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TECHNICAL DIVISION QUARTERLY PROGRESS REPORT OCTOBER 1 - DECEMBER 31, 1976

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IDAHO NATIONAL ENGINEERING LABORATORY

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TECHNICAL DIVISION QUARTERLY PROGRESS REPORT
OCTOBER 1 - DECEMBER 31, 1976

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ALLIED CHEMICAL CORPORATION
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ABSTRACT

The report is the first in a series of quarterly progress reports on ERDA budgeted activities subcontracted to Allied Chemical Corporation at the Idaho National Engineering Laboratory. The work is performed by the Technical Division and is divided into three subjects.

Fuel Cycle Research and Development includes fluidized-bed calcination and post treatment of commercial nuclear fuel process waste; the storage of fission product noble gas; the catalyzed reaction between NO_x and NH_3 ; the adsorption and storage of ^{129}I ; evaporation of radioactive wastes; the removal of actinides from commercial high-level waste; reprocessing and waste treatment of HTGR fuel; and studies on natural fission reactors.

Special Materials Production covers long-term management of ICPP high-level waste; ICPP fuel process improvements; advanced graphite fuels reprocessing; buried pipeline transfer systems; and ICPP waste management assistance.

Other Projects Supporting Energy Development include geothermal energy development; inplant source term measurements; burnup methods for FBR fuels; nuclear materials security; absolute thermal fission yield measurements; analytical support to LWBR program; research on analytical methods; and environmental iodine species behavior.

SUMMARY

FUEL CYCLE RESEARCH AND DEVELOPMENT

I. FLUIDIZED-BED CALCINATION AND POST-TREATMENT OF COMMERCIAL WASTES

1. Calcination Studies

Fluidized-bed solidification of simulated Allied General Nuclear Services High-Level Liquid Waste-Intermediate-Level Waste (AGNS HLLW-ILLW), concentrated to 150 gal/MTU, was demonstrated in a 10-day run using the pilot-plant, 12-inch-diameter calciner. About 7200 liters of feed were solidified at 500°C to 1100 kg of calcined solids.

Ruthenium volatility during calcination of simulated AGNS waste at 800°C with in-bed combustion heating was measured to be 0.001%. A steady-state bed was formed at 500°C with in-bed combustion heating and the ruthenium volatility measured. The value obtained $(3 \pm 2) \times 10^{-3}\%$, verified the result $(2 \pm 1) \times 10^{-3}$ obtained earlier using a non-steady-state bed. The properties of the steady-state bed, which was formed from feed containing uranium, indicate that a harder product is formed than that formed when rare earths are substituted for the uranium in the feed.

Denitration of the feed by in-bed reaction of formic acid causes poor combustion of the kerosene at 500°C, but not at 550°C.

2. Post Calcination Treatment of Commercial Wastes

Simulated fluidized-bed commercial calcine was pelletized and cast in an aluminum alloy matrix using bench-scale equipment. Glasses containing 25 and 35 wt% of the above commercial calcine were prepared using BNWL Frit 73-1. Weight loss on Soxhlet leaching at 95°C was 0.21%/100 hr.

II. FISSION PRODUCT NOBLE GAS STORAGE DEVELOPMENT

Equilibrium sorption of krypton on extracted sodalite was compared with non-equilibrium sorption (at 5 hr) as a function of temperature and pressure. Preliminary design criteria for a pilot-scale encapsulation system were prepared, and three potential vendors and two laboratories involved in high pressure research were visited to finalize pilot-plant design. An economical alternative to the hydrogen recombiner system was identified for recovery of ^{85}Kr from zirconium fuels. A preliminary design of an engineered ^{85}Kr storage facility using pressurized cylinders was completed and maximum storage cell temperatures

and pressures following loss-of-cooling capacity were calculated. Safe operating conditions would not be exceeded in such a pressurized cylinder storage facility. The first set of pressurized cylinder material γ -exposure tests in liquid rubidium was completed. Visual and metallographic analyses revealed extensive corrosion in the aluminum (6061 T6) sample.

III. LIGHT WATER REACTOR (LWR) OFF-GAS TREATMENT

The design of a test apparatus to study the NO_x - NH_3 reactions over hydrogen mordenite has been prepared. Materials and capital equipment are being ordered and procured for construction of the test apparatus.

IV. IODINE-129 ADSORBENT AND STORAGE DEVELOPMENT

Under similar test conditions and based on Ag content, the iodine loading capacity of silver-exchanged mordenite Zeolon-900 (AgZ) is about the same as that observed in silver-exchanged faujasite Type Bx (AgX). Iodine desorption tests were run which indicate that the matrix effect of the zeolites Types X and Z on chemisorbed AgI is small. The response surface for HI desorption from AgIZ as a function of bed temperature and superficial hydrogen face velocity has been generated. Comparison of desorption rates defined by this surface indicates that AgZ beds can be regenerated up to ten times faster than they can be loaded.

V. WASTE MANAGEMENT

A bench-scale storage tank is being designed and constructed for long-term studies of solution mixing, solids suspension, and heat transfer phenomena. The tank is being patterned after the liquid waste storage facilities at the Barnwell Nuclear Fuel Plant (BNFP). Design criteria for the bench-scale unit are described.

Laboratory refluxing of HLLW solutions shows that solids continue to form for more than 200 hr in either dilute or in concentrated waste. Precipitates formed can be redissolved in Turco Alkaline Rust Remover; 2 M oxalic acid dissolves about 65% of the solids.

Analyses from laboratory evaporations show that simulated HLLW containing less expensive substitutes for palladium, rhodium, and technetium will provide valid data in the small-scale evaporator and the bench-scale storage tank units with respect to solids formation and heat transfer data.

Laboratory tests using Type 304L stainless steel coupons indicate that one of the fission product substitutes may cause an increase in the corrosion rate. The effects of low level chloride, ruthenium, and low level fission products (<0.001 M) in typical HLLW solutions were also investigated. Work is continuing to develop synthetic HLLW solutions

which will accurately simulate actual waste with respect to materials behavior in small-scale and bench-scale equipment.

VI. STUDY OF BIDENTATE COMPOUNDS FOR SEPARATION OF ACTINIDES FROM COMMERCIAL LWR REPROCESSING WASTE

A program was initiated under subcontract to ORNL for the removal of actinides from commercial LWR reprocessing waste using bidentate extractants. For the study synthetic LWR waste is being prepared and the extractant, dihexyl-N,N-diethylcarbamylnmethylenephosphonate (DHDECMP), prepared in purified form.

VII. HTGR FUEL RECYCLE WASTE TREATMENT

1. HTGR Semi-Volatile Fission Product Removal

Laboratory tests using a tube furnace are being conducted to develop vaporization and deposition data for the semi-volatile fission products that will be released in High Temperature Gas-Cooled Reactor (HTGR) fuel reprocessing. The tests involve combusting the simulated fission product oxide with graphite powder at 900°C and estimating the condensing temperature from the temperature profile of furnace tube.

2. Catalytic Oxidation of Carbon Monoxide

A batch-recycle laboratory-scale catalytic reactor for studying the kinetics of CO oxidation is in operation. Analysis of preliminary data by computer program indicates that the rate of reaction follows a mathematical model based on bimolecular surface kinetics.

VIII. NATURAL FISSION REACTOR STUDIES

In 1972, the first known example of a neutron-chain reaction in nature was reported to have occurred at the Oklo mine site in Gabon. An important aspect of the study of the Oklo phenomenon is the behavior of the fission products and heavy elements in the Oklo environment as related to the isolation of reactor products from the biosphere through proposed geologic disposal. Because the Oklo environment successfully managed its nuclear waste for two billion years, the program is actively seeking the possible location of other natural fission reactor sites. Basic studies relative to this phase of the program are discussed.

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SPECIAL MATERIALS PRODUCTION

I. LONG-TERM MANAGEMENT OF ICPP HIGH-LEVEL WASTES

1. Post Calcination Treatment of ICPP Wastes

Pellets of Idaho Chemical Processing Plant (ICPP) calcined high-level waste formed with wet and dry binders were tested for retrieval from storage bins or incorporation into metal or concrete matrices. Pellets prepared on a bench-scale were attrition-resistant during pneumatic transport. Dissolution rates for Zr-Al-type calcine or pellets in nitric acid were slow.

2. Actinide Removal

Distribution measurements of actinides and other elements between synthetic zirconium-aluminum first-cycle raffinate and DHDECMP are continuing.

3. Calcined Solids Retrievability and Handling

The major effort during the quarter concentrated on determining the effect of calcine fines on the retrieval of stored calcine. Mixtures of bed material and fines containing greater than 15 wt% fines severely restrict calcine flowability.

4. Defense Waste Document

Work continued on preparation of a Defense Waste Document for ICPP high-level waste. Initial drafts describing the state of technology for treating the waste were completed. Risk evaluations and pre-conceptual designs for representative processes were initiated.

II. ICPP PROCESS IMPROVEMENTS

Fluorinel hot dissolution tests with irradiated fuel were successfully completed.

III. ADVANCED GRAPHITE FUELS REPROCESSING

Specific secondary burner operating parameters were identified based on operation of the 4-inch-diameter Rover pilot plant burner.

IV. WASTE TRANSFER SYSTEMS

A program has been established to evaluate materials and methods necessary for safe interplant transfer and containment of radioactive liquid wastes and to develop standards for guidelines for the design and installation of such transfer facilities. Laboratory evaluations

of methods for studying corrosion of bare and coated stainless steel pipe are in progress. Test sections are being prepared for extensive laboratory and field testing of coatings.

V. ICPP WASTE MANAGEMENT DEVELOPMENT

1. Waste Feed Chemistry Studies

Two methods developed to suppress fluoride and chloride volatility during calcination of a blend of zirconium and second-cycle wastes with minimum production of gelatinous solids in calciner feed were evaluated in a 4-inch-diameter calciner. One method is to increase the aluminum concentration of the blend prior to calcium nitrate addition; the other is to substitute magnesium nitrate for calcium nitrate. Both methods suitably suppressed fluoride and chloride volatility during calcination, resulted in calciner operation free from fluidized-bed particle agglomeration, and produced a suitable calcine product.

2. WM-183 Flowsheet Development

Flowsheets are being developed to calcine the waste in ICPP storage tank WM-183 which contains 15 g/l sodium nitrate and 250 ppm chloride. Both differential thermal analyses (DTA) and a 4-inch-diameter calciner run indicate that addition of powdered iron to WM-183 waste may prevent fluidized-bed particle agglomeration during calcination of the waste. DTA indicates blending of WM-183 waste with zirconium waste may also prevent agglomeration.

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OTHER PROJECTS SUPPORTING ENERGY DEVELOPMENT

I. NUCLEAR MATERIALS SECURITY

Measurement Equipment for Chemical Plants

Components of a computer-based on-line system for Special Nuclear Materials (SNM) theft detection and process surveillance were installed in the ICPP. The remote signal and data transmission capabilities for the system were successfully demonstrated. An improved transit-time flowmeter sensor was built and tested and the flowmeter electronics were completed. An analysis was made of factors affecting high accuracy level measurements in "organ pipe" critically safe storage tanks. Data taken with a stressed quartz crystal pressure transducer indicate that level changes of as little as one millimeter can be detected in organ pipe tanks using the tank pneumatic level probes. A precision of 0.5% or better was obtained for uranium isotope ratio measurements of reference standards with the developmental quadrupole mass spectrometer.

II. GEOTHERMAL ENERGY DEVELOPMENT

The liquid fluidized bed heat exchanger is designed to prevent fouling on heat transfer surfaces exposed to geothermal water when they are cooled while transferring heat to a secondary working fluid. The heat exchanger tubes are surrounded by a bed of (typical) sand particles fluidized by the hot entering stream of geothermal water. Agitation around the tubes of the fluidized sand particles prevents scale deposition and increases heat transfer from the brine to the tube surfaces.

These beneficial results have been demonstrated in bench-scale and small pilot plant exchangers when both artificial and actual geothermal waters were used. Initially, only vertical one-stage exchangers were used. The most recent tests have been conducted in a horizontal exchanger, 8-inch-diameter x 15.5 inches long. It contained 49, 3/8-inch tubes. This unit represents one stage of a horizontal exchanger which has many of the construction features of a conventional one. Heat transfer coefficients have matched those obtained in the vertical exchanger.

Initial cost estimates were made comparing a conventional exchanger to be used as a preheater in the 5 MW Thermal Loop at Raft River, with a fluidized-bed exchanger. These estimates showed little difference in cost between the two types of exchangers.

III. INPLANT SOURCE TERM MEASUREMENTS

The inplant source term program is designed to collect data in operating commercial Pressurized Water Reactors. The data collected will be used to verify or modify existing predictive models concerning the source, transport and process equipment effectiveness for radionuclides in the radwaste system. The program will include a total of six power reactor sites, two from each of the major PWR vendors. Initial measurements have been started at two sites.

IV. BURNUP METHODS FOR FAST BREEDER REACTOR FUELS

Fission Product analyses were completed for the ^{240}Pu and ^{242}Pu capsules. Preliminary fast reactor fission yields for the heavy mass peak for ^{242}Pu were reported. Analysis of the two ^{237}Np capsules for selected major fission products is nearing completion.

V. ABSOLUTE THERMAL FISSION YIELD MEASUREMENTS

Recently, selected fission yields for ^{239}Pu and ^{235}U were remeasured as part of a nuclear measurements program. Significant differences were observed when the ^{239}Pu fission yield values for ^{138}Ba and the stable xenon isotopes were compared to the accepted literature values. A report has been issued describing this work and additional funding has been received to further evaluate these discrepancies.

VI. LIGHT WATER BREEDER REACTOR (LWBR) - ANALYTICAL SUPPORT

A series of seven irradiated ($\text{ThO}_2\text{-UO}_2$) fuel pellets from the LWBR Proof-of-Breeding Program was received and analyzed. Accuracy of the uranium content analysis was 0.67% at the 95% C.I. This special custom work is expected to continue for one to two years.

VII. RESEARCH ON ANALYTICAL METHODS

1. Low-Level System Contamination in Isotopic Dilution Mass Spectrometry

An uncommonly large negative bias was observed for ^{235}U in the quality control data on the zirconium fuel control samples (ID-RB-ZR). Because such a bias is not normally indicative of any problem with the spectrometer itself, the entire chemical separation and mass spectrometry procedure was investigated and it was determined that the source of the bias was almost certainly due to the presence of a natural uranium contamination in the reagents used in the separation procedure.

2. Determination of Mercury in Organic Solid Samples

The method of Woodriff and Siemer has been used to determine fractional part per million levels of mercury in solid organic samples. The method is described briefly, as well as a less-sensitive, alternate method of mercury determination developed by Hatch and Off.

3. X-Ray Fluorescence Analysis of Fluorinel Samples for Process Control

The X-Ray fluorescence procedure developed for the rapid multielement analysis of highly radioactive fuel samples has been successfully tested on Fluorinel pilot plant runs using both unirradiated and irradiated fuels. The method was extended to include the analysis of cadmium, and calibration ranges were increased to permit the determination of higher concentration levels of Zr and U.

4. Preparation of Samples for the X-Ray Fluorescence Determination of Uranium in Residues from Rover Fuel Dissolution

An X-ray fluorescence procedure is under development for the direct determination of uranium in the insoluble residue remaining after the dissolution of Rover fuel. Two procedures have been reviewed and evaluated; the one promoting greater simplicity of remote operations involved is preferred.

5. Fission Product Volatility Study

A project has been initiated to determine the volatility, transport, and deposition of fission products present in HTGR fuels when the fuel particles are burned in a fluidized bed in the headend process for uranium recovery. A combustion tube has been designed and a method developed to determine the approximate temperatures at which specific fission products volatilize and plate out in the system, and where maximum plating occurs.

6. Modification of ICPP Sampling System

After encountering several operational problems with the current ICPP fuel sampling system, and at the request of the Operations Branch, EG&G was contacted and requested to provide design modifications of ICPP's current system. Three alternative options were provided. After evaluation, modifications and improvements to the most promising system were suggested.

7. Determination of the O/U Ratio of Uranium Dioxide by Controlled Potential Coulometry

Although both gravimetric and volumetric methods have been used for O/U ratio measurements on unirradiated UO_2 , adaptation of these methods to use on irradiated material is difficult because large samples are required to obtain accurate results. The controlled coulometric methods for determining the stoichiometry of UO_2 , originally reported by Stromatt and Connally, was successfully tested on unirradiated fuel and it is likely that in the near future, the procedure will be adapted to determining the stoichiometry of irradiated PBF fuel pellets.

8. Improved ^{237}Np Method

Analysis of ^{237}Np on various plant process feed solutions is frequently required. A method developed for aluminum fuel matrices which assumed 100% neptunium yield, gave poor precision when applied to feed solutions from stainless steel and zirconium fuels. A procedure, developed at Los Alamos Scientific Laboratories for obtaining tracer quantities of ^{239}Np from ^{243}Am was used and the separation procedure for ^{237}Np is now corrected for yield.

9. Bulk Fuel and Waste Assay Unit

A major effort the past several months has been to improve the response characteristics of the Bulk Fuel and Waste Assay Unit. To minimize problems of sample position dependency, an optimum location for the source was determined. System operation in the presence of a high gamma source was also determined. Calibration curves using a sand and boron matrix were prepared.

VIII. ENVIRONMENTAL IODINE SPECIES BEHAVIOR

Studies relative to the formation of volatile hypoiodous acid, HOI, as a function of initial I_2^0 concentration and temperature at a constant pH were started. Elevated temperatures and decreasing initial I_2^0 concentrations enhance the fraction of HOI which is volatilized.

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FUEL CYCLE RESEARCH AND DEVELOPMENT

I. FLUIDIZED-BED CALCINATION AND POST-TREATMENT OF COMMERCIAL WASTES

1. AGNS Waste Calcination Studies

1.1 Flowsheet Development Studies (R. E. Schindler)

A 10-day flowsheet verification run was conducted using the pilot-plant, 12-inch-diameter calciner to demonstrate solidification of simulated AGNS HLLW-ILLW. About 7200 liters of simulated HLLW-ILLW were solidified at 500°C (using in-bed combustion) to 1100 kg of solids. The feed was a blend of simulated HLLW and ILLW at a concentration of 150 gal (combined waste)/MTU with rare earths substituted for uranium. The normal gross solidification rate was 9 gal/hr-ft² (based on the cross-sectional area of the fluidized bed). After reaching steady state, the product/fines weight ratio ranged mostly between 2.5 and 3.0.

Two fuel nozzles were used during the run: an unshrouded oxygen-atomized nozzle and a shrouded Sonicore nozzle. No serious problems were observed with the unshrouded nozzle. However, small clinkers were formed during operation of the Sonicore nozzle as a result of solids sticking to the shroud.

Plans for Next Quarter

Simulated AGNS HLLW-ILLW will be solidified in a 5-day run in the 12-inch-diameter calciner using an unshrouded nozzle to further verify that clinkers are not formed with the unshrouded nozzle.

1.2 Ruthenium Flowpath Studies (J. D. Christian)

Measurements of ruthenium volatility during short-term fluid-bed calcination of simulated AGNS-blended HLLW-ILLW were extended to 800°C using the 3-inch-diameter calciner with in-bed combustion (IBC) heating. The measured ruthenium volatility was 0.001%. Earlier values measured with IBC heating were 0.01% at 670°C, 0.002% at 570°C, and 0.002% at 500°C. Evidently, the reducing conditions created by the burning kerosene suppress ruthenium volatility, even at elevated temperatures.

A steady-state bed was formed at 500°C with IBC heating to verify data obtained at unsteady state; the ruthenium volatility at steady-state bed conditions was measured to be $(3 \pm 2) \times 10^{-3}\%$; the error limits give the range of results for duplicate measurements. These results are similar to earlier results, obtained using an unsteady-state bed, of $(1.7 \pm 0.8) \times 10^{-3}\%$ and verify the validity of results obtained at other conditions using an unsteady-state bed.

Properties of the 500°C, IBC steady-state bed, which was formed using uranium in the feed, were as follows: mass mean particle diameter (MMPD) = 0.65 mm, attrition resistance index (ARI) = 55, product to fines ratio (P/F) = 9. Values typically measured for the properties when the bed is formed in the 4-inch-diameter calciner using feed which contains rare earths substituted for the uranium are: MMPD = 0.35 mm, ARI = 17, P/F = 2.6. Evidently, uranium in the feed results in formation of a much more attrition-resistant product.

Studies of the effect of feed denitration by reaction with formic acid on the fluidized-bed calcination process were continued using the 3-inch-diameter calciner. Denitration may be used to control ruthenium volatility, as well as NO_x, in the calciner off-gas. In-bed denitration was studied using the IBC heating mode. At 500°C, poor burning occurs, probably due to the lack of combustion-catalyzing nitrates. At 500°C, where there is less dependence on nitrates for the combustion of kerosene, smooth burning is observed.

Plans for Next Quarter

A steady-state run at 400°C with indirect heating will be completed using the 3-inch-diameter calciner in which the feed is denitrated in bed with formic acid. Results of analysis of the off-gases for NO_x and of the final product for residual nitrates will be reported. A steady-state in-bed denitration run at 550°C (using IBC heating) will be made and similar measurements obtained.

2. Post Calcination Treatment of Commercial Wastes

(K. M. Lamb and H. S. Cole)

Bench-scale pelletizing and pellet-metal matrix incorporation studies using simulated fluidized-bed calcine continued. The calcine readily forms durable pellets using metakaolin and an H₃PO₄-HNO₃ spray, but the pellets tend to agglomerate on drying. Pellet formation conditions, such as spray-to-calcine feed rates, still need to be defined. Also, methods to minimize pelletizer disc and scraper coatings or methods to remove these coatings must be investigated. Uniform pellets 3/16-inch-diameter were made at a solids feed rate of 50 lb/hr. Lower feed rates produce larger pellets (~1/2-inch-diameter @20 lb/hr), while high feed rates (200 lb/hr) produce pellets with diameters of ~1/16-inch. Two-hundred lb/hr is probably near the capacity limit of the 16-inch-diameter disc pelletizer. These feed rates correspond to those required for approximately a 3 MTU/day plant.

Pelletizing and metal matrix casting units are presently separately operated. The metal matrix system consists of a 5-inch ID x 4-ft-long tube furnace capable of 1100°C, a vacuum pump to evacuate the canister prior to casting, and valves to control air flow through the canister while heat treating the pellets and to control metal flow. Presently, canisters are filled with green pellets and welded before being cast, but flange connections are being prepared. Castings made from pellets externally heat treated and those made from pellets heat treated in the canister were similar in uniformity, but castings made with directly loaded green pellets have slightly higher pellet volumes.

Aluminum alloy castings up to 2-1/2 inches diameter x 18 inches long of pelleted waste have been prepared. During pellet heat treatment, air flow through the canister is maintained at ~0.6 ft/sec to sweep gases and provide a uniform temperature profile. In one hour, the canister is heated to 500°C to dry and begin denitrating the pellets. The pellets are then heated to 700°C in one more hour, and maintained at 700°C for an hour to complete the denitration and to react the binder and calcine. While at temperature, the canister is evacuated to 1 torr or less within 5 - 10 minutes. The molten metal at 600 - 650°C is drawn through the canister to make the casting. Vacuums above 1 torr tend to leave voids in the casting when aluminum is used. The aluminum A-380 casting alloy used (melting temperature, 565°C) appears to wet the pellet surfaces well when heated to 600°C or above, as determined by sectioning and visual inspection. Castings made with canister-to-pellet diameter ratios of 4 or 5 were over 60 vol% aluminum due to the poor pellet packing configuration. Castings with over 50 vol% pellets were achieved with canister-to-pellet diameter ratios >8.

Uniform glasses were prepared using BNWL Frit 73-1^a with 25 and 35 wt% simulated commercial (mixed HLLW-ILLW) fluidized-bed calcine. The waste glass was prepared by melting at 1100°C for approximately two hours. The weight loss on Soxhlet leaching in distilled water of the 35 wt% glass (-16 to +60 mesh) at 95°C after 100 hr was 0.21 wt%. This glass will also be tested for leach resistance to simulated ground water brines which may exist in the vicinity of salt strata, and to acid and caustic solutions.

Settled densities of a recently prepared, fluidized-bed calcine representative of a mixed commercial HLW-ILW waste were determined as follows: bed, 2.22 g/cc; fines, 1.47 g/cc; and for a 2.9/1, bed-to-fines ratio, 2.44 g/cc. At this bed-to-fines ratio, the fines fill the void spaces, increasing bulk densities.

Long-term thermal stability tests were made on two specimens (1/2-inch high x 3/4-inch diameter) of calcine (MMPD = 0.52) cast in aluminum alloy. Weight losses on storage at 400°C after the first day were 0.27 and 0.17%, respectively. After 179 days, the specimens increased

^a J. L. McElroy, Quarterly Progress Report Research and Development Activities Waste Fixation Program, April-June 1974, p 29, BNWL-1841.

slightly in weight, probably due to aluminum oxidation, recovering a portion of the initial loss, for a net loss of 0.16 and 0.07 wt%.

A mixture of 10 wt% metakaolin and 90 wt% calcine is being evaluated for possible caking on storage at elevated temperatures. After five days at 600°C, the mix remained uncaked. Higher temperatures will be tested to determine storage temperature limits for mixtures such as this, as they may have to be temporarily stored prior to pelletizing short-term decay wastes.

Plans for Next Quarter

Pelletizer operation and pellet formation studies will continue. Improvements in the bench-scale casting unit and larger size castings will be made. Integration of the pelletizing and metal matrix casting system will begin. Glasses prepared from fluidized-bed calcine and BNWL Frit 73-1 will be leach tested with acid and base solutions and three simulated ground water brines.

II. FISSION PRODUCT NOBLE GAS STORAGE DEVELOPMENT

(R. Benedict, A. B. Christensen, L. T. Cole,
M. Hoza and D. A. Knecht)

1. Zeolite Encapsulation

A glovebox was installed for weighing encapsulated zeolite samples in a dry environment. Discussions were held with R. L. Porter of Autoclave Engineers, Inc., concerning our laboratory-scale encapsulation system and high pressure safety. A series of encapsulation experiments (lasting ~6 months) to obtain data for a detailed model was begun.

Pressure-Volume-Temperature data for krypton at high pressures and temperatures were used to correlate pressure and volume with the Redlich-Kwong^a equation parameters as a function of temperature. Using Vaughan's data for krypton sorption on sodalite,^b equilibrium loadings were predicted as a function of temperature and pressure. The results are shown in Figure 1. As the temperature increases, higher pressures are required to achieve the same equilibrium loading. Loadings achieved at nonequilibrium conditions (Figure 2) are expected to show a similar qualitative behavior at high temperatures, but an opposing behavior at low temperature, resulting in constant loading curves which pass through a minimum. The equilibrium sorption results will be used together with the nonequilibrium results in modeling the encapsulation behavior.

^a J. M. Prausnitz and P. L. Chueh, Computer Calculations for High Pressure Vapor-Liquid Equilibria, Prentice-Hall, Englewood Cliffs NJ, 1968.

^b R. M. Barrer and D.E.W. Vaughan, "Trapping of Inert Gases in Sodalite and Cancrinite Crystals", J. Phys. Chem. Solids, vol 32, pp. 731-743, 1971.

FIGURE 1. KR SORBED ON EXTRACTED SODALITE AT EQUILIBRIUM

FIGURE 2. KR SORBED ON EXTRACTED SODALITE AT 5 HR

Preliminary design criteria for a pilot-scale encapsulation system were prepared. Pressure vessel and system capabilities were selected based on laboratory scale experience and on estimates of process requirements. The pilot system will test design features which may be necessary for a process-scale system. While features and materials suitable for use with 6% ^{85}Kr will be incorporated, the system will be operated using only "cold" krypton or argon. Three potential vendors of the pilot-scale system and two research laboratories currently using high pressure systems were visited. The design criteria as well as rubidium corrosion of potential pilot plant materials were discussed.

Pilot-scale development will involve the following:

Evaluate detailed design concept. Pilot-plant design can also serve as a preliminary process-scale design and will lead to the process-scale conceptual design.

Determine processes which will require pilot-scale operation prior to obtaining production-scale conceptual design, such as the following:

- 1) Operate an $\sim 5\text{-l}$ vessel to determine reliability of remote closure, sample introduction and removal, and system remote handling;
- 2) Test safety barricade for gas containment (and possibly for missile containment);
- 3) Determine cooling capability while at high pressure using an internal heat source to simulate ^{85}Kr decay;
- 4) Determine processes which will require mock-up simulation prior to design of pilot-scale and/or production-scale system, including:
 - a) Test remote handling of zeolite sample, systems designs for handling material flow, system layout;
 - b) Determine cooling capability of mock-up high pressure vessel, using internal heat source to simulate ^{85}Kr decay.

The cost of a hydrogen recombiner to remove ^{85}Kr released during the dissolution of zirconium fuel has been thoroughly investigated; the minimum cost of about \$1,300,000 is not justified by program needs. The ^{85}Kr needed for hot encapsulation and long-term storage tests can be met with less krypton than would be recovered by the hydrogen recombiner system, and an alternate system based on the existing N_2O catalytic separator (WN-107/108/109) has been identified. New reactor vessels would be needed with two types of catalysts. A storage tank (about 200 psig) could be provided in the middle cell which would hold all of the off-gas from processing one batch of Zr fuel. A conceptual design will be prepared by an architect-engineer for the alternate system, to be completed by the last quarter of FY 1977. If the project appears feasible, and the cost is less than $\sim \$800,000$, capital equipment funds can be committed by the end of FY 1977.

About 20,000 Ci of ^{85}Kr will be required for hot encapsulation and long-term zeolite and cylinder storage tests, as 6% ^{85}Kr in krypton. This estimate is higher than the 10,000 Ci previously estimated for hot encapsulation and zeolite long-term tests only. Recovery of approximately one-tenth of the ^{85}Kr released during the Zr fuel dissolutions projected for FY-1979 through FY-1980 would provide the 20,000 Ci needed. If more ^{85}Kr can be recovered, additional hot long-term cylinder storage tests can be provided with ~5-10 years' lead time over possible commercial storage facilities. If ^{85}Kr is available earlier from normal ICPP production, hot tests can begin as early as FY-1978.

2. Pressurized Cylinder Storage

A preliminary conceptual design of an engineered ^{85}Kr storage facility using pressurized cylinders was completed. It consists of a shielded hot cell and a cylinder storage area containing storage cells. The hot cell is used to examine and service the gas cylinders and to transfer ^{85}Kr from any leaking cylinder into a new cylinder. After being processed through the hot cell, the ^{85}Kr -filled cylinders are loaded into a shielded transfer container and transferred through an air lock into the isolated storage area.

The storage facility (for the 40-year operation) is a 1700-ft-long air-tight building, designed as a secondary containment to the cylinder storage cells. A central rail track runs the length of the storage area to provide for movement and positioning of the shielded container transfer carriage. Along both sides of the track are arranged the gas storage cells. Each cell is a shielded enclosure capable of storing 104 gas cylinders in a horizontal position. Each cell is equipped with isolation valves, as well as equipment required for removal of decay heat and for detecting the presence of leaking cylinders.

Heat transfer calculations were made for a storage cell containing 104 gas cylinders (at 500 psi of 6% ^{85}Kr in krypton) evenly spaced in a horizontal position to estimate steady-state temperatures after a postulated cell cooling system failure. Table 1 lists the results for various temperatures outside the cell.

TABLE 1			
EQUILIBRIUM TEMPERATURES IN STORAGE CELL ^a			
Outside Cell T, °C	Cell Air T, °C	Cylinder T, °C	Cylinder P, Atm
27	64	109	55.1
47	85	130	58.4
67	106	150	61.7
87	127	171	65.0
107	147	192	68.3

^a 104 50-liter capacity cylinders containing 6% of ^{85}Kr in krypton, initially at 35 atm (500 psi) and 60°C.

3. Rubidium Corrosion

C-ring specimens were machined, characterized, and calibrated for diameter of compression versus tensile strength. One set of pre-stressed C-ring specimens was exposed at 127°C and 1 atm Ar to γ radiation in a liquid Rb environment. Visual and metallographic tests showed that the aluminum specimen was corroded. Some corrosion was also observed near the bolt and nut location on the 4130 steel specimen and was shown by metallography to be a surface effect only. (Its origin may have been due to cleaning after the exposure.) Two new batches of C-ring γ exposure tests (to last six months) were started at the respective conditions: 1200 psi Ar, 127°C, and 1000 psi Ar, 300°C.

Plans for Next Quarter

A report on methods of immobilizing ^{85}Kr (which had been delayed by work on the Energy Research and Development Administration Generic Environmental Impact Statement for Waste Management) will be completed. Encapsulation experiments will be continued to provide data for a detailed model. Bid packages will be issued for AE services for, (1) designing the alternative hydrogen recombiner system (costing less than ~\$800,000), and for (2) preparation of the conceptual design of a commercial-scale demonstration ^{85}Kr storage facility using pressurized cylinders. Bids will be issued for the design and fabrication of a pilot-scale encapsulation system.

III. LWR OFF-GAS TREATMENT (I-466)

(R. A. Brown)

1. Catalytic Reaction of NO_x and NH_3

(D. H. Munger, T. R. Thomas)

The design of a test apparatus to study the $\text{NO}_x\text{-NH}_3$ reaction over hydrogen mordenite has been prepared. The apparatus will include: (1) electronic mass flow controllers to maintain a constant composition feed gas of air, NO , NO_2 , and NH_3 , (2) a 5 cm (diameter) by 30 cm stainless steel reactor to contain the catalyst. The instruments for analyzing reactant and product distribution will include: (1) a chemiluminescence monitor for NO , NO_2 , and NH_3 , (2) a hygrometer for H_2O , and (3) an infrared spectrophotometer for N_2O . Data from the flow controllers, thermocouples, pressure sensors and analyzers will be recorded by a multipoint data logger with sequential switching. Materials and capital equipment are being ordered and procured for construction of the test apparatus.

Using NO_x concentrations of 0.1 to 1% in air, H_2O concentrations of 0 to 5%, a superficial face velocity of about 107 m/min and bed temperatures of 300 to 500°C, the kinetics of NH_3 reacting with NO , NO_2 , O_2 , and H_2O will be studied.

Plans for Next Quarter

Techniques for analyzing and correlating gaseous effluent data will be studied. Preparation of a topical report on NO_x - NH_3 literature review test apparatus description, and test plans, will be initiated.

IV. IODINE-129 ADSORBENT AND STORAGE DEVELOPMENT (I-187)

(L. P. Murphy, J. T. Nichols, B. A. Staples, T. R. Thomas)

The loading capacity of silver-exchanged mordenite Zeolon 900 (AgZ) for airborne-elemental iodine has been determined for the following conditions: bed depth, 5 cm; superficial face velocity, 15 m/min; bed temperature, 100°C ; mesh size, 10-20; carrier gas, dry air. For a set of four replicate tests, a loading of 59.5 ± 6.7 mg I_2/g AgZ (at the 95% confidence level) was obtained at an average DF of 250. The AgZ contains 20 wt% Ag; therefore, the above loading corresponds to 298 mg I_2/g Ag. Based on the Ag content, the iodine loading of AgZ is about the same that has been observed in silver-exchanged zeolite Type 13X (AgX). Using similar test conditions, replicate tests gave a loading of 113 ± 13 mg I_2/g AgX which corresponds to 313 mg I_2/g Ag (i.e., 36 wt% Ag).

Iodine desorption tests were run on AgZ beds which had been loaded with iodine (AgIZ) in dry air. The beds were purged with pure hydrogen at bed temperatures between 400 and 550°C and superficial face velocities between 1 and 15 m/min. Figure 3 illustrates the observed partial pressure of HI (P_{HI}) from AgIZ, iodine loaded AgX (AgIX), and the P_{HI} calculated from AgI. As shown, the P_{HI} from AgIZ ranged between 0.14 to 1.8×10^{-3} atmospheres and closely approximated the P_{HI} calculated by the equation:

Figure 3. Partial pressures of HI over AgI, AgIX and AgIZ.

$$\log P_{\text{HI}} = -\Delta G^0/4.6 RT \quad \text{for the reaction:}$$

The observed and calculated data were fitted by least squares to the equation:

$$\log P_{\text{HI}} = A + \frac{B}{T + 273}$$

The data indicate that the matrix effects of Type X and Z zeolites on the chemisorbed AgI is small and that equilibration of the above reaction is essentially instantaneous in the range of face velocities used.

The response surface shown by Figure 4 for the desorption of HI from AgIZ was generated by fitting the data to the second order model:

$$Y = 0.585 + 0.456 X_1 + 0.477 X_2 + 0.064 X_1^2 + 0.0045 X_2^2 + 0.352 X_1 X_2$$

where $Y = \text{mg HI/min-cm}^2$ (i.e., rate of HI desorbed per cross-sectional area of bed), $X_1 = (\text{temp}-475)/75$, and $X_2 = (\text{face velocity}-369)/246$.

Figure 4 Desorption rate of HI from AgIZ (mg HI/min-cm^2). Contours are constant desorption rates.

The coordinates at which duplicate data points were obtained are shown by the symbol "o" in Figure 4. All observed desorption rates agree within $\pm 11.1\%$ (at the 95% confidence level) of the rates predicted by the response surface.

A typical set of conditions for bulk-iodine removal from the dissolver off-gas of an LWR fuel reprocessing plant might be to treat a $4 \text{ m}^3/\text{min}$ air stream containing $300 \text{ mg I}_2/\text{m}^3$ on the average. If the AgZ bed is designed for a superficial face velocity of 15 m/min during iodine loading, then the cross-sectional area would be 2700 cm^2 . The loading rate would be $0.44 \text{ mg I}_2/\text{min-cm}^2$. If the bed were regenerated with H_2 at 500°C and a superficial face velocity of 15 m/min , the desorption rate would be $4.5 \text{ mg HI/min-cm}^2$ or about ten times faster than the loading rate. All sets of temperatures and face velocities which yield desorption rates greater than $0.5 \text{ mg I}_2/\text{min-cm}^2$ would provide adequate bed regeneration rates for the example loading rate.

Plans for Next Quarter

The effects of NO , NO_2 , and water vapor on loading capacity will be investigated. The stability of HI-loaded lead-exchanged Type 13X (PbI_2X) will be investigated. An HI photometer will be added to the regeneration apparatus.

V. WASTE MANAGEMENT (I-457)

(L. C. Lewis, B. E. Paige)

In order to increase storage capacity and thereby reduce the cost of chemical reprocessing of commercial reactor fuels, high-level liquid wastes (HLLW) and intermediate-level liquid wastes (ILLW) are concentrated prior to and/or during interim storage in tanks. The objectives of the current studies are (1) to investigate solids production, fouling tendencies, and off-gas behavior during concentration and storage of LWR liquid wastes, and (2) to evaluate materials of construction for process evaporators and storage tanks.

Simulated fuel reprocessing solutions are being used for the current investigations of wide ranges of variables in order to avoid the difficulties and expenses of experimenting extensively with actual radioactive fuel solutions. The simulated HLLW solutions used were described previously.¹ The composition and preparation of these solutions are designed to produce wastes which resemble as closely as possible the actual liquid LWR wastes in evaporation and storage studies. Work is continuing to evaluate the use of chemically similar substitutes in these studies.

1. Evaporation

Laboratory evaporations of simulated HLLW have been continued to obtain data for the design and operation of commercial HLLW evaporators, to characterize solids which are formed, and to identify any other unexpected phenomena associated with the evaporation of these solutions. The compositions of the HLLW solutions studied are based on three types of commercial flowsheets. HLLW-0, which represents waste containing minimal process additives, has been used for most of the laboratory studies during this quarter. The other two solutions studied previously are HLLW-Fe and HLLW-UP. HLLW-Fe represents waste from a process in which a high iron content results from the use of a consumable iron basket liner for transporting fuel pieces to the dissolver. HLLW-UP represents waste from a process in which substantial solvent degradation is assumed and in which the waste from the solvent clean-up step is combined with the first cycle raffinate to yield a solution with high phosphate and high uranium concentrations. All solutions contain concentrations of fission product elements based on a fuel burnup of 33,000 MWd/MTU and a 150-day cooling period. Fission products with concentrations less than 0.001 μ at 378 ℓ /MTU are not included. The concentrations of the corrosion products and the phosphate concentration are based on previous estimates² of LWR liquid waste compositions.

1.1 Laboratory Evaporation of HLLW (P. A. Anderson, C. B. Millet)

In batch laboratory evaporations, the three types of HLLW solutions were concentrated from 1512 ℓ /MTU (400 gal/MTU) containing 2 M HNO_3 down to at least 378 ℓ /MTU containing about 7 M HNO_3 . Physical and chemical properties, including boiling point rises, densities, and amounts of undissolved and total solids, have been reported previously^{1,3}. Analyses of the solids from these evaporations have now been completed and reviewed. The effect of substituting some of the more expensive fission product elements in solutions used for evaporations has been investigated. Redissolution of the precipitated solids is being investigated to find solvents for descaling heat transfer surfaces and for tank sludges. The precipitation of solids during extended periods of boiling with reflux is being investigated for concentration levels found within a typical LWR process flowsheet.

1.11 Characterization of Solids

The compositions and physical properties of the undissolved solids in evaporated HLLW slurries are of interest in projecting the behavior of waste during concentration and storage. Solids obtained from HLLW solutions concentrated to 378 ℓ /MTU were examined by emission spectroscopy to obtain a semiquantitative analysis, by x-ray fluorescence to determine the absence or presence of the less abundant elements, and by x-ray diffraction to identify precipitated compounds.

The major component in solids precipitated in HLLW-0 is probably hydrated forms of ZrMo_2O_8 . X-ray diffraction data indicate that the compound is probably similar to that obtained by Campbell and Buxton⁴;

however, the particles shown in Figure 5 do not have the same crystalline appearance. After the solids are heated overnight at 600°C, the predominant compound is ZrMo_2O_8 . Quantitative analyses of the supernate from HLLW-0 solutions indicate that the zirconium and molybdenum precipitate in approximately equal molar quantities; therefore, ZrMo_2O_8 accounts for only about half of the zirconium in the precipitated solids. About 30% of the original zirconium and 20% of the original molybdenum remained in the supernate after concentration to 378 g/MTU indicating that further precipitation of these elements could occur during additional evaporation and, therefore, could cause scaling.

The balance of the precipitated solids consists of unidentified compounds of zirconium, tellurium, and phosphorus with trace amounts of iron, chromium, and lanthanides. The solids precipitated from HLLW-Fe contain more iron while solids from HLLW-UP solutions contained uranium and more phosphorus than comparable solids from HLLW-0. Evaporations of HLLW-0, HLLW-Fe, and HLLW-UP solutions containing ruthenium, palladium, rhodium, and rhenium (simulant for technetium) were compared to solutions omitting ruthenium and substituting less expensive nickel, cobalt, and manganese, respectively. Ruthenium was omitted rather than substituted because no available substitute is known to simulate its unique properties with respect to solids formation and volatility. The compositions of precipitates from solutions with and without substitutes were not detectably different by emission spectroscopy or x-ray diffraction.

Figure 5. Precipitate from evaporated HLLW-0
(Scanning electron microscope at 4900 x magnification)

Neither the ruthenium, palladium, rhodium, and rhenium nor the substituted nickel, cobalt, and manganese were found in the solids by x-ray fluorescence. It was concluded that solutions containing the substitutions for the less expensive elements in simulated waste should yield valid data in small-scale evaporator and the bench-scale storage tank studies with respect to solids formation and heat transfer data.

Plating and caking of the undissolved solids on the surface of the glass evaporator from boiling HLLW solutions are greater in the more concentrated solutions and occurs particularly on the heat transfer surfaces. The plating and caking were most pronounced in the solutions with the higher nitric acid concentrations at all concentration levels. Since there are actually more undissolved solids at the lower acid levels, indications are that solids formed in the lower acid solutions did not have as great a tendency to form scales.

1.12 Rate of Precipitate Formation in Boiling HLLW

Freshly prepared HLLW solutions, which were made by combining clear stock solutions, contain some undissolved solids. The amount of undissolved solids increases when the solution is heated to the boiling point. This indicates that boiling is essential to produce a simulated waste which can approximate the dissolution of actual fission products from irradiated fuel in boiling nitric acid. The amount of precipitate present in HLLW-0 at all concentration levels appears to be a function of time, temperature, and concentration. The rate of precipitation appears to increase at higher temperatures and to decrease in higher concentrations of nitric acid. To study this effect, the amounts of undissolved solids in HLLW-0 solutions were measured at time intervals as the solutions were boiled under total reflux at various concentrations of nitric acid.

At 4536 μ /MTU (1200 gal/MTU), which approximates the concentration level of unevaporated HLLW from the first extraction cycle, the formation of undissolved solids at the boiling point continued for more than 200 hr at all levels of nitric acid investigated (1, 4, and 7 M). The rate of formation was higher during the first 20 hours at 1 and 4 M HNO_3 . Since the solids content increase at the boiling point was relatively small, the undissolved solids content in the dilute HLLW should not change significantly for a period of several days when the solution is stored at ambient temperature during reprocessing.

When the first cycle raffinate is concentrated to 1512 μ /MTU (400 gal/MTU) or lower, the amount of solids formed can be minimized by keeping the nitric acid concentration at approximately 7 M. This high-volume waste is normally concentrated in-tank; however, these rate data indicate that additional precipitation may occur during storage even if the solution is not concentrated further.

At 378 μ /MTU (100 gal/MTU), precipitate still continued to form for more than 200 hours at the boiling point showing that the continued precipitation is not unique to any one level of concentration of the waste. At 10M HNO_3 , which was investigated at this concentration level,

the precipitation of barium nitrate due to the salting effect of nitric acid resulted in increased amounts of precipitates.

A comparison of the data obtained from these rate studies with data obtained from similar waste stored at 35 to 60°C indicates that the rate of formation of solids is more rapid at the boiling point.

1.13 Redissolution of Precipitates Solids

The long-term operation and the decontamination of HLLW evaporation, transfer, and storage equipment may require the periodic removal of undissolved solids and scale by the addition of solvents. The redissolution of undissolved solids from HLLW-0 was investigated using aliquots of solids suspended in distilled water and adding the reagent being tested; the mixture contained 83 vol% of the added reagent. The weight percents of the original undissolved solids which were dissolved in 2 hr at 95°C are reported in Table 2.

TABLE 2

REDISSOLUTION OF HLLW-0 PRECIPITATES

<u>Solvent</u>	<u>Precipitate Redissolved, wt%</u>
2 M HNO ₃	13
8 M HNO ₃	25
2 M Oxalic Acid	65
2 M H ₃ PO ₄	4
2 M H ₂ SO ₄	31
10% Acetic Acid	5
10% NaOH	39
10% Turco Alkaline Rust Remover	100
2 M HCl	12
14 M HF	100

The 10% solution of Turco Alkaline Rust Remover^a, which contains 65% sodium hydroxide, dissolves the solids. A solution of 10% NaOH dissolved only 39% of the solids. The second best solvent was 2 M oxalic acid which is used as a decontamination reagent for process equipment. Sulfuric acid at 2 M and nitric acid at 8 M, which is about the same concentration as the parent HLLW solution, dissolved

^a Turco Products, Inc., Division of Purex Corporation, Carson, California.

about one-quarter of the precipitate and could possibly be effective in descaling heat transfer surfaces. Phosphoric acid and acetic acid are ineffective as solvents. Hydrofluoric acid is a very good solvent, but 2 M HCl dissolved only about 10% of the solids. In actual chemical process equipment, solvents containing fluorides and chlorides are not considered acceptable because of the excessive corrosion attack on stainless steel equipment. Redissolution studies are continuing.

1.2 Small-Scale Evaporation (G. R. Villemez)

The small-scale thermosyphon evaporator unit has been constructed, installed and pressure-tested. Installation of the steam supplies, insulation, controls, and instrumentation, which are currently in progress, will complete the waste concentration system.

2. Storage of Evaporated Waste

Long-term studies are being made to determine the behavior of stored HLLW and to provide design and operational data for commercial liquid waste storage facilities. Evaporated simulated HLLW solutions are being tested for solution stability and undissolved solids formation. A bench-scale storage tank is being designed and constructed for long-term studies of solution mixing, solids suspension, and heat transfer phenomena using equipment patterned after facilities at the Barnwell Nuclear Fuels Plant. Design and operational experience can be applied to similar studies using actual LWR waste in a hot cell.

2.1 Long-Term Storage of Evaporated HLLW (P. A. Anderson, C. B. Millet)

Samples of concentrated HLLW solutions resulting from laboratory evaporations of the three types of waste with and without substituted fission product elements have been stored without agitation at constant temperatures. Samples stored up to 4 months at 35°C show essentially no change in the amounts of undissolved solids. After the storage temperature was increased to 60°C for 4 weeks, there appeared to be a slight increase in the amount of undissolved solids in the stored solutions.

2.2 Bench-Scale Storage Tank (G. R. Villemez, P. A. Anderson)

Calculations were completed for the design of the bench-scale equipment which will be used to simulate the storage of HLLW. The design calculations of the bench-scale equipment were based on operating conditions similar to conditions expected at the BNFP. A 12-inch-diameter tank containing 3.6 gallons of simulated waste was selected for the bench-scale equipment so that the size would be suitable and data obtained would be applicable to future work with irradiated LWR fuel solutions in hot cell experiments.

The maximum heat load in HLLW, used as the basis for cooling calculations for BNFP⁵, is 123 Btu/hr/gal of waste. In the current bench-scale tank, this LWR fission-product-heat input will be simulated by immersed electric heating elements with a capacity of approximately

900 watts. The constant input heaters are designed to operate below the boiling point of the waste solution in order to reduce the potential for scaling of the heating elements.

The size of the cooling coils required for the bench-scale tank were calculated using a heat-transfer-area to volume ratio of 0.074 ft²/gal. The heat load required for the bench-scale unit makes it necessary for the cooling water flow rate to be in the laminar flow region with a Reynolds number at 1000 and turbulent flow of the cooling water in the BNFP tanks cannot be duplicated. The turbulent flow in the cooling coil is not necessary to make heat transfer correlations with full scale tanks. Using four feet of 1/4-inch stainless steel tubing, the velocity for the cooling water will be 0.6 ft/sec. Assuming an overall heat transfer coefficient of 32 Btu/hr/ft²/°F, the temperature rise in the cooling water will be 17°F. The temperature of the HLLW will be investigated over the range from 140 to 175°F.

Solution mixing and undissolved solids suspension will be accomplished with two ballast tank agitators and two airlift circulators. The proposed BNFP operating conditions, which were used as the design basis for the mixers, include an air feed rate to the airlift of 1×10^{-3} scfm of air per gallon of waste, a velocity at the ballast tank nozzle of 60 ft/sec, and a ballast tank refill rate of 1 ft/sec through the nozzle. The ballast tank volume is 4.75% of the storage tank volume.

The relative distance from the discharge nozzles to the depth of the solution stored has been initially set at 10% of the depth of the stored solution to duplicate the most severe mixing conditions which will occur when the storage tank is completely filled. The BNFP ballast tank agitators are scheduled to discharge solution for approximately one-minute periods at one-hour intervals. In the bench-scale unit, discharge rates will be controlled by the inlet air pressure and refilling rates will be controlled by the discharge of the air into the tank through vents. A cycling timer and solenoid valves will be used to vary the discharge and refill frequency. Additional mixing will be accomplished by two airlift circulators which are designed to discharge up to 1×10^{-3} scfm of air per gallon waste. The airlift circulators are designed for either intermittent or continuous operation.

3. Materials and Corrosion

3.1 Laboratory Corrosion Tests (C. B. Millet)

Modified Huey tests are being used to determine corrosion rates for the materials of construction for evaporators, storage tanks, and auxiliary equipment. Unwelded coupons are submerged to determine the corrosion rates in the solutions, and welded coupons are suspended at the liquid-vapor interface to observe weld behavior and possible preferential attack at the interface or in the vapor phase.

In order to establish the requirements for simulated waste solutions in the small-scale evaporator studies, tests have been performed to determine the effects of low level chloride, substitution for rare and expensive fission product elements, and ruthenium on the corrosion of Type 304L stainless steel. Chloride at 200 ppm did not affect the corrosion rate of HLLW solutions at 378 g/MTU containing 7 M HNO_3 . Solutions containing rhodium, palladium, and rhenium (simulant for technetium) exhibited a corrosion rate approximately two-thirds (260 μ/yr) that of the solution containing the substitutes, respectively, cobalt, nickel, and manganese (375 μ/yr). In solutions containing 0.059 M ruthenium, the corrosion rate doubled with reference to solutions containing neither a ruthenium nor a ruthenium substitute. The inclusion of fission products (antimony, indium, selenium, and tin) which have low concentrations (<0.001 M) and, therefore, have previously been omitted, had no effect on the corrosion. These data showed that a substitute for ruthenium which will produce similar corrosion on stainless steel is needed for materials studies in the small-scale thermosiphon evaporator. Additional laboratory tests will be made to determine the source of corrosion in the substitutes for the rare and expensive elements. Fission products which are present at low concentrations (<0.001 M) can be omitted.

The effect of agitation by bubbling air was investigated and determined to decrease the corrosion rate in a solution containing high iron concentration (0.66 M) and increase the rate in HLLW-0 (minimal process additives and degradation products).

Two new Jessop alloys, JS700 (21Cr, 25Ni, 4.5Mo) and JS777 (21Cr, 25Ni, 4.5Mo, 2Cu), were tested and determined to have approximately the same corrosion resistance as Type 304L stainless steel in HLLW-0 solutions.

No preferential interface or vapor phase attack has been observed in any of the tests.

3.2 Monitoring of Storage Tanks

Three types of simulated waste (HLLW-0, HLLW-Fe, and HLLW-UP) are being monitored for corrosion of stainless steel. Individual Type 304L stainless steel electronic probes are submerged in waste solutions at 60°C. Solutions are stirred at 1-hour intervals to resuspend the solids. The rates of corrosion are being measured with an electronic corrosometer to evaluate continuous monitoring of waste storage tanks.

Plans for Next Quarter

Solutions approximating the composition of HLLW from the Barnwell Nuclear Fuel Plant will be prepared for laboratory evaporations. Evaporated HLLW slurries and supernates will be measured for viscosity.

Construction of a small-scale thermosiphon evaporator will be completed and the unit will be tested with water and nitric acid.

Laboratory corrosion coupon tests will be conducted to determine the effects of possible descaling agents and corrosion products upon the corrosion rate of Type 304L stainless steel. Laboratory corrosion coupon tests will evaluate the corrosion rate of various metals in stored HLLW slurries for comparison with data obtained from electronic corrosion monitoring probes.

4. References

1. LWR Fuel Reprocessing and Recycle - Progress Report for April 1 - June 30, 1976, ICP-1101 (December 1976).
2. Alternatives for Managing Waste from Reactor and Post-Fission Operations in the LWR Fuel Cycle, ERDA-7643 vol. 2, (May 1976) Section 6.1 - 6.4.
3. LWR Fuel Reprocessing and Recycle - Progress Report for July 1 - September 30, 1976, ICP-1108, (December 1976).
4. LWR Fuel Reprocessing and Recycle Program Quarterly Report for Period April 1 - June 30, 1976, ORNL/TM-5547 (July 1976).
5. Final Safety Analysis Report, Barnwell Nuclear Fuel Plant Separations Facility, Dolset 50-322 (October 1973) Section 8.

VI. STUDY OF BIDENTATE COMPOUNDS FOR SEPARATION OF ACTINIDES FROM COMMERCIAL LWR REPROCESSING WASTE

(L. D. McIsaac, N. C. Schroeder, R. E. LaPointe)

Bidentate organophosphorus compounds have been under study for about three years as possible extractants of actinides from ICPP high-level wastes. The expertise gained with these extractants is presently being applied to the problem of actinide removal from high-level liquid waste generated by reprocessing commercial LWR fuel. As is the case with our work on ICPP waste, attention will focus principally on the use of the bidentate compound, DHDECMP. This work is under subcontract to Oak Ridge National Laboratory.

The bidentate extractants proposed for this study are presently obtainable only in a crude form which is not satisfactory for use. At this time, we are using a "small" high vacuum distillation system to obtain approximately 86% pure DHDECMP after two distillations. This is a very slow process and by no means will we be able to come close to obtaining the ultrapure DHDECMP needed until a preparative high pressure liquid chromatograph system is installed. We will, however, be able to use this 86% DHDECMP for preliminary studies.

Radioactive nuclides to be used for extraction studies have been ordered, some are in our possession now, and a few will be made locally when we have sufficient amounts of extractant. We are also investigating methods of selectively stripping actinides from the extractant and subsequent cleanup of the solvent for recycling purposes.

1. Preparation of Synthetic Waste Solution

Initial studies will be conducted using synthetic waste solution prepared by mixing nitric acid solutions of nitrate salts of nonradioactive isotopes of fission product elements. The quantities are based on those that were calculated by the ORIGEN code for typical LWR fuel irradiated to 33,000 MWd/metric ton. The fission product content is based on a fuel reprocessing time of 160 days and storage of wastes for five years after reprocessing. The volume, acid concentrate and fission product content values correspond to approximately those expected, after the co-decontamination step, in the HAW column (5569 liters, 2.9 M HNO₃) before exhaustive extraction with 30% TBP. This step was chosen because this is a possible location for our bidentate extraction process. For our early experiments, 2 liters of solution would be sufficient; however, a solution that was made by dissolving all water solubles plus the elements dissolved in conc HNO₃ proved unsatisfactory. With time, a precipitate appears. It is assumed to be a zirconium molybdenum complex but we are awaiting test results on it at this time. We have found that ZrO(NO₃)₂·4H₂O will dissolve in 2.9 M HNO₃, but does precipitate with time. Tin and antimony are not stable with regard to precipitation. We had much trouble trying to dissolve dry Pd(NO₃)₂ in water and in 2.9 M HNO₃ but palladium sponge dissolved into concentrated nitric acid and stayed in solution. Filtration of the waste solution just after preparation showed that some Pd had precipitated.

We will continue to investigate other methods of solution preparation which will give a stable product. However, it appears that our procedure will be to add solutions of the troublesome elements to aliquots of the stable solution, when needed for daily experiments.

Table 3 shows: the elements, their quantities in the synthetic waste solution, the starting compounds, and the methods of dissolution.

TABLE 3

Synthetic Commercial Waste Solution

<u>Element</u>	<u>Quantity g/l</u>	<u>Compound</u>	<u>Dissolved in</u>
Sr	0.163	Sr(NO ₃) ₂	water
In	2.47 x 10 ⁻³	In ₂ O ₃	2.9 <u>M</u> HNO ₃
Cd	0.017	Cd(NO ₃) ₂	water
Cs	0.482	CsNO ₃	2.9 <u>M</u> HNO ₃
Se	9.89 x 10 ⁻³	Metal	9.75 <u>M</u> HNO ₃
Ba	0.332	Ba(NO ₃) ₂	water
Te	0.112	Metal	9.75 <u>M</u> HNO ₃
Mo	0.680	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	2.9 <u>M</u> HNO ₃
Sn	9.89 x 10 ⁻³	Metal (20 mesh)	2.9 <u>M</u> HNO ₃

TABLE 3 (Continued)

<u>Element</u>	<u>Quantity g/l</u>	<u>Compound</u>	<u>Dissolved in</u>
Ag	0.012	AgNO ₃	water
Zr	0.724	ZrO(NO ₃) ₂ •2H ₂ O	2.9 <u>M</u> HNO ₃
Br	0.003	NaBrO	water
I	0.053	HIO ₃	water
As	1.855 x 10 ⁻⁵	As ₂ O ₃	water
Sb	2.47 x 10 ⁻³	Metal	9.75 <u>M</u> HNO ₃
Pd	0.282	Sponge metal	conc HNO ₃
Rh	0.077	Rh(NO ₃) ₃	2.9 <u>M</u> HNO ₃
Rb	0.066	Rb NO ₃	2.9 <u>M</u> HNO ₃
Ru	0.426	RuNO(NO ₃) ₃	2.9 <u>M</u> HNO ₃
La	0.254	La(NO ₃) ₃ •6H ₂ O	water
Y	0.093	Y(NO ₃) ₃ •6H ₂ O	2.9 <u>M</u> HNO ₃
Nd	0.816	Nd(NO ₃) ₃ •6H ₂ O	water
Pr	0.239	Pr(NO ₃) ₃ •5H ₂ O	2.9 <u>M</u> HNO ₃
Ce	0.492	Ce(NO ₃) ₃ •6H ₂ O	2.9 <u>M</u> HNO ₃
Sm	0.177	Sm(NO ₃) ₃ •6H ₂ O	2.9 <u>M</u> HNO ₃
Gd	0.024	Gd(NO ₃) ₃ •6H ₂ O	2.9 <u>M</u> HNO ₃
Eu	0.034	Eu ₂ O ₃	2.9 <u>M</u> HNO ₃
Fe	0.140	Fe(NO ₃) ₃ •9H ₂ O	2.9 <u>M</u> HNO ₃
Cr	0.024	Cr(NO ₃) ₃ •9H ₂ O	2.9 <u>M</u> HNO ₃
Ni	9.28 x 10 ⁻³	Ni(NO ₃) ₂ •6H ₂ O	2.9 <u>M</u> HNO ₃

VII. HTGR FUEL REPROCESSING AND WASTE TREATMENT

1. HTGR Semi-volatile Fission Product Removal

(K. L. Wagner, H. S. Meyer, J. A. Rindfleisch, G. O. Haroldsen)

In HTGR fuel reprocessing, the fuel particles will be crushed, then burned in a fluidized bed burner. A number of fission-product oxides will be volatilized in the process. The purpose of this task is to develop the technology for successful handling and removal of these particular fission products. They will be those oxide species that will be volatilized at 900°C and will condense and either become airborne as very fine, difficult-to-filter particulates, or else will plate out on internal surfaces of equipment. The suspected species are oxides of Se, Rb, Mo, Tc, Ru, Cd, Sb, Te, Cs, Ce and possible others.

Preliminary laboratory investigation has been undertaken to determine the approximate vaporization and deposition temperatures, and the nature of the deposited material. These tests have involved mixing 0.5 g of the candidate material with 2.5 g of fine graphite and combusting in a tube furnace at 900°C. A temperature profile of the furnace tube was determined in advance to establish the approximate deposition temperatures. The results are summarized in Table 4. Of special note was the evidence that SeO_2 and RuO_2 passed through a fiber filter downstream of the furnace.

In addition to the preliminary laboratory work, vapor pressure data and thermodynamic data from the literature and associated HTGR development work going on at other sites are being consolidated and put into usable form to give insight into the volatilizing and deposition steps that will transpire in the HTGR processing system. This information, plus that from the tube furnace tests, are being used in evaluating possible semivolatile removal methods and devices.

Plans for the Coming Quarter

In the coming quarter, the volatility and deposition data that are being acquired will be used for preliminary evaluation to assess deposition problems and the promise of possible removal systems. The first task will involve bringing more information to bear on depositions that are likely to occur between 900°C, the combustion temperature, and 500°C, the proposed in-vessel sintered metal-filter temperature. Laboratory tests will then be undertaken to verify and quantify the magnitude of the problems and its implication on burner design and operation. The tube furnace tests will be continued to aid in providing a better perspective of the volatility and deposition problems. Also, planning will be completed for laboratory tests of removal devices that will collect and promote deposition under controlled regimes between 500°C and ambient temperature. More specifically, these will be designs of test systems for fluidized-bed quenching and fixed-bed quenching of the off-gas stream to promote condensing and deposition at the desired location. Other promising systems will also be evaluated.

2. Catalytic Oxidation of Carbon Monoxide

(J. A. DeDebbio and T. R. Thomas)

Experimental

During reprocessing of HTGR fuel it may be necessary to substantially reduce the concentrations of CO and O_2 in the gaseous effluent to eliminate potential interference with krypton recovery. Therefore, a batch recycle reactor is being used to study the kinetics of CO oxidation over an alumina-supported platinum catalyst in a CO_2 atmosphere. This is a closed system consisting of a heated 2.5 x 2.5 cm bed of catalyst in series with a 35-liter reservoir and a recirculating pump. The experimental apparatus also includes a precision pressure gauge (0.001 Torr resolution) for producing both standard and experimental concentrations of CO and O_2 and an infrared gas analyzer to measure CO.

The reactant gases are circulated through a bypass loop until the catalyst bed is brought to temperature. At this time, the gas mixture is allowed to pass through the bed marking the beginning of the kinetic run. Test parameters include temperature (200 - 300°C), gas concentration (0.2 - 2% CO and O₂) flow rate (0.2 - 1.55 scfm) and superficial face velocity (70 - 240 ft/min).

TABLE 4
RESULTS OF TUBE-FURNACE VOLATILITY TESTS

<u>Species</u>	Grams/FSVR* Element (6 yr burnup, 1 yr cooling, fissile plus fertile)	*Ft.St. Vrain Reactor
		<u>Observation</u>
Antimony	0.356 g	Volatile at 900°C
Sb ₂ O ₃		Volatile at 700°C
Sb ₂ O ₄		Volatile at 900°C - changed to Sb ₂ O ₃
Sb ₂ O ₅		Volatile at 800°C - changed to Sb ₂ O ₃
SbCl ₃		Volatile at 500°C
Barium	56.7 g	Not volatile at 900°C - forms BaCO ₃
BaO ₂		Not volatile at 900°C - forms BaCO ₃
CdO	0.699 g	Volatile at 900°C
Cerium	99.2 g	No vapor observed - forms CeO ₂
CeO ₂		No vapor observed - (to be repeated)
Cs O	76.9 g	Volatile at 900°C
Eu ₂ O ₃	3.84 g	No vapor observed - (analyses pending)
La ₂ O ₃	41.0 g	No vapor observed - (analyses pending)
MoO ₃	105. g	Volatile at 600°C
Nb ₂ O ₅	0.243 g	Not volatile at 900°C
Rb ₂ O ₄	18.6 g	Volatile at 900°C
RuO ₂	47.5 g	Volatile at 900°C
Selenium	2.69 g	Volatile at 400°C
SeO ₂		Volatile at 200°C
Ag ₂ O	0.129 g	Vapor observed - forms metallic silver - may be a volatile contaminant.
Strontium	39.2 g	Vapor observed - forms SrO <2% Sr found on the filter
SrO		Vapor observed - analyses pending - may be a volatile contaminant
TeO ₂	18.2 g	Volatile at 700°C
SnO ₂	1.05 g	Not volatile at 900°C
ZrO ₂	139 g	Not volatile at 900°C

Kinetic Model

Assuming a bimolecular surface reaction between CO and O₂ on a pelleted platinum-alumina catalyst, Voltz and co-workers (Ind. Eng. Chem. Prod. Res. Develop. 12, pp 294-301 (1973)) were successful in fitting the experimental data to the following rate expression:

$$r = - \frac{d(\text{CO})}{dt} = \frac{K(\text{CO})(\text{O}_2)}{[1 + k(\text{CO})]^2}$$

where r = rate of CO oxidation, K = rate constant and k = equilibrium adsorption constant for CO. We have expanded this expression to include adsorption constants for O₂ and CO₂ as follows:

$$r = - \frac{d(\text{CO})}{dt} = \frac{K k(\text{CO})k'(\text{O}_2)}{[1+k(\text{CO})+k'(\text{O}_2)+k''(\text{CO}_2)]}$$

where K = fundamental rate constant, and k' and k'' = adsorption constants for O₂ and CO₂, respectively.

A computer program has been written which (1) fits the empirical data (conc vs time) by linear regression, (2) differentiates the empirical regression equation, and (3) uses iterative, non-linear least squares analysis to estimate all constants. Preliminary data indicate that the above equation is a valid description of the kinetics involved.

Plans for Next Quarter

Using the above mentioned CO concentrations and operating temperatures, the rate and equilibrium adsorption constants will be generated for the bimolecular surface reaction model.

VIII. NATURAL FISSION REACTOR STUDIES (OWI FUNDING via LASL)

(W. J. Maeck, W.A. Emel, R. L. Eggleston, J. E. Delmore, R. A. Nielsen)

A unique approach to the study of the long-term behavior of waste fission products and the actinide elements in geologic environments is through the analysis of the remains of natural fossil fission reactors. In 1972, the discovery of the natural fission reactor at the Oklo pit in the Republic of Gabon provided us with such a case. Initial studies conducted both by the French CEA and United States ERDA laboratories and reported at the IAEA Conference on the Oklo Phenomenon^a showed that most of the fission products had remained in place for a period of ~2000 million years. Of particular importance was the high immobility of plutonium and the higher actinides in this environment.

^a"The Oklo Phenomenon", Proceedings of an IAEA Symposium, Libreville, Gabon, June 1975.

In the search for other natural fission reactors through analysis of various ore samples, the lack of an observed depleted ^{235}U sample does not preclude the occurrence of a natural fission reactor for two reasons. First, it is possible that the reactor could have operated in a near breeder mode such that the amount of ^{239}Pu produced and decaying to ^{235}U is equal to the amount of ^{235}U fissioned; and second, it is possible that wide dispersion of a fossil reactor remains could be masked by the relatively large amount (1-3 ppm) of uranium which occurs in nearly all geologic specimens. To minimize the possibility of overlooking such cases, the measurement of selected fission product elements is being conducted, in particular the isotopic measurement of Ru. This element is highly suited as a monitor for fossil reactor remains because the natural occurrence of Ru in the earth's crust is very small, being approximately one part in 10^9 . Thus, the isotopic composition of natural occurring Ru could be significantly altered if contaminated with fission product Ru whose isotopic composition is significantly different from that of natural. A large number of selected U ore samples are currently being analyzed for Ru.

Because the amount of Ru in most ore samples is expected to be small, a considerable amount of development time has been devoted to the study of the separation of Ru from ore samples and its subsequent mass spectrometric measurement. In the past irradiated fuel samples and Oklo samples have been successfully analyzed where the amount of Ru on the mass spectrometer filament approximated 1 microgram (μg). To obtain 1 μg of Ru from normal U ores where the concentration may be as low as 1 part in 10^9 , would require the processing of 1000 grams of ore. This is unreasonable for a subsequent mass spectrometric measurement. Therefore, we have attempted to reach the desired sensitivity by improving the measurement technique. Currently, Ru spectra have been obtained on as little as 7 ng of Ru; however, at this level we are experiencing interfering levels of Mo and Zr which may be either in the separated sample or the filament material, or both. The study of this problem is being continued.

The separation technique is distillation of Ru as the tetroxide from sulfuric acid using sodium bismuthate as the oxidant. When using very clean glassware, 5 ng or less of Ru can be distilled. One interference in this method is the presence of large quantities of Pb which precipitates as lead sulfate in the distillation flask resulting in excessive bumping. Improvements in the design of the distillation flask are being investigated.

To date several isotopic measurements have been obtained for Ru separated from relatively rich U ores. The results given in Table 5 are neither indicative of natural Ru nor that expected from ^{235}U thermal fission. Although the natural Ru component has not been subtracted because of interfering Mo and Zr spectra the data are surprisingly consistent which could indicate little or no natural Ru contamination. We believe these results may be characteristic of the isotopic composition of Ru produced by spontaneous fission of ^{238}U or a mixture of ^{238}U spontaneous fission and ^{235}U -induced fission. Studies are currently underway to determine the predominant mode of fission in these samples.

TABLE 5
RUTHENIUM ISOTOPIC MEASUREMENTS

<u>SAMPLE</u>	<u>Ru Isotopic Ratios</u>			
	<u>99/101+102</u>	<u>101/102</u>	<u>101+102/104</u>	<u>102/104</u>
3.1 Pitchblend (NWT Aust.)	0.423	0.926	3.59	1.86
3.14 Uraninite (Congo)	0.425	0.919	3.52	1.84
3.61 Uraninite (Canada)	0.432	0.890	3.66	1.94
8.01 NWT Australia	0.431	0.916	3.70	1.93
8.02 NWT Australia	0.462	0.909	3.50	1.87
Cluff Lake (Canada)	0.446	0.911	3.52	1.84

Oklo Reactor Ores	Variable	1.20	4.92	2.23
²³⁵ U Thermal Fission	0.66	1.21	5.05	2.30
Natural Ru	0.261	0.541	2.62	1.70

Because the quantity of Ru produced by ²³⁸U spontaneous fission may be related to the age of the U mineral and hence provide a new age-dating mechanism, we are currently attempting to define the isotopic composition and fission yields of ²³⁸U spontaneous fission produced Ru. Sample selection and measurement criteria are being developed in cooperation with the Los Alamos Scientific Laboratory.

*

SPECIAL MATERIALS PRODUCTION

I. LONG-TERM MANAGEMENT OF ICPP HIGH-LEVEL WASTES

1. Post Calcination Treatment of ICPP Wastes

(H. S. Cole and K. M. Lamb)

Alternative post treatment methods for ICPP high-level waste include storing pelleted calcine in on-site bins or incorporating these pellets in a matrix. The forming of pellets from calcine was studied using a laboratory-scale pelletizer and both solid and liquid chemical binders. Pellets with adequate mechanical strength are required for bin storage or matrix incorporation; leach-resistant pellets are also desired for ultimate storage. Table 1 shows the pellet compositions and leach rates for the more favorable of the more than sixty pellet formulations tested. A simulated zirconia calcine was used in all cases. All pellet preparations were evaluated for green, dried, and heat-treated strength on the basis of resistance to crumbling while green, and to breaking or dusting when rolled or dropped after heat treatment at 750°C for one hour. As shown in Table 1, calcine mixed with several binder formulations produced pellets having leach resistances between 0.1 and 0.5 wt% loss after 50 to 100 hours of Soxhlet leaching at 95°C.

All of the pellets listed, whether prepared with metakaolin, metakaolin plus H_3BO_3 , or $Ca(OH)_2$, were sufficiently consolidated to resist breakup while handling before being dried. Of the dried pellets, those containing $Ca(OH)_2$ exhibited the least dusting on abrasion, but all are probably satisfactory for use. All of the heat-treated pellets were hard, dust-free, and free-flowing.

Pelletizing studies using the 16-inch-diameter disc pelletizer show that balance between liquid spray and solid feed rate must be carefully controlled to prevent production of non-uniform or off-sized pellets. At proper feed rates, uniform pellets are produced which do not agglomerate and have sufficient green strength to prevent slumping.

The 16-inch disc pelletizer can be used to make pellets ranging in size from 1/2 to 1/16-inch. Size control appears to be largely dependent on spray location and feed composition and to a lesser extent upon throughput rates. Pellets were made with zirconia calcine using the 16-inch disc pelletizer and a 2:1 volume ratio of H_3PO_4/H_2O as a liquid binder and 10 wt% slaked lime [$Ca(OH)_2$] as a solid binder. After drying at 200°C and sintering at 750°C for 1 hour, the pellets had a leach rate of 4.4×10^{-4} g/cm²-day. Pellets were also made using a 3:1 volume ratio of H_3PO_4/HNO_3 and 20 wt% metakaolin. These pellets were tested for attrition resistance during pneumatic transport. After traveling about 50 ft vertically and horizontally through two 90° bends at 55 ft/sec, and then dropping 30 ft, 95 wt% of the pellets remained intact; loss was due to slight surface abrasion (see Table 2).

TABLE 1

LEACH RATES OF PELLETED ZIRCONIA CALCINE

<u>Calcine</u> <u>Wt%</u>	<u>Solid Binder, Wt%</u>			<u>Liquid Binder</u>		<u>Leach Rate, wt%</u>	
	<u>Meta-Kaolin</u>	<u>H₃BO₃</u>	<u>Ca(OH)₂</u>	<u>H₃PO₄/ HNO₃</u>	<u>H₄PO₄/ H₂O</u>	<u>100 hr</u>	<u>50 hr</u>
80	20			3:1	3:1	1.1	0.13
70	30			3:1		0.24	
70	30				3:1		0.13
80	20				2:1	0.50	
90	10			2:1			1.2
80	20			2:1		0.45	
85	5	10		3:1			0.1
85	5	10			3:1		1.3
85	10	5		3:1			1.1
85	10	5			3:1		1.2
90			10	3:1			1.1
80			20	3:1			0.20
90			10		3:1	0.55	
90			10		2:1		0.31
80			20	2:1			0.23

TABLE 2

PELLET ATTRITION DURING PNEUMATIC TRANSPORT

<u>Mesh Size</u>	<u>Weight,g</u>	<u>Cumulative %</u>
+ 14 ^a	79.5	95.0
+ 16	.5	95.6
+ 20	.5	96.2
+ 24	.6	96.9
+ 28	.9	98.0
+ 32	.8	99.0
+ 35	.9	100.0

^a non-attrited pellets

Preliminary studies of pellet and calcine dissolution indicate that complete dissolution will be difficult if bin-stored calcine or pellets are to be redissolved for actinide removal. Phosphoric acid, which is a good binder for making durable pellets, forms zirconium phosphate which is difficult to redissolve (see Tables 3 and 4). Boiling HNO₃ solutions were used in all cases. Dissolution time was 10 min. The highest percentage dissolution (>97%) for calcine was obtained with 4 to 8M HNO₃, but the calcine concentration was only 5 g/100 ml. To achieve 99% dissolution will require multiple passes or likely addition of HF.

TABLE 3

DISSOLUTION OF CALCINE AND PELLETTED CALCINE

<u>Material (5 Gram Quantity)</u>	<u>Conc. Nitric Acid (100 ml Boiling)</u>	<u>Percent Dissolved (10 Minutes)</u>
Calcine	15.4 <u>N</u>	95 - 97
Pellets (3:1 H ₃ PO ₄ /H ₂ O Binder)	8.0 <u>N</u>	67

Plans for Next Quarter

Bench-scale pelletization and matrix incorporation studies will continue. Pellet impact and compression strength tests will be made.

TABLE 4

DISSOLUTION OF CALCINE IN HNO_3					
HNO_3	Calcline Concentration (g/100 ml of acid)				
<u>M</u>	5g	10g	15g	20g	50g
Percent Dissolved					
1	75.2	24.2	7.1	- -	- -
2	90.1	67.2	40.0	11.9	- -
4	97.2	87.8	77.8	67.7	- -
6	97.5	90.5	82.8	84.2	- -
8	97.9	91.5	86.9	86.8	54.4
12	93.5	88.5	84.0	83.6	70.6

2. Actinide Removal from ICPP Wastes

(L. D. McIsaac)

Distribution studies with synthetic zirconium-aluminum process first-cycle raffinate and DHDECMP are continuing. Tracers produced in the Advanced Test Reactor and Coupled Fast Reactivity Measurement Facility at the Test Reactor Area are being used for these measurements. Distribution coefficients for Cr, Sr, Y, Mo, Tc, Pd, Ag, In, Sn, Sb, Te, Cs, Ba, La, Nd, and Hg were also measured. Distribution data for a 6 M HNO_3 scrub and stripping with 0.05 M HNO_3 -0.05 M oxalic acid were also obtained where activity levels permitted.

A small amount (0.2 ml) of 98 mole% DHDECMP purified extractant was prepared by silica gel liquid chromatography. Distribution coefficients for Am and Hg were also measured using this purified extractant diluted to 33 vol% in xylene. Synthetic raffinate tagged with ^{241}Am and ^{203}Hg was used. The distribution coefficients (E_a^0) for Am and Hg were 9.6 and 1.6, respectively. The E_a^0 for Am is consistent with previous measurements with less pure DHDECMP; that for Hg is lower than expected. Impurities present in the extractant as received from the producer appear to affect Hg extraction.

Plans for Next Quarter

Distribution measurements using DHDECMP as extractant will continue. The few remaining extraction coefficients to be measured will be run as appropriate tracers.

A literature search will be made to obtain information regarding the stripping of Hg from organic extractants. This information could be useful in the ultimate solution of the problem of stripping of Hg from DHDECMP.

3. Calcined Solids Retrievability and Handling

(B. D. Rose)

A final report on the properties of WCF calcine as they pertain to retrieval of calcine and the design of future storage bins was received from a consulting firm specializing in the design of bins and hoppers. The prime conclusion was that storage of calcine fines (separately or mixed with bed material) for later retrieval is very complex and costly. Calcine fines and mixtures of calcine and fines have high cohesive strength and do not flow readily. Recommendations were that fines should be agglomerated before storage, or processing conditions in the calciner altered to eliminate fines generation.

Specified proportions of fines and bed material were tested to determine the maximum amount of fines that could be tolerated during pneumatic retrieval. A mixture consisting of 10 wt% fines (MMPD = 0.48 mm) gave flow properties acceptable to pneumatic retrieval; 15 wt% fines (MMPD = 0.45 mm) resulted in a stable 5-inch-diameter "rat hole", which is larger than the proposed retrieval suction nozzle.

Using conditions similar to those in the WCF transport system and calcine with 15 wt% fines (approximately 20 wt% are produced in the WCF) resulted in a fines increase to 24 wt% (MMPD = 0.3 mm) for the equivalent transport distance to storage. Therefore, a significant quantity of fines exists in storage.

Plans for Next Quarter

Plans will be made to probe the storage bins to determine if obstructions to retrieval exist and to provide representative samples for analysis. A sample of simulated calcine will be subjected to representative storage bin temperature and pressure conditions to determine the possibility of agglomeration. Retrieval nozzle design configuration testing will continue with recommendations following.

4. Defense Waste Document

(R. L. Nebeker, A. P. Roeh, R. M. Drake, H. R. Maxey, W. B. Kerr)

A Defense Waste Document (DWD) is being written to define alternatives for long-term management of ICPP waste. This document is being prepared at ERDA's request to allow the public to comment on waste management alternatives prior to selection of the process and disposal method. The DWD will describe methods for treating and storing ICPP high level waste, discuss processing and storage risks, and present preconceptual designs of selected representative processes and rough cost estimates for major alternatives

The DWD will describe the state of existing technology for treating and storing ICPP waste. Although many options will be described, certain options will be discussed in more detail because they are representative of groups of methods presently being considered for use at ICPP. The options which will be discussed in detail include: calcine dissolution and actinide removal, calcine retrieval and conversion of calcine to pellets, incorporation of calcine in a metal matrix, and conversion of the calcine to a sintered glass-ceramic material. Cost estimates will be prepared only for these options. Storage alternatives which will be discussed include: shipping the waste to a Federal Repository, storing the waste at the INEL, and removing the actinides and shipping them to a Federal Repository while storing the actinide-free waste at the INEL.

The various processes being considered for post-calcination treatment of the ICPP high-level waste are in an early state of development. Significant R&D efforts are required before a process can be selected and design initiated. Consequently, all costs will be preliminary, and risk discussion will be general. Because of the preliminary nature of the projects, probability numbers will not be used. However, a methodology will be presented by which a cost/risk evaluation can be completed at a later time as the development for the processes progresses.

Storage and processing risks will be discussed separately. Because of the status of the process development, no attempt will be made to estimate routine or accidental radioactive and chemical releases for specific processes. Rather, the routine releases incurred in the past during operations at the ICPP will be discussed and used to show the maximum type and magnitude of typical releases expected during the routine operations of the planned facilities. Calculations will be completed to show the effects on the off-site environment of accidental releases of specific quantities of calcine and chemicals. The radiation doses resulting to the public from accidental releases will be compared with background and other doses routinely received by the public. The many lines of defense to prevent releases to the environment that will be included in any post-calcination treatment process will be discussed in detail. Plots showing the quantity of calcine that must be released to result in a dose to the public corresponding to doses normally received (such as medical x-rays) will be presented.

On-site storage risks also will be discussed in general terms. The barriers separating stored waste from the environment will be tabulated. The effects of leach rate and surface-to-volume ratio on transport of radioactivity to the aquifer will be discussed. The expected concentration of radioactivity in water resulting from transfer of waste activity to bodies of water in the area will be compared to the maximum permissible concentrations in drinking water. Doses resulting from atmospheric releases as a function of time after storage will be compared with other routinely received doses.

Initial drafts of the document sections containing technical descriptions and state-of-technology assessments for the major alternative processes have been completed and reviewed. Consultant services for work on the risk evaluation section were obtained, and a risk assessment methodology for both processing and storage was formulated. Preliminary design criteria were completed and architect-engineering work on the preconceptual design was initiated. Preliminary flowsheets for two processes were completed.

II. ICPP PLANT PROCESS IMPROVEMENT

For the reporting period, effort on this program was given exclusively to chemical and engineering development for the Fluorinel process to be installed at ICPP.

The Fluorinel Headend System will be installed in existing process cells in the main ICPP process building and will consist of several dissolvers, several complexing and surge tanks, and a liquid feed clarification system. Auxiliary equipment required to support the headend process includes a hot cell for fuel preparation and charging, off-gas cleanup systems, several casks, an improved analytical system, and various safety and control systems. Existing facilities at the ICPP will be used to extract uranium from the dissolver product.

1. Hot Fuel Dissolution Demonstration

The Fluorinel Hot Fuel Dissolution Demonstration program was successfully completed. A total of nine runs was made, four using unirradiated fuel and five using irradiated fuel. Preliminary observations indicate that (1) the improved flowsheet produces solution with acceptable stability; (2) the dissolution rates for various components of the irradiated and unirradiated fuels are comparable; and (3) the use of cadmium as a soluble nuclear poison produces no detrimental solution stability effects.

2. Pilot Plant Centrifuge

Installation of the Bird centrifuge and associated instrumentation for the Fluorinel Pilot Plant is complete. Preliminary checkout of the equipment and instrument calibration is in progress. Testing of the system with simulated process slurry is scheduled to start in January 1977.

3. Cadmium Nuclear Poison Studies

The high solubility of CdSO_4 salt in water has been verified in the laboratory. The use of this method to prepare poisoned solutions for the proposed Fluorinel process flowsheet was determined to be acceptable.

The dissolution of Cd metal in HF-H₂O₂ (as proposed in the Fluorinel process flowsheet) is also being studied in the laboratory. The reaction rates of the Cd-acid reaction will be determined for various HF and H₂O₂ concentrations and at various temperatures in order to optimize the process makeup flowsheet.

An experimental study has been prepared to evaluate the stability of cadmium in various solutions representing each process step in the proposed Fluorinel flowsheet. These data are needed for input into the PSAR for the Fluorinel Process.

4. Pilot Plant Filter System

Design of a filter system for installation in the Fluorinel pilot plant dissolution module has been completed. A Mott sintered-metal inertial filter and a Cacco etched disc filter will be tested as an alternate method to the Bird centrifuge for removal of insoluble solids from Fluorinel process solutions.

5. Fluorinel Dissolver Mockup

Design has been completed for a pilot plant mockup of the bottom portion of the proposed Fluorinel plant dissolver. The mockup will be installed in the pilot plant to test solids agitation and removal capabilities of a new design proposed by Fluorinel Project Architect-Engineer.

6. Hastelloy C-4 Weld Development

A weld development program to study various weld processes in welding Hastelloy C-4 has begun. The Gas Tungsten Arc Welding (GTAW) process, has been qualified to weld this alloy to a thickness of 1.75 inches. The weld's mechanical properties were excellent but some porosity was evident which could have an adverse effect on corrosion resistance. The Gas Metal Arc Welding (GMAW) process will be evaluated later for welding of thicker sections of this alloy. The development of a procedure to weld C-4 to stainless steel using the GTAW process is now in progress.

7. Fluorinel Corrosion Studies

Corrosion studies on materials of construction for the Fluorinel Process is continuing. A new test vessel fabricated out of Hastelloy C-4 is currently under test using dissolver product solution at 80°C. The C-4 material used in this vessel is of very low carbon content and the results of the test will help determine the role of carbon content in weld area corrosion.

III. ADVANCED GRAPHITE FUELS REPROCESSING (KK 080201)

For the reporting period, effort in this program was devoted exclusively to definition of operating conditions and design verification for the Rover combustion-leach headend being installed at ICPP.

In the process for Rover graphite fuels, the bulk of the graphite matrix is converted to CO_2 in the primary burner. The residual graphite is combusted in the secondary burner. All of the U_3O_8 , all of the $\text{Nb}_3\text{UO}_{10}$, and 30% of the Nb_2O_5 contained in the secondary burner ash is dissolved by a sequential dissolution scheme in a dissolver vessel. The residual undissolved Nb_2O_5 is removed from the dissolver effluent by a continuous solid bowl centrifuge. The solids go to waste storage and the supernate is transferred to the extraction system.

1. Rover Secondary Burner

Nine runs were made using the 4-inch-diameter pilot plant secondary burner to specifically verify operating parameters. Tests were conducted to determine the most satisfactory bed temperature and the maximum concentration of oxygen in the fluidizing gas that prevents bed sintering. An operating temperature of $830\text{--}840^\circ\text{C}$ was found to provide satisfactory burner control and burning characteristics using fluidizing gas concentrations of both 70% O_2 - 30% air and 80% O_2 - 20% air; no bed sintering was detected. Temperature during burning was easily controlled using the shroud cooling air, and the combustion efficiency remained high.

Four additional runs were made to determine the maximum ash-to-bed ratio at which the burner can be operated. Tests so far show the burner will operate satisfactorily with up to 30% U_3O_8 and 10% graphite in the bed. A higher ash-to-bed ratio will be used in future tests until poor burner operation is apparent or bed sintering occurs.

2. Neutron Interrogator

The wet borated sand used as the matrix in previous tests was dried to represent a more realistic matrix for calibration of the neutron interrogator. A calibration curve using 20 g uranium samples and the dry matrix gave better sensitivity and compared quite well with calibration curves made using the wet matrix.

Tests were also conducted using 1 g vials of ^{235}U distributed evenly throughout a dry bed of sand and boron to more closely simulate uranium being deposited in the Rover dissolver solids. The sensitivity was found to increase approximately 30% relative to the 20 g samples containing the same quantity of uranium.

3. Rover Filter Testing System

The filters planned for use in the Rover processing system will be "blown back" by air pulses on a regular cycle to prevent plugging of the filters. Tests were conducted to determine the volume of air required for several blowback pulse durations. The pressure drops across the distributor plate and cluster filters without solids showed a pressure drop to air flow relationship:

$$\Delta P_{in.H_2O} = X_i e^y$$

where $y = (0.05)$ (Airflow in scfm) and the X_i is the coefficient for each filter tested. For a clean unused cluster filter

$$X_1 = 0.3$$

Three other cluster filters used in previous solids tests resulted in coefficient $X_2 = 0.6$, $X_3 = 0.9$, $X_4 = 1.0$. The coefficient (X_i) measures the degree to which a filter is plugged.

The pressure drop across cluster filters (six 3/4-inch-diameter filters 19-inches long having a 5 micron, mean pore size) was determined for various gas flowrates for clean filters and solid loaded filters. The filters were loaded using a fluidized bed of Rover graphite.

Blowback tests indicate that a 0.4 or 1 sec blowback pulse length will successfully clear a cluster filter at a filter pressure differential of 100-inch H_2O . The filter was located 27 ft from the solenoid valve and the gas flow through the filter was 10 cfm/ft². A 0.1 sec pulse with the solenoid valve located 27 ft from the filter could only successfully blow the filter back against 20-inch H_2O at a 7 cfm/ft² flowrate. Two cluster filters being blown back from the same solenoid were limited to 20-inch H_2O at 12 ft from solenoid at 7 cfm/ft² flowrate and a 0.4 sec pulse length.

4. Capacitance Type Level Detector

Testing of the Rover Drexelbrook 508-1101 capacitance level detector indicates that it can be used to determine whether solids are flowing into or out of a vessel. Curves in which solids level is plotted vs. detector output (ma) were obtained using sand and a mixture of graphite, iron filing, sodium carbonate, and aluminum oxide. The level indicator had to be recalibrated when switching from sand to the mixture. This confirms that the level detector will not give accurate level indications if there is a variance in the electrical properties of the solids.

5. Rover Solids Transport Test System

Modifications to the pilot plant solids transport system resulted in maintaining the pressure drop across the filters under 2 psig as specified in the design criteria. A complete study of the filter blowback systems is planned.

Solids handling capacities for Penberthy Jets 62A and 63A were tested. Known weights of simulated secondary burner ash were transported from a glass vessel to the filter vessel.

Solids discharged readily from a 1-inch opening in a stainless steel 60°C coned vessel when aspirated by the jet. Less than 2% of the solids were held up in the container after transfer was complete.

IV. WASTE TRANSFER SYSTEMS (KK 08 03 02)

This program is directed toward evaluation of the materials of construction and methods of containment of radioactive waste during intraplant transfer. The primary goal of the program will be the creation of standards or guides for the design and construction of lines, encasements and other features of such waste transfer systems.

The following studies are included in the program: corrosion and corrosion control for various kinds of stainless steel in underground service; cathodic protection of buried stainless steel pipe; use of coatings for protection from corrosion and improvement in cathodic protection; evaluation of nonmetallic pipe materials; and evaluation of encasement designs for cost and earthquake resistance. Both laboratory and field testing will be used for the experimental efforts.

Pipe coating vendors and manufacturers of coated pipe have been contacted to determine which types of coatings should most logically be evaluated for stainless steel pipe in buried waste line service. The following types of coatings are under evaluation: (1) hot applied coal tar tape and primer, (2) extruded polyethylene with butyl rubber primer, (3) thin film coal tar epoxy and primer, (4) polyethylene tape, and (5) fusion bonded epoxy powders. Pipe specimens are being fabricated from Type 304L stainless steel for application of these coating types.

Special consideration is being given to the chloride content of pipe coatings because of previous occurrences of stress corrosion cracking in stressed stainless steel pipe coated with polyvinyl chloride tape. Samples of approximately a dozen common pipeline coatings, primers, and insulation materials have been obtained and analyzed at ICPP for chloride content. Polyethylene tape and primer, the coal tar tapes and primers, and calcium carbonate insulators are all below the 250 ppm total chloride level used as a guideline at Savannah River Laboratory. Fusion bonded epoxies are slightly below 1000 ppm total chloride, while coal tar epoxies, polyurethane foam insulations, and Gilsonite derived insulators are >2000 ppm total chloride.

A fiberglass reinforced polyester pipe is being tested to determine its suitability for use as a secondary containment pipe for the transfer of high level radioactive wastes. It is presently being exposed to 5 M nitric acid at 18 and 60°C.

The laboratory studies are currently focused on determining overprotection and disbonding characteristics of laboratory applied coatings on stainless steel pipe. Laboratory studies are being carried out in liquid electrolytes and saturated soil. Modified ASTM procedures are being used. Results will be applied to the field studies.

V. ICPP WASTE MANAGEMENT DEVELOPMENT

1. Waste Feed Chemistry Studies

(B. J. Newby)

Two methods were developed in the laboratory to suppress fluoride and chloride volatility during calcination of a blend of 3 vol first-cycle zirconium waste with 1 vol ICPP second-cycle waste with minimum production of gelatinous solids in calciner feed. The methods are: (1) increase the aluminum to fluoride mole ratio from 0.25 (normal concentration) to 0.32 and add calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) prior to calcination, or (2) substitute magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$). These methods were evaluated during 4-inch-diameter, fluidized-bed, in-bed combustion calciner runs to determine their effect on fluoride and chloride volatility, calciner operability, and calcine properties. Fluoride and chloride volatility suppression, fluidized-bed operability, and nature of calcine solids produced during calcination when using $\text{Ca}(\text{NO}_3)_2$ are independent of the aluminum to fluoride mole ratio between 0.28 and 0.32. $\text{Mg}(\text{NO}_3)_2$ effectively suppresses fluoride volatility during calcination of the blend (with normal aluminum concentration) without agglomerate formation and produces a calcine product of suitable hardness without nodules. Use of $\text{Mg}(\text{NO}_3)_2$ to suppress chloride volatility during the calcination of the blend (with normal aluminum concentration) retained an average of 66% of the chloride in the calcine; use of $\text{Ca}(\text{NO}_3)_2$ under the same conditions retained an average of 70% of the chloride in the calcine. Most of the chlorides are contained in the

overhead fines rather than in the calcine product when $\text{Mg}(\text{NO}_3)_2$ is used; the reverse is true when $\text{Ca}(\text{NO}_3)_2$ is used. Fines produced when $\text{Mg}(\text{NO}_3)_2$ is used are less dense than those produced when $\text{Ca}(\text{NO}_3)_2$ is used.

Plans for Next Quarter

No further work is planned for the next quarter.

2. WM-183 Flowsheet Development

(A. P. Hoskins, B. J. Newby)

ICPP storage tank WM-183 is filled with a combination of aluminum waste, electrolytic waste, evaporator bottoms, decontaminating solutions, etc., containing about 15 g/l sodium nitrate and 250 ppm chloride. Calcination of waste containing sodium nitrate causes fluidized-bed particle agglomeration; calcination of wastes with chloride can cause excessive corrosion of off-gas equipment. It was found that the waste could be concentrated by 40% while still maintaining its stability. Differential thermal analyses (DTA) were used to scope potential flowsheets. DTA showed that calcination of WM-183 waste without additives would cause agglomeration of a fluidized bed. DTA also showed that the addition of powdered iron to or the blending of first-cycle zirconium waste with WM-183 showed promise for eliminating agglomeration during calcination of the waste. Short-term solution stability studies show that the zirconium WM-183 waste blends most likely to be used (blends from 3 vol WM-183:1 vol zirconium to 1 vol WM-183:2 vol zirconium) contain only a trace of solids after one month of storage without calcium nitrate, and with calcium nitrate contained no more solids than the recommended blend of zirconium and ICPP second-cycle waste with calcium nitrate.

Two scoping runs were completed using a 4-inch-diameter, fluidized-bed, in-bed combustion calciner to determine the calcinability of the waste in WM-183. The first run was an attempt to calcine the simulated waste with no preconcentration or additives. The run ended after 5.5 hr; the feed appeared to be too dilute to produce sufficient bed material for particle growth. The simulated feed was then concentrated to 60% of the original volume; after 9 hr, the bed material began to agglomerate due to the sodium nitrate in the WM-183 waste. A third, short-term run with powdered iron (0.5 mole iron per mole of sodium nitrate) added to the concentrated feed to suppress the caking tendency of the high sodium waste was successfully completed. No significant operating problems or agglomeration were experienced.

Plans for Next Quarter

Short term stability studies will be made on blends of WM-183 waste concentrated by 40% with zirconium waste. The hydrogen concentration will be determined in the off-gas evolved when powdered iron is added to WM-183 waste. A study will be made to see if addition of silver

nitrate to calciner feed will keep chloride in the bed during calcination of WM-183 waste. Four-inch-diameter calciner runs will be made to determine the amount of powdered iron and chloride volatility suppressing reagent required to prevent fluidized-bed particle agglomeration and to keep chloride in the bed. If 4-inch calciner runs with powdered iron show promise, a 12-inch calciner run will be made using the most promising flowsheet.

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OTHER PROJECTS SUPPORTING ENERGY DEVELOPMENT

I. NUCLEAR MATERIALS SECURITY

1. Measurement Equipment for Chemical Plants

1.1 In-Plant Process Surveillance System (W. J. Harris, H. R. Deveraux)

Components for a proposed on-line Special Nuclear Materials (SNM) theft detection, process surveillance system have been installed in the Idaho Chemical Processing Plant. These components include transfer valve position monitoring switches with high precision tank level and solution density transducers for input accountability and first cycle extraction feed tank monitoring. Design has been completed for operation with a remotely located computer-based data acquisition and data analysis system. Continuous monitoring of the sensors and instruments in the plant provides immediate detection of attempts to steal SNM. Computer programs including the required theft detection algorithms will be developed and applied to give pattern recognition or "signature" comparison output in the form of suitable alarm signals when non-allowed sequencing of transfer and control valves occurs or if non-standard operating modes, process flow configurations, or operating sequences are detected. The design goal is to provide the generated alarm response at an appropriate level to counteract each diversion attempt, but with minimum impact on plant production. Operational tests are scheduled by July 1977, after electrical signal cabling is completed and a transit-time flowmeter, gamma absorptimeter, and additional valve monitoring signals are plant installed. The construction and checkout of the various electronic subsystems are on schedule. Remote signal and data transmission, and remote interface control capability has been demonstrated through as much as 1000 feet of cable. Two-way signal transmission and remote interface control has also been demonstrated over the telephone line network, permitting monitoring from any telephone location.

2. Component Development

(H. R. Deveraux, W. J. Harris)

2.1 Transit Time Flowmeter

This sensor was developed to measure the volume of SNM solution entering the sensitive plant loadout area. Accuracy of 0.3% has been demonstrated in laboratory tests. Periodic recalibration is not required, the precision increases at low flows, and the sensing unit is not susceptible to plugging or corrosion. This flowmeter measures the transit time of a small bubble with ultrasonic detectors mounted on the outside of plant lines. Combined with the previously developed gamma absorptimeter, these sensors permit an independent and immediate measurement of the amount of SNM transferred between plant modules or material balance areas. A transit-time flowmeter unit has been

fabricated by precise machining from stainless steel bar stock to ensure a properly defined ultrasonic beam through the contained liquid, and slots were milled adjacent to each ultrasonic crystal mounting area to highly attenuate acoustic energy following the path around the circumference section of the transducer. The electronic system for remote operation of this flowmeter, including the remote cable line drivers has been completed.

3. Precision Tank Level Measurement

(F. O. Cartan)

Tests, evaluation, and report preparation have been continued on commercial pressure measurement transducers for applications to increased accuracy tank content measurement and tank leak detection caused by intentional diversionary activities, or non-intentional plant operations or equipment failures.

Calculations were made on experimental measurements obtained on a pilot model of an "organ pipe" geometry, critically safe storage tank. Analysis was made of a number of factors which must be considered for high accuracy measurements. Factors studied included bubble volume, evaporation, sparge line air flow, and thermal expansion of both tank and liquid. Results indicate that with a stressed quartz crystal transducer level measurement accuracy of within 0.01% can be obtained and that level changes of one millimeter can be detected.

4. Safeguards Isotope Ratio Mass Spectrometer

(M. W. Echo)

Plant safeguards and operation personnel, as well as ERDA and IAEA inspectors need rapid, convenient, and independent measurement capability to obtain isotopic composition and concentration of uranium and plutonium. A developmental model mass spectrometer is being tested that is small, sturdy, does not need cooling water or air or liquid nitrogen, and is portable so that it can be rolled about the plant or moved in a van to wherever immediate measurements are needed. This instrument is of the quadrupole mass filter design, which does not require a heavy magnet assembly.

Sample requirements are one microgram or less. Precision or isotope ratio measurements is 0.5% or better on major peaks based on data collected from standard reference material having uranium-235 ratios corresponding to natural 3%, 20%, 50%, and 93% enrichment. Several instrument design deficiencies are being corrected, including sealing of the vacuum lock mechanism on the sample head.

5. Plans for Future Activities

- Preparation of the safeguards isotope ratio mass spectrometer for routine laboratory operation.
- Pilot plant testing of the bubble transit time flowmeter and installation as part of the plant load-out area, plant input accountability, remote monitoring system.
- Plant demonstration of initial phase of the on-line SNM theft detection, process surveillance system.

II. GEOTHERMAL ENERGY DEVELOPMENT

1. Liquid Fluidized Bed Heat Exchanger

(C. A. Allen, A. F. Fanous*, O. Fukuda, R. E. McAtee)

This concept is designed to prevent fouling on heat transfer surfaces when heat is transferred from geothermal fluids to working fluids such as clean water, fluorocarbons, or isobutane. In this exchanger, geothermal brine passes through the shell side and the working fluid through the tubes. The tubes are surrounded by a bed of particles, which is typically silica sand. The velocity of the brine agitates the particles, and the fluidized particles scrub the heat transfer surfaces. This concept has been shown to prevent fouling and to increase the heat transfer coefficient by approximately a factor of two.

1.1 Horizontal Configuration

Early experiments were conducted in vertical vessels. A horizontal unit was conceived which is simpler to build and with features more like conventional tube and shell units. In this case, the geothermal fluid flows vertically through the shell and the working fluid horizontally through the tubes, so the exchanger is of cross flow design.

The vessel and tube bundle are constructed of carbon steel. The vessel is 8 inches in diameter and 18 inches long. The tube bundle contains 49 tubes and is 15.5 inches long. A more detailed description appears in the previous report.

This vessel was installed on the Raft River test loop trailer and hydraulically tested to 150 psi. Problems were encountered with the O-ring seal between the back tube sheet and the vessel. This was corrected by going to harder O-ring material. Finding a distribution system took considerable effort. The best result was obtained with a sandwich structure. The lower plate has 3/8-inch holes on 1-inch centers with a triangular pitch. The upper plate supports the bed and has 1/32-inch holes with 30% free area. A plume still appears in the

*EG&G Idaho

center of the bed due to the outlet flow. This plume is associated with the outlet, since there are 3 inlets longitudinally along the bottom of the vessel, but the plume only appears under the single outlet. A retaining screen was mounted above the bed to keep the bed from slowly elutriating. The modifications are shown on Figure 1.

Figure 1. Cross section of the horizontal vessel showing distributor plates, retaining screen and outlet plume.

Flow rate tests were run where the cooling water flow has held constant at 50 gpm which corresponds to tubeside velocity of 4.6 ft/sec and the geothermal flow rate was varied between 15 and 100 gpm.. Bed material is silica sand closely screened to 1 mm diameter.

Heat transfer coefficients were calculated and compared with similar experiments from vertical assemblies (see Figure 2). At low flows the bed-to-tube heat-transfer coefficients (h_o) are slightly higher in the horizontal configuration. The vertical experiments were not carried to fluidizing velocities as high as the horizontal, but the pattern appears to be continuous. The magnitude of the coefficients at high velocity seems high and these values are being verified.

A six-week extended test is being conducted with corrosion coupons mounted above and in the bed. Various alloys are being tested including several stainless steels, a Hastelloy and carbon steel. This experiment will be terminated on January 31.

The vessel with an improved tube bundle will be transported to the Geothermal Component Test Facility at East Mesa in Imperial County, California by March 1 for a 90-day scale control test. Wells in this area have greater scaling potential than Raft River Wells.

1.2 Dimensional Analysis

Previous attempts to correlate liquid fluidized-bed heat transfer data with existing correlations have proved fruitless. However, recent publications on liquid fluidized-bed heat transfer provide several new equations to be tried. These equations do not pertain to bed-to-tube heat transfer, but with modifications they appear to approximate the data. They have the general form:

$$Nu = a Re_t^b Pr^c E^{-d} (E-1)^e \left(\frac{dp}{dt}\right)^f \quad (1)$$

where

Nu = Nusselt number

Re_t = Reynolds number at particle terminal velocity (the velocity which entrains the particles)

Pr = Prandtl number

E = porosity

dp = particle diameter

dt = distance between nearest neighbor tubes

a, b, c, d, e and f are constants.

Applied to data obtained from the horizontal experiments Equation (1) becomes

$$Nu = (1.82 \pm 10\%) \left(\frac{dp}{dt}\right)^{0.2} Re_t^{0.52} Pr^{1/3} E^{0.52m} (1-E)^{0.48} \quad \text{for } (2) \\ 0.4 < E < .76$$

Figure 2: LIQUID FLUIDIZED BED HEAT TRANSFER

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where $m = \frac{8.85}{\log dp}$.

There has been observed in all other liquid fluidized-bed heat transfer experiments a maximum in the heat transfer coefficient. This has not been seen in these experiments probably because of the scarcity of data above 0.76 void fraction. Assuming this system behaves like other liquid fluidized beds, then above void fraction = 0.76 Equation (1) would become:

$$Nu = (1.87) \left(\frac{dp}{dt}\right)^{1.2} Pr^{1/3} Re_t^{0.52} E^{0.48m} (1-E)^{0.52} \quad 0.76 < E < 1 \quad (3)$$

The experimentally determined bed-to-tube heat transfer coefficients are displayed along with the curves generated from Equations (2) and (3) in Figure 3.

1.3 Preliminary Size-Cost Analysis

Prior to further development of liquid fluidized-bed heat exchangers it was important to determine the cost of an LFB unit relative to conventional tube and shell units. This first cut effort was based on the low pressure preheater intended for installation in the 5Mw electric Thermal Loop designed for Raft River. Properties of the fluids are described in Table 1.

	TABLE 1	
	Shell Side	Tube Side
Fluid Circulated	Liquid Geothermal Fluid	Liquid Isobutane
Mass Flow Rate, lb/hr	1,040,000	934,000
Liquid Density, lb/ft ³	60.8	31.3
Liquid Viscosity	0.9047	0.2718
Liquid Specific Heat, but/lb. deg. F	1.000	0.676
Temperature in, °F	190	105
Temperature out, °F	144	180
Operating Pressure, psia	150	410
Velocity, ft/sec		8
Fouling Resistance, hr. ft ² deg. F/btu	0	0.001
Heat exchanged btu/hr	47,200,000	47,200,000

Several assumptions were made for this analysis as follows.

The study was based on the following assumptions:

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Figure 3

- 1) Average size of sand particles = 3 mm
- 2) Number of stages = 6
- 3) Velocity of liquid isobutane = 8 ft/sec
- 4) Velocity of geothermal fluid between tubes, at entrance or at exit does not exceed 75% of the terminal velocity
- 5) The shell side heat transfer coefficient (h_o) was based on the superficial velocity, defined as:
 Geothermal Fluid Flow
 Shell Longitudinal Cross-Sectional Area Diameter
- 6) Tubeside heat transfer coefficient (h_i) = 250 Btu, /hr-ft²-°F.

No attempt was made to determine the efficiency of any of these parameters. All of the assumptions will lead to a conservative cost estimate.

Standard calculations were used to generate values for heat transfer area, shell diameter and length, and number of tubes. A standard formula based on the heat transfer area was used to calculate the cost. In this calculation each stage was assumed to be a separate exchanger so the total cost is the sum for six exchangers in the fluidized bed case.

Two parameters were varied in these calculations. Five tube diameters from 3/8 to 3/4-inch were investigated. Pitch-to-tube diameter was varied between 1.5 and 2.5. This ratio is larger than normally seen in conventional units, because of the requirement that the distance between tubes must be several times greater than the particle diameter. Results of these calculations for fluidized bed exchangers are shown in Table 2 and a conventional tube and shell unit size and cost is shown in Table 3.

Based on these calculations, three conclusions can be drawn with the reservation that the efficiency of the liquid fluidized-bed unit operating parameters was not sufficiently evaluated.

- 1) In fluids of low scaling potential like Raft River, the capital cost of liquid fluidized bed and conventional heat exchangers is comparable.
- 2) Shell size of a liquid fluidized-bed unit may be 50% longer than conventional unit.
- 3) Liquid fluidized-bed heat exchangers require less than half the heat transfer surface of conventional tube and shell exchangers.

Table 2

Overall Dimensions and Estimated Cost of Fluidized Bed Heat Exchanger

Tube O.D. Inches	No. of Stages	No. of Tubes	Ratio Pitch Tube OD	Overall Heat Transfer coeff. Btu/hr-ft ² -°F	Heat Transfer Area Per Stage ft ²	Effective Length of Tubes Per Stage Feet	Shell ID, Inches	Estimate Cost Thousand Dollar
50	3/4	557	1.50	131	2920	26.7	38	128
			1.75	127	3014	27.6	45	136
			2.00	124.5	3081	28.2	51	160
			2.25	117	3274	29.9	57	165
			2.50	111	3433	31.4	64	166
			1.50	135	2842	22.9	38	128
	5/8	775	1.75	130	2951	23.6	44	135
			2.00	125	3065	24.2	50	143
			2.25	119	3230	25.5	57	157
			2.50	116	3308	26.6	63	161
			1.50	143	2685	18.3	35	128
			1.75	139	2766	19.4	41	132
	1/2	1023	2.00	135	2847	19.9	46	136
			2.25	128	2990	20.9	52	143
			2.50	120	3198	22.6	58	154
			1.50	145	2646	14.7	35	127
			1.75	141	2741	14.3	41	128
			2.00	135	2843	15.6	47	136
	3/8	1867	2.25	131	2952	15.9	53	136
			2.50	125	3060	17.3	58	143

Table 3

Overall Dimensions and Estimated Cost of Conventional Heat Exchanger
(for Comparison)

Tube OD Inches	No. of Stages	No. of Tubes	Ratio Pitch Tube OD	Overall Heat Transfer coeff. Btu/hr-ft ² -°F	Heat Transfer Area ft ²	Effective Length of Tubes, ft	Shell ID Inches	Estimated Cost, Thousand Dollars
3/4	1	1634	1.25	51.3	42779	54	50	133
		(two tube passes)				(two tube passes)	(two shell passes)	
		817				108	36	
		(theoretical single pass)				(theoretical single pass)	(theoretical single pass)	

III. INPLANT SOURCE TERM MEASUREMENTS

(J. H. Keller, B. G. Motes, D. Akers, T. E. Cox, S. W. Duce, J. Tkachyk)

The inplant source term program is a joint effort between Allied Chemical Corporation-ICP and EG&G Idaho with EG&G being the lead contractor under the direction of the NRC. This program is an outgrowth of a previous AEC effort which made measurements in commercial Boiling Water Reactors (BWR). The current program is concerned primarily with Pressurized Water Reactors (PWR) with the major objectives being the collection of data in operating commercial nuclear power plants so that the validity of existing predictive models can be accessed or modified where needed. The emphasis is to:

- 1) determine the specific sources of radionuclides,
- 2) determine the pathways for movement through the plant,
- 3) quantify the amount of each radionuclide present,
- 4) determine the DF's of process equipment.

In general, the responsibilities for the technical part of the program are divided with ACC being responsible for radionuclides in the gas phase and EG&G Idaho working with the liquid samples and doing counting of short-lived nuclides on site. The general plan is to make measurements in two plants from each of the three major PWR vendors. Conceptually, the work plan and sampling schedule at each plant or station will cover several months, preferably beginning with a "dirty" core prior to a major refueling outage, continuing through the refueling outage and into a period of full power operation with a "clean" core after the outage.

Measurements at two sites were begun late in FY-76 and are continuing at this time. The first station in which measurements were made was the Zion Generating Station owned and operated by Commonwealth Edison Company. This is a two-unit 1100 MWe Westinghouse plant. The station has separate containments but common areas for fuel handling, turbines and radwaste processing (auxiliary building). The gaseous effluents are discharged through twin stacks adjacent to each containment structure. The effluents from the auxiliary building are filtered before discharge and, depending on the exhaust fan configuration, can go to either one of the two stacks or be split between the stacks. Samplers have been installed in the exhaust ducts leading to the stacks and in five major feed ducts upstream of the exhaust filters.

The samplers are operated continuously with the sampling media changed on a one- to two-week interval. The samplers collect particulates, iodines, tritium, and carbon-14. The samples are returned to the INEL for analysis. Additional grab samples are taken from process gas systems on a periodic basis. These samples may or may not be counted at the plant site depending on the nuclides of interest.

The second plant selected for the study was the Fort Calhoun Station of the Omaha Public Power District. This is a single unit Combustion Engineering plant. Samplers were again installed in the major exhaust duct branches; however, it was not possible to obtain a sample from the exhaust stack.

The program generates a considerable volume of data which must be cleared with the plants before publication. The first preliminary report is presently being reviewed by the Fort Calhoun staff and the NRC. These data should be available in the near future.

IV. BURNUP METHODS FOR FAST BREEDER REACTOR FUELS (RRD FUNDED)

(W. A. Emel, D. E. Adams, A. L. Erickson, R. L. Tromp, W. J. Maeck)

The purpose of this program is to measure absolute fast reactor fission yields and to develop methods for the determination of fuel burnup for Fast Breeder Reactor (FBR) fuels.

In the reporting time period, analyses of the ^{240}Pu and ^{242}Pu capsules were completed and initial data reduction studies started. Preliminary fast reactor fission yields for the heavy mass peak for ^{242}Pu are given in Table 4.

The majority of the chemical separations and mass spectrometric measurements for two irradiated capsules of ^{237}Np were completed. The balance of the work should be completed in the second quarter of FY-77. The dissolution of two irradiated capsules of ^{241}Am is planned for January 1977.

V. ABSOLUTE THERMAL FISSION YIELD MEASUREMENTS (DPR FUNDED)

(W. A. Emel, F. A. Duce, R. L. Tromp, W. J. Maeck)

As an outgrowth of another nuclear measurement program which required the measurement of relative fission product concentrations, it was determined that some of the ^{239}Pu thermal fission yields were significantly different from previous measurements. Because of the importance of these new data to users of fission yield data, a report "Discrepancies and Comment regarding ^{235}U and ^{239}Pu Thermal Fission Yields and the Use of ^{148}Nd as a Burnup Monitor", (ICP-1092) by W. J. Maeck, W. A. Emel, J. E. Delmore, F. A. Duce, L. L. Dickerson, J. H. Keller, and R. L. Tromp, was prepared and issued in December 1976.

The summary of that report follows:

Relative thermal fission yields measured on thermally irradiated samples of ^{235}U and ^{239}Pu for Kr, Rb, Cs, Xe, Ba, and Nd show large differences for several isotopes compared to previous

TABLE 4

PRELIMINARY ^{242}Pu FAST REACTOR
FISSION YIELDS FOR THE HEAVY MASS PEAK

MASS-ELEMENT ISOTOPE	CAPSULE-9	CAPSULE-22	$\bar{X}$
125-Sb	0.063	0.055	0.059
126	0.18 ^a	0.18 ^a	0.18
127	0.33 ^a	0.32 ^a	0.32
128	0.58 ^a	0.57 ^a	0.58
129	1.02 ^a	1.02 ^a	1.02
130	1.79 ^a	1.75 ^a	1.77
131 Xe	3.18	3.14	3.16
132 Xe	4.61	4.56	4.59
133 Cs	6.94	7.01	6.97
134 Xe	7.62	7.55	7.59
135 Cs	7.07	7.20	7.13
136 Xe	7.04	6.99	7.02
137 Cs+Ba	6.39	6.53	6.46
138 Ba	6.22	6.33	6.28
139 La	6.00	5.98	5.99
140 Ce	5.04	4.85	4.95
141	4.80 ^b	4.73 ^b	4.77
142 Ce	4.55	4.62	4.58
143 Nd	4.65	4.64	4.65
144 Nd+Ce	4.32	4.31	4.32
145 Nd	3.44	3.43	3.43
146 Nd	2.95	2.94	2.94
147 Sm	2.40	2.40	2.40
148 Nd	2.03	2.03	2.03
149 Sm	1.61	1.62	1.62
150 Nd	1.34	1.33	1.33
151 Sm	1.00	1.00	1.00
152 Sm	0.77	0.77	0.77
153	0.60 ^c	0.60 ^c	0.60
154 Sm	0.43	0.43	0.43

^a Extrapolated values between mass 125 and 131.

^b Extrapolated value between mass 140 and 142.

^c Extrapolated value between mass 152 and 154.

measurements made in this laboratory^a and compared to data in current fission yield compilations^b. Particularly significant are 14% higher values for ^{138}Ba and 8.5% higher values for the Xe isotopes for ^{239}Pu thermal fission. A major impact is that all of the ^{239}Pu fission yields will have to be adjusted to preserve mass balance. Small differences obtained for the Xe isotopes for ^{235}U cause only a slight effect on the mass yield curve.

Differences also were obtained for the isotopic distribution of Nd, in particular, an increase in ^{148}Nd abundance with increasing neutron flux. This results from a large neutron capture cross section for ^{147}Nd . Previously measured ^{148}Nd fission yields tend, therefore, to be high relative to the nearly instantaneous fission yields measured in the work. Thus, burnup values based on ^{148}Nd and measured on fuels exposed to a low flux could be biased low and for fuels exposed to a high flux biased high.

The primary purpose of this preliminary report is to draw attention to the observed differences and their effect on fission yields, especially for ^{239}Pu , and to caution chemists who are measuring burnup of thermal irradiated fuels by techniques using ^{148}Nd as a burnup monitor.

Because of the significance of these data, funding (189-I-439) has been requested to complete the absolute yield measurement for ^{235}U and ^{239}Pu . It is anticipated that this effort will commence in the second quarter of FY 1977.

VI. LIGHT WATER BREEDER REACTOR (LWBR) - ANALYTICAL SUPPORT

(D. E. Adams, W. A. Emel, J. E. Delmore)

Since 1965 ERDA has sponsored the Light Water Breeder Reactor Program. As part of that program, the Proof-of-Breeding Experiment is designed to show that more fissile material can be produced than consumed in existing commercial pressurized water reactors. Proof-of-Breeding requires very high accuracy uranium analyses. To demonstrate our capabilities, six unirradiated fuel pellets were analyzed for uranium content with acceptable accuracy. After qualifying on the unirradiated pellets a series of seven irradiated ($\text{ThO}_2\text{-UO}_2$) fuel pellets from the LWBR

^a F. L. Lisman, R. M. Abernathy, W. J. Maeck, J. E. Rein, Nuc. Sci. Eng. 42, 191-214 (1970).

^b IAEA Fission Product Nuclear Data Conference, Bologna, Italy, (Nov. 1973), IAEA-169, Review Paper No. 11a.

Proof of Breeding program were received from the Bettis Laboratory and analyzed during this quarter. The procedure consists of removing the fuel from the cladding, weighing the fuel sample and dissolving the fuel in a special Pyrex bottle in an autoclave at $\sim 200^{\circ}\text{C}$ and 200 psig. The dissolvent is 13M HNO_3 - 0.05M HF. The dissolution times ranged from 18 to 48 hours. After dissolution, the sample was filtered, weighed and analyzed. The analyses required for the fuel solution were: weight percent uranium, U isotopic, ^{232}U , ^{144}Ce , ^{137}Cs , and ^{95}Zr . The fuel cladding from each pellet was also dissolved and analyzed for ^{54}Mn and total iron for neutron spectra information.

Bettis required an accuracy on the weight percent uranium results of better than 1% at the 95% C.I. The overall propagated uncertainty for the wt% U for the seven irradiated pellets and one unirradiated control pellet was 0.67% at the 95% C.I. The precision of the uranium results averaged 0.18% (one sigma) with a range of 0.05-0.38%.

A second series of twelve pellets will be shipped in the next quarter. It is expected that this special custom work on the LWBR program will continue for one to two years.

VII. RESEARCH ON ANALYTICAL METHODS

1. Low-Level System Contamination in Isotope Dilution Mass Spectrometry

(E. E. Filby, D. R. Trammell, N. R. Zack, S. D. Reeder)

The purpose of this study was to find the source of the bias so that it could be corrected. Similar corrective measures would, of course, also apply to plant samples. An analysis has been made of isotope dilution mass spectrometry (IDMS) data to determine the source of the negative bias observed for ^{235}U in the quality control data on the zirconium fuel control (ID-RB-ZR). This quality control data showed a -0.12% bias on the ^{235}U isotopic value, and a +0.46% bias for ^{238}U . This transforms to a -0.183% bias per mass unit (pmu) on the 235:238 ratio. This is an uncommonly large bias. Moreover, a negative bias is not normally observed if the problem is associated with the mass spectrometer.

Results

This study indicates that this bias is almost certainly due to natural uranium contamination of the reagents used. A separate study by S. D. Reeder showed that the chemistry of the U-Sep-1 procedure is working and does not appear to contribute to the bias.^a

^a S. D. Reeder, Analytical Chemistry Branch Progress Report for June 1976 (July 26, 1976).

The U-Sep-1 procedure was used both by Shift Lab and Quality Control Lab personnel. All mass spectrometry data was generated during routine operation of the instruments. A wide variety of sample types were run, and the results confirmed that the deviation observed on ID-RB-ZR was a consistent factor on all samples run through the Shift Lab.

	<u>Bias</u>
ID-RB-ZR	-0.183% pmu
ZR Matrix Control	-0.192% pmu
NBS-750	-0.170% pmu
79% Control	-0.155% pmu

The overall bias observed for all types of samples run through the Shift Lab (weighted according to the number of samples run) was -0.177% pmu.

Samples which were directly loaded for the mass spectrometer (no U-Sep-1 or other manipulation) showed an overall bias of only -0.014% pmu.

	<u>Bias</u>
NBS-750	-0.014% pmu
79% Control	-0.016% pmu
3:5:8 blend	-0.012% pmu

This is a negligible quantity, though it does seem to indicate that the daily calibration may be slightly over-correcting the data. Assuming this to be so, the overall Shift Lab bias becomes -0.163% pmu.

Reagents Used in the Quality Control Lab

A significant negative bias was obtained when the U-Sep-1 procedure was used in the Quality Control Lab; however, the bias was much less than that shown by the Shift Lab.

	<u>Bias</u>
Zr Matrix Control	-0.065% pmu
NBS-750	-0.070% pmu
79% Control	-0.107% pmu

The overall bias for samples run through the Quality Control Lab was -0.077%, which becomes -0.063% pmu when the above-mentioned over-correction is taken out.

Using the low-level spike, it was possible to identify and measure about 98 ng/sample of natural-uranium contamination in the U-Sep-1 reagents used in the Quality Control Lab and in the zirconium matrix material used to prepare the control solutions (the aluminum nitrate

solution contributed by far the greatest proportion of this contamination). It may be assumed that perhaps 20 ng/sample of contamination is spread out at unmeasurable levels as a general laboratory background (glassware, etc.). When the analytical results are corrected for these levels of natural-uranium contamination, the negative bias essentially disappears (now -0.008% pmu). (Even if only the quantities actually measured are used, the bias still decreases to a negligible -0.019% pmu.)

Shift Lab Reagents

Though the same reagents are presumably used in the Shift Lab, testing of their U-Sep-1 sequence with low level spikes and controls identified a total of 253 ± 26 ng/sample of natural-uranium contamination. Various possible sources besides the reagents were investigated, level contamination was almost certainly the problem, the various sets of data can be used as a measure of the magnitude of the natural-uranium contamination in the ID-RB-ZR analysis sequence (in some cases, the measured zirconium-matrix contamination level must also be factored in).

	<u>Contamination (ng)</u>
LL Spike/Control (+ Matrix)	284 ± 29 (12 points)
79% Control (+ Matrix)	301 ± 68 (5)
NBS-750 (+ Matrix)	303 ± 124 (3)
ID-RB-ZR	308 ± 150 (28)
ZR-Matrix Control	310 ± 170 (11)
ZR Blend	274 ± 98 (16)
	(± 1 Std Dev)

A weighted average of this data gives a total contamination in the U-Sep-1 sequence of 297 ± 124 ng natural uranium for the data examined.

When the ID-RB-ZR results are corrected for this level of natural contamination in the Shift Lab U-Sep-1 sequence, the bias again essentially disappears (-0.006% pmu).

To put the 297 ng/sample quantity in perspective, it should be noted that just 29 μ g of natural uranium added to 500 ml of salting reagent will give this level. And that would require less than one-tenth of a drop of a 6 g/l solution.

Other Possible Sources of Contamination

Among the possible sources of contamination, the remote pipetter in the Remote Analytical Facility was also tested. This was not a problem, as a general rule. However, a definite problem was seen when the sample isotopic composition was changed drastically to test for this possibility.

<u>Sample</u>	<u>Sample U</u>	<u>²³⁸U (%)</u>
High Level Natural U	0.438 mg	99.276
Low Level		
Spike 1	3.39 µg	3.303
Spike 2	3.39 µg	0.615
Spike 3	3.39 µg	0.535

It is apparent that not all of the more concentrated initial solution had been rinsed out when the first low level sample was pipetted. However, most of this had been washed away by the time that spike 2 was handled.

The possibility that some contamination might arise from material carried by the air flow system was also checked in the Remote Analytical Facility and in the Mass Lab glovebox. This proved to be no problem.

Summary

The existence of the negative bias was shown to be a consistent problem during the entire period of this study. Checks on various standards where direct sample loading could be used showed a negligible mass spectrometer bias though there was evidence for a slight over-correction resulting from the dialy calibration. Contamination by natural uranium of the U-Sep-1 reagents was found to be a problem in both the Quality Control and Shift Labs, being considerably worse in the Shift Lab. Corrections for the postulated levels of contamination reduced the projected biases to negligible levels.

	<u>Raw Bias</u>	<u>Bias w/o Over-Correction</u>	<u>Bias w/o Contamination</u>
Direct Load Samples	-0.014 %	-0-	-0-
QC Lab	-0.077 %	-0.063	-0.008
Shift Lab (all)	-0.177%	-0.163	-0.999
ID-RB-ZR	-0.183%	-0.169	-0.006

Contamination by a sort of "gentle rain" in the RAF or the Mass Lab glovebox was found to be negligible problem. It was demonstrated that the remote pipetter can be a problem when there is a significant difference in the isotopic composition or concentration for successive samples.

Solution Make-Up

ID-RB-ZR: Approximately 77% ²³⁵U, 22% ²³⁸U blend in nitric acid with added "Zirc Matrix", concentration ~0.5 g/l. Used for process IDMS control samples.

Zr Matrix Control: Essentially the same as above. Originally submitted as check on solution make-up.

- NBS-750: Certified 75.129 wt% ^{235}U dissolved in nitric acid, concentration ~ 1 g/l. Used for mass spectrometer calibration, etc.
- 79% Control: Approximately 79% ^{235}U blend in nitric acid without matrix, concentration ~ 1 g/l. Previously used as process IDMS control as "ID-RB" series.
- Low Level Control: Highly diluted 79% control, concentration ~ 15 $\mu\text{g/g}$. Used as control for intermittent low-level work.
- Low Level Spike: ^{233}U spike containing $\sim 0.2\%$ ^{238}U , concentration ~ 6.7 $\mu\text{g/g}$. Dilution of old IDMS spike, used for running IDMS on low-level samples.
- Zr Blend: Essentially the same as ID-RB-ZR. Run as a group over a relatively short period of time.
- 3:5:8 Blend: Approximately equal fractions (33%) of ^{233}U , ^{235}U , and ^{238}U metal dissolved in dilute nitric acid, concentration ~ 1.5 g/l. Isotopic standard heavily characterized by use in the Safeguards Analytical Laboratory Evaluation Program.

2. Determination of Mercury in Organic Solid Samples

(D. A. Pavlica, R. W. Stone)

Various modifications of furnace or cold vapor atomic absorption for the determination of mercury have become standard in many laboratories. The most popular method is that of Hatch and Ott.^a The mercury is reduced (usually with Sn^{2+}) and aerated from solution in a closed system. The mercury vapor passes through a quartz absorption cell of an atomic absorption spectrometer where its absorption is measured. Since gold dissolves in mercury to form an amalgam, some workers have concentrated the elemental mercury in the gas stream onto gold surfaces and released the mercury suddenly (by heating the gold substrate) into the atomic absorption cell. This approach significantly increases the sensitivity. Finally, in order to eliminate digestion or extraction steps, some workers have applied the above concentration technique directly to the combustion gases of samples burned in oxygen.^b

Recently in the Spectrochemical Laboratory, the method of Woodruff and Siemer^c was used to determine fractional part per million levels of

- ^a W. R. Hatch, W. L. Ott, "Determination of Sub-Microgram Quantities of Mercury by Atomic Absorption Spectrophotometry", Anal. Chem., **40** (December 1968) pp 2085-2087.
- ^b V. Liddums, U. Ulfvarson, "Mercury Analysis in Biological Material by Direct Combustion in Oxygen and Photometric Determination of the Mercury Vapour", Acta Chem. Scand., **22**, (February 1968) pp 2150-2156.
- ^c D. Siemer, R. Woodruff, "Application of the Carbon and Rod Atomizer to the Determination of Mercury in the Gaseous Products of Oxygen Combustion of Solid Samples", Anal. Chem., **46** (April 1974) pp. 597-598.

mercury in solid organic samples. From 5 to 200 mg of sample is placed in a quartz combustion boat and then heated in an oxygen atmosphere. A sodium carbonate and calcium oxide fusion adsorbent removes any organic compounds which were not completely oxidized prior to trapping of the elemental mercury. The evolved mercury is flushed from the system with oxygen and collected on the inner surface of a porous, gold-plated, graphite crucible. The porosity of the crucible allows the carrier gas to pass through the graphite while the mercury is concentrated on the gold substrate. The atomic absorption is then measured by heating the crucible in a Woodruff furnace atomic absorption spectrometer to release the collected mercury. This technique of combining the sensitivity of the Woodruff furnace atomic absorption spectrometer with the direct combustion of organic solid samples permits good results for mercury in a wide range of matrices. The sensitivity of the technique is $\sim 1 \times 10^{-10}$ g, and the detection limit is $\sim 0.5 \times 10^{-10}$ g.

3. X-Ray Fluorescence Analysis of Fluorinel Samples for Process Control

(A. M. Delmastro)

The X-ray fluorescence procedure developed for the rapid analysis of highly radioactive fuel dissolution samples^a has been tested for process control during three preliminary Fluorinel pilot plant runs with unirradiated fuel. The X-ray method operated satisfactorily and the analysis data obtained provided project personnel with essential information concerning the dissolution process.

As a result of these studies, the X-ray method was extended to include the analysis of cadmium in the process. The calibration ranges for Zr and U also were increased to permit the determination of higher concentration levels. These ranges are:

Zr: 10 - 110 g/l

U: 0.05 - 15 g/l

Cd: 1 - 25 g/l

The X-ray fluorescence method has also been used successfully with highly radioactive fuel as during five Fluorinel pilot plant runs made in the Multicurie Cell. Samples prepared for the X-ray analysis measured 3 to 5 R/hr near contact. The effects of the radiation were minimal on the Norelco wavelength dispersive vacuum X-ray spectrometer used for the analyses. No significant change in background readings were observed. The effects of this radioactivity also was evaluated for the Nuclear Semiconductor energy dispersive X-ray spectrometer used in pilot plant studies with unirradiated fuel. Although a spectrum could be collected, the system electronics were overloaded by the high

^a R. C. Shank et al, Analytical Chemistry Branch Annual Report Fiscal Year 1976, ICP-1103, 1976.

radiation field, resulting in the loss of optimum performance. Comparison of X-ray analysis results with values determined by Methods U-Fluor-1, Zr-AA-1, and Isotope Dilution Mass Spectrometry indicate that the accuracy of the X-ray method is within the ± 5 to 10% rsd required for process control.

4. Preparation of Samples for the X-Ray Fluorescence
Determination of Uranium in Residues from
Rover Fuel Dissolution

(S. D. Reeder, A. M. Delmastro)

An insoluble residue remains after the dissolution of Rover fuel. The uranium content in this residue must be determined so that the effectiveness of the uranium dissolution can be ascertained and the residue appropriately treated prior to disposal. An X-ray fluorescence procedure is under development for the direct determination of uranium in the insoluble residue. This method will require remote operations such as washing, drying, weighing, and mounting of the sample. Two procedures have been evaluated for performing these operations: (a) filtration of the sample directly onto a modified X-ray sample cup, washing these solids, and then analyzing them by X-ray fluorescence prior to drying and weighing the sample, and (b) separating the solids by centrifuging in a test tube, washing, drying, weighing, and the loading a known weight of the solids onto a sample holder for X-ray analysis. Both oven and microwave drying have been investigated. Results of these studies indicate microwave drying has few advantages over conventional oven drying. Procedure (b) outlined above appears to be more promising than Procedure (a) because the remote operations are simpler.

To accomplish Procedure (a), a hardened-paper filter was first secured to the top of a plastic cylindrical sample holder with a plastic retaining ring. With controlled vacuum applied, synthetic liquid-solids samples were pipetted onto the filter paper and the liquid drawn through the filter. After rinsing with water and acetone, a Mylar film was placed over each sample and secured with a second retaining ring. Drying of the samples in the holder by a microwave and conventional drying oven were studied. Microwave drying did not offer any time advantage over a conventional 105 to 110°C drying because the plastic holder does not absorb enough microwave energy to heat much above 100°C and thus evaporate moisture from its surface. With either drying method, the constancy of the weighings was about 1 mg. When dry, the fine sand-like sample is free to move within the space bounded by the Mylar film and filter paper, and a convenient sample geometry is not obtained. If the assembly is not dried, the sample will generally retain a fixed geometry on the paper long enough to perform the X-ray analysis. However, the solids are not always evenly distributed on the filter, which can cause significant error in the X-ray analysis.

Procedure (b) which has been evaluated for preparing a sample of undissolved Rover solids involves centrifugation rather than filtering. A liquid-solids sample containing approximately the amount of solids needed for the determination of uranium by X-ray fluorescence is centrifuged in a test tube and the aqueous phase discarded. The solids are washed with water and again separated by centrifugation. After a similar rinse with acetone to promote rapid drying, the test tube and sample are dried and weighed. The dried sample then can be dispensed from the test tube to a suitable sample holder and the sample weight obtained from a reweighing of the test tube.

Sample drying for this procedure is a simple matter with a microwave or conventional oven. Microwave drying is aided by use of an energy absorber to rapidly heat the test tube to a temperature above 110°C. The energy absorber used in this study consisted of a 1:1 mixture of copper oxide (CuO) and sodium chloride (NaCl). The mixture was placed in a 150-ml centrifuge tube and a tube slightly larger in diameter than the one used for the sample was vertically imbedded in the powder. The sample tube then was placed within the larger tube and the unit placed in a microwave oven. Using reduced energy input, the sample is dried in about 3 min. Without dilution with sodium chloride, the copper oxide reaches a "red heat" which is too high a temperature for this purpose.

Since the sample holder is not used during the separation and drying of the solids sample, the choice of a holder is more flexible than is the case with Procedure (a). One which is being tested consists of a standard 9.5-mm-diam x 19-mm-long copper fitting used to join sections of copper tubing. A Mylar film is cemented to one end of the copper tube and the dried sample is placed inside and evenly distributed on the surface of the Mylar film. A small quantity of cellulose fiber is added to the tube and compressed against the sample and Mylar film by applying pressure with a close fitting metal rod. The cellulose effectively holds the sample in place for X-ray analysis.

5. Fission Product Volatility Study

(D. R. Trammell)

At the request of J. A. Rindfleisch of Process Support and Technology, a project has been started to determine what may happen to fission products in HTGR fuels when the fuel particles are crushed and burned in the headend process for uranium recovery. The fuel particles are uranium and thorium carbide particles coated with porous graphite, pyrolytic carbon, silicon carbide, and another pyrolytic carbon coat. The porous graphite absorbs any of the fission products that may migrate from the fuel kernel. The chemical state of the fission products is not known. The fission products could be present in the particle as the element, as the carbide, or even as a reaction compound with other fission products. However, when the fuel particles are crushed and burned, the fission products will probably be converted to the

oxides. The graphite is to be burned in a fluidized bed with oxygen. As the oxygen passes through the bed, all the oxygen possibly could be consumed producing an atmosphere of carbon monoxide and carbon dioxide. This would create a reducing condition that could reduce the fission product oxides to the metals. At high temperatures, the elemental form would, in most cases, be more volatile than the oxides. Even in the presence of oxygen the graphite can reduce the oxides and may form volatile species that could be carried by the fluidizing gases.

To determine what happens to fission products under these conditions, a fairly large amount of the oxides of the major fission products will be heated to 900°C in the presence of graphite. A stream of air or carbon monoxide and carbon dioxide will be flowing over the mixture. The carbides and elemental forms, where available, also will be ignited in the presence of graphite with various atmospheres.

Figure 4 shows apparatus to be used for this investigation. A temperature profile of the furnace has been obtained and the temperature at points along the tube is known with respect to the pyrometer setting. The sweep gas is passed through a magnesium perchlorate drying tube and then controlled at a maximum flow rate of 5 scfh. The samples will be heated in quartz boats, and visual observations will be made as the temperature is increased. Pictures will be taken, when possible, to visually record what is occurring as the reaction proceeds. The sample will be ignited in the furnace until the graphite is completely burned. After cooling, the boat, the filter holder, and the filter will be weighed to determine the amount of deposit collected. The tube and boat will be photographed, and then the deposits will be dissolved to determine how much material volatilized from the boat and where it plated out in the system. The scrub solution will be analyzed to determine what may have passed through the filter.

From the temperature profile of the combustion tube, it will be possible to determine the approximate temperatures at which the fission products volatilize and then plate out and where maximum plating occurs.

6. Modification of ICPP Sampling System

(M. A. Wade)

Operations has requested EG&G to design a new sampling system. The present system collects samples in 5, 10, or 15-ml bottles that have rubber diaphragms in the lids. The sample ports, located in shielded compartments behind lead glass, are two needles connected to the appropriate tanks. When a sample is to be pulled, a sample bottle is forced over the needles of the sample port, and vacuum is applied to circulate liquid from the tank through the sample bottle. After complete mixing and circulation through the lines, the sample bottle is removed, placed in a hand "pig" and carried to the Shift Laboratory for subsequent analyses. The problems with this system that prompted the request to EG&G are:

Fig. 4 Apparatus for determining volatility of fission products.

- 1) The sample port needles are easily bent and often get plugged. They are a high maintenance item and personnel take up considerable radiation in repairing and/or replacing them.
- 2) The tongs used to handle the sample bottles remotely often get bent and are high maintenance items.
- 3) When the sample bottles are removed from the needles, liquid drips onto the bottles and contamination often is spread when the bottles are removed from the system and transferred to the hand pigs.

EG&G presented three proposals at an October meeting to which Chemical Research and Analysis (CR&A) personnel were invited. Two of the proposals use the same bottles and needles to collect the samples but have external mechanisms designed that handle the bottles and transfers them directly to casks that can then be taken to the Shift Lab. These two systems solve the problems of contamination spread at the sampling source, eliminate the need for tongs, and reduce the probability of bending the needles.

The third proposal, which Operations supervision prefers, eliminates the needles. The needles are replaced with a sampling reservoir through which the tank solution is continually circulated. When a sample is to be pulled, the circulation is stopped, and a 5-ml disposable tip pipet is inserted into the reservoir and is filled with liquid. The pipet is contained in a lead pig equipped with a mechanism to operate the pipet remotely. This pig then is transferred to the Shift Lab.

At the meeting in October, CR&A personnel were asked to evaluate the three systems from the standpoint of any problems they would create for us. We have no objections to either of the first two systems because the samples are delivered in bottles that the Remote Analytical Facility (RAF) is designed to handle. The third (pipet) system does, however, pose problems for us as outlined below.

- 1) The RAF is not designed to handle such large and cumbersome items as the disposable tip pipets.
- 2) It is our experience with such pipets (we use the Eppendorf) that they often leak, and we may be receiving a pig that contains highly radioactive liquid in the bottom. This will result not only in possible spread of contamination in our laboratory but also a possible loss of sample.
- 3) The liquid in the pipets must be transferred to containers that can be stored and handled in the RAF. Preferably, the containers should be the bottles containing the rubber diaphragm because the RAF is designed to handle these bottles. A system must be designed to make this transfer remotely.

- 4) These pipets are fairly expensive (\$25 to \$50) and should be reused. If they do become contaminated, they must be discarded to avoid cross contamination of accountability samples and to avoid radiation to personnel handling them.

Because of the advantages of the third (pipet) system to Operations, we have suggested a modification of this system that retains these advantages and also eliminates the disadvantages for CR&A. In place of the pipet, an evacuated sample bottle (containing the rubber diaphragm) is used to take the sample. A double tipped hypodermic needle (similar to those used to take blood samples in evacuated test tubes) is inserted into the sample reservoir. The evacuated sample bottle is then faced down over the other end of the needle and liquid is drawn into the bottle. The sample is now in a container that will not leak and that is compatible with the RAF. The only change required in the design proposed by EG&G is that the system be designed to handle the bottle rather than the pipet. The advantages of this system over the EG&G systems are:

- 1) Eliminates the use of expensive pipets.
- 2) Eliminates the need of transferring sample from the pipet to a sample bottle.
- 3) Item 2 reduces design and fabrication cost.
- 4) Item 2 reduces the chance of spreading contamination.
- 5) Item 2 reduces the time required to take the sample.
- 6) Pulls the sample directly into a container compatible with the existing equipment in the RAF.
- 7) Experimental samples taken with this system did not leave any liquid on the surface of the rubber diaphragm; this will reduce contamination spread.
- 8) Evaporation of samples from the bottles is a problem with the present system and would be with the first two systems proposed by EG&G. This evaporation occurs because the large sampling needles often tear the rubber diaphragms. In the third system only disposable hypodermic needles penetrate the diaphragm. In fact, vacuum has been maintained for over a week in bottles penetrated by the hypodermic needle.
- 9) The needles should not plug because the sample will not be taken while the liquid is flowing through the sampling reservoir. Time can be allowed for solids, if present, to settle to the bottom prior to sampling.
- 10) If a needle does plug, it will be disposed of and a new one used without any involvement of maintenance personnel.
- 11) A cask of much smaller size can be used for the sample bottles than for the large (~305-mm long) pipets. This will not only

reduce the cost of fabrication but will also make delivery to the laboratory easier. The larger cask will probably require a cart for delivery whereas the smaller cask may be delivered by hand as presently is the case.

7. Determination of the O/U Ratio of Uranium Dioxide
by Controlled Potential Coulometry

(J. R. Delmastro)

An oxygen to uranium ratio approaching the stoichiometric value of 2.000 is a requirement for reactor grade uranium dioxide (UO_2). Occasionally, samples are received at ICPP for this determination. Although both gravimetric and volumetric methods have been used previously for O/U ratio measurements on unirradiated UO_2 , these methods are difficult to perform on irradiated material primarily because large sample sizes are required in order to obtain accurate results. The controlled potential coulometric method for determining the stoichiometry of UO_2 originally reported by Stromatt and Connally^a appears to be more suitable for analyzing such samples. This method involves a controlled potential coulometric titration of U(VI) and total uranium in an oxide sample after dissolution in hot cone H_3PO_4 in the absence of oxygen. The total uranium is determined coulometrically in 1M H_2SO_4 by reduction at -0.38 V vs. SCE at a mercury pool electrode after chemical oxidation of all the uranium to U(VI) with excess Ce(IV) and reduction of the excess Ce(IV) at +0.05 V vs. SCE. The U(VI)/U ratio is determined directly on a single sample aliquot containing 5-10 mg total uranium and the O/U ratio is calculated from the equation $\text{O/U} = 2 + \text{U(VI)/U}$. This method is independent of uranium concentration, which eliminates errors due to the presence of inert material in the sample. The presence of ions which can reduce U(VI) or oxidize U(IV) upon dissolution of the UO_2 will cause an error in the ratio determination. This method was investigated and found suitable for the analysis of unirradiated UO_2 . The O/U ratio in an unirradiated LOFT UO_2 fuel pellet was determined by this procedure.

Preliminary coulometric investigations to gain an estimate of the precision attainable in the O/U determination were performed using solutions containing 1 to 10 mg U(VI) in 1M H_2SO_4 . After a pre-reduction at +0.05 V vs. SCE and coulometric reduction of the U(VI) at -0.38 V vs. SCE at a mercury pool cathode, a two-fold excess of ceric sulfate was added, and the solution was allowed to set for ~3 min. The excess Ce(IV) then was titrated by reduction at +0.05 V vs. SCE and the U(VI) in the solution again determined by reduction at -0.38 V vs. SCE. From the results obtained at the various levels of uranium, it appears that

^a R. W. Stromatt and R. E. Connally, "Determination of the Stoichiometry of Uranium Dioxide by Controlled Potential Coulometry", Anal. Chem., 33, (1961) pg 345.

an O/U ratio of greater than 2.05 can be determined to better than 0.2% when the total uranium in the sample aliquot is ~10 mg. The error in the O/U ratio increases as the deviation from stoichiometry becomes smaller because quantities of U(VI) in the sample aliquot smaller than 0.5 mg cannot be determined with high precision (<2%) due to limitations caused by background currents in the coulometry cell.

The LOFT fuel pellet was analyzed after crushing the entire pellet to a fine powder with a Plattner's Diamond mortar and pestle. Approximately 0.6 g of the powdered sample was transferred to a 100-ml volumetric flask containing 20 ml of deoxygenated 85% H_3PO_4 . With a flow of argon over the solution, the flask was swirled occasionally to mix. Not all the sample dissolved before the H_3PO_4 was dehydrated. The flask was cooled, swirled, and heated again. These operations were repeated until all the UO_2 dissolved. Approximately 30 min were required for sample dissolution. After cooling, sufficient deoxygenated 1M H_2SO_4 was added to dilute to 100-ml volume. A gelatinous precipitate formed but redissolved upon mixing. This solution was stored in a well-stoppered volumetric flask under an inert atmosphere and 1 to 2-ml aliquots were taken for the controlled potential determination. Coulometric determinations of U(VI) originally present in the sample aliquots indicated only small differences from the electrolyte blank (5 ml 1M H_2SO_4), indicating that the UO_2 was nearly stoichiometric. After addition of excess Ce(IV), waiting 3 min, and reducing the excess Ce(IV), the total uranium in the sample aliquots was determined. Based upon the analysis of 3 sample aliquots, an O/U ratio of 2.001 was obtained. In the near future, it may be necessary to adapt this procedure to determine the stoichiometry of irradiated PBF fuel pellets. Procedures would have to be developed for remotely crushing and dissolving such samples.

8. Improved ^{237}Np Method

(L. E. Trejo)

The Radio and Special Analysis Group is required to analyze plant process feed solutions for ^{237}Np . In the present method, neptunium is oxidized to Np(VI) and extracted into hexone from an acid-deficient aluminum nitrate salting solution. Uranium and plutonium also were oxidized to the +6 valence state and extracted. A solution of 0.25M FeCl_2 , 0.5M $\text{NH}_2\text{OH}\cdot\text{HCl}$, and 1M HCl is used to strip the Np(VI) from the hexone and reduce it to the +4 valence state. Uranium and plutonium also strip from the hexone; however, U(VI) is not reduced by the reducing strip tractred into thenoyltrifluoroacetone (TTA) xylene while the Pu(III) and U(VI) remain in the strip solution. An aliquot of the TTA-xylene phase is evaporated to dryness on a stainless steel plate and alpha counted for ^{237}Np . The counting plate also is checked by alpha pulse height analysis so the results may be corrected if any alpha emitting particles besides ^{237}Np have extracted into the

TTA-xylene. This method was developed for aluminum fuel matrices and assumed 100% neptunium yield. Recently, poor precision on feed solutions from stainless steel and zirconium fuels resulted in an effort to improve this method.

The main problem was that the procedure contained no provision to determine yield. Neptunium-239 can be used as an internal standard to determine the yield but has a short (2.35 days) half-life. A literature search uncovered a method developed at Los Alamos Scientific Laboratory which uses ^{243}Am which decays to ^{239}Np to obtain a fresh supply of the Np standard. The ^{243}Am is absorbed on a column of Dowex 50-X4, 200-400 mesh resin, and at weekly intervals, the ^{239}Np is oxidized with a few drops of periodic acid and eluted from the column.

For our study, the ^{239}Np solution was standardized and yields determined by gamma-ray spectroscopy using a high resolution Ge(Li) detector computer linked to a dedicated Nova 1200 data reduction system. Initial results obtained using a composite feed solution as a matrix and spiked with the ^{239}Np solution for yield determinations were encouraging. The feed solution used contained a known ^{237}Np value. The solution was spiked with a known amount of ^{237}Np (288 d/s/ml) and analyzed several more times. Results are tabulated below.

Feed Solution

<u>Trial</u>	<u>Results (d/s/ml)</u>	
1	77.7	
2	78.3	$\bar{X} = 80 \text{ d/s/ml}$
3	84.2	

Feed Solution (~80 d/s/ml) Plus ^{237}Np Known (288 d/s/ml)

<u>Trial</u>	<u>Total Results (d/s/ml)</u>	<u>Results Minus ^{237}Np in Feed Soln.</u>
1	381	301
2	359	279 $\bar{X} = 291 \text{ d/s/ml} \pm 16$
3	393	313
4	356	276 (1 σ S.D. of 5.5%)
5	368	288

Further study is required using a more concentrated solution of ^{239}Np which will reduce counting times and also, hopefully, increase the precision of the yield determination. When more concentrated ^{239}Np becomes available in about 3 weeks, the study will be continued.

Another problem encountered in the method is the small build-up of solids on the planchet as the sample is evaporated to dryness. The solids are caused by iron which is introduced into the system by reducing scrub solution and are undesirable for quantitative alpha measurements. More work is planned using different reductants that will contribute less solids.

9. Bulk Fuel and Waste Assay Unit

(J. P. Henscheid)

In the past several months, considerable progress has been made in the calibration of the Bulk Fuel and Waste Assay Unit. This work has been directed in three major areas. First, a neutron source position was required which gave the same net counts for a given amount of uranium whether the uranium was located near the side or center of the sample can. Second, the effect of a high-level gamma source on the detector was tested. Third, a calibration curve for the instrument was prepared.

A position was found for the neutron source in which the count rate was independent of the sample position. This was done by preparing standard curves with the uranium in both the center and side positions of the sample can. The neutron source was moved for each set of curves until a position was found that resulted in the curves merging. The final graph showing just the merged single curve is shown in Figure 5. Each point is the average of 4 counts and one standard deviation is shown on the curve.

To check the effects of a gamma source on the detector, a special source was prepared consisting of irradiated ATR fuel pieces encapsulated in a plexiglass tube with 6-mm of lead shot shielding to reduce the beta field. This source was greater than 50 R/hr gamma at 12.7 mm. The source was placed in front of the detector and 6-mm pieces of lead then were placed between the source and the detector until the gamma-source no longer affected the detector. This test was run with and without the neutron source and also with and without uranium in the sample can. It was found that 32-mm of lead was required to keep the gamma source from affecting the detector. All subsequent tests will be performed with 32-mm of lead in front of the detector. As expected, the sensitivity of the instrument was not decreased very much by the addition of the 32-mm of lead. The results of this test are shown in Table 5. Columns 2 and 3 both show that the addition of 38-mm of lead only decreases the sensitivity by about one-third. This is due more to a change in geometry of the system than to the lead itself. A drop in sensitivity of only one-third should not have too great an adverse effect on the overall performance of the system.

A calibration curve using 20-g increments of ^{235}U (as UO_3) was prepared. For this curve the samples were counted at least twice in each position and then the sample tubes were reversed and counted at least twice more. The sample was scanned and rotated to ensure uniform measurement. The matrix for this curve was sand containing boron. Several months

ago, the curve was prepared using sand saturated with 3.5 g/l boron in water and without any lead shielding in front of the detector. This curve is shown in Figure 6. There is some indication that the slope of the curve was changing slightly with uranium concentration. The cause of this change has not been investigated because this matrix system will not be used. If time permits, a study will be made to try to identify contributing factors. The ranges shown are one standard deviation. The curve was prepared again after the addition of the lead shielding in front of the detector. However, notification was given that instead of using 3.5 g/l borated water, the plant samples are going to be dry. Therefore, the sand was dried before this curve was prepared. This curve is shown in Figure 7. The ranges shown are one standard deviation of the data collected. Comparison of these two curves showing the sensitivity for Figure 7 is actually better than that for Figure 6 and is not decreased by the one-third that would be expected from the addition of the 32-mm of lead shielding. This reversal is due to the removal of the water from the sand matrix. Water is a known moderator for neutrons, and its removal is believed to be the cause of the increase in sensitivity.

TABLE 5

DATA FROM TESTS WITH 50 R γ -SOURCE^a

<u>Amounts of Pb (mm)</u>	<u>Without γ-Source</u>	<u>With γ-Source</u>
0	0.64	
12.7	0.59	163.5
19.05		2.64
25.40	0.47	0.52
31.75		0.48
38.10	0.41	

^a All tests were done with a constant amount of uranium with results in counts/second.

In progress is another test with the gamma source to make sure it will not affect the calibration. A test then will be made to determine if dispersing the 20-g increments of uranium over a larger volume will have any effect on the performance of the system. An early 1977 completion date is anticipated for this project.

Fig. 5 Sand and boron matrix.

Fig. 6 Wet boron sand without lead shield.

Fig. 7 Dry boron sand and 32-mm lead shield.

VIII. ENVIRONMENTAL IODINE SPECIES BEHAVIOR

(J. H. Keller, J. W. Tkachyk, F. A. Hohorst)

The Environmental Iodine Species Behavior program is concerned with the evaluation of, 1) the transport of various iodine species from a source, such as a reactor stack, to a site downwind in the environment, 2) the deposition of these species on vegetation under wet and dry conditions, and, 3) the interconversion of the various species in environment after release from the source. This phase of the effort involves the measurement of the iodine source, Q , including species at the point of release, environmental measurement of the same species in air, the quantity of iodine deposited on vegetation, the quantity of iodine in milk and the various meteorological parameters during the transport.

In order to better understand the chemistry involved, a laboratory study has been undertaken to establish the formation rates, distribution coefficients and lifetimes of the various iodine species under a variety of conditions. The work in this period has been entirely involved with the laboratory studies because of unfavorable weather conditions for field studies. Emphasis has been placed on the study of HOI, the least well-understood of the volatile iodine species.

The generation of HOI was undertaken by adding elemental iodine tagged with ^{131}I to an aqueous solution at a constant pH. This solution was sparged with air to sweep out any volatile species. The initial iodine concentration was varied as was the temperature. At a constant temperature, the lower the initial iodine concentration, the higher the fraction of HOI in the volatile species. The fraction of HOI in the volatile iodine released from the solution also increases with the increasing temperature.

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