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Consolidated Fuel Reprocessing Program Progress Report for Period October 1 to December 31, 1978

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CONSOLIDATED FUEL REPROCESSING PROGRAM PROGRESS REPORT FOR PERIOD OCTOBER 1 TO DECEMBER 31, 1978

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FOREWORD

This quarterly progress report on the Fuel Reprocessing Program covers the ongoing development program at ORNL.

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. During this period when the future of several proposed fuel cycles is so 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.

Future CFRP progress reports will be expanded to cover the overall reprocessing development program of the Department of Energy.

1. HIGHLIGHTS

1.1 PROCESS RESEARCH AND DEVELOPMENT

B. L. Vondra

Reference spectra for plutonium(III), (IV), (V), (VI), and polymer were obtained in 0.1 to 4.0 *M* HNO_3 at 22 to 50°C. These spectra will allow more accurate quantification of spectrophotometric measurements of plutonium concentration and the identification of valence states.

Coprocessing flowsheets were evaluated by batch solvent extraction to test the use of concentrated (1.5 *M*) hydroxylamine nitrate to strip all the plutonium plus a portion of the uranium. Plutonium recoveries of about 99.9% were achieved with about 12% of the uranium costripping. The addition of about 0.1 *M* HNO_2 to the loaded organic phase had only a minor adverse effect on plutonium stripping and did not alter uranium stripping behavior.

Hydrazine "carbonate" is being evaluated as a replacement for sodium carbonate in the solvent wash system. Suitable methods were identified for the engineering-scale preparation of hydrazine "carbonate" solutions. Initial experimental results suggest that hydrazine bicarbonate may be the species present in solution.

Continued investigation of the reaction of hydroxylamine nitrate with nitric acid has led to the finding that nitrous acid is a reaction product, in addition to nitrous oxide. The presence of nitrous acid may help to explain the unpredictable plutonium reoxidation events reported by others.

Hot-cell experimental work was initiated with PNL-3 fuel. This is (25% Pu, 75% $^{238}U)O_2$ clad in stainless steel and irradiated to about 60,000 MWd/t in the EBR-2 fast flux; thus, it is typical of LMFBR core fuel. To supply fuel for voxolidation/dissolution experiments, 14 rods were sheared with the new semiautomatic single-rod shear.

Nonoxidative heat treatment methods for tritium removal were evaluated using H. B. Robinson fuel. Heating at 1000°C in a flowing inert atmosphere gave good tritium release (99.9%) from broken fuel fragments.

Three 16-stage mini-mixer-settlers were installed in alpha-containment glove boxes, along with associated pumps, tanks, and instrumentation. Initial hydraulic testing was satisfactory. This system will be used in future cold uranium-plutonium flowsheet evaluation experiments.

Radioactive operations were begun in the Solvent Extraction Test Facility. Work this quarter included (1) eight dissolutions (2 kg of heavy metal per batch) of sheared H. B. Robinson fuel irradiated to 31,000 MWd/t and cooled 4.5 years; (2) four feed

adjustments (4 kg of heavy metal per batch) to approximately 3 *M* HNO_3, 300 g/liter of uranium and greater than 95% plutonium(IV); (3) clarification of the four batches of adjusted feed solution by filtration through a precoated, etched-disk filter having 1-μm pores; and (4) three sets of solvent extraction runs, with a total of eight test periods. Equipment performance was satisfactory, and evaluation and analysis of the data are in progress.

Eight runs were completed at Rockwell-Hanford to test thermal denitration and hydrogen reduction for product conversion in the same vessel. Uranium, plutonium, or uranium-plutonium powders were prepared. Minor equipment changes are under way to alleviate some mechanical problems.

Corrosion studies at Battelle (Columbus) showed that titanium and tantalum are not subject to stress corrosion cracking or pyrophoric reactions in 90 to 98% nitric acid; and thus, these metals may be promising materials for use in portions of the Iodox process equipment. Additional work at ORNL confirmed that zirconium alloys undergo cracking and will not be suitable.

1.2 ENGINEERING RESEARCH

W. S. Groenier

The 0.5-t/d rotary kiln voloxidizer has been operated at elevated temperatures for a total of 170 h while individual subsystems were being checked out. The flight cartridge is being prepared for installation. All subsystems will be available, and the experimental program is expected to begin next quarter.

Heat transfer tests using the small voloxidizer to determine the effects of solids dispersion using simulated fuel were completed.

A rotary kiln seals development program has begun with the assistance of the FMC Corporation. A reference design of the concept chosen in the selection study has been completed. Fabrication should be complete in time for testing during the summer of 1979.

Continuing problems have forced an additional delay in beginning the rotary dissolver erosion-corrosion study. The main problem remaining has to do with excessive acid leakage into the housing, which is caused by drum misalignment and will require that the waste tank be insulated to contain heated acid. Operation should begin next quarter.

Nitrogen oxide scrubbing experiments have been continued to provide data for mathematical model development. These tests have recently explored wider ranges of gas and liquid flow rates than previously used. These ranges were made possible with the installation of a larger scrubber tower. Scrubbing efficiencies varied as expected, being influenced by the gas-liquid interfacial area and the gas residence time.

Annular centrifugal contactor tests have demonstrated uranium extraction efficiencies of about 100% for various operating conditions. In a single run, where the residence time was only 3 s, an efficiency of 96% was measured. The design of a second model with improved features has begun. Stripping coefficients for plutonium in the presence of a reductant have

been measured for various contact times. This was done as part of an effort to determine if short residence-time contactors can be applied in this case.

In a parallel effort, calculations are being made to determine the operating conditions necessary to strip plutonium in the absence of a reductant.

Temperature and ^{85}Kr gamma-scan profiles have been measured for the combination-column fluorocarbon absorption process to determine optimum column operating conditions. Distribution coefficient data for krypton and xenon in dichlorodifluoromethane have been obtained for a solute concentration of 10%. Previous work involved Henry's law (infinite dilution) constants.

The development of a ^{14}C removal process has continued with additional studies to develop process instrumentation, to characterize a $Ba(OH)_2$ hydrate solid reactant, and to measure removal efficiencies in a $Ca(OH)_2$ slurry stirred-tank reactor.

1.3 ENGINEERING SYSTEMS

M. J. Feldman

The methodology for evaluating the cost basis of various options for a fuel reprocessing facility configuration within a nuclear energy center has been issued in an interim report.

A brief study to evaluate the proliferation-resistant characteristics of a typical pyrochemical reprocessing facility has been completed. This type of facility is being evaluated for potential use as an "exportable" technology to nonweapons nations who desire to obtain energy independence via use of nuclear power. A report is being prepared.

All components for the normal-feed alligator shear test have been installed on the shear. When the control system is received and installed, testing will begin.

The conceptual design of a prototype voloxidizer is 90% complete. A concept for testing and developing the seal mechanism for the unit has been completed.

The support system installation for the rotary dissolver is essentially complete. Operations of the dissolver were curtailed to permit repair of the failed drum support rollers.

Corrosion experiments on unirradiated fuel cladding material have been completed. Material previously exposed to liquid sodium, and then exposed to water for 10 to 12 months, did not show any signs of failure.

A scoping study to evaluate the benefits of various methods of taking and transporting in-cell samples was concluded. The study presents a method which uses a remotely operated tract guide vehicle and pneumatic tube transfer.

The *Hot Experimental Facility Interim Design Report,* has been issued. This report describes the reference HEF concept for a pilot-scale reprocessing facility capable of demonstrating reprocessing technology and storage for typical breeder reactor and light-water reactor (LWR) fuels, using either the uranium-plutonium or the thorium-uranium-plutonium fuel cycles. The facility will be licensable and will meet or exceed the federal

requirements for fuel reprocessing plants. The requirements cover such subject areas as safeguards, saboteur resistance, release of contaminants to the environment, radiation exposure to the public and plant personnel, natural phenomena, and decommissioning.

1.4 TECHNICAL SUPPORT

W. S. Groenier

Major accomplishments in the safeguards task include (1) the completion of a computer code (INSIM) to simulate the movement of fissile material through a reprocessing plant, (2) the design of a material balance system for the continuous rotary dissolver, and (3) completion of an analysis of a Kalman filtering technique as applied to pulsed columns. Work has started toward the organization of a proliferation-resistant engineering effort which will include a demonstration of data handling techniques in an existing facility.

In the nuclear safety task, a series of criticality experiments with concrete reflected arrays of Fast-Flux Test Facility fuel has been completed; conceptual designs have been prepared for a series of solution experiments.

Work in the instrumentation and controls sensors development task has included (1) an investigation of refractometry as a method of monitoring the acidity of pure nitric acid streams, (2) the design of an in-line photometric analyzer for uranium product streams, (3) efforts to design neutron poison and free acid monitors, and (4) an evaluation of angular momentum and ultrasonic flowmeters. Nondestructive assay techniques have been further investigated by performing follow-on experiments with simulated spent fuel to refine system precision, to measure long-term stability, and to study the application of these techniques to leached hull monitoring. Additional tests were made to further establish the feasibility of using vibration signals to monitor material flow through a rotary dissolver.

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 IET and the 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 are confirming tritium release from irradiated fuel specimens by voloxidation. A hot-cell facility (Solvent Extraction Test Facility) with an irradiated fuel capacity in the kg/d range has been made operational and is being used to test flowsheet options and coprocessing and low-decontamination factor options, as well as high decontamination partitioning flowsheets. Through product conversion activities, methods are being established to convert mixed oxide nitrate solutions to fabricable powders.

2.1 LABORATORY DEVELOPMENT

J. C. Mailen

2.1.1 Plutonium (IV) polymer reaction in aqueous solutions

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

The plutonium polymerization studies[1] have been temporarily interrupted in order to obtain reference spectra for the various plutonium species in nitric acid solution. Although the need for accurate molar absorbtivity data is encountered by all users who monitor plutonium species spectrophotometrically, there is no complete set of such calibration data for Pu(III), (IV), (V), (VI), and polymer as a function of temperature and nitric acid concentration. Previous reports may have been satisfactory for their own purposes, however, variables such as temperature[2] or the nature of the species and the medium[3] have been disregarded; consequently, the more general applications of such data have been left with much uncertainty. Reference spectra data have been obtained for 0.1 to 4.0 *N* HNO_3 and temperatures of 22 to 50°C [some tests were made at 10°C in order to get Pu(IV) and (V) at low acid values]. Final data refinement and presentation will be made upon delivery of digital equipment. In their present form, however, several useful observations can be made.

The spectrum of Pu(IV) changes substantially in going from 0.1 to 4.0 *N* HNO_3 primarily because of the shift in the nature of the Pu(IV) species according to:

$$Pu^{4+} + NO_3^- \rightleftharpoons Pu(NO_3)^{3+} .$$

At 0.1 *N* HNO_3, bands due to Pu^{4+} and $Pu(NO_3)^{3+}$ can be resolved at 470 nm, $\epsilon = 38$, and at 476 nm, $\epsilon = 82$ liter $mole^{-1}$ cm^{-1}, respectively; at 2.0 *N* HNO_3, the 470-nm band disappears. The net result is that ϵ^{476} for Pu(IV) in nitric acid varies from approximately 50 at 0.1 *N* HNO_3 to 80 at 2.0 *N* HNO_3 and then falls in going to 4.0 *N* HNO_3 as higher nitrates of Pu(IV) are formed. Although Hindman described these phenomena[2] some years ago, these observations are typically ignored. Temperature effects on the Pu(IV) spectrum, which were not considered in Hindman's treatment, should shift the above equilibrium and cause dramatic changes in the ϵ^{476} values for Pu(IV).

The only spectrum of Pu(V) which is regularly cited is that by Cohen[4] in $HClO_4$ at 10°C. We have measured the spectrum of Pu(V) generated in 0.1 *N* HNO_3 in an electrochemical-spectrophotometer cell and have data over the 10 to 35°C range.

Finally, Pu(IV) polymer spectra have been measured, where possible, as a function of temperature, acid concentration, and aging effects to check the previous assumptions[1] regarding $\epsilon_{50°}^{400nm}$ for plutonium polymer. Little change in ϵ^{400} with respect to these variables has been found. A value of $\epsilon_{22°}^{400} = 147 \pm 3$ liter $mole^{-1}$ cm^{-1} for fresh and aged polymer from 0.1 to 4.0 *N* HNO_3 has been measured. A negative temperature coefficient of 0.1% per degree Centigrade was measured over the 22 to 50°C interval.

2.1.2 Plutonium reductive stripping studies

M. H. Lloyd and S. E. North

Studies were continued to evaluate coprocessing stripping procedures in which all of the plutonium is stripped with part of the uranium using hydroxylamine nitrate (HAN) both as the plutonium reductant and as a salting agent to retard uranium stripping. The primary impetus for this study was to evaluate process concepts that will be used in the Solvent Extraction Test Facility (SETF) campaigns. Since low aqueous-to-organic ratios will be used in these tests, the acid concentration in the organic feed is an important variable. Therefore, batch-stripping experiments were conducted in which the effects of both the organic feed and aqueous strip acid concentrations on plutonium and uranium stripping behavior were evaluated. When high aqueous phase concentrations of HAN are used to retard uranium stripping, significant variations in HAN concentration should not adversely affect plutonium reduction; therefore, the use of a holding reductant such as hydrazine may not be required. However, because of the low aqueous volume ratios employed, a large stoichiometric excess of HAN in the system and HAN decomposition by reaction with HNO_2 could be significant. The effect of HNO_2 concentrations in this system has been determined.

In these tests, organic feed solutions were prepared by contacting an equal volume of 30% TBP–NDD with a 3 *M* HNO_3 aqueous feed which contained 1.7 g/liter of plutonium and 110 g/liter of uranium. Typically, the organic feed solutions contained about 1 g/liter of plutonium, 90 g/liter of uranium, and 0.2 *M* HNO_3. The organic phase acidity was adjusted by contact with two 1/5-volume aqueous scrub stages which contained 6 *M* NH_4NO_3 and the desired acid concentration. The organic feeds were stripped with four 1/7-volume stages. The stripping solutions contained 1.5 *M* HAN and the desired acid concentration.

Batch-stripping experiments were performed in which the HNO_3 concentrations in the organic phase and the strip acid concentrations were varied from 0.05 to 0.20 *M*. Extraction times were varied from 2 to 5 min, and settling times varied from 5 to 10 min.

Plutonium stripping behavior for two of these experiments is shown in Fig. 2.1. In these experiments, the organic phase acidity was adjusted from 0.2 *M* to ~0.05 *M* with

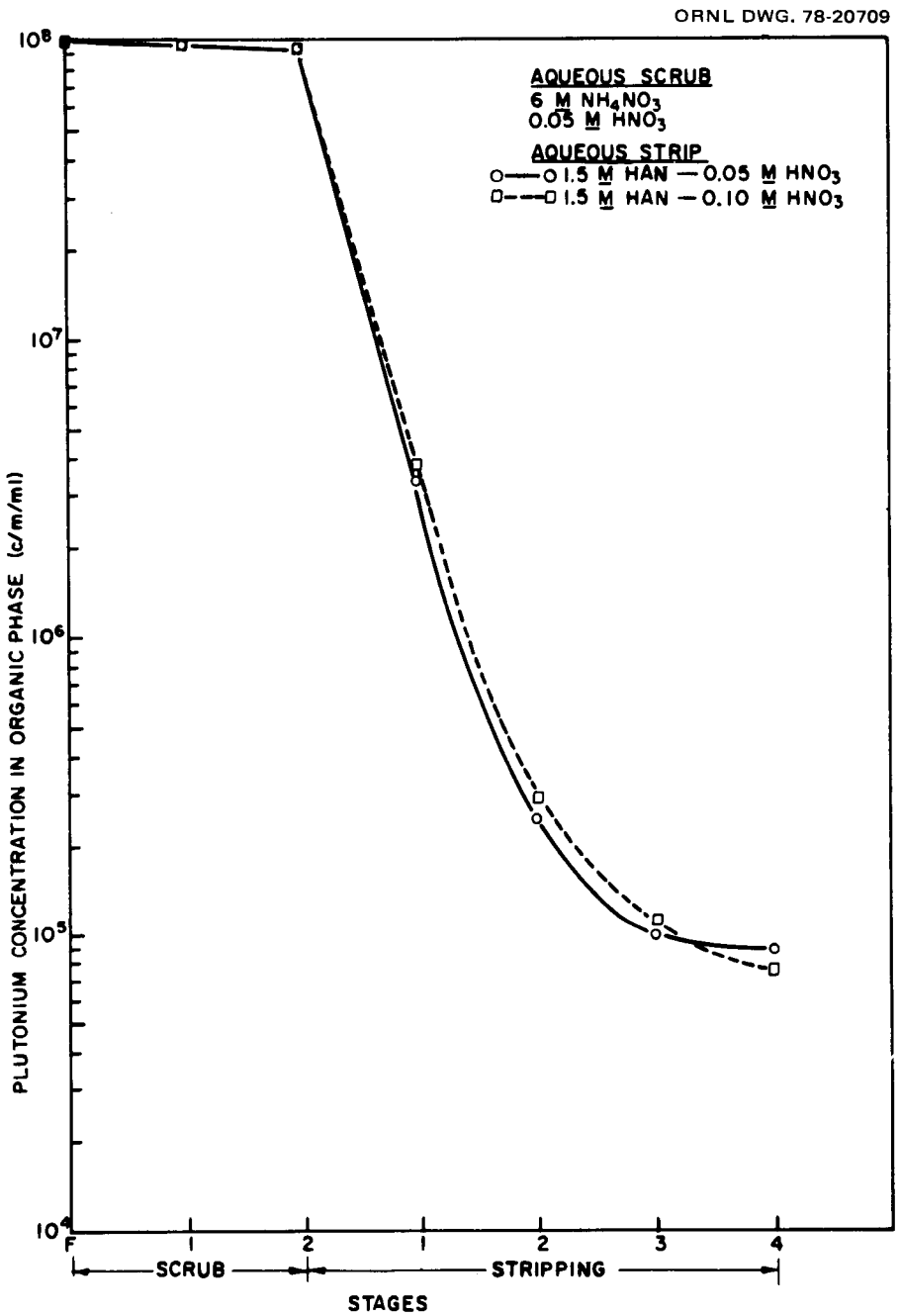

Fig. 2.1. The effect of HNO_3 concentration on plutonium reductive stripping behavior.

two scrub stages, and the strip acid concentrations were 0.05 and 0.10 *M*. The data indicates that little or no plutonium was stripped with the fourth stripping stage. It seems most likely that this effect is not real, but results from the inability of alpha counting techniques to reliably detect small amounts of plutonium in organic solutions that contain high concentrations of metal ions. This point, however, cannot be resolved unambiguously with the current available analytical techniques.

The indicated plutonium recovery in four stages (~99.90%) did not vary with acid concentration in the range studied or with variations in extraction and stripping contact times. Uranium stripping behavior was also unaffected by these variables. About 12% of the uranium was stripped with the plutonium in all cases.

Next, studies were initiated to evaluate the effects of HNO_2 on this stripping system. As the study progressed, it became apparent that the addition of known concentrations of HNO_2 to the organic phase cannot be easily accomplished. In initial experiments, KNO_2 was added to 3 *M* HNO_3 feed solutions and contacted with the organic phase. It was found that HNO_2 reacted so rapidly with 3 *M* HNO_3, that it was not possible to introduce detectable concentrations of HNO_2 into the organic phase by this procedure. Organic feed solutions containing HNO_2 and the desired concentrations of uranium and plutonium can be prepared by first extracting nitrous acid from a water or dilute nitric acid solution of KNO_2 and then contacting the organic phase with a 3 *M* HNO_3 solution of uranium and plutonium. Typically 60 to 70% of the HNO_2 in the organic phase was decomposed during contact with the acid-metal phase. Using this procedure, the maximum concentration of HNO_2 that can be introduced into the organic phase appears to be about 0.45 *M* and the maximum concentration retained in the organic phase after contact with the aqueous feed solution is about 0.15 *M*.

Nitrous acid was stable in the organic phase provided it was stored in a closed container with limited vapor space. Under these conditions, HNO_2 stability was not affected by the organic phase HNO_3 concentration. Nitrous acid can be readily removed by air sparging, however, and HNO_2 stability in the organic phase was sensitive to variations in the vapor space of a closed container. The HNO_2 concentration in 30% TBP-NDD was reduced from 0.45 *M* to 0.11 *M* by air sparging the solution for 30 min at room temperature. The effects of vapor space on HNO_2 retention by TBP-NDD was demonstrated in two types of experiments. In the first experiment, 50 ml of a 30% TBP-NDD solution was stored in a closed 500 ml container for 16 h at room temperature. The HNO_2 concentration decreased from 0.13 *M* to 0.06 *M* during this storage period. In a similar experiment, a 30% TBP-NDD solution which contained 0.26 *M* HNO_2 was stored in a closed bottle with very little vapor space and in an open bottle. After 24 h, the organic solution in the closed bottle contained 0.24 *M* HNO_2 whereas the organic solution in the open bottle contained only 0.02 *M* HNO_2.

These factors seriously complicate the ability to reliably analyze organic solutions for HNO_2. A reliable analysis will require standardized procedures involving sample volume, sample bottle size, and handling procedures during the analysis.

The effect of HNO_2 on plutonium reductive stripping behavior is shown in Fig. 2.2. These stripping experiments were performed in the same way as the experiments previously described (Fig. 2.1) except that HNO_2 was introduced into the organic phase by initially equilibrating the organic phase with aqueous solutions of KNO_2 at concentrations of 0.4, 2.0, and 4.0 *M*.

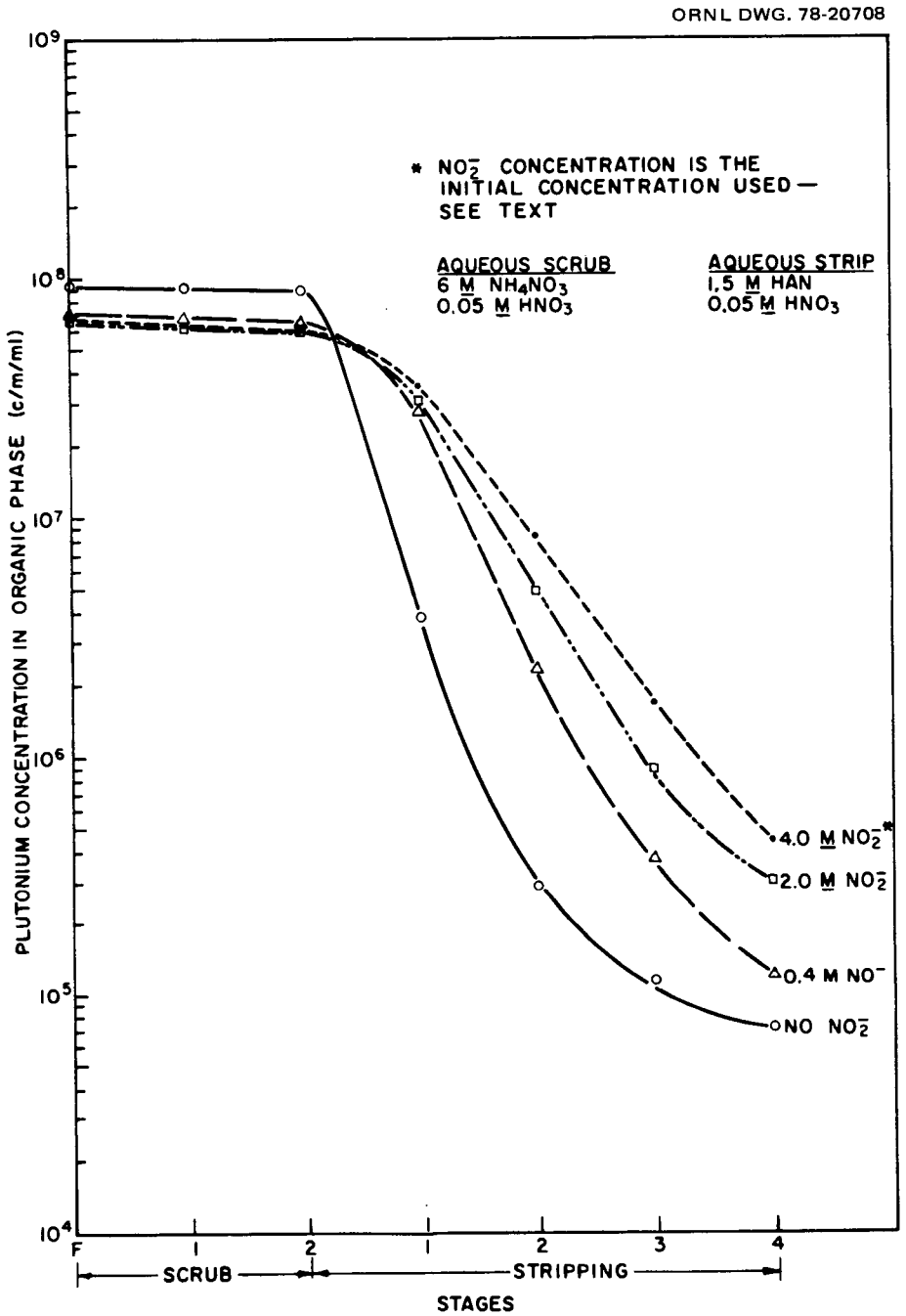

Fig. 2.2. The effect of HNO_3 concentration on plutonium reductive stripping behavior.

An analysis of the organic phase prior to stripping indicated that the HNO_2 concentration was about 0.1 *M* in all three cases and does not reflect an increasing HNO_2 concentration. This appears to be due to the loss mechanisms described above rather than to actual HNO_2 concentrations; because plutonium stripping behavior shows a regular decrease in plutonium stripping with increasing nitrite concentration initially used in the experiment.

The addition of HNO_2 to the experiment did not affect uranium stripping behavior. About 88% of the uranium remained in the organic phase in all four experiments. The presence of HNO_2 in the organic phase does noticeably affect both uranium and plutonium extraction behavior. However, as shown in Fig. 2.2, organic feeds that contain HNO_2 extracted only about 75% of the plutonium compared with the experiment that did not contain HNO_2. This same behavior was observed for uranium. Uranium concentration in HNO_2 containing organic solutions was decreased about 20%. This could be due to solvent loading effects in which the HNO_2 extracted by TBP effectively reduces the concentration of TBP available for metal ion extraction.

2.1.3 Plutonium-uranium-thorium coprocessing studies

J. B. Knauer, J. T. Barker, and M. H. Lloyd

Experiments were continued to obtain plutonium, uranium, and thorium distribution coefficients for the 30 vol % TBP-NDD system as a function of HNO_3, uranium, and thorium concentrations. During this report period, a series of experiments containing 1 g/liter plutonium and no uranium was completed. The feed acid concentrations in these experiments were varied from 0.1 *M* to 4.5 *M* HNO_3, and the thorium concentrations were varied from 5 to 250 g/liter. A series of experiments was also completed in which the aqueous feeds contained a significantly higher plutonium concentration (15 g/liter). The acid, uranium, and thorium concentrations in this series are shown in Tables 2.1 and 2.2.

Results obtained in experiments with aqueous feed concentrations of 1 g/liter of plutonium-no uranium-varying thorium-varying acidity show the same trends in extraction behavior for plutonium and thorium as those reported[5] with 15 g/liter of uranium present. For example, plutonium distribution coefficients increased regularly with increasing HNO_3, and the effect of nitrate salting at high thorium concentrations on plutonium distribution coefficients was again observed. This effect caused the plutonium distribution coefficients to increase with increasing thorium concentrations at HNO_3 concentrations of less than 2 *M*, but to decrease with increasing thorium concentrations at acidities greater than 2 *M*.

There was essentially no change in plutonium distribution coefficients when the plutonium concentration was increased from 1 to 15 g/liter and the same general trends in plutonium extraction behavior were observed for the higher plutonium concentration.

Regions of third-phase formation for aqueous feed solutions containing 1 g/liter of plutonium are shown in Table 2.1 and regions of third-phase formation with 15 g/liter of plutonium are shown in Tables 2.2 and 2.3. These tables show the vol % of the organic phase appearing as third phase and the percentage of extracted metal ions that are present in the third phase when a third phase is formed. When uranium was not present, third-phase formation first occurred at an organic phase thorium concentration of about 29 g/liter.

Table 2.1. Third-phase formation at aqueous feed concentrations of 1 g/liter of plutonium, no uranium, varying thorium, and varying acidity

Acid (*M*)	No thorium	Thorium, g/liter						
		5	15	45	100	150	200	250
0.1	None	None	None	None	*a*	*a*	*a*	*a*
0.3	None	None	None	None	None	*a*	*a*	*a*
0.6	None	None	None	None	None	19%[b] / 45.4,[c,d] 41.7[e]	32% / 81.5, 79.6	32% / 88.3, 87.4
1.0	None	None	None	None	None	28% / 70.6, 67.7	32% / 83.8, 83.5	34% / 89.7, 88.4
2.0	None	None	None	None	30% / 75.4, 68.8	31% / 80.8, 81.3	35% / 88.5, 89.5	32% / 88.4, 90.0
3.0	None	None	None	None	33% / 77.1, 80.4	33% / 84.6, 87.6	35% / 87.5, 92.2	34% / 89.3, 93.7
4.0	None	None	None	None	35% / 81.4, 86.6	35% / 86.0, 91.0	35% / 87.7, 94.1	35% / 89.6, 95.6
4.5	None	None	None	22% / 43.4, 44.9	34% / 81.4, 88.0	34% / 85.7, 92.7	35% / 88.0, 94.6	35% / 89.6, 95.6

[a] The acidity of stock solutions did not permit the preparation of this feed solution.
[b] The vol % of organic extractant appearing as third phase.
[c] The percentage of plutonium in organic extractant present in third phase.
[d] The percentage of uranium in organic extractant present in third phase.
[e] The percentage of thorium in organic extractant present in third phase.

Table 2.2. Third-phase formation at aqueous feed concentrations of 15 g/liter of plutonium, 15 g/liter of uranium, varying thorium, and varying acidity

Acid (*M*)	Thorium, g/liter			
	100	150	200	250
0.6	None	27% / 69.4, 42.2, 66.1	30% / 83.1, 54.3, 79.3	34% / 88.5, 59.3, 87.5
1.0	20%[a] / 49.4,[b] 32.2,[c] 45.2[d]	29% / 77.3, 41.9, 76.1	31% / 85.0, 61.6, 86.3	34% / 89.0, 64.3, 86.8
2.0	31% / 74.6, 47.2, 75.8	32% / 81.6, 58.5, 82.4	33% / 86.6, 66.0, 88.4	35% / 87.8, 56.5, 89.8
3.0	31% / 77.1, 50.1, 78.8	34% / 84.2, 64.1, 88.0	34% / 86.0, 66.6, 91.6	35% / 88.4, 68.5, 91.4
4.0	33% / 81.4, 53.5, 85.5	34% / 83.0, 64.5, 90.5	34% / 86.0, 70.2, 93.1	35% / 86.8, 68.6, 91.2
4.5	33% / 78.9, 55.8, 86.4	35% / 84.8, 68.5, 91.5	35% / 87.4, 66.6, 93.7	35% / 87.4, 72.4, 92.1

[a]The vol % of organic extractant appearing as third phase.
[b]The percentage of plutonium in organic extractant present in the third phase.
[c]The percentage of uranium in organic extractant present in third phase.
[d]The percentage of thorium in organic extractant present in third phase.

Table 2.3. Third-phase formation at aqueous feed concentrations of 15 g/liter of plutonium 100–150 g/liter of uranium, varying thorium, and varying acidity

Acid (*M*)	Thorium, g/liter			
	100 g/liter uranium			150 g/liter uranium
	100	150	200	100
0.6	None	None	9%[a] 28.4,[b] 15.2,[c] 29.7[d]	None
1.0	None	None	9% 25.7, 15.2, 31.3	None
2.0	None	None	16% 42.9, 27.5, 55.1	None
3.0	None	11% 29.6, 19.4, 35.1	19% 49.0, 34.2, 63.5	None
4.0	4% 9.6, 8.9, 14.4	20% 49.7, 35.8, 64.9	22% 56.7, 41.5, 75.6	None
4.5	12% 27.7, 19.4, 39.8	22% 56.2, 41.9, 74.3	23% 55.3, 43.8, 76.1	None

[a]The vol % of organic extractant appearing as third phase.
[b]The percentage of plutonium in organic extractant present in third phase.
[c]The percentage of uranium in organic extractant present in third phase.
[d]The percentage of thorium in organic extractant present in third phase.

Equipment has been designed and fabricated for the determination of distribution coefficients at elevated temperatures. The extraction vessel consists of a water-jacketed centrifuge cone that can be agitated in a vortex mixer. A constant temperature is obtained with a recirculating water bath. Experiments to evaluate the performance of this equipment are presently in progress.

2.1.4 Plutonium losses due to solution instability and solids formation

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

The solids formation mechanisms involving thorium in fuel reprocessing solutions have been the subject of continued investigations. Studies during the past year have emphasized thorium molybdate precipitation. Initial tests indicated that these precipitates would form very rapidly at feed acid concentrations of 2 to 4 *M* at 40°C or less at the thorium concentrations typically proposed for thorium-containing fuels. This means that thorium molybdate precipitates would occur at many flowsheet conditions presently proposed for fuel reprocessing. The solids that are formed can be expected to selectively carry significant amounts of plutonium. We have new evidence from solubility data, for example, that thorium molybdate precipitates or gels can form in solutions containing as little as 20 g/liter of thorium. On the other hand, in competition with 1.5 g/liter of zirconium, equimolar quantities of thorium result in the formation of zirconium molybdates that carry up to 6% thorium.

The focus of the thorium studies has been on the solubility of thorium molybdate in nitric acid, its precipitation behavior, and characterization of the precipitates. The bulk of the completed experimental work has been in refluxing nitric acid since the solutions come to equilibrium much faster at high temperatures. A significant amount of lower temperature experimental work is still in progress because of slow equilibration times; the results of these experiments will be reported at later dates. Because of the recent deemphasis of thorium investigations, no new experiments are currently planned.

X-ray evidence exists for two distinct types of thorium molybdate precipitates formed under differing acid conditions. The metal stoichiometry of the precipitate from 1 *M* nitric acid corresponds to a compound of the formula $Th(MoO_4)_2 \cdot XH_2O$. The stoichiometry of a different precipitate (from 10 *M* nitric acid) is currently unresolved.

The important process variables influencing the solubility and precipitation behavior of these thorium molybdates are the thorium and molybdenum concentrations (activities), nitric acid concentration, temperature, and ionic strength. Selective complexing of the molybdenum by adding a stronger complexing cation, which forms a more soluble molybdate (such as Fe^{3+}), should probably be considered as an important variable also.

The precipitation reaction is not a first-order reaction. The solutions appear to be clear and stable for an induction time, *t*, and predicting this time seems to be most pertinent to reprocessing operations. Following the induction time, the precipitation starts very slowly, accelerates, and then slows when approaching equilibrium.[6] Predicting the induction would allow corrective steps to be taken prior to precipitation if the solids would

adversely affect reprocessing operations. A plot of the acid concentration vs induction time (Fig. 2.3) exhibits a maximum in 6 *M* nitric acid with "minima" at the boundaries of the acid range studied (0.6–12 *M*). The thorium molybdate solubility also exhibits a maximum in 6 *M* nitric acid and the solubility at constant acid concentration is consistent with the classical solubility product-type relation.

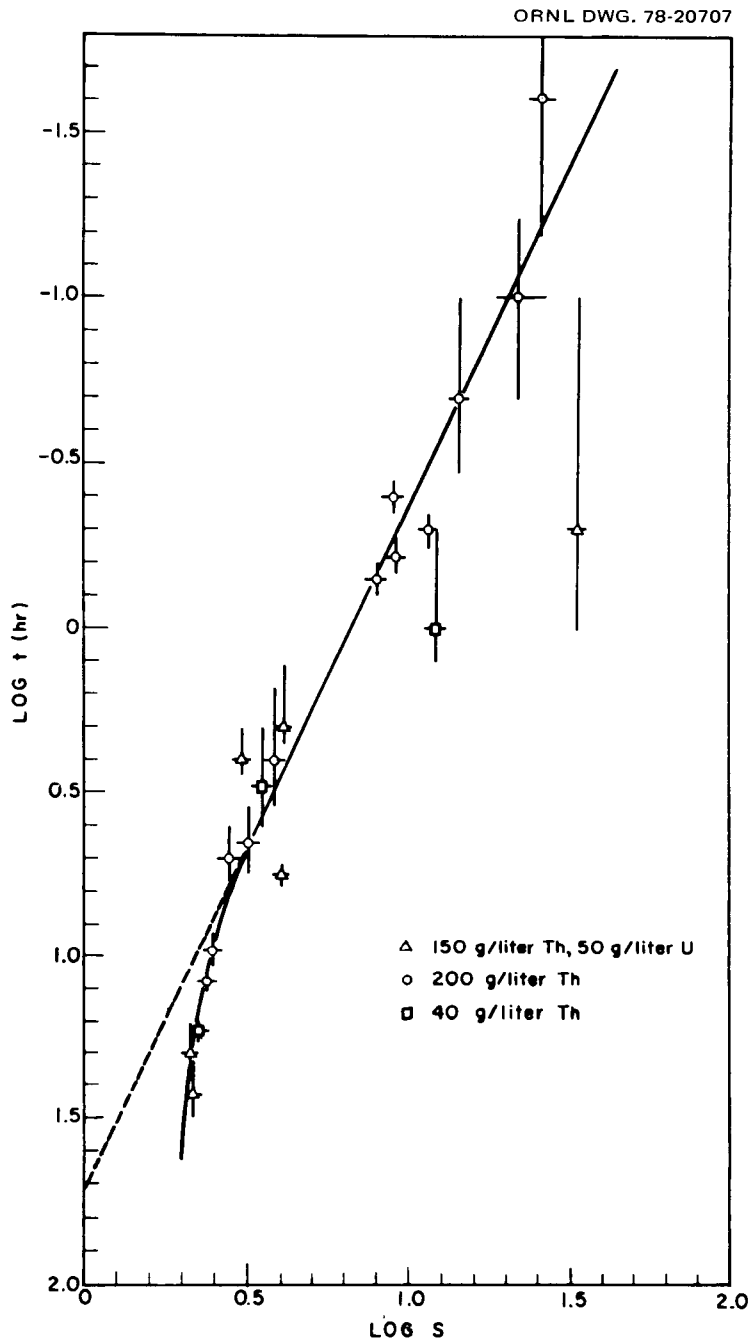

Fig. 2.3. The precipitation induction time vs nitric acid concentration for refluxing nitric acid solutions containing 200 g/liter of thorium and 1.5 g/liter of molybdenum.

The relation of induction time and saturation ratio can be used to predict the induction time for thorium- and molybdenum-containing solutions. The saturation ratio, s, is the ratio of the initial solution concentration to the equilibrium concentration. The saturation ratio also determines the degree of super-saturation of the solution. Molybdenum is the limiting component in these precipitation reactions and, thus, its concentration is used in the calculation of the saturation ratio. Data from several different experiments at reflux temperatures are plotted in Fig. 2.4 as log t vs log s. These experiments cover nitric acid concentrations of 0.6 M to 12 M, a molybdenum concentration range of 1.5 to 5 g/liter, and a thorium concentration range of 40 to 200 g/liter. The nonlinear shape of the log t vs log s function is consistent with a mechanism of homogeneous nucleation and crystal growth. Precipitate formation occurs spontaneously and has not been intentionally induced by additions such as seed crystals. The effect of temperature on the $t - s$ relationship is substantial, but experiments at lower temperatures have not yet been concluded.

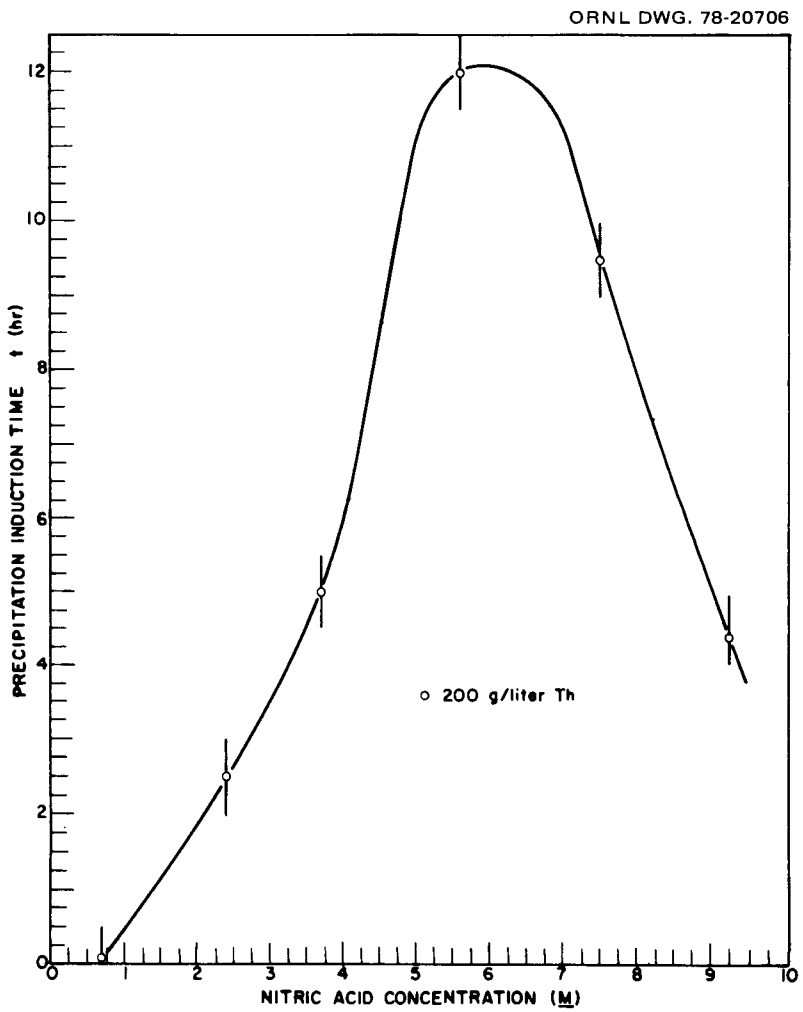

Fig. 2.4. Log of the precipitation induction time vs log of the saturation ratio for thorium molybdate precipitation from nitric acid. The estimated uncertainties are indicated for each data point. △ 150 g/liter of thorium, 50 g/liter of uranium; ○ 200 g/liter of thorium; and □ 40 g/liter of thorium.

The effect of some additional process variables has been studied. The addition of 25% uranium appears to have an insignificant effect on the precipitation kinetics. Lithium nitrate and aluminum nitrate additions to 1.4 *M* decrease the molybdate solubility by up to 60%, but the induction times appear to be consistent with those in Fig. 2.4.

Although the precipitation induction times at reflux temperatures are predictable under varying conditions, it must be emphasized that the solubilities used to calculate the saturation ratio cannot yet be quantitatively predicted. Experiments and calculations in progress and anticipated for next quarter are intended to remedy this situation and finalize the thorium work.

2.1.5 Solvent cleanup studies

O. K. Tallent, D. J. Pruett, and K. E. Dodson

Studies are evaluating hydrazine "carbonate" as the solvent wash reagent to remove products which result from hydrolytic and/or radiolytic degradation of the TBP[7–9] and associated complexes formed with actinides and fission products. If not removed in a wash operation, the degradation products form stable, organic-soluble complexes with fission products which cause operational problems (emulsions, precipitation, slow phase separation, phase inversion, etc.)[5,10,11] and can result in decreased decontamination of fission products from the actinides or process upsets. Recent German work[12] has utilized ~1 *M* aqueous hydrazine or hydrazine "carbonate" for the organic wash followed by electrolytic decomposition of the spent hydrazine reagent. The major potential advantage of hydrazine reagents over the standard wash reagent, sodium carbonate, is that the hydrazine compounds can be decomposed to gaseous products, thus eliminating a significant source of solid waste.

A method for preparing hydrazine "carbonate" solution by contacting gaseous CO_2 with aqueous hydrazine has been investigated in this report period. Two types of reactions are reported to occur between carbon dioxide and hydrazine[13–15]

$$CO_2 + N_2H_4 \cdot H_2O \rightarrow N_2H_5^+ + HCO_3^- \quad , \tag{2.1}$$

and

$$CO_2 + 2N_2H_4 \cdot H_2O \rightarrow NH_2NHC(=O)N_2H_5 + 2H_2O \quad . \tag{2.2}$$

The product in Eq. (2.1) is hydrazine bicarbonate and the product in Eq. (2.2) is hydrazine carbazate. The chemistry of hydrazine carbazate was discussed previously.[16] During this report period, however, it was found that the reaction in Eq. (2.1) usually occurred under conditions where CO_2 at ~0.97 atm of pressure was reacted with 1.0, 3.0, and 6.0 *M* $N_2H_4 \cdot H_2O$ in aqueous solution at temperatures ranging from 2 to 60°C. Under these conditions, ~1.0 mole of CO_2 is consumed per mole of $N_2H_4 \cdot H_2O$ present. The reaction

in Eq. (2.2) appeared to occur in an experiment at 80°C where only 0.5 moles of CO_2 was consumed per mole of $N_2H_4 \cdot H_2O$ present. Similar results have been reported for the ammonium carbonate-ammonium carbamate system,[17] except the carbonate in that system was stable only up to 33°C.

The progress of the reaction to form hydrazine bicarbonate can be monitored by pH measurements. In the initial stages of the reaction [Eq. (2.1)] using 1.0, 3.0, or 6.0 *M* $N_2H_4 \cdot H_2O$ solution at 25°C, the pH ranges from 10.0 to 10.5. During the reaction as CO_2 is contacted with the solutions the pH decreases and the reaction is completed at a pH of ~7.0. The reaction can be monitored further by measuring density and/or conductivity changes. The density of aqueous hydrazine is approximately the same as that of water. The density of 6.0 *M* $N_2H_4 \cdot H_2O$ solution at 25°C increases linearly from ~1.01 g/cm^3 to ~1.13 g/cm^3 as the $N_2H_4 \cdot H_2O$ is converted to $N_2H_4 \cdot H_2CO_3$. The conductance of aqueous solutions of $N_2H_4 \cdot H_2CO_3$ in the concentration range from 0.5 to 6.0 *M* at 25°C is approximately defined by the following equation:

$$C\Lambda = 1730\ 1/\Lambda - 16 \quad , \tag{2.3}$$

where Λ is equivalent conductance in mho/cm^2 and C is molar concentration. The equivalent conductance at infinite dilution calculated from Eq. (2.3) is 108.1 mho/cm^2. The equivalent conductance at 25°C of the $N_2H_5^+$ ion[18] at infinite dilution is reported to be 59.4 and that of the HCO_3^- ion[19] to be 44.5 mho/cm^2 with the sum of the two being 103.9 mho/cm^2 which compares well with the 108.1 mho/cm^2 obtained from Eq. (2.3).

At a constant CO_2 pressure of ~0.97 atm, the reaction rate for Eq. (2.1) varies with $N_2H_4 \cdot H_2O$ concentration and temperature. The initial reaction rate is defined by a first-order rate equation

$$\log C = -(A/V)\, k/2.3\, t + \log C_o \quad , \tag{2.4}$$

where C, A, V, k, t, and C_o, respectively, denote unreacted $N_2H_4 \cdot H_2O$ molar concentration, interfacial contact area between the gaseous CO_2 and the aqueous phase in cm^2, volume of aqueous phase in ml, rate constant which varies with temperature, elapsed reaction time in minutes, and initial molar $N_2H_4 \cdot H_2O$ concentration. The value of k at a given temperature can be determined from the following equation

$$\log k = 1.00 - 569.1/T(°K) \quad . \tag{2.5}$$

With 1.0 *M* $N_2H_4 \cdot H_2O$, the first-order kinetics applies until the reaction is at least 95% complete. In 3.0 or 6.0 *M* $N_2H_4 \cdot H_2O$, the above rate constants apply until the reaction is ~50% complete after which the rate becomes slower.

The activation energy calculated from Eq. (2.5) is 2.72 kcal/mole. Low activation energies are expected in neutralization reactions such as that in Eq. (2.1).

A −7.35 kcal/mole heat of neutralization was found experimentally for the gaseous CO_2-aqueous hydrazine reaction [Eq. (2.1)] at 30°C. The overall reaction is thought to include the following separate reactions:[20–23]

	$\Delta H_{25°}$ (kcal)	Estimated $\Delta H_{30°}$ (kcal)
$CO_{2(g)} + H_2O_{(aq)} \rightleftharpoons H_{aq}^+ + HCO_{3aq}^-$	−2.56	−2.14
$N_2H_4 \cdot H_2O_{(aq)} \rightleftharpoons N_2H_{5(aq)}^+ + OH_{(aq)}^-$	10.60	8.40
$H_{(aq)}^+ + OH_{(aq)}^- \rightleftharpoons H_2O_{(aq)}$	−13.82	−13.13
	−5.78	−6.87

The sum of the reactions is equal to Eq. (2.1). The value of −7.35 kcal, experimentally measured for the heat of reaction at 30°C, is in reasonable agreement with the estimate of −6.87 kcal calculated from the literature data.

Precipitates did not form in 1.0 and 3.0 *M* $N_2H_4 \cdot H_2CO_3$ solutions when these solutions were allowed to stand in sealed or unsealed containers at 25°C for a period of two weeks. Precipitation did occur, however, in 6.0 *M* solutions at pH <7.0. The precipitates were redissolved by adding small amounts of 6.0 *M* $N_2H_4 \cdot H_2O$ to the solution-precipitate slurry.

Hydrazine bicarbonate solutions should be stored in closed vessels or under a slight CO_2 atmosphere such that the partial pressure of the CO_2 in the cover gas is in equilibrium with the CO_2 dissolved in the $N_2H_4 \cdot H_2CO_3$ solution at a pH of 7.0. There is decomposition of the $N_2H_4 \cdot H_2CO_3$ in solutions left vented to the atmosphere; this can be detected by an increase in the pH of the solutions. The decomposition does not occur to a significant extent in samples stored in closed containers.

The total hydrazine concentration in aqueous solutions containing hydrazine, hydrazine bicarbonate, or a mixture of both can be determined by potentiometric titrations using HCl titrant. The concentration of hydrazine bicarbonate can be determined by a back titration method in which a known excess of NaOH is added and the sample is back-titrated with HCl.

Hydrazine, carbonate, and bicarbonate ions all exhibit spectra in the ultraviolet region; however, these spectra appear to be of little value for purposes of this work.

Solids have been obtained from 1.0 *M* $N_2H_4 \cdot H_2O$ solutions using a freeze-drying technique and from precipitation of 6.0 *M* $N_2H_4 \cdot H_2CO_3$ solutions. These solids have been subjected to elemental, infrared, and nuclear magnetic resonance (NMR) analyses. The infrared spectrum for the solids exhibits absorption peaks normally found in spectra for

bicarbonates.[24] The peak at 1700 cm^{-1}, which is characteristic for the carbonyl group in carbamates, is notably absent; however, a similar absorbance peak would have been expected for carbazate, if present. An NMR analytical method indicates that the compound in the solids contains six hydrogens. The elemental analyses of the solids are consistent with the solids containing primarily $N_2H_4 \cdot H_2CO_3$ along with a small amount of $N_2H_4 \cdot H_2O$ which could be present due to a slight $N_2H_4 \cdot H_2CO_3$ decomposition.

2.1.6 Nitrogen compound chemistry

F. J. Smith, M. R. Bennett, L. Maya, and D. R. McTaggart

The chemistry of the compounds formed between hydrazine and CO_2 has received little attention. The few references[25–27] which have been located indicate that hydrazine, like ammonia, forms a carbonate $[(N_2H_5)_2CO_3]$, bicarbonate $[N_2H_5HCO_3]$, and a carbamate $[N_2H_3COON_2H_3]$. The relative stabilities and kinetics of formation and breakdown for these compounds have not been fully investigated and no information exists for potential fuel reprocessing conditions. No information is available in the literature on the solubilities of the hydrazine carbonate, bicarbonate, and carbamate. Studies have been initiated to define solid and solution species in the N_2H_4-CO_2-H_2O system. Future work will establish the solubilities, stabilities, and kinetics.

Solids have been isolated from the N_2H_4-CO_2-H_2O system by sparging CO_2 gas through 6-, 10-, and 18-*M* hydrazine-water solutions at 25°C. The initial pH was about 12 and decreased to 7 as CO_2 neutralized the hydrazine. The white solids appeared after about 2 to 4 h for the 10 and 18 *M* hydrazine solutions, but about 18 h of continued CO_2 sparging was required to produce a precipitate in the 6 *M* hydrazine solution. All of the solids gave identical infrared spectra which are not characteristic of a carbamate. The solids are now being further characterized.

In previous work on the reaction between hydroxylamine nitrate (HAN) and nitric acid in the range 65–100°C, only the gaseous products were analyzed. The work is now being extended to include in-situ analyses of the liquid phase as well. This is being done by spectrophotometric means using ultraviolet cells as the containers for the reaction. The cells are sealed with serum caps to contain the gaseous products which are analyzed, as before, by gas chromatography. The cell holder in the spectrophotometer is equipped with a heated jacket so that the reaction mixture can be examined at temperatures up to 80°C. It was found that HAN in the concentration range 0.01 to 0.04 *M* in 3 *M* HNO_3 reacts spontaneously at room temperature to produce nitrous acid. The reaction is complete within 3 min. The yield of nitrous acid is about 0.2 mole per mole of HAN. The reaction also produces about 0.4 mole N_2O per mole HAN. The yields of N_2O and HNO_2 increase to 0.55 and 0.5 mole per mole HAN, respectively, at 75°C. Under these conditions, the nitrous acid concentration initially reaches a maximum and slowly decays, apparently due to thermal decomposition. This explains the detection of NO_x as gaseous products in previous runs.

The detection of nitrous acid in the reaction medium at room temperature is significant since HAN does not react rapidly with dilute nitric acid; however, it cannot be assumed that a reaction will not take place at higher concentrations.

The difference between the yield of nitrous acid at room temperature and at a higher temperature indicates the presence of an intermediate or a competing reaction. A preliminary qualitative test for the presence of hyponitrous acid in the reaction medium at room temperature was positive. This aspect will be explored further. However, it is evident that the reaction between HAN and nitric acid is much more complicated than what the stoichiometry proposed by Bercaw & McKibben[28] would indicate.

2.1.7 Fission product chemistry

L. Maya, J. A. Haas, and C. D. Bopp

Ruthenium. Nitrosyl ruthenium extracted into 30% TBP-dodecane undergoes a reversible reaction in the organic phase to produce a species not readily back-extracted into 3 *M* HNO_3. This property is used as an analytical tool to determine the proportion of the ruthenium present in that form and will be referred to as retained ruthenium. Apparently, this reaction involves displacement of aquo ligands in the inner coordination sphere by TBP. The following set of reactions is postulated as a possible mechanism leading to the formation of retained ruthenium:

$$RuNO(NO_3)_3(H_2O)_2 + 2TBP \rightleftharpoons RuNO(NO_3)_3(TBP)_2 + 2H_2O \qquad (2.6)$$

$$2H_2O + 2TBP \rightleftharpoons 2TBP\cdot H_2O \qquad (2.7)$$

$$RuNO(NO_3)_3(H_2O)_2 + 4TBP \rightleftharpoons RuNO(NO_3)_3(TBP)_2 + 2TBP\cdot H_2O \qquad (2.8)$$

A series of experiments was conducted to determine the effect TBP, water, and acid concentrations have on the proportion of retained ruthenium in the organic phase. Nitrosyl ruthenium solutions in nitric acid of different concentrations were equilibrated with TBP-dodecane solutions. The organic phase was allowed to stand for a 2-h period to complete the reaction, and was then stripped with fresh acid to determine the amount of retained ruthenium. The results obtained are given in Table 2.4. The proportion of retained ruthenium was used to calculate a quotient Q, which is the ratio of ruthenium in the retained and strippable forms. This value relates to a generalized expression describing the equilibrium in the following form:

$$Ru_s + nX \rightleftharpoons Ru_r + zY \quad ,$$

where the subscripts s and r refer to strippable and retained respectively.

$$Q = Ru_r/Ru_s \text{ and } K = Q\cdot(aY)^z/(aX)^n \quad ,$$

where a denotes activity

$$\log Q = n \log aX + \log K/(aY)^z \quad .$$

According to this expression, a linear correlation between the log of Q and the log of the TBP activity should exist if TBP is a reactant involved in the equilibrium as postulated in Eq. (2.8). The TBP activities in solutions such as those examined in these experiments are not available in the literature. Two sources for these values were considered. In both cases, assumptions had to be made since neither covered exactly the conditions examined. The first set of activities, given under a_1 in Table 2.4, is based on data of Alcock et al.,[29] who reported TBP activity coefficients for TBP-dodecane solutions of different concentrations in equilibrium with 1 M HNO_3. In this case, it is assumed that no large departures would occur by using these values for acid concentrations other than 1 M HNO_3. The second set of activities, given under a_2 in Table 2.4, is based on values derived by Davis[30] for TBP activities in aqueous nitric acid of different concentrations. Those values were corrected to account for the presence of diluent by using a factor derived from data obtained by Davis[31] in a study of the extraction of nitric acid by TBP-diluent mixtures.

It was found that plots of log Q vs log a_{TBP} gave a linear relation up to 3 M HNO_3 in the aqueous phase. A linear least-squares fit of the data obtained with 30% TBP and the a_2 values gave a regression coefficient of 0.99. Inclusion of the data for 20% TBP gives a regression coefficient of 0.96 which is further lowered to 0.89 and 0.82 after inclusion of the values for 60 and 100% TBP. The correlation is significant considering the wide variation in the TBP concentration. Similar regression coefficients were obtained using the a_1 values. The slopes of the plots are 4.86 for the a_1 values and 2.74 for the a_2 values. The uncertainties in this treatment preclude obtaining the actual stoichiometric ratio of TBP to ruthenium; but, it appears that this number is larger than one. The values of Q are inversely proportional to the nitric acid activity in the solution. This would suggest participation of nitric acid in the reaction, but that is highly unlikely. Rudstam[32] found that nitration and denitration of nitrosyl ruthenium in the organic phase are slow reactions with half-lives on the order of 20 h, which are much longer than the time required for the reaction considered. Apparently, the effect observed is due to the fact that nitric acid also reacts with TBP and, therefore, lowers the activity of the TBP which is the actual reactant. The water activity in the organic solutions is the same as the water activity in the nitric acid used in the equilibrations. The values of the water activities, which are somewhat constant in the range considered, are listed in Table 2.4; these were taken from a tabulation given by Davis.[33]

The results obtained at acid concentrations higher than 3 M do not follow the correlation between log Q and log a_{TBP}. It appears that the proportion of the retained ruthenium goes through a minimum at about 3 M acid. It is possible that beyond that concentration the reaction mechanism changes. Coincidentally, beyond 3 M acid the sum of the water and acid molarities in the organic phase exceed the TBP molarity. This effect is independent of the TBP concentration in the diluent. In the range $\geqslant 3M$ HNO_3, the formation of species

Table 2.4. Ruthenium retention in TBP-dodecane mixtures

Aqueous H^+ (*M*)	Organic H^+ (*M*)	Organic H_2O (*M*)	Water activity	"Free" TBP[a] (*M*)	TBP activity a_1	TBP activity a_2	Q[b]	Retained Ru (%)
				20% TBP (0.73 *M*)				
1.0	0.126	0.268	0.97	0.604	0.18	0.137	1.84	64.8
2.0	0.236	0.24	0.93	0.494	0.147	0.08	0.33	24.8
3.0	0.42	0.215	0.88	0.31	0.092	0.044	0.06	5.7
4.5	0.584	0.14		0.146			0.27	21.4
5.0	0.604	0.12		0.126			0.40	28.6
				30% TBP (1.09 *M*)				
0.5	0.081	0.49	0.985	1.014	0.233	0.213	5.58	84.8
1.0	0.21	0.52	0.97	0.885	0.204	0.164	3.85	79.4
2.0	0.45	0.51	0.93	0.645	0.148	0.096	0.9	47.5
3.0	0.62	0.396	0.88	0.475	0.109	0.053	0.2	17.0
4.5	0.86	0.27		0.235			0.285	22.2
5.5	0.95	0.2		0.145			0.37	27.0
6.0	1.0	0.183		0.095			0.43	30.0
				60% TBP (2.19 *M*)				
3.0	1.25	1.01	0.88	0.94		0.073	1.19	54.5
				100% TBP (3.65 *M*)				
3.0	1.93	2.48	0.88	1.72		0.113	5.29	84.1

[a] Free TBP = Molarity TBP minus molarity HNO_3.
[b] Q = retained/strippable.

such as $TBP \cdot HNO_3 \cdot H_2O$ and $TBP \cdot 2HNO_3$ becomes more important. It is apparent that the formation of retained ruthenium is complex and may involve a set of sequential equilibria, such as those described by Eqs. (2.6) and (2.7). In the range $\geqslant 3\ M\ HNO_3$, where uncomplexed TBP is exhausted, Eq. (2.7) might occur through the participation of $TBP \cdot HNO_3$.

The temperature dependence on the equilibrium concentration of retained ruthenium was examined for 30% TBP solutions obtained after equilibration with 3 *M* HNO_3. The following results were obtained:

Temperature (°C)	50	40	35	25	15	5
Q	0.051	0.111	0.175	0.205	0.285	0.63

A plot of $\ell n\ Q$ vs the reciprocal of the temperature in degrees Kelvin gives the relation $\ell n\ Q = 4451.7\ T^{-1} - 16.51$ from a least-squares regression with a coefficient of 0.94. Estimates of the thermodynamic functions are $\Delta H = -8.8$ kcal/mole and $\Delta S = -33$ cal/mole °K. These values are only indicative since the activities of other reactants or products are not considered in the quotient. However, no gross deviations are anticipated since the free TBP and water concentrations of the extracts are approximately constant in the temperature range examined. The decrease in entropy is consistent with the postulated set of reactions given above.

The kinetics of the reaction was examined once more, this time using a bath thermostated at 25 ± 0.1°C. The half-life for the conversion of retained ruthenium into a strippable form is 6.5 min, whereas the reverse reaction has a half-life of 29.7 min. These values refer to 30% TBP in equilibrium with 3 *M* HNO_3. It is calculated that the proportion of retained ruthenium will reach 50% of the equilibrium concentration after 6.2 min, 90% in 17 min, and 99% in 35.6 min. The half-lives for the reaction for a solution in equilibrium with 2 *M* acid were obtained in an independent run and were 10.0 and 12.5 min for the decomposition and formation of the retained species.

The processing implications of these findings are in line with operating procedures arrived at by empirical observations. Ruthenium contamination can be minimized by high loadings of the extract. This has the effect of lowering the proportion of free TBP available for ruthenium extraction and the subsequent transformation of a fraction of the ruthenium into a species not easily back-extracted; also, from the temperature effect observed, it is seen that a heated scrub would be beneficial. Furthermore, because of the kinetics of the reaction, use of fast contactors in the extraction step and longer equilibrations in the strip and scrub section would tend to improve ruthenium decontamination.

Zirconium. Monobutylphosphoric acid (MBP) appears to form two distinct complexes with zirconium depending on the initial ratio of the reactants and the acidity of the reaction medium. The MBP-to-zirconium stoichiometry of these complexes is either 2:1 or 1:1. Observations on the behavior of these complexes are summarized below:

The 2:1 complex is formed instantaneously in either an aqueous or organic medium. This complex is quite insoluble ($\sim 10^{-7}\ M$) and settles at the interface in mixtures of HNO_3

and 30% TBP. It has been found that this material adsorbs niobium and cesium. The 1:1 complex is formed under conditions of low acidity over a period of a few hours. The solubility of this compound in 30% TBP containing dialkylphosphoric acid exceeds 10^{-3} *M*. This complex cannot be back-extracted into nitric acid (0.5–3 *M* H^+), and it is only partially decomposed by treatment with 0.2 *M* Na_2CO_3. On the other hand, it can be adsorbed onto active carbon. The 1:1 complex can be converted into the 2:1 complex by the addition of one equivalent of MBP; but, the 2:1 complex cannot be converted into the 1:1 complex in the presence of excess zirconium. A scheme for crud control would involve the addition of inert zirconium to prevent the formation of the 2:1 complex and treatment of the washed solvent with active carbon to remove any 1:1 complex that had formed.

A more detailed description of the work performed during this reporting period is given below. The 2:1 complex was prepared in 6 *M* HNO_3 by adding zirconium to a MBP solution. The reaction took place immediately, forming a gelatinous precipitate. A sample of the washed and dried material gave an x-ray diffraction pattern with very diffuse lines indicative of small crystallites. The solubility of freshly precipitated material in 3 *M* HNO_3 is 5×10^{-7} *M*, and is 3.2×10^{-6} *M* in 30% TBP. The solubility decreases by about two orders of magnitude for a precipitate that has been aged overnight. An analysis of the 2:1 complex indicates the presence of one oxygen in excess of the eight required by the MBP-zirconium stoichiometry. The compound can be formulated as $ZrO(MBP)_2$ or $Zr(MBP)_2 \cdot H_2O$. The first formulation corresponds to a compound that would have two hydrogens that are potential sites for ion exchange, whereas no such property would be shown by the second. The infrared spectrum of the material shows that the formulation as the hydrate is the correct one. It appears that the water is bound in the lattice and possibly coordinated to the zirconium. Extensive drying did not eliminate the water bands. Small weight losses (~2%) were not due to water loss but rather to partial decomposition, as shown by the elemental analysis of the dried material. Furthermore, chemical tests with ^{134}Cs showed no ion exchange behavior; on the other hand, it was found that this compound adsorbed a significant amount of the cesium. Adsorption of niobium onto this material was shown previously, thus giving a reason for additional concern about the formation of precipitates in the form of interfacial crud because of their ability to adsorb additional activity. In studying the 1:1 complex, it was found that it could be converted to the 2:1 complex by adding one equivalent of MBP. On the other hand, the 2:1 complex could not be converted into the 1:1 complex after prolonged contact with excess zirconium. The 2:1 complex can also be prepared in an organic medium. The solubility of this material is similar to that of the complex prepared in an aqueous medium.

The 1:1 complex has been prepared in TBP-dodecane solutions by the addition of MBP in an amount not to exceed a 1:1 molar relation to zirconium extracts or by contact of MBP solutions in 30% TBP with an aqueous solution containing zirconium. The zirconium cannot be back-extracted into 3 *M* after aging the extract under conditions of low acidity $\leqslant 0.1$ *M* H^+. The extent of the retention has been established by the Martin-Kenny technique. An alternative technique to distinguish between the complexed and uncomplexed zirconium has recently been developed. This is based on the selective adsorption

of uncomplexed zirconium onto silica gel. The solubility of the 1:1 complex in TBP-dodecane containing butyllaurylphosphoric acid exceeds 10^{-3} *M*. The 1:1 complex formed in the organic phase is partially removed by a 0.2 *M* Na_2CO_3 wash, and is completely removed by adsorption onto active carbon. Attempts have been made to prepare the 1:1 complex according to a procedure described by Solovkin et al.[34] which requires 0.2 *M* HNO_3 as the reaction medium. Solids have been isolated but full characterization is not complete. Preliminary solubility determinations show a value of 6 X 10^{-3} *M* in 3 *M* HNO_3 and 4 X 10^{-4} *M* in 30% TBP.

2.1.8 Electrochemical methods evaluation

G. M. Brown

This task was initiated this report period to provide laboratory evaluation of electrochemical methods for selected processing applications. The initial emphasis is on the assessment of electrophoretic methods for clarifying dissolver solutions. Other areas of interest are in cleanup of organic solvents for recycle and removal of traces of plutonium from the organic phase in coprocessing flowsheets for fast reactor fuels.

In evaluating the feasibility of electrostatic methods for clarifying dissolver solutions, we have first analyzed the available data from the literature concerning the chemical composition of the insoluble residue from fuel dissolution. Approximately 0.2–0.3 wt % of $(U, Pu)O_2$ fuel is insoluble in the 6 *M* HNO_3 dissolver solution.[35] A chemical analysis of the residue[36] and an assessment[37] of the chemical state of fission products in UO_2 fuel have been previously reported. Noble metals and elements with an atomic number between 43 and 52 should be present as the zero-valent metals or mixed-metal alloys. Molybdenum will be present as the metal or as MoO_2, depending on the extent of burnup and the initial stoichiometry of the fuel (M:O ratio).[37] The reported chemical composition of the residue[36] is in agreement with these expectations. The small size of the particles suggests that they may be present as a colloidal dispersion. A review has been made of the literature relevant to the use of electrostatic methods for removing or breaking up colloidal dispersions in high ionic strength aqueous media. Based on this review, it is concluded that electrophoretic methods for fuel clarification are impractical in the high ionic strength media involved. A more detailed report describing this assessment is in preparation.

Electrodeposition or amalgamation is a viable alternative to a removal technique based on the zeta potential of a colloidal particle. An evaluation of these techniques will be made, particularly as applied to the use of porous electrodes with a flowing stream of dissolver solution. The surface composition of these metal particles is also important. A passivating oxide layer may exist on the surface of these particles which kinetically inhibits aggregation. Electrochemical reduction of this oxide coating should allow aggregation or amalgamation to occur more readily.

Ruthenium was found to be the principal component (~40 wt %) of the dissolver residue.[36] Current efforts are being directed toward methods of generating cold-simulated colloidal dispersions of ruthenium metal. The surface composition of these ruthenium particles in nitric acid solutions will be examined.

2.1.9 Evaluation of alternate extractants

W. D. Arnold and F. I. Case

Compounds similar to TBP, but with longer alkyl chains, appear from initial studies to have significant advantages over TBP for reactor fuel reprocessing.[38,39] Evaluation of tri(n-hexyl) phosphate (THP) and tri(2-ethylhexyl) phosphate (TEHP) is being emphasized. These extractants have negligible aqueous solubility, do not form a third phase at high thorium loadings, and have a lower tendency toward precipitate formation than TBP. Studies were initiated this quarter to compare their stability toward acid hydrolysis with that of TBP.

Thorium extraction isotherms. Isotherms for the extraction of thorium with 1.09 *M* TEHP in n-dodecane from 3 *M* HNO_3 are compared in Fig. 2.5 with isotherms obtained earlier with THP and TBP solutions. Two different batches of TEHP, one from FMC and one from Union Carbide were tested. Extraction behavior was about the same for both batches although the latter sample, which has an advertised purity of 99.6%, loaded with thorium to a slightly lower level than the FMC sample. The TEHP is a somewhat weaker thorium extractant than TBP and THP. As with THP, TEHP did not form a third phase at high thorium loadings. The nitric acid extraction in these tests was essentially the same for all three extractants, but the water extraction was on the order of TBP > THP > TEHP. There were no apparent differences in phase separation rates for the different solvents.

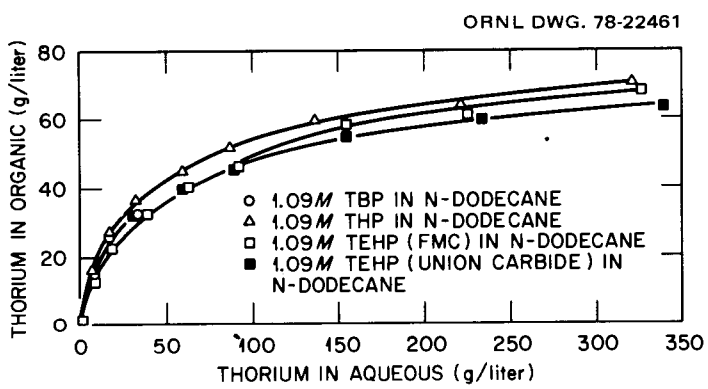

Fig. 2.5. Isotherms for extraction of thorium from 3 *M* HNO_3 at ~25°C.

Hydrolytic stability. A recent Russian study[40] showed that hydrolysis of TBP in nitric acid is about five times faster than hydrolysis of triisobutyl phosphate. This suggests that TEHP, which like triisobutyl phosphate has branching at the second carbon, may be more resistant to hydrolytic degradation than TBP.

Tests were initiated to compare the stabilities of TBP, THP, and TEHP. The solvents will be contacted with nitric acid and the rate of degradation determined by measuring the concentration of the dialkylphosphoric acid which is the principal degradation product.

Direct determination of this concentration by gas chromatographic and ion chromatographic methods is being investigated in the Analytical Chemistry Division. Both methods appear to have the capability for detecting the dialkylphosphoric acid concentration in the range of 10^{-5} and 10^{-3} *M* even though some problems have been encountered with each method in application to at least one of the candidate solvent systems.

Indirect methods for estimating the degradation product concentration are also being examined. Attempts to do this by measuring uranium retention after extraction and stripping with dilute acid were not successful. Better results have been obtained by measuring the extraction coefficient for ^{95}Zr-^{95}Nb. For 1.09 *M* TBP solution with added dibutylphosphoric acid (HDBP) in the concentration range 10^{-4} to 10^{-3} *M*, the extraction coefficient had about a 1.8 power dependence on the HDBP concentration. Results were about the same when the ^{95}Nb was removed from the traced solution (3 X 10^{-5} carrier Zr, 1 *M* HNO_3) prior to the extraction (Fig. 2.6). The ^{95}Zr-^{95}Nb extraction coefficients were 0.01, 0.05, and 2.5, respectively, for added HDBP concentrations of 0.0, 10^{-4}, and 10^{-3} *M*. Standard curves are also being obtained for the other solvent systems prior to the stability tests.

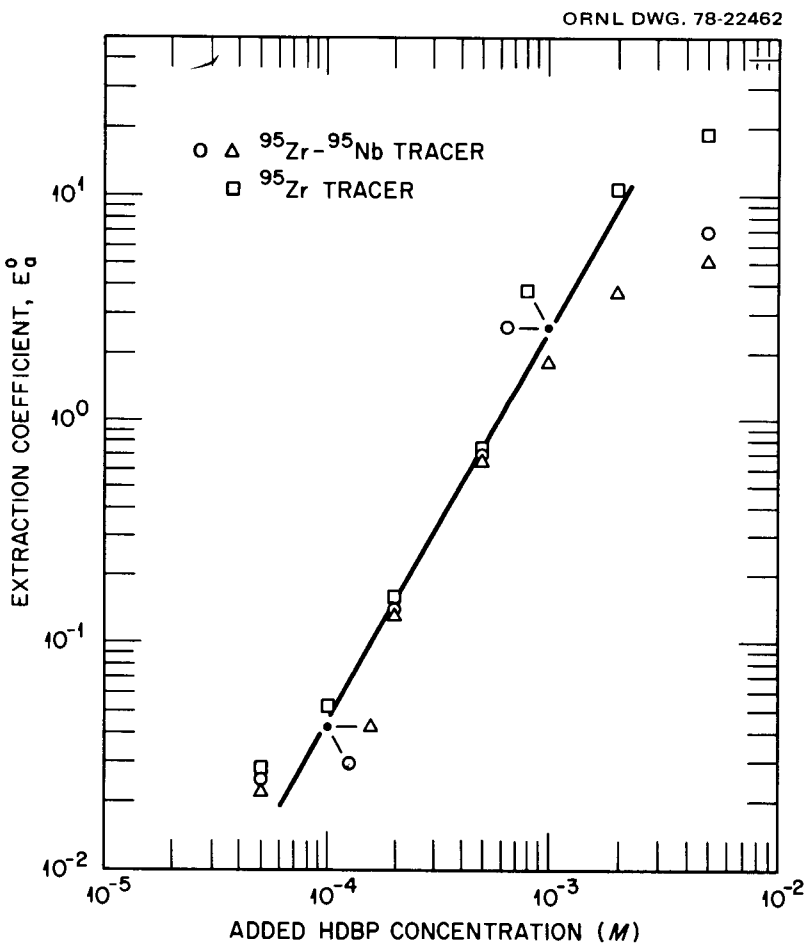

Fig. 2.6. Extraction of ^{95}Zr-^{95}Nb from 1 *M* HNO_3 with 30% TBP–HDBP solutions.

2.2 HOT-CELL DEVELOPMENT

V. C. A. Vaughen

2.2.1 Fuel procurement, fabrication, and irradiation history

J. H. Goode, E. C. Hendren, R. G. Stacy, V. J. Tennery, J. R. Travis, C. S. Webster, and V. C. A. Vaughen

Procurement of advanced fuels. A listing of irradiated (U, Pu)C specimens available at the Los Alamos Scientific Laboratory (LASL) was reviewed as a possible source of advanced fuels for future hot-cell studies. Most of the fuels on the list were early specimens fabricated by the United Nuclear Company; therefore, discussions are being held with LASL for the acquisition of newer, better-characterized specimens from more recent irradiations by Westinghouse and LASL.

Fabrication and irradiation of HEDL experiment PNL-3. The Hanford Engineering Development Laboratory (HEDL) experiment PNL-3 contained 37 unencapsulated fuel pins in a subassembly (S/A) fabricated by the Fast-Flux Test Facility/Liquid Metal Fast Breeder Reactor Driver Fuel Development Program at HEDL and irradiated in the fast flux of the EBR-2 reactor. The purpose of the experiment was to collect statistically significant data on swelling behavior, gas release rates, and general irradiation performance of fuel pins fabricated according to the initial reference design parameters and irradiated under approximate Fast Test Reactor (FTR) conditions.[41]

Irradiation history for the subassembly is:

	Charged in reactor		Discharged from reactor	
S/A	Run	Date	Run	Date
X051	32B	12/17/68	45B	9/16/70
X051A	52A	10/20/71	60A	1/10/73
X051B	63	5/23/73	70B	4/9/74

The final burnup was estimated to be about 60,000 MWd/t at a peak linear power of 5 kw/ft.

A total of 10 intact and one sectioned rods were released by HEDL for reprocessing studies at ORNL. Each of the rods, clad in 0.250-in. OD by 0.016-in. wall type 304 stainless steel tubing, contained a 13.5-in.-long fuel column (~80 g) of mechanically blended 75% UO_2–25% PuO_2 pellets and 0.5 in. of UO_2 insulator pellets at the top and bottom of the

fuel column. The uranium in the fuel and insulator pellets was of natural enrichment prior to irradiation. The rods in the S/A were cooled by the sodium of the reactor, which had an inlet temperature of about 700°F. Figure 2.7 is a schematic diagram and typical gamma scan of one of the rods, PNL-3-11.

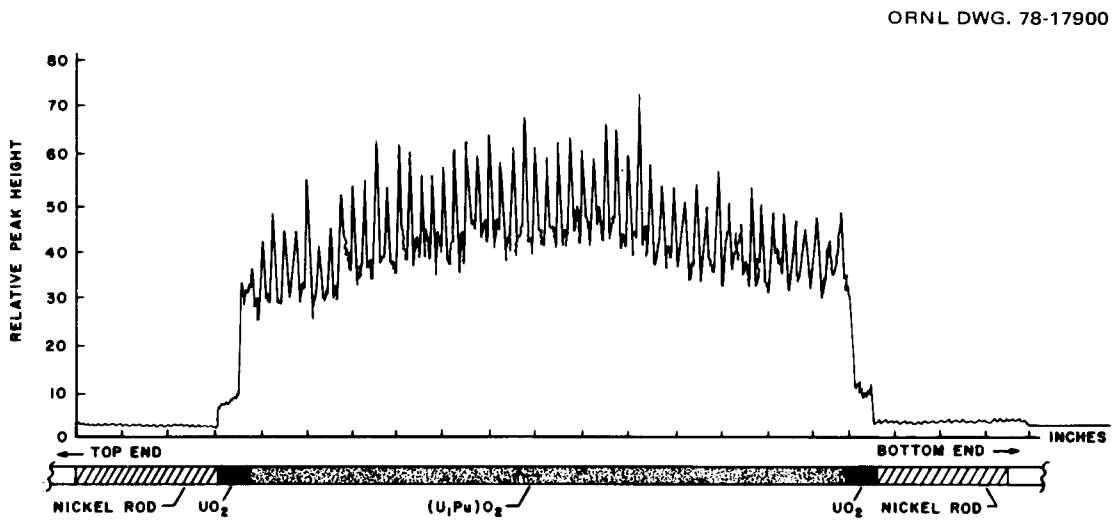

Fig. 2.7. Gamma scan and schematic cutting diagram for rod PNL-3-11.

For our reprocessing tests, the rods were divided into two main batches: those pins containing (U, Pu)O_2 fuel pellets sintered during fabrication at 1510 to 1540°C and those containing pellets sintered at 1650 to 1675°C, both sintered for at least 6 h. Rods selected for each batch were:

Sintering temperature	
1510–1540°C	1650–1675°C
Rod 3-1	Rod 3-4
3-6	3-11
3-9	3-12
3-28	3-13
3-31	3-17
3-35	3-18
3-50	3-19

The 15th rod, PNL-3-51, had a lower burnup and was held for other studies. Fission gas release measurements on six of the rods were reported earlier.[42]

Transfer of fuel and cleanout of storage canal. The Building 3597 storage canal was emptied of long-decayed fuel not needed for the hot-cell program. The fuel was transferred from under water into 3- to 8-in.-diam by 84-in.-long retrievable storage containers and then moved in a 14,000-lb shipping cask to the Solid Waste Storage Area (SWSA) for retention. The canal was emptied of water, scrubbed, and cleaned with a pressure washer; the walls and floor still require further decontamination before the pool can be decommissioned.

The fuel stored in the Building 4507 hot cells that was not to be used during FY 1979 has been sent to storage at Building 3597 (Hot Garden) and to the new fuel storage facility at the SWSA. Two trips with a 2000-lb cask and 12 trips with an 8600-lb cask were required to move the stainless steel storage container. In all, 60 kg of fuel was moved.

2.2.2 Flowsheet parametric studies

J. H. Goode, R. G. Stacy, G. K. Ford, E. C. Hendren, J. R. Travis, C. S. Webster, and V. C. A. Vaughen

Shearing. To supply increased amounts of sheared, irradiated reactor fuels, a new semi-automatic, single-rod fuel shear was designed and fabricated at ORNL (Fig. 2.8). An electrically-operated pump remotely controls a horizontal 1-in.-diam hydraulic piston attached to a hardened steel blade. The fuel rod segments are fed vertically by gravity. The fitting on the top of the shear is removable and can be changed to accept rods from 0.25 to 0.65

ORNL PHOTO. 5377-78

Fig. 2.8. Single-rod fuel shear with an automatic hydraulic pump.

in. in diameter. The sheared segments fall into a cup (not visible) stationed in the compartment directly below the feed point. The cut length is adjustable from 0.25 to 2.0 in. The steel cutting blade may be replaced remotely. The hydraulic cylinder is remotely removable and also interchangeable with a double-action cylinder should the pump ever be modified for hydraulic blade return. (A spring-action return mechanism is currently used.) Installation of the quick-disconnect hydraulic fittings will enable us to automate the manual fuel shear[43] which was installed in the cell two years ago. That will provide another semi-automatic shear as backup.

During this report period, 14 PNL-3 stainless steel clad rods (0.236-in. OD) containing 60,000 MWd/t (U, Pu)O_2 were sheared to supply fuel samples for future parametric studies. Rods with oxide sintered at 1500 to 1540°C were separated from those containing oxide sintered at 1600 to 1675°C. The ends of each rod segment (Fig. 2.7) were removed leaving approximately 12.5 in. for shearing into experimental specimens. Each rod was then subdivided into three sections; one section was sheared into 2-in.-long pieces, another was sheared into 1-in.-long pieces, and the remaining section was sheared into 0.125-in.-long cuts (for unclad fuel). Because the gamma scan profile shown in Fig. 2.6 indicated that burnup of the core (U, Pu)O_2 was slightly higher at the center of each rod, locations for the different cut lengths were alternated from rod to rod to ensure that the fuel sample sizes (1 in., 2 in. clad, and 0.125 in. unclad) were approximately uniform in burnup.

The new shear was used in preparing the 1-in.- and 2-in.-long clad fuel segments. The amounts of fuel dislodged from the cut sections were about the same for the two sintering temperatures (Table 2.5). However, there was some difference in sizes. The ends of the 1-in. and 2-in. pieces were generally clean cut; only a few had rough edges, and pillowing was minimal. The shorter cuts (~0.125-in. long) were made on the manual shear. The forces during the shearing of the PNL-3 were not measured because of a failed pressure gauge. A replacement gauge and pressure relief by-pass valve for the hydraulic pump were subsequently installed.

Table 2.5. PNL-3 (U, Pu)O_2 dislodged from cladding during shearing

	Sintering temperature	
	1500–1540°C	1600–1675°C
Total fuel weight, g	343.8	337.7
Total cuts[a]	35	33
Fuel weight dislodged, g	50.6	46.0
Total dislodged, %	14.7	13.6
Dislodged per cut, g	1.45	1.39
Dislodged per cut, %	0.42	0.41

[a] Number of shear cuts at 1-in. and 2-in. lengths.

Size distribution of dislodged fuel. The unclad fuel specimens, collected during shearing of the PNL-3 rods, were characterized according to sieve sizes. An automatic sieve shaker, which was designed and fabricated at ORNL, was installed in the hot cell for this purpose (Fig. 2.9). The skaker, which is mostly constructed of stainless steel, consists of a motorized vibrator plate on which either four 5-in.-diam sieves or six 3-in.-diam sieves can rest. A motor-driven tapping hammer contacts the retainer bar on top of the sieves.

ORNL PHOTO. 5378-78

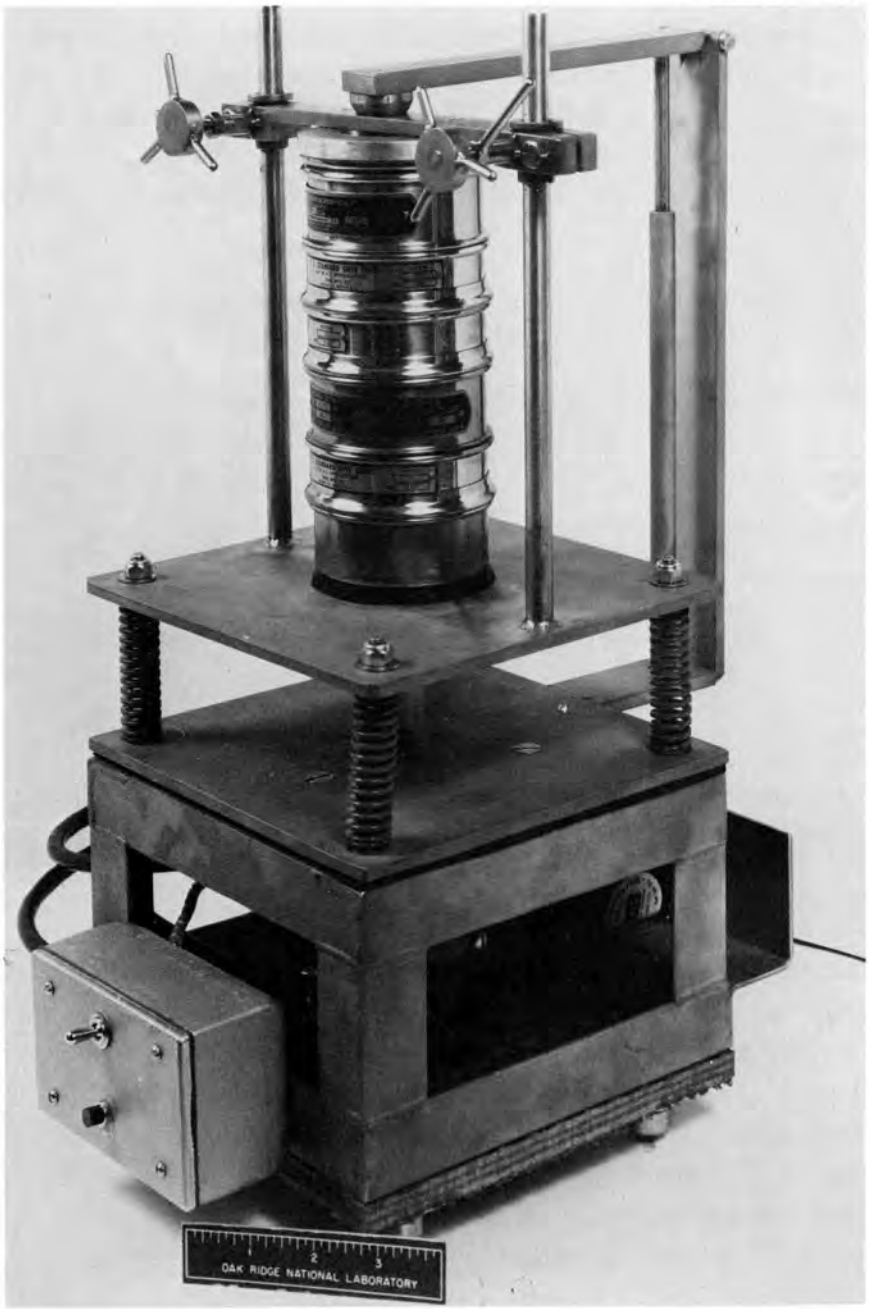

Fig. 2.9. Automatic sieve shaking device.

The fuel materials dislodged from the cladding during shearing was sieved to determine the size distributions. These materials were kept segregated by sintering temperature, but the materials from the 1- and 2-in. cladding cuts were combined for analysis. Although data interpretation is not complete, some preliminary results are reported (Tables 2.6 and 2.7). In general, the material from the lower sintering temperatures as well as the material completely removed from the cladding were found to have larger average sizes. The shapes of the distribution curves appeared to be very similar, and diverged from a straight line on a Rosin-Rammler plot to an asymptote value approaching half the original tubing dimension (~3 mm). The slopes of the straight line portions of the curve were clustered between about 40 to 50°. The same range of slopes was found for the NUMEC B-7 and C-13 rods studied earlier; however, the average sizes for NUMEC B-7 and C-13 were smaller.[44] For example, the amounts of the material larger than 500 μm were 60 to 70% for the NUMEC materials, whereas about 70 to 85% of the materials from these tests was larger than 500 μm.

Table 2.6. Size distribution of (U, Pu)O_2 dislodged from combined 1-in.- and 2-in.-long shear cuts

Mesh no.	Opening (μm)	Sintering temperature 1500–1540°C Wt., g	%	1600–1675°C Wt., g	%
14	1400	12.8	25.3	7.0	15.2
18	1000	11.2	22.1	8.6	18.7
20	850	5.9	11.7	7.2	15.6
35	500	7.5	14.8	8.9	19.4
50	300	4.0	7.9	4.8	10.4
100	150	3.7	7.3	4.2	9.1
200	75	2.1	4.2	2.2	4.8
	<75	3.4	6.7	3.1	6.8
Total		50.6	100.0	46.0	100.0

Voloxidation. A concluding voloxidation experiment was made in the series of UO_2 fuel tests using H. B. Robinson fuel (irradiated to 28,000 MWd/t). Experiments in the series have involved oxidation of clad and unclad fuel samples at different temperatures and oxygen feed rates. The current run was made using 1-in.-long pieces of Zr-4 clad UO_2, oxidized in pure oxygen at 480°C. The analyses and data reduction are not yet completed. As with unclad UO_2, oxidation in pure O_2 was completed in less than 1 h at the voloxidation temperature. Voloxidations in air made on similar samples took between 2 to 3 h to reach completion.[45] Preliminary tritium and ^{85}Kr analyses on samples from this experiment were typical for this UO_2 fuel. Tritium recovery in the off-gas system was high (>80% of the inventory was adsorbed on the silica gel trap); the krypton that evolved

during oxidation was only about 5% of the total fuel inventory. Release profiles for both radionuclides were measured as sharp peaks in the off-gas concentrations which closely paralleled the O_2 consumption peak.

Table 2.7. Size distribution of (U, Pu)O_2 dislodged from 0.125-in.-long shear cuts

Mesh no.	Opening (μm)	Sintering temperature 1500–1540°C Wt., g	%	1600–1675°C Wt., g	%
14	1400	86.6	44.3	62.0	34.0
18	1000	41.6	21.3	42.5	23.3
20	850	16.7	8.5	22.4	12.4
35	500	21.9	11.2	23.5	12.9
50	300	10.7	5.5	12.0	6.6
100	150	8.5	4.3	10.8	5.9
200	75	3.9	2.0	5.0	2.7
325	44	1.8	0.9	1.5	0.8
400	38	2.2	1.1	1.0	0.6
635	20	1.4	0.7	1.3	0.7
	<20	0.3	0.2	0.2	0.1
Total		195.6	100.0	182.2	100.0

2.2.3 Solution stability and precipitates

D. O. Campbell and W. L. Pattison

A new x-ray fluorescence analysis system was installed on an existing shielded scanning electron microscope for studying radioactive solids occurring in fuel reprocessing studies. Despite delays in operation resulting from inoperable components, x-ray spectra of test samples and one sample of dissolver residue were obtained. The instrument is not fully operational yet, but these tests were encouraging. Individual solid particles were identified in the dissolver residue consisting of zirconium cladding fragments, ruthenium and molybdenum from insoluble fission products, silicon which is a common impurity, and zinc from an unknown source.

2.2.4 Alternates to voloxidation

D. O. Campbell and W. L. Pattison

A series of experiments has been completed on the effectiveness of non-oxidative heat treatments for removing tritium from irradiated fuel, and of any related side effects; the results for tritium are summarized in Table 2.8 for UO_2 fuel from the H. B. Robinson reactor and in Table 2.9 for mixed oxide fuels. Some fission product analyses, however,

Table 2.8. Tritium release from H. B. Robinson UO_2 (%)

Temperature (°C)	Time (h)	2-in.-long clad fuel			Fragmented fuel		
		Argon	4% H_2-He	Vacuum[a]	Argon	4% H_2-He	Vacuum[a]
1000[b]	24	97					
1000	6	53			96		98.6
1000	24	80	80	89	99.95	99.87	99.98
1000	72	87			99.97		
900	24				92		
800	24				92	93.5	99.5
600	24				24		

[a]Partial oxidation from in-leakage of air could enhance tririum release.
[b]Thermocouple failed; temperature exceeded 1000° for 1–2 h, possibly 1150°C.

Table 2.9. Tritium release from fragmented mixed oxide fuel (%)

Temperature (°C)	Time (h)	4% UO_2-ThO_2			LMFBR
		Argon	4% H_2-He	Vacuum	Argon
1000	24	99.97	99.96	99.88	99.4
900	24	99.90	99.83		

are not yet complete. After heating at 1000°C for 24 h tritium release was typically 80% for clad fuel sheared into 2-in. lengths and about 99.9% for broken fuel fragments. The fraction released was smaller after 6 h and somewhat greater after 3 d. These observations are in agreement with expectations for a process controlled by diffusion. The higher release for the "vacuum" tests probably resulted from partial oxidation (to a composition intermediate between UO_2 and U_3O_8) because of in-leakage of a small amount of air. More extensive tests with fragmented fuel demonstrated a more rapid tritium release, and even at 800°C, 90% was released in 24 h. Material balance measurements indicate that tritium contained in the cladding is released, along with that in the fuel, at high temperatures. Tritium might be slowly removed from fuel assemblies by a heat treatment prior to shearing; however, an analysis of the residual cladding must be made to verify this.

Similar tests with a mixed oxide fuel that does not undergo a phase change when oxidized (4% UO_2 in ThO_2) demonstrated excellent tritium removal at both 900 and 1000°C. A single test with 20% PuO_2 mixed oxide LMFBR fuel gave a slightly smaller tritium removal (99.4%); however, there was so little tritium in this fuel initially, that the residual after heating was very small and, therefore, subject to some uncertainty. This LMFBR fuel lost more than 99% of its tritium during irradiation, and the test indicated that

another 99% can be removed; however, the benefit appears to be limited since only about 1% of the total tritium produced remains in the fuel and can be recovered.

2.2.5 Plutonium transfer kinetics
D. E. Horner, J. C. Mailen, and R. G. Yates

The solvent extraction kinetics of actinides and fission products are being examined to assist in predicting the behavior of solvent extraction systems. During this quarter, additional information on the behavior of uranium and thorium was obtained and an experimental plan was developed for measuring kinetic behavior of plutonium in solvent extraction.

Recently obtained information has shown the following:

1. The activation energy for the aqueous-to-organic transfer of thorium is 5 kcal/mole; that for the organic-to-aqueous transfer is 8.1 kcal/mole. The difference of these two quantities gives the heat of reaction of thorium nitrate with TBP: –3.1 kcal/mole. This is similar to that found earlier for the reaction of uranyl nitrate with TBP: –3.7 kcal/mole.

2. The pseudo-first order rate constants for thorium increase as the 1.3 power of the TBP concentration in the aqueous-to-organic direction and as the –0.7 power in the organic-to-aqueous direction.

3. An extensive examination of data from Lewis cell tests indicated that the results from this method tend to be slightly lower than those obtained in drop or Kenics mixer tests. A new starting technique and a new sampling technique have been introduced which give more reproducible data and produce excellent agreement in uranium transfer rate constants determined by the Lewis cell and other techniques. In the new starting technique, the cell is set up and stirring begun with barren phases; a concentrated solution of the ion under study is then introduced into one or the other phases. By doing this, the interface is not disturbed by the introduction of a bulk phase. A new sampling technique allows sampling the phases near the interface to partially alleviate effects caused by relatively poor bulk phase mixing. Sampling near the interface was shown to result in increasing the calculated values of the rate constant to correspond with those found by the drop method. The indications are favorable for obtaining good plutonium transfer kinetics by the modified procedure.

A topical report entitled, *Interphase Transfer Kinetics Using the Drop Method, Lewis Cell, and Kenics Mixer. I. Uranium,* is being prepared.

2.2.6 Plutonium flowsheet development
W. D. Bond and B. A. Hannaford

The objectives of this work are to develop and evaluate solvent extraction coprocessing flowsheets with plutonium-containing solutions prior to their testing in the Solvent

Extraction Test Facility hot cells and to evaluate new process options. Three 16-stage mini-mixer-settlers in alpha glove boxes comprise the principal experimental apparatus.

Work that was accomplished included the installation and preliminary testing of the mixer-settlers in an open glove box. The liquid feed tanks and the liquid metering capillaries were installed and calibrated, and the satisfactory operation of the metering pumps was demonstrated.

Three mini-mixer-settlers, recently fabricated according to drawings provided by Savannah River Laboratory, were fitted with 0 to 3000 rpm servo motors and installed in a 6-ft-long glove box (Fig. 2.10). Flexible connections of 1/8-in.-diam Teflon tubing permit the introduction of aqueous and organic streams to any chosen mixing chamber. Organic flow is generally right-to-left, with transfer pumps providing a means for automatically controlling and recording the flow between mixer-settler banks A (extraction) and B (partitioning), and between B and C (stripping). The metered aqueous phase flows from left-to-right in individual mixer-settler banks, overflows a weir, and travels to one of the three glass receivers located in the connecting glove box. The receivers are maintained at a slightly negative pressure.

ORNL PHOTO. 5608-78

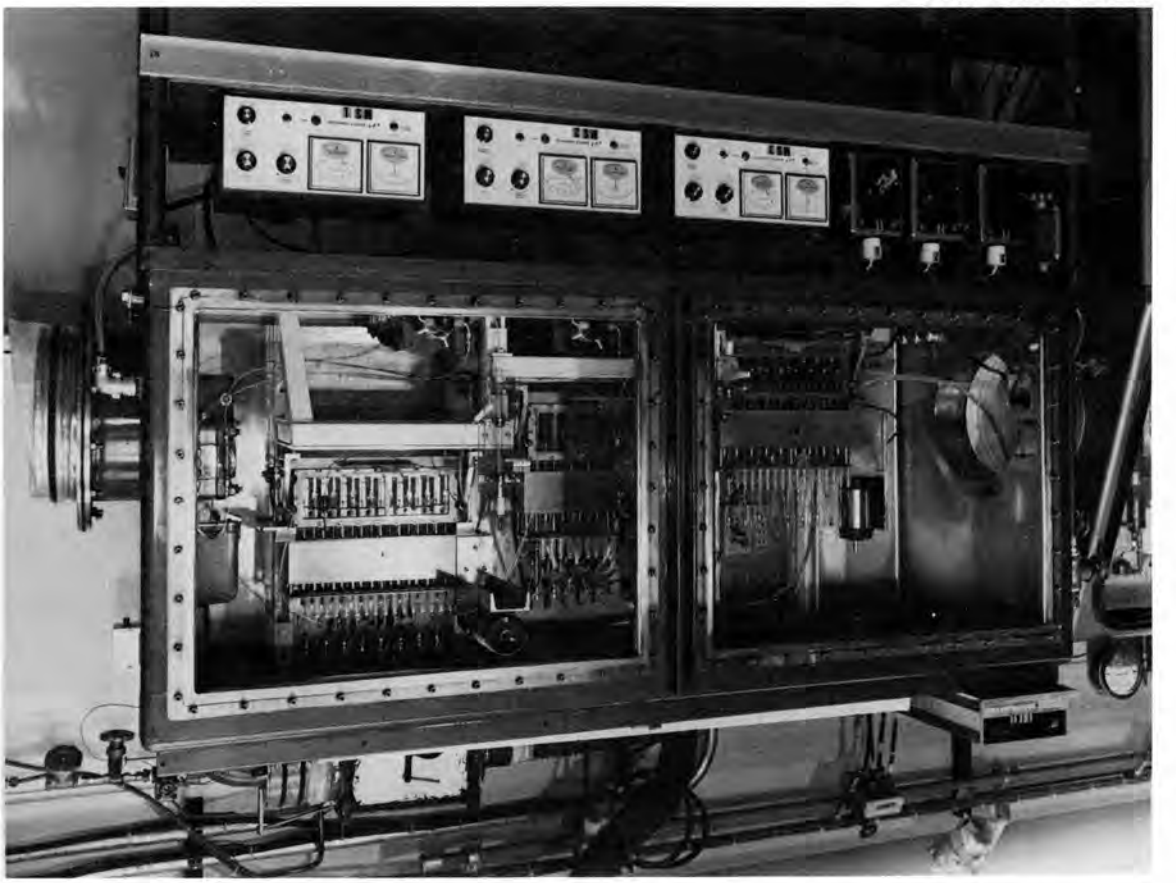

Fig. 2.10. Installation of three mini-mixer-settlers in an open glove box. Heater controls and agitator drive controls are located below the glove box.

Samples of aqueous and organic phases from individual settling chambers are withdrawn via 1/16-in.-diam dip tubes which are connected to an array of 32 Vacutainer holders located above the gear box on each mixer-settler bank. Because of the very low aqueous phase holdup in each settling chamber, perhaps 2 out of about 10 ml total volume, the sample volume must be limited to approximately 1 ml. Since this size Vacutainer was not available, a device was designed and fabricated which evacuates 10-mm-diam X 65-mm-long Vacutainers to the absolute pressure required to draw any desired volume up to 3 ml. In general, only the eight settling chambers on the front side of each bank will be sampled; samples will be withdrawn at the conclusion of a period of steady-state operation.

Required liquid feed rates to the mixer-settlers fall in the range 0.2 to 4 ml min^{-1}. The metering systems were designed around a valveless pump head (Model RH 1CKC, Fluid Metering Inc.) with variable displacement of 0.01 to 0.10 ml per revolution. Gear-head servo motors (0—100 rpm) were coupled to the pump heads. Modifications to the servo motor controllers (586BV, Electrocraft Corp.) and interfacing with Foxboro pneumatic recorder-controllers were specified by J. M. Madison and D. R. Miller, of ORNL Instrumentation and Controls Division. The nearly completed liquid metering system is shown in Fig. 2.11. Although delivery of needed pressure-to-voltage transducers was incomplete, all pumping control circuits were operable. Calibration of all capillaries with water, dilute HNO_3, or 30% TBP-NDD showed the response to be linear over the full range of flow rates. A housing was installed around the differential pressure (d/P) cells and capillaries to provide a thermostated air bath for stable capillary calibrations.

Hydraulic tests were started with the mixer-settlers in order to establish the workable range of aqueous and organic flow rates and stirrer speeds.

2.2.7 Application of the SEPHIS-MOD4 program to flowsheet evaluation

A. D. Mitchell and V. C. A. Vaughen

The SEPHIS-MOD4 computer program is a model of the solvent extraction operations and is designed to be used in flowsheet development and to predict the effects of variations in operating conditions. Cold uranium mixer-settler tests were run to investigate coprocessing flowsheets which might be used to produce a product stream with 20% plutonium and 80% uranium. The SEPHIS-MOD4 program was used to determine the experimental conditions which would give the desired product, and the experimental concentrations in the mixer-settlers were compared with the calculated values. The conditions for these runs (PS-5 and PS-6) were previously reported.[46] The aqueous uranium and nitric acid profiles for the partial partitioning mixer-settler bank in run PS-5 are shown in Figs. 2.12 and 2.13 respectively. The lines indicate the concentrations calculated by SEPHIS-MOD4, whereas the crosses signify the experimentally determined concentrations. The results are very close throughout the bank for both components. These results indicate the usefulness of SEPHIS-MOD4 in scouting new flowsheet conditions, and also that the flowsheet conditions used in PS-5 will result in the desired uranium concentration in the product streams.

Unfortunately, the high nitric acid concentration in stages 10 to 16 for run PS-5 would probably prohibit the complete reduction of plutonium by hydroxylamine. SEPHIS-MOD4 was used to determine how this acidity might be reduced while still stripping only

ORNL PHOTO. 5607-78

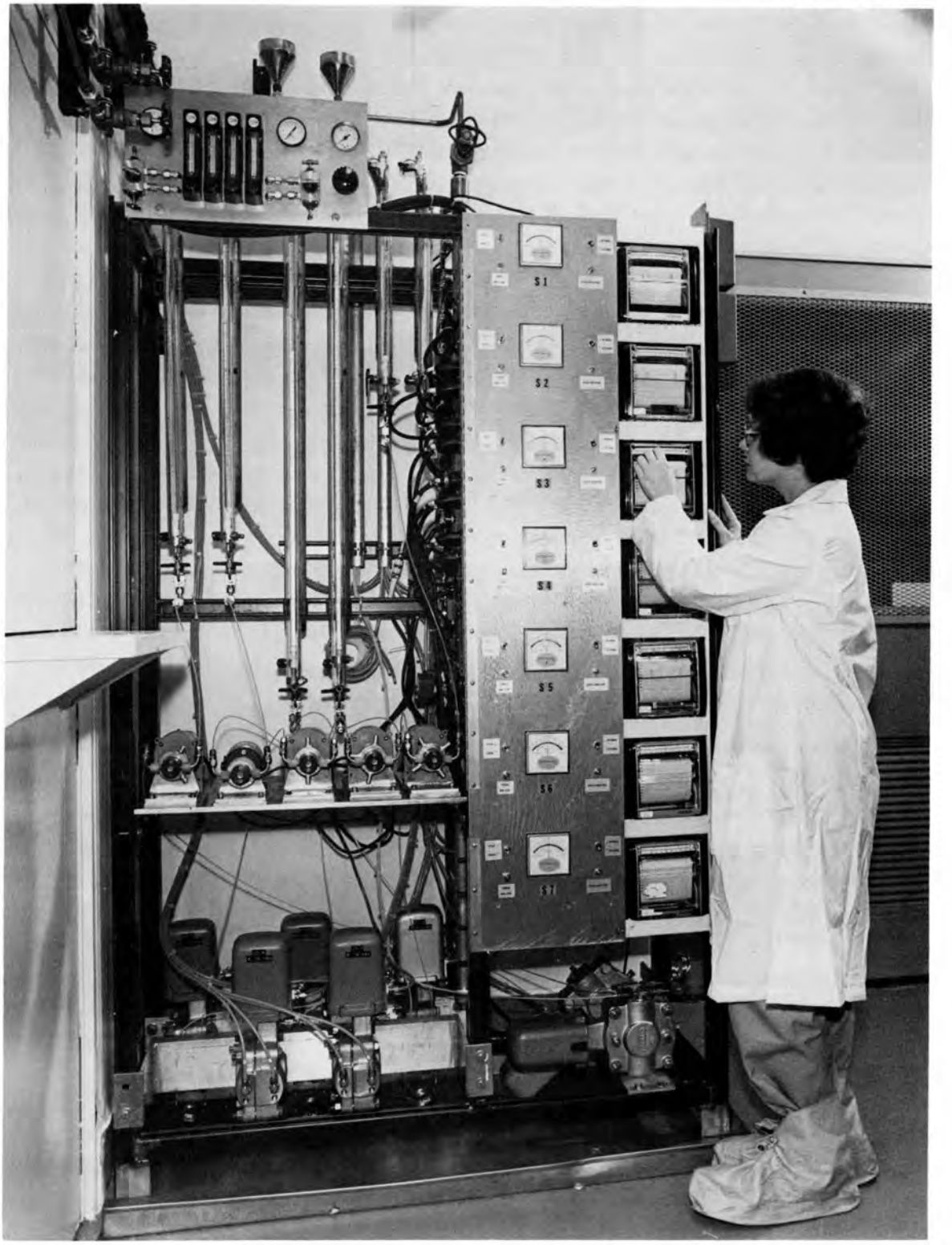

Fig. 2.11. Liquid metering system. Flow-measuring capillaries (0.042-in. ID, 4-15 ft. long) permit automatic control and recording of flow rates.

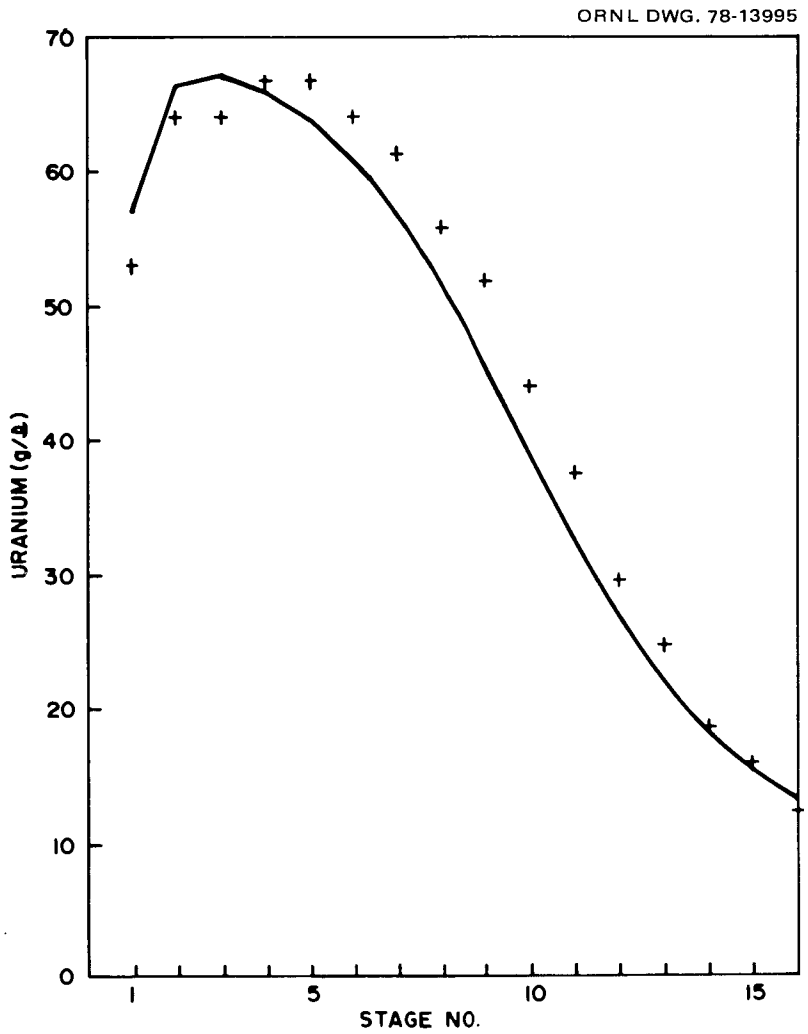

Fig. 2.12. A comparison of the predicted (line) and experimental (crosses) uranium concentrations in the aqueous phase in the partial partitioning bank of run PS-5.

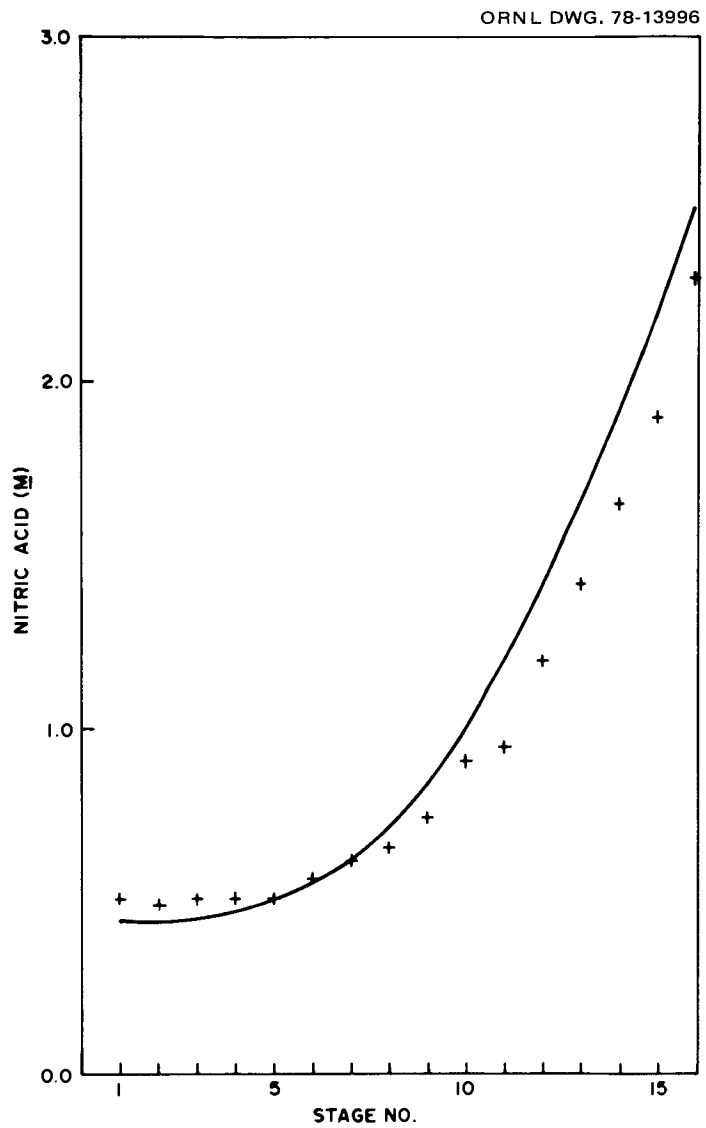

Fig. 2.13. A comparison of the predicted (line) and experimental (crosses) nitric acid concentrations in the aqueous phase in the partial partitioning bank of run PS-5.

5% of the uranium into the aqueous product; the resulting flowsheet conditions were used in run PS-6. The uranium and nitric acid profiles for both the extraction and partial partition banks are shown in Figs. 2.14 and 2.15. The uranium profile was predicted reasonably well by SEPHIS-MOD4, although the experimental results show more refluxing of the uranium than was anticipated. The nitric acid profile was predicted very well. The acidity in stages 15 and 16 is still above 1.0 *M* which may hinder the reduction of plutonium, but this profile is an improvement over that in PS-5.

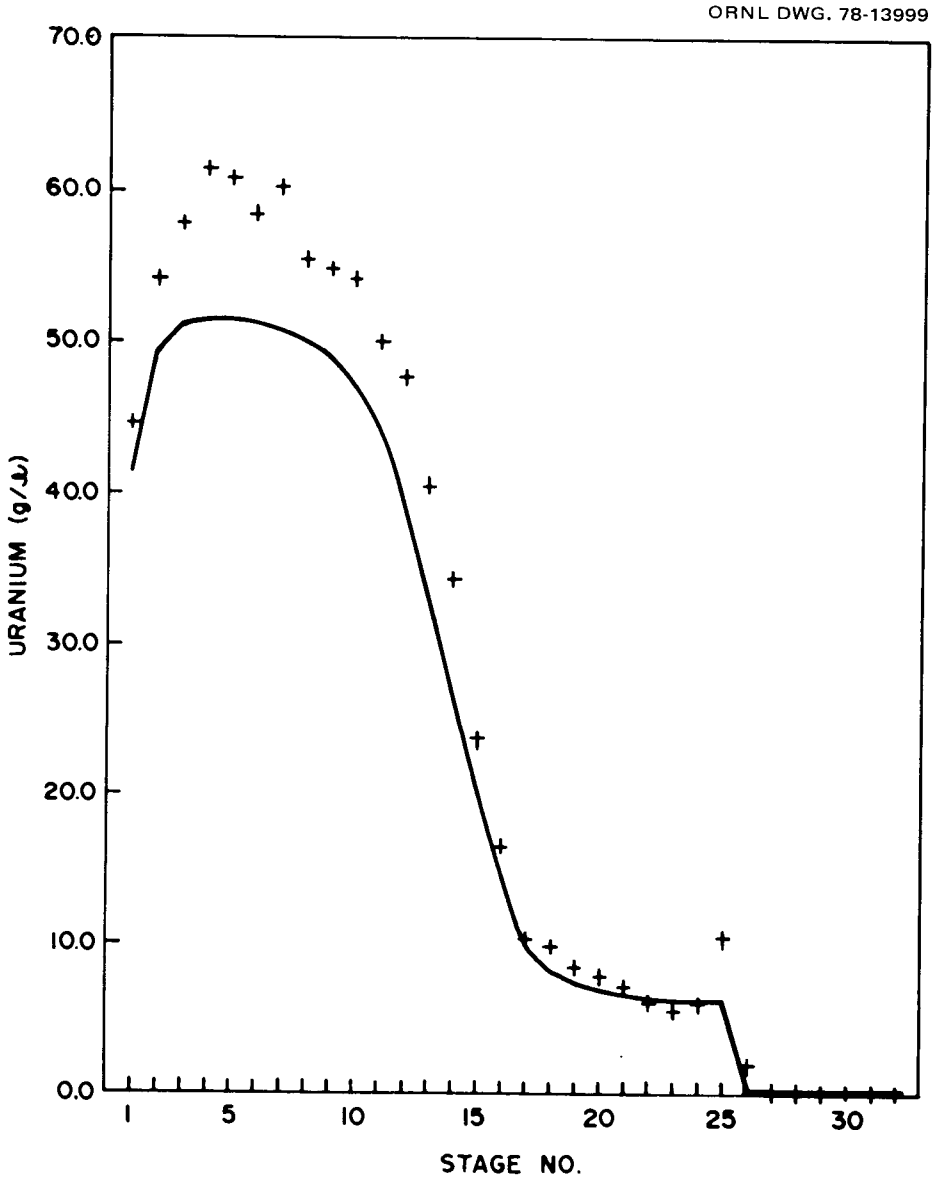

Fig. 2.14. A comparison of the predicted (line) and experimental (crosses) uranium concentrations in the aqueous phase of run PS-6.

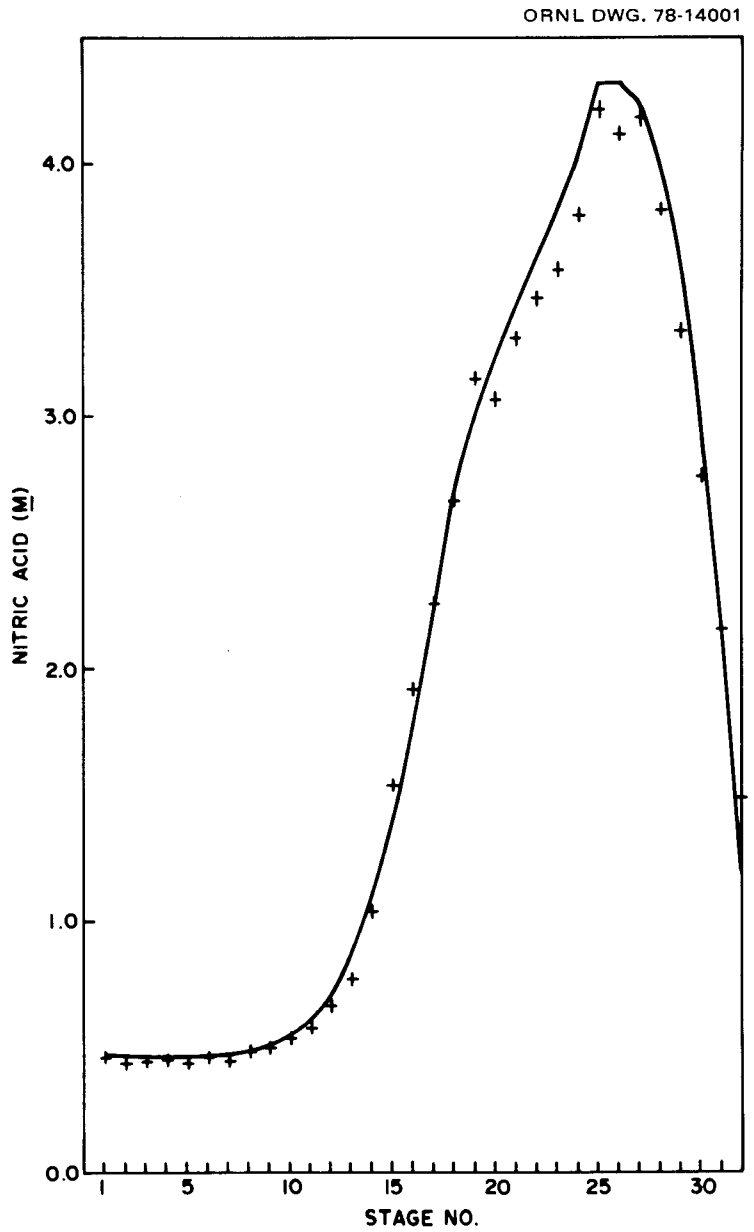

Fig. 2.15. A comparison of the predicted (line) and experimental (crosses) nitric acid concentrations in the aqueous phase of run PS-6.

2.2.8 Analysis of data from the reduction of plutonium(IV) by hydroxylamine

A. D. Mitchell and V. C. A. Vaughen

Experimental rate data for the reduction of plutonium(IV) by hydroxylamine have been obtained by M. H. Lloyd and S. E. North.[47,48] A rate expression for the reaction

$$2NH_3OH^+ + 2Pu^{+4} \rightleftharpoons 2Pu^{+3} + N_2 + 2H_2O + 4H^+ \qquad (2.9)$$

has been reported by G. S. Barney[49]

$$-\frac{d[\mathrm{Pu(IV)}]}{dt} = k\,\frac{[\mathrm{Pu(IV)}]^2[\mathrm{NH_3OH^+}]^2}{[\mathrm{H^+}]^4[\mathrm{Pu(III)}]^2\,(0.33 + [\mathrm{NO_3^-}])^2}\ . \tag{2.10}$$

To determine whether the ORNL experimental data can be fitted with this rate expression, the rate equation was integrated by assuming constant acidity and nitrate concentration during the course of the reaction. The resulting equation gives an integrated value dependent upon the initial reaction mixture and the fraction of the Pu(IV) which was not reduced after a period of time. For a good fit, a plot of the integrated value vs time should follow a straight line with a slope determined by

$$\text{slope} = k'e^{-E/RT}\,\frac{[\mathrm{Pu(IV)}]_{\mathrm{init}}[\mathrm{NH_3OH^+}]^2_{\mathrm{init}}}{[\mathrm{H^+}]^4(0.33 + [\mathrm{NO_3^-}])^2}\ . \tag{2.11}$$

This slope can be used to determine the dependence of the rate on the various variables in the system, and to calculate a value for the rate constant, k'.

The reduction data were integrated and plotted to determine how well they matched the form reported by Barney.[49] (The results were also compared with calculations from SEPHIS-MOD4 which employs the Barney kinetics.) In many cases, the plots were similar to that in Fig. 2.16. The straight line for the experimental data confirms the applicability of the assumed rate equation. The difference in the slopes of the experimental and calculated lines indicates a discrepancy in the value used for the rate constant.

Further analysis of the data dealt with the rate dependence on temperature, acidity, and hydroxylamine. The activation energy (E) reported by Barney[49] was confirmed and the fourth order dependence on acidity was confirmed except for cases of $[\mathrm{H^+}] < 0.3\ M$. It is thought that in this low acidity region, the reduction reaction may be impeded by plutonium hydrolysis. The second order hydroxylamine dependence was not confirmed.

2.3 SOLVENT EXTRACTION

L. J. King

2.3.1 Solvent Extraction Test Facility

L. J. King, D. E. Benker, J. E. Bigelow, F. R. Chattin, E. D. Collins, D. B. Owsley, R. G. Ross, H. C. Savage, R. C. Shipwash, B. J. Strader, C. E. Waddell, and L. C. Williams

The Solvent Extraction Test Facility (SETF) is cell 5 of the Transuranium Processing Facility (TRU) is being used to evaluate and demonstrate 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.

During this period, the installation of the SETF equipment was completed and radioactive operation was begun.

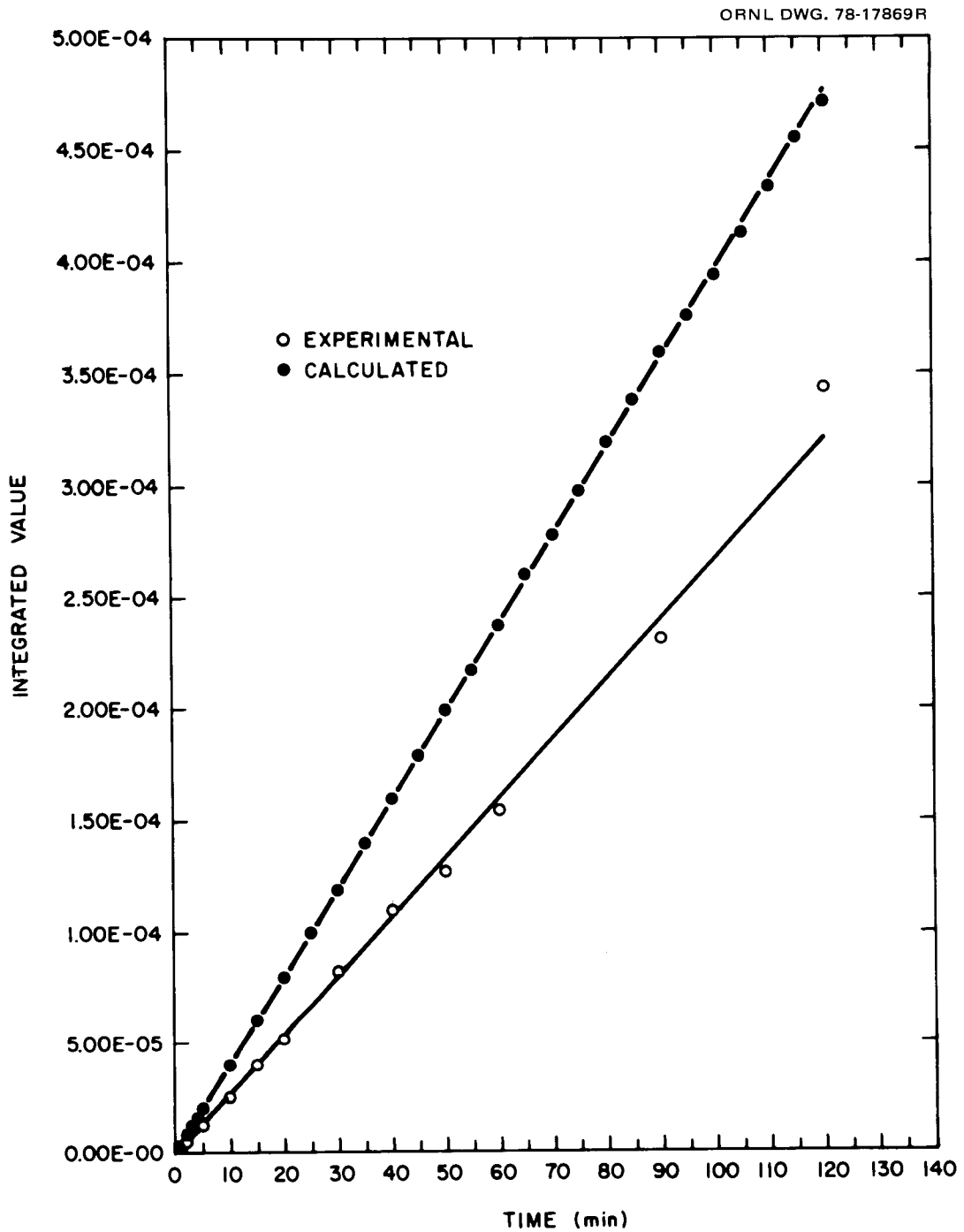

Fig. 2.16. Comparison of plutonium reduction data with an assumed kinetic form and calculated values from the same form.

Installation. The third of three equipment racks was installed in cell cubicle 5. All of the jumper-line connectors were installed and all lines were tested for routing and leak-tightness.

Figures 2.17 through 2.19 are photographs of the three equipment racks that are in cell cubicle 5. The rack frames are approximately the same size — 3 ft wide and 6 ft high.

The major components of the mixer-settler rack (Fig. 2.17) are the three 16-stage mixer-settler banks and the two drive motors on each bank. The two glass vessels (T-550 and T-551) are effluent-solution handling tanks. The multistage sampling devices were not installed when this photograph was taken.

The dissolver and feed equipment rack is shown in Fig. 2.18. The dissolver is located near the bottom of the rack to the left. The perforated basket, which holds the 1- to 2-in.-long pieces of sheared fuel, is shown attached to the basket lifting device and partially withdrawn from the top of the dissolver. The feed adjustment tank (T-556) is located within the rack frame to the right of the dissolver and the condensate collection tank is located behind the dissolver. The centrifuge (for feed clarification) is located at the bottom of the rack just to the right of the dissolver. The centrifuge can be replaced by a low-porosity filter. The two glass tanks in the upper portion of the rack are dual feed tanks. The feed flow rate is controlled by varying the air pressure applied to the feed tank in response to an electronic signal from a differential pressure transmitter in the feed line. The transmitter is located on the extreme left of the bottom of the equipment rack.

Figure 2.19 is a photograph of the solution-transfer, ion-exchange, and sampling equipment rack.

Equipment checkout. The UO_2 pellets (4 kg of natural uranium) were dissolved and processed to test the dissolution equipment and procedures, the feed adjustment equipment and procedures, the in-cell radioactive feed system, and the mixer-settlers.

A dissolving procedure developed at SRL was used. The UO_2 pellets were placed in the dissolver and covered with 3 *M* HNO_3. Then, approximately 10 *M* HNO_3 was added while holding the temperature at 50°C. This was followed by a digestion period at 90°C for 1 to 2 h. The specific gravity instrumentation was found to be useful for monitoring the dissolution rate.

The electronic flow transmitter for the hot feed flow control system was calibrated using water and uranyl nitrate solution. The flow control system was given an extended test (12 h) by metering uranyl nitrate (300 g/liter of uranium) from one feed tank to the other and observing the depletion and buildup rates in the tanks. In this system, the flow rate is controlled by varying the air pressure on the feed tank in response to signals from a differential pressure transmitter in the feed line. The flow rate (~0.5 liter/h) varied within ±5% as the feed tank liquid level decreased from full to empty. Following hydraulic tests using HNO_3 solutions and solvent, the solvent extraction equipment was tested for operability using the uranyl nitrate solution. The mechanical and hydraulic performance was satisfactory.

ORNL PHOTO. 5466-78

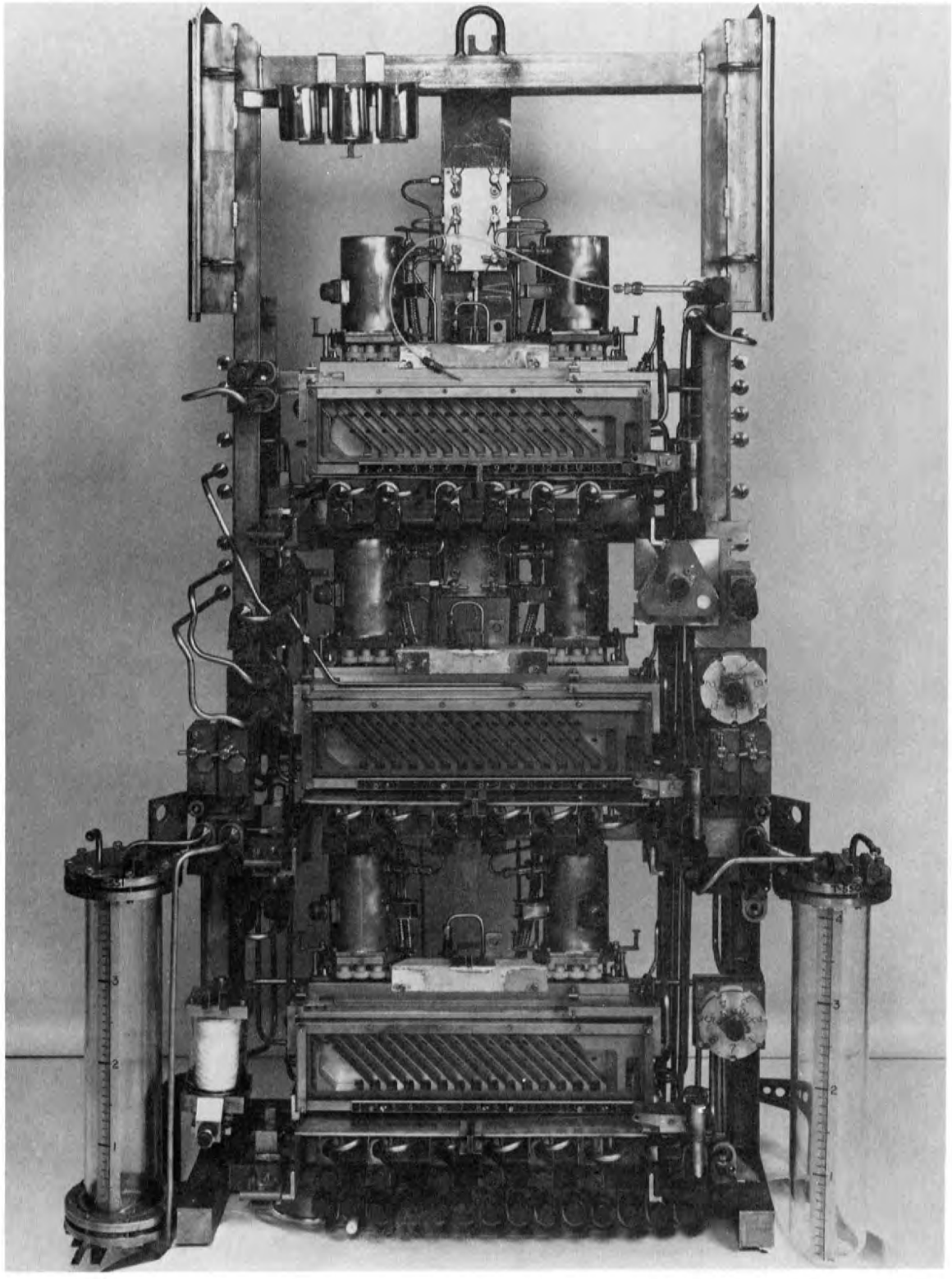

Fig. 2.17. Mixer-settler equipment rack in the Solvent Extraction Test Facility.

ORNL PHOTO. 5181-78

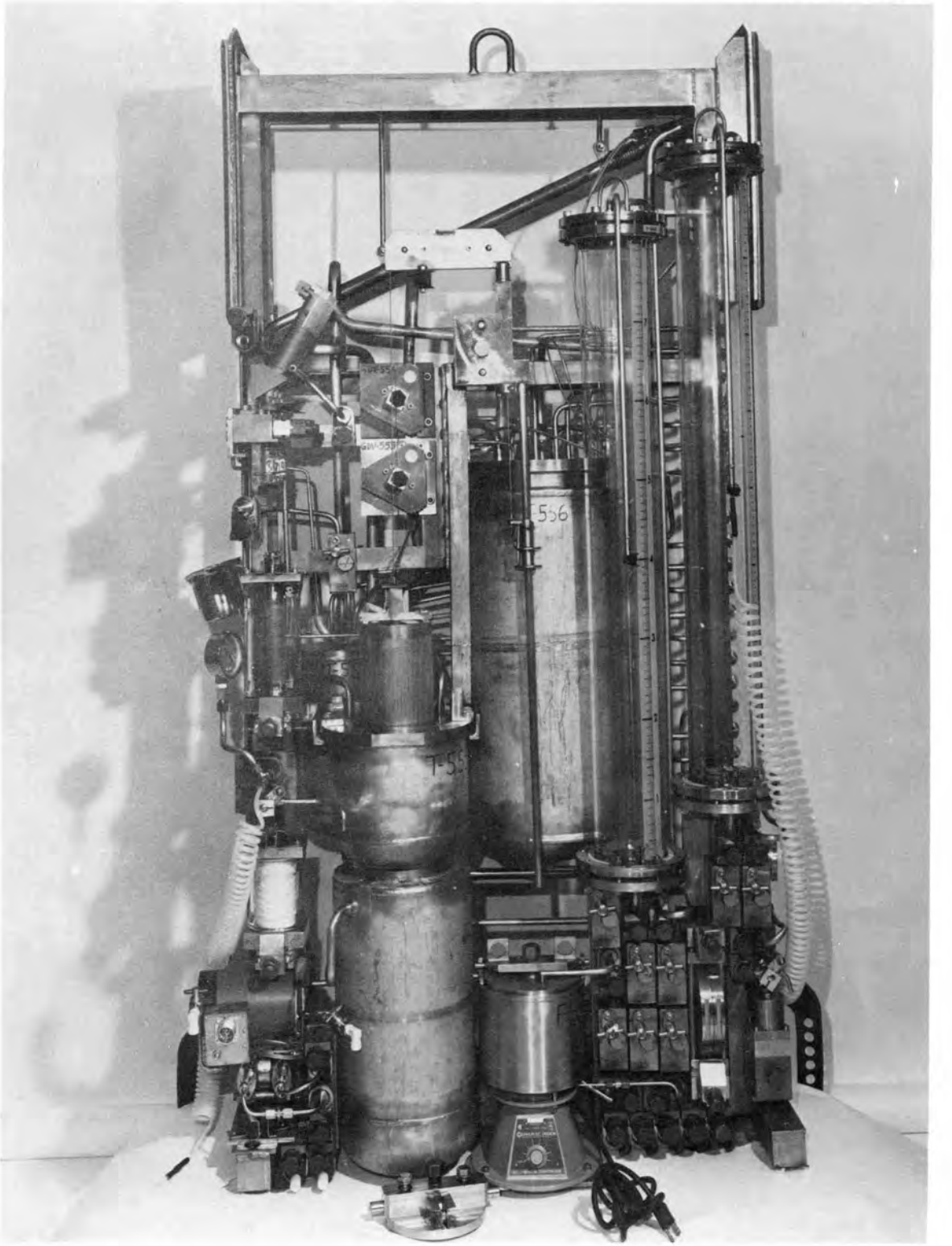

Fig. 2.18. Dissolving and feed system equipment rack in the Solvent Extraction Test Facility.

ORNL PHOTO. 3336-78

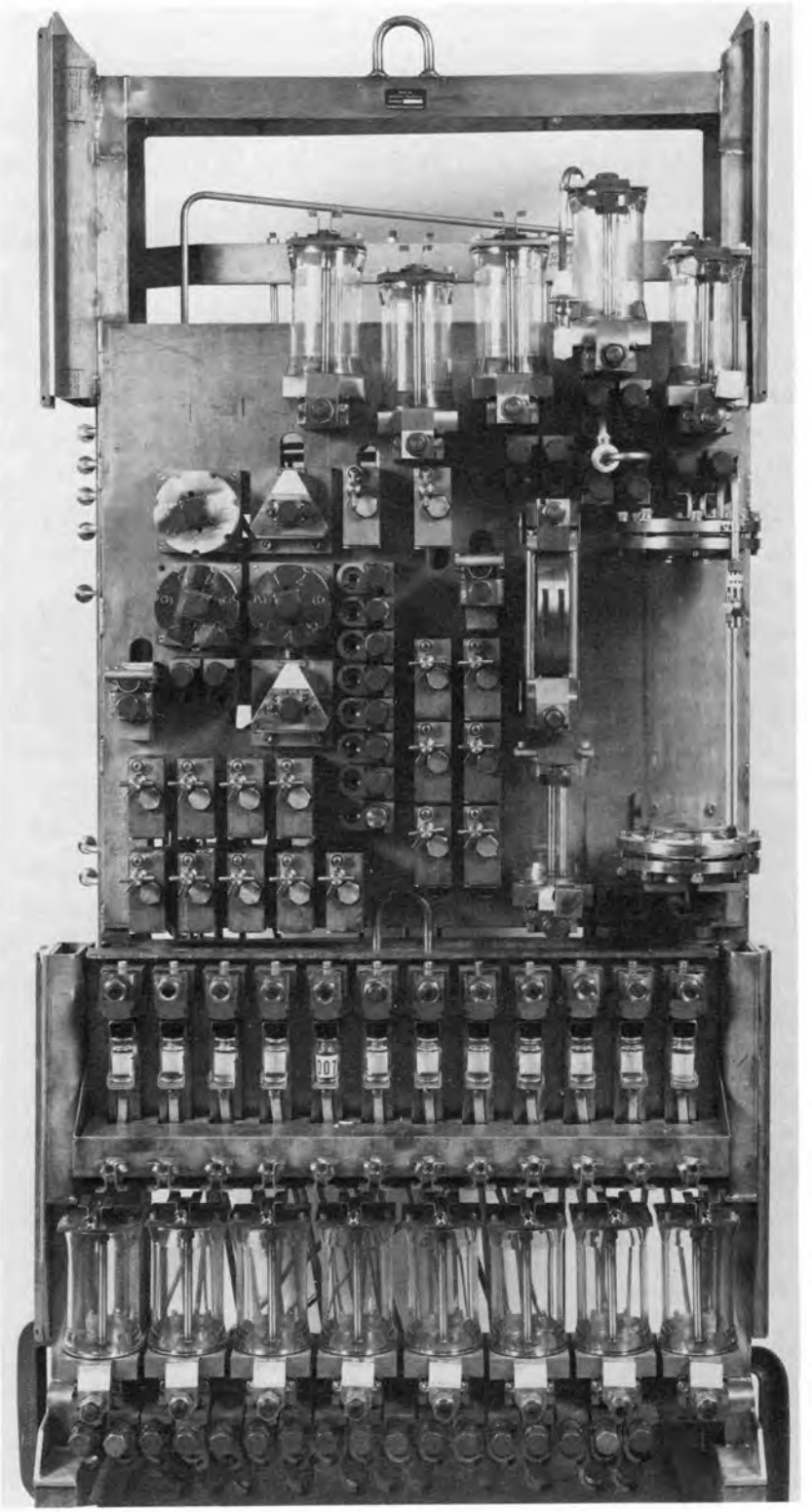

Fig. 2.19. Solution transfer, ion exchange, and sampling equipment rack in the the Solvent Extraction Test Facility.

Boiling tests in the plutonium product evaporator (T-503) demonstrated that the heating and cooling systems were adequate, evaporation rates were adequate, and there was no entrainment problem.

Radioactive operation. Hot operations during this period included (1) eight dissolutions of heavy metal (2 kg per batch) from sheared fuel rods which had been irradiated to 31,364 MWd/MTU in the H. B. Robinson-2 PWR and cooled for 4.5 yr; (2) four feed adjustments (4 kg of heavy metal per batch) to approximately 3 *M* HNO_3, 300 g/liter of uranium, and greater than 95% Pu(IV); (3) clarification of the four batches of adjusted feed solution by filtration through a precoated, etched-disc filter having 1-μm pores; and (4) three sets of solvent extraction runs, in which there were a total of eight test periods.

The three sets of solvent extraction runs were intended to demonstrate a variety of flowsheet concepts, some of which are well-established and others newly developed. These included (1) "high DF" extraction-scrub conditions, (2) partitioning of the plutonium along with enough of the uranium to form a product in which the plutonium content is from 5 to 12% or from 25 to 40% of the heavy metal content, and (3) costripping of all the uranium and plutonium.

In the extraction-scrub bank, most of the run conditions were kept constant throughout all the tests. Only the acidity of the scrub solution was varied. Seven extraction and nine scrub stages were used. Solution flow rates were constant (0.4 liter/h feed, 1.6 liters/h solvent, and 0.17 liter/h scrub). The solvent was 30% TBP in normal paraffin hydrocarbon (NPH) and the feed concentration was 300 g/liter of uranium and 3.0 *M* HNO_3. The mixer-settler temperature was held constant at 40°C. The acidities of the scrub solutions were 1.0 *M*, 0.5 *M*, and 3 *M* HNO_3 in the first, second, and third sets of tests respectively.

During all of the tests, the third mixer-settler bank was used to contact the waste solvent with a solution of 2 *M* HNO_3–0.05 *M* $Fe(SO_3NH_2)_2$ to strip any residual plutonium prior to disposal of the solvent. The run conditions for the second mixer-settler bank varied widely as is discussed below.

During the first set of tests, the scrub solution in the extraction-scrub bank was 1.0 *M* HNO_3. The amount of uranium costripped with the plutonium in the partitioning (second) mixer-settler was controlled by means of inextractable nitrate salting. There were four tests in the set, each lasting about 15 h, and each using a different strip solution. The number of partitioning stages (4), the temperature (40°C), and the flow rates (strip-solvent ratio was 0.17) were held constant. The strip solutions used in the four tests and the desired product compositions were:

Test	Composition	Desired Product Pu in U-Pu (%)
1A	2 *M* hydroxylamine nitrate (HAN) – 0.1 *M* HNO_3	25–40
1B	0.5 *M* HAN–0.1 *M* HNO_3	5–12
1C	0.035 *M* HAN–2 *M* NH_4NO_3–0.2 *M* HNO_3	25–40
1D	0.035 *M* $Fe(SO_3NH_2)_2$–2 *M* NH_4NO_3–0.2 *M* HNO_3	25–40

The objective of the second set of tests was to investigate the use of an organic bank-extractant (30% TBP in normal paraffin hydrocarbon) in the partitioning mixer-settler bank to regulate the amount of uranium in the U-Pu product. Essentially all of the uranium and plutonium was stripped from the pregnant organic (from the extraction-scrub bank) in five stages using a 0.2 *M* HNO_3 strip solution containing 0.1 *M* hydroxylamine nitrate and 0.05 *M* hydrazine. Then, a fraction of the uranium was back-extracted in three stages using 30% TBP in NPH. The temperature was held constant at 40°C. The flow ratios and the desired product compositions for the two tests in the second set were:

Test	Flow ratios		Desired Product Pu in U-Pu (%)
	Strip-solvent	Strip-backscrub	
2A	0.16	0.75	25–40
2B	0.16	2.1	5–12

During the third set of tests, the uranium and plutonium in the pregnant solvent from the extraction-scrub bank were costripped. This test was divided into two parts. In part A, the plutonium was stripped as Pu(IV) using 0.1 *M* HNO_3; and in part B, the plutonium was reduced and stripped using 0.1 *M* HNO_3–0.05 *M* HAN–0.025 *M* N_2H_4 solution. The mixer-settler temperature (40°C), the number of stages (16), and the flow rates (strip solvent ratio was 1.15) were held constant.

The feed preparation operations (dissolution, feed adjustment, and clarification) were performed without significant difficulty. The precision of flow control, both for the hot feed stream and the cold chemical solutions, was generally within 5%, as expected; however, intermittent incidents of plugging were somewhat troublesome. Effluent stream handling methods (flow rate measurement, batch diluent washing of aqueous solutions, and solution transfer) were satisfactory. The sensitivity of the five in-line alpha detectors was not uniform and will require some adjustment; however, some readings were obtained and will be useful for data interpretation. The multistage sampling device, using pre-evacuated TRU sample bottles, operated satisfactorily.

Evaluation and analysis of the data are in progress.

2.4 PRODUCT CONVERSION

D. J. Crouse

2.4.1 Direct thermal conversion

J. T. Knight and C. R. Sherman (Rockwell-Hanford Operations)

Eight test runs were completed in the batch-stirred thermal reactor which is designed to permit thermal denitration and subsequent hydrogen reduction in the same vessel. Nitric

acid solutions of uranium nitrate, plutonium nitrate, and uranium-plutonium nitrate (25% Pu) were calcined in air at temperatures in the range of 430 to 465°C. The resulting oxide powders were reduced in flowing 96% N_2–4% H_2 at 750 or 840°C.

In this system, the feed solution (100 or 200 g of heavy metal per liter) is pumped into the reactor which, initially, is empty except for a small amount of oxide heel. The feed solution flow rate in the runs was varied from 1/4 to 4 ml/min with the optimum range being 2 to 3 ml/min. With this low flow rate, run times were long with low capacity throughput. Also, phase transformation (liquid to mastic to solid aggregate) and viscosity changes caused the agitator to stall occasionally resulting in discontinuous denitration and nonuniform temperature distribution. Sampling data from these first denitration test runs are incomplete.

Minor equipment changes including redesign of the agitator blade, spider, and crucible are now under way to alleviate the stall or "lockup" problem. Other changes include using a higher torque motor with improved motor to shaft torque transfer, surface hardening of the agitator blade and crucible, and improved filter and condenser designs.

Results of the DTA and TGA tests performed earlier with uranium, plutonium, and uranium-plutonium solutions have been difficult to interpret. Recent analyses indicate that sodium and aluminum impurities are present at concentrations that may be high enough to have affected the test results. However, the results indicate that a flowable, ceramic-grade oxide may be produced by direct thermal denitration. Final conclusions regarding the quality of the oxide product and the efficiencies of the thermal denitration test must await more complete analytical results.

Plans for continued testing and analyses include:

1. more precise control and measurement of temperature, gas flow rate, and solution feed rate;
2. performance of test runs with purified plutonium nitrate feed solution;
3. additional time-temperature, feed rate, and concentration studies to optimize the calcination and reduction parameters;
4. resolution of present inconsistencies in the DTA-TGA results and in analytical results for O/M, crystallinity, and impurities.

2.5 ANALYTICAL CHEMISTRY DEVELOPMENT

D. A. Costanzo

2.5.1 Chemical methods development

D. A. Costanzo

Potentiometric titrimetry (C. S. MacDougall). Development of the potentiometric thorium assay was completed. A literature survey of analytical techniques for the determination

of plutonium was made, and a potentiometric method was selected for application to ORNL tasks. This technique consists of oxidizing the plutonium to Pu(VI), reacting the plutonyl with excess Fe(II), and titrating the remaining Fe(II) with standardized Ce(IV). The necessary reagent chemicals were procured; solutions were prepared and standardized. A Mettler modular titration system was installed in a hot facility in Building 2026; a series of titrations was then performed to verify that the equipment was operational.

Liquid and gas chromatography (D. L. Manning). Liquid and gas chromatographic separation capabilities are being established to assist the solvent extraction studies. A liquid chromatograph was assembled from components consisting of a Milton Roy mini-pump, a Rheodyne high-pressure injection valve, and ultraviolet plus differential refractive index detectors. The stationary phase is a 25-cm Partisil-10 ODS-2 reverse-phase column; methanol-water is the mobile phase. The gas chromatograph (GC) is a Schimadzu model 6A with a model E1A data processor for data readout and a Schimadzu model R-11 recorder for display of chromatograms. The GC uses a Dexil-300 column which is noted for its stability at high temperatures.

A study of elution parameters with GC using the Dexil-300 column is in progress. Methyl derivatives of dihexyl phosphate and trihexyl phosphate have been prepared and run through the chromatograph. The data obtained show that well-defined separations of trihexyl phosphate, dihexyl phosphate, and n-dodecane can be obtained.

2.5.2 Mass spectrometry development

J. A. Carter

Spark source mass spectrometry development (R. J. Warmack, D. L. Donohue, W. H. Christie, and J. A. Carter). The initial checkout of the mass spectrometer to be used for high-gamma spark source analysis was begun this period and the first mass spectra have been recorded from this instrument.

Mass spectrometry of uranium and plutonium (R. L. Walker, W. R. Musick, and J. R. Sites). The evaluation of the isotope dilution (IDMS) procedure for determining the amount of uranium and plutonium in spent dissolver solutions has been completed using the two-stage mass spectrometer for mass analysis, the resin bead sample preparation, and the filament loading method. The precision of measurement on synthetic samples using the hot-cell facilities is ±1% RSD. The two-stage mass spectrometer was upgraded recently with the installation of new electronic counting equipment and an interface-controller-PDP-11 computer system for data accumulation and processing. It is anticipated that the internal precision using this equipment will improve the precision over that of the old counting system. Future work will be directed toward the determination of the overall precision with the new system.

2.5.3 Nuclear and radiochemical methods development
J. R. Stokely

Technetium-99 by neutron activation (L. C. Bate and J. R. Stokely). A method for determining ^{99}Tc through neutron activation analyses has been developed and is currently being evaluated. Technetium-99 is separated from other fission products by a carrier-free separation procedure prior to determination by activation analysis. The separation involves a cyclohexanone extraction of ^{99}Tc from basic carbonate media. Technetium is stripped into water by diluting the cyclohexanone with carbon tetrachloride. Small amounts of remaining fission products are scavenged with iron hydroxide. Technetium is concentrated on an ion exchange resin which is air dried. The ^{99}Tc-loaded resin is irradiated for 11 s to produce ^{100}Tc, which is determined by gamma-ray spectrometry. The decontamination factor from fission products is greater than 10^4, and it is possible at the present time to determine ^{99}Tc at the 10-nanogram level. The sensitivity of the method is presently limited because of chloride impurities in the ion-exchange resin, which causes an interference in the activation analysis. Efforts are under way to find ultra-high purity resins that could be used in the analysis to improve sensitivity.

2.5.4 X-ray spectrometry development
R. S. Crouse

Scanning electron microscope (R. S. Crouse). Installation and checkout of an energy dispersive x-ray spectrometer system (EDX) for the scanning electron microscope (SEM) in the High Radiation Level Examination Laboratory has been completed. Problems that were encountered with the software were corrected by the vendor, and personnel training for operation of the system has been completed.

The heavy-metal collimator which protects the Si(Li) detector of the EDX system has been put in place and a "hot" residue sample on a graphite mounting has been introduced into the SEM for the initiation of work with a group of radioactive samples now on hand. The graphite mounting of samples is used because it does not introduce extraneous substrate peaks which can complicate data interpretation.

X-ray fluorescence development (J. H. Stewart, Jr.). A survey of quantitative x-ray fluorescence (XRF) techniques has been completed for the analysis of materials of the nuclear fuel cycle, particularly fuel reprocessing. The XRF has certain inherent advantages which make it a powerful analytical tool: it is sensitive and accurate, independent of chemical form and isotopic composition, it is rapid and nondestructive, and it is capable of analyzing complex mixtures without chemical separations because of the limited number of fluorescence emission lines available.

Two distinct techniques, the wave-length dispersive XRF and the energy-dispersive XRF have been studied in order to evaluate special analytical advantages of each with the significant capital equipment differential. A preliminary study has been made using existing equipment at the Y-12 Plant laboratory. This study showed that both techniques were viable candidates and should be evaluated further.

A more detailed experimental program was designed which would be performed in the applications laboratories of equipment vendors. The experiments were conducted to:

1. Demonstrate the ability of the system to detect multiple elements at the μg/g concentration level.
2. Demonstrate the ability to provide rapid quantitative analyses of selected elements of specific interest in complex fission product (FP) solutions.
3. Determine the feasibility of using the U Kα and the Th Kβ emission lines for the analysis of uranium and thorium at the μg/g level employing a ^{57}Co excitation source.
4. Determine the feasibility of the quantitative analysis of zirconium in the presence of variable quantities of uranium.
5. Verify the use of filter paper substrate in the accurate analysis of uranium as suggested by early Karlsruhe documents.[51]

The experimental program was successful. The fission product solutions were prepared to contain 22 elements at or above 10 μg/g, and 18 were detected. The computer program was able to deconvolute the complex FP spectrum and perform quantitative analysis for U, Th, Zr, Sr, and Rb. (These elements were chosen because they cause serious inter-element effects as well as direct line interferences; therefore, they vigorously test the XRF equipment and software programs.)

Zirconium was accurately determined in zirconium-uranium standards in TBP. Uranium and thorium were easily detected at 50 μg/g with the ^{57}Co source. Uranium was measured at the 98.4 keV Kα1 line, and thorium was measured at the 105.6 keV Th Kβ1 line.

The accuracy claimed for the use of filter paper as sample substrate was not obtained in these experiments. According to the personnel at Lawrence Livermore Laboratory, they have been notably unsuccessful in attaining the accuracy claimed in the Karlsruhe report.

The results of the experimental series show that the less costly energy-dispersive analysis system is suitable for the requirements of the Consolidated Fuel Reprocessing Program.

2.6 MATERIALS COMPATIBILITY

J. C. Griess

Most of the experimental program for this task is performed at Battelle Columbus Laboratories and at Westinghouse Advanced Reactor Division under subcontracts with Oak Ridge National Laboratory. At the end of fiscal year 1978 both contracts expired; the Battelle contract was renegotiated in early November, however, the Westinghouse subcontract has not yet been approved. Consequently, the amount of work performed during this quarter has been limited.

2.6.1 Corrosion tests at Battelle Memorial Institute

J. A. Beavers, R. E. Visintainer, and W. K. Boyd (Battelle Memorial Institute, Columbus, Ohio)

Since the results presented in the last report[52] showed that zirconium alloys are subject to stress corrosion cracking in 70 to 98% HNO_3 from room temperature to the boiling point, most of the tests during this quarter were concerned with titanium and tantalum which are promising materials for construction of Iodox process equipment. Constant-extension-rate stress corrosion cracking tests in 90 to 99% HNO_3 and in commercially available red fuming nitric acid (~5% H_2O) from room temperature to the boiling point failed to produce cracks in either material. Similarly, no cracks developed in the vapors above boiling 100% HNO_3 when the metal temperature was 130°C.

Teflon equipment has been constructed so that specimens of titanium and tantalum can be exposed to nitric acid containing varying amounts of NO_2 at temperatures up to the boiling point without a loss of NO_2 from the system. Stress corrosion cracking tests can be performed in these vessels and coupons exposed for various times can subsequently be impact-tested to check for pyrophoric reactions. The literature[53] indicates that nitric acid must contain less than 1.4% water and greater than 6% NO_2 to produce pyrophoric reactions with titanium. Experiments will be conducted to confirm these values, and hopefully, to demonstrate that tantalum neither cracks nor undergoes pyrophoric reactions under any conditions that could exist in Iodox process equipment.

Coupon specimens of tantalum and titanium were exposed to 90% (21.2 *M*) and to 95% (22.6 *M*) HNO_3 at 85°C for 500 h. All specimens corroded insignificantly; tantalum showed no visible changes but titanium developed thin interference films.

Experiments with several different materials have been conducted in the vapors above 8 *M* HNO_3 heated at 25 to 85°C to approximate the off-gas from the dissolver. In these initial tests, the specimens were mounted horizontally above the solution and a few iodine crystals were placed on their surfaces. After 100 h, the pitting characteristics of the materials were examined. Titanium, zirconium, Hastelloys G and C-276, Inconel 625, and a ferritic stainless steel containing 29% Cr and 4% Mo were the only materials that remained free of pits at all temperatures. Carpenter 20, 304L and 316L stainless steel, Inconel Alloys 600, 671, and 690, Incoloy Alloys 800 and 825, and E-Brite 26-1 developed deep pits under the iodine crystals. The results clearly show that in iron- and nickel-base alloys, the higher the molybdenum content, the better the resistance to attack by iodine.

Equipment is being assembled to determine the influence of iodine and water partial pressures in air streams on the behavior of 304L stainless steel at different temperatures. Titanium specimens will also be tested under the same conditions.

The Battelle report entitled *Materials Performance in Nitric Acid Solutions Containing Fluoride* was revised in response to ORNL comments and is presently being prepared.

2.6.2 Corrosion tests conducted at ORNL

J. C. Griess

When stress corrosion cracks were noted in the zirconium process equipment used in laboratory testing of the Iodox process, several U-bend specimens made from Zircaloy-4

sheet and one specimen, made by axially sawing a length of Zircaloy-2 tubing and bending one of the halves into a U, were placed in 22 *M* HNO_3 at room temperature. After 6700 h for the U-bends and 6000 h for the half tube, the test was stopped and the specimens were examined metallographically. The half tube of Zircaloy-2 showed one major crack along the axis of the tube with numerous secondary cracks approximately perpendicular to it. The Zircaloy-4 U-bends showed small cracks originating on sheared edges. Thus, these results further confirm the cracking susceptibility of zirconium alloys in nitric acid solutions and show that zirconium alloys should not be used in Iodox process equipment.

2.7 ADVANCED PROCESSES

B. L. Vondra

2.7.1 Sodium effect on voloxidation and dissolution

A. D. Kelmers

A report entitled *Chemistry of the System Na-U, Pu-O Relevant to LMFBR-Type Fuel Voloxidation and Dissolution Processing Operations* was issued; the summary follows:

> The chemistry of sodium uranates and plutonates was reviewed to evaluate the potential effects of the presence of small amounts of sodium in failed LMFBR-type fuel on the voloxidation and dissolution processing steps. No significant problems were defined. Small amounts of sodium present in sheared fuel should exit the kiln as sodium salts of uranium and/or plutonium, which would be readily soluble during HNO_3 dissolution. Most of the sodium would be present in the spent fuel as Na_3MO_4 (M = U, Pu) and probably would be oxidized to $Na_2M_2O_7$ during voloxidation. Lesser amounts of elemental sodium could enter the voloxidizer where it should rapidly form sodium oxide and then react with fuel during voloxidation to form $Na_2M_2O_7$. Any sodium that is hydrolyzed to NaOH during cleaning or water storage should react similarly with the fuel during voloxidation.
>
> No process research and development effort seems warranted, since no significant potential problems or processing unknowns have been identified; however, this is an interesting area for basic chemical research. In the past, very little attention has been directed toward studying sodium plutonates, and the existence of $Na_2Pu_2O_7$ (which should be isomorphous with the known $Na_2U_2O_7$) has not been experimentally established. Little work has also been reported with sodium uranates, and no phase diagrams of the pertinent systems, that is, Na_2O-U_3O_8, Na_2O-PuO_2-O, or Na_2O-U_3O_8-PuO_2-O have been determined.

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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.

The engineering research activities reported below are either ongoing or new activities from the Advanced Fuel Recycle Program and from ORNL's involvement in the Converter Fuel Reprocessing Program. Other Consolidated Fuel Reprocessing Program activities will be described in subsequent quarterly reports.

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 and M. E. Whatley

An experimental voloxidation system scaled to 0.5-t/d is being provided to study (in nonradioactive experiments) certain important process parameters, to study 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. At the end of this reporting period the project was on schedule and no major problems have been encountered during the initial testing phase.

During FY 1978, the kiln was installed and operated at high temperature for the first time. The internal flight cartridge was delivered but was not installed because several of the welds were found to be defective.

During this quarter, two runs were carried out, bringing the total operating time at elevated temperatures to 170 h. The furnace cooling system, off-gas system, and new instruments and controls were tested.

In addition to these experiments, each of the voloxidizer subsystems has been tested. The vibratory feeders have been operated successfully, and the tip bucket, which weighs a feed charge, has been installed and is being tested. The rotary shroud feeder is being fabricated.

The flight cartridge required extensive reworking and is being prepared for installation. The furnace cooling system was modified to improve control and operability. A 3-in.-diam off-gas line and a particulate filter were installed.

All subsystems will be available for use during the next quarter, and we will begin our experimental program with the integrated system. The shroud feeder and flights will be installed. Unit process-controlled programmed startup and shutdown of the furnaces will also be tested.

3.1.2 Rotary-kiln heat transfer studies
B. B. Spencer and M. E. Whatley

Nineteen additional heat transfer experiments were performed using the small rotary-kiln voloxidizer. The first six experiments in which the solids feed rate and holdup were both zero were performed to determine the heat requirements necessary to maintain specified temperature profiles in the kiln. These experiments featured maximum wall temperatures ranging from 300 to 600°C. The following 13 experiments were also performed at zero feed rate [with high solids (hulls) holdup] to determine the effects of solids dispersion alone. Both ends of the kiln were sealed to maintain solids holdups of 40 to 45% of the kiln volume. Again, the heat requirements necessary to maintain given temperature profiles were determined; wall temperatures ranged from 300 to 600°C. Experimentation and data analysis are continuing.

Experiments at similar conditions to those described above and using sand as the solid material to simulate fines will be performed.

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.

Experimental runs using Linde type 3A molecular sieves have continued during this quarter. These runs have consisted of standard runs (using I_2-H_2O-air mixtures to verify findings from earlier runs) and certain nonstandard runs (i.e., first loading the bed with iodine-air mixtures then adding H_2O-air mixtures) to determine the behavior of iodine under a variety of operating modes.

A contract extension to continue these studies in FY 1979 has been finalized. The object of these studies is to determine how various operating parameters (e.g., sieve-type, temperature, and regeneration temperature) affect the iodine retention of the adsorption bed. The goal is to determine the best operating conditions for maximizing water retention and minimizing iodine retention in the bed.

Work on an apparatus to determine equilibrium isotherms of molecular sieves in the presence of iodine has continued. Several runs using 3A sieves showed no detectable change in the isotherms obtained with and without I_2 in the air-water mixture. The apparatus was modified to maintain better temperature control and is now back in operation. This work will continue during FY 1979.

3.1.4 Seals development

M. E. Whatley

Among the most important mechanical features of 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. of water. Firm design criteria have not yet been established for the seals since any inleakage is detrimental from the point of view of the process, and the degree to which the leakage is limited will depend on the results of conceptual design studies.

During the past year many seal concepts have been reviewed; those most unsuitable to the process have been eliminated from consideration. Since September, the FMC Corporation has been assisting in the selection of a reference design for testing purposes. A reference design has been developed which consists of a stationary monolithic graphite ring held against a rotating polished stainless steel surface by the action of springs reacting through rolls against a ring on the rotating drum. The thermal expansion of the drum, and any other small axial displacement, is accommodated by a flexible diaphragm in the reference design

rather than by a bellows such as is used in the present full-scale experimental voloxidizer. Conventional bellows have the tendency to collect dust in the convolutions, which is not acceptable. Seal replacement is accomplished by removing the entire end-breeching section and the part of the drum with the seal.

The design of a prototype reference seal has been completed and approved for fabrication. Purchase orders have been placed for the monolithic graphite ring and diaphragm. The design for a test stand has also been completed, and construction and installation are planned on a schedule which will allow testing to begin in the summer of 1979.

3.1.5 Rotary-kiln corrosion test

W. D. Holland and M. E. Whatley

Two identical drums (18-in.-diam × 20-in.-long) containing test specimens of type 316 stainless steel and Incoloy 800H were loaded with a charge of 10 kg of ceramic-filled stainless steel hulls and then rotated for 4 months at 1 rpm in an oven maintained at 650°C. Thickness measurements (using an ultrasonic technique) of the test specimens made at 42 specified locations showed no significant change as a result of exposure.

A failed drum-drive unit was recently replaced, and the system was operated for approximately 1 month using a mixture of ½-in. and ¼-in. steel rods in place of the stainless steel hulls originally used. Although testing has been suspended because of another drive unit failure, an examination of the contents of the drums indicated that the steel rods were wearing away much too rapidly to be of further use. Plans are to resume testing with new larger drive units and to use sheared stainless steel rods to simulate loaded hulls.

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. Dissolution characteristics of the fuels can vary widely, depending on plutonium content, method of preparation, and irradiation history. Consequently, in the overall program, extensive leaching data will be obtained to determine the effects of such variables. Other efforts are directed toward understanding the behavior of iodine in the dissolver system. Criticality control and off-gas considerations call for dissolver design and operation to be performed within rather narrow limits. Continuous dissolving methods, which appear to offer superior solutions to these problems, are being emphasized.

During this report period, emphasis has been on the ongoing development of a continuous rotary dissolver. In addition, work has started on an advanced dissolver design concept and on the development of a method for providing solids agitation in a digestor tank. Dissolver flow-modeling studies have also resumed.

3.2.1 Rotary dissolver erosion-corrosion tests
B. E. Lewis

All instrumentation for the 4-ft-diam dissolver erosion-corrosion test has been calibrated, and checkout of the dissolver system has begun with 8 *M* HNO_3 at 100°C. After about 1 h of exposure to the nitric acid environment, a valve in the acid line failed. All valves in the system were required to be stainless steel due to the presence of nitric acid. On closer investigation, it was discovered that three of the system valves, including the failed one, were fabricated of carbon steel. A quality assurance deviation report was submitted. It was also noted that some of the failed valves contained rubber o-rings. These have been replaced with Teflon. All failed valves were replaced with certified stainless steel valves. The system checkout was then resumed, and a small acid leak was noticed under the drum housing around the proximity probe at the north end. On inspection, it appeared that the sensor on the proximity probe and the o-rings and gaskets on the probe mount had been physically destroyed in the acid environment. The location of the failed probe was such that acid leaking from the drum fell directly on the sensor. The probe at the south end of the dissolver does not normally experience such contact with the nitric acid. The opening where the failed probe was located was sealed, and all o-rings and gaskets associated with both probe mounts have been replaced with Teflon. Shortly after restarting the system, the second probe failed. This failure did not appear to be due to the physical destruction of the sensor. Replacement probes have been ordered and will be installed when received. Checkout of the system is continuing.

A marked increase in the leak rate of acid from the dissolver drum into the housing has been observed. It has been estimated that about 75% of the acid flow coming into the dissolver is leaking into the housing. On the basis of this high leak rate, it appears that the dissolver drum has shifted axially away from the liquid receivers attached to the dissolver housing. This creates an excessive amount of heat loss in that the primary flow of acid out of the dissolver goes into an uninsulated waste drum before being recycled into the make-up tank. In order to maintain the system temperature at about 100°C while operating with the large leak rate, it will be necessary to insulate the waste tank. Testing will begin as soon as checkout and repairs are completed.

3.2.2 Rotary dissolver flow modeling studies
B. E. Lewis

Background information on component development criteria is being collected in preparation for additional efforts to develop an analytical model for rotary dissolver flows. The desired model will utilize dissolver flow characteristics and chemical data to formulate design equations.

Material balance equations for the major components of interest have been written for the nth dissolver stage. The material and energy balances will be written for the non-steady-state conditions immediately after a solids transfer into a compartment of the rotary dissolver.

3.2.3 Advanced rotary dissolver development
B. E. Lewis

An advanced rotary dissolver concept originated by E. L. Nicholson is one that should offer greater ensurance against solids hang-up, although no blockage of internals has occurred in existing continuous dissolvers. Blockage of the solids exit chute has occurred on one occasion using long strips of shroud material. The new design is being developed for possible application in a later phase of the program. In this concept, the drum contains a continuous welded spiral screw baffle, leaving the center portion completely open. Solids will be fed countercurrent to the fluid flow and will gradually move through the dissolver and be agitated by the slow rocking motion of the drum. Process fluids will be carried to various locations within the dissolver via piping running through the open area in the center of the drum. The drum will be positioned within a sealed housing similar to the pilot plant dissolver. As provided by a slight slope, fluids will flow by gravity over the spiral baffle and exit the drum into the housing. Small flights will be attached to the drum between the spiral baffle windings to provide increased agitation. The drum will contain areas for both fuel dissolution and hull rinsing. The rinsing liquid will be sprayed over the cladding as it passes through the rinse area and exits the dissolver. This dissolver concept does not appear to provide the degree of agitation that current designs offer. However, the simplicity of the internals of the advanced dissolver greatly decreases the chances of a blockage. Sketches of the drum concept are being prepared.

3.2.4 Digester study
B. E. Lewis

Background information on the digester tank is being obtained to devise a means for testing various ways to maintain solid particles in suspension. Concepts available from the literature and from contacts with program personnel will be included in the overall study. Plans are to fabricate a critically safe tank similar to that being considered for the Integrated Equipment Test (IET), to select a suitable material for particle simulation, and to equip the system with promising devices for maintaining particle suspension (jets, sparge ring, thermal convection loop, or other).

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 Iodox process for removing iodine from gas streams, the development of a method to remove these contaminants is receiving considerable attention.

3.3.1 Solids separation

B. E. Lewis

Background information is being obtained to assess various candidate methods for clarifying dissolver product solutions. Previous efforts to initiate a scoping study will be reviewed along with new data now available from solids characterization tests and from the development of methods employing flocculating agents (SRL).

Data on the type and quantity of insoluble particles expected in the dissolver product streams are being collected. Not only is it necessary to consider slowly soluble and insoluble particles in the product streams but also solution instabilities due to the occurrence of precipitation prior to solvent extraction. In general, the particles appear to range in size from about 44 μm down to submicron size. We will be concerned with solids-liquid separations immediately following the dissolver digester tanks, after secondary dissolution, and prior to solvent extraction. After more is known about the quantity, size, and type of solids in the product streams, recommendations will be made concerning the equipment required to accomplish the separations.

An initial contact meeting was held with General Atomics Company to review and discuss the evaluation of a Sharples continuous vertical centrifuge. A definitive work package description will be prepared (according to the WAA system) for inclusion in the overall Consolidated Fuel Reprocessing Program.

3.3.2 Iodine evolution tests

J. G. Morgan

Studies have continued on iodine evolution from a 4 *M* HNO_3 feed stream using steam stripping in a flowing system. When the feed concentration is 2×10^{-4} *M* iodine, a 10% distillate cut removes about 98% of the iodine. Experiments were carried out using a lower iodine concentration in the feed (4×10^{-5} *M*). Data from these tests are being analyzed.

When iodine is steam-stripped from the 4 *M* HNO_3 feed stream, helium is swept over the iodine-rich product condensate. The sweep stream contains helium, water vapor, and iodine. A radioiodine molecular species sampler was used to identify the iodine compounds present in the sweep stream. Supplied by Science Applications, Incorporated, the sampler is a series of filters to preferentially trap particulates, I_2, HOI, and CH_3I. The results for a 1-h sweep at a flow rate of 35 cm^3/min are shown in Table 3.1.

Air sparging tests to measure the iodine release from a ¼-scale digester tank are being continued using a ring bubbler with air flows of 0.1 to 1.0 scfm. The tank contains 4 liters

Table 3.1. Iodine species present in sweep gas

Filter	Iodine species	Fraction of total
Paper	Particulate	0.03
CdI_2	I_2	0.97
4-iodophenol on Al_2O_3	HOI	0.0004
TEDA-impregnated charcoal	CH_3I	0.002
Charcoal (backup)		$<10^{-4}$

of 4 *M* HNO_3 with an iodine concentration of 2 to 3 $\times$ 10^{-5} *M*. Sparging during heatup, sparging after heating to 70 or 90°C, and sparge rate are the parameters being studied. Preliminary results indicate that greater than 90% of the iodine can be removed from the digester tank, with the removal rate as a direct function of the sparge rate.

3.3.3 Accountability
J. G. Morgan

An activity to evaluate Integrated Equipment Test and Hot Experimental Facility accountability concepts and to review current safeguards and Instrumentation and Controls Division efforts in accountability and in-line analysis has begun. The primary objective is to provide a scoping study that will summarize results and efforts from a variety of sources into a single document and describe any needed additional development program.

In-line analytical methods to measure uranium and plutonium in the product stream are being studied. This is a joint effort between the Instrumentation and Controls and Analytical Chemistry Divisions. A spectrophotometric method for uranium analysis is under investigation. Gamma irradiation effects on both optical windows and fiber optics will be determined in support of remote monitoring. An accountability station has been established after the feed clarification step in the feed preparation flowsheet. The safeguards effort will also include material balance assessments using the prototype continuous rotary dissolver.

3.3.4 Nitrogen oxide scrubbing tests
R. M. Counce

Experiments have been conducted using a new pilot-plant-scale packed tower for nitrogen oxide absorption. The data from these experiments will be used to further test a nitrogen oxide absorption model.[1] The tower has sufficient diameter and packing size for scale-up purposes.[2] The results reported here provide a preliminary indication of the scrubber efficiency for varied gas and liquid rates.

Attempts to mathematically model the nitrogen oxide absorption and desorption phenomena are proceeding simultaneously with the experimental investigation. The following absorption mechanisms appear to be adequate descriptions of the phenomena when the scrubber liquid is dilute nitric acid:[3,4]

$$2NO_2(g) \leftrightarrows N_2O_4(g) \tag{3.1}$$

$$NO_2(g) \leftrightarrows NO_2(l) \tag{3.2}$$

$$2NO_2(l) + H_2O(l) \rightarrow HNO_2(l) + HNO_3(l) \tag{3.3}$$

$$N_2O_4(g) \leftrightarrows N_2O_4(l) \tag{3.4}$$

$$N_2O_4(l) + H_2O(l) \rightarrow HNO_2(l) + HNO_3(l) \tag{3.5}$$

$$NO_2(g) + NO(g) \leftrightarrows N_2O_3(g) \tag{3.6}$$

$$N_2O_3(g) \leftrightarrows N_2O_3(l) \tag{3.7}$$

$$N_2O_3(l) + H_2O(l) \rightarrow 2HNO_2(l) \tag{3.8}$$

$$NO_2(g) + NO(g) + H_2O(g) \leftrightarrows 2HNO_2(g) \tag{3.9}$$

$$HNO_2(g) \leftrightarrows HNO_2(l) \tag{3.10}$$

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \tag{3.11}$$

At high partial pressures of nitrogen oxides (NO_2, N_2O_4, N_2O_3, HNO_2) in the gas phase, and with a significant fraction of these as NO_2 and N_2O_4, absorption reaction (3.5) will predominate. Otherwise, all of the above absorption routes should be taken into consideration to describe the absorption process.

Nitric acid is fairly stable in the liquid phase, while nitrous acid is relatively unstable. The following equilibrium reactions involving nitrous acid appear to predominate in the liquid phase:[5,6]

$$2HNO_2(l) \leftrightarrows NO_2(l) + NO(l) + H_2O(l) \tag{3.12}$$

$$4HNO_2(l) \leftrightarrows N_2O_4(l) + 2NO(l) + H_2O(l) \tag{3.13}$$

The decomposition of liquid nitrous acid can involve the desorption of nitric oxide from the liquid phase coupled with reactions (3.3) and (3.5), or the desorption of nitric oxide coupled with the desorption of NO_2 and/or N_2O_4.[7] Additionally, the decomposition of liquid nitrous acid may be accomplished by the reverse of reactions (3.7) and (3.8) or reaction (3.10).[7] The decomposition of liquid nitrous acid has in some cases proved to be a limiting phenomenon in the aqueous scrubbing of nitrogen oxides from gas streams[8] and thus warrants inclusion in a mathematical model that predicts nitrogen oxide scrubbing efficiency.

The experimental system has been previously described.[1] The absorption column used in these studies is 0.10 m in diameter and is packed with 13-mm Intalox saddles.

The oxidation state of the gaseous nitrogen oxide mixture has proven to be an extremely important parameter in predicting scrubbing efficiency.[9] The oxidation state, along with gas and liquid loads, will be investigated in planned experiments. The experimental results in Fig. 3.1 show the effect of gas and liquid loads on scrubbing efficiency. Column efficiency is defined as:[10]

$$E = \frac{1 - P_{NO_x,out}/P_{NO_x,in}}{1 + \epsilon_{NO_x} P_{NO_x,out}/P_{NO_x,in}}, \tag{3.14}$$

where

$P_{NO_x,\,in}, P_{NO_x,\,out}$ = partial pressure of nitrogen oxides entering and leaving the tower,

ϵ_{NO_x} = fractional gas volume change due to absorption of nitrogen oxides.

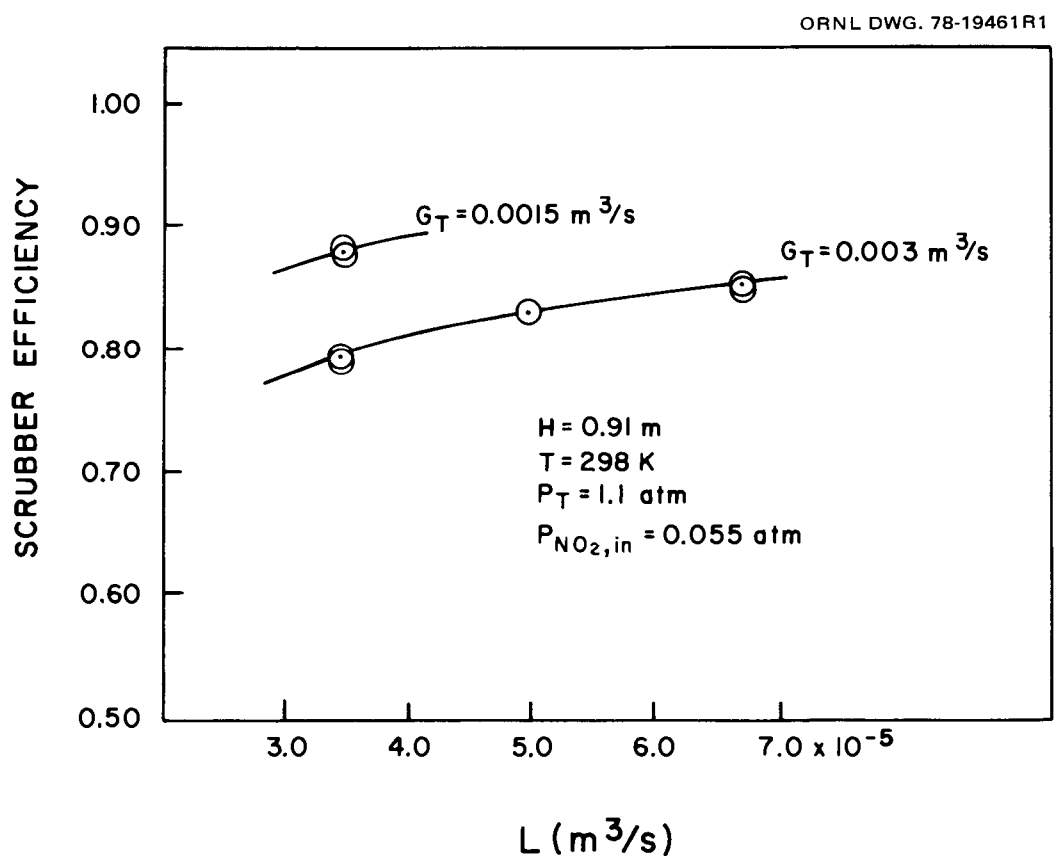

Fig. 3.1. Nitrogen oxide removal efficiency for varying gas and liquid loads (nitrogen oxides in feed gas were in $NO + N_2O_4$ state, H is height of packing, T is temperature, P_T is total pressure, and $P_{NO_2,in}$ is the partial pressure of $NO_2 + N_2O_4$ in the feed gas).

These effects are predictable since increased liquid rates increase the gas-liquid interfacial area and the liquid-phase mass transfer rates; at the same time, the lower gas rates provide increased gas-phase residence time in the column.

The experiments are expected to continue until sufficient data exist for the development of a mathematical model to predict nitrogen oxide scrubber efficiency. Model development is proceeding simultaneously with the experimental phase.

3.3.5 Fluid transfer and metering

R. M. Counce

Preliminary planning is under way for a facility to test fluidic pumps. A double-nozzle diode pump[11] is being designed to provide flow rates of 1.25×10^{-4} to 2.50×10^{-4} m^3/s for fluids having densities of about 1000 kg/m^3 and lifts up to 18 m. The testing of this unit is expected to begin in April.

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 to study extraction kinetics, plutonium reduction techniques and kinetics, and solvent clean-up techniques that may involve the use of short residence-time contactors.

Efforts are also under way at ORNL to improve and apply the SEPHIS computer code for flowsheet engineering studies, to evaluate a mixed-cell contactor for solvent washing, and to investigate engineering aspects of intercycle feed adjustments. Work at other sites on pulsed columns and other solvent extraction contactors is also being reviewed.

3.4.1 Contactor development

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

Laboratory testing of the 0.5-t/d (0.9-cm rotor) annular centrifugal contactor is continuing. A series of mass transfer efficiency tests using uranium and thorium has been completed. Analytical results are available for measuring uranium extraction efficiency.

Uranium extraction efficiency tests. A series of nine tests was made to measure uranium extraction efficiency at various flow rates and organic-to-aqueous (O:A)-phase flow ratios. All the tests except one were performed at the standard rotor speed of 1765 rpm; one test was made at a rotor speed of 2500 rpm. Aqueous feed composition was approximately 0.06 *M* U and 0.5 *M* HNO_3; organic extractant composition was 30% tributyl

phosphate (TBP) in normal dodecane (NDD). Extraction efficiencies were very close to 100% in all tests except that at maximum flow rate where the efficiency was about 96%. Conditions and results of the extraction tests are given in Table 3.2.

Table 3.2. Extraction efficiency tests in a 0.9-cm annular centrifugal contactor (aqueous phase: 0.06 *M* U, 0.5 *M* HNO_3; organic phase: 30% TBP-NDD)

Test	Rotor speed (rpm)	Total flow (liters/min)	Flow ratio (O:A)[a]	Continuous phase[b]	Uranium balance (%)	Extraction efficiency (%)
1	1765	4	1.0	O	104.1	100.9
2	1765	8	1.0	O	100.5	95.9
3	1765	2	1.0	O	101.6	99.5
4	1765	1	1.0	O	101.8	98.8
5	2500	4	1.0	O	101.4	100.4
6	1765	4	0.2	A	101.9	100.9
7	1765	4	0.5	A→O	101.5	100.1
8	1765	4	0.5	O	101.0	101.3
9	1765	4	2.0	O	100.4	99.4

[a]Organic-to-aqueous.

[b]At an O:A ratio $\geq$ 0.5, the organic phase is normally the continuous phase in the mixing annulus. In test 7, the contactor was started with the annulus full of aqueous phase and then was allowed to convert to organic- continuous before effluent samples were taken.

The slightly lower extraction efficiency found in test 2 suggests that the residence time in the mixing zone may have been borderline for achieving full mass transfer. The residence time is estimated to have been nearly 3 s, which is about what is needed for 100% mass transfer.

The high stage efficiencies found in using a rotor speed of 1765 rpm indicates that higher rotor speeds are not needed for achieving good phase mixing.

Several additional tests were made to measure uranium stripping efficiency and thorium extraction efficiency. Analytical results are not yet available.

Design of 0.5-t/d contactor M-2. Work has started on the design of a second model (M-2) of a 0.5-t/d annular centrifugal contactor. This contactor will incorporate features compatible with remote servicing and should serve as a prototype of the contactor that will eventually be used in an eight-stage contactor bank for installation in the IET facility at ORNL.

The rotor diameter in the M-2 contactor has been increased from 9 to 12 cm and the annular gap has been increased from 0.64 to 1.27 cm. Rotor speed is being kept at 1765 rpm. The larger rotor and annular gap should lead to a significant increase in throughput capacity; therefore, the maximum capacity will be about twice the projected flow rate based upon the tentative ORNL flowsheet for a 0.5-t/d fuel processing rate.

The first 0.5-t/d unit was built with a minimal-size rotor (9-cm-diam rotor) and annular gap in order to evaluate the performance of a contactor with minimum residence time. As reported previously,[12] a significant improvement in ruthenium and zirconium decontamination could not be projected at contactor residence times achievable in that size contactor. In addition, current interest in flowsheets aimed at emphasizing nonproliferable processes reduces the need for achieving high decontamination from these fission products. Accordingly, the design of the M-2 contactor is directed toward improving capacity and achieving more reliable hydraulic and mechanical performance.

The dimensions selected for the M-2 contactor are well within the limitations for critical safety as determined by preliminary ORNL calculations. These calculations will be extended and will be reevaluated before the M-2 contactor design is finally accepted.

3.4.2 Reduction of plutonium by hydroxylamine nitrate-hydrazine

E. A. Huff, A. Siczek, and J. Meisenhelder (ANL)

The reduction of tetravalent plutonium (Pu IV) to trivalent plutonium (Pu III) in 30% TBP-NDD by hydroxylamine nitrate (HAN)-hydrazine (HZ) was tested, along with the subsequent transfer of Pu(IV) and Pu(III) from the organic phase to an aqueous phase. These tests were conducted on a batchwise basis to determine whether this reductant was suitable for use in short residence-time contactors.

The composition of the organic and aqueous phases employed in these tests is given in Table 3.3. The aqueous solution, A, was equilibrated with 30% TBP-NDD at a volume ratio of 1:1 to form the organic solution, B, which was then used in the reduction tests. A 9-ml batch of solution B was shaken manually with 3 ml of the reducing solution, C, for periods of 1, 5, and 10 min. After each time period, aliquots of 0.1 ml of each phase were withdrawn for analysis. The analytical results are given in Table 3.4.

Table 3.3. Composition of solutions used in plutonium reduction tests

Solution	U (*M*)	Pu (*M*)	HNO_3 (*M*)	HAN (*M*)	HZ (*M*)	TBP-NDD (%)
A	0.4	0.134	2.0			
B	*a*	0.0446	*a*			30
C			0.25	0.16	0.10	

[a] Not analyzed.

Table 3.4. Plutonium reduction by hydroxylamine nitrate-hydrazine

Extraction time (min)	Volume ratio (O:A)[a]	Pu (*M*) Organic	Pu (*M*) Aqueous	DC_{Pu}[b]
1	2.97	0.0182	0.0796	0.23
5	3.03	0.0138	0.0930	0.15
10	3.10	0.0111	0.0988	0.11

[a]Organic-to-aqueous.
[b]Distribution coefficient; in the absence of the reducing agent, $DC_{Pu} \simeq 0.26$.

3.4.3 Flowsheet engineering
R. T. Jubin and M. E. Whatley

Solvent extraction systems in radiochemical plants are called upon to meet several objectives within a variety of constraints which have traditionally been quantified only loosely. Early solvent extraction plants were designed from rapidly compiled data and then built with an urgency prompted by military necessity. Modifications were responses to particular operational problems, and innovations were rare. Generally, new flowsheets contained minimal engineering input and were contrived by experienced chemists. The flowsheets usually limited the number of stages (or column height) in a more or less arbitrary manner to conform to available equipment or cell height. Optimization of the overall system was left to a small group of responsible individuals who, after reflecting on their understanding of the most important factors, made definitive decisions based on "judgment." Such judgment in the past has been adequate and reasonable, taking into consideration the state of the technology at the time. The more severe process requirements for today's power reactor fuels, the wide variety of fuel types, the sizeable additions of relevant information (both in chemical effects and in equipment performance), and the availability of better calculational techniques suggest that an analytical approach to flowsheet optimization should be attempted.

The questions to be addressed include the selection of a contactor, the number of stages in each section of the extractor, appropriate flow rates, specifications for flow control, and specifications for instrumentation. It is conceivable that feed concentration might also be included as a study variable and that recommendations for startup and shutdown procedures be established. It is likely that analysis will point to particular areas of development to improve performance, such as flow control, or that it will establish regions of sensitivity or insensitivity. The drafting of objective functions for optimization will be an important aspect of this activity. These functions will call attention to the relative importance of competitive process objectives and constraints as well as criteria for performance, including decontamination factors, recovery, and solvent degradation.

The work will start from the reference flowsheet for the HEF and will identify and list process performance criteria and constraints that led to its selection. The relative importance of each criterion and constraint will be quantified. An exhaustive search for hidden or obscure criteria will then be made to complete the list. From this list, a tentative objective function will be derived from which optimization can be made.

A survey of candidate equipment for use in future plants will be made, in addition to a quantitative description of that equipment. Existing correlations will form the bases for describing conventional contactors; new correlations, as they are made available, will be used for high-performance contactors now under development.

The SEPHIS computer program, which is used to calculate Purex and Thorex flowsheet performance, will initially be used in parametric studies. Subsequently and as required, modifications to the program will be made, or a new flowsheet-dedicated program will be written to fit a more definitive role. Work will then be assessed and future direction determined.

The final product is to be a procedure (possibly in the form of a computer program) for formally incorporating all significant aspects of the system into a quantitative determination of an optimum flowsheet, which would be applicable to the various solvent extraction cycles of a fuel reprocessing plant. An ancillary effort is already under way, that is, an evaluation of the separation of Pu(IV) from U(VI) as an alternative to the valence adjustment steps now required in conventional flowsheets.

The UCOR subroutine of the SEPHIS code, which generates the distribution coefficients of uranium, plutonium, and nitric acid, was used this quarter to generate a series of distribution coefficient tables and curves as functions of uranium and plutonium concentration. These calculations will be compared with experimental results to determine whether or not UCOR can be used to accurately predict values under particular experimental conditions, which, in effect, will identify the range limitations for SEPHIS.

Using SEPHIS, a series of 16 runs was made to statistically determine the variables having major and minor effects on a solvent extraction partitioning system in which no plutonium reductant is used. Analysis of the results is incomplete at this time. However, as expected, the plutonium concentration in the solvent stream leaving the contactor is very sensitive to operating parameters; therefore, a wide variation is seen, that is, from 0.0002 to 21.1% of the plutonium in the feed stream leaves in the organic product stream. The wide variation in numerical values is posing some problems in the data analysis. Possible alternate methods of analysis are being examined.

A modification of SEPHIS or the writing of a new code for steady-state flowsheet studies and optimization is also being examined. Literature on various multicomponent separation computer codes is being gathered and evaluated for potential applicability.

3.4.4 Solvent washing contactor

W. E. Eldridge

The solvent washing mixed-cell contactor was reinstalled after the replacement of defective parts. Initial trial runs of the system revealed several design inadequacies in the

gravity flow tubing, which has since been corrected. The solvent washing system has been operated using both 0.25 *M* Na_2CO_3 and water as the aqueous phase in contact with 30% TBP in normal paraffin. The 0.25 *M* Na_2CO_3 washing showed rapid phase separation and a narrow dispersion band, with a small amount of organic remaining in the aqueous product as fine droplets. Water washing resulted in a somewhat slower separation of the fine droplets and a nondispersing emulsion band which formed at startup. Modifications to the system were made (to allow for direct recycle of the aqueous feed stream to the contactor, with minimum standing time). Further shakedown tests were conducted, and the aqueous recycle leg of the system was found to be functioning properly. A 48-h continuous run was made to monitor fluctuations in variables such as contactor impeller speed, aqueous flow, and organic flow. Aqueous and organic samples were taken each hour; many of the samples will be analyzed to determine the degree of phase separation. All mechanical aspects of the run were successful, with the contactor impeller speed being monitored by a phototachometer. We were able to determine some operating conditions which allow for adequate dispersion in the contactor while still permitting distinct phase separation at the interface within the settler.

3.4.5 Alternate contactor studies
M. E. Whatley

Initial contact meetings were held this quarter to review and discuss pulsed-column and Robatel contactor work at General Atomics Company and flowsheet activities in pulsed columns at Allied General Nuclear Services. Definitive work-package descriptions will be prepared according to the WAA system for inclusion in the overall Consolidated Fuel Reprocessing Program.

3.4.6 Feed adjustment
J. G. Morgan and M. E. Whatley

The HEF reference solvent extraction flowsheet for U-Pu calls for the reduction of plutonium to the trivalent state with hydrazine between the H (first) cycle and the partitioning cycle. An aqueous product stream from partitioning will contain uranium, plutonium, and hydrazine. This stream will probably not be further decontaminated but sent directly to product conversion. In either case, the hydrazine must be quantitatively destroyed, and the plutonium must be oxidized to the four state. The most attractive approach to the problem is to contact the stream with NO_2. Because of the insidious nature of the hydrazine hazard, an experimental study of this operation will be conducted. The applicability of a short tower as well as a sparged tank will be considered. Work will be done without plutonium. This activity will also respond to all other intercycle feed adjustment operations in accordance with flowsheet requirements.

3.5 OFF-GAS PROCESSING

W. S. Groenier

This task consists of the development of various processes for the treatment of reprocessing plant off-gases to ensure that environmental goals are met. Work includes the accelerated 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 Iodox demonstration system incorporates iodine scrubbing with hyperazeotropic nitric acid, the collection of solid pentavalent iodine, and acid recovery. Studies of the Iodox 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 under way.

3.5.1 Fluorocarbon absorption process development

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

Recent program emphasis has been directed toward further experimental verification of the combination absorber-fractionator-stripper column. In particular, the operational versatility and stability of the column was explored. Experimental column temperatures and external gamma-scan profiles have been obtained over a wide range of operating conditions to define the operating characteristics of the pilot plant combination column. Equipment details and relevant theory have been previously reported.[13–15] The combination column operates under a sizeable temperature gradient. Soluble gas concentration is brought about by gross internal condensation of the stripping vapor in the middle section of the combination column. The concentrated noble gas product is collected as a side stream. Figure 3.2 shows two typical combination column temperature profiles and demonstrates, in general, the mobility of the internal condensation zone. Over the range of flow rates of 1.5 to 0.75 gpm covered during the testing period, the condensation zone was found to move 44 in. from column position 108 to 152 respectively. As implied by the sharpness of the temperature gradient, the bulk of the solvent vapor condensation occurs in a narrow section of the column. The location of the zone is primarily a function of the solvent flow rate; lower rates result in the zone being formed higher in the intermediate section and, consequently, result in a more concentrated product. The product withdrawal point is fixed by the construction of the column; therefore, the solvent flow rate must be specified so as to properly locate the condensation zone and product concentration peak. The main product takeoff point of the pilot plant column is located at column position 120 (120 in. from the bottom of the

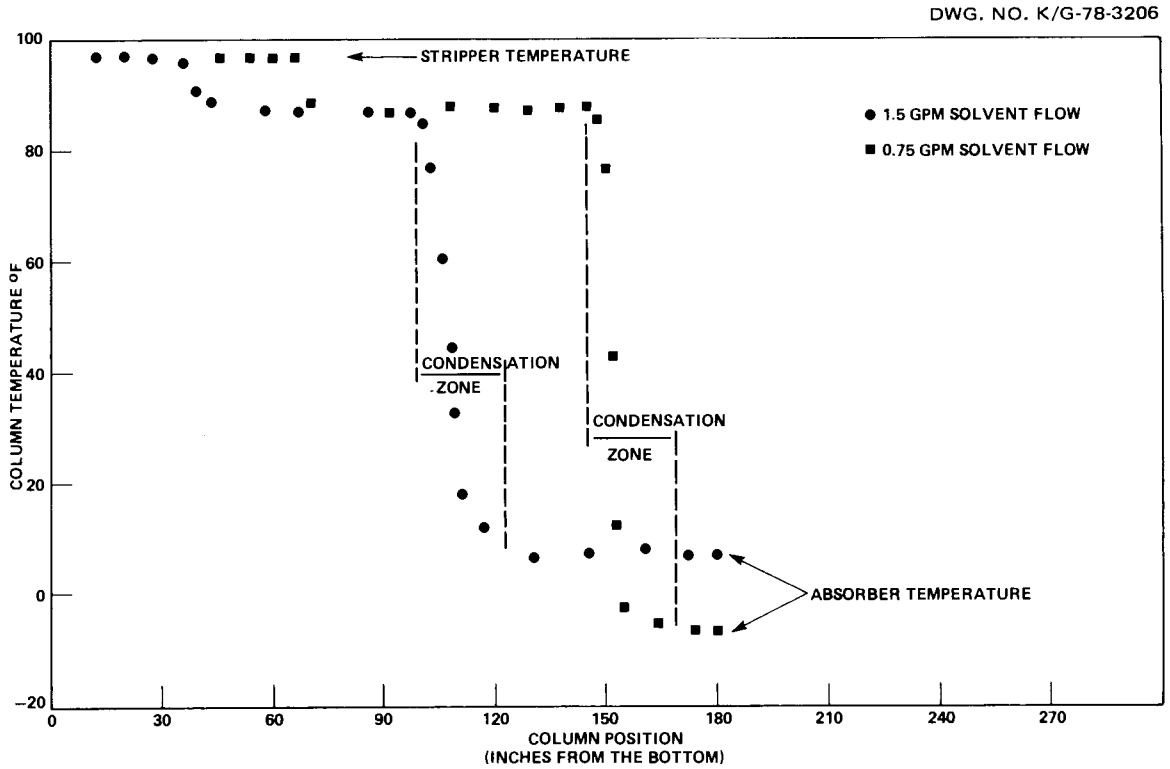

Fig. 3.2. Combination column temperature profile.

column). The required or optimum solvent flow rate in this case was found to 1.0 gpm. A gamma scan of the combination column operating at this solvent flow is shown in Fig. 3.3.

The inlet solvent temperature was found to affect the location of the condensation zone only slightly within the range investigated. Reproduction and stability of the soluble gas peak was well established. In general, with good column control, the concentration peak could be located and maintained for any desired period of time within a 2-in. interval around the product takeoff point. Only conventional process control instrumentation is required.

In conjunction with the stability tests, improvements were made with regard to the general operation of the column. Specifically, start-up time was reduced from 4 h to only 1 h, with near steady-state conditions being achieved within the second hour. Operation of the new molecular-sieve solvent drying station eliminated the formation of a refrigerant-12 hydrate which previously caused operational problems.

Current tests involve removing and concentrating the noble gas in a continuous system. This pilot plant data will allow further verification of the single column concept and, ultimately, will provide the necessary information upon which to make operational and performance comparisons with the conventional three-column process. Other work is under way to evaluate various final product purification schemes.

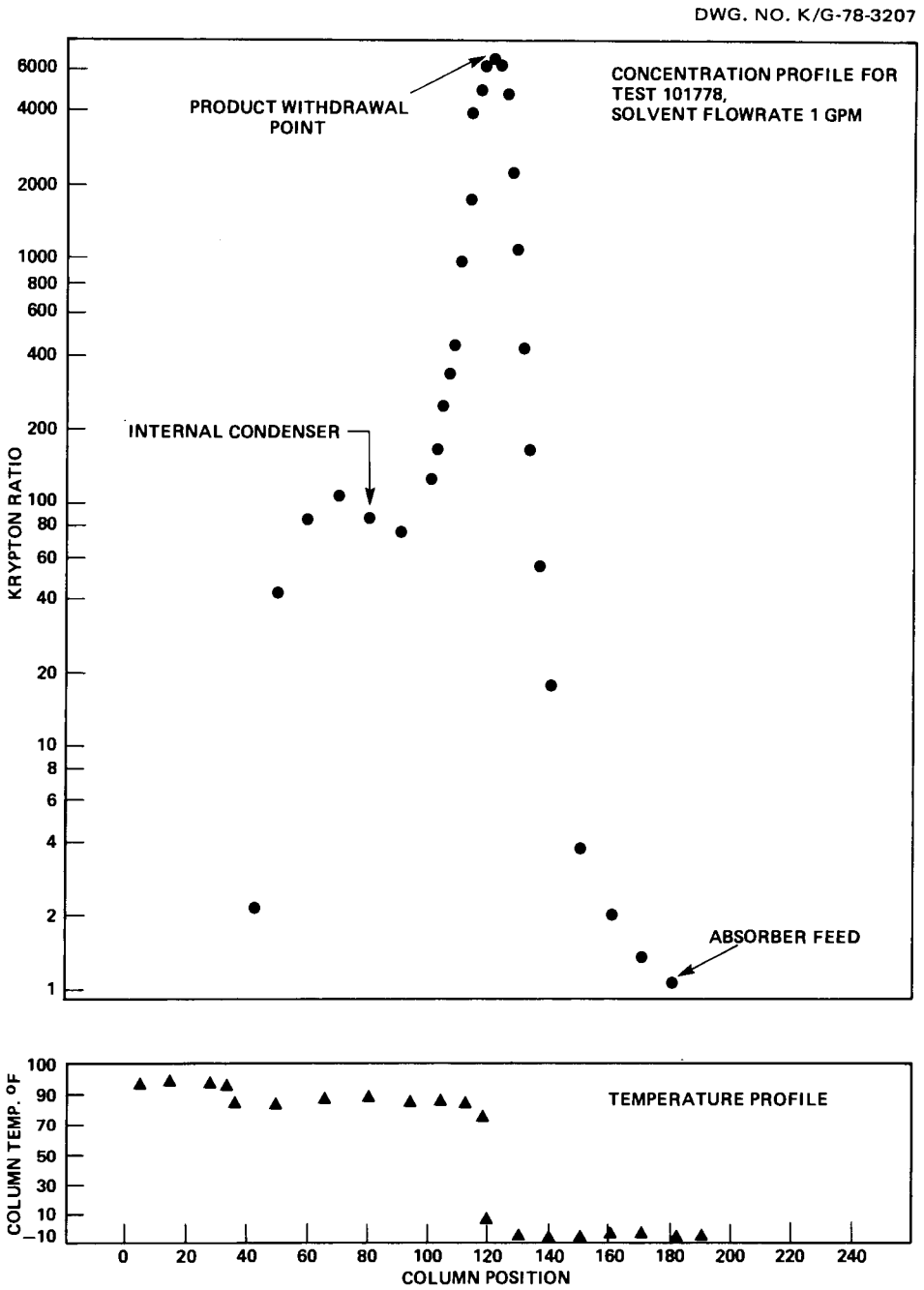

Fig. 3.3. Combination column gamma and temperature profiles for operation at optimum solvent flow rate.

Process design models have been completed for the absorber, fractionator, and stripper. A topical report[15] that details the fractionator and stripper operation and analysis is currently available; a similar document[16] for the absorber will be available within the coming quarter. Work will then be initiated to combine the component models into an overall design document applicable to either the three-column or combination-column process.

3.5.2 Noble gas solubility studies

J. H. Shaffer

A systematic study of the solubility behavior of krypton and xenon in dichlorodifluoromethane (refrigerant-12) was continued. Measurements of the behavior of these solutes at infinite dilution in R-12 at its saturation pressure were completed during the previous quarter. The data were calculated as Henry's constants over a temperature interval of −30 to +50°C. The current program will examine the effects of solute concentration on the solubility behavior in each of the two binary systems over the same temperature range.

The experimental procedure is essentially the same as that used for studies at infinite dilution. However, additional material balance calculations are required to determine the chemical composition of the two phases and to assess the total system pressure. Direct pressure measurements were not planned for the current test series unless large departures from ideal solute gas behavior were encountered. Data are derived from the molar distribution of radioactive solute gas, solvent density and saturation pressure values, and the material balance on components initially charged to the containment cylinder.

Experiments with the first test series for the two solute gases are in progress. The material balance for krypton in the system was calculated for a solute concentration of about 10% in the gas phase at 25°C. The corresponding xenon concentration was set at approximately 1%. The results obtained thus far are summarized in Tables 3.5 and 3.6 for krypton and xenon respectively. Values for Henry's constants obtained from the previous study of solutes at infinite dilution are also tabulated. A comparison of these values with equilibrium constants calculated for the solutes at higher concentrations and at corresponding temperatures shows a small but consistent effect on solute concentration. The significance of this effect will be examined during subsequent solubility determinations at higher solute concentrations.

Table 3.5. Krypton solubility in dichlorodifluoromethane

Temperature (°C)	Total pressure (atm)	$Y_{(Kr)}$ mole fraction	$X_{(Kr)}$ mole fraction	Equilibrium coefficient (atm)	Henry's constant (atm)
50	12.848	0.0634	0.00621	131.2 ± 0.5	128.9 ± 0.6
40	10.283	0.0780	0.00615	130.3 ± 0.1	127.0 ± 0.4
30	8.131	0.0958	0.00614	126.8 ± 1.2	124.1 ± 0.5
20	6.354	0.1188	0.00614	117.0 ± 0.3	113.4 ± 0.2
0	3.728	0.1830	0.00624	109.3 ± 0.5	105.8 ± 0.4

Table 3.6. Xenon solubility in dichlorodifluoromethane

Temperature (°C)	Total pressure (atm)	$Y_{(Xe)}$ mole fraction	$X_{(Xe)}$ mole fraction	Equilibrium coefficient (atm)	Henry's constant (atm)
50	12.121	7.216×10^{-3}	1.356×10^{-3}	64.5 ± 0.4	62.6 ± 0.2
40	9.562	8.518×10^{-3}	1.366×10^{-3}	59.7 ± 0.1	58.1 ± 0.4
30	7.426	1.008×10^{-2}	1.379×10^{-3}	54.3 ± 0.1	53.3 ± 0.3
10	4.239	1.451×10^{-2}	1.411×10^{-3}	43.6 ± 0.1	43.6 ± 0.2
−10	2.211	2.177×10^{-2}	1.451×10^{-3}	33.2 ± 0.1	32.1 ± 0.2
−20	1.532	2.728×10^{-2}	1.472×10^{-3}	28.4 ± 0.2	27.4 ± 0.2

3.5.3 Solid sorbent studies

R. T. Jubin

Equipment has been designed to allow solid sorbents to be evaluated for the removal of elemental iodine or methyl iodide from gas streams containing mixtures of air, water vapor, nitric oxide, nitrogen dioxide, and traces of other halogen gases. Specifically, we plan to evaluate silver-exchanged mordenite (AgZ) for methyl iodide removal. This particular combination has not been previously tested, as noted in a literature survey[17] and in an earlier progress report,[13] and is of interest because of the general ability of mordenite-based sorbents to be regenerated. Included in the planned series of tests are two life-cycle studies to follow the change of the AgZ filter-bed capacity to remove either CH_3I or I_2 after an extended number of bed regenerations.

The fabrication of the solid sorbent test equipment is nearing completion. Installation of this equipment should proceed during January. The glass shop has not yet received many of the glass joints required for the filter housings. These 5-cm-diam housings will be loaded with up to six 2.5-cm-thick layers of sorbent material. The materials are expected to arrive by the end of December.

The silver zeolite-mordenite exchange column has been fabricated and is now being mounted as a self-contained unit, with a pump to circulate the $AgNO_3$ solution and required quick disconnects on a moveable stand so as not to tie-up valuable hood space.

The present hood exhaust duct work with mechanical seals is slated for replacement with welded stainless steel ducting. Fabrication of this new duct work has begun and installation is expected in mid-January.

Solid sorbent evaluation activities at General Atomic Company and at Science Applications, Incorporated, were reviewed and discussed this quarter in preparation for a definition of work in the overall Consolidated Fuel Reprocessing Program.

3.5.4 Carbon-14 removal process development

G. L. Haag and A. D. Ryon

The development of processes for the removal and fixation of $^{14}CO_2$ released in the reprocessing of breeder-based fuels is being conducted, with major emphasis being placed on the treatment of high volumetric gas streams containing less than 1000 ppm CO_2. 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.

Analytical instrumentation. The reliable determination of CO_2 in the sub-ppm regime is of importance in the development of a CO_2 removal and fixation process for the treatment of low CO_2 content gas streams. The acquisition of capable instrumentation and accurate calibration in the regime of interest have been difficult. Two instruments, a gas chromatograph equipped with a nickel-catalyst methanizer and a flame ionization detector (FID), and a variable wavelength, variable pathlength infrared analyzer, have been obtained. The calibration gases containing sub-ppm concentrations of CO_2 were obtained from the Bureau of Mines (BOM) Helium Operation Center in Amarillo, Texas. These gases were analyzed by BOM using a freeze-out preconcentration technique followed by mass spectrometry. The analysis accuracy was stated as ±15%.

The gas chromatograph utilizes a Porapak column to separate the components of interest, a methanizer to convert CO_2 to CH_4, and a flame ionization detector for hydrocarbon analysis. Detection capabilities have been improved by operating at more optimum helium, hydrogen, and air flow rates and by increasing the instrument gain. These new operating conditions have also enabled the time between samples to be reduced from 20 to 10 min. Deactivation of the nickel-catalyst methanizer has been observed, and the conversion efficiency is now routinely monitored with a CO_2-CH_4 standard. Using reference gases, the instrument has been calibrated to a lower limit of 100 ppb. Personnel at the BOM Helium Operation Center have suggested the use of an exponential dilution system for calibration purposes. The approach is under study since only two reference gases would be required to obtain a calibration curve over the entire sub-ppm regime of interest.

The variable wavelength, variable pathlength infrared analyzer was installed in a glove box where the instrument is maintained under an argon atmosphere to minimize baseline noise level and drift. The infrared light source and window are separated by the ambient atmosphere. The instrument provides in-line monitoring capability since the cell volume is only 5.6 liters. Using an absorbance wavelength of 4.3 μ, a pathlength of 21.75 m, a cell pressure of 5 psig, and a cell temperature of 50°C to avoid the possibility of H_2O condensation, the instrument was calibrated with reference gases down to 100 ppb. Tests were run to determine the possibility of water interference at this wavelength and low CO_2 concentrations. The results were negative.

The possibility of extending the calibration curves of both instruments below 100 ppb has been examined; the major problem is the lack of reference gases. However, the present calibration curves for both the gas chromatograph and the infrared analyzer have been extrapolated; remarkable collaboration between the instruments was obtained in the 30- to 100-ppb regime.

A second variable of importance in determining the operating characteristics of the $Ba(OH)_2$ hydrate system is the determination of water content in various streams. A Panametric model 2100 hygrometer was obtained to provide in-line monitoring capability of six streams over the dew point range of importance. After numerous problems, the instrument has been returned to the factory for recalibration and alternative methods are being examined.

$Ba(OH)_2$ hydrate solid reactant. A comprehensive literature review of $Ba(OH)_2$ hydrate chemistry has been conducted. The literature has indicated that $Ba(OH)_2 \cdot H_2O$ and $Ba(OH)_2 \cdot 8H_2O$ exist as stable compounds. Under special conditions, $Ba(OH)_2 \cdot 2H_2O$ has been verified by x-ray diffraction and infrared resonance patterns.[18] The reactants used in experimental studies were obtained from the vendor as $Ba(OH)_2 \cdot H_2O$, $Ba(OH)_2 \cdot 5H_2O$, and $Ba(OH)_2 \cdot 8H_2O$. Conversations with the vendor have indicated that the stoichiometric coefficients for the degree of hydration were determined on a mass basis; therefore, the composition of $Ba(OH)_2 \cdot 5H_2O$ is likely 43% $Ba(OH)_2 \cdot H_2O$ and 57% $Ba(OH)_2 \cdot 8H_2O$. X-ray diffractions are being obtained for verification.

Previous studies have indicated that the role of water in the overall gas-solid reaction is quite illusive. For the treatment of a dry air stream (−70°C dewpoint) containing 330 ppm CO_2, $Ba(OH)_2 \cdot H_2O$ was found to be unreactive, whereas $Ba(OH)_2 \cdot 8H_2O$ was initially reactive. However, gradual conversion of the octahydrate to the monohydrate resulted in an overall loss in reactivity. When the same feed gases were water-saturated, $Ba(OH)_2 \cdot H_2O$ exhibited greater reactivity and conversion than the octahydrate. However, final conversion of the octahydrate was greater than when a dry feed gas was used. The literature has indicated that the octahydrate will decompose to the mono- when the water vapor pressure is less than 6 mm Hg (2°C dewpoint).[19,20] However, the rate of water removal will be affected by diffusional limitations. Similarly, the conversion of the mono- back to the octahydrate has been termed reversible, although the rate is considerably slower. Because of the slower rate, there are indications that appreciable amounts of water may be adsorbed before the actual conversion of the lattice from that of mono- to octahydrate. Very little information was found on the conversion of $Ba(OH)_2 \cdot H_2O$ to $Ba(OH)_2$ (and vice versa) at ambient conditions. Diffusional difficulties for the transfer of water out of the crystal lattice appear to be greater, making vapor pressure data extremely difficult to obtain.

Experimental studies have been initiated to verify some of the information in the literature and to more fully understand the effect of humidity and reactant on the CO_2 removal rate and final bed conversion. Present studies have been hampered by difficulties with analytical instrumentation for water measurement.

$Ca(OH)_2$ slurry stirred-tank reactor. Studies were conducted to determine the CO_2 removal efficiency of the $Ca(OH)_2$ slurry stirred-tank reactor for treatment of a 330-ppm CO_2 gas. Considerable data had been obtained pertaining to CO_2 removal from higher gas concentrations. The main purpose of the study was to determine the effect of gas flow rate, impeller speed, impeller diameter, and slurry concentration on the overall CO_2 removal efficiency. Attempts will be made in the future to correlate this and other data to various system parameters.

The 27.3-cm-ID, stirred-tank reactor was used for these studies. The reactor is of standard design with a liquid height to tank diameter ratio of 1 and is fully baffled, with four baffles (width of $1/10$ the tank diameter) located at 90° from one another. The slurry volume is 16 liters. The impellers are standard six-straight-bladed disk turbines with diameters of 5.0 and 5.38 in. Impeller speeds of 350, 450, 550, and 650 rpm were used. Although the reactor does not have torque measurement equipment to determine power input, the correlations by Rushton have indicated $P = \alpha n^3 d^5$ for an unsparged system, where P is the total power input, n the agitator speed, d the agitator diameter, and α a proportionality constant.[21] However, corrections must be made for the gas sparging effect. Solid densities of 0.5, 1.0, and 1.5 *m* and gas flow rates of 10 to 80 liters/min were used. To obtain the higher gas flow rates, the pressure drop across the sparger was reduced by enlarging the sparge holes from $1/16$ to $1/8$ in. Initial comparison with previous data has indicated that the sparger modification had a detrimental effect on CO_2 removal efficiency at the lower gas flow rates.

A total of 92 datum points were taken in this study; a portion of the results is presented in Figs. 3.4 and 3.5. The effect of agitator speed and gas flow rate on CO_2 removal efficiency is presented in Fig. 3.4. The data indicate that for a nominal DF of 100, superficial velocities in excess of 30 cm/min (~18 liters/min) must be avoided, and staging of units would be required for higher superficial velocities. Further information would be required (on larger equipment) to determine scale-up criteria. However, from the preceding data, one may speculate that the equipment to treat a reference 500 ft^3/min stream would be extremely large. A rather surprising result (Fig. 3.5) was the effect of slurry concentration upon CO_2 removal efficiency. The decontamination factor was found to increase as the slurry concentration decreased. As previously stated, this and other data are undergoing further analyses, and attempts will be made to model the system from theoretical and empirical perspectives.

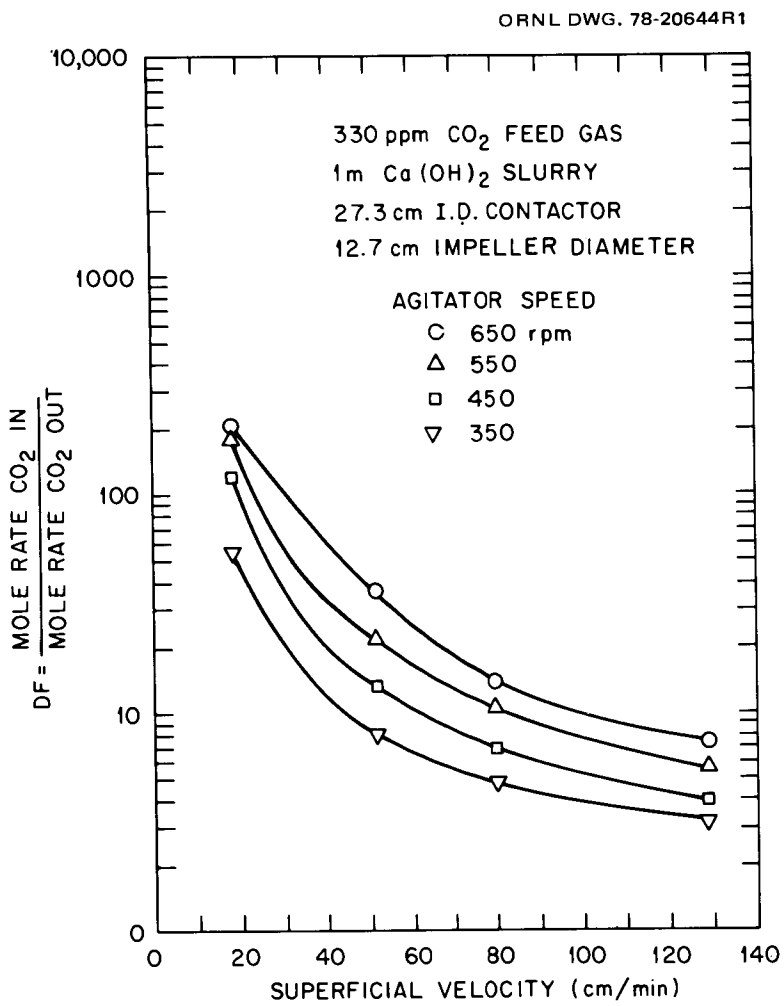

Fig. 3.4. Effect of agitator speed on CO_2 removal efficiency in the 27.3-cm-ID, stirred-tank reactor.

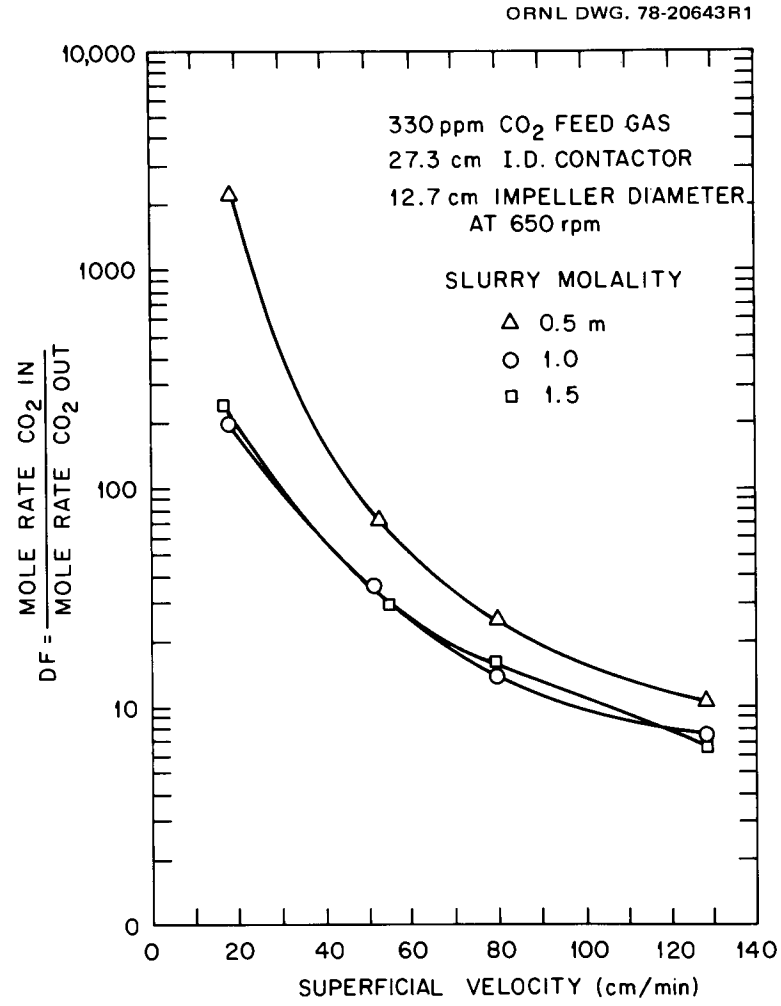

Fig. 3.5. Effect of slurry concentration on CO_2 removal efficiency in the 27.3-cm-ID, stirred-tank reactor.

3.6 ENGINEERING RESEARCH INSTRUMENTATION SUPPORT

W. F. Johnson, S. S. Gould, and G. R. Wetherington, Jr.

3.6.1 Full-scale experimental voloxidizer

Hulls and fines feeder systems have been made operational. The weigh tables for the hulls and fines have been calibrated and the tip bucket has been installed. Experimentation with the tip-bucket feed-system hopper has verified the Tridyne Corporation hopper design for feeding hulls and fines. An alternate design for feeding shroud pieces is being implemented.

The oxygen analyzers have been installed and are ready to be tested. The bag-type flowmeter in the off-gas system and the heater power calculators have been made operational.

Experimental data has been recorded on a Techtran digital cassette recorder and then transferred to the DEC PDP-10 computer system for further analysis. The color cathode ray tube (CRT) display unit is ready for installation.

3.6.2 Small experimental voloxidizer

The electrical interconnections have been completed between the general purpose Engineering Research unit process controller and the small experimental voloxidizer. Software written to satisfy an approved system design requirements document is being compiled.

3.6.3 Fluidic diode process pump test facility

A preliminary system design requirements document and an instrumented flowsheet have been prepared. Most of the instrumentation will soon be placed on order.

ACKNOWLEDGMENT

The following support personnel contributed to the activities reported in this section: C. F. Bertsch (Sect. 3.5.4); W. T. Bostic (Sects. 3.1.1 and 3.1.2); E. C. Brantley (Sects. 3.3.4 and 3.4.4); S. L. LeStrange (Sect. 3.1.1); J. F. Lockmiller (Sect. 3.2.1); L. M. Marlar (Sects. 3.1.1 and 3.1.2); J. L. Patton, ORGDP (Sect. 3.5.1); and J. D. Randolph (Sect. 3.3.2).

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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 synergistic testing of the 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 development efforts.

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

4.1 ENGINEERING ANALYSIS

O. O. Yarbro

4.1.1 Study of reprocessing facilities at a nuclear energy center

M. J. Haire and D. C. Hampson

The first phase of a study to determine the probable nature of, the relative costs of, and the unique development requirements for, the reprocessing facilities at a nuclear energy center (NEC) was completed, and the interim report was issued on schedule. The report consists of three volumes, with the first volume as the main text, including the basis and methodology for evaluating the relative cost of various reprocessing configurations. Volumes II and III are appendices; Volume II contains an evaluation of the status of reprocessing technology, and Volume III contains detailed flowsheets and equipment concepts developed specifically to support this study.

The second phase of the study, to be completed in FY 1979, will apply the methodology and cost data developed in phase I to optimize reprocessing plant configurations applicable to a nuclear center.

4.1.2 Cost impact of remote maintenance on fuel reprocessing plants
N. R. Grant

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

This study is divided into six tasks. A more detailed description of each task was reported previously.[1]

Task 1 — Current State of the Art

The maintenance approaches used at existing domestic and foreign facilities and facilities currently being designed are summarized.

Task 2 — Requirements for Future Reprocessing Plants

This task includes a description of the regulations which it is anticipated must be applied to future licensable reprocessing facilities.

Task 3 — Estimated Facility Cost for Remote Maintenance

This task investigates the cost items in a reprocessing facility that are affected by the decision to use contact or remote maintenance. Cost items include the areas of construction, operation, and decommissioning.

Task 4 — Categorization of Contaminated Systems

The major contaminated systems and subsystems of a model process are classified into categories and analyzed in terms of reliability, plant availability, care of decontamination, and other factors.

Task 5 — Alternate Design Approaches for Cost Reduction

This task will define alternate design schemes that could be used to reduce cost of equipment and facilities.

Task 6 — Evaluation of Alternate Design Approaches and Conclusions

This evaluation will include factors such as reliability, effect of downtime, and decommissioning, as they are related to overall cost impact. It will also summarize all of the tasks and state the conclusions of the overall study.

A draft report of each of the first four tasks has been completed. Drafts on the last two tasks are to be complete by June 1979. It is planned to combine the critical portions of each of the task reports into one final document during the last quarter of this fiscal year.

4.1.3 Pyrochemical reprocessing study

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

The current approach to providing foreign nations, especially a small, nonweapons, nonsupplier nation, with the opportunity to employ nuclear power is through a guaranteed supply of low enriched ^{235}U or ^{233}U and to require that spent fuels be returned to secured centers for storage or reprocessing. An alternative, which would provide a nation with a greater degree of energy independence, could be to supply that nation with reprocessing technology that has certain necessary antiproliferation characteristics; in short, an "exportable technology."

A study was completed during the past quarter to evaluate the applicability of a reprocessing system based on a prototypical pyrochemical flowsheet to meet the above requirements. Technical inputs from the major contributors to the study have been received and a draft report is in preparation. The complete report will be issued next quarter.

4.2 COMPONENT DEVELOPMENT

O. O. Yarbro

The Component Development effort is a general follow-on to the Engineering Research effort. Component Development goals include the design, fabrication, and operation of pilot-plant scale-process equipment capable of being both remotely operated and maintained.

The current tasks of Component Development include disassembly and cutting, voloxidation, and dissolution. In the future, feed preparation, solvent extraction, and product conversion will be included.

4.2.1 Disassembly and cutting

S. A. Meacham (Westinghouse Advanced Reactors Division) and B. S. Weil

An overall head-end systems requirement document will be prepared to interface the disassembly and cutting task requirements with those of voloxidation, dissolution, and waste handling. The following development efforts are in progress.

Disassembly system. The first draft of the system design requirements (SDR) document has been reviewed and comments are being incorporated. A flowsheet, stating the alternatives, has been prepared and issued. The equipment required to carry out each function of disassembly is being identified.

Plasma torch development. Installation of the support systems in Building 7608 is well under way, and installation of the purchased plasma torch components should begin on schedule in January.

Instrumentation and Controls has reviewed and approved the control system drawings. Arrangements have been made to measure the radio frequency noise around Building 7608

to assure that the installed plasma torch system meets Federal Communications Commission regulations. A concepetual design of a brush-type grounding device for the plasma torch is being prepared. A commercial rotating grounding device was procured and will be used in baseline tests.

The fabrication of feed material for the plasma torch tests is in progress. A ceramic pellet loading device has been assembled; all materials for the system have been received with the exception of the wire needed to wrap the fuel rods in four of the 29 dummy subassemblies.

Laser-cutting development. The United Technologies Research Center (UTRC) has been selected to develop specific baseline information required to support the design of a laser cutting system. The development program to be carried out by UTRC will include (1) a review of spent fuel subassembly designs, (2) material degradation studies, (3) laser cutting tests, (4) design and testing of the focus head, (5) design and testing of the control system, and (6) total system design.

Shear Systems.

Tooling fabrication. Tooling designs VII and VIII, including fabrication and heat treatment, have been completed, and the tooling has been received.

Tooling evaluation. The latest compactor die guide block failed during the compaction stroke against a Pressurized Water Reactor (PWR) dummy subassembly. The design-limiting throat of the shear and the load required for compaction are generally accepted as the cause of the failure. Major modifications of the Birdsboro shear will be necessary in order to complete the testing. In view of the recent program redirection and modification requirements, testing of PWR dummies will be deferred until the tooling has been evaluated.

The design VII tooling, which slits the shroud during compaction, was tested. The tests successfully demonstrated that this task can be accomplished, but the product generated with this particular design is unattractive as the shroud typically fractures into two C-shaped pieces. However, some modifications could be incorporated into the tooling to deliver a more acceptable product consisting of smaller shroud pieces.

Alligator shear development. All the components for the normal feed alligator shear test have been installed on the shear. While testing the 200-ton compactor, it was determined that the hold-down arm was deflecting the 6-in.-thick work table. Minor design changes have been made to correct the deflection. A control pedestal is being built for the alligator system and is scheduled for delivery in January. Testing will begin soon after the control system is checked out.

Remote shear development. Gulf and Western and Sundstrand have started their preconceptual design studies on force transmission for a remote shear. A mid-phase II review was held and progress was determined to be on schedule with the work proceeding satisfactorily.

4.2.2 Prototypic voloxidizer

J. E. Van Cleve, Jr. and M. E. Whatley

The FMC Corporation is providing a conceptual design of this unit. The machine was separated into ten subsystems that require design effort. At the present time, concepts have been developed for nine of the ten subsystems. The remaining subsystem, the furnace concept, should be completed in early January 1979.

The development of a rotating seal for the voloxidizer is a subtask that interfaces closely with the design of the prototypical voloxidizer. It has long been recognized that the seal used on the full-scale experimental voloxidizer is unacceptable for HEF service and that any new design will require experimental testing.

FMC has assisted in the development of a conceptual design of a seal, and the fabrication of special parts is being discussed with prospective suppliers. Detailed attention must be given to specifics, such as a two-foot monolithic graphite ring and a four-foot diameter bellows. The design of a test stand for evaluation of the seal is now being completed.

4.2.3 Dissolution

J. Q. Kirkman and J. P. Drago

Prototypical rotary dissolver. Corrective actions to repair the dissolver drum support rollers, which failed last quarter, have required suspension of dissolver operations throughout this report period.

The support roller failure, which was described in detail in the last report,[1] basically involved binding of the graphitar-bearing sleeves in the rollers on their stainless steel roller shafts. This binding hampered or stopped roller rotation. The rolling surfaces of the dissolver drum that were in contact with the failed rollers were seriously galled.

Redesigned graphitar-bearing sleeves have been fabricated and inserted into the rollers with an interference fit of 0.155 mm to ensure that the graphitar-bearing material remains in compression under all operating conditions. In addition to the large interference fit, key design improvements in the bearing include provisions for forced lubrication with water and a helical groove on the inside diameter of the bearing to distribute the lubricant and collect wear products. Instrumentation to sense proper roller rotation completes the planned modifications for the correction of the roller failure. The new drum support roller assemblies are being installed and aligned.

Dissolver support systems and process equipment. The necessary support systems have been integrated with the 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.

Accomplishments during this report period include completion of (1) several NO_x scrubbing system performance tests, (2) installation of a density analyzer in the dissolver off-gas line and two capillary flow elements in the dissolver fresh liquid feed streams, and

(3) repair of a failed dissolver product diversion valve. Operations of the entire system with hot nitric acid and follow-up runs with U_3O_8 were again deferred pending completion of the repairs to the dissolver drum support rollers.

The NO_x scrubbing system tests are significant because they represent the first opportunity to operate a large portion of the dissolution system under automatic control utilizing written operating procedures. The testing conducted on the scrubbing system, shown in Fig. 4.1, was divided into two parts. The first set of scrubbing tests were scouting runs to determine the performance of the packed scrubber column over a wide range of parameters, investigate the effect of temperature on the removal of nitrous acid from the scrubber bottoms tank, check the reliability of the NO_x analyzer instrumentation, and obtain data for completing a material balance. From the scouting tests, information was gained not only about the basic scrubbing process but also about equipment problems, equipment operational limits, and operating procedure adequacy. From a process standpoint, the tests suggested that a key factor in improving system scrubbing efficiency would be a reduction in the nitrous acid concentration of the scrubber bottoms liquid, a fraction of which is recycled to the top of the column as scrubbing liquid (see Fig. 4.1). With the scrubber bottoms tank operated at a high temperature to promote dissociation of HNO_2, the scouting tests identified three parameters which should affect nitrous acid behavior in the system and consequently the scrubber performance. The three parameters were air sparge rate of the scrubber bottoms tank, recycle acid flowrate, and recycle acid temperature.

To determine the significance of each of the three parameters identified in the scouting tests, a second set of NO_x scrubber system tests is presently in progress. This set of tests consists of four steady-state runs, the conditions for each run being based on a half-fraction factorial design for three parameters. The results of the four runs will assist in determining which of the three parameters significantly improves scrubbing efficiency. Specifically, the testing will provide information on what effect the impact sparge rate has on reduction of nitrous acid in the scrubber bottoms tank, the degree to which nitrous acid is stripped from the recycle acid stream at the top of the column, and the effect temperature has on tower performance and nitrous acid dissociation within the tower. Partial results to date indicate the ability to maintain a 0.5 mole % NO_x in the outlet gas with an inlet gas stream to the column containing 5.4 mole % NO_x.

4.2.4 Instrumentation and controls

W. F. Johnson, R. M. Tate, and G. R. Wetherington, Jr.

Shear instrumentation. An apparatus to allow additional testing of the fluidic shear sensors has been fabricated and assembled. Preliminary data on the multiple sensor block indicate less displacement sensitivity than that obtained by electron microprobe x-ray (EMX) on their experimental sensor block. This discrepancy is being investigated. Tests are also being run on commercially available sensors, and the possibility of utilizing these sensors is being investigated.

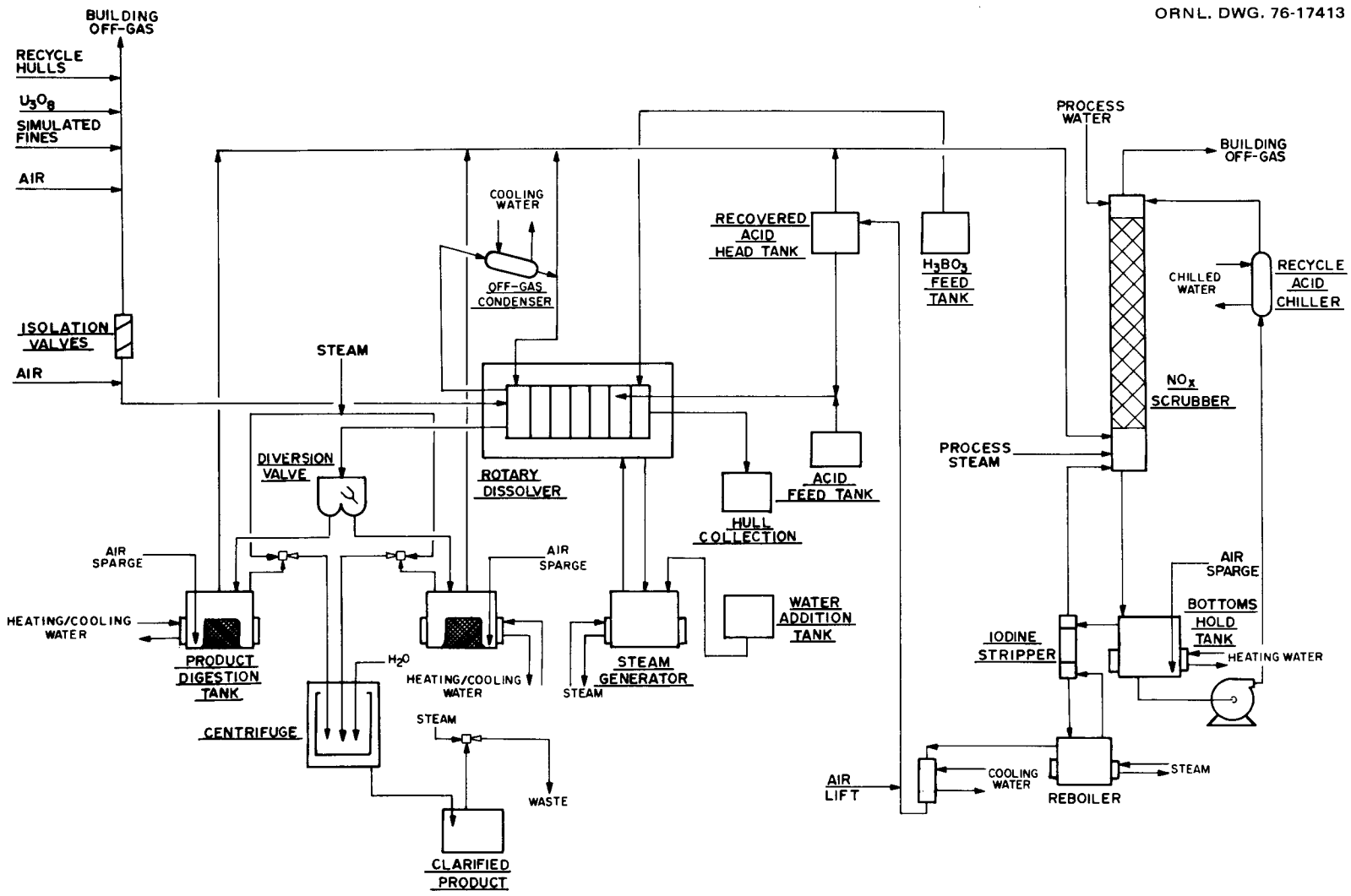

Fig. 4.1. Rotary dissolver system flow diagram.

Prototype dissolver instrumentation and controls. Three instrumentation related items have been accomplished this period. First, a gas density analyzer, which monitors the dissolver off-gas entering the NO_x scrubber column and the scrubbed stream leaving the column, has been installed and calibrated. This instrument measures the thermal conductivity of the gas stream and infers density from this measurement. Second, the accuracy of measuring the fresh acid feed flow and fresh water feed flow to the dissolver has been improved significantly by the installation of capillary flow elements in the feed lines. Third, a conductivity flow cell holder and transmitter have been installed and calibrated for the scrubber bottoms tank. The cell holder minimizes conductivity measurement errors by stripping gas bubbles out of the solution to be measured prior to passing the solution through the conductivity element. The successful operation of this unit has led to modifications which will allow a flow cell holder to be used on each of the product tanks. The continuous recirculation system for the cell holder is essentially an air-lift-assisted jet that draws fresh product tank solution continuously through the cell and then returns it to the tank.

The Analytical Chemistry Division has provided the necessary data for the determination of the uranium and acid concentrations of the product tanks from temperature, density, and conductivity measurements. The algorithms relating the measurements to concentrations have been determined, and final statistical analysis of the accuracy of measurement is being determined.

Disassembly and cutting. A manual control station for the alligator shear has been designed and is being fabricated. It provides for the operation of the fuel feeder assembly, the fuel scoring compactor, and the alligator shear. Limit switches will soon be added to the feeding mechanism.

A drum programmer has been purchased for controlling the gas sampling system for the plasma torch facility, and its electrical connections have been included in the facility electrical drawings.

Component development data acquisition and control system (CODEDACS). The final memory expansion for the system has been ordered; delivery is expected in February. The disk expansion is expected to arrive in January.

The cable tray and cables between the shear and CODEDACS have been installed.

4.3 SYSTEMS DEVELOPMENT

N. R. Grant

Systems Development is directed toward the major components that are closely associated with the operations and maintenance aspects of the HEF. None of these tasks are directly process related. The goals in Systems Development are the design, fabrication, and operation of full-scale, remotely operable equipment.

The tasks assigned to this area are the Integrated Equipment Test (IET) facility, the receiving and storage systems, the remote maintenance systems, the waste handling systems, and the procurement of depleted uranium fuel to be used for equipment and process development.

The program budget for FY 1979 has required reductions in some tasks.[2] The receiving and storage and waste handling tasks were selected as the best candidates for reduced funding. Reports this quarter for these two tasks reflect this reduction in that some subcontracts were closed and others are being allowed to close; very few new activities are being initiated. A few basic programs will continue in these two tasks this fiscal year.

4.3.1 Integrated Equipment Test facility

J. G. Stradley, H. W. Harvey, 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 establishes an area where specific pieces of process equipment can be operated as an integrated system. These are equipment components that have evolved from the development 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 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.

Design and schedule. The IET design is the responsibility of UCC-ND Engineering. Title II design began in January 1978; the status of the three phases is as follows:

1. The IPD design effort is on schedule (40% actual vs 40% scheduled).
2. The design for ROMD is still behind schedule with approximately 38% complete vs 49% scheduled.
3. The GPF design is complete; however, a review of some of the drawings, the general specifications, and the procurement package remains to be completed. It is now anticipated that the procurement package will be released in January 1979 and that construction will start by May.

Integrated Process Demonstration. As indicated earlier,[1] the materials of construction for the Iodox and its acid concentration systems continue to be a problem. Battelle Memorial Institute (Columbus, Ohio) has continued to conduct stress-corrosion cracking experiments on various materials by means of constant-extension rate tests. These are being performed under the acid conditions (22 *M* HNO_3) expected in the Iodox and its acid

concentration systems. Recommendation for construction materials is scheduled to be made in February so that Title II design of these units can be reinitiated in March.

Procurement packages for some equipment items have been released. The Integrated Crane and Manipulator System (Fig. 4.2) procurement package, consisting of hoist, trolleys,

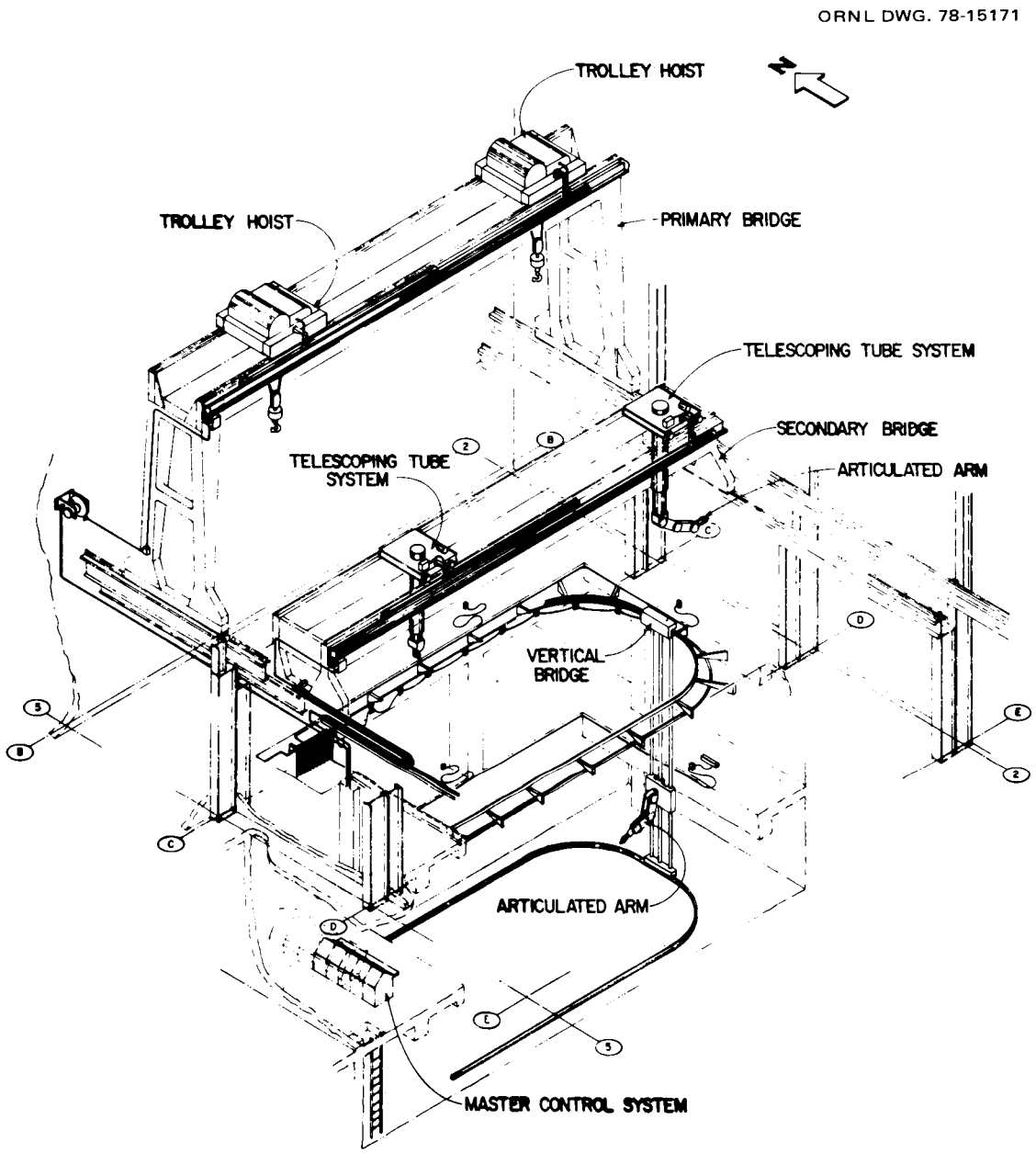

Fig. 4.2. Remote handling equipment in ROMD.

telescoping tubes (with hooks or articulated arms), and a wall-mounted bridge/trolley and boom (with articulated arm capability), has been released for quotation. The contract for this system is expected to be awarded by June 1979.

Detailed specifications covering the TV positioning system, television system, master/slave manipulators, simulated shielding, and other miscellaneous ancillary equipment have been issued for review. It is currently anticipated that the individual contracts for this equipment should be awarded by July 1979.

The ROMD model has been completed to reflect the Title I design level and will be upgraded, as appropriate, to reflect the final facility configuration.

4.3.2 Receiving and storage

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

The work breakdown structure for the receiving and storage task identifies eight subtasks, including (1) systems integration control; (2) cask shipping, receiving, and maintenance; (3) cask unloading station; (4) fuel receiving and handling; (5) sodium removal and decontamination; (6) nondestructive assay; (7) storage; and (8) fuel receiving cell. The objectives of these subtasks have been described in previous progress reports. Programmatic requirements necessitated a major reduction in efforts for this area. Work is being completed or phased out for many of these subtasks. The progress of this task during this report period is discussed in the following sections.

Systems integration. A report is being prepared which summarizes the results from all the conceptual design studies and experimental test efforts performed within each subtask for the period from August 1976 to September 1978. The report will provide a basis for resuming design of the various items in the task when funding of this task is resumed.

Fuel receiving and handling. The conceptual design study for the local instrument and control system (LICS) in the fuel receiving cell and fuel storage pool was received this quarter. Westinghouse Advanced Reactors Division (WARD) prepared the study under the direction of the Instrumentation and Controls Division of ORNL.

The final report presents a two-level hierarchical instrument and control system for the receiving and storage (FRS) areas. The top level is the supervisory control system (SCS), which provides both supervisory data functions for the operations management staff and centralized control and data functions for the fuel receiving and storage system operators. The lower level of the hierarchy is the subsystem local control (SLC) and data functions, which will permit the FRS system operators to run the subsystems in an independent fashion. The SCS is capable of performing all necessary FRS operations independent of the overall HEF plant supervisory system. In addition, the SLC is able to continue the FRS subsystem operations in the event of failure within the SCS.

The SCS and SLC provide for three selectable modes of operation for FRS subsystems. The three modes are (1) manual, (2) semi-automatic, and (3) automatic. The automatic

mode applies to all FRS operations, with the exception of cask handling and unloading. The supervisory control system will be designed for automatic computer based operations to the extent practicable.

Nondestructive assay system (NDA). The scoping study for the mechanical systems of the NDA station is nearing completion. The study provides information on the functions and requirements of the nondestructive assay station for use in the subsequent conceptual design of the equipment.

Storage. During this reporting period, the unirradiated corrosion experiments (corrosion II) of the WARD/ORNL corrosion program were completed. The cold- and hot-leg sodium-exposed cladding specimens completed their intended water exposure without failure. Before the experiment was terminated, the hot-leg specimens accumulated over 12 months of water exposure and the cold-leg specimens accumulated over 10 months. The specimens are currently being evaluated, and the results will be presented in a topical report.

The water exposure of the irradiated cladding specimens of the WARD/ORNL corrosion III program continued during this period. The specimens to date have accumulated over six months of water exposure without failure of the sodium-exposed cladding.

4.3.3 Remote maintenance

R. Blumberg, J. Garin (Westinghouse Advanced Reactors Division), and W. F. Schaffer, Jr.

The remote maintenance task is concerned with improving the technology for maintaining the radioactive systems of nuclear fuel reprocessing plants. Along with the primary goal of reducing personnel exposure, the improvements will make the maintenance systems more reliable, more easily maintained, and more efficient, thus, contributing to increased plant availability.

The principal effort under way at this time consists of setting up an unused cell at the Thorium-Uranium Recycle Facility (TURF) to test and demonstrate several of the improvements under development. It is planned to conduct integrated tests involving remotely operated piping connectors, improved crane controls, impact wrenches, and television viewing. For the next two or more years, this facility will be our major remote maintenance test area until ROMD becomes available for this purpose. Following is a description of several other activities in progress.

Electromechanical system (B. J. Bolfing, J. Garin, P. E. Satterlee, and J. W. Switzer). This subtask is involved with improving the overhead handling systems and their auxiliaries. This equipment includes remotely operated bridge carriage, hoist and manipulator systems, as well as the tools (such as impact wrenches) that are used with the manipulators to operate on the process equipment.

Manipulator and crane controls. The laboratory checkout of the three-axis position indication and control system has been completed. The installation of the electronic control boxes onto the trolley of the cell E bridge at TURF is 50% complete. Figure 4.3 is a view of

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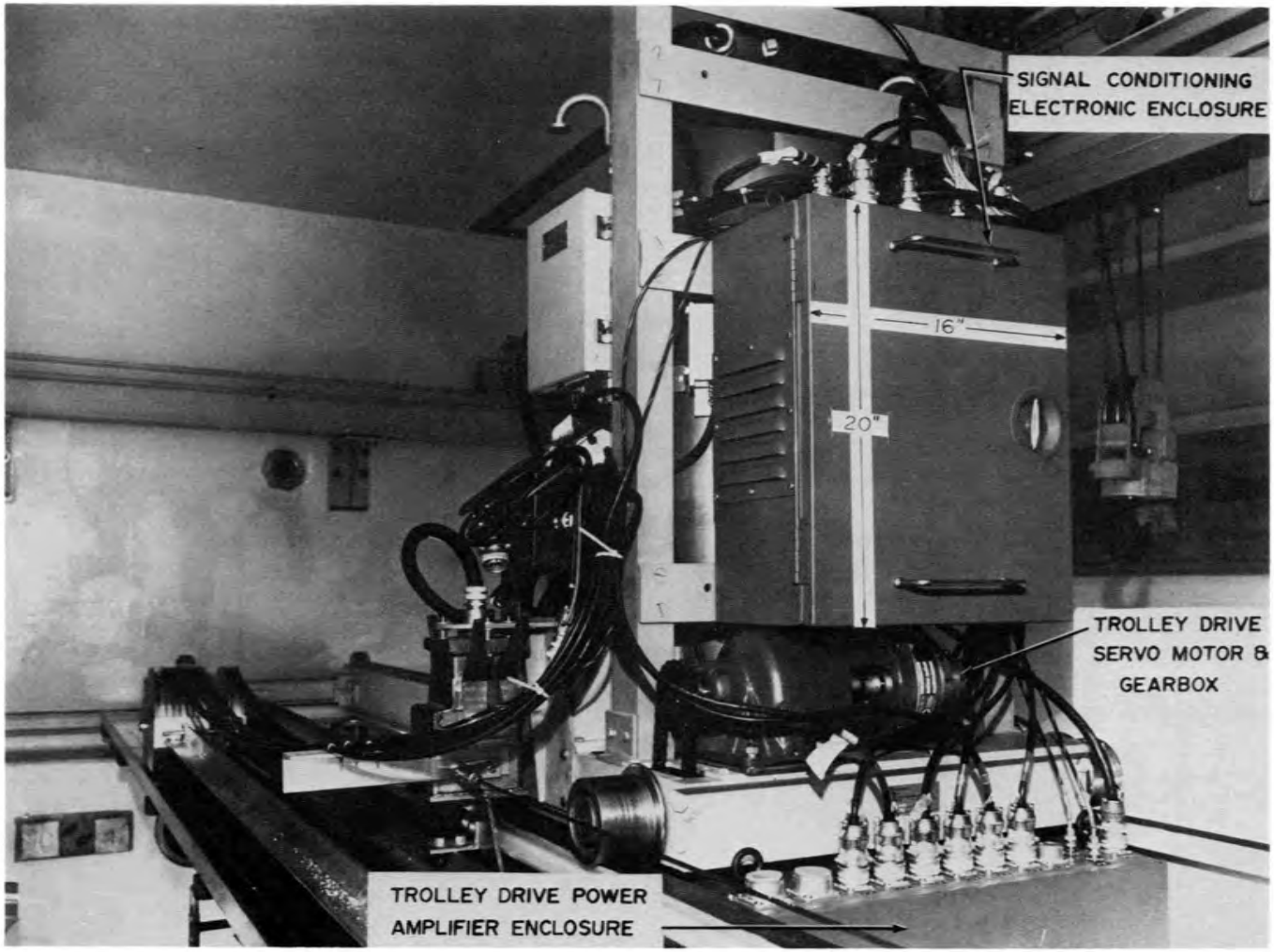

Fig. 4.3. New electronic controls for TURF cell E bridge.

the installation showing the relative sizes of the electronic control enclosures and the drive motor. The system has been designed with modular, plug-in components and some redundancy in order to ensure availability of the operating equipment for testing of the impact wrench and remote disconnects.

The PDP 11/34 minicomputer to be used with this system has been received and the acceptance tests run. A joy stick control has been received and is being wired as a substitute for the existing multiswitch manipulator control.

Power transmission. A study has been completed by WARD on the use of batteries as a means of powering overhead systems for the remote maintenance task. The study was a small scoping effort wherein several battery types (lead-acid, nickel-zinc, and iron-nickel) were examined on a preliminary design basis to supply the power needs estimated for an overhead crane system. The systems were evaluated in terms of life cycle characteristics, maintenance features, operating performance, commercial availability, and cycle costs. All three battery types were judged to be feasible for the power requirements. The lead-acid type was considered to be the best choice for the present, based on commercial availability, while the iron-nickel system was rated best on the basis of performance. The design of a system that could be installed and tested in ROMD constitutes the second phase of this program.

Impact wrench. The design and fabrication of an electrically driven, remotely operable impact wrench is 95% complete. The design of a control system to operate this wrench with regulation of torque output is under way. At least two new methods of torque regulation are being considered; namely, direct sensing of mechanical torque and a system based on sensing or counting hammer blows. In addition, two other electrically driven torque wrenches have been designed using other types of hammer mechanisms as a basis.

Remote maintenance studies. Three studies which support this subtask are in various stages of completion.

1. Criteria have been prepared for a conceptual design of an extended-reach manipulator which incorporates some features of advanced technology, such as force feedback, component identification, and internally wired television. This device is a response to the manipulative requirements of the deep cells of the HEF configuration and the needs for additional capability to accomplish in situ maintenance. A subcontract has been recently awarded to MBAssociates of San Ramon, California, for this design.

2. A contract for a remote maintenance plant availability study was awarded to Nuclear Services Associates (NSA) of Fullerton, California. They have completed the first phase which provides an equipment list that tabulates 13 columns of remote maintenance data for each item of equipment in the process cells. Among the data tabulated is maintenance frequency from which NSA will estimate values of plant availability. From this kind of analysis, our development program will derive guidance on how much emphasis to place on the development of in situ maintenance tooling. The NSA will also prepare a maintenance plan and submit a final report by the end of May.

3. The final draft of a remote maintenance design guide manual has been prepared. Its primary purpose is to serve the needs of component developers and subcontractors who do not have experience in remote maintenance. This manual will be revised periodically as we gain more experience in what information is required and in what form it is best communicated.

Remote connectors and jumpers (W. F. Schaffer, Jr.). The objective of this subtask is to develop remotely operable fluid and electrical connectors for use in the HEF. Specific to the development of fluid connectors is the need for developing a radiation resistant seal. The present practice in reprocessing plants is to use a Hanford-Purex (H-P) connector with a Teflon seal. The development is organized into four general activities.

1. Adaptation of the H-P connector with a radiation-resistant seal. At present, jumpers have been constructed with H-P connects modified to accept Grafoil, Gamah, Graylor, and "C" ring seals. (The last three are stainless steel.) This assortment represents a diversity of sealing techniques. They are available for testing as described below in items 3 and 4.
2. Develop alternates to the H-P design. Three subcontracts have been placed with outside firms for procurement of detailed designs and fabrication of connectors, and a fourth design was fabricated at ORNL. The design, fabrication, and acceptance testing of these items are in various stages of completion; however, all subcontracted connector design work is expected to be finished and received at ORNL by April 1979.
3. Testing for remote handling characteristics. Very little work has been done on tests set up in Building 7601 due to the lack of precise control capabilities of the overhead crane. The test stand will be moved to cell E of TURF for these tests after the three-axis system is installed there.
4. Evaluation of the sealing performance of various connectors. The fabrication of the facility to test seal performance has encountered delays in procurement. The responses to the first bid package were unsatisfactory. The bid package has been revised by dividing it into four parts, and the new request for bids will be sent out early in the next quarter.

Sampling systems (R. Blumberg and W. F. Schaffer, Jr.). The scoping study on liquid sampling, previously described,[1] has been completed, and a report has been issued. Additional work in this area has been stopped due to lack of funds. The study developed and compared designs for three different types of liquid sampling systems: (1) a system based on existing technology (a station located at a shielded window equipped with a master slave), (2) an advanced technology liquid sampling (ATLS) system using a remotely operated track-guided vehicle, and (3) a system utilizing pneumatic tube transfer.

System (2), which was considered the best of the three designs, has features that offer significant benefits in HEF maintenance, operation, and cell layout. In the ATLS system, liquid is withdrawn and circulated between the vessels and a sampling station mounted on the wall of the cell. The driving force for liquid circulation is a conventional vacuum jet/air-lift method. The sampling station contains piping, air jets, and a needle block. The

mechanical operations required for the sampling cycle are provided by a remotely operated, battery-powered service vehicle which is mounted on a track running around the perimeter of the cell. These operations include

1. bringing empty sample bottles to the sample station,
2. pushing the bottle up into the fill position on the needle block,
3. reading and transmitting the sample bottle identity to operations control center,
4. removing the filled bottle,
5. delivering the filled bottle to the analytical cell.

Remote maintenance has been designed into this system by providing four removable packages and by having most of the complex mechanical parts mounted on an easily removed subassembly of the service vehicle. The need for operator attention, monitoring, and involvement in sampling operations is minimized.

4.3.4 Waste handling

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

The development or selection of methods for the conversion of all of the different radioactive wastes of a fuel reprocessing plant (e.g., 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 the waste development work of other laboratories, provide input when specific problems are not fully investigated, and consider the adaptability of resolutions to the HEF design. Where little or no development is being performed outside ORNL, such as metallic waste packaging, this task will follow through on all of the equipment-development phases of scoping studies, design, fabrication, and testing.

A molten-salt burner potentially provides a method for the disposal of all miscellaneous liquid wastes resulting from breeder fuel reprocessing operations. These wastes include caustic liquids, ion exchange resin slurries, spent solvents, and organics for which this process had not been previously considered. The molten-salt burner tests (performed by the Energy Systems Division of Rockwell International) have been completed. They have demonstrated the capability of their unit to safely combust an aqueous stream consisting of NaOH, $NaNO_3$, kerosene, PVC, TBP, and an ion exchange resin. This stream was mixed with methanol to provide the required heat content in the stream. The NO_x emissions were materially reduced by injecting ammonia above the molten-salt level. A patent disclosure has been filed on this technique, and the terminal report covering this work is presently in preparation.

The inductoslag melting tests performed at Pacific Northwest Laboratory have been completed, and a terminal report has been received. The report will be issued as an ORNL/CFRP document.

The work at Georgia Tech on the effect of adding a central billet of cast fuel hulls to the vitrified high-level waste canister is complete. The terminal report is in preparation.

The proof-of-principle experiments for the NDA monitoring of leached fuel hulls for residual plutonium are under way. These experiments will investigate the feasibility of using active neutron interrogation and the detection of the prompt neutrons produced during fission. Passive gamma and passive neutron methods will also be investigated in case the active system fails. The merit of a measurement strategy which involves both pre- and postdissolution assays will also be determined. The predissolution measurement could enhance the confidence level for the postdissolution measurement.

4.3.5 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, (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.

Twenty dummy fuel assemblies are expected to be fabricated and delivered to ORNL by June.

The response to a bid package to convert 30,000 kg of uranium as uranyl nitrate to oxide over a 12- to 18-month period was not satisfactory. One bid was received, but the quoted price was much higher than estimated. We are investigating the possibility of obtaining this service from a DOE contractor. A decision will be made next quarter; meanwhile, the first dissolver test is expected to be run with depleted uranium.

4.4 HOT EXPERIMENTAL FACILITY

J. R. White

The *Hot Experimental Facility Interim Design Report,* dated October 1978, has been published. This report describes the reference HEF concept for a pilot scale reprocessing facility that will be capable of demonstrating storage and reprocessing technology for typical breeder-reactor and LWR fuels using either the uranium-plutonium or the thorium-uranium-plutonium fuel cycles. The facility will be licensable and will meet, or exceed, the federal requirements for fuel reprocessing plants; these include safeguards, saboteur resistance, natural phenomena, release of contaminants to the environment, radiation exposure to the public and plant personnel, and decommissioning. The HEF will use equipment that can be scaled up for use in production-sized plants. It will also be versatile so that initially installed equipment can be replaced with more advanced designs as they evolve through CFRP developmental efforts. A summary description of the reference HEF concept is included in this progress report.

The previous quarterly report described the HEF design studies that were to be performed during fiscal years 1979 and 1980. The plan then was to defer the HEF concept design until fiscal year 1981. Verbal redirection has been received from the DOE to

continue with the HEF concept design and to issue the Conceptual Design Report early in fiscal year 1981. Schedules, budgets, and staff needs are being prepared to implement this redirection.

A comprehensive description of the design criteria applicable to the overall HEF conceptual design has been prepared and submitted to the DOE for review. The major requirements in this criteria document are summarized in Table 4.1, which includes a definition of the input material to the HEF, functional requirements for fuel storage and reprocessing, operations and maintenance guidelines, and waste-effluent management.

Table 4.1. Summary of HEF design criteria

Item	HEF requirement
A. Input material	
(1) Fuel assemblies	• Store and reprocess fuel from: FFTF Thorium breeders Plutonium breeders Gas-cooled reactors Light water reactors (includes zirconium cladding) • Reprocess carbide fuels (with modification or replacement of HEF equipment)
(2) Decay time	• Receive and store fuel with a minimum decay of 60 days • Reprocess uranium-plutonium fuel with a minimum decay of 90 days and 250 days for thorium fuel
(3) Shipping cask	• Accept fuel shipped in casks filled with air, sodium, inert gas, or water
(4) Cask transporter	• Accept fuel casks shipped by rail or truck
B. Functional	
(1) Reprocessing capacity	• Have a reprocessing capacity of 0.5 metric ton of heavy metal per day (and capable of operation at 0.25 metric ton of heavy metal per day) of uranium-plutonium fuel and 0.2 metric ton of heavy metal per day for thorium fuels
(2) Process description	• Be equipped to recover and purify source and fission material, convert products to solid form, treat off-gases, purify and recycle liquid and acid, and package waste
(3) Feed material storage	• Store 500 fueled, plus 100 control, assemblies in water with a total pool heat dissipation of 2.0×10^6 W
(4) Process cell ventilation system	• Ventilation system in main process cell to have two modes of operation: Low-volume air-inleakage operation with local cooling and exhaust through vessel off-gas system Once-through high-volume, flow-through operation with an independent gas filtration-treatment system. Flow rate based on cell cooling • Ventilation system in all other cells to be low-volume mode of operation

Table 4.1. (continued)

Item	HEF requirement
(5) Process off-gas	• Process off-gas, including dissolver off-gas, to be once-through flow
(6) Product storage and shipping	• Products to be stored and shipped in oxide form include: $U^{238}O_3$ ThO_2 Mixture of 25% PuO_2 and 75% $U^{238}O_2$ Mixture of 25% $U^{233}O_2$ and 75% $U^{238}O_2$
	• Product storage capacity for 100 days of operation of U-Pu or Th-U fuels
	• Storage of $U^{238}O_2$-PuO_2 and $U^{238}O_2$-$U^{233}O_2$ to be in common vault and comply with safeguards requirements
(7) Cask external contamination	• Decontamination and monitoring of casks after receipt and before offsite shipment
(8) Cask maintenance	• Removal of cask coolant, decontamination of cask internals, and space for limited cask maintenance
C. Operation and maintenance	
(1) Support facilities	• Independent site providing all facilities and services for routine operation and maintenance
	• Existing facilities to be used for support of nonroutine operation
(2) Plant availability factor	• Target on-stream availability is 60% of time-rated capacity
	• Demonstrate feasibility of operating a 5 metric ton of heavy metal per day production plant at 80% availability
(3) Design life	• Facility life is 30 years
	• Spare parts inventory and equipment repair time based on plant factor
(4) Development equipment	• Development equipment to be prototypic for production plant
(5) Contaminated equipment maintenance	• Maximum radiation level in routinely occupied areas $\leqslant$0.1 mrem/h
	• Contaminated equipment maintenance usually performed remotely
	• Contact maintenance to be consistent with goal of 500 mrem/year personnel exposure
	• Containment to be provided for transfers from contaminated areas
	• Equipment to be included for remote decontamination and maintenance, contact maintenance storage, cutup, and packaging
(6) Equipment interfaces	• In-cell equipment to be compatible with environmental provisions, as well as remote viewing manipulation, and maintenance

Table 4.1. (continued)

Item	HEF requirement
D. Waste and effluent management	
(1) Fission product emissions	• Demonstrate retention factors that yield site boundary whole-body dose ≤0.1 mrem/year at HEF capacity
	• Design objective to provide minimum overall plant retention factors as follows for typical breeder fuels:

Contaminant	Retention factor
C^{14}	5
H^{3}	5
Kr^{85}	100
I^{131}	1×10^{7}
I^{129}	4×10^{4}
Ru	5×10^{10}
Particulates	2×10^{11}
Transuranics	2×10^{11}

	• Additional tritium retention factor of about 25 for LWR fuels
	• Radon retention for thorium fuels as needed to meet 0.1 mrem/year maximum site boundary dose
(2) High-level liquid waste	• To be solidified and packaged in containers acceptable in federal repository (casks and transporters not included in HEF)
	• Maximum allowable temperature of solidified waste in 12-in. diam can to be 800°C. To meet this requirement, the following have been established: Store waste in liquid form for two years before solidification Install five liquid waste tanks at 20,000 gallons each (one is a spare) Provide 2.5×10^{6} W heat removal for each tank, with a total capacity for all tanks of 5×10^{6} W
	• Maximum power generation per waste can sent to federal repository to be 5 kW. To meet this requirement, the following have been established: Waste can size 12 in. diam by 10 ft high Waste storage capacity for 400 cans (six years' capacity) Waste storage pool heat removal capacity of 3.5×10^{6} W
(3) Disposition of metal scrap	• To be consolidated and packaged acceptable for transfer to federal repository (waste casks and transporters not included in HEF)
	• Storage for six months of operation at 0.5 metric ton of heavy metal per day
	• Design objective to maintain U^{233}/Pu content of scrap within total measured plant loss to all waste ≤0.1 % of U^{233} plant input
(4) Process liquid recycle and disposition	• To contain equipment for recovery, purification, and recycle of water and acid used in all process functions

4.4.1 Process systems

E. D. North and F. L. Peishel

During review of the various proposed proliferation-resistant fuel cycles, it was concluded that the HEF must be able to process three broad classes of fuel: uranium-plutonium, uranium-plutonium-thorium, and thorium-uranium.

The HEF will house equipment to reprocess spent fuel from any of the fuel cycles shown in Fig. 4.4. Further, the fissile products must be denatured during reprocessing to protect against diversion of strategic fissile material.

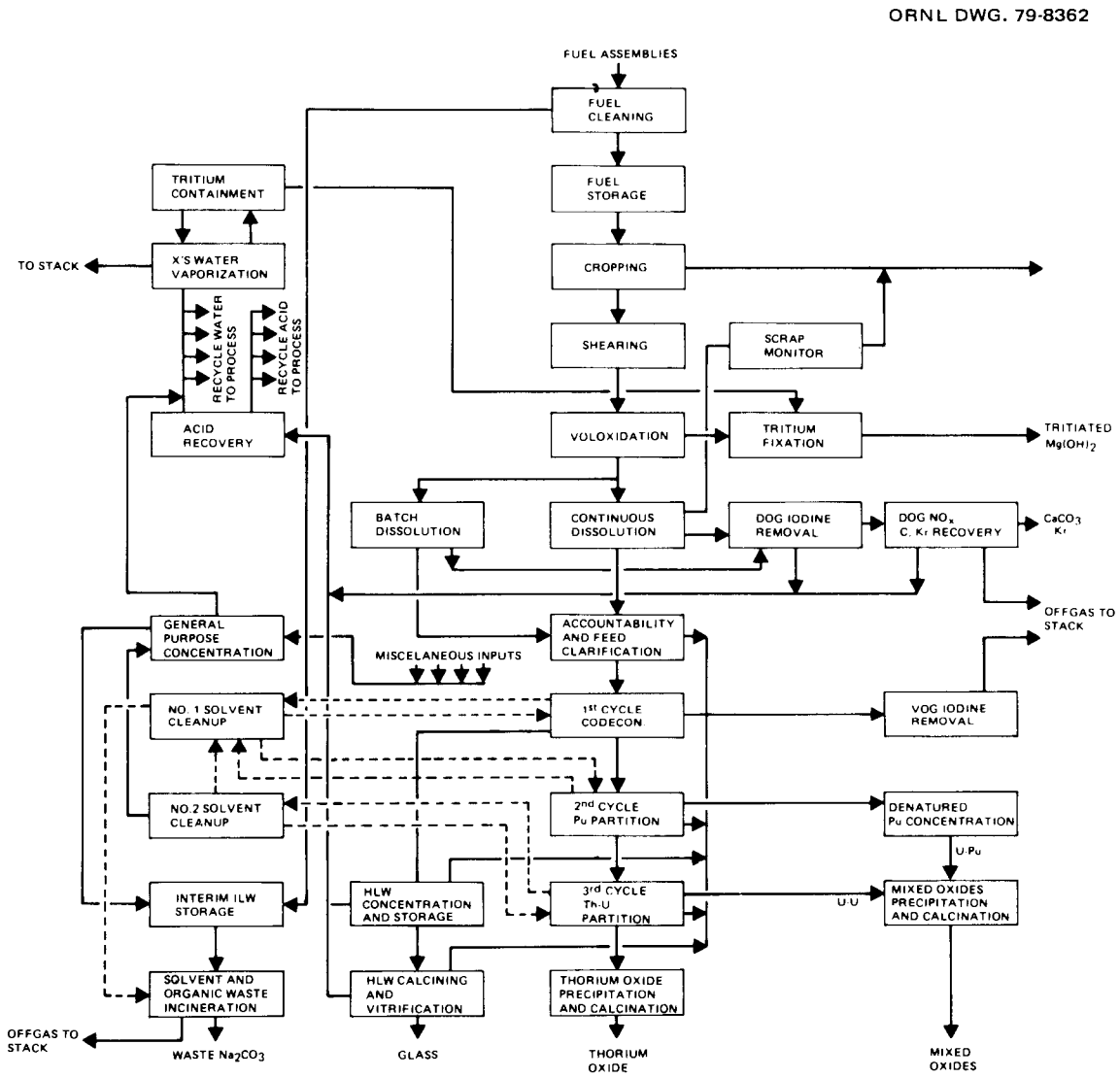

Fig. 4.4. Uranium-plutonium-thorium simplified block flow diagram.

All types of fuel assemblies will be removed from shipping casks, cleaned of sodium (if necessary), nondestructively assayed, and transferred to the fuel storage pool, using common equipment in the fuel receiving cell (Figs. 4.5 and 4.6). Similarly, all fuel assemblies will be prepared for processing in the same shear/disassembly machine in the fuel disassembly cell (Fig. 4.7). All sheared fuel pins will discharge into the voloxidizer, which heats the fuel in the presence of oxygen. This releases tritium, which will be recovered from the off-gas system for disposal. Tritium removal from thorium fuels in the voloxidizer is not expected to be effective; therefore, tritium will accumulate in the recycle acid and water stream. A separate tritium removal system will be installed from these streams.

Fuels will discharge from the voloxidizer into a rotary dissolver which will be fed countercurrently with acid. A modified form of the acid Thorex process will be used in the HEF for the sequential separation of plutonium and uranium from thorium. The solvent extraction system, which includes one cycle for codecontamination, will process all three types of fuel. Common systems will also be used to convert the ^{238}Pu and $^{233-238}U$ product streams into oxide form and to package, store, and ship the products.

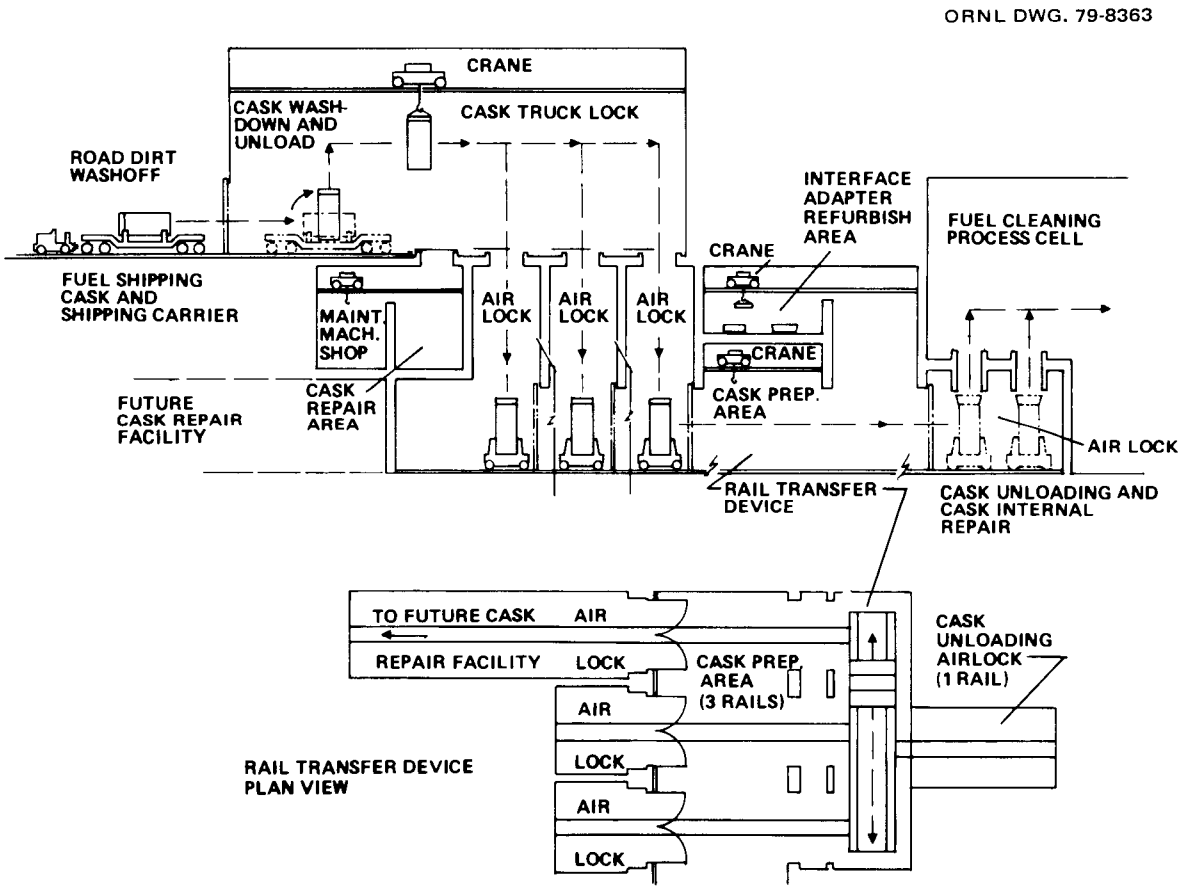

Fig. 4.5. Fuel shipping cask handling.

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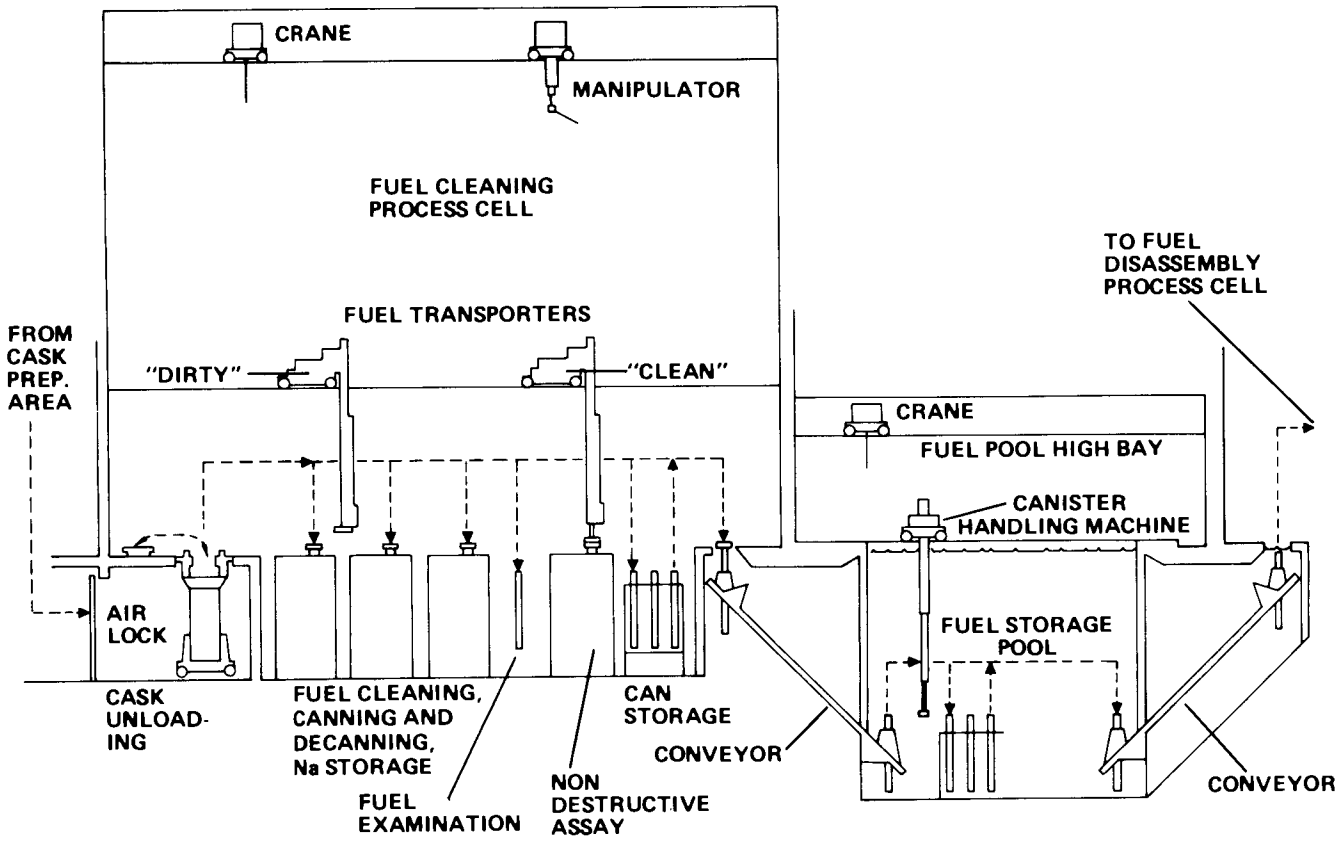

Fig. 4.6. Fuel receiving, cleaning, and storage.

ORNL DWG. 79-8365

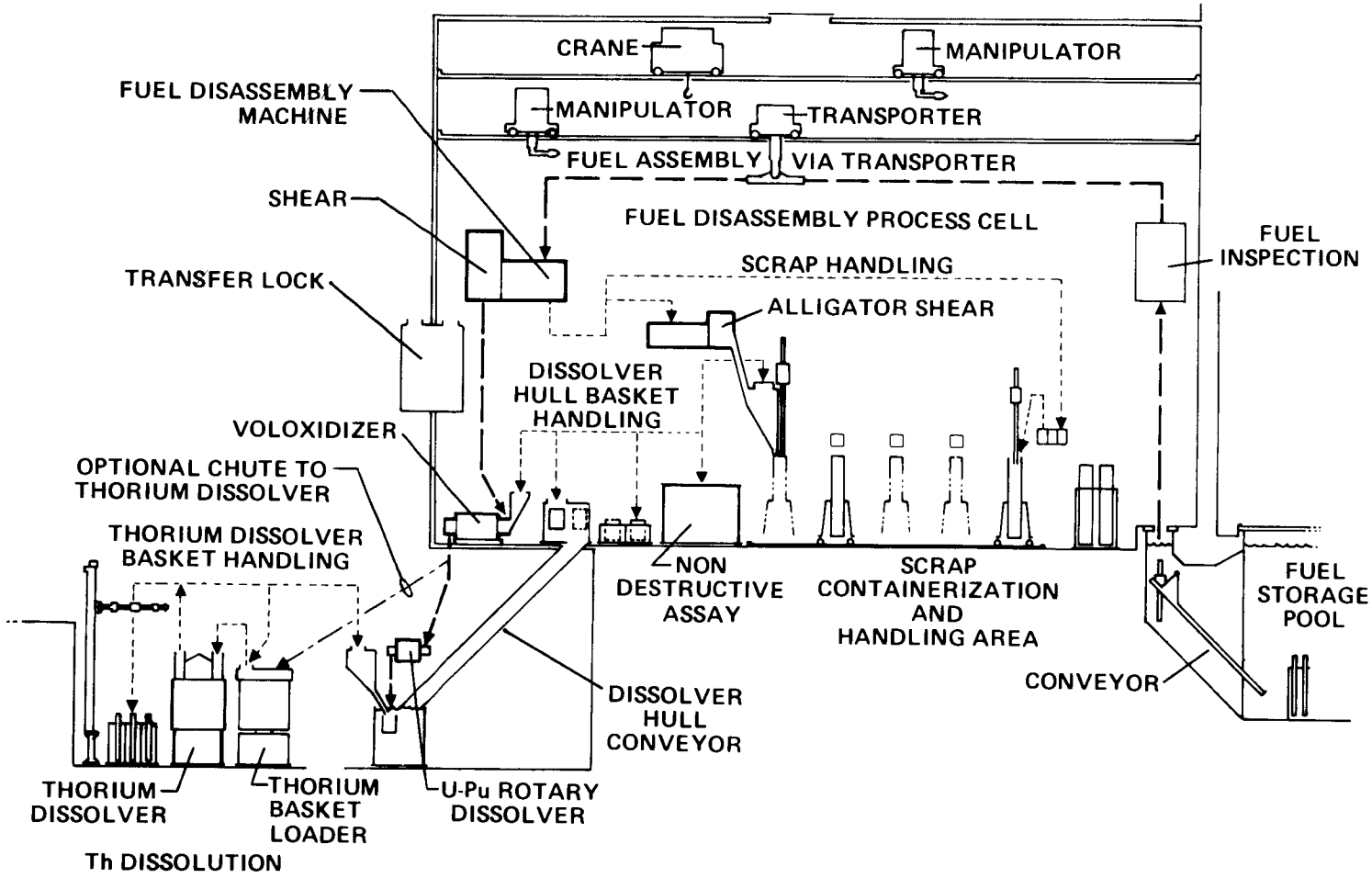

Fig. 4.7. Fuel inspection, disassembly, shearing, voloxidation, and dissolver loading.

High-level liquid wastes will be solidified and vitrified for subsequent transfer to a federal repository. The vitrified waste will be packaged into 12-in.-diam by 10-ft-tall canisters and stored in the waste pool. Metal scrap from the fuel assemblies and other process operations will also be compacted into waste cans and stored in the waste pool. Equipment will be provided for the recovery, purification, and recycle of water and acid. No process liquids will be discharged to the environment. Off-gases will be treated extensively to remove tritium, iodine, krypton, xenon, carbon-14, and radon, as shown in Fig. 4.8.

Process equipment will be designed for remote installation and maintenance using the manipulative equipment provided in the cells. In general, this means that all equipment will be arranged in modules or assemblies sized for transfer in and out of the cells. Components that may fail frequently or require service (such as motors, bearings, heaters, and shell-and-tube heat exchangers) will be fabricated as assemblies that can be remotely replaced without moving the larger module to which they are attached. All process and service connections to the module assemblies will be capable of remote disconnect and reconnect, which will be accomplished by "piping jumpers" between the modules, service connections in the cell wall, process lines in the in-cell pipeway, and adjacent modules. The majority of piping jumpers between each module, the in-cell pipeway, and the service feed-throughs in the cell wall will be positioned so that the jumper disconnect fittings will be within a specified range of elevations which will allow convenient servicing by in-cell maintenance equipment.

ORNL DWG. 79-8366

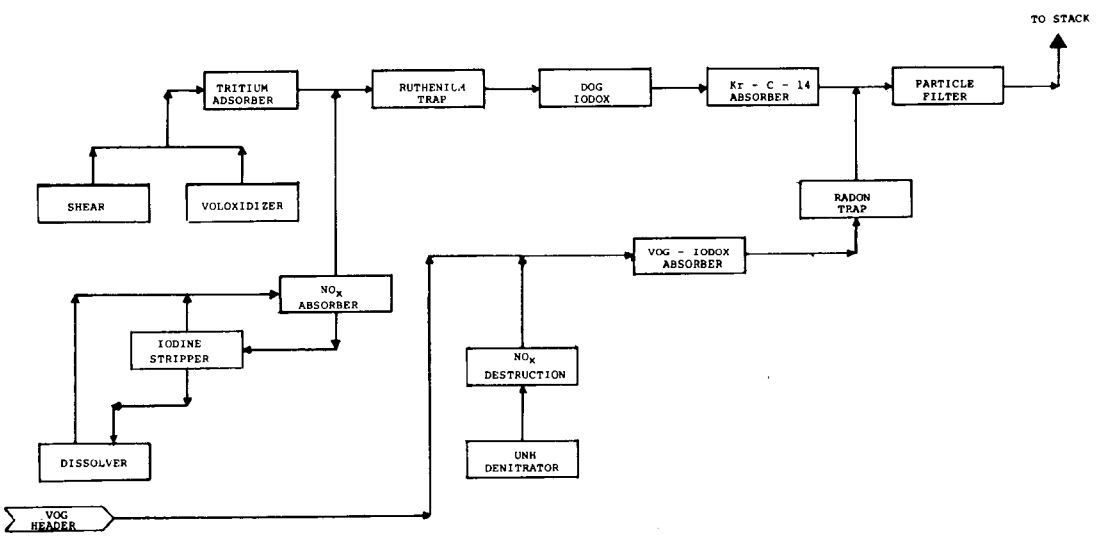

Fig. 4.8. Off-gas treatment systems.

4.4.2 Facility design

J. R. White and J. N. Herndon

The reference HEF conceptual design includes all facilities and equipment needed to meet the design criteria, except those for carbide fuels. The project has been organized by the work breakdown structure shown in Fig. 4.9. Wherever possible, the concepts selected for the facilities and equipment are based on existing state-of-the-art technology. However, in areas where there was no technological base, the concepts selected were based on relatively brief design trade-off studies and/or input provided by CFRP developmental activities. The facility design has not been optimized, and a number of technical problem areas are unresolved. Further, the design has not been analyzed for reliability and cost effectiveness. The reference design (and cost estimate) was prepared to identify and resolve problem areas and to obtain optimal cost effectiveness.

A site for the HEF has not been designated. At present, without firm commitments to construct the HEF, no serious site selection process is under way. However, it has been assumed for the reference conceptual design that the site will be in Oak Ridge. The reference site used for this phase of the conceptual design is about 2 miles east of the proposed Clinch River Breeder Reactor (CRBR) and 1 mile south of the proposed Exxon reprocessing plant (Fig. 4.10). Limited field work has been performed on this site, including topographic mapping and preliminary subsurface investigations based on bore holes, auger holes, and subsurface excavation.

The HEF will be an essentially independent site, with all the facilities necessary for routine operation and maintenance of the fuel storage and reprocessing activities. Existing ORNL and UCC-ND facilities will be used wherever possible to support nonroutine activities. The reference HEF complex plot plan is shown in Fig. 4.11.

The site will be zoned and fenced to provide (1) a protected area in which nuclear materials are safeguarded against intrusion and/or diversion, (2) a controlled area in which unauthorized personnel are excluded, and (3) a boundary area that defines the site. Fencing and cleared zones will be installed around these areas.

The HEF process building, shown in Fig. 4.12, will contain all of the cells, building areas, and equipment used for fuel storage, fuel reprocessing, product conversion, waste processing, and contaminated equipment maintenance operations. The building will be located within the controlled area. The major portion of the building will be of reinforced concrete, with overall dimensions of about 450 by 780 ft. Structural requirements for the building will be in accordance with established codes and regulations. The outer shell will be hardened for tornadic missile resistance. Access will be limited to a minimum number of locations, and security systems will be incorporated at these entrances for safeguard purposes. The outer shape of the building will retain, to the extent possible, a smooth configuration to an elevation of 5 m above grade for maximum visibility of external surfaces. Access gates will be provided through the protected area fences for railroad cars and trucks to the fuel, waste, and product truck locks contained in the building.

ORNL DWG. 79-8367

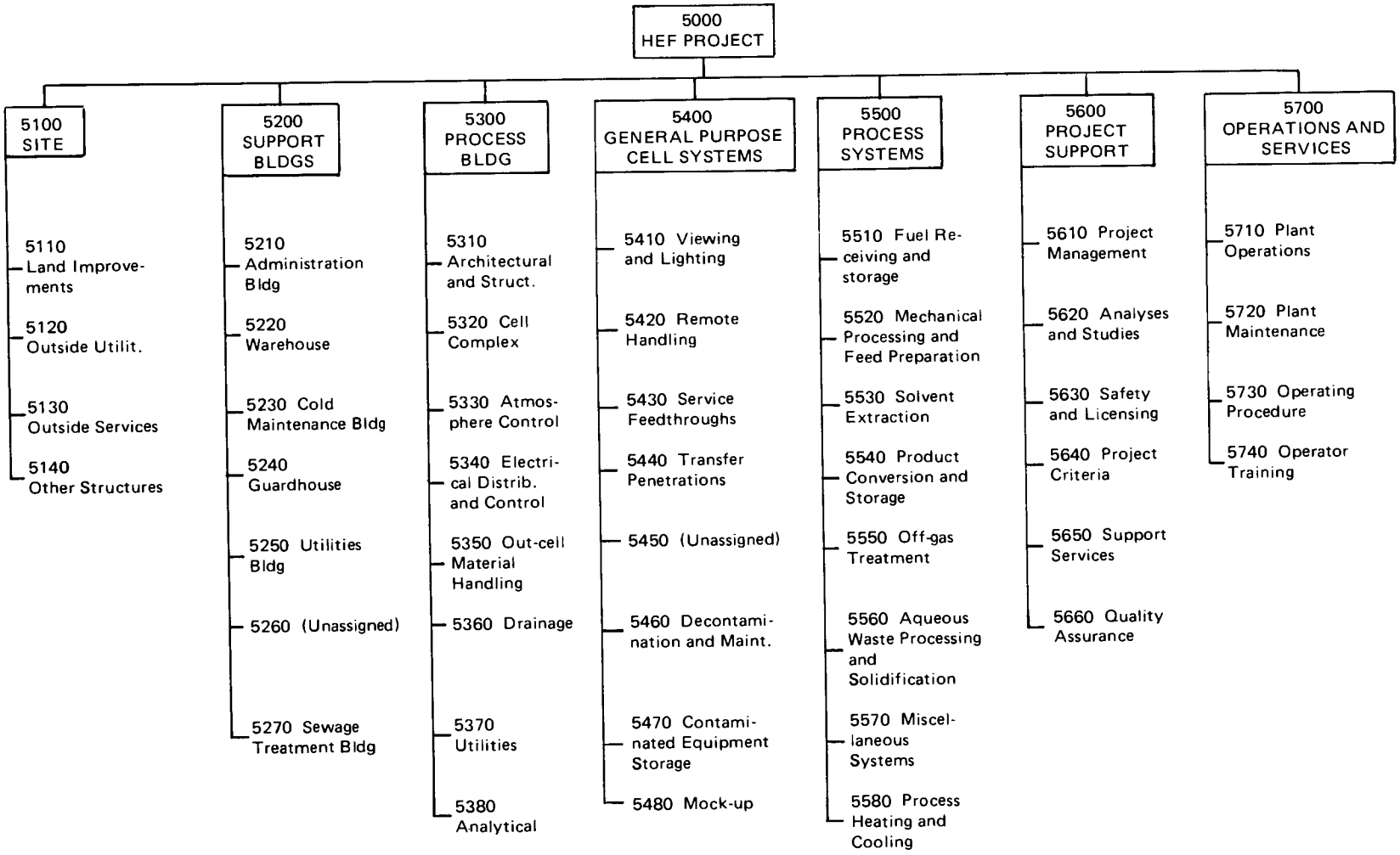

Fig. 4.9. Hot Experimental Facility work breakdown structure.

ORNL DWG. 79-8368

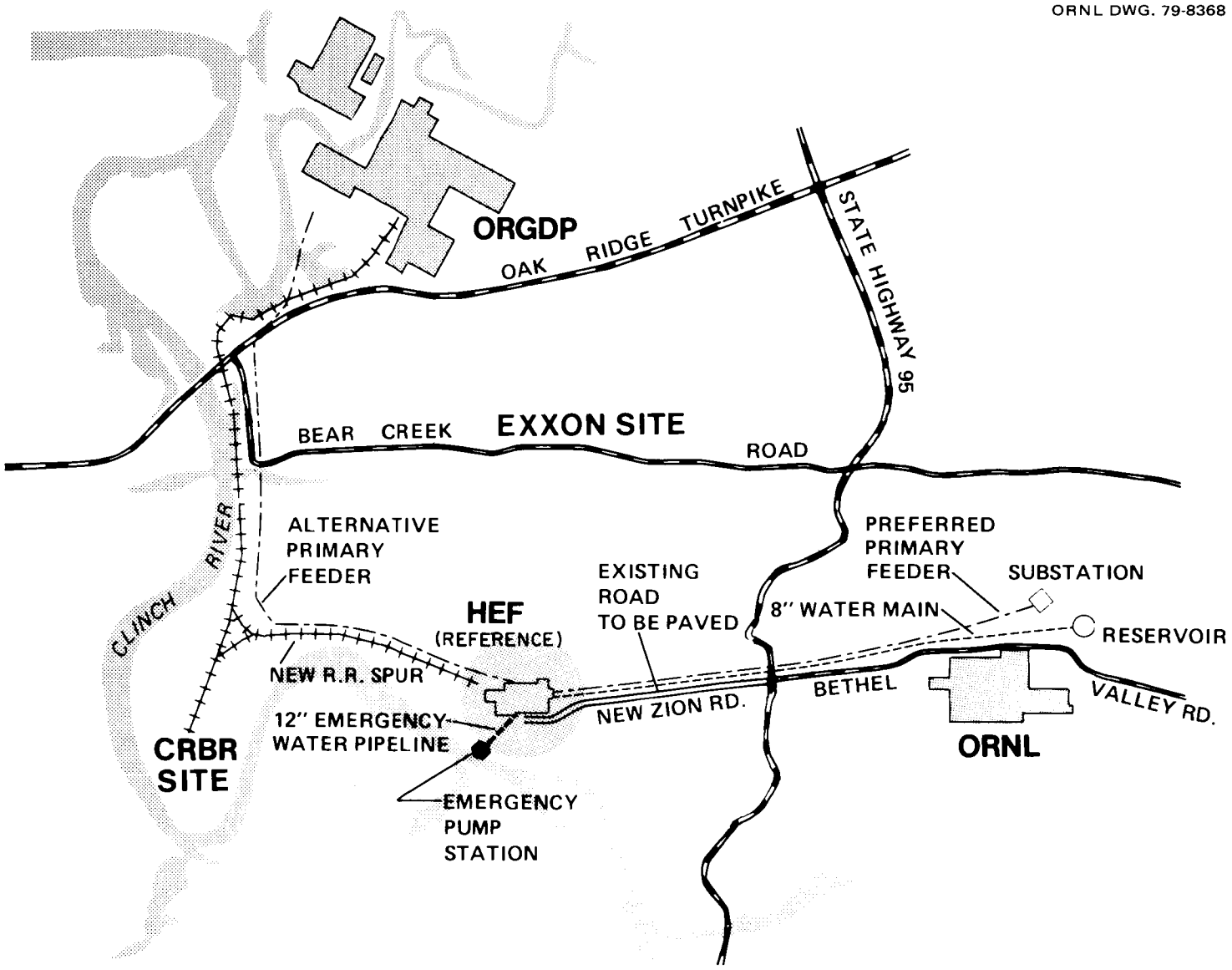

Fig. 4.10. Oak Ridge area plan.

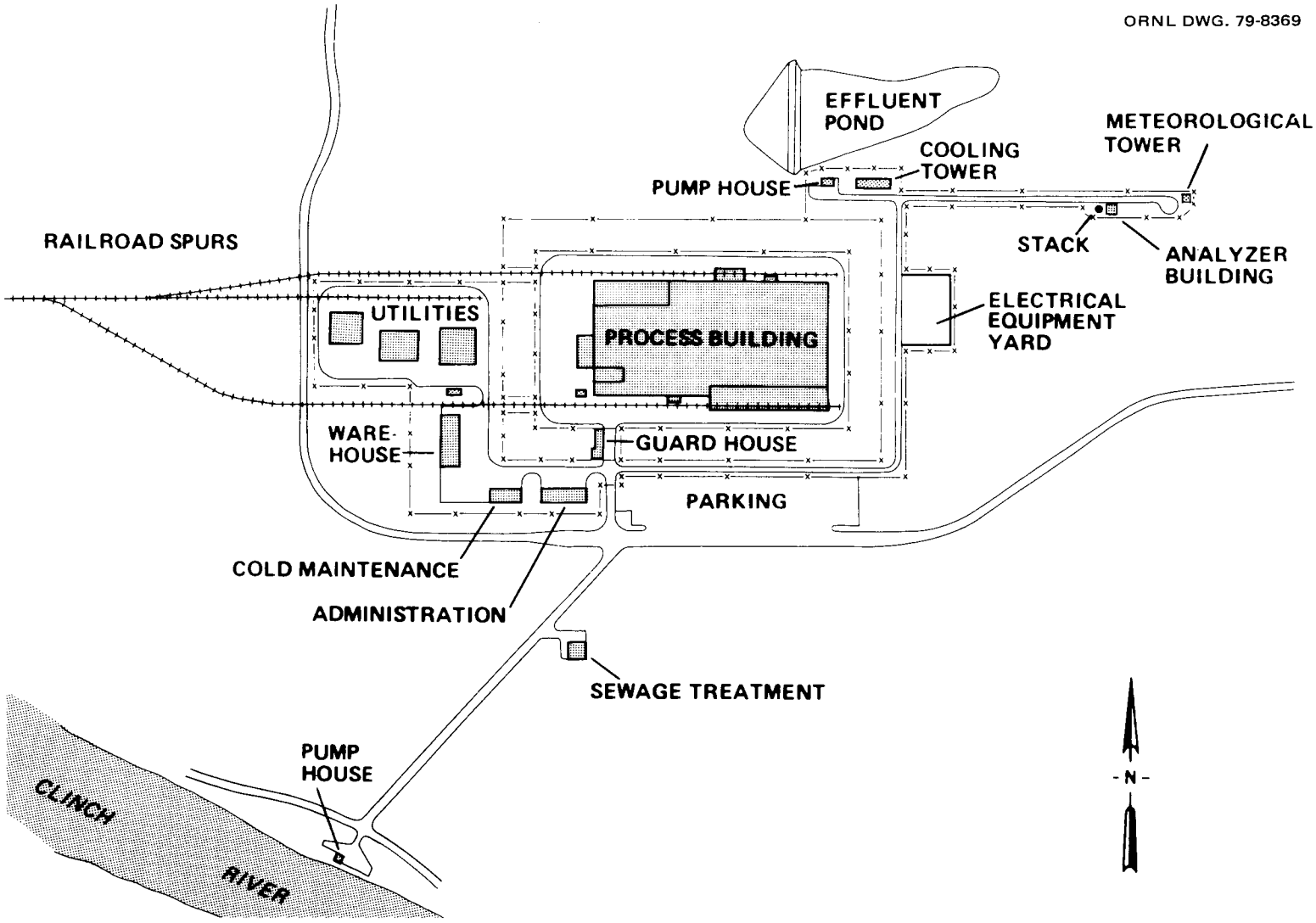

Fig. 4.11. Reference Hot Experimental Facility site plan.

ORNL DWG. 79-8370

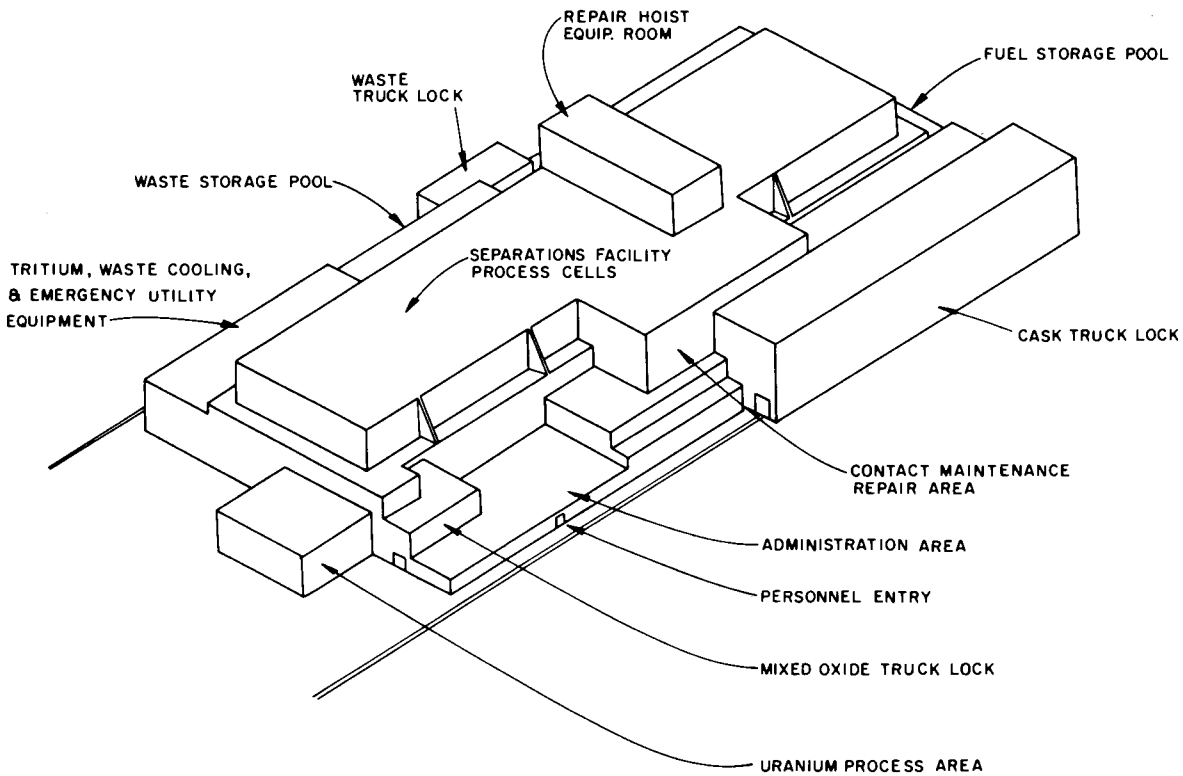

Fig. 4.12. Hot Experimental Facility process building.

The interior of the building will be subdivided into two functional areas: the cell complex and the building areas that surround the cell complex. The cell complex will include all of the shielded and special contamination-confinement enclosures, as shown in Fig. 4.13. Figure 4.13 shows the number and names of each cell area, the major functions performed in each area, and the flow of materials between the areas.

The major feature of the cell complex is the division of process equipment into two main process cells arranged in parallel, with access corridors on all sides. The north cell will house process operations having high radiation levels; the south cell will house operations having intermediate radiation levels. The fuel shearing, voloxidation, and scrap packaging operations will be enclosed in a ventilation barrier in the north process cell to protect the equipment from acid vapors. Similarly, ventilation enclosures will be installed around the fuel cleaning and product packaging operations in the south cell. The fuel cleaning enclosures will have roof hatches so that process cell cranes can remove and replace failed equipment.

The decontamination and maintenance cell is provided to remotely decontaminate, repair, and dispose of (cut up and package) equipment from the two process cells. It will also be the path for transferring large new equipment to the process cells. A contact maintenance area will be used to service equipment that has been decontaminated to acceptable levels.

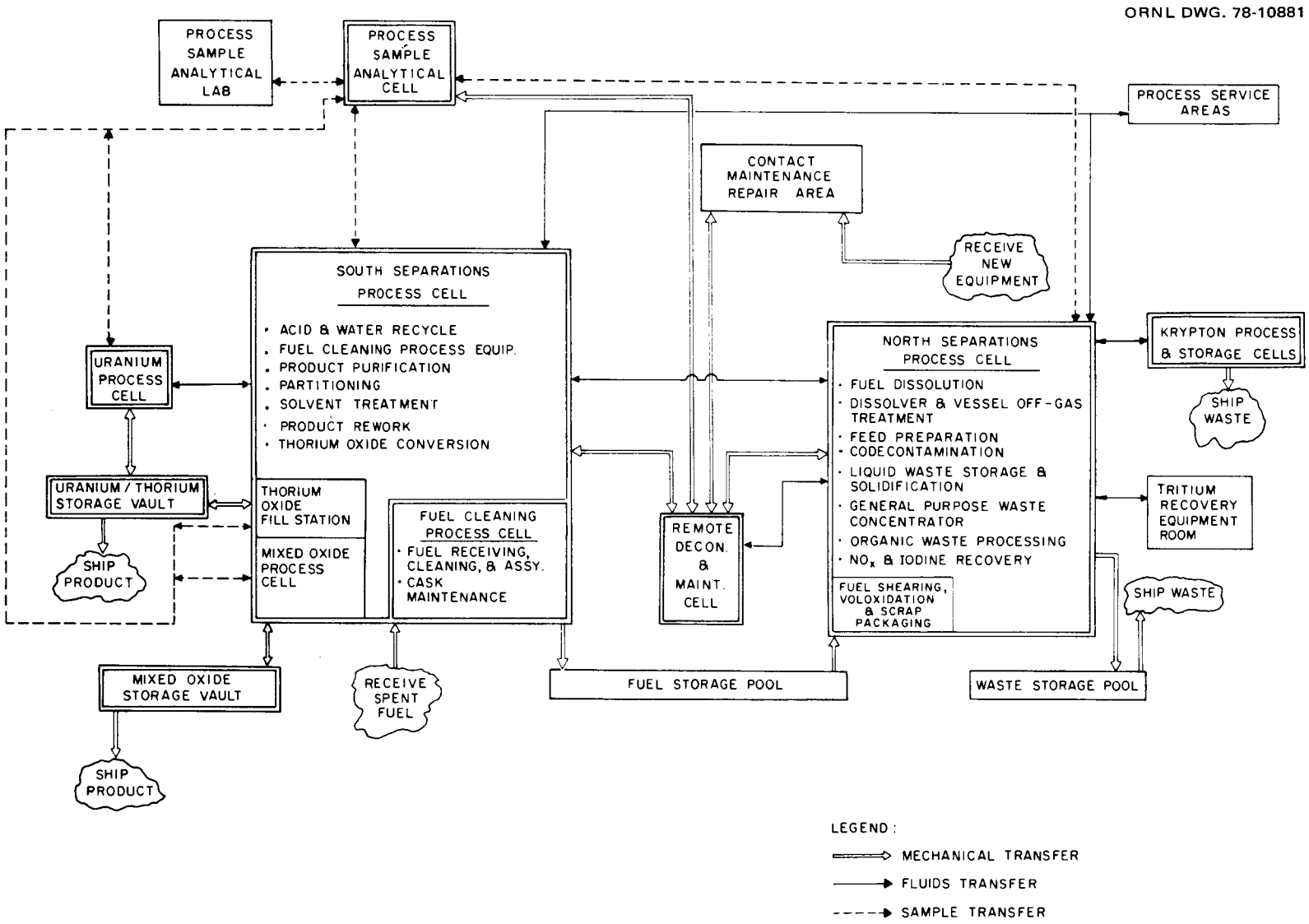

Fig. 4.13. Schematic of Hot Experimental Facility cell complex.

The fuel storage pool will be linked with the fuel shearing area in the north process cell and with the fuel receiving and cleaning area in the south process cell via water-filled canals. The pool will have the capacity for storing over 600 fuel assemblies. The fuel assemblies will not be enclosed in secondary containers; as a result, it is possible that fission gases released from failed fuel pins could occasionally prevent personnel from entering the pool area. Therefore, the pool will be remotely operated although equipment will be maintained by contact means. All solidified process waste, fuel assembly hardware, and contaminated filters, equipment, etc., will be held in the waste storage pool before transfer to a federal repository. All waste will be contained in leaktight cans. A small shielded cell will be used to remove waste cans from the pool and to dry load them into top-loading waste casks.

A process sample analytical cell will be used to perform analytical chemistry operations. Samples will be taken in the process cells and transferred via pneumatic tube to the analytical cell. Pneumatic tubes will also be provided to transfer dilute samples to glove boxes within the analytical laboratories. The analytical cell will interconnect with the decontamination and maintenance cell for the repair of large equipment. In addition, a contact repair shop will be connected directly to the analytical cell for repairing small equipment, if radiation levels permit.

A mixed-oxide storage vault will be provided for special nuclear materials. The product cans will be loaded into shipping casks directly from this vault. Uranium oxide product conversion and packaging will be performed in a separate cell. It is expected that equipment in this cell can be repaired following remote decontamination. The nonfissile uranium product will be stored in a common vault with the uranium-thorium product. Krypton gas will be collected in bottles and stored in a separate cell.

The HEF concept differs from that of other reprocessing plants in that considerably more of the process equipment will be located within shielded enclosures and repaired by remote means to meet the design goal of limiting operating personnel exposure to 500 mrem/yr. Also, much more process equipment will be involved, so that current federal regulations for the emission of contaminants to the environment will be met. Process equipment includes that for filtration and purification of gaseous discharges, purification of gaseous discharges, purification and recycling of acids and water, tritium collection, solid waste compaction and packaging, material accountability, safeguards and saboteur resistance, natural disasters, and decommissioning. An additional complication for the HEF is the requirement to change out equipment for testing and demonstration purposes.

The combination of the above factors has led to a concept of total remote maintenance in the process cells, in decontamination and maintenance cells, in analytical cells, and in product vaults. Contact maintenance may be permissible in other cells, provided that the total annual plant personnel exposure for operation, maintenance, and equipment change out will not exceed the allowable radiation exposure objectives. Another factor that contributed to the total remote maintenance concept is the specified 60% availability factor, which requires not only equipment reliability and redundancy but an integrated process equipment maintenance system that minimizes downtime for repairs.

Each of the remotely operated cells will be equipped with an overhead crane and manipulator system for maintaining in-cell equipment. These systems, coupled with in-cell television cameras and lighting, will be capable of replacing failed components on the larger process equipment modules in situ or of transferring an entire module to the decontamination and maintenance cell for extensive manipulation and viewing. An intrinsic element of the HEF remote maintenance philosophy is that the handling system must have remote repair capability and be able to recover remotely from all credible failures. To accomplish these functions, special features will be installed on the remote handling systems.

REFERENCES

1. W. D. Burch et al., *Advanced Fuel Recycle Program Progress Report for Period July 1 to September 30, 1978,* ORNL/TM-6577 (December 1978) p. 4-1.
2. Ref. 1, pp. 4-6 through 4-14.

5. TECHNICAL SUPPORT

W. S. Groenier

Various generic studies that are not specific to functional research and development areas but are important to the overall program are reported here. The particular areas under analysis and study include nuclear engineering, safeguards, and environmental matters. Notable facility improvements and overall process instrumentation and control studies are also reported. Beginning with this report, the development of instrumentation and control equipment and methods is included since these efforts are also nonspecific to functional areas.

Ongoing activities from the Advanced Fuel Recycle Program are reported in summary fashion; the details of these activities will be described in topical reports. Subsequent quarterly reports will include other activities of the Consolidated Fuel Reprocessing Program.

5.1 FACILITY OPERATIONS

J. M. Chandler and D. E. Dunning

General facility expenditures were moderated early in the fiscal year to provide reserve funds for any carry-over charges from FY 1978. To date, the only unscheduled outlay of money was in equipping and modifying the analytical laboratory in Building 7603, which will be occupied by Analytical Chemistry Division personnel who will analyze samples submitted by the technical staff of the Consolidated Fuel Reprocessing Program.

Analytical laboratory modifications included the replacement of ceiling tile, the replacement of a vacuum pump, the rearrangement of water and air supply lines, the installation of demineralized water services to the laboratory sink, and improvements to the hood and off-gas system.

A temporary portable diesel-electric emergency generator has been installed and tested. This unit provides emergency power to process off-gas fans, the voloxidizer drive, and cooling for motors.

A caustic storage tank and pump has been insulated and installed. A salvaged stainless steel tank was used to replace a leaking mild steel tank.

Valves were replaced in the nitric acid supply system and in other locations where stainless steel construction is required. A quality assurance investigation revealed that the supplier had shipped mild steel valves by mistake. In the future, valves will be inspected by the stores receiving and inspection personnel using a magnet to detect strongly magnetic materials such as mild steel.

A scrubber for process off-gas treatment has been designed and is being procured. This project is almost five months behind schedule because of conflicts in scheduling manpower in the UCC-ND Engineering sections. The scrubber will be used to remove oxides of nitrogen from the process off-gas stream being discharged to the environment.

The facility emergency manual has been updated and reissued.

The CFRP facility has recently become a major point of interest, and increasing numbers of people are being brought on tour. A considerable amount of time and effort is being expended to prepare for these tours.

Building 7608 (formerly the chlorination facility, which is located east of the main 7600 complex) is being refurbished for use in plasma torch development work.

Building 7602 is being emptied of stored items, in preparation for the startup of the Integrated Equipment Test (IET) during the second quarter of FY 1979.

The facility operations group continues to work with the IET Title II design effort in the review of design drawings and equipment criteria.

Work has begun on writing procedures for facility operations; five have been completed.

Drawings for an off-gas extension to Building 7602 have been completed; a request for engineering services to accomplish physical installation has been issued.

Work has begun on updating drawings and identifying the facility's electrical services equipment, much of which has been radically modified to meet program needs.

5.1.1 Instrumentation for the off-gas collection scrubber

W. F. Johnson

Design of the instrumentation annunciator and control cabinet for the CFRP off-gas scrubber has been completed, and informal drawings have been prepared. The material is on order, and construction of the cabinet will begin as soon as the items are received.

5.2 SAFEGUARDS

J. E. Rushton

The safeguards task includes activities related to the design and evaluation of physical protection, material control, and material accounting systems. The principal accomplishments during this period were (1) the completion of a computer code (INSIM) to simulate the movement of fissile material through a reprocessing plant, (2) the design of a practical material balance system to be applied to the continuous rotary dissolver experimental setup, and (3) the completion of an analysis of a Kalman filtering technique as applied to pulsed columns.

5.2.1 Simulation of fissile material flow through a reprocessing plant
R. D. Hurt

A computer program has been written to simulate the flow of liquid through a fuel reprocessing operation. The code (INSIM) can be applied to any reprocessing flowsheet merely by changing the numbers in an input array. Batch operation, continuous operation, and the transition from one to the other can easily be simulated. In its more general applications, INSIM is attached to a series of subroutines which mathematically model the individual steps of the process to predict fissile material concentrations. There is one subroutine for each generic category of process vessel, that is, continuous flow tank, batch-operated tank, pulsed column, evaporator, etc. A preliminary series of mathematical models has been developed and is being tested. While these models are simple, it is possible to link more sophisticated unit process models to INSIM without affecting the simulation itself. This feature enables the user to tailor INSIM to suit particular needs.

The simulation model will be used in the analysis of material control and accounting systems (Fig. 5.1). In the absence of a real data base, the only way to assess the effectiveness of such systems is to apply them to simulated data. This assessment procedure is beginning in earnest now that INSIM is nearly completed and the HEF safeguards philosophy is more firmly defined.

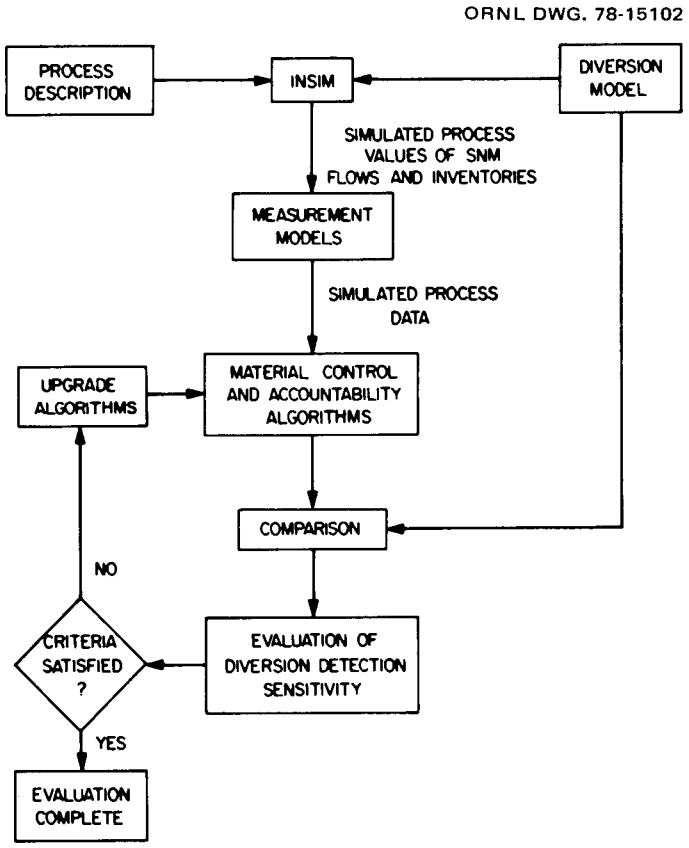

Fig. 5.1. Procedure for evaluation of material control and accountability systems.

5.2.2 Parametric analysis and dissolver mass balances
E. D. Blakeman

Two reports, *A Parametric Analysis of Material Accountability for an Advanced Fuel Reprocessing Facility* and *On-Line Material Balances Around a Rotary Dissolver,* have been completed and are in preparation.

The first report describes the results of a study to investigate the statistical relationship between measurement accuracies and material accountability for the HEF.[1] The second report describes ongoing work to perform uranium, acid, and total mass balances in conjunction with the prototype continuous rotary dissolver. The purpose of this work is to study and assess the feasibility of real-time material balances for special nuclear material (SNM) safeguards. A computer code to perform these balances has been written. Work remains to implement this code on the CODEDACS system and to link the CODEDACS system with the rotary dissolver, such that real-time computations may be performed.

5.2.3 Application of the Kalman filtering analysis to a pulsed column model
E. D. Blakeman and G. W. Morrison (ORGDP)

An analysis has been conducted to investigate the use of the Kalman filtering technique[2] for detecting SNM diversion losses in a simulated pulsed-column mode.* Inventory measurements in the column were assumed to be provided by two passive neutron detectors located outside the column above and below the feed stream stage at stages where maximum plutonium concentrations occur. It is currently planned to continue analysis using the SEPHIS[3] code to simulate a pulsed extraction column from the HEF design. Results will be published in an ORNL/CFRP report.

5.2.4 Safeguards instrumentation
W. R. Hamel, W. F. Johnson, and L. E. Ottinger

Criteria have been established for the selection of sensors to be used for pipe penetration monitoring. The selection criteria are being applied to several promising techniques to identify candidates for further test and evaluation.

5.2.5 Proliferation-resistant engineering
J. E. Rushton

The goal of the proliferation-resistant engineering studies is to identify and evaluate design and operational features that will enhance the proliferation resistance of nuclear fuel cycle facilities by providing prompt detection mechanisms and increasing the time required

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*Simulation model obtained from Prof. G. L. Patterson, Chemical Engineering Dept., University of Missouri, Rolla, Missouri.

to obtain weapons-usable material from these facilities. A plausibility study on proliferation-resistant design was initiated by the Nuclear Alternative System Assessment Program of the DOE in January. The present studies initiated by the CFRP are a follow-up of this plausibility study. Currently, efforts are focused on three main tasks.

The first task, which is being conducted by Pacific Northwest Laboratory (PNL), is the development of design and process concepts and operational modes that can be incorporated into reprocessing facilities to enhance proliferation resistance. The second task, also being conducted by PNL, involves the development of a method to systematically evaluate the proliferation-resistance effectiveness of the reprocessing plant features developed in the first task and in other studies.

The third task, which is being conducted at ORNL, involves the development and testing of a monitoring system for fuel cycle process operations for the purpose of providing a safeguards authority with prompt detection of diversion or modification attempts. This task will use the solvent extraction and product concentration processes in the Building 3019 pilot plant as a test bed for the monitoring system. A computerized accountability system is being installed in this facility as a part of a laboratory safeguards upgrading program. This computer system will be available for use in the monitoring demonstration.

The process sensors that will be used in the first phase of the demonstration have been identified. The demonstrations will be based, to the extent possible, on process instrumentation as distinguishable from special purpose safeguards monitors. This approach was selected to determine the sensitivity to bulk material losses of a system based on instruments that have already been fully proved for hot-cell applications. Additional measurements which would increase the monitoring sensitivity will also be identified in this task.

Visits to Systems Planning Corporation (SPC) in Arlington, Virginia, and to Allied General Nuclear Services (AGNS) in Barnwell, South Carolina, were made to discuss activities related to proliferation resistance. Systems Planning is completing a study for the DOE Division of Fuel Cycle Evaluation on a command, communication, and control concept for monitoring facility operations and initiating in-plant response mechanisms to delay material acquisition in the event of a national takeover of an internationally operated fuel cycle facility. Allied General is studying methods that would permit a safeguards authority to remotely disable or inhibit reprocessing operations. Further contacts that would enhance the integration of these studies with the proliferation-resistance tasks are planned by the CFRP.

5.3 NUCLEAR SAFETY

H. T. Kerr and J. F. Mincey

Considerable progress has been made in several areas during this quarter. The series of experiments with concrete-reflected arrays of Fast-Flux Test Facility (FFTF) fuel pins was successfully completed, and the series of experiments with fixed-poison arrays began and is about one-third complete. Validation of some computational models has been

accomplished, and efforts are being made to eliminate unresolved discrepancies in other models. Conceptual designs were prepared for a series of solution experiments planned for 1979, and preliminary criticality safety analyses have been made for some HEF component designs. An invited paper[4] on soluble neutron poisons for criticality control was presented at the winter ANS meeting, and an article[5] describing the results of water-moderated and reflected FFTF fuel-pin-array experiments was submitted to *Nuclear Technology.* A decision was made to suspend further use of the solid-state track recorders (SSTR) for neutron spectral measurements.

5.3.1 Partially concrete-reflected water-moderated fuel arrays

Four critical experiments on square lattice patches of 9.677, 12.446, 15,392, and 19.355 mm have been completed with water reflection on the top and bottom of the arrays and concrete reflection on the four sides. Documentation of this experimental series by the Battelle staff is nearing completion; validation of appropriate computational models will begin as soon as the data are compiled.

5.3.2 Fixed-poison experiments (water-moderated and reflected FFTF fuel)

All components for the fixed-poison experiments have been fabricated. Ten of the scheduled 35 (~ 30%) experiments (involving cadmium and boral plates and gadolinium pins) have been completed. All experiments are expected to be completed by March. Considerable difficulty was encountered in cold-working operations involving metallic gadolinium; stress cracking occurred during normal cold-working. The cracking problem was eliminated, however, by rapidly performing the cold-working operation in such a manner that self-annealing occurred.

5.3.3 Validation of computational models

The Nuclear Regulatory Commission (NRC) is currently standardizing neutron cross-section processing codes for their evaluations.[6] Interim versions of these codes are being used to provide essential criticality safety guidelines for designing the HEF. By validating these interim versions against the criticality benchmark data being acquired through the experimental program, anomalies can be identified and resolved for several neutronic systems. By proceeding in this manner, much of the preliminary work necessary for validating computational techniques will be complete when the NRC adopts its official version of these codes. However, design guidelines, based in part on results obtained with interim versions of these codes, will necessarily be conservative.

A paper is being prepared for publication which describes the calculational results obtained by modeling the water-moderated and reflected FFTF fuel-pin-array experiments with the KENO-IV[7] Monte Carlo Code using ENDF/B-IV cross-section data. The cross sections were processed with an interim version of the AMPX system.[8] Calculated k_{eff} values are only slightly higher than the experimental value of unity; the differences can probably be reduced by further refinements of the computational models.

Considerable effort has been expended in trying to validate computational models of the plutonium thermal eta experiment. The calculated k_{eff} values have consistently been at least 2.2% above unity. Since no error has been found in the computational model, the experimental data are being reexamined. Samples of the plutonium solution are being reanalyzed, and other potential sources of error are being evaluated. Hopefully, this additional effort will resolve this anomaly.

5.3.4 Conceptual design of solution experiments

Experimental criticality data are needed for soluble neutron absorbers (poisons) to accurately determine their effectiveness in preventing criticality for solutions bearing fissile materials. These data are needed for better criticality control in storage, handling, and processing of the fissile materials. These data are also needed to validate criticality control calculational techniques used in the analysis of poisoned systems. A conceptual design has been developed to summarize the experiments required to fulfill the needed data and to give detailed concepts for some of the equipment and experimental work. Also, preliminary cost estimates have been made for three methods by which experiments might be performed. Additional detailed designs will be developed and reported.

5.3.5 Publications

An invited paper entitled "Soluble Neutron Poisons for Industrial Criticality Control: Are We Ready?" was presented at the winter ANS meeting in Washington, D.C. The paper provided a summary of historical applications of soluble poisons, reviewed technical considerations, identified data needs, and described typical applications in the HEF design. The paper was well received, and requests were made that the paper be expanded and published in the *Nuclear Safety* journal.

The initial series of water-moderated and reflected FFTF fuel-pin-array experiments has been completed and thoroughly analyzed. An article describing the results of these experiments was prepared and submitted to *Nuclear Technology* by the Battelle staff. Additional experiments of this type are under way to experimentally determine leakage effects and the repeatability of the critical array sizes.

5.3.6 Suspension of SSTR use

Solid-state track recorders were used in some of the earlier criticality experiments in an attempt to determine a neutron spectral index. The SSTR's were moderately successful in that isotopic fission rates could be measured to within a precision of about 5%. However, the spectral indices derived from the SSTR data were somewhat inconsistent and could not be correlated with calculational results. Furthermore, the use of the SSTR's caused considerable increases in the time required to complete a given experiment. Resolution of these problems could be accomplished but would involve considerable expense. Consequently, the decision was made to suspend the use of the SSTR's until additional funds are available and to concentrate all resources on the completion of criticality experiments.

5.4 INSTRUMENTATION AND CONTROL SYSTEMS

W. R. Hamel and S. M. Babcock

This task will develop instrumentation systems and engineering techniques for the Consolidated Fuel Reprocessing Program 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 Control and data systems development

J. W. Spitzer, R. W. Tucker, Jr., and W. L. Zabriskie

Data management and communications development. Estimates are being compiled for the purchase of EMC-distributed process control system components for test and evaluation.

Progress has been made in efforts to identify a technique for achieving communication between the CODEDACS computer and the Bristol UCS-3000 unit process controllers.

Bristol UCS-3000 compiler update. After attempting several new execution options that are now available with ACCOL"E," it was found that one of the Bristol-supplied compiler data files was incomplete. Bristol has shipped the information necessary to complete this file, and several new compilations have been completed. The reverse compiler will soon be operational.

5.4.2 Sensors development

R. L. Anderson, D. A. Bostick, W. W. Johnston, D. D. McCue, H. H. Ross, and J. E. Strain

Analytical sensors. Refractometry is being investigated as a possible method for monitoring the acidity of pure nitric acid feed streams. The relationship of the refractive index to nitric acid concentration can be approximated by a quadratic equation over the range of 0.3 to 13 *M*. The refractive index remains essentially constant in more concentrated acid solutions. If the reading error is assumed to be $\pm 10^{-4}$ refractive index units, and the sample temperature is controlled to within 1°C, then pure nitric acid streams can be monitored with a precision of ± 0.05 *M*.

The design of the in-line photometric analyzer, for initial application on uranium product streams, is continuing. The effects of gamma radiation on optical components such as quartz fiber optics and potential cell wall materials, including sapphire and suprasil, are being investigated.

Work on the design of the neutron poison monitor has included an investigation of a technique to allow a 40-ft separation between the neutron detector and the sense amplifier. This separation would allow the amplifier, normally in close proximity to the neutron detector, to be located outside the shielded area. Initial experiments indicate a significant improvement in signal-to-noise ratio when an essentially open reference line is used in conjunction with the signal line.

The design and evaluation of the free-acid monitor based on vapor-phase condensation is complete; a report detailing its design and performance is in preparation. The monitor samples the dissolver solution by means of a continuous-flow loop that raises the sample to a temperature of 74°C, separates an equilibrium vapor phase, cools the sample, and returns it to the sampled vessel. The vapor phase is transported via a heated tube and then condensed into an acid measuring device. The use of conductivity to measure the condensate acidity provides a useful range of 0.5 to 10.5 *M* feed acid. The refractive index measurement of condensate acidity permits a feed acid range of 4 to 13 *M*. If automatic titration is used for condensate acidity, the useful range of the monitor can be extended from 4 to more than 15 *M*. A small correction is necessary to eliminate the effects of solute concentration and undissolved solids. The prototype monitor requires 2 min to detect a change in feed acid concentration and 8 min to indicate the new acid concentration.

Preliminary investigations have been initiated for the development of in-line sensors to monitor hydrazine concentration in the HCP reduction vessel for indicating the Pu(III): Pu(IV) ratio and low-level acid in recovered organic solvent streams and the low-level plutonium and uranium in waste streams.

Physical sensors. The control system of the automatic flow calibration loop has been made operational; trial runs with two different types of flowmeters have been used to debug the flow loop. The loop was modified to reduce flow noise, and the Teflon seats of the digital valves were replaced with neoprene seats to reduce the through-the-seat leakage. As a result of these efforts, the imprecision of the flow measurements was reduced from about 1 to 0.15%.

Flow measurements from an angular momentun (Coriolis force) flowmeter and an ultrasonic flowmeter appear to be reproducible to within 1%. Although the cause of the imprecision has not yet been determined, the ultrasonic flowmeter appears to have timing-based problems and is subject to transient temperature effects.

The flowmeter scoping study was completed and reviewed within the Instrumentation and Controls Division. Reviewer comments have been incorporated into a second draft which has been resubmitted for approval.

5.4.3 Special measurements

G. L. Ragan, C. W. Ricker, G. G. Slaughter, M. M. Chiles, C. M. Smith, and D. N. Fry

Head-end nondestructive assay (NDA). A detailed activity plan for the remainder of FY 1979 has been drafted and is currently being reviewed. This plan places full emphasis on the development of a system to measure the isotopic composition of spent fuel subassemblies. Studies related to this development effort were initiated during the quarter.

The possibilities for demonstrating the performance of the NDA system, using spent plutonium fuel subassemblies, have been investigated. At this time, it appears that a demonstration that would be of technical value cannot be arranged for the immediate future.

Follow-on experiments using proof-of-principle experimental equipment have been performed. The need for and the effectiveness of a gain-monitoring channel was evaluated.

The gain-monitoring channel shares the same high voltage supply as the four measuring channels; furthermore, it is identical to the other channels, except that the methane-filled proton recoil detector is spiked with 1% ^{3}He and the preamplifier and amplifier are followed by two single-channel analyzers rather than one. These two single-channel analyzers include narrow windows on the upper and lower slopes of the 764-keV peak, resulting from the ^{3}He (n,p) reaction in the 1% ^{3}He present in the detector. The high-window to low-window count rate ratio is a sensitive indicator of channel gain; a gain change corresponding to a 1% change in count rate is indicated by a 30% change in this high-low ratio. Since the four measuring channels are so nearly identical to the gain-monitoring channel and share the same environment and high voltage, their count rates can be corrected on the basis of gain shifts indicated by the gain-monitoring channel.

Long-term stability measurements demonstrated the need for and the effectiveness of the gain-monitoring channel. A series of seventeen 1-h counts with a fuel subassembly in place showed a 0.39% standard deviation of the distribution before gain correction and a 0.09% deviation after correction, based on the gain-monitoring channel. The extremes of the count rate distribution differed by 1.2% before correction and by 0.1% after correction.

The sensitivity of the assay system was investigated by the removal of one pin of a 61-pin array in the 7.1% enriched uranium fuel subassembly. The 1.6% change in loading resulted in a 1.4% change in signal when the pin was removed from the center of the subassembly, and a 1.6% change in the signal when the pin was removed from a position at the outer surface of the subassembly. These results are consistent with those obtained previously using enrichment changes rather than the pin-removal approach.

The feasibility of using a similar system for the assay of fresh ^{233}U fuel was investigated. Calculations indicate that the system will perform well for ^{233}U. The radial sensitivity is approximately the same as that for ^{235}U and ^{239}Pu fuels and, because of the low neutron and gamma backgrounds, sources of lesser intensities can be used. Four 1-Ci ^{124}Sb-Be sources will permit the detection of a change in fissile content of 0.5% with a 3-σ confidence level, that is, assuming the detector system to be subject to a standard deviation of 0.1% and allowing for a total counting time (including a background run) of 1 h. An assay system having this capability could be of considerable value to a fuel fabrication facility.

G. L. Ragan was one of three ORNL representatives who attended a DOE meeting on "Measurement Problems in the Fabrication of Alternate Breeder Fuels" held at Los Alamos Scientific Laboratory (LASL) November 14 and 15. He presented a paper suggesting the feasibility of using an NDA system similar to the one developed at ORNL for the assay of completed fuel subassemblies of various types of alternate fuels, in either fresh or spent condition.

Leached hulls nondestructive assay. Studies that will lead to the design of a proof-of-principle experiment for leached hulls assay have been initiated. The experiment will investigate (1) the feasibility of using active neutron interrogation of the leached hulls and (2) the detection of the prompt neutrons produced by fissions induced in the fissile material retained by the hulls. The studies will also include a further evaluation of the passive-gamma

and passive-neutron methods of assay that were considered in the scoping study. The passive methods are being evaluated as alternatives to the active neutron method should it fail to meet expectations.

The merit of a measurement strategy that involves both pre- and postdissolution assays is being investigated. The predissolution assay of chopped fuel would provide a direct reference standard, thus enhancing the confidence level for the measurements made by the leached hulls monitor.

Mechanical surveillance — four-foot dissolver. Vibration signals generated by the movement of simulated nuclear fuel material through a three-stage, continuous rotary dissolver were analyzed to determine whether or not these signals contained characteristic signal patterns that would identify each of five phases of operation in the dissolver and, therefore, would indicate the proper movement of material through the dissolver. This characterization of the signals is the first step in the development of a system for monitoring the flow of material. Five phases of operation are present during the movement of material through the three-stage dissolver: (1) introduction of material into the inlet stage, (2) transfer of material from the inlet stage to the dissolution stage, (3) mixing of material in the dissolution stage, (4) transfer of material from the dissolution stage to the exit stage, and (5) discharge of material from the exit stage.

Studies on the three-stage dissolver were organized to accomplish three goals: (1) to determine whether each of the five phases of dissolver operation could be characterized by the vibration signal associated with that phase of operation; (2) to determine whether the characterization of each phase could be identified during continuous operation, that is, when two or more phases might occur simultaneously; and (3) to determine if improper movement of material through the dissolver would result in significant changes in the characterization of the phases of operation.

To achieve the first goal, several single 20-kg batches of simulated fuel material were processed individually. With only one batch of material in the dissolver at a time, the signals associated with each of the five phases of operation were separated and individually recorded and examined.

To achieve the second goal, several tests were conducted where 2-kg batches of material were added at 30-s intervals (simulating continuous operation) until 60-kg of material had been added. The dissolver was operated on approximately a 5-min cycle; thus, material loads of approximately 20 kg were collected in the dissolution stage before transfer.

Two series of tests were conducted to achieve the third goal: in one, an artificial blockage was installed in the transfer chute between the dissolution and exit stages, and in the second, an artificial blockage was installed in the exit chute approximately 2 ft from the entrance. For both series, tests were conducted with both single 20-kg loads and individual 2-kg loads introduced at 30-s intervals.

It was concluded that a vibration monitoring system can be developed to detect abnormal material movement in a rotary dissolver. It has been established that (1) all five phases of dissolver operation can be characterized by vibration signatures, (2) four of the

five phases of operation can be readily and directly identified by a characteristic vibration signature during continuous prototypic operation, (3) the transfer of material from the inlet to the dissolution stage can be indirectly monitored by one of the other four vibration signatures (the mixing signature) during prototypic operation, (4) a simulated blockage between the dissolution and exit stages can be detected by changes in one or more characteristic vibration signatures, and (5) a simulated blockage of the exit chute cannot be detected.

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