337
1/4/78

AB. 1719

ICP-1132

MASTER

TECHNICAL DIVISION QUARTERLY PROGRESS REPORT JULY 1 - SEPTEMBER 30, 1977

CYRIL M. SLANSKY

B. C. MUSGRAVE

B. R. DICKEY

K. L. ROHDE

October 1977

Allied
Chemical

IDAHO CHEMICAL PROGRAMS

IDAHO NATIONAL ENGINEERING LABORATORY

DEPARTMENT OF ENERGY

IDAHO OPERATIONS OFFICE UNDER CONTRACT EY-76-C-07-1540

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161
Price: Printed Copy \$9.00; Microfiche \$3.00

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

ICP-1132

Distributed Under Category:
UC-2
General, Misc., Progress. . .
UC-10
Chemical Separations Proc., Pu . .

TECHNICAL DIVISION QUARTERLY PROGRESS REPORT

JULY 1 - SEPTEMBER 30, 1977

Cyril M. Slansky, Editor

Work performed under the direction of:

B. C. Musgrave, Manager
Technical Division

B. R. Dickey, Assistant Manager
Technical Division

K. L. Rohde, Assistant Manager
Technical Division

Date Published - October 1977

ALLIED CHEMICAL CORPORATION
IDAHO CHEMICAL PROGRAMS - OPERATIONS OFFICE

PREPARED FOR THE
DEPARTMENT OF ENERGY
IDAHO OPERATIONS OFFICE
UNDER CONTRACT EY-76-C-07-1540

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

leg

ABSTRACT

Progress for the third quarter of 1977 is reported on ERDA-budgeted activities contracted to Allied Chemical Corporation at the Idaho National Engineering Laboratory. The work is divided into three categories.

Fuel Cycle Research and Development

Results are presented on the fluidized-bed calcination of simulated radioactive waste from the reprocessing of spent commercial nuclear fuel, on the post treatment of the calcine, and on the removal of actinide elements from the waste prior to calcination. Other programs include the development of storage technology for ^{85}Kr waste; a study of the hydrogen mordenite catalyzed reaction between NO_x and NH_3 ; the adsorption and storage of ^{129}I on silver exchanged mordenite; physical properties, materials of construction, and unit operations studies on the evaporation of high-level waste; the behavior of volatile radio-nuclides during the combustion of HTGR graphite-based fuel; and the use of the uranium-ruthenium system in age-dating uranium ore bodies.

Special Materials Production

The long-term management of defense waste from the ICPP covers post-calcination treatment of ICPP calcined waste; the removal of actinide elements from first-cycle raffinate; the retrieval and handling of calcined waste from ICPP storage vaults; and the preparation of the "Defense Waste Document". Process improvements are reported on the Fluorinel headend process for Zircaloy-clad fuels and on uranium accountability measurements. Other development results cover the process for recovering spent Rover fuel, buried pipeline transfer systems, support to the Waste Management Program, and effluent monitoring methods evaluation and development.

Other Projects Supporting Energy Development

In this category are studies on nuclear materials security; application of a liquid-solid fluidized-bed heat exchanger to the recovery of geothermal heat; inplant reactor source term measurements; burnup methods for fast breeder reactor fuels; absolute thermal fission yield measurements; analytical support to light water breeder reactor development; research on analytical methods; and the behavior of environmental species of iodine.

SUMMARY

FUEL CYCLE RESEARCH AND DEVELOPMENT

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

1. Fluidized-bed Calcination of Commercial Waste

The fluidized-bed calcination of two projected Allied General Nuclear Services (AGNS) high-level liquid waste-intermediate-level liquid waste (HLLW-ILLW) feed compositions -- 1974 steady-state and 1976 steady-state -- containing uranium was demonstrated in 100-h tests in the enclosed, 10-cm-dia calciner. Two additional tests with feeds of increased nitric acid concentration (increased from 4N to 6N) were terminated by clinker formation, possibly due to operating misjudgements. Ruthenium volatility increased with increasing nitric acid concentration.

2. Post-Calcination Treatment of Commercial Waste

A study of the characteristics and limitations of microwave power and a study of the present methods of waste processing are being used as the basis for writing a document on how microwave heating can most likely be used in nuclear waste processing.

3. Study of Bidentate Compounds for Separation of Actinides from Commercial LWR Reprocessing Waste

Additional distribution coefficients for actinides and other key elements between reduced synthetic LWR waste solution and 30% DHDECMP in DIPB have been measured. Distribution coefficients for extraction, scrub and strip contacts for americium between cadmium modified synthetic HAW and 30% DHDECMP in DIPB have been obtained. Distribution coefficients for Cf(III) between 30% DHDECMP in DIPB and various concentrations of nitric acid have been determined. Diluent scoping studies indicate that kerosene mixtures with p-DIPB are slightly better diluents for DHDECMP compared to technical grade DIPB. Further efforts to obtain pure (> 99%) DHDECMP have been made using preparative liquid chromatography.

II. KRYPTON-85 STORAGE DEVELOPMENT

Two reports which evaluate methods of (a) immobilizing krypton-85 in solids and of (b) further immobilizing the solids loaded with krypton-85 have been published. Pressurized cylinder test specimens in a rubidium environment were exposed to gamma radiation at 54 to 185°C for 2½ months. Krypton loadings on sodalite of $\geq 40 \text{ cm}^3$ per g were obtained in the laboratory at 193 MPa (28,000 psi) and 410°C for 24 h or at 193 MPa and 510°C for 2 h. From rates of leakage measured for oven-dried and spray-dried sodalite powder, temperature dependence of diffusion rates identical to that reported in the literature was observed. Using measured leakage

values, maximum net leakage of ^{85}Kr was predicted to be 3% for spray-dried, 0.5% for oven-dried sodalite, and 0.3% for the sodalite reported in the literature. A pilot-scale encapsulation system will be designed, but construction and operation will be delayed. The report, "Technological Assessment of Pilot-Scale System for Encapsulation of Krypton-85 in Zeolite" was published. Measurements of krypton and argon loading on zeolites after up to 370 days at ambient laboratory conditions show no leakage for oven-dried sodalite samples loaded with krypton. Some zeolite A samples showed leakage above experimental error. Zeolite samples loaded with krypton were exposed to gamma radiation for 28 days at temperatures of 52-68°C. No leakage occurred in sodalite; ~ 80 to ~ 95% leakage was found in zeolite A. No structural damage was detected in the zeolite samples.

III. LWR OFF-GAS TREATMENT

The final draft of a report entitled, " NO_x Abatement with Ammonia by Hydrogen Mordenite at Nuclear Reprocessing Plants", has been prepared.

IV. IODINE-129 ADSORBENT AND STORAGE DEVELOPMENT

Tests to determine the effects of water vapor, NO and NO_2 on the elemental-iodine (I_2) loading of silver-exchanged mordenite were completed. The highest iodine loadings were obtained with NO in the gas stream. Using simulated dissolver off-gas streams, loadings of about 170 mg I_2/g adsorbent and a decontamination factor of 10^3 to 10^4 were obtained. This represents about 72% conversion of the silver-to-silver iodide. The data indicate that NO keeps the silver in the metallic state, which has a higher capacity for iodine than the oxide. In the absence of NO, NO_2 appears to slowly oxidize silver-to-silver oxide, and cause lower iodine loadings. This should not present a problem as the primary NO_x species in dissolver off-gases will be NO. Water vapor appeared to have no effect on the iodine loadings.

Recycle tests on a bed of silver-exchanged mordenite, in which the iodine was repeatedly loaded as I_2 and stripped as hydrogen iodide (HI), were completed. The bed was recycled 13 times. The data indicate a 20% loss in the initial iodine-loading capacity would occur after 13 recycles. The loss in loading capacity is believed due to a slow but progressive pore collapse which blocks access to the silver sites.

Tests to determine the iodine loadings of lead-exchanged zeolites, which were used to chemisorb HI during the recycle tests, were completed. Loadings up to 408 mg HI/g substrate were obtained. This represents about 90% use of the lead to form chemisorbed iodine. The iodine-vapor pressures over the substrates were predicted to be 10^{-6} , 10^{-8} and greater than 10^{-16} atm for lead-exchanged mordenite, lead-exchanged faujasite and reduced lead-exchanged faujasite, respectively. All of the above substrates may be suitable for long-term storage of ^{129}I . The topical report covering the information given in this and in the previous quarterly report (ICP-1122) is being prepared.

The iodine adsorbent program will end this quarter. Additional work should be done to:

- (1) Measure the loading capacity of silver-exchanged mordenite for airborne-organic iodides.
- (2) Determine the effects of water vapor, NO and NO₂ on the iodine loadings of silver-exchanged mordenite not pretreated with hydrogen.
- (3) Conduct design verification studies on the regeneration and recycle of silver-exchanged mordenite in pilot plant studies.
- (4) Search for other silver-loaded substrates that might be more suitable for regeneration and recycle than silver-exchanged mordenite.
- (5) Complete the evaluation of recycle life of Ag[°]Z; i.e., measure the complete life cycle of the adsorbent.

V. LIQUID WASTE MANAGEMENT: EVAPORATION AND STORAGE

The small-scale thermosiphon evaporator was operated successfully with a titanium reboiler tube section for the evaporation of both nitric acid and simulated high-level liquid waste (HLLW). The heat transfer coefficient for the titanium reboiler tube with dilute nitric acid was approximately the same as with the Type 304L stainless steel reboiler tube. However, significantly lower heat transfer coefficients were obtained during the evaporation of more concentrated nitric acid and both dilute and concentrated HLLW. The lower heat transfer coefficients are attributed to the buildup of solids on the titanium reboiler tube surface. After 432 hours of operation the titanium reboiler tube had no measurable weight change attributable to corrosion.

The Laboratory Storage Tank was operated with both nitric acid and HLLW. The cooling water coils showed significantly lower heat transfer coefficients for nitric acid and HLLW than for water.

The characteristics of undissolved solids particles in freshly stored HLLW slurries were compared to those of aged slurries and to the scale deposited on the heat transfer surfaces of the small-scale thermosiphon evaporator.

Evaluation of the remote electronic corrosion monitoring techniques continued with a comparison to rates for corrosion coupons in the same solutions.

VI. HTGR FUEL REPROCESSING

1. Laboratory Burner Operation

Five runs were made in the laboratory quartz glass burner with MoO₃ and

RuO_2 added to the bed. These semivolatiles vaporized into the off-gas stream as expected and condensed out on the upper burner surfaces and on the sintered-metal filter in the top of the burner. During the runs, RuO_2 was converted to RuO_4 , which passed through the filter and was recovered in a scrub solution. The amount converted was dependent upon the O_2 concentration in the burner off gas.

2. Laboratory Testing of Semivolatiles Removal Device

The laboratory fluidized-bed condenser was effective in cooling the burner off gas from approximately 770 K to less than 370 K. Tests were performed to determine a means of keeping the distributor plate at approximately the incoming gas temperature to prohibit condensation of the semivolatiles in the holes of the plate. A combination of superheating the gases before they enter the condenser and adjusting the flow to give incipient fluidization just above the distributor has been successful.

VII. NATURAL FISSION REACTOR STUDIES

Analyses were completed on 11 samples from the perimeter of the Oklo natural reactors. Ruthenium analyses showed that ^{99}Ru was enhanced relative to the other Ru fission product nuclides. Earlier work on core samples showed the opposite effect. The proposed explanation is that the ^{99}Ru precursor, ^{99}Tc , leached at a faster rate than the Ru itself.

SPECIAL MATERIALS PRODUCTION

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

1. Post Calcination Treatment of ICPP High-Level Wastes

New glass formulations were prepared and tested for leachability and thermal conductivity. A glass high in silica showed higher leach rates than past compositions. The waste glasses have lower thermal conductivities than most industrial glasses. Experiments on volatility of fluoride during melting of waste glass were begun.

Calcine containing a high percentage of bed particles (0.3 to 0.5 mm diam) resulted in poorly agglomerated pellets. Calcine reduced in size to 0.1 to 0.2 mm by grinding resulted in good quality pellets, but the dried pellets were dusty.

Design criteria for the post-calcination treatment pilot-plant to verify the pelletizing process are being prepared. A mockup of a rotating tray heat treater has been designed and is being fabricated. A microwave heated pellet drying system is also being evaluated for use in the pelletizing process.

Scoping neutron activation analyses were performed to determine required

sample sizes, irradiation times, and detectable radionuclides on both pelleted and glass waste forms as a means to determine elemental content and losses during waste form preparation and leach testing.

Calcine dissolution studies for actinide removal show that approximately 70% of the calcine can be dissolved in 8 M HNO_3 in 30 minutes at 70°C. Dissolution is increased to ~ 80% at 90°C. Addition of HF to HNO_3 reduces total solids dissolution. Two-stage dissolution with HNO_3 or HF gives only a slight increase in total calcine dissolution (from 3 to 10%). Up to 93% of the calcine can be dissolved using near boiling (95°C) HNO_3 .

2. Actinide Removal from ICPP Wastes

A hot minimixer settler actinide extraction experiment was completed using ICPP-produced Zr-Al first cycle raffinate. Twenty percent dihexyl, N-N, diethylcarbarylmethylenephosphonate (DHDECMP) in 2:1 decalin-diisopropylbenzene was used as the extractant. Mercury extraction and its electrolytic removal from DHDECMP was studied. Also, several commercially available solvents were tested as alternate diluents for DHDECMP.

3. Calcined Solids Retrieval and Handling

A detailed program plan for the period FY-77 through FY-83 was completed and issued. Design work is approximately 70% completed for special equipment needed for the calcine bin sampling project. The safety review for the latter will be started by October 1, 1977. Most of the off-the-shelf equipment required for the bin sampling project has been ordered. A set of design bases was written for the cold prototype retrieval equipment and will be issued by Oct. 1, 1977. The existing solids retrieval pilot plant in CPP-620 was upgraded, and standardization tests were completed on the existing nozzle. Calcine simulant comparison tests were completed and indicate that CaCO_3 is a better calcine simulant than MgO for retrieval testing.

4. ICPP Defense Waste Document/Programmatic Environmental Impact Statement

The "Alternatives for Long-Term Management of Defense High-Level Radioactive Waste" (DWD) document was technically edited and revised in format. Comments received from WPR were incorporated as the document was final typed on mats. The DWD was submitted to WPR for final review and publication on August 5, 1977.

ERDA has directed that a Programmatic Environmental Impact Statement (PEIS) be prepared for the several candidate alternatives for the management of defense high-level radioactive waste generated at the ICPP. Preliminary scheduling and cost estimates were completed. A detailed outline has been submitted for review and comment by ERDA-ID and WPR.

II. ICPP PLANT PROCESS IMPROVEMENT

1. Zirconium Fuel Recovery Process

Scoping studies were completed on the operating characteristics of the etched-disc filter system and the horizontal, continuous, decanting centrifuge system. Both systems were tested with simulated solutions from the proposed Fluorinel process flowsheets. The results indicate that either system could be designed to provide adequate removal of solids from the dissolver product.

Design verification studies of the degree of solids agitation in the proposed Fluorinel dissolver bottom design were completed. The results indicate that the proposed design cannot adequately agitate the process solids. Special studies are underway to identify an acceptable design.

2. Corrosion of METGLAS

Corrosion laboratory screening tests of METGLAS of formulation $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ indicate that the material is not suitable for use as a solid nuclear poison at ICPP because it deteriorates in contact with boiling acid solutions used routinely at ICPP.

3. Uranium Accountability Measurements

A comparison has been made of three possible methods for sample cleanup prior to isotope dilution mass spectrometry on uranium accountability samples. A method using the compound triisooctylamine was found to offer significant savings in manipulation time; however, this procedure has not been thoroughly proven for radioactive samples. The method U-Sep-2 (tentative) has been proven in routine use, but requires more time for final acceptance. A conventional column-type anion exchange method also worked well, but has not been proven in high-throughput use and requires more time.

III. ADVANCED GRAPHITE FUELS REPROCESSING

Testing of erosion on the Rover solids transport system jets and elbows has continued. The effect on erosion of the percentage Al_2O_3 in burner ash was determined. Two means of reducing wear on elbows were tested: (a) using capped tees in place of the elbows and (b) increasing the distance from the jet to the elbow. Both were effective in reducing erosion wear in the system.

The erosion tests on the Tribaloy 700 weld overlay on the pilot-plant centrifuge auger were completed. The wear on this coating was similar to the chromium oxide ceramic coating previously tested.

IV. WASTE TRANSFER SYSTEMS

The laboratory tests to evaluate the bonding of coatings on pipes

subjected to 1.5, 3, 5, and 10 volts dc cathodic protection overvoltage have shown some failure of fusion bonded epoxy.

Laboratory corrosion tests using corrosometer probes in ICPP soil have shown an average corrosion rate for mild steel of 3 mpy and no measurable rate for stainless steel during a two month period.

Readings of current requirements on the field lab specimens indicated that the coatings were not being disbonded.

V. ICPP WASTE MANAGEMENT DEVELOPMENT

1. Tank WM-183 Flowsheet Development

Three runs have been made in the 10-cm diameter calciner with a feed blend of two volumes zirconium fluoride waste and one volume tank WM-183 waste (concentrated to 60% of its original volume). None of these runs were completely successful in preventing the buildup of chloride in the scrubbing solution. Some formation of agglomerates on the fuel nozzle occurred in all the runs.

2. Sodium-Bearing Waste Flowsheet Development

The proposed flowsheet for calcining sodium-bearing waste (3 vol zirconium - 1 vol sodium-bearing waste blend using a calcium to fluoride mole ratio of 0.7) resulted in chloride volatility and rough calcine when tested in the WCF. Scoping tests were made in a 10-cm diameter calciner to evaluate alternate flowsheets. Flowsheets consisting of blends of zirconium waste with sodium-bearing waste using calcium nitrate showed the most promise for preventing fluidized-bed particle agglomeration. Differential thermal analyses -- X-ray studies did not show why powdered iron added to commercial waste prevents bed agglomeration during calcination of the waste, but will not prevent agglomeration when added to ICPP sodium-bearing waste.

3. Calciner Feed Flowmeter Testing

A survey is being conducted to find a flowmeter which will perform more reliably and accurately and will have less restriction to feed flow than the EM flowmeters presently used in the WCF. Preliminary tests of a cross-correlation flowmeter were successful.

4. Transport System Moisture Monitor

A moisture analyzer probe installation in the transport air return line at the WCF will be delayed due to a lack of welder radiation exposure time. The monitoring system, which consists of the moisture analyzer probe and a thermocouple on the transport air return line in the calciner cell, will provide data to be used in controlling the moisture content of the solids transport system, thereby reducing the possibility of condensation and subsequent plugging in the line. The thermocouple has been installed in the calciner cell, and the moisture analyzer will be installed at the next available opportunity.

5. Waste Feed Chemistry Studies

The use of magnesium nitrate to suppress fluoride and chloride volatility during calcination of a blend of 3 vol of zirconium and 1 vol sodium-bearing wastes with minimum production of gelatinous solids in calciner feed was evaluated in a 10 cm-diameter calciner. A minimum magnesium to fluoride mole ratio of 0.6 is required to effectively suppress chloride volatility.

6. Alternate Sodium Waste Solidification Process

A preliminary evaluation of alternate sodium-bearing waste solidification processes has been completed. Further pilot-plant development is necessary before any of the alternate processes could be considered for a plant-scale facility at ICPP.

7. Calciner Alternate Startup-Bed Material

Fluorapatite has been shown to produce substantially less metal erosion than dolomite, while showing 2 to 3 times the resistance to particle attrition. A 10-cm diameter calciner run, simulating WCF startup, was successful with a uniform coating of aluminum oxide being applied to the fluorapatite particles.

VI. EFFLUENT MONITORING METHODS EVALUATION AND DEVELOPMENT

The test system has been fabricated and is being installed for the evaluation of the dioctylphthalate method used for testing HEPA filter efficiencies in a corrosive environment. Another project involves the development of a method to chemically separate low-energy emitting radio-nuclides from stack effluents for continuous monitoring. This program was initially funded in FY-77 with major emphasis scheduled for the second half. Therefore, the projects are in the initial stages of testing and development.

OTHER PROJECTS SUPPORTING ENERGY DEVELOPMENT

I. NUCLEAR MATERIALS SECURITY

Significant improvements were made to the data acquisition and display capabilities of the plant safeguards monitoring system. The computer programming requirements for monitoring the process activity in the plant have been completed. Testing of the plant surveillance system included a successful demonstration of remote monitoring and control capabilities using a telephone link between the ICPP and ERDA Headquarters in Germantown. A pilot-plant system is being installed to test the use of a special designed gamma absorbtimeter and transit-time flowmeter for on-line measurement of uranium in flowing streams.

II. LIQUID-FLUIDIZED-BED HEAT EXCHANGER FOR GEOTHERMAL APPLICATIONS

Scale formation on heat transfer surfaces reduces the efficiency of the production of power from hydrothermal resources. Because of the abundance of low temperature resources, binary systems are attractive, but scale buildup must be controlled. Allied Chemical Corporation-Idaho Chemical Programs at the IENL is responsible for the development of dense-phase liquid-fluidized-bed heat exchangers. A 2100-hour scale control test was completed at the East Mesa, California, geothermal site. The outside surfaces remained clear, except for the top of the tubes; the bed-to-tube transfer coefficient decreased about 8%. The overall heat transfer coefficient decreased about 30% during each of two cycles because of fouling on the inside of the tubes by the low quality cooling water. Specifications for the six-stage, liquid-fluidized-bed 60-kW preheater have been prepared. The system will be used in second-phase testing of the Raft River binary-cycle power plant. Both horizontal and vertical heat exchanger shells will be tested. A gas-fluidized-bed industrial dryer will be designed in cooperation with EG&G. The proposed first test is sludge from a potato processing plant secondary waste stream; previous attempts to dry the sludge in a rotary kiln were unsuccessful.

III. INPLANT SOURCE-TERM MEASUREMENT PROGRAM

The inplant source-term measurement program is an NRC-funded program intended to measure the movement of radionuclides through commercial power reactor systems. Plants three and four have been selected for the measurement program. Turkey Point Station will be the next plant studied with Rancho Seco Station to follow. The measurement program at Zion Station has been suspended during repair of the plant's ventilation system.

IV. BURNUP METHODS FOR FAST BREEDER REACTOR FUELS

The analysis of the two ^{241}Am capsules was finished. The data will not be of as high quality from the other capsules, but will be adequate for the programmatic needs. An improved technique for La and Ce analyses has been applied to all the Pu and Np capsules and is being applied to the U capsules. The ANL capsules were received and analyses have begun on them.

V. ABSOLUTE THERMAL FISSION YIELD MEASUREMENTS

Work was initiated on the 14 ATR fuel plate punchings with all the samples dissolved and Kr and Xe analyzed on all of them. Uranium, Nd and Cs analyses are finished on the ^{235}U ETR capsules. Analyses of the ^{239}Pu ETR capsules will start in October.

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

Preliminary data for uranium depletion and fluence analyses on the high priority LWBR fuel segments have been reported to Bettis Atomic Power Laboratory. Schedule commitments for the final report, which will include a complete error analysis for the measurements, should be met. Relatively few problems were encountered, while related development work provided specific procedures for analyses of thorium and manganese in these samples.

VII. RESEARCH ON ANALYTICAL METHODS

1. Evaluation of Ion Chromatography as a Technique for Analysis of Geothermal Effluent Brines

Ion chromatography was evaluated as a technique for the determination of selected anions and cations in geothermal effluents.

2. Gas Chromatographic Determination of Freon 113 in Geothermal Effluent Brines

In support of the geothermal energy research program, a gas chromatographic method was developed for the determination of Freon 113 in geothermal effluent brines. The method uses a Porapak Q column and a hydrogen ionization detector. Calibration of the method is performed using 1,2 dichloroethane as an internal standard.

3. Installation of Electron Spectrometer System

An ESCA/SAM electron spectrometer has been installed in the Spectrochemical Laboratory to be used for nondestructive surface composition analysis. The system can identify all the chemical elements except hydrogen and helium on a surface and distinguish between different oxidation and chemical states.

4. Installation of Automatic Titration System in the Remote Analytical Facility (RAF)

A Mettler automatic titration system was installed in the RAF to facilitate the determination of acidity. This system will make acid titrations in the RAF more precise.

5. The Determination of Manganese in Solutions Used as Neutron Detectors

Recent analytical support to a nuclear physics experiment which uses manganous sulfate solution as a neutron detector has resulted in the adaption of a highly selective potentiometric method to determine manganese in these solutions. The method is based upon the titrimetric oxidation of Mn^{+2} to Mn^{+3} with potassium permanganate in a neutral pyrophosphate medium. This method was applied to the determination of manganese in a solution used in similar nuclear physics experiments performed in England. Results

were about 1% lower than their nonselective gravimetric method. This difference was accounted for in a determination of solution impurities by atomic absorption and spark source mass spectrometry.

6. Induction-Coupled Plasma Source

The application of the induction-coupled plasma to elemental solution analysis is being investigated. Calibration curves and detection limits have been obtained for several elements.

7. Determination of Sulfate in Synthetic Waste Calcination Feed Solutions by Ion Chromatography

Sulfate was determined by ion chromatography in synthetic second cycle waste feed solutions. A precision and accuracy study was performed using a control which simulated the feed solutions. Based on six determinations of sulfate in this control, a relative standard deviation of 0.6% and a positive bias of 3.8% can be expected for the synthetic feed solutions.

8. Analysis of Solid Samples for Fluoride by Fluoride Specific Ion Electrode

A new method is being developed for the analysis of fluoride in solid samples. The method will eliminate a recently observed interference with the present method and will be faster when analyzing more than two samples.

9. The Determination of Uranium by REDOX Titrimetry

A precise and selective potentiometric method previously developed to determine 5-25 mg of uranium in the titration volume has been improved by using a temperature controlled bath to eliminate the adverse effects of temperature sensitive reactions. In addition, the HP 9830 titrator control programs have been modified to give reliable automatic titrations even when the electrode potentials are not reproducible.

10. Dissolution of Stainless Steel Containing Chromium Boride

A stainless steel sample containing chromium boride (CrB) was dissolved using a sequential dissolution. Aqua regia was used to dissolve the stainless steel and then sulfuric was used to dissolve the CrB. The described procedure gave total dissolution with minimum problems associated with the formation of insoluble sulfates.

11. Investigation of Ion Chromatography for Determination of Dibutylphosphate

An ion chromatography study of the determination of DBP in uranium processing streams was performed. Promising results were obtained for this determination by stripping the DBP from the TBP-kerosene mixtures with a sodium phenate solution before injection onto the chromatograph. Results obtained thus far for eight determinations at the 20 ppm and

50 ppm levels indicated an insignificant bias at the 95% confidence interval and standard deviations of 2.69 and 2.38%, respectively. Additional work is planned to complete the development of a method suitable for routine use.

12. Mass Spectrometric Analysis of Thorium

A tentative procedure has been developed for thermal ionization mass spectrometric analysis of thorium. The performance of the method depends upon extremely precise control of the filament heating time and temperature, and on the timing of the data collection. Additional development would be required to obtain a totally routine method.

VIII. ENVIRONMENTAL IODINE SPECIES BEHAVIOR

The environmental iodine species behavior program is intended to measure the release of radionuclides, primarily radioiodine, from nuclear facilities and to determine their behavior in the environment. Field measurements at the Quad Cities Nuclear Power Station have been initiated. Several sampling systems for different nuclides have been established at two sites, and iodine measurements are being made at three additional sites.

CONTENTS

ABSTRACT	i
SUMMARY	ii
RESULTS - FUEL CYCLE RESEARCH AND DEVELOPMENT	1
I. FLUIDIZED-BED CALCINATION AND POST-TREATMENT OF COMMERCIAL WASTES.	1
1. AGNS Waste Calcination Studies.	1
1.1 Flowsheet Development Studies.	1
2. Post-Calcination of Commercial Waste.	3
2.1 Feasibility of Applying Microwave Power to Solidifying High-level Nuclear Wastes.	3
3. Study of Bidentate Compounds for Separation of Actinides From Commercial LWR Reprocessing Waste.	4
3.1 Synthetic LWR Waste.	4
3.2 Cadmium Modified Synthetic HAW.	4
3.3 Diluent Scoping Studies.	6
3.4 Preparation of Pure DHDECMP.	7
3.5 Extraction Studies	7
II. KRYPTON-85 STORAGE DEVELOPMENT.	11
1. Storage Alternatives.	11
2. Pressurized Cylinder Storage.	14
2.1 Rubidium Corrosion	14
3. Zeolite Encapsulation Storage	14
3.1 Laboratory-Scale	14
3.2 Pilot-Scale.	17
4. Long-Term Testing of Krypton-85 Storage Media	18
III. LWR OFF-GAS TREATMENT	22
IV. ¹²⁹ I ADSORBENT AND STORAGE DEVELOPMENT.	22
V. LIQUID WASTE MANAGEMENT: EVAPORATION AND STORAGE	29
1. Evaporation	30

1.1	Operating Characteristics of Evaporator.	31
1.2	Heat Transfer of Evaporator.	31
1.21	Rate	32
1.22	Scaling and Fouling.	32
2.	Waste Storage	36
2.1	Laboratory Storage Tank.	36
2.11	Heat Transfer.	36
2.12	Physical Mixing of Stored Slurries	38
2.2	Storage of Evaporated HLLW	38
2.21	Stability of Stored HLLW Slurries.	38
2.22	Characteristics of the Undissolved Solids in Stored HLLW Slurries.	40
2.23	Comparison of Precipitates and Evaporator Scale.	40
2.3	Design of Small-scale Storage Tank	43
3.	Materials and Corrosion	43
3.1	Monitoring Storage Tanks	43
3.2	Reboiler Tube Evaluation	43
3.3	Laboratory Corrosion Tests	44
VI.	HTGR FUEL REPROCESSING.	47
1.	Deposition and Plate-out Testing.	47
2.	Condensation and Removal of Volatile HTGR Fission Products.	51
VII.	NATURAL FISSION REACTOR STUDIES	54
	<u>RESULTS - SPECIAL MATERIALS PRODUCTION.</u>	55
I.	LONG-TERM MANAGEMENT OF ICPP HIGH-LEVEL WASTES.	55
1.	Post Calcination Treatment of ICPP Wastes	55
1.1	ICPP Waste Vitrification	55
1.2	Pelleted Waste Form Development.	57
1.3	Pelletizing Pilot-Plant Development.	58
1.4	Determination of Pelleted and Glass Waste Form Properties	59
1.5	Calcine Dissolution Study.	59
2.	Actinide Removal From ICPP Wastes	62

2.1	Minimixer Settler Experiment.	62
2.2	Radiolysis of DHDECMP	63
2.3	Mecury Extraction Studies	63
2.4	Diluent Studies	64
2.5	DHDECMP Purification.	64
2.6	Engineering Studies	64
3.	Calcined Solids Retrieval and Handling	64
3.1	Program Management.	64
3.2	Retrieval Nozzle Development.	65
3.3	Bin Sampling.	65
3.4	Cold Prototype Retrieval Equipment.	67
4.	ICPP Defense Waste Document/Programmatic EIS	67
II.	ICPP PLANT PROCESS IMPROVEMENT	69
1.	Zirconium Fuel Recovery Process.	69
1.1	Solids Characterization	69
1.2	Pilot Plant Filter System	69
1.3	Pilot Plant Centrifuge.	72
1.4	Fluorinel Dissolver Bottom Mockup	80
2.	Corrosion of METGLAS	86
3.	Uranium Accountability Measurements - Comparison of Separation Methods for Uranium IDMS.	87
III.	ADVANCED GRAPHITE FUELS REPROCESSING	92
1.	Solids Transport Systems Testing	92
1.1	Performance Tests with Model 23A Ejector.	92
1.2	Erosion by Simulated Primary Burner Ash	93
1.3	Erosion in Capped Tee	93
1.4	Erosion as a Function of Distance From the First Elbow	98
2.	Erosion of Tribaloy 700 in the Rover Pilot Plant Centrifuge	99
3.	Rover Process Support Dissolver.	101
IV.	WASTE TRANSFER SYSTEMS	104
1.	Laboratory Disbonding Tests.	104
2.	Laboratory Corrosion Testing	105
3.	Field Test	105

V.	ICPP WASTE MANAGEMENT DEVELOPMENT.	106
1.	Tank WM-183 Flowsheet Development.	106
2.	Sodium-Bearing Waste Flowsheet Development	106
3.	Calclner Feed Flowmeter Testing.	108
4.	Transport System Moisture Monitoring	108
5.	Waste Feed Chemistry Studies	109
6.	Alternate Sodium Waste Solidification Process.	109
7.	Alternate Calclner Startup Bed Material.	111
VI.	EFFLUENT MONITORING METHODS EVALUATION AND DEVELOPMENT . .	112
1.	Evaluate In-Place Test Methods for Determining HEPA Filter Efficiencies.	112
2.	Methods Evaluation for Monitoring of Radionuclides with Low-Energy Emissions	112
	RESULTS - OTHER PROJECTS SUPPORTING ENERGY DEVELOPMENT	114
I.	NUCLEAR MATERIALS SECURITY	114
1.	Development of Monitoring Systems for Chemical Plants	114
1.1	In-Plant Monitoring System Demonstration.	114
1.2	Computer Programming Requirements for Plant Monitoring	115
2.	In-line Density Measurement.	118
3.	Transit Time Flowmeter	118
II.	LIQUID-FLUIDIZED-BED HEAT EXCHANGER FOR GEOTHERMAL APPLICATIONS	119
1.	Scale Control Test	119
2.	60-kW Preheater.	122
3.	Fluidized-bed Dryer.	122
III.	INPLANT SOURCE TERM MEASUREMENTS	123
IV.	BURNUP METHODS FOR FAST BREEDER REACTOR FUELS.	123
V.	ABSOLUTE THERMAL FISSION YIELD MEASUREMENTS.	124

VI. LIGHT WATER BREEDER REACTOR (LWBR) - ANALYTICAL SUPPORT. .	125
VII. RESEARCH ON ANALYTICAL METHODS	125
1. Evaluation of Ion Chromatography as a Technique for Analysis of Geothermal Effluent Brines	126
1.1 Anion Analysis.	126
1.2 Cation Analysis	129
2. Gas Chromatographic Determination of Freon 113 in Geothermal Effluent Brines.	130
3. Installation of Electron Spectrometer System	134
4. Installation of Automatic Titration System in the Remote Analytical Facility	134
5. The Determination Manganese in Solutions Used as Neutron Detectors.	136
6. Induction - Coupled Plasma Source	137
7. Determination of Sulfate in Synthetic Waste Calcination Feed Solutions by Ion Chromatography	138
8. Analysis of Solid Samples for Fluoride by Fluoride Specific Ion Electrode	141
9. The Determination of Uranium by Redox Titrimetry . . .	143
10. Dissolution of Stainless Steel Containing CrB.	144
11. Investigation of Ion Chromatography for Determination of Dibutylphosphoric Acid.	146
12. Mass Spectrometric Analysis of Thorium	149
VIII. ENVIRONMENTAL IODINE SPECIES BEHAVIOR	149

FIGURES AND TABLES (by Section)

FUEL CYCLE RESEARCH AND DEVELOPMENT

Figures

1. Percent purity of DHDECMP obtained vs preparative liquid Chromatography.	10
2. Maximum temperature produced in a 23-cm horizontal cylinder in air at 27°C as a function of krypton loading, 0 to 125 cm ³ Kr/cm ³ solid	12

3. Maximum temperature produced in a 23-cm horizontal cylinder in air at 27°C as a function of krypton loading, 100 to 1000 cm ³ Kr/cm ³ solid	12
4. Radiation absorbed at the center of a polymer matrix and at the outside surface of the stainless steel cylinder (130 cm length, 0.5 cm wall thickness, and 11 cm inside radius) containing 78 TBq·L ⁻¹ ⁸⁵ Kr Loaded on zeolite . . .	14
5. Radiation absorbed at the center of a cement matrix and at the outside surface of the stainless steel cylinder (130 cm length, 0.5 cm wall thickness, and 11 cm inside radius containing 82 TBq·L ⁻¹ ⁸⁵ Kr loaded on zeolite. . . .	15
6. Radiation absorbed at the outside surface of a porous stainless steel cylinder (130 cm long, 0.5 cm wall thickness, and 11 cm radius) containing 85 TBq·L ⁻¹ ⁸⁵ Kr loaded on zeolite.	16
7. Krypton loading on leached sodalite at 410° and 510°C, 124 MPa (18000 psi), MPa (23000 psi), and 193 MPa (28000 psi), as a function of encapsulation time	16
8. Iodine loadings in the saturation zone of Ag ^o Z vs gas stream composition	24
9. Iodine loadings of recycled Ag ^o Z	26
10. Iodine desorbed vs regeneration cycle of AgIZ	27
11. Heat transfer for a titanium reboiler tube in nitric acid	33
12. Heat transfer for a titanium reboiler tube in HLLW	34
13. Solids on feed end of reboiler tube	35
14. Solids on top end of reboiler tube	35
15. Scale on feed end of reboiler tube	37
16. Scale on tube sheet of reboiler tube	37
17. Heat transfer coefficients for cooling of the laboratory storage tank	39
18. Precipitate from freshly stored HLLW (scanning electron microscope at 5000X magnification)	41
19. Precipitate from HLLW after two months storage (scanning electron microscope at 5000X magnification).	41
20. Rinsed precipitate from HLLW after five months storage (scanning electron microscope at 5000X magnification) . .	42

21. Scale deposited on Type 304L stainless steel reboiler tube during evaporation of HLLW (scanning electron microscope at 5000X magnification).	42
22. Schematic diagram of the fluidized-bed burner apparatus . . .	48
23. In-bed filter deposits (deposition on sintered stainless steel filter following five fluidized bed burner runs with MoO_2 and RuO_2 added is shown).	51
24. Fluidized-bed burner deposits (deposition on the quartz fluidized-bed burner after five runs with MoO_3 and RuO_2 added is shown)	52
25. Bed-above-bed quenching apparatus (lower insulated section is stainless steel)	53

Tables

1. Calcining tests summary	2
2. Distribution coefficients for key elements from reduced synthetic LWR waste solution.	5
3. Extraction, scrub and strip distribution coefficients for Am and Pu from reduced synthetic LWR waste solution	6
4. Distribution data for Cd modified HAW	6
5. Solvent effect studies of americium distribution between 30% DHDECMP and synthetic HAW	8
6. Distribution coefficient for Cf(III) between 30% DHDECMP in DIPB and nitric acid.	9
7. Measured E and D_0 , and calculated maximum net leakage for krypton diffusion in sodalite	17
8. Krypton and argon loading on zeolite stored at ambient laboratory conditions	19
9. Krypton and argon loadings on zeolite after gamma-exposure	20
10. Iodine loading and distribution vs contaminant gases. . . .	22
11. Iodine loadings in saturation and mass-transfer zones vs contaminant gases	23
12. Iodine loading on $\text{Ag}^{\circ}\text{Z}$ vs number of recycles	26
13. Hydrogen iodide loadings on lead-exchanged zeolites in dry hydrogen at 150°C	27

14. Iodine vapor pressure data for chemisorbed iodine on lead-exchanged zeolites	28
15. Corrosion rates for Type 304L stainless steel at 60°C . . .	44
16. Operating conditions for the fluidized - bed burner runs . .	50

RESULTS - SPECIAL MATERIALS PRODUCTION

Figures

1. Thermal conductivity of two waste glasses from 300 to 500 K Temperature range	56
2. Retrieval nozzle used for standardization tests	66
3. Etched-disc filter loop schematic.	72
4. Etched-disc filter solids loading at 51.5 L/min·m ²	74
5. Etched-disc filter solids loading at 103.0 L/min·m ²	75
6. Etched-disc filter solids loading at 128.8 L/min·m ²	76
7. Backflush waste system design.	77
8. Dissolver bottom mockup schematic	81
9. Sparge tube exit velocity vs nitrogen pressure	82
10. Performance of original 1/5 scale mockup (280 g ZrO ₂ solids)	83
11. Effect of increased sparge tube volume at constant velocity	84
12. Effect of increased solids loading at constant velocity and volume	85
13. Extraction of uranium from hydrochloric acid onto anion exchange resin	90
14. Extraction of uranium from hydrochloric acid into triisooctylamine, TIOA, (%5 in Xylene), Reference	91
15. Rover solids transport test apparatus	94
16. Erosion of elbows.	96
17. Amount of erosion on capped tee during 84 H Test (all measurements in micrometers. N = Negligible).	97
18. Schematic diagram of centrifuge bowl section	100

Tables

1. Composition of glass frits	57
2. Calcine dissolution in nitric and hydrofluoric acid . . .	60
3. X-ray analysis of undissolved solids	62
4. Thermogravimetric analysis of typical fluorinel process solids	70
5. Solids recovery vs backflush pressure.	71
6. Centrifuge solids removal efficiency	78
7. Centrifuge discharged solids appearance	79
8. Corrosion tests of Metglas	87
9. Comparison of methods for sample preparation	88
10. Comparison of performance of Model 23A and Model 63A . . .	92
11. Results of erosion tests on Rover process elbows	95
12. Erosion measurements on the centrifuge auger	102
13. ICPP sodium waste composition	110
14. ⁹⁹ Tc content of ICPP stack gas	113

RESULTS - OTHER PROJECTS SUPPORTING ENERGY DEVELOPMENT

Figures

1. Bed side and overall heat transfer coefficient during 80 days of the east mesa scale control test	121
2. Ion chromatogram of anions in geothermal water. Recorder sensitivity: 10 $\mu\text{mho F}^-$, 3 $\mu\text{mho Br}^-$ and NO_3^- , 30 $\mu\text{mho SO}_4^-$. . .	128
3. Ion chromatogram of cations in geothermal water. Recorder sensitivity 3 $\mu\text{mho Li}^+$ and Na^+ , 1 $\mu\text{mho NH}_4^+$ and K^+ . . .	131
4. Chromatogram of Freon 113 determination sensitivity: 1×10^{-12} ampere full scale	135
5. Aluminum calibration curve	139
6. Digestion apparatus	145

Tables

1. Operating conditions during the scale control test at East Mesa.	120
2. Anion and cation determinations in geothermal effluent brines.	127
3. Bias and precision data for the determination of ions in geothermal effluent brines	129
4. ICP detection limits in 0.05N HNO ₃ solutions.	138
5. Analysis of fluoride-containing solids by modified procedure	142
6. Comparison of potentiometric to volumetric procedures for analysis of fluoride in solid calcined sample	143

RESULTS

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 (J. H. Valentine, G. G. Simpson, R. E. Schindler)

Four calcining tests have been made in the enclosed 10-cm-dia calciner since the last reporting period. The runs were scheduled for 100 hours; approximately 0.25 m³ of simulated waste was calcined during each run. The calciner operated at 775 K with in-bed combustion. The purposes of the runs were to demonstrate the calcinability of projected AGNS HLLW-ILLW compositions and to measure the volatility of ruthenium over a range of acid concentrations.

The feed characteristics and available results of the four tests plus those of previously reported Run EM-1 are summarized in Table I. The feeds for the first three tests were simulated 1974 projected AGNS HLLW-ILLW with varying acid concentrations. The feeds for Runs EM-4 and -5 were simulations of the two 1976 projected HLLW-ILLW compositions which (compared to the 1974 projection) contain an increased (by a factor of 2 or 3) gadolinium concentration and a reduced phosphate concentration. Except for Run EM-1, the feeds contained uranium. The 1974 projected feeds were difficult to feed because of a high concentration of undissolved solids containing iron molybdates and zirconates and barium phosphate. The 1976 projected feeds were easier to handle, because the reduced fission-product and phosphate concentrations results in lower concentrations of undissolved solids.

The three feeds with the moderate -- about 4 N -- acid concentrations were calcined successfully. However, both of the feeds with the high acid concentrations -- about 6 N -- produced clinkers which forced shutdowns. The shutdown in Run EM-5 may have been caused by operating errors -- insufficient nozzle-air and fluidizing-air flows.

The ruthenium volatilities measured during the tests ranged from <0.01% to 0.14%. The ruthenium volatility appears to increase with increasing acid or nitrate concentration: the highest ruthenium volatility was measured with feed with the highest acidity (6 N); and all the measured ruthenium volatilities were higher than those -- 10^{-3} to $10^{-2}\%$ -- observed earlier in tests with low-acid feed -- about 1 N -- in the 7.5-cm-dia calciner.

Plans for Next Quarter

Another test will be made with the 1976 projected steady-state feed composition. A summary report covering all development work on calcining commercial reprocessing wastes will be issued.

TABLE 1
CALCINING TESTS SUMMARY

Run	1	2	3	4	5
Feed Flowsheet	Steady-state HLLW-ILLW (1974)	Steady-state HLLW-ILLW (1974)	Steady-state HLLW-ILLW (1974)	Early-op HLLW-ILLW (1976)	Steady-state HLLW-ILLW (1976)
Feed Conc. (m ³ /MTU)	0.8	0.57	0.57	0.62	0.79
Acidity, N	3.9	3.8	5.8	4(est)	6 (est)
U conc., kg/m ³	0	18.7	22.5	35 (est)	31 (est)
Duration, h	104	93	74	100	79
Product:fines ratio	*	*	*	3	5
Attrition index	37	41	32	---	---
Bed mmpd, mm	0.42	0.50	0.50	---	---
Ru volatility, %	< 0.01	< 0.08	0.14	< 0.03	---
Comments	---	---	Clinkers	---	Uncontrolled particle growth, clinkers

*Accurate data not available due to cyclone plugging

2. Post-Calcination Treatment of Commercial Wastes

2.1 Feasibility of Application of Microwave Power to Solidifying High-Level Nuclear Wastes (T. Piper)

Microwave heating may have unique capabilities in the treatment of high-level wastes. A study of microwave applicator techniques, electromagnetic wave propagation and standing wave modes, and microwave power sources available was made to evaluate possible applications to waste treatment processes. The study showed the multi-mode applicators are generally used unless the product has very long length (such as yarn or paper) or some other unique property requiring a special applicator design. Multimode applicators can be designed to permit continuous product entry and exit without microwave leakage. Microwave power sources are available as relatively efficient (75%) magnetrons to 6 kW microwave output at 2450 MHz and as less efficient (60%) klystrons to 50 kW microwave output. Klystrons are really amplifiers rather than oscillators and thus can be "ganged" together for even more than 50 kW of microwave power.

The present methods under study for solidifying nuclear waste are fluid-bed, spray, and rotary kiln calcination. Joule heated glass melters and wiped film evaporators are also possible solidification processes. Conventional resistive heating for in-can glass melting is of course also being developed.

The areas considered applicable for microwave heating are being documented in a report, a draft of which has been completed for internal review. Following is a summary of potential applications and restrictions in the use of microwave heating for nuclear wastes.

- (1) Microwave offers no advantage in evaporation of liquid wastes, because of its lower energy efficiency compared to conventional means.
- (2) Although microwave heating may be used to calcine waste, it likely will not give improved product characteristics over fluidized bed or spray calcining.
- (3) Microwave heating appears advantageous for drying or heating a pelleted waste, because its uniform heating characteristics prevent large temperature gradients within the pellet.
- (4) Microwaves are possibly competitive with a Joule heated glass melter in that electrode consumption is eliminated and melter start-up is no problem.

Plans for Next Quarter

Laboratory-scale experiments on microwave heating to solidify and melt wastes are planned.

3. Study of Bidentate Compounds for Separation of Actinides From Commercial LWR Reprocessing Waste

(L. D. McIsaac, J. D. Baker, J. F. Krupa, N. C. Schroeder)

3.1 Synthetic LWR Waste

Additional distribution coefficients for actinides and other elements between reduced synthetic commercial LWR waste solution and 30% dihexyl-N,N-diethylcarbamylnmethylenephosphonate (DHDECMP) in diisopropylbenzene (DIPB) have been measured. These data are shown in Table 2 which is a composite of newly obtained data and values reported in the previous quarterly progress report. Experimental procedures for the reduced system ($0.01M \text{ Fe (SO}_3\text{NH}_2)_2 - 0.02M \text{ HSO}_3\text{NH}_2$) were the same as in that report. For comparison, values obtained using $0.1M \text{ NaNO}_2$ are listed in the far right hand column. Previous work¹ on oxidized synthetic LWR waste solution ($0.1M \text{ NaNO}_2$) showed that groups or families of elements such as the alkali metals, alkaline earths or lanthanides showed similar trends in their distribution coefficients. For this reason, only representative elements from these various groups are included in Table 2. In addition, other key elements from the actinides and transition elements are included in Table 2. As expected, those elements whose oxidation states do not change between the two systems give similar distribution coefficients. Slight differences that do occur are probably due to media effects or weak complexing by sulfamate anion. For elements such as neptunium and plutonium, whose oxidation states change between systems, there is a marked difference in their distribution coefficients.

After extraction from reduced synthetic LWR waste solution, americium and plutonium were subjected to two 1/5-volume scrubs with $3.0M \text{ HNO}_3 - 0.05M$ oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) followed by three strips with $0.05M \text{ HNO}_3 - 0.05M$ hydroxylamine nitrate (HAN) and a final strip of $0.05M \text{ HNO}_3 - 0.05M \text{ H}_2\text{C}_2\text{O}_4$. The distribution data in Table 3 show that americium and plutonium, once extracted from reduced waste solution, behave similarly to the oxidized system reported in the previous quarterly.

3.2 Cadmium Modified Synthetic HAW

The possibility of adding a neutron poison such as cadmium nitrate to HAW to prevent criticality problems during uranium reprocessing steps has been suggested.² To see what effect this modified HAW would have on actinide removal, the distribution coefficients for extraction, scrub and strip were measured for americium.

Synthetic HAW with contents reported earlier³ but made to $3.5M \text{ HNO}_3$

¹C. M. Slansky, Ed., et al., Alternative Fuel Cycle Technology Progress Report for April 1 - June 30, 1977, ICP-1122, July 1977.

²D. W. Tedder, Oak Ridge National Laboratory, Oak Ridge, TN, personal communication, September 1977.

³C. M. Slansky, et al., Technical Division Quarterly Progress Report for October 1 - December 31, 1976, ICP-1111, March 1977.

TABLE 2**DISTRIBUTION COEFFICIENTS FOR KEY ELEMENTS FROM REDUCED
SYNTHETIC LWR WASTE SOLUTION**

<u>Element</u>	<u>Distribution Coefficient</u>	
	<u>0.01M $\text{Fe}(\text{SO}_3\text{NH}_2)_2$-0.02M HSO_3NH_2</u>	<u>0.1M NaNO_2</u>
Np	98	2.2
Am	4.2	4.3
U	50	51
Pu	20	304
Ce	5.8	5.8
Eu	2.9	2.9
Mo	0.37	0.39
Nb	1.6	0.51
Tc	2.2	2.3
Zr	2.0	1.8
Pd	0.54	0.53
Ru	0.40	0.27
Ba	0.011	0.013
Cs	0.0004	0.0005
Rh	0.05	0.018
Sb	0.015	0.036

TABLE 3

EXTRACTION, SCRUB AND STRIP DISTRIBUTION COEFFICIENTS FOR Am
AND Pu FROM REDUCED SYNTHETIC LWR WASTE SOLUTION

	Extraction	Scrub		Strip			
		1	2	1	2	3	4
D_{Pu}	20	134	26	0.54	0.04	0.18	0.05
D_{Am}	4.3	4.3	5.3	0.71	0.12	0.10	0.13

and 0.156M $Cd(NO_3)_2$ was tagged with ^{241}Am and extracted with 30% DHDECMP in DIPB. The extractant was the same used in earlier distribution studies. One scrub was made with 1/5-volume of 3.5M HNO_3 -0.05M $H_2C_2O_4$ and the organic, then stripped with three successive equal volume portions of 0.05M HNO_3 -0.05M HAN. The results are given in Table 4. All runs were made in duplicate. All contacts were made at 23°C for 5 minutes.

The extraction distribution observed for ^{241}Am is considerably higher than with synthetic HAW at 2.9M HNO_3 where $D_{Am} = 4.3$ was observed. Higher acidity and salting due to $Cd(NO_3)_2$ is responsible for the increase. Stripping is less efficient due to increased initial acidity in the organic phase.

TABLE 4

DISTRIBUTION DATA FOR Cd MODIFIED HAW

		Extraction	Scrub	Strip		
				1	2	3
D_{Am}	Run 1	6.4	6.4	0.81	0.14	0.17
	Run 2	6.3	6.7	0.84	0.14	0.20

3.3 Diluent Scoping Study

The effect of solvent used to dilute DHDECMP has been shown earlier^{4,5}

⁴L. D. McIsaac, J. D. Baker, and J. W. Tkachyk, Actinide Removal from ICPP Waste, ICP-1080, August 1975.

⁵C. M. Slansky, et al., Waste Management Development Technology Progress Report for July - September 1976 ICP-1106, November 1976.

to strongly influence the distribution of americium from acidic nuclear waste generated at the Idaho Chemical Processing Plant. Straight chain aliphatic diluents were shown to produce a second organic phase from nitric acid solutions (i.e., 1.5M HNO_3). Decalin was marginally useful but also produced a second phase when used with 6M HNO_3 .

We are conducting a diluent scoping study for the use of DHDECMP in synthetic HAW. All measurements are being made with the same batch of DHDECMP (~90% pure) and synthetic HAW tagged with americium. The data obtained to date are shown in Table 5. When compared with technical grade DIPB (50% meta, 40% para, 10% ortho), only kerosene mixtures with p-DIPB are significantly better diluents. Preliminary results with decalin mixed with p-DIPB indicate increased americium distribution but coalescence appears to be slow.

3.4 Preparation of Pure DHDECMP

Preparative liquid chromatography is being used to obtain pure DHDECMP. The liquid chromatograph is a Jobin Yvon "Chromatospac-Prep 100" which uses a gas driven piston to vertically compact the column packing material. Parameters that have to be established for this system are column size, flow rates, loading, vertical column packing pressure, solvent strength and type of column packing. Presently, 800 grams of Silica Gel (Merck H-60, 10-40 μm particle size) are being used for the column packing. A slurry of this packing in 1% methanol in dichloromethane is vertically compressed to 6.7 atmospheres, resulting in a column approximately 7.5 cm in diameter and 40 cm in length. Preparative runs, using loadings of up to 40 mL of various purities of DHDECMP, have been attempted on this column. Eluent for these runs was 1% methanol in dichloromethane with flow rates of approximately 70 mL per minute.

Figure 1 shows the percent purity of DHDECMP obtained versus fractions collected when a loading of 40 mL of 62% pure DHDECMP was added to the column. The majority of DHDECMP comes off the column between fractions 15 and 20. The highest purity obtained in this run was 99% at fraction 19. Major impurities are also identified in Figure 1. The dihexyl-hexylphosphonate, dihexylmethylphosphonate and the ester interfere with the leading edge of the DHDECMP peak. An unidentified compound starting at about fraction 21 interferes with the tailing DHDECMP peak. The octyl homologue is not a serious impurity since it is considered just as useful as DHDECMP for actinide partitioning.

Methods to improve this separation include increasing the column length, varying the methanol concentration in dichloromethane and starting with purer DHDECMP.

3.5 Extraction Studies

Distribution coefficients for Cf(III) between 30% DHDECMP (88% pure) and various concentrations of nitric acid have been determined. This data is shown Table 6. Purified californium tracer⁶ was taken to incipient

⁶Moore, Fletcher L., New Extraction Chromatographic Method for Rapid Separation of Americium from Other Transuranium Elements, Anal. Chem., 40, No. 14, p. 2130, December 1968.

TABLE 5

SOLVENT EFFECT STUDIES OF AMERICIUM DISTRIBUTION BETWEEN
30% DHDECMP AND SYNTHETIC HAW

<u>Solvent</u>	<u>D_{Am}^a</u>
Tech. Diisopropyl Benzene	4.4
p-Diisopropyl Benzene	4.7
Ter-Butyl Benzene	4.1
n-Amyl Benzene	4.6
1 part Kerosene-1 part p-Diisopropyl Benzene	b
1 part Kerosene-2 parts p-Diisopropyl Benzene	6.6
1 part Kerosene-3 parts p-Diisopropyl Benzene	5.5
1 part Kerosene-4 parts p-Diisopropyl Benzene	5.4
AMSCO F65 ^c	4.5
Isopropyl Cyclohexane	b
n-Propyl Cyclohexane	b
Ter-Butyl Cyclohexane	b
n-Butyl Cyclohexane	b
n-Amyl Cyclohexane	b

^a All values have an uncertainty of $\pm 10\%$.

^b Second organic phase formed.

^c Product of Union Oil Company.

dryness in concentrated nitric acid. It was taken up with the particular nitric acid concentration being studied and allowed to stand 1 hour. After this period, 1:1 extractions were performed in the manner described in previous reports. Aqueous and organic phases were counted by liquid scintillation spectroscopy.

TABLE 6
DISTRIBUTION COEFFICIENT FOR Cf(III) BETWEEN 30% DHDECMP
IN DIPB AND NITRIC ACID

<u>M</u> HNO ₃	0.1	0.5	1.0	3.0	6.0
D _{Cf}	0.024	0.23	0.62	3.0	6.0

Plans for Next Quarter

Preparative liquid chromatography will be used to produce pure (>99%) DHDECMP. This will be used to determine various physical and chemical properties of the compound. In addition, definitive distribution coefficients for key elements in synthetic LWR waste solution will be determined. Investigations into diluents for DHDECMP will be continued. Efforts will be continued to define extraction, scrubbing, and stripping parts of an actinide partitioning flowsheet for both oxidized and reduced HAW.

ACC-B-2830

Figure 1. Percent Purity of DHDECMP Obtained vs Preparative Liquid Chromatography

II. KRYPTON-85 STORAGE DEVELOPMENT

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

1. Storage Alternatives

Reports have been published which evaluate methods of immobilizing krypton-85 in solids⁷ and of further immobilizing the solids loaded with krypton-85 to prevent dispersal during handling and storage.⁸ A paper based on ICP-1125⁷ was accepted for presentation at the winter ANS meeting.

Three methods of immobilizing krypton-85 in solids were evaluated: (a) high temperature/pressure sorption in zeolites, glass, metal, and other solids, (b) ion implantation/sputtering in solids, and (c) low temperature metal vapor deposition. Method (a) using zeolites and method (b) using crystalline or amorphous metals appear to be the most promising based on Kr loading, Kr leakage, and thermal properties of the solids. Using loadings achieved in the laboratory, the weight and volume of the solids which would be required to immobilize the amount of ⁸⁵Kr (6% in krypton) which is produced annually by 67 light water reactors (1000 MWe at 28,700 MWd burnup) are:

4.8 Mg or 7.3 m³ of sodalite zeolite (26 STP cm³ Kr/cm³ solid, Method (a))

12.0 Mg or 1.3 m³ of nickel (142 STP cm³ Kr/cm³ solid, Method (b))

1.5 Mg or 0.2 m³ of amorphous metal (888 STP cm³ Kr/cm³ solid, Method (b))

In comparison, the required weights and volumes of 49.6-L pressurized cylinders are:

8.3 Mg or 6.5 m³ at 3.4 MPa (500 psi or 29 STP cm³ Kr/cm³ container)

2.5 Mg or 1.9 m³ at 13.8 MPa (2000 psi or 100 STP cm³ Kr/cm³ container)

Figures 2 and 3 compare maximum temperatures attained in various storage media, assuming that each medium is placed in a horizontal 23-cm-dia steel cylinder in ambient air at 27°C. Krypton stored as a pressurized gas is included in Figure 2 (with loading expressed in STP cm³/cm³ container). Since data of physical properties of solids containing encapsulated Kr are not yet available, the properties of the host solid are used; in amorphous metals, the density was assumed to be 7 g·cm⁻³ and the thermal conductivity (k) was assumed to be 0.01 W·cm⁻¹·K⁻¹ for Figure 2, and 0.01, 0.05, or 0.1 W·cm⁻¹·K⁻¹ for Figure 3 (the corresponding value for solid glass, also an amorphous material, is ~ 0.01).

If only interstitial diffusion is considered (and diffusion via crystal

⁷D. A. Knecht, An Evaluation of Methods for Immobilizing Krypton-85, ICP-1125, Allied Chemical Corporation-ICP, Idaho Falls, ID, July 1977.

⁸R. W. Benedict, An Evaluation of Methods for Immobilizing Solids Loaded with Krypton-85, ICP-1130, Allied Chemical Corporation - ICP, Idaho Falls, ID, August 1977.

Figure 2. Maximum Temperature Produced in a 23-cm Horizontal Cylinder in Air at 27°C as a Function of Krypton Loading, 0 to 125 cm³ Kr/cm³ Solid

Figure 3. Maximum Temperature Produced in a 23-cm Horizontal Cylinder in Air at 27°C as a Function of Krypton Loading, 100 to 1000 cm³ Kr/cm³ Solid

damage is ignored), the measured diffusivities of krypton in sodalite result in negligible leakage during long-term storage at the calculated maximum storage temperatures;⁹ even lower diffusivities (and less leakage at the calculated maximum storage temperature) can be estimated from Kr diffusion in nickel. No measurements of Kr diffusion in amorphous metal are available; at a loading of 90 STP cm³ Kr·g⁻¹, (or 630 STP cm³ Kr/cm³ solid) the crystallization temperature (~ 800°C) is not reached, assuming a thermal conductivity for the amorphous metal similar to glass (rapid krypton release has been observed at the crystallization temperature).¹⁰

While processes (a) and (b) appear promising for long-term storage of ⁸⁵Kr, further loading, leakage, and physical property characterization are needed before a conceptual design and cost estimate can be made.

Some of the methods of immobilizing krypton-85 produce solid granules, such as powders or pellets. To prevent accidental dispersal of the solid during handling, shipping, and storage, it may require immobilization.

Seven methods of immobilizing solids granules using (a) glass matrices, (b) metal matrices, (c) polymer matrices, (d) pressed (isostatic) matrices, (e) cement blocks, (f) bitumen blocks, and (g) porous metal containers, were evaluated.⁸ Glass matrices and some cast-metal matrices are not feasible because of high process temperatures.

Figures 4 and 5 give the radiation dose absorbed in a polymer and cement matrix, respectively. The radiation dose at the outside surface of a stainless steel cylinder containing the cement and polymer matrices is also shown. Radiation damage would be too large to use bitumen and cement blocks. However, polymer matrices with increased radiation-stability could be used.

Sintered-metal and pressed (isostatic) matrices appear to be good storage forms, and require further development. If disposable porous metal containers are used to hold the solid during the gas immobilization process, direct handling of the solid loaded with krypton-85 can be eliminated. After the gas is immobilized, the porous containers can be placed inside a second container which meets storage and handling requirements. Radiation absorbed at the outside surface of a porous stainless steel cylinder (130 cm long, 0.5 cm wall thickness, and 11 cm radius) filled with zeolite containing 85 TBq ⁸⁵Kr per litre zeolite is shown in Figure 6.

Determination of leakage rates, effect of beta radiation on the matrix material, and storage conditions are needed so that the most satisfactory krypton-85 storage method can be selected.

⁹R. A. Brown, M. Hoza, and D. A. Knecht, "⁸⁵Kr Storage by Zeolite Encapsulation", Proc. Fourteenth ERDA Air Clean. Conf., 1976, CONF-760822 Vol. 1, pp. 118-131, Springfield, VA, February 1977.

¹⁰J. J. Cuomo and R. J. Gambino, "Incorporation of Rare Gases in Sputtered Amorphous Metal Films", J. Vac. Sci. Technol. Vol. 14, pp. 152-157, 1977.

Figure 4. Radiation Absorbed at the Center of a Polymer Matrix and at the Outside Surface of the Stainless Steel Cylinder (130 cm Length, 0.5 cm Wall Thickness, and 11 cm Inside Radius) Containing $78 \text{ TBq} \cdot \text{L}^{-1}$ ^{85}Kr Loaded on Zeolite.

2. Pressurized Cylinder Storage

2.1 Rubidium Corrosion

A stainless steel assembly containing pressurized cylinder test specimens in a rubidium and argon environment was gamma-exposed for $2\frac{1}{2}$ months. Temperatures varied from 54 to 185°C during the exposure. The assembly was shipped to Colorado School of Mines, where the specimens will be analyzed.

3. Zeolite Encapsulation Storage

3.1 Laboratory-Scale

Results of some detailed scoping krypton encapsulation experiments

Figure 5. Radiation Absorbed at the Center of a Cement Matrix and at the Outside Surface of the Stainless Steel Cylinder (130 cm Length, 0.5 cm Wall Thickness, and 11 cm Inside Radius) Containing $82 \text{ TBq} \cdot \text{L}^{-1}$ ^{85}Kr Loaded on Zeolite.

are shown in Figure 7 for leached sodalite. Although the experimental accuracy is $\pm 2 \text{ cm}^3 \cdot \text{g}^{-1}$, the decrease in loading at 510°C for long times may be significant, possibly due to destruction of the crystal structure. A run at 410°C , 193 MPa (28000 psi), and 96 h (not shown in Figure 7) gave a loading of $44.1 \text{ cm}^3 \cdot \text{g}^{-1}$ as compared to $47.6 \text{ cm}^3 \cdot \text{g}^{-1}$ at 24 h. Krypton loadings near saturation ($\sim 50 \text{ cm}^3 \cdot \text{g}^{-1}$) are reached at 410°C for long times and at 510°C for short times for 193 MPa.

Leakage rates of krypton from two different leached sodalite samples, spray dried (SD) and oven dried (OD), were measured at different temperatures. The diffusivities were calculated⁹ and are compared with Vaughan's results.^{11,12} The activation energies, E , and pre-exponential, D_0 calculated from the data are:

¹¹D. E. W. Vaughan, Encapsulation of Rare Gases, Ph.D. Thesis, Imperial College, London, 1967.

¹²R. 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 6. Radiation Absorbed at the Outside Surface of a Porous Stainless Steel Cylinder (130 cm Long, 0.5 cm Wall Thickness, and 11 cm Radius) Containing $85 \text{ TBq} \cdot \text{L}^{-1}$ ^{85}Kr Loaded on Zeolite

Figure 7. Krypton Loading on Leached Sodalite at 410°C and 510°C , 124 MPa (18000 psi), 159 MPa (23000 psi), and 193 MPa (28000 psi), as a Function of Encapsulation Time

TABLE 7

MEASURED E AND D_0 , AND CALCULATED MAXIMUM NET LEAKAGE
FOR KRYPTON DIFFUSION IN SODALITE

SODALITE SAMPLE	E, $\text{kJ}\cdot\text{mol}^{-1}$	D_0 , $\text{cm}^2\cdot\text{sec}^{-1}$	^{85}Kr Max. Net Leakage, %
SD, This Work	162	3.85×10^{-3}	3
OD, This Work	168	4.1×10^{-4}	0.5
Vaughan's Work ⁶	159	1.1×10^{-5}	0.3

Although the activation energies are similar, the D_0 values are significantly different, possibly due to different intercrystal diffusion characteristics of the SD and OD structures.

The E and D_0 values can be used to calculate³ the maximum net leakage of original krypton-85 inventory for each sample, shown as "Max Net Leakage" in Table 7; Sample OD has better long-term storage characteristics than SD, based on these measurements.

3.2 Pilot-Scale

A short-form data sheet for line item construction of a pilot-scale encapsulation system was submitted to ERDA-ID. Upon further consultation with ERDA-ID and HQ, it was agreed to proceed only with AE conceptual design of the pilot-scale system and to hold up detailed design and construction until a selection of ^{85}Kr immobilization technologies (ion implantation/sputtering or zeolite encapsulation) can be made. A conceptual design and cost estimate of a commercial-scale encapsulation system will be made concurrently.

M. Hoza attended the Sixth AIRAPT International High Pressure Conference in Boulder, CO July 25-29, 1977. Sessions in design and safe use of high pressure equipment were attended and contacts with high pressure equipment vendors and users were renewed.

On August 1, M. Hoza visited Monsanto Chemical Company's high pressure facility in St. Louis, MO. Monsanto pioneered the design of a high pressure test chamber for explosive pressure media.¹³ He viewed their film of the testing of such a barricade to destruction,¹⁴ and will borrow a copy to show at ICPP. Monsanto has a computer program for the design of concrete walls for barricades, and will help us design the high pressure room for our pilot-scale system.

¹³H. C. Browne, H. Hileman, and L. C. Wegner, "Barricades for High Pressure Research", Ind. Eng. Chem., Vol. 53, pp. 52A-58A, October 1961.

¹⁴J. P. Weber, J. Savitt, J. Krc, Jr., and H. C. Browne, "Detonation Tests Evaluate High Pressure Cells", Ind. Eng. Chem., Vol. 53, pp. 128A-131A, November 1961.

A report, "Technological Assessment of Pilot-Scale System for Encapsulation of Krypton-85 in Zeolite", is being written. The operating temperature of the high pressure vessel required that internal heating with insulation be used to keep the pressure-bearing wall below creep temperatures. Vessel pressure seals need to be tested further before the best seal design can be determined. Special requirements of the pilot-scale system include non-contaminating compressors and vacuum pumps, and materials capable of withstanding a high radiation field. Other design considerations are standard technology.

4. Long-Term Testing of Krypton-85 Storage Media

Tests are being carried out with zeolites loaded with non-radioactive krypton at simulated storage temperatures, with and without an external radiation field. These tests include:

- (1) Periodic loading measurements of samples kept at ambient laboratory conditions to look for slow leakage and sample degradation.
- (2) Long-term exposure to external gamma radiation of loaded zeolite samples at elevated temperatures, with subsequent analyses to detect leakage and sample degradation.

The results in Table 8 illustrate (1) above. For oven-dried sodalite, no leakage occurred, within experimental accuracy; for spray-dried sodalite, if some leakage occurred, it is still within experimental error at 210-343 days. If some krypton is trapped between crystals (or in the macropores) in spray-dried sodalite, it could leak out at ambient temperatures; in Section 3 the measured D_0 for krypton diffusion was larger in spray-dried than in oven-dried sodalite.

Potassium-exchanged zeolite A shows some leakage at room temperatures; the large leakage found with Cs-exchanged zeolite A may be due to a low level of ion exchange (currently being measured) or to the inability of the large Cs ion to take up a blocking position on the zeolite A cage opening. While Rb-exchanged zeolite A may be more promising, further leakage tests are required.

The first test under part (2) involved gamma exposure of zeolite samples loaded with krypton or argon for 28 days at temperatures of 52-68°C. Dosage calculations have not yet been completed. The results are shown in Table 9. No leakage was evident with sodalite samples; however, ~ 80 to ~ 90% leakage occurred with zeolite A. Unleached sodalite samples containing intercalated NaOH (not shown in Table 9) change color from grayish white to pink during irradiation. X-ray crystallography showed that no structural changes occurred in the zeolites during irradiation.

TABLE 8
KRYPTON AND ARGON LOADING ON ZEOLITE STORED
AT AMBIENT LABORATORY CONDITIONS

Zeolite Type	Gas	Measured Loading ^a , cm ³ ·g ⁻¹		Time Elapsed, d
		Initial	Final	
Sodalite, OD2 ^b	Ar	20.9	20.3	329
Sodalite, OD2-L2 ^c	Ar	37.7	37.3	329
	Kr	13.4	15.2	238
	Kr	13.4	16.9	370
	Kr	12.3	11.2	238
	Kr	20.4	25.3	341
	Kr	20.1	20.6	349
	Kr	30.3	28.0	210
Sodalite, SD-L2 ^d	Kr	26.1	24.5	343
	Kr	26.8	24.6	337
	Kr	60.8	57.3	236
Zeolite 3A, Commercial	Kr	56.0	50.8	273
Zeolite A, 99% K-Exchanged	Kr	64.3	62.7	212
	Kr	64.6	64.0	270
	Kr	64.6	53.3	347
	Kr	47.7	2.0	327
Zeolite A, Cs-Exchanged	Kr	49.6	46.8	326

(a) Mass spectrometric measurement, STP cm³ Kr per g unencapsulated sample, with estimated accuracy of ± 2 cm³·g⁻¹.

(b) Oven-dried, unleached.

(c) Oven-dried, leached.

(d) Spray-dried, leached.

TABLE 9
KRYPTON AND ARGON LOADINGS ON ZEOLITE
AFTER GAMMA-EXPOSURE^a

<u>Zeolite Type</u>	<u>Gas</u>	<u>Measured Loading^b, cm³·g⁻¹</u>		<u>Heated and Gamma-Exposed Samples</u>
		<u>February, 1977</u>	<u>Control Samples^c</u>	
Sodalite, OD2-L2 ^d	Ar	39.2	42.0	38.3
	Kr	12.0	13.1	12.4
Zeolite 3A, Commercial	Kr	57.3	54.1	10.4
Zeolite A, 99% K-Exchanged	Kr	50.8	37.6	2.1

(a) 28 days at 52 - 68°C.

(b) Mass spectrometric measurement, STP cm³·g⁻¹, with estimated accuracy of ± 2 cm³·g⁻¹.

(c) Unheated control samples analyzed at same time as gamma-exposed sample.

(d) Oven-dried, leached.

Future long-term storage (and encapsulation) tests will require a supply of krypton-85. A conceptual design and cost estimate was made by Fluor for installing a hydrogen recombiner at ICPP in order to allow ⁸⁵Kr recovery from the zirconium dissolver off-gas. The cost of a full-scale recombiner was \$1.5 to 2.0 million, and for a reduced-scale recombiner was \$1.2 million. Since our programmatic needs alone cannot justify a \$1.2 million expense, we have explored two other options for increased ⁸⁵Kr recovery at ICPP:

- (1) Dilute a portion of the hydrogen-rich zirconium dissolver off-gas with nitrogen to below the explosion limit of H₂ in air, and process the gas through the rare gas plant after it has been upgraded.
- (2) Upgrade the rare gas plant to improve the recovery efficiency, and process only aluminum fuel dissolver off-gas.

Upon completion of the cost estimate for (1) and (2), an Expenditure Authorization will be submitted for either option, depending on the expense.

Plans for Next Quarter

A strategy analysis of krypton-85 storage options will be issued. Pressurized cylinder test specimen analyses will continue. Encapsulation and leakage tests will continue. An Expenditure Authorization for laboratory-scale hot encapsulation system will be completed. A new set of long-term radiation tests for zeolites loaded with argon and krypton will be started. Long-term leakage tests at ambient laboratory conditions will continue. An Expenditure Authorization for the hydrogen dilution system and for the Rare Gas Plant upgrade will be submitted and design criteria will be completed.

RESULTS

III. LWR OFF-GAS TREATMENT

(R. A. Brown, D. H. Munger, and T. R. Thomas)

The final draft of a report entitled, "NO_x Abatement with Ammonia by Hydrogen Mordenite at Nuclear Reprocessing Plants", has been prepared.

Plans for Next Quarter

The LWR off-gas treatment program will be terminated this quarter. Reactor engineering studies should be made to determine a design equation and product distribution for the above NO_x abatement technology.

IV. IODINE-129 ADSORBENT AND STORAGE DEVELOPMENT

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

Tests to determine the effects of water vapor, NO and NO₂ on the iodine loadings of silver-exchanged mordenite Zeolon 900 (AgZ) have been completed. The AgZ was pretreated with H₂ at 500°C for 24 hr to reduce the silver to the metallic state (Ag⁰Z) before testing. All loading tests were run in airstreams using the following conditions: bed weight, 270 g; bed depth, 15 cm; bed diameter, 5 cm; superficial face velocity, 15 m/min; bed temperature, 150°C; airborne-elemental iodine concentration, about 1500 mg I₂/m³; and decontamination factor at breakthrough, 10³ to 10⁴.

The iodine-distribution and -loading data are given in Table 10.

TABLE 10
IODINE LOADING and DISTRIBUTION vs. CONTAMINANT GASES

Test Conditions			mg I ₂ /g Ag ⁰ Z in each 2.5 cm Segment ^b							
Water Vapor (%) ^a	NO ₂ (%)	NO (%)	1	2	3	4	5	6	Avg. Loading (mg I ₂ /g Ag ⁰ Z)	
0	0	0	174	160	141	121	69	15	113	
6	0	0	155	136	123	89	35	3	91	
0	2	0	97	100	91	73	39	9	68	
6	2	0	125	127	119	121	81	17	98	
0	0	2	163	171	170	134	93	22	129	
6	0	2	169	167	143	123	74	10	115	
0	2	2	187	181	185	169	103	21	141	
6	2	2	181	172	163	129	65	9	120	

^a Dew point = 35°C

^b The average value of duplicate or triplicate tests

The data in Table 10 indicate that the first 5 to 7.5 cm of the test beds attain a saturation loading; the distribution of iodine is about constant. The remaining 7.5 cm is in the mass-transfer zone.

In Table 11, the average iodine loadings in the saturation and mass-transfer zones are given.

An analysis of the saturation-zone data based on a three-level factorial design and the 95% confidence interval of an effect indicate:

- (a) NO effect = 40 ± 12 mg I₂/g Ag^oZ; adding NO to the gas stream enhances the iodine loading.
- (b) NO₂ effect = -12 ± 12 mg I₂/g Ag^oZ; within the confidence limits of an effect, the negative influence of NO₂ is not clearly established.

TABLE 11
IODINE LOADINGS IN SATURATION AND MASS-TRANSFER
ZONES VS CONTAMINANT GASES

Test Conditions			Loadings (mgI ₂ /g Ag ^o Z) ^a		
Water Vapor (%)	NO ₂ (%)	NO (%)	Saturation Zone ^b	Mass-transfer Zone ^c	Over-all Average
0	0	0	159 ± 17	69 ± 17	113 ± 12
6	0	0	138 ± 17	43 ± 17	91 ± 12
0	2	0	96 ± 17	41 ± 17	68 ± 12
6	2	0	124 ± 17	73 ± 17	98 ± 12
0	0	2	168 ± 14	90 ± 14	129 ± 10
6	0	2	159 ± 17	69 ± 17	115 ± 12
0	2	2	185 ± 14	98 ± 14	141 ± 10
6	2	2	171 ± 17	67 ± 17	119 ± 12

^a The error limits represent the 95% confidence interval for duplicate or triplicate tests based on a pooled variance.

^b The average loading on the first three segments in Table 10.

^c The average loading on the last three segments in Table 10.

- (c) H_2O effect = $-4 \pm 12 \text{ mg I}_2/\text{g Ag}^\circ\text{Z}$; the presence or absence of water vapor has no significant effect on the iodine loadings.
- (d) $\text{NO} \times \text{NO}_2$ interaction = $25 \pm 12 \text{ mg I}_2/\text{g Ag}^\circ\text{Z}$; the interaction between NO and NO_2 is large; at low levels of NO , the effect of increasing NO_2 is a reduction in loading. At higher NO levels, the NO_2 effect becomes small.
- (e) $\text{H}_2\text{O} \times \text{NO}_2$ interaction = $11 \pm 12 \text{ mg I}_2/\text{g Ag}^\circ\text{Z}$; the interaction between water and NO_2 is insignificant.
- (f) $\text{H}_2\text{O} \times \text{NO}$ = $7.5 \pm 12 \text{ mg I}_2/\text{g Ag}^\circ\text{Z}$; the interaction between water and NO is insignificant.

A similar analysis of the data in the mass-transfer zone and the overall average loading both indicate a large positive effect due to NO . However, no other main effects or interactions were found significant.

A graphical presentation of the effect-test data (Figure 8) illustrates the positive influence of NO on the iodine loadings. In the absence of NO , NO_2 has a negative influence. However, the large $\text{NO} \times \text{NO}_2$ interaction (i.e., $25 \pm 12 \text{ mg I}_2/\text{g Ag}^\circ\text{Z}$) identified in the three-level factorial designs prevents a clear statistical interpretation of the positive and negative effects of NO and NO_2 , respectively.

ACC-A-2822

Figure 8. Iodine Loadings in the Saturation Zone of Ag°Z vs Gas Stream Composition

The effects of NO and NO₂ may be due to the equilibrium:

In the absence of a matrix effect by the mordenite, the free energy of reaction for converting the metal to the oxide would be 6.3 kcal/mol at 150°C. Oxide formation is thermodynamically unfavorable, and could only occur in the absence of NO in the test gas. The presence of NO acts as a reductant to hold the silver in the metallic state even in the presence of O₂(g). AgZ has about half the iodine-loading capacity of Ag[°]Z (ICP-1122). This result was checked by running a test with AgZ using a test gas containing 2% NO₂ and 6% H₂O at 150°C. The loading was 69 mg I₂/g AgZ, which is about half the value obtained for Ag[°]Z (124 ± 17 mg I₂/g Ag[°]Z in Table 10). In the absence of NO, NO₂ is partially oxidizing the Ag[°], and causing lower iodine loadings. The primary NO_x species in the dissolver off-gases of reprocessing plants will be NO. Consequently, the Ag[°]Z should remain in the reduced state, and the maximum iodine loadings given in Table 11 and Figure 8 should be obtainable. A loading of 170 mg I₂/g Ag[°]Z represents about 72% conversion of the Ag[°] to silver iodide.

The recycle of a bed of Ag[°]Z was continued. The experimental conditions and results of the first five cycles are given in the previous quarterly report (ICP-1122). The test bed has been recycled 13 times; the results of the loading tests, along with the distribution of iodine are given in Table 12.

The iodine loading reaches a maximum on the second cycle. This is attributed to elimination of zeolitic waters and further reduction of silver to the metal during the first three exposures to H₂ at 500°C during regeneration. Beyond the second recycle, reduction in iodine loading is attributed to progressive pore collapse and decreasing accessibility of the silver atoms.

Figure 9 illustrates the iodine loading in the saturation zone vs the number of recycles. A linear least-squares fit of the data was made on the iodine loadings for recycles 2 through 13. Extrapolation of the data indicate a 50% loss in initial iodine-loading capacity would occur by cycle 18. However, further tests are needed to verify the extrapolation. The actual curve may be leveling out (at 20% loss in loading capacity) as indicated by the similar loadings obtained beyond Recycle 9. The amount of iodine that could be stripped with H₂ from the iodine-loaded Ag[°]Z bed (AgIZ) vs the regeneration cycle is given in Figure 10. The data indicate that complete iodine stripping is obtainable for the first five cycles (the low point on the second cycle resulted from incomplete drying of the test bed before stripping). Beyond the seventh cycle, an additional 16 hr was needed to achieve greater than 90% iodine removal. The increasing resistance to total iodine removal is believed due to diffusion resistance from progressive pore collapse.

During the regeneration tests, the desorbed HI from the AgIZ bed was chemisorbed on lead-exchanged zeolites downstream. The bed temperature was 150°C and the superficial face velocity about 8 m/min. All other

TABLE 12

IODINE LOADING ON $\text{Ag}^{\circ}\text{Z}$ VS NUMBER OF RECYCLES

Cycle	mg I_2/g $\text{Ag}^{\circ}\text{Z}$ in each 2.5 cm segment						Avg. Loading (mg I_2/g $\text{Ag}^{\circ}\text{Z}$)
	1	2	3	4	5	6	
0	179	174	164	132	60	7	119
1	182	170	161	127	71	10	120
2	212	201	178	147	76	13	138
3	192	192	180	150	70	5	131
4	194	189	179	145	67	8	130
5	191	180	176	147	80	10	131
6	169	166	154	142	94	21	124
7	188	174	169	139	61	12	124
8	165	182	158	142	47	8	117
9	137	129	125	88	46	11	89
10	149	143	128	103	42	6	95
11	141	117	154	85	95	36	105
12	137	130	129	114	70	18	100
13	143	140	131	107	51	13	98

ACC-A-2823

Figure 9. Iodine Loadings of Recycled $\text{Ag}^{\circ}\text{Z}$

Figure 10. Iodine Desorbed vs Regeneration Cycle of AgIZ

test conditions were identical to those given for iodine stripping of the AgIZ bed (see Table 1 in the previous quarterly, ICP-1122). Table 13 gives the results of the loading tests.

TABLE 13
HYDROGEN IODIDE LOADINGS ON LEAD-EXCHANGED
ZEOLITES IN DRY HYDROGEN AT 150°C

Zeolite	No. of Tests	Iodide Loadings (mg HI/g Zeolite)	
		Average	Range
PbX ^a	5	408 ± 22 ^d	378-436
Pb ⁰ X ^b	1	192	-
PbZ ^c	2	380	361-398

^a Lead-exchanged faujasite

^b PbX exposed to H₂ at 500°C for 24 hr

^c Lead-exchanged mordenite

^d The 95% confidence interval of the average

The data indicate that the best loadings are obtained on PbX and about 90% of the lead is being used to chemisorb HI.

Tests were completed to determine the vapor pressures of iodine chemisorbed in PbX, PbOX and PbZ (PbIX, Pb^OIX, and PbIZ, respectively). Solid samples were placed in a heated optical cell and the vapor pressure of I₂(g) vs temperature determined from the absorption intensity of the I₂(g) visible spectrum. The data were fitted by least squares to the equation:

$$\ln P_{I_2} = A \pm B/T$$

where P = the vapor pressure of elemental iodine and T is in K. The values of A and B for the substrates and the predicted value of P_{I₂} at 20°C by extrapolation are given in Table 14.

TABLE 14
IODINE VAPOR PRESSURE DATA FOR CHEMISORBED
IODINE ON LEAD-EXCHANGED ZEOLITES

Substrate	Gas Blanket	A	B	P _{I₂} at 20°C (atm)
PbIX	Air	15.3	9.47x10 ³	4.0x10 ⁻⁸
	Nitrogen	17.3	1.01x10 ⁴	3.4x10 ⁻⁸
Pb ^O IX	Air	44.5	2.65x10 ⁴	9.5x10 ⁻²¹
	Nitrogen	51.6	3.02x10 ⁴	2.3x10 ⁻¹⁶
PbIZ	Air	6.6	5.53x10 ³	4.4x10 ⁻⁶
	Nitrogen	8.0	6.20x10 ³	1.8x10 ⁻⁶

The above extrapolated vapor pressures are related to the strength of the lead-iodine bond. Pure PbI₂ has an iodine-vapor pressure of about 10⁻²⁸ atm at 20°C. The chemisorbed bonds are considerably weaker than the iodide bond. However, the iodine-vapor pressures may be small enough that all the above listed substrates would be suitable for long-term storage of ¹²⁹I in sealed containers at ambient temperatures.

A mass-balance test was run to determine if I₂(g) were the only significant iodine species that would desorb from PbIX. A gas stream of nitrogen was passed through the optical cell containing the PbIX at 175°C for 16 hr. The absorbance of the I₂(g) was monitored continuously. The iodine desorbed from the PbIX was calculated by graphical integration of the equation:

$$\text{mg } I_2(g) = \frac{f \cdot m}{a \cdot b} \int_0^t \text{Abs} \cdot dt$$

where Abs = the observed absorbance, t = time in hr, f = nitrogen flow

rate in cm^3/hr , $m=254 \text{ mg I}_2/22.4 \text{ cm}^3$, a = the molar absorptivity of iodine (18.54 atm^{-1} at 520 nanometers, and b = the path length of the cell (10 cm). The weight of iodine desorbed as determined by the above equation was compared to the gravimetric weight loss on the PbIX. The two methods gave a weight loss within 10% of each other which indicates the primary, if not the sole volatile species, to be $\text{I}_2(\text{g})$.

Plans for Next Quarter

The iodine-129 adsorbent and storage program will be terminated this quarter. The first draft of a topical report covering the information in this and the previous quarterly report (ICP-1123) is being prepared. The final draft will be completed in October 1977.

Based on the results of this program, the following work should be done:

- (1) Study the loading capacity of Ag°Z for airborne-organic iodides
- (2) Determine the effect of water vapor, NO and NO_2 on the iodine loadings of AgZ .
- (3) Conduct design verification studies on the regeneration and recycle of Ag°Z in pilot-plant studies.
- (4) Search for other silver-loaded substrates that might be more suitable for regeneration and recycle than Ag°Z .
- (5) Complete the evaluation of recycle life of Ag°Z , i.e., measure the complete life cycle of the adsorbent.

V. LIQUID WASTE MANAGEMENT: EVAPORATION AND STORAGE^a

(B. E. Paige, P. A. Anderson)

The reprocessing of spent nuclear fuel by several of the presently considered alternative fuel cycles generates liquid wastes which must be stored for short or intermediate periods pending solidification. The liquid storage volume of waste tanks can be increased and more efficiently utilized if the waste is concentrated to the smallest practical volume before and/or during storage.

The present studies are concerned with the nitric acid wastes which result from the tributyl phosphate extraction of uranium. Simulated solutions are used to avoid the difficulties and expense of experimenting with actual radioactive solutions. The objectives are to investigate the quantities and nature of the undissolved solids and materials of construction for process operating conditions during the concentration and storage of high-level liquid wastes (HLLW).

Factors being investigated include the effects of solids deposition on heat transfer surfaces in two separate phases of processing: (1) the thermosiphon evaporation of dilute HLLW and (2) the interim storage

^aPart of the Alternative Fuel Cycle Technology program administered by Savannah River Operations and Savannah River Laboratory.

of concentrated HLLW during which fission product heat is removed by cooling-water coils. Data from earlier laboratory investigations in both of these areas,¹⁶ in addition to data on the physical properties of evaporated HLLW,¹⁷ provided the bases for the design of the present experimental equipment and the selection of physical and chemical properties to be studied. Evaluation of the corrosive effects of individual and combined species in liquid wastes are continuing.

1. Evaporation

The small-scale thermosiphon evaporator was operated this quarter with a titanium reboiler tube using nitric acid and simulated HLLW solutions as was done during the previous quarter with the Type 304L stainless steel specimen.¹⁶ The evaporator unit is constructed of Type 304L stainless steel; only the reboiler tube sections are changed as subsequent alloys are tested. The two levels of evaporation which were selected were 340 L/MTU (90 gal/MTU) and 1380 L/MTU (365 gal/MTU). Based upon earlier laboratory evaporation of HLLW, 340 L/MTU represents the upper practical concentration limit from the standpoint of total solids content. A concentration of 1380 L/MTU was selected as a lower concentration limit for short-term cooled fuels and also allows for the possibility of considerable in-tank concentrating during interim storage. Based on these limits, runs were made under the following operating conditions:

- (1) The continuous evaporation of solution from 4900 L/MTU containing 2.5 M nitric acid to 1380 L/MTU containing 7 M nitric acid for 48 h.
- (2) The continuous evaporation of reconstituted solutions from run (1) from 4900 L/MTU containing 2.5 M nitric acid to 340 L/MTU containing 7 M nitric acid at vapor velocities of 0.3 and 0.6 m/s (1 and 2 ft/s) for 68 h.
 - (2a) The recirculation of the solution from run (2) at 340 L/MTU for an additional 48 h while recycling all condensate.
- (3) The continuous evaporation of reconstituted solution from run (2) from 4900 L/MTU containing 2.5 M nitric acid to 340 L/MTU containing 7 M nitric acid at vapor velocities of 0.9 and 1.2 m/s (3 and 4 ft/s) for 52 h.

A complete set of runs was first made with nitric acid to establish a baseline for the titanium reboiler tube material. The runs were then repeated under the same operating conditions using simulated HLLW solution.

¹⁶ Alternative Fuel Cycle Technology Progress Report for April 1 - June 30, 1977, ICP-1122 (April 1977).

¹⁷ LWR Fuel Reprocessing and Recycle Progress Report for January 1 - March 31, ICP-1116 (April 1977).

The HLLW feed contained 6 g/L total fission products which represent extraction raffinate at 4900 L/MTU from fuel irradiated to 33,000 MWd/MTU and cooled for 150 days. The HLLW feed also contained 2 g/L uranium, 7 g/L gadolinium, 0.34 g/L phosphate and 0.01 g/L dissolved corrosion products.¹⁷

To minimize the time required to obtain steady state operating conditions, the evaporator was charged with HLLW which was already adjusted to the expected concentration of the evaporator product.

1.1 Operating Characteristics of Evaporator (G. R. Villemez, C. B. Millet)

Plugging problems which were previously experienced with the settling of undissolved solids in concentrated HLLW (340 L/MTU) were eliminated with the removal of the preheater. An automatic control valve was installed in the feed line, eliminating the previous problem of unstable operating conditions.¹⁶

The maximum waste solution temperature allowed in the waste evaporator is 130°C due to the explosion hazard of tributyl phosphate and nitric acid above 140°C.¹⁸ The evaporator can be operated with a throughput of 300 to 1200 g/h of vapor condensate consisting of approximately 2 M nitric acid. This corresponds to a vapor velocity range of 0.3 to 1.22 m/s (1 to 4 ft/s).

1.2 Heat Transfer of Evaporator (G. R. Villemez, C. B. Millet)

The heat transfer for the titanium reboiler tube was calculated on the same basis as the Type 304L stainless steel reboiler tube.¹⁶ The rate of heat transfer (q), is defined as the product of the overall heat transfer coefficient (U), the area of heat transfer surface (A), and the apparent temperature difference (ΔT). The heat transfer expression is:

$$q = U \cdot A \cdot \Delta T$$

The rate of heat transfer, q , was calculated as the product of the vapor rate at the atmospheric pressure of 84.7 kPa (12.3 psi) at 1585 metres (5200 ft) elevation and the latent heat of the evaporation of water at the saturated vapor temperature. The area is based on the inside diameter of a 1-inch reboiler tube with 30 cm (12 in.) of reboiler tube exposed to condensing steam; an additional 7.5 cm (3 in.) portion of the reboiler tube was exposed to the steam condensate. The feed solution was preheated by the steam condensate to the temperature of the recirculated solution, which was near the boiling point at the feed end for the reboiler section. The apparent temperature difference was calculated from the measured saturated vapor temperature above the boiling liquid and the condensing steam temperature. The calculated heat transfer rates are estimated to be within 10% of the actual value.

¹⁸Hanford Atomic Products Operation, Purex Technical Manual, HW-31000 DEL. March 25, 1955, Part III, p 1007.

1.21 Rate

The apparent overall heat transfer coefficients with the titanium reboiler tube were calculated from operating data obtained during steady state conditions.¹⁶ Data from the first nitric acid evaporation to 1380 L/MTU indicated little, if any, effect on the heat transfer coefficients from solids formation in the titanium reboiler tube. However, the solids buildup appeared to reduce the heat transfer coefficients during runs with the nitric acid to 340 L/MTU. The overall heat transfer coefficients for titanium were approximately 55% of the values for Type 304L stainless steel in the nitric acid solutions evaporated to 340 L/MTU. These data are shown in Figure 11.

The heat transfer coefficients for titanium during the evaporation of the HLLW solutions to 340 L/MTU were essentially the same as the baseline nitric acid values at this concentration. The overall heat transfer coefficients for titanium were 65 to 95% of the values for Type 304L stainless steel in HLLW solutions evaporated to 340 L/MTU as shown in Figure 12.

As shown in Figures 11 and 12, the overall heat transfer coefficients increased with an increase in the vapor velocity but decreased with the accumulation of operating time on the titanium reboiler tube. The decreased values in the second and third evaporation runs are apparently due to scaling effect.

Even though the scale deposition appeared to continuously reduce the overall heat transfer coefficient during evaporation, the titanium material is preferable to Type 304L stainless steel due to its superior corrosion resistance as reported in Section 3.2.

1.22 Scaling and Fouling

Solids were formed in the titanium reboiler tube section during the evaporation of 7 M nitric acid. The solids which deposited on the feed end of the reboiler tube are shown in Figure 13, and those which deposited on the tube sheet are shown in Figure 14.

The loose dark gray scale which formed on the surface of the titanium reboiler tube section during the evaporation of nitric acid, contained major amounts of iron and silicon and minor amounts of nickel and chromium. This scale has not formed on either the Type 304L stainless steel reboiler tube or the Nitronic-50 reboiler tube currently being tested. Since all waste solutions contain some stainless steel corrosion products from the process, a plating out of these materials may be the cause of poor heat transfer which has been observed in all titanium evaporators.¹⁹

The scale which formed in the feed end of the reboiler tube section

¹⁹M. W. Wilding and B. E. Paige, Survey on Corrosion of Metals and Alloys in Solutions Containing Nitric Acid, ICP-1107 (December 1976).

Figure 11. Heat Transfer for a Titanium Reboiler Tube in Nitric Acid

Figure 12. Heat Transfer for a Titanium Reboiler Tube in HLLW

TITANIUM REBOILER TUBE EXPOSED TO
7-MOLAR NITRIC ACID

Figure 13. Solids on Feed End of Reboiler Tube

TITANIUM REBOILER TUBE EXPOSED TO
7-MOLAR NITRIC ACID

Figure 14. Solids on Top End of Reboiler Tube

during the evaporation of the simulated HLLW solution, shown in Figure 15, is a hard thin layer which appears to build up with operating time. The scale deposit was thicker on the tube sheet, shown in Figure 16, than on the feed end. Since these scales continuously reduce the overall heat transfer coefficient during the evaporation, long-term operation may require periodic scale removal processes to maintain an adequate heat transfer rate in the titanium reboiler tubes. Most of the scale from the tube surface was removed after a 6-hour treatment with boiling 10% Turco Alkaline Rust Remover.^a However, some scale was still visible in the heat transfer area even after scrubbing with a nylon brush.

The scale formed in the titanium reboiler tube section during the evaporation of HLLW consisted mostly of zirconium and molybdenum with traces of iron, which is essentially the same scale formed during previous evaporations of HLLW with a Type 304L stainless steel reboiler tube section. HLLW scale is compared to precipitates from laboratory evaporations in Section 2.23.

2. Waste Storage

The present storage studies with simulated HLLW are designed to provide design and operational data for the safe and economical storage of evaporated liquid wastes pending solidification. The data obtained will be applicable to a variety of types of HLLW's anticipated from any of several possible alternative fuel cycles, including existing defense wastes.

During this quarter, the major effort was directed toward operating the Laboratory Storage Tank, continuation of long-term stability studies with stored HLLW slurries, and further characterization of precipitated solids.

2.1 Laboratory Storage Tank (P. A. Anderson)

Long-term storage studies have been initiated in the Laboratory Storage Tank to obtain preliminary data on heat transfer, mixing, and chemical stability of stored HLLW. Experience with experimental equipment will be utilized in the design and construction of a small-scale storage tank. The tank has been operated with water,¹⁶ 12.8 M nitric acid, and HLLW with a composition representative of waste from an LWR reprocessing plant. A nitric acid concentration of 12.8 M was initially selected because laboratory batch evaporations yielded slurries with this acidity. Recent experience with the small-scale thermosiphon evaporator indicates that 7 M is a more likely acidity for concentrated HLLW slurries. The HLLW slurry which is presently stored is the adjusted product from the small-scale thermosiphon evaporator.

2.11 Heat Transfer

Heat transfer coefficients at various flowrates of cooling water for stored water, 12.8 M nitric acid, and HLLW at 1380 L/MTU in

^aTurco Products, Inc., Division of Purex Corporation, Carson, California.

TITANIUM REBOILER TUBE EXPOSED TO LWR WASTE
SOLUTION

Figure 15. Scale on Feed End of Reboiler Tube

TITANIUM REBOILER TUBE SHEET EXPOSED TO LWR
WASTE SOLUTION

Figure 16. Scale on Tube Sheet of Reboiler Tube

5.3 M HNO_3 are shown in Figure 17. Measurements were made while the solutions were thoroughly mixed for uniform temperatures throughout the stored solutions. The cooling water flow through the Type 304L stainless steel cooling coil is entirely in the laminar flow region. The initial heat transfer coefficients for both the nitric acid and the HLLW were substantially lower than for water at nominal storage conditions. In all three cases, measurements were made after the solution was in the tank for only a few days. Future heat transfer measurements will determine effects due to scaling on the heat transfer surfaces during long-term storage at 60°C.

2.12 Physical Mixing of Stored Slurries

The present experimental equipment was designed to agitate the stored solution in a manner which duplicates the conditions in a large storage tank.¹⁶ One selected parameter is a ballast tank nozzle exhaust velocity of 18 m/s. The ballast tank agitators and convection currents provide vigorous agitation for the lower one third of the 13.6-litre tank, decreasing to only gentle circulation at the top. Temperature gradients of 2 to 4°C are observed within the storage tank at the nominal storage temperature of 60°C after only a few minutes of operation when no other form of mixing is applied. Uniform temperatures throughout the tank were obtained only with auxiliary mixing from the airlift circulators. The ballast tank agitators effectively suspend the undissolved solids near the exhaust nozzle; however, those solids on the tank floor opposite the ballast tank nozzles are not entirely dislodged. This indicates that the ballast tank nozzles must be situated to sweep as much of the tank floor as possible.

2.2 Storage of Evaporated HLLW (P. A. Anderson)

During this quarter, the investigation of the stability of stored slurries with respect to quantities of undissolved solids was continued with HLLW solutions containing a wide variety of process additives. X-ray fluorescence, X-ray diffraction, and scanning electron microscope (SEM) techniques were used to compare the undissolved solids from laboratory evaporated slurries and the scale which plated on heat transfer surfaces of small-scale thermosiphon evaporator. The effects of nitric acid and water rinsing upon the solids were also studied.

2.21 Stability of Stored HLLW Slurries

Simulated HLLW slurries from laboratory evaporations have been stored up to 13 months at constant temperatures and without agitation. The data from 18 samples, which were obtained at intervals of one to two months, show no significant changes with respect to quantities of undissolved solids. The storage of these slurries will continue with future analyses made at six-month intervals.

Figure 17. Heat Transfer Coefficients for Cooling of the Laboratory Storage Tank

2.22 Characteristics of the Undissolved Solids in Stored HLLW Slurries

The quantities of total undissolved solids reported^{17, 20, 21} in evaporated HLLW slurries have been based upon analyses in which the filtered solids were not rinsed because of the possibility that rinsing would be likely to dissolve a portion of the solids. X-ray fluorescence and X-ray diffraction data show that thorough rinsing of HLLW solids with water and dilute nitric acid does not alter the chemical composition or the crystalline structure of the particles. Total undissolved solids analyses will continue with the non-rinsing technique.

The solids from a HLLW slurry, which contains 12.8 M nitric acid, 67 g/L gadolinium as a nuclear poison, 0.005 M phosphate, and 0.125 M uranium to simulate total actinides, were examined with a scanning electron microscope (SEM). The precipitate from the slurry when freshly stored, shown in Figure 18, contains cubic particles with a definite crystalline structure. After two months storage at 60°C without agitation, precipitate from the same slurry, illustrated in Figure 19, shows a coating on the particles. Precipitate from the same solution, after three additional months of storage, was thoroughly rinsed with dilute nitric acid and water before SEM examination. Some of the coating material, shown in Figure 20 was still present. Coating effects were not observed after eight months of storage in the non-crystalline particles precipitated from HLLW-0 in previously reported studies.²² X-ray fluorescence and X-ray diffraction analyses detected no differences in the compositions and crystalline structures of solids due to either the rinsing or the coating material.

The undissolved solids which settle to the bottom of a stored HLLW slurry can be easily resuspended with gentle agitation every few days. Slurries which stand for several months without agitation require more vigorous agitation to resuspend the solids. This indicates that continuous agitation in an actual HLLW storage tank should help prevent caking on the tank floor.

2.23 Comparison of Precipitates and Evaporator Scale

The precipitates from laboratory evaporated HLLW were compared to the scale which formed on the Type 304L stainless steel reboiler tube of the small-scale thermosiphon evaporator during operation with HLLW. Analyses by X-ray diffraction and X-ray fluorescence showed the chemical compositions to be essentially identical except for small amounts of

²⁰LWR Fuel Reprocessing and Recycle Progress Report for April 1 - June 30, 1976, ICP-1101 (November 1976)

²¹LWR Fuel Reprocessing and Recycle Progress Report for July 1 - September 30, 1976, ICP-1108 (December 1976)

²²LWR Fuel Reprocessing and Recycle Progress Report for October 1 - December 31, 1976, ICP-1110 (January 1977)

Figure 18. Precipitate from Freshly Stored HLLW
(scanning electron microscope at 5000X magnification)

Figure 19. Precipitate from HLLW after Two Months Storage
(scanning electron microscope at 5000X magnification)

Figure 20. Rinsed Precipitate from HLLW after Five Months Storage
(scanning electron microscope at 2000X magnification)

Figure 21. Scale Deposited on Type 304L Stainless Steel
Reboiler Tube during Evaporation of HLLW
(scanning electron microscope at 5000X magnification)

$\text{Fe}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ which have appeared in the evaporator scale. However, scanning electron microscope examination of the scale, shown in Figure 14, does not indicate the presence of any definite crystalline structure or regular shape of particles as have been found in all of the precipitates which have been examined from laboratory evaporations.

2.3 Design of Small-scale Storage Tank (P. A. Anderson)

A small-scale storage tank is being designed for HLLW storage studies with advanced simulated waste slurries. The tank is being designed for possible application to studies with actual waste solutions generated from hot cell dissolution of irradiated fuels. Improved solution heating will be obtained by stratified heating coils to simulate fission product heat generation differences from suspended and settled components. Solution mixing will be accomplished with ballast tank agitators and thermal convection currents. Water flow in the cooling coils will be in the turbulent range. Type 304L stainless steel will be used as much as possible for the construction of components which contact the stored solutions. The tank will be installed adjacent to the small-scale thermosiphon evaporator and will be filled with evaporator product.

3. Materials and Corrosion

Materials and corrosion studies are being conducted with simulated HLLW slurries in the laboratory and in the small-scale thermosiphon evaporator. The corrosive effects of waste solutions on materials of construction for evaporators, waste tanks, and auxiliary equipment are being studied to identify suitable alloys for fuel reprocessing facilities. Methods for monitoring corrosion of tanks and internal components during interim storage of liquid wastes are being evaluated.

3.1 Monitoring Storage Tanks (P. A. Anderson)

Studies are continuing to evaluate the dependability and accuracy of electronic corrosion monitoring probes in waste tanks and lines. Corrosion monitoring probes, which are constructed of the test alloys, are continuously exposed to the environment being monitored. They are activated weekly, or when desired, to determine accumulated amounts of corrosion. Electronic probes offer the advantage of rapidly obtaining corrosion rate data by remote operation.

Separate Type 304L stainless steel probes were exposed for one to three months to HLLW and 12.8 M nitric acid at 60°C with gentle agitation for one minute each hour to simulate ballast tank mixing in an actual waste tank. A probe was also exposed for one month to HLLW at 1380 L/MTU in 5.3 M nitric acid in the Laboratory Storage Tank. During the three month test period, the electronic equipment indicated continuous corrosion at relatively steady rates. The equipment has operated within the manufacturer's limits of accuracy for the instruments. The corrosion rates indicated by the electronic probes are compared in Table 15 to the rates determined by individual corrosion coupons in the same test solutions.

TABLE 15

CORROSION RATES FOR TYPE 304L STAINLESS STEEL AT 60°C

Type of solution	Corrosion rates from the electronic probes, $\mu\text{m/yr}^{(a)}$	Corrosion rates from coupons, $\mu\text{m/yr}$
HLLW at 1380 L/MTU in 7.0 M HNO_3	32	14
HLLW at 1380 L/MTU in 5.3 M HNO_3 with substitutes for Rh, Pd, Tc, and no Ru	8	6.4
12.8 M HNO_3	10.5	10

(a) 1 $\mu\text{m/yr}$ is equivalent to 3.9×10^{-2} mils/yr

These data show that the corrosion rates obtained with the electronic probes are very low and are comparable to the rates determined by corrosion coupons. This is consistent with previous tests in three selected types of HLLW slurries.¹⁷ The evaluation of the performance of electronic corrosion monitoring equipment under simulated process conditions is continuing.

3.2 Reboiler Tube Evaluation (G. R. Villemez, C. B. Millet)

The entire lengths of reboiler tube sections in the small-scale thermosiphon evaporator are used as corrosion specimens. The corrosion rate of the titanium reboiler tube during 432 hours of evaporative service was essentially zero.

3.3 Laboratory Corrosion Tests (C. B. Millet)

Modified Huey tests are being used to determine the corrosion effects of chemical species which are present in actual waste but are not present in simulated waste solutions. Loss of weight by corrosion coupons is determined for three 24-hour periods and one 96-hour period to complete one week of total exposure. Unwelded coupons are submerged in solutions for weight loss measurements and welded coupons are suspended at the vapor-liquid interface to observe weld behavior and possible preferential attack at the interface or in the vapor phase.

Laboratory corrosion tests were performed to determine the effect of the radioactive fission product technetium. Technetium exists only as a radioactive isotope and requires special handling; therefore, it has previously been simulated in HLLW by rhenium or manganese. Technetium

is a corrosion inhibitor for iron and carbon steel,²³ but rhenium does not have a similar effect. Oxidized manganese (Mn[VII]) can be a corrosion accelerator.²⁴ Since technetium provides inhibition by forming a protective coating, it was not anticipated that it would further protect stainless steel which is already protected by a passive oxide coating.

Three solutions containing technetium at 2.18 g/L, which represents HLLW at 378 L/MTU (100 gal/MTU), were tested at the boiling point on Type 304L stainless steel. The first solution, 7 M nitric acid containing technetium, was found to be nearly twice as corrosive as a pure nitric acid solution. In the second solution, HLLW without ruthenium, the corrosion rate was decreased slightly in the first periods of the test, but by the end of the test, the rate was equivalent to the rate (210 $\mu\text{m}/\text{yr}$) found in previous tests without ruthenium. Overall, the presence of technetium did not change the corrosion rate in HLLW with ruthenium omitted. In the third solution, HLLW containing ruthenium, the corrosion accelerating effects of ruthenium^{22 25} were nullified by the technetium. The average corrosion rate (208 $\mu\text{m}/\text{yr}$) was the same as if both ruthenium and technetium had not been present. The observed corrosion in all three tests was general attack in the liquid phase with no preferential vapor phase or interface attack.

The technetium metal dissolved in nitric acid yielded a dark brown solution. At the beginning of these tests, all three solutions were dark brown from the addition of technetium. After boiling for thirty minutes the 7 M nitric acid and the HLLW solution without ruthenium returned to their original color. The color change indicated an oxidation-reduction reaction involving technetium which inhibits valences ranging from seven to zero.²⁶ The color change was either masked or did not occur in the solution containing ruthenium.

Plans for Next Quarter

The small-scale thermosiphon evaporator will be operated with a Nitronic 50 and Sandvik 2R12 reboiler tube to evaluate fouling tendencies, heat transfer coefficients, and off-gas behavior. Additional operating runs

²³Cartledge, G. H., "Inhibition of Corrosion by the Pertechnetate Ion", Isotope and Irradiation Technology, 1, pp 125-129 (Winter 1963-64).

²⁴Coriou, H., Hure, J., and Plante, G., "Electrochemical aspect of the Corrosion of Austenitic Stainless Steel in Nitric Medium and in the Presence of Hexavalent Chromium", Electromchimica Acta, 5, pp 105-11 (1961).

²⁵McIntosh, A. B., and Evans, T. E., "The Effect of Metal Species Present in Irradiated Fuel Elements on the Corrosion of Stainless Steel in Nitric Acid", 2nd United Nations Conference on Peaceful Uses of Atomic Energy, Vol. 17 (1958).

²⁶Peacock, R. D., The Chemistry of Technetium and Rhenium, New York: American Elsevier, 1966.

will determine corrosion rates for Sandvik 2RE69 and Type 310 stainless steel during the evaporation of simulated HLLW waste solutions. Characterization studies of precipitates and scale deposits will continue. The designing and ordering of construction materials for the small-scale storage tank will be completed.

Laboratory corrosion tests will continue to determine corrosion rates for various rare earth fission products and their substitutes. The effects of technetium and ruthenium will be verified and further investigated.

VI. HTGR FUEL REPROCESSING

(L. W. McClure)

High Temperature Gas-Cooled Reactor (HTGR) fuel blocks consist of fuel particles in a graphite matrix. During reprocessing, the blocks are crushed, and the graphite is burned in a primary burner to expose the fuel particles. The fuel particles are then crushed and burned in a secondary burner. During this step, fission products in the fuel will vaporize. Previous laboratory tests have identified which fission products will vaporize in the burner environment.

The tests this quarter have determined the vaporization and condensation characteristics of MoO_3 and RuO_2 . Also, preliminary heat transfer tests were performed with a fluidized bed condenser as a means for removal of the vaporized fission products.

1. Deposition and Plate-Out Testing (K. L. Wagner, G. O. Haroldsen)

A tube furnace study conducted earlier identified the fission products that are most likely to be volatile in a HTGR secondary, fluidized-bed graphite burner.²⁷ This quarter, simulated fission products were added to a model fluidized-bed burner, and their volatilities in an actual burner environment were studied. Three checkout and five experimental runs were conducted using an externally heated quartz burner. In the previous tube furnace study, RuO_2 and MoO_3 showed very different volatilities. When RuO_2 was heated, it distributed throughout the experimental apparatus. When MoO_3 was heated, it formed thick crystals of MoO_3 just downstream from the sample boat. Since these two compounds represent two extremes in volatility and since they are much less toxic than the other volatile fission products, MoO_3 and RuO_2 were used for the first series of burner tests as simulated fission products.

A schematic drawing of the experimental apparatus is shown in Figure 22. Preheated air at a flow rate of approximately 0.3 L/s (0.6 scfm) enters the 5 cm O.D. section of the quartz burner and passes through a quartz distributor plate. Then, the air fluidizes a bed of 60 mesh alumina which is heated by a vertical tube furnace. Next, the gas is cleaned by a 3.8 cm O.D., sintered, stainless steel, H porosity filter. After passing through the inbed filter, the air enters the off-gas system and passes through a glass fiber filter. Finally, the off-gas is scrubbed in a 50% HCl, 50% ethyl alcohol solution before being vented to a fume hood.

In the standard experimental procedure, 10.4 g of MoO_3 and 3.2 g of RuO_2 were added with 104 g of ground (< 20 and > 60 mesh) graphite to an alumina bed. The apparatus was closed, fluidized, and then heated to the combustion temperature of the graphite. At that point, the burning

²⁷C. M. Slansky, Ed., Technical Division Quarterly Progress Report, April 1 - June 30, 1977, ICP-1123 (July 1977).

Figure 22. Schematic Diagram of the Fluidized-bed Burner Apparatus

graphite raised the temperature in the bed to over 1170 K. After the majority of the graphite had burned, O_2 was added to the fluidizing air, and fluidization was continued for three hours under a 60% O_2 atmosphere at approximately 1070 K. Following this "thermal soak" period under the high O_2 concentration, the furnace was turned off and the apparatus was cooled. Throughout the runs, the sintered stainless steel filter was blown back at a frequency of 2 times per minute. The filter was blown back to keep it from plugging with graphite fines.²⁸

Table 16 presents the conditions for each of the five experiments conducted. The first three runs were conducted using the standard procedure. During these three experiments, much more ruthenium was observed throughout the off-gas system during the "thermal soak" portion than during combustion of the graphite. The last two experiments were performed under different conditions, and the ruthenium volatility was compared with that of the previous runs.

The fourth experimental test was conducted using air only. No O_2 was added during the "thermal soak" period. The ruthenium concentration of the scrub solution after this run was 160 times less than the concentration measured after the third run.

The fifth run used dry N_2 as the fluidizing gas, and air was used for the filter blowback. No graphite was added during this run, but graphite fines from the previous runs were present. The Ru concentration in the scrub of this run was less than the analytical detection limit of 0.1 $\mu\text{g/mL}$.

The reduced volatility of Ru during the final two runs was attributed to less conversion of the RuO_2 to highly volatile RuO_4 . Less O_2 was available to react with the RuO_2 therefore less RuO_4 was formed. The maximum amount of ruthenium in the scrub solution was only $\sim 1\%$ of the total amount of ruthenium placed in the burner.

During the course of the five runs, the pressure drop across the in-bed filter increased from 2.44 kPa (9.8 in. H_2O) at a flow rate of approximately 0.6 L/s air to 8.22 kPa (33 in. H_2O) at the same flow rate. By the conclusion of the fifth experiment, the deposition on the filter (see Figure 23) had become great enough that the fluidizing gas was venting through the pressure relief device at the top of the vessel rather than passing through the filter.

Considerable deposition also occurred on the walls of the quartz burner, (see Figure 24). The pending analyses of the bed material and the deposits are expected to provide more information on the reactions of MoO_3 and RuO_2 within a fluidized-bed burner.

²⁸W. S. Rickman, Interim Development Report for Secondary Burning, GA-A13540 (December 25, 1975).

TABLE 16
OPERATING CONDITIONS FOR THE FLUIDIZED - BED BURNER RUNS

Run No.	Fluidizing Gas	Maximum Fluidized Bed Temperature During Combustion (°C)	Maximum Off-Gas Temperature During Combustion (°C)	Duration of Combustion (min)	Average Fluidized-Bed Temperature During "Thermal Soak" (°C)	Average Off-Gas Temperature During "Thermal Soak" (°C)	Duration of "Thermal Soak" (min)
1	Air with O ₂ added during the "Thermal Soak"	955	100	50	804	112	175
2	Air with O ₂ added during the "Thermal Soak"	934	96	60	814	96	170
3	Air with O ₂ added during the "Thermal Soak"	916	104	60	796	104	170
4	Air	904	109	65	814	73	165
5	Dry N ₂	--- (a)	---	--	756	82	180

(a) Combustion of graphite was not done. Run performed only to compare "Thermal Soak" portion with previous runs.

Figure 23. In-bed Filter Deposits (deposition on sintered stainless steel filter following five fluidized bed burner runs with MoO_2 and RuO_2 added is shown)

2. Condensation and Removal of Volatile HTGR Fission Products (G. O. Haroldsen)

Preliminary runs have been conducted with the experimental fluidized-bed over-bed quenching apparatus.²⁷ In this apparatus, the lower fluidized bed heats the carrier gas and volatilizes simulated fission products. The upper bed, with a cooling coil immersed in the bed, cools the gases from the lower bed and condenses the volatilized materials. The objective of this particular task is to demonstrate rapid cooling of the gas from approximately 1170 K to less than 370 K and removal of the volatilized fission products by condensation and deposition on the bed particles.

The first version of this apparatus consisted of two 46-cm-long quartz glass sections flanged together at the middle. The main body of each section was 5.8 cm in diameter, and had enlarged ends at the flanges of 7.6 cm. This gave the upper bed a truncated cone shape.

Figure 24. Fluidized-bed Burner Deposits (deposition on the quartz fluidized-bed burner after five runs with MoO_3 and RuO_2 added is shown)

The lower-bed section had thirteen 400-watt cartridge heaters that were inserted through 1.27-cm-dia. nipples in the wall of the vessel.

Although this apparatus was found to be too fragile for extensive testing, preliminary data collected from two checkout runs indicated very good cooling characteristics in the upper quenching bed. In the first experiment, the incoming gas at 970 K was cooled to 340 K in a bed depth of 23 cm of 50-60 mesh nickel particles. The second run used fused alumina in place of nickel particles. Essentially the same rapid cooling was achieved. Therefore, the bed material used doesn't appear to have a significant effect on overall heat transfer.

In a second version of the apparatus (see Figure 25), the fragile lower quartz section was replaced with a section of stainless steel pipe, while the upper quartz section remained unchanged. This apparatus is presently in use and is proving satisfactory. With this apparatus, preliminary runs have been conducted to identify operating limits and

Figure 25. Bed-above-bed Quenching Apparatus (lower insulated section is stainless steel)

design requirements for maintaining the upper distributor plate temperature above the condensing temperatures of the volatile species to avoid deposition in the orifices of the plate.

By limiting the degree of fluidization taking place at the upper surface of the distributor and by superheating the gas entering the distributor, the desired distributor temperature can be maintained.

With the truncated-cone shaped bed, it is possible to have little or no fluidization at the bottom of the bed while the upper portion of the bed is fluidized where the cross-sectional area is smaller. A run of six hours' duration successfully maintained the desired temperatures and demonstrated that the truncated-cone concept has potential in maintaining the desired distributor plate temperatures and cooling of the gas by the fluidized portion of the bed.

Plans for Next Quarter

Further testing will be conducted to define the limits of the

truncated-cone shaped bed with regard to gas velocities, cooling rate, cooling coil distance above the distributor, and other significant parameters. Through theoretical calculations, an assessment will be made of the required slope of the wall of the vessel to give desired flexibility of operation. Tests will then be devised to verify by experiment the effect of wall slope.

Other ways of maintaining desired distributor plate temperature will be investigated including direct heating of the distributor, and partial insulation of the distributor. After proper temperature control and temperature distribution have been achieved, tests will then be conducted with simulated volatile fission products.

The lab-scale burner will be operated with additional simulated fission products to determine their volatilization and deposition characteristics.

VII. NATURAL FISSION REACTOR STUDIES

(W. J. Maeck, R. L. Eggleston, F. A. Duce, J. E. Delmore,
R. A. Nielsen, F. W. Spraktes)

An extensive overview of this program was given in the previous quarterly report (ICP-1123). The major experimental activity for the quarter has been the analysis of 11 uranium ore samples taken from the perimeter of the Oklo natural reactor. These ores were dissolved and analyzed for U, Ru, Nd, and Sm. These samples were unusual in that the measurements of the ruthenium isotopes showed enhancement of mass 99. Samples taken from the cores of the Oklo reactors showed the opposite effect. Since ^{99}Ru is preceded by ^{99}Tc , which has a $2 \cdot 10^5$ -year half-life, the obvious conclusion is that Tc migrated from the reactor zones at a faster rate than Ru.

RESULTS

SPECIAL MATERIALS PRODUCTION

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

1. Post Calcination Treatment of ICPP Wastes

1.1 ICPP Waste Vitrification (H. S. Cole and D. Gombert)

An alternative waste form for ICPP wastes is monolithic glass; the calcined waste would be converted into a leach-resistant glass. Experiments on glass formation were continued using 50 mL alumina crucibles to hold the sample melts in a furnace for 3 to 6 hours at temperatures ranging from 1050 to 1100°C. Melting time and temperature were varied for qualitative comparison of the finished glass to determine degree of vitrification and internal stress.

Leach tests were made on two new glass formulations, 13 and 14, and compared to 12. Glass 12 contained P_2O_5 which would be introduced if pelleted calcine were ever vitrified. Glasses 13 and 14 are borosilicate glasses, but 14 had a higher SiO_2 content to improve temperature stability (see Table 1 for compositions). In the 100 hr Soxhlet tests at 95°C (particle size -16 to +60 mesh) glass 13 leached 1.95% and glass 14 leached 3.08%, versus an overall average of 3.01% for other glasses studied to date. (Glass 13 had the lowest leach rate of the 14 glasses.) In the brine, acid, and caustic leaches (leach time 19 h at ambient), glass 12 ranged from 0.002 to 1.62%. Glass 14 leached more than 23% in the acid, and glass 13 leached over 31% in the acid; brine and caustic results averaged 0.001 to 0.341% for both glasses. Leach rates may have been affected by any of 3 factors now under investigation. The alumina crucibles tend to dissolve in the glass to a slight degree which adds aluminum oxide to melt and makes vitrification more difficult. Platinum crucibles are on order to avoid this problem. Another factor possibly influencing the leach data is the new method employed for crushing glass 14. Instead of grinding the annealed glass, the samples were heated to about 350°C, then quenched in water to fracture the glass. The micro-cracking caused by this process may lead to a misleadingly high leach rate. The other consideration is the composition of the glass itself.

The thermal conductivities of glasses 13 and 14 were measured and are shown graphically in Figure 1. These conductivities average about 40 to 50% of the value for a commercial window glass (0.052 vs. 1.13W/m·K at 373 K). The heat generation rate of ICPP waste is low, therefore, the glass has ample conductivity for heat dissipation.

Figure 1. Thermal Conductivity of Two Waste Glasses
from 300 to 500 K Temperature Range

ACC-A-2777

One problem unique to vitrification of ICPP calcine is the high fluoride content of the waste introduced as hydrofluoric acid in the fuel dissolution process; the fluoride is present in the calcine as CaF_2 . During the melting period, some of the fluoride in the waste is vaporized and could cause serious corrosion to both the refractories and off-gas system in continuous melters.

Experiments to study the degree to which fluoride is volatilized during melting have begun. The experiments involve heating the glass components (frit and calcine in a 2:1 mixture) in a quartz tube constantly purged with a wet ammonia vapor. The fluoride is collected as NH_4F before it can react with the glass tubing of the experimental equipment. The off-gas is then scrubbed in a series caustic bubbler system which collects any residual fluoride as NaF for analysis. An experiment has been run and samples submitted for chemical analyses.

TABLE 1
COMPOSITIONS OF GLASS FRITS*

	12 (wt%)	13 (wt%)	14 (wt%)
SiO_2	50.1	51.8	59.4
Na_2O	26.9	28.3	21.7
B_2O_3	16.2	12.9	11.2
ZnO	1.7	2.1	2.3
CaO	0.0	2.8	3.1
Li_2O	1.7	2.1	2.3
P_2O_5	3.4	0.0	0.0

*Glasses are made from a melt of 66 wt% frit and 34 wt% simulated calcine.

1.2 Pelleted Waste Form Development (K. M. Lamb)

Experiments were run to pelletize calcine containing the additives boron and zinc.¹ A mixture of 60 wt% bed calcine, 20 wt% calcine fines and 20 wt% metakaolin (Run-P-13A) did not produce uniform spherical pellets using a solution of 3.5M H_3PO_4 and 1.6 M HNO_3 as a liquid binder, because of excessive large bed particles (0.3-0.5 mm diameter). Only the smaller particles pelletized well; thus, the product was essentially bed particles with a thin coating of metakaolin and calcine fines. To improve agglomeration, the calcine bed particles were reduced by grinding to a range of 0.1 to 0.2 mm diameter. This calcine was mixed with 20 wt%

¹C. M. Slansky, et al., Technical Division Quarterly Progress Report, April 1-June 30, 1977, pp. 49-52, ICP 1123, July 1977.

metakaolin and 20 wt% calcine fines and pelletized (Run-13B) using a solution of 3.5M H_3PO_4 and 1.6M HNO_3 as the liquid binder. Uniform spherical pellets were readily formed; the pellets had good green strength. After air drying for ~48 hours, these pellets of 3 to 6 mm diameter were dusty and fragile, probably due to the low amount of H_3PO_4 used in the liquid binders. A pelletizing run (13C) was also made using 20 wt% metakaolin, 20 wt% calcine fines, 45 wt% ground bed, and 15 wt% ordinary bed calcine with a liquid binder of 6.5M H_3PO_4 and 1.7M HNO_3 . The 15 wt% bed was added as seed material for pellet growth. The pellets formed were < 3 mm in diameter, hard and slightly irregular in shape. The ground calcine requires more liquid binder than does a 3:1 mix of calcine bed and fines because a greater surface area must be wetted. For a solid feed rate of 210 grams/min, the ground calcine needs ~75 cm^3/min liquid binder compared to 26 cm^3/min for regular calcine. Additional pelletizing experiments to better define the feed and binder ratios needed are pending the preparation of more simulated calcine.

The Soxhlet leach rate of the pellets made from run 13C was 4×10^{-4} g/ cm^2/d for the first 100 hours of leaching. This compares to 1.6×10^{-4} g/ cm^2/d Soxhlet leach rate for pellets made from 60 wt% zirconia calcine bed, 20 wt% fines and 20 wt% metakaolin using a solution of 11M H_3PO_4 and 3.9M HNO_3 as a liquid binder.²

Experiments were begun to determine the feasibility of spraying colloidal silica as a liquid pellet binder. DuPont's Ludox HS-30 colloidal silica is 30 wt% SiO_2 and can be readily sprayed at flow rates as low as 12 cm^3/min because of its relatively low viscosity (4.5×10^{-3} Pa·s at 25°C) compared to H_3PO_4 . Colloidal silica is a possible replacement for H_3PO_4 as a liquid binder, because it may react well at the pellet heat treating temperatures to form leach-resistant silicates.

1.3 Pelletizing Pilot-Plant Development (S.J. Priebe)

The design for a mockup of a rotating tray heat treater has been completed and the unit is being fabricated. It will consist of a set of rotating slotted trays. Paddles will force the pellets from one tray to the next. Experiments concerning rotational speed, tray spacing, and paddle arrangement will provide information which will be incorporated into the design of the pilot-plant unit.

On a laboratory scale, microwave heated drying was proven fast and effective for simulated ICPP waste.¹ The system under consideration for the pilot plant will use a 6 kW microwave generator manufactured by Cober Electronics. The drying cavity will be about 1m x 1m x 1m. Pellets will pass through the chamber on a vibrating tilted tray made of ceramic or glass. An estimate of the power required for drying and heating the pellets to 200°C (31 kg pellets/h) is 3-4 kW. With heat losses, the 6 kW unit will be able to handle the largest anticipated pilot-plant throughput of pelletizer.

²C. M. Slansky, et al., Technical Division Quarterly Progress Report, October 1-December 31, 1977, pp. 27-30, ICP 1111, March 1977.

The pelletizing pilot-plant design criteria have been started. These criteria will be specific enough to submit to design engineering for detailed design. The design criteria are primarily for the module system, the off-gas system, and utilities and instrumentation. Some equipment (screens, oversize particle grinder, and heat treater) has not been specified, but will be designed into the system as information is provided. A bin and feeder system will be used to feed the calcine and solid binder.

1.4 Determination of Pelleted and Glass Waste Form Properties (H. S. Cole)

Analysis by neutron activation of pelleted and glass waste forms was made to determine if more accurate analyses than by chemical means could be obtained, especially for Cs. Activation analysis is being evaluated to determine loss by volatilization of elements when waste forms are prepared and elemental loss due to leaching. The CFRMF reactor at the Test Reactor Area was used to irradiate the samples at a nominal thermal flux of 5.5×10^{11} n/cm²/s. For pelleted waste, 100 mg samples were irradiated for one hour will give better accuracy for elements such as Cs and Ca. Flux monitors and elemental standards are used to calibrate the irradiations. Modification to an automatic sample counter on the gamma spectrometer is being made to improve counting geometries. Preliminary results indicate ²⁸Al and other short-lived nuclides can be determined immediately after activation, while ²⁴Na, ¹⁴³Ce, ¹⁵³Sm, ¹⁴⁰La, etc., can be determined after a decay period of a few hours. Longer-lived nuclides such as ⁴⁷Ca, ⁵¹Cr, ⁶⁵Zn, ⁹⁵Zr, ¹¹³Sn, ¹³⁴Cs, and ¹⁸¹Hf and other rare earths can be measured after a decay time of 1-3 weeks. Counting times of 180 minutes were used for the longer lived elements. The method appears promising as a reliable technique to determine overall material balance of the waste product components at various stages of product testing.

1.5 Calcine Dissolution Study (P. C. Butler, D. R. Trammell)

The solubility of ICPP simulated and radioactive waste calcine is being determined to provide preliminary dissolution data for the Programmatic Environmental Impact Statement related to removal of actinides from stored ICPP calcines.

The dissolution study was restricted to the use of nitric and hydrofluoric acids. Work was directed toward determining the concentration of acids which produce the greatest dissolution of simulated calcine. Various ratios of HNO₃ to HF at a calcine-to-acid ratio of 200 g/L were studied. The calcine (representative of actual wastes) was placed in the acid mixtures and heated for either 30 or 60 min at 70 to 95°C. Solutions were then filtered and the undissolved solids dried and weighed. In some cases, the solid compositions were identified by x-ray analysis. Both single and two-stage dissolutions were studied. In the two-stage experiments, dissolution was carried as far as possible with nitric acid alone followed by a nitric-hydrofluoric acid mixture.

The results of the study are summarized in Table 2. The data show that HNO₃ alone gives the most rapid and complete dissolution. At 8M HNO₃, about 72% of the solid was dissolved. Increasing the acid strength did

TABLE 2
CALCINE DISSOLUTION IN NITRIC AND HYDROFLUORIC ACID

First Dissolvent	Time & Temperature	% Dissolved	Second Dissolvent	Time & Temperature	Additional % Dissolved	Total % Dissolved
<u>M: HNO₃</u>	<u>30 min</u>		<u>M HF:M HNO₃</u>	<u>30 min</u>		
4	70°C	58.7		70°C		
6	"	68.4		"		
8	"	71.6	1.6:7.1	"	13.2	74.3
8	"	57.7	2 -	"	21.9	66.0
8a	"	70.2	- 8	"	37.1	81.4
10	"	70.4				
12	"	71.4				
8a	80°C	75.1	- 8	80°C	29.0	82.8
8a	"	78.5	1.6:7.1	"	12.7	82.3
6	90°C	79.9				
10	"	82.9				
8a	95°C	86.1	- 8	95°C	47.6	93.4
	<u>60 min</u>			<u>60 min</u>		
8a	70°C	72.8	6 -	70°C	14.0	76.1
<u>M HF:M HNO₃</u>	<u>30 min</u>			<u>30 min</u>		
7.0:4.0	70°C	19.0				
4.7:5.3	"	5.5	4 -	70°C	26.2	29.5
4.0:10.0	"	-8.9				
2.8:6.4	"	17.8				
2.0:6.8	"	45.1	4 -	"	5.4	47.6
1.6:7.1	"	49.1				
1.0:4.0	"	-23.5	- 8	"	24.6	17.6
1.0:10.0	"	48.9				
4.7:5.3	90°C	10.1				
1.6:7.1	"	51.2				
	<u>60 min</u>					
1.6:7.1	70°C	47.7				
	<u>30 min</u>					
2 ^a -	70°C	48.9				
4 ^a -	"	16.0				
6 ^a -	"	21.6	- .8	"	11.0	31.2

(a) Bed calcine ground to approximate fines particle size.

not increase the amount of solid dissolved. The addition of HF to HNO_3 at ratios from 7:4 to 1:10 significantly reduced the amount of solids dissolved. In fact, at high ratios of HF/ HNO_3 (2:5 and 1:4) the weight of solids remaining actually increased over the starting weight. X-ray analyses (Table 3) show that when only HNO_3 is used as a solvent, the solids remaining are CaF_2 and ZrO_2 . When HF is used, the residues also contained calcium fluozirconate.

Dissolution (Table 1) using HF/ HNO_3 mixtures following a straight HNO_3 dissolution did not significantly increase the amount of solids dissolved. It appears that in order to dissolve calcine to near completeness, very low calcine concentrations or acids other than HNO_3 -HF are needed.²

Plans for Next Quarter

Fluoride volatility and annealing point temperature studies will be continued. Glass compositions will be varied to evaluate glass properties such as volatility, leach resistance, and thermal conductivity. Visits to Savannah River and Hanford will be made exchange information and to investigate the possibility of getting a small laboratory-scale melter for research.

More synthetic calcine will be prepared for experimental use. Experiments to pelletize zirconia calcine will continue using colloidal silica and aluminum phosphate as liquid binders.

Detailed pellet pilot-plant design work will begin. Layout of the module in the gamma facility at TRA, the necessary additional utility lines, power requirements, and ventilation system will be determined.

A microwave heated pellet dryer will be tested, pending arrival of the microwave applicator unit. Tray angles, drying times, and weight of pellets to be dried will be determined. The rotating tray heat treater will be completed and tested.

Pelleted samples before and after heat treating and/or leaching will be evaluated for elemental losses by activation analysis. Losses due to melting and leaching of glass products will be determined.

Calcine dissolution with 8M HNO_3 will be repeated using a solid to acid ratio of 100 g/L. A "hot" calcine sample will be dissolved and the fraction of solids dissolved will be determined based on the best dissolution rate from cold experiments. The distribution of Pu between the solid and liquid fractions will also be determined. Volatiles from the dissolution will be trapped in 1M NaOH and any volatile radioactive and cationic species will be determined.

TABLE 3

X-RAY ANALYSIS OF UNDISSOLVED SOLIDS

<u>Dissolvent</u> <u>(M HNO₃)</u>		<u>Crystalline</u> <u>Components</u>
4		CaF ₂ , ZrO ₂
10		" "
<u>(M HF - M HNO₃)</u>		
7.0	4.0	CaF ₂ , CaZrF ₆ ·2-2.5 H ₂ O
1.6	4.0	CaF ₂ , CaZrF ₆ ·2-2.5 H ₂ O
1.0	4.0	CaF ₂ , CaZrF ₆ ·2-2.5 H ₂ O

2. Actinide Removal from ICPP Wastes

(L. D. McIsaac, J. D. Baker, J. F. Krupa, N. C. Schroeder)

2.1 Minimixer Settler Experiment

During this quarter, DHDECMP that had been purified on a CVC molecular still (88% pure) was used in a hot minimixer settler run to extract actinides from ICPP Zr-Al first cycle raffinate. Batch extraction studies indicated that 20% DHDECMP in 2:1 decalin-diisopropylbenzene was required to get an Am separation factor of 1000 at 23°C with a six-stage extraction and a 1:2-volume ratio of organic to aqueous flows. Decalin-diisopropylbenzene was chosen as the preferred diluent. This was the best choice based on extraction properties, dispersion and coalescence characteristics of the solvents.

Cerium-144 was used as an internal tag on extraction efficiency because of the prominence of its 133 keV gamma-ray which is easily detected using a Ge(Li) spectroscopy system and because of its similarity in extraction behavior to Am.

Based on batch extraction data and known extractor efficiency and temperature correction factors, it was calculated that 98% of the ¹⁴⁴Ce should be removed. This is in good agreement with the measured value of 98.4%. Mass analyses for Pu and Am decontamination factors are in progress. Samples were purified for mass analysis by methods previously reported.³

³Baker, J. D. and McIsaac, L. D., Isotope Dilution Analysis of Pico-gram Quantities of Plutonium, Americium, and Curium in Nuclear Fuel Processing Plant Waste Streams, ICP-1094 (June 1976).

The actinides coprecipitated on a rare earth oxalate precipitate which formed in the first several stages of the strip minimixer settler. Precipitation was caused by a combination of higher concentration of rare earths (roughly a factor of two) and the use of a lower acidity strip (.005 M vs .05 M HNO_3) than previously used in batch strip experiments. From this experience, it was decided that a two-step strip, 0.005 M HNO_3 -0.05 M hydroxylamine nitrate (HAN) followed by 0.005 M HNO_3 0.05 M $\text{H}_2\text{C}_2\text{O}_4$, would be used in subsequent minimixer settler experiments to prevent rare earth oxalate precipitation. The first strip (0.005 M HNO_3 -0.05 M HAN) would reduce the rare earth concentrations below the solubility product of their oxalate complexes. When the stripping minimixer settler was stopped, Am was removed to less than detectable levels while $\sim 0.02\%$ of the Pu remained in the organic phase.

A quantity of DHDECMP which had been through the entire mixer-settler experiment was sequentially washed with equal volumes of 0.05 M Na_2CO_3 and H_2O . The extraction characteristics of this material are nearly identical to those of the initial extractant. This information shows that DHDECMP can be recycled. Further studies in this area are needed to determine how many times DHDECMP can be recycled.

2.2 Radiolysis of DHDECMP

Batch extraction experiments were performed using radioactive Zr-Al waste and 20% DHDECMP in 2:1 decalin-diisopropylbenzene. The removal of Pu from DHDECMP was studied. One set of measurements was made with DHDECMP that had received the radiation dose of once through a pulse column. The other set of measurements was made with DHDECMP that had received the radiation dose of 100 passes through a pulse column ($\sim 20 \text{ Wh}\cdot\text{L}^{-1}$). After three strips with 0.005 M HNO_3 - 0.05 HAN and three strips with 0.005 M HNO_3 -0.05 $\text{H}_2\text{C}_2\text{O}_4$ strips, the residual Pu was $\sim 0.005\%$ in each case. This shows that radiolysis degradation of DHDECMP does not affect actinide stripping.

2.3 Mercury Extraction Studies

Mercury has been extracted from synthetic Zr-Al waste using $\sim 97.5\%$ pure DHDECMP. The distribution coefficient for Hg is higher than reported earlier for 97 + % pure DHDECMP (31 vs 1.6). Previously, it was felt that impurities in the DHDECMP were the principal cause for Hg extraction. It is now thought that residual isopropanol, used in the purification of DHDECMP, interfered with the extraction of Hg in the previous experiments.

The problem of stripping Hg from DHDECMP has been reported earlier.⁴ This quarter Hg has been successfully removed from DHDECMP. The technique utilizes an electrolytic flow cell with a residence time of 15 minutes and an electrode gap of 3 mm. The anode and cathode were platinum and mercury, respectively. DHDECMP was loaded with mercury to

⁴Buckham, J. A., Idaho Chemical Program Annual Report for FY-1975, ICP-1086.

to the equivalent of one pass through an extraction column (0.004 M). This was accomplished by extracting the appropriate amount of mercury from 1.5 M HNO_3 . Therefore, the organic was ~ 0.025 M in HNO_3 . At a potential of 100 V dc and current of ~ 0.9 mA, approximately 75% of the mercury was removed.

2.4 Diluent Study

Several commercially available solvents received from Amsco division of Union Oil Company were tested as possible diluents for DHDECMP. Of the solvents studied, high flashpoint Naphtha, D65, F65 and "F" exhibited the highest influence on Am extractability. On the basis of the D_{Am} , none of the solvents were superior to technical grade diisopropylbenzene.

2.5 DHDECMP Purification

DHDECMP has been purified to $\sim 98\%$ using liquid chromatography techniques. The method and results are discussed in the section of this document entitled "The Study of Bidentate Compounds for Separation of Actinides from Commercial LWR Reprocessing Waste".

2.6 Engineering Studies

One hundred and twenty litres of DHDECMP have been ordered so that cold pilot plant extraction tests can begin. The contract was awarded to Wateree Chemical Company which has been the sole supplier of the extractant up to this time.

Methods for tracing an upcoming pilot plant run using rare earths as simulators for americium are being studied.

Plans for Next Quarter

The study of mercury extraction and removal will continue. A method of following the cold pilot plant run using rare earths as simulators for americium will be developed. The extraction behavior of highly purified (99 + %) DHDECMP will be studied with selected elements.

3. Calcined Solids Retrieval and Handling

3.1 Program Management (J. S. Schofield)

The program plan for calcined solids retrieval and handling was completed. The plan covers the period FY-77 through FY-83 and includes bin sampling, cold prototype retrieval equipment development, calcine stabilization, calcine packaging, retrieval nozzle development, and plant-scale equipment conceptual design.

Work is proceeding on schedule in all areas with the exception of the calcine bin sampling project. This has been delayed approximately two months due to the involvement of cognizant Waste Management and Plant Engineering personnel in fuel storage basin work. This delay can be made up provided the basin support work can be terminated soon and additional personnel brought on board.

3.2 Retrieval Nozzle Development (T. R. Byrnes)

Upgrading of the existing solids retrieval equipment in CPP-620 has been completed with the exception of substituting a vertical pipe for the present one containing several bends after discharge of the rotary feed valve. Equipment upgrade included addition of (1) a new rotary feed valve, (2) various air flow rotameters, (3) nozzle holder, (4) miscellaneous piping revisions and repairs, and (5) a receiving drum lid.

Standardization tests were run on the existing retrieval nozzle using a cold zirconia calcine granules and fines mixture. Standardization tests are run to determine a nozzle's performance as influenced by various operating parameters.

The highest retrieval rate obtained for the calcine through the two-inch diameter nozzle was approximately 1600 kg/h (3500 lb/h). An average rate of ~ 340 kg/h (750 lb/h) would be necessary to completely empty a bin in Bin Set 2, 3, or 4 in about one month.

Each standardization test has been run by allowing the retrieval nozzle to feed under its own weight into the calcine in a vertical position. Parameters varied included the air flow rate from the nozzle annulus, air injection of the nozzle throat and the overall flowrate. Use of the air injection reduces the retrieval rate in all but a few instances where there is no flow through the annulus. Maximum retrieval through the two-inch-diameter nozzle appears to occur at a flow rate of ~ 25 m³/h (15 cfm) through the annulus regardless of the total air flow. While the retrieval rate increases with increasing air velocity, it appears the most efficient retrieval rate (in kg calcine transferred/m³ air) occurs at a total air velocity of ~ 11.5 - 12.0 m/s, except for instances where the ratio of air flow through the annulus to total air flow is $\leq \sim 0.01$. The retrieval nozzle is shown in Figure 2.

Comparison retrieval tests were run using the CaCO₃ and MgO fines recommended by Jenike and Johanson for use as calcine simulants. The MgO was ineffective and would cake up and plug the retrieval line. The CaCO₃ retrieved at the same rate as calcine, or greater, in most of the tests. Further testing will be done using a CaCO₃ granules and fines mixture.

Equipment was designed and is being fabricated to test a rotating nozzle concept for eliminating ratholing problems during retrieval. This system is a rotating (~ 0 - 2 rpm) nozzle head equipped with spring loaded arms which should effectively break up any packed calcine material as it rotates, allowing the calcine to fall down to the feed nozzle where it can be retrieved pneumatically. The spring-loaded arms should prevent damage to bin internals.

3.3 Bin Sampling (J. A. Hendricks and J. S. Schofield)

Calcine will be sampled in bins 3 and 7 in Bin Set 2. A commercially available soil sampler will be used to obtain a core through the entire depth of each bin. The core will be made up of 2-ft lengths of split

ACC-A-2188

Figure 2. Retrieval Nozzle Used for Standardization Tests

wall sampler tubes. These tubes will be drawn up through a platform surrounding each bin riser into a sample container cask. Each section is unscrewed remotely from the core, using a device built into the platform, and stored inside the cask. Each cask can hold up to seven 2-ft core sections. These casks are then stored until they can be transferred to the Multicurie Cell for sample removal and inspection.

The core driller and associated sampling pipes, clamps, etc., have been ordered. Most of the sample analysis equipment to be used in the Multicurie Cell has also been ordered. Design work is approximately 70% complete on the major equipment items to be fabricated. Most of these will go out for bid during October.

The safety review for the bin sampling project will be started about October 1, 1977. This is approximately two months behind schedule. This delay has been due to Plant Engineering personnel who were assigned to the calcine sampling project equipment design, and Waste Management personnel assigned to the safety review, having to work on various CPP-603 projects.

3.4 Cold Prototype Retrieval Equipment (J. A. Hendricks)

A draft of the design bases and requirements for the cold prototype retrieval equipment has been issued for comments. The final copy will be issued by October 1, 1977. These will be used as the basis for subsequent equipment design by an A-E. A formal request was made to EG&G for use of the MTR reactor containment building to house the retrieval equipment.

Plans for Next Quarter

Approval for use of MTR containment structure for housing retrieval equipment will be obtained. An A-E for equipment design will be selected and conceptual design and performance specifications started.

Bin sampling safety review will be completed and O&ES and Safety Review Board (SRB) approval obtained. The drilling apparatus and core samplers will be tested; design for the sample cask storage rack will be completed. A draft outline of sample analysis operations in the Multicurie Cell will be prepared.

Comparison tests with CaCO_3 granules and fines mixture will be conducted. A rotating nozzle for eliminating ratholing problems will be installed and tested. Testing on miscellaneous other nozzle design will be conducted and design work on other means of eliminating ratholing during retrieval and on agglomerated calcine started.

4. ICPP Defense Waste Document/Programmatic Environment Impact Statement

(N. A. Chipman, W. B. Kerr, M. S. Carr)

The "Alternatives for Long-Term Management of Defense High-Level Radioactive waste" (DWD) document was submitted to WPR on August 5, 1977,

after being edited and revised by Ford, Bacon, and Davis, Utah, Inc. The technical editing and format revision were required to make the DWD conform with style content and format of a similar document written at Savannah River. Comments received from WPR were incorporated at this time. The DWD was final typed on photographic mats and submitted to WPR for final review and publication on August 5, 1977.

Preliminary work has been started to prepare a Programmatic Environmental Impact Statement (PEIS) for several candidate alternatives for the management of the Defense High-Level Radioactive Waste generated at the ICPP. The candidate alternatives selected for the document are:

- (1) No action -- continue current operations. Dispose of calcine (with actinides) in licensed bins at INEL.
- (2) Calcine (with actinides) is pelletized; disposal is in licensed bins at INEL.
- (3) Calcine (with actinides) is converted to glass; disposal is at INEL.
- (4) Actinide-free calcine disposal in licensed bins at INEL. Actinide-fraction is solidified for disposal at Federal Repository.
- (5) Stabilized calcine (with actinides) for disposal at Federal Repository.
- (6) Calcine (with actinides) is converted to glass for disposal at Federal Repository.

Preconceptual designs will be completed (for those alternatives not included in the DWD) by an A-E. A scope of work has been prepared for this work. Preliminary schedules, costs, and manpower estimates were developed. The document is scheduled to be completed for submittal to WPR by August 1978. A detailed outline of the PEIS was submitted to ERDA-ID and WPR for review and comment.

II. ICPP PLANT PROCESS IMPROVEMENTS

1. Zirconium Fuel Recovery Process (M. L. Gates)

For the reporting period, efforts were expended exclusively in chemical and engineering verification studies for the Fluorinel process to be installed at ICPP.

The Fluorinel headend system for zirconium alloy fuel will be installed in a new 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 facilities for fuel storage and handling, off-gas cleanup systems, several casks, improved analytical systems, and various safety and control systems. Existing facilities at the ICPP will be used to extract the uranium from the dissolver product and process the radioactive waste.

1.1 Solids Characterization (S. Wildman)

Solids which occur during Fluorinel fuel processing were characterized to determine: (a) the temperature of transition for loss of water bound to the solids, and (b) an estimate of the water in the sample which could be removed by exposure to elevated temperatures. This information is required for the design of a neutron interrogator to analyze these solids.

Test solids were obtained by dissolving small quantities of a typical Fluorinel fuel. This was followed by separating the residue and drying to constant weight at ambient temperature (298 K). Water losses of the solids were measured at 7 different temperatures using a DuPont Model 26-321 High Temperature Solids Moisture Analyzer. This instrument is designed to determine moisture release at any specified temperature by measuring the current required to electrolyze the moisture after it is removed from the sample by a heated carrier gas stream. The maximum temperature used was 973 K. X-ray fluorescence was used to determine changes in sample composition. The test results are summarized in Table 4.

X-ray analysis indicated that the first detectable change in the crystal structure of the residue occurred at 623 K, followed by another change at 973 K. The crystalline specie(s) present could not be identified.

1.2 Pilot Plant Filter System (K. F. Childs)

Scoping studies on the suitability of using an etched-disc filter to remove solids from the Fluorinel dissolver product are underway. Slurries composed of 0.1% by weight ZrO_2 in water were used to simulate the Fluorinel dissolver product. The equipment used for the filter studies consists of a feed tank, progressive cavity pump, etched-disc filter, backflush gas accumulator, waste can, vent tank, and associated

TABLE 4

THERMOGRAVIMETRIC ANALYSIS OF TYPICAL FLUORINEL PROCESS SOLIDS

Sample No.	Temperature (K)	Moisture Released (Weight %)
1	373	3.62
2	398	4.39
3	423	4.91
4	473	6.02
5	523	7.36
6	623	7.52
7	973	7.23

piping, valves, and gauges. A schematic of the test loop is shown in Figure 3. Filter element solids loading was studied as a function of the differential pressure, flow rate, and particle size. Solids recovery versus backflush pressure was also studied.

The data shows the following trends: (a) At constant differential pressure, the solids loading varies inversely with the flow rate, (b) at constant differential pressure, the solids loading varied directly with the particle size, and (c) the design criteria particle size mixture behaved as would particles of a single size equal to the weighted average of the mixture. The solids loading versus the differential pressure across the filter for three flow rates tested is shown in Figures 4 to 6. The results in Table 5 indicate that backflush pressures of 690 kPa (100 psi) and 2070 kPa (300 psi) are most effective on the initial backflush. The backflush at 1380 kPa (200 psi) was poorer on the initial backflush. The differential pressure across the filter was returned to initial levels in all cases after one backflush. The differential pressure can be reduced to initial levels after one backflush even though all solids are not removed from the filter as can be seen in Figures 4, 5, and 6. The differential pressure versus solids loading curves are very flat until loadings of over 60% of the maximum are reached.

Total solids recovery was excellent in all cases; however, more solids were carried over into the vent line from the waste can as the backflush pressure was increased. This could be eliminated by modifying the waste can design as shown in Figure 7.

The filtrate was sampled and refiltered. No significant amounts of fines were lost in the filtrate. Pumping the ZrO_2 slurry results in some particle size reduction. The fines generated were retained on the filter except for some lost in the first minutes of operation, probably

TABLE 5
SOLIDS RECOVERY VS BACKFLUSH PRESSURE^a

Backflush Pressure (kPa)	Filter ΔP (kPa)			Solids Loading (g)	% Solids Recovery		% Solids in Vent
	Fully Loaded	1st Backflush	2nd Backflush		1st	2nd	
690	407	17.2 ^b	20.7	3300	93	101	2
1380	393	20.7	20.7	3400	58	97	8
2070	289	20.7	20.7	3400	96	100	12

^aResults for < 44 μm solids at 129 L/min·m² of filter element

^b17.2 kPa (2.5 psi) is equivalent to 20.7 kPa (3.0 psi) within experimental accuracy

before enough solids were collected to act as a precoat. The fines recovered with the filter cake during backflushing appeared as a milky colored, very slow settling slurry with a particle size estimated to be less than 37 μm .

The overall performance of the filter was excellent. Solids loadings under the most severe conditions (128 L/min·m² and < 44 micron particles) were up to 3400 g at 413 kPa differential pressure. This corresponds to a 10.9 kg solids loading on a full scale filter (30 L/min and 0.233 m²). This would allow more than one complete batch of dissolver product at 7.5 kg solids per batch to be processed before backflushing. The solids loading obtained with the design mixture at 129 L/min·m² was 3950 g at 413 kPa differential pressure, which would correspond to a 12.7 kg loading in a full scale unit.

Pump performance was less than satisfactory. Excessive noise and vibration were generated when pumping slurries at temperatures above 300 K. Below this temperature the noise and vibration were present for 2 to 4 minutes after startup and intermittently thereafter. The use of a water flush for the packing eliminated the symptoms except for 1 to 2 minutes at startup. The noise and vibration were probably due to cavitation since the symptoms were the same when the pump was artificially cavitated by injecting nitrogen gas into the feed line. Slippage in the pump was also a problem. The flow rate dropped from 12.7 L/min at 138 kPa differential pressure to 6.6 L/min at 689 kPa differential pressure. The pump is rated at 11.4 L/min at 689 KPa. The manufacturer has been unable to determine the cause of the noise and vibration or a solution to the drop in flow rate at higher pressures. Therefore, a progressive cavity-type pump is not recommended.

The overall performance of the pilot plant filter system was very

Figure 3. Etched-Disc Filter Loop Schematic

satisfactory. A filter system utilizing an etched-disc filter could be a viable means of removing solids from the Fluorinel dissolver product. The selection of a suitable pump should present no major problems. A survey of the vendor literature is underway to identify pumps that have the potential for satisfying Fluorinel process design requirements. The selection of a pump(s) for future testing will be made on the basis of this survey.

1.3 Pilot Plant Centrifuge (K. F. Childs, D. H. Preussner)

Initial testing of the horizontal, continuous, solid bowl centrifuge with simulated process slurries of 0.1% ZrO_2 in water has been completed. Independent variables tested were: (a) rotational velocity, (b) particle size, and (c) feed flow rate. Solids were recovered, dried, and weighed both from the solids discharge port and from the liquid effluent to yield data on solids removal efficiency.

During the runs, slurry was gravity fed to the centrifuge in 50 L batches. When the amount of solids recovered out the discharge port per batch stabilized, the system was assumed to be at a steady state (i.e., solids cake in bowl at maximum capacity). Approximately 680 g of ZrO_2 solids were fed into the centrifuge before solids were obtained out of the discharge port, thus the bowl holdup is assumed to be this amount. Solids recovery data were then taken on the next 3 to 4 batches. The results obtained are presented in Tables 6 and 7.

The material balance on the tests was fairly good, averaging approximately 92%. Solids were detected in the liquid effluent at a ratio of less than one gram per 150 g of solids fed. However, for the purpose of calculating the percent solids removed, it was assumed that all losses occurred via the liquid effluent. This probably makes the percent removal results more conservative than they actually are since the unaccounted for solids are likely due to a combination of changes in bowl holdup due to changes in particle size, cake moisture content, or flow rate.

The results show that feed flow rate and centrifuge rotational velocity appear to have little effect on solids removal efficiency. Particle size also appears to have little effect, although the percent removal appears to decrease slightly as the particle size decreases. However, higher rotational velocity, increased particle size, and decreased feed flow rate all tend to decrease the moisture content of the discharged solids.

No significant evidence of erosion of the centrifuge internals was seen after 30 hours of operation with ZrO_2 and water slurries. The equipment ran relatively quietly and with minimal vibration.

The overall performance of the pilot plant centrifuge system was very satisfactory. A system utilizing a horizontal, continuous decanting centrifuge could be a viable means of removing solids from the Fluorinel dissolver product. The performance of the centrifuge compared well with that of the etched-disc filter.

Figure 4. Etched-Disc Filter Solids Loading at 51.5 L/min.m²

Figure 5. Etched-Disc Filter Solids Loading at 103.0 L/min.m²

Figure 6. Etched-Disc Filter Solids Loading at 128.8 L/min.m²

Figure 7. Backflush Waste System Design

ACC-A-2779

TABLE 6
CENTRIFUGE SOLIDS REMOVAL EFFICIENCY

157 rad/s (1500 rpm)

<u>Particle Size μm</u>	<u>Percent Removal</u>			
	<u>Feed Flow Rate (L/s)</u>			
	<u>0.09</u>	<u>0.18</u>	<u>0.40</u>	<u>Average</u>
<88 >74	98%	108%	87%	98%
<74 >44	83%	98%	86%	89%
<44	108%	86%	78%	88%

204 rad/s (2290 rpm)

<u>Particle Size μm</u>	<u>Percent Removal</u>				
	<u>Feed Flow Rate (L/s)</u>				
	<u>0.09</u>	<u>0.18</u>	<u>0.40</u>	<u>0.52</u>	<u>Average</u>
<88 >74	75%	97%	105%	90%	92%
<74 >44	a	93%	99%	90%	94%
<44	a	91%	84%	91%	98%

318 rad/s (3040 rpm)

<u>Particle Size μm</u>	<u>Percent Removal</u>			
	<u>Feed Flow Rate (L/s)</u>			
	<u>0.18</u>	<u>0.40</u>	<u>0.52</u>	<u>Average</u>
<88 >74	88%	99%	99%	95%
<74 >44	91%	97%	97%	94%
<44	91%	97%	85%	91%

^aData not available.

TABLE 7

CENTRIFUGE DISCHARGED SOLIDS APPEARANCE

157 rad/s (1500 rpm)

		Appearance		
		Feed Flow Rate (L/s)		
Particle Size μm		0.09	0.18	0.40
<88	>74	dry powder	slight caking	wet mud
<74	>44	dry powder	slight caking	wet mud
<44		slight caking	wet mud	fluid mud

240 rad/s (2290 rpm)

		Appearance			
		Feed Flow Rate (L/s)			
Particle Size μm		0.09	0.18	0.40	0.52
<88	>74	dry powder	dry powder	dry powder	slight caking
<74	>44	a	dry powder	caking	damp cake
<44		a	dry powder	damp cake	damp cake

318 rad/s (3040 rpm)

		Appearance		
		Feed Flow Rate (L/s)		
Particle Size μm		0.18	0.40	0.52
<88	>74	dry powder	dry powder	dry powder
<74	>44	dry powder	dry powder	dry powder
<44		dry powder	dry powder	slight caking

^aData not available

1.4 Fluorinel Dissolver Bottom Mockup (K. F. Childs)

Initial testing of the proposed dissolver bottom design for the Fluorinel process indicated that the proposed design would not satisfy the design criteria. The design criteria specifies that the agitation provided in the dissolver must be capable of suspending the solids encountered during dissolver operation. Therefore, special studies were undertaken to determine the modifications to the design which would be necessary to satisfy the design criteria. The results of both the initial studies and the special studies completed to date are presented here.

The dissolver bottom mockup was designed as a 1/5 scale model based on cross-sectional area of the lower 0.6 metre height of the proposed Fluorinel dissolver. The glass mockup was 40.6 cm I.D. with three 2.8 mm I.D. sparge tubes located around the perimeter of the inverted dish bottom, spaced as designed by the architect/engineer, as shown in Figure 8. The liquid height in the tubes was 246 cm and was controlled by a standpipe. A timing device controlled the sparge pulse sequence such that the three tubes could be pulsed successively or simultaneously for variable lengths of time and at variable intervals. ZrO_2 and lead powders in water were used to simulate the various solids and liquids to be encountered during dissolver operation.

After initial testing showed the 2.8 mm I.D. tubes to be ineffective, the sparge tube I.D. was increased to 5.7 mm resulting in a 4.7 increase in sparge liquid volume. The tubes were further increased to 7.7 mm I.D. resulting in an additional 1.8-times increase in volume. Larger I.D. tubes could not be used without major modifications so reservoirs were installed in the 7.7 mm I.D. lines to provide additional sparge liquid volume. Initially, 350 mL reservoirs were installed resulting in a 4-times increase in volume. Then the reservoir volume was doubled to 700 mL, resulting in an additional 1.7-times increase in volume and giving a total sparge volume increase of 59-times the original 1/5 scale mockup. This is 12-times the volume available in the proposed full scale dissolver. In tests with each of the tube sizes mentioned, the nitrogen motive gas pressure was varied from 27 to 207 kPa. Tube exit velocities corresponding to these pressures are shown in Figure 9. The effects of the variables described above on the agitation of the solids are presented in Figures 10, 11, and 12. The sketches illustrate a side view of the suspended solids and a bottom view of the areas cleared by the sparge tubes. The areas covered with drifts of solids are darkly shaded and the suspended solids are lightly shaded on the sketches.

It can be seen in Figure 10 that the effect of increased sparge velocity at constant sparge liquid volume (for the 2.8 mm I.D. tubes) was to increase the cleared area at each tube at the expense of creating deeper drifts. Very little solids transfer between clear zones was seen. Velocities greater than 3 m/s show little additional gain in clear area due to the reduced sparge duration (due to the fixed volume) and the flow profile not being fully established in vessel.

In Figure 11, the effect of increased sparge duration (volume) at constant

Figure 8. Dissolver Bottom Mockup Schematic

Figure 9. Sparge Tube Exit Velocity vs Nitrogen Pressure

Figure 10. Performance of Original 1/5 Scale Mock-up (280 g ZrO_2 Solids)

280g ZrO_2 SOLIDS

4.6 m/sec EXIT VELOCITY

ACC-A-2781

Figure 11. Effect of Increased Sparge Tube Volume at Constant Velocity

7.7 mm I.D. TUBES WITH 2-350 ml RESERVOIR 4.6 m/sec. SPARGE TUBE EXIT VELOCITY

SIDE VIEW

BOTTOM VIEW

500g ZrO_2
90% solids
suspended

2600g ZrO_2
20% solids
suspended

500g Pb
70% solids
suspended

2600g Pb
15% solids
suspended

ACC-A-2782

Figure 12. Effect of Increased Solids Loading at Constant Velocity and Volume

velocity can be seen. The increase in cleared area is not a direct function of the increase in sparge duration. For example, the change between the 7.7 mm I.D. tube, without and with the 350 mL reservoir, results in a sparge duration increase of four times, but the change only doubles the cleared area.

Figure 12 shows the effects of the particle density and total solids loading on sparging at constant velocity and volume. Increased solids loading at constant density acts to damp out the effect of the sparge jets reducing the clear area; however, the total amount of solids in suspension was relatively unchanged. The mass of lead in suspension was less than the mass of ZrO_2 but not as low as expected. The clear areas with the 2600 g of lead loading are actually larger than with 2600 g of ZrO_2 , thus it is apparent that the lesser volume of lead with respect to ZrO_2 at a given solids loading offsets the effects of the higher density to some extent.

The results indicate that all of the design modifications tested failed to satisfy the design criteria for complete dissolver agitation. The major variables affecting sparge efficiency were found to be sparge duration (volume) and velocity. Pulse sequencing had only minor effects at the conditions tested. The nozzle orientation (0 to 90° from the tangent to the vessel wall) and nozzle designs were also of minor effect, changing solids drift patterns rather than improving solids suspension. The dissolver bottom mock-up studies will continue with alternate bottom designs and with different tube designs.

PLANS FOR THE NEXT QUARTER

The dissolver bottom mockup studies will continue during the next quarter. A full-scale dissolver bottom mockup will be designed and installed. Studies will be conducted on the dissolution characteristics of typical Fluorinel process solids using conditions with no effective solids sparging. Other design verification studies will be conducted as scheduling permits.

2. Corrosion of METGLAS^a (C. A. Zimmerman)

METGLAS, a boron containing material, has possible application as a fixed nuclear poison. One formulation alloy 2826A has a nominal composition of $Fe_{40}Ni_{40}P_{14}B_6$, but can be varied to contain up to about 5.5% boron. METGLAS alloy 2826A has exhibited corrosion resistance in tests made by the manufacturer in 6% ferric chloride ($FeCl_3$) solution at 60°C, and in a solution of salts in 1M nitric acid (HNO_3) at 40°C. Additional laboratory screening tests on the above formulation have been made recently at the ICPP using boiling process and decontamination reagents routinely used at ICPP. The corrosion results are shown in Table 8.

^aTrade mark of Allied Chemical Corporation

TABLE 8

CORROSION TESTS OF METGLAS

<u>Boiling Solution</u>	<u>Corrosion Rate ($\mu\text{m}/\text{month}$)</u>
2 <u>M</u> Nitric Acid	20.48
8 <u>M</u> Nitric Acid	Totally Dissolved (Less than 77 hours)
6 <u>M</u> Sulfuric Acid	Totally Dissolved (Less than 17 hours)
2 <u>M</u> Nitric Acid - 7 <u>M</u> Hydrofluoric Acid	Totally Dissolved (Less than 78 hours)
8 <u>M</u> Nitric Acid - 1 <u>M</u> Hydrofluoric Acid	Totally Dissolved (Less than 18 hours)
1.5 <u>M</u> Nitric Acid - 0.2 <u>M</u> Hydroxylamine Sulfate	31.5
6% Turco 4502 (Alkaline Permanganate)	0.053
10% Oxalic Acid - 2% Citric Acid	6.93

Samples tested in highly corrosive solutions such as 8 M nitric acid, 6 M sulfuric acid, and mixtures of nitric acid and hydrofluoric acid were totally dissolved.

The total dissolution of the four specimens in boiling acid media indicates that this particular formulation of METGLAS is not applicable as a fixed neutron poison in contact with solutions used at ICPP. Additional testing of METGLAS material is planned if new formulations are produced which might be applicable to ICPP process conditions.

3. Uranium Accountability Measurements - Comparison of Separation Methods for Uranium IDMS (S. Kelly, Jr.)^a

This study was made to compare the effectiveness of three different separation methods used to prepare samples for isotopic dilution mass spectrometry (IDMS). The methods are: (a) U-Sep-2 (tentative), used routinely during the recent copressing run at the ICPP; (b) resin column anion

^aThe author wishes to thank the following people for their help and useful discussions: The mass spectrometer operators, E. E. Filby, S. D. Reeder, and D. R. Trammell.

exchange, used commonly for non-routine separations; and (c) liquid anion exchange, adapted recently from a literature method.^{5,6} The methods were judged on the basis of uranium recovery, time of analysis, running behavior in the mass spectrometer, "forgiveness" of the methods to mistakes, and possible unusual features.

Each of the methods starts after the hexone extraction since the decontamination steps (U-Sep-1) are the same in all three. A natural uranium solution (NBS-308) was extracted into hexone and standardized at 1.630 mg/mL uranium. Regular testing of this stock solution verified that the concentration remained constant.

Table 9 contains data collected for uranium recovery, time of analysis, running behavior, and the total time.

TABLE 9
COMPARISON OF METHODS FOR SAMPLE PREPARATION

Method	Average % Recovery	Analysis* Time	Running Behavior	Total Time Analysis & Drying
U-Sep-2 (tentative)	62.2±7.06	~50 min	Good	2.5 h
Liquid Anion Exchange	89.9±2.87	~40 min	Good	.75 h
Column Anion Exchange	85.3±1.56	~75 min	Good	3.0 h

*Time of analysis per set of five samples; does not include drying or evaporation time.

Method U-Sep-2 (tentative) has a consistent recovery of 50-70%. The loss is largely due to the inability to quantitatively transfer the resin to a column after it has been contacted with the uranium-bearing hexone and also to the residual uranium left on the column after the short elution step.⁷ To elute all the uranium would require numerous washes. The analysis time is moderate, ~ 50 min per set of five samples, but a 1-2 h sample drying time must also be considered.

Liquid anion exchange yields the highest recovery of 88-93%. The method

⁵S. D. Reeder, Technical Division Quarterly Report, April - June 30, 1977.

⁶F. L. Moore, Anal. Chem., **30** (5), p 909 (1958).

⁷Trammel, D. R. and Wade, M. A., "Investigation of Ion Exchange Purification of Uranium Samples after Method U-Sep-1 for Mass Spectrometric Analysis", PSAB Progress Report (March 1977).

uses triisooctylamine (TIOA) as the exchange agent, and TIOA is like other high molecular weight amines which are highly efficient as extractants. Liquid anion exchange also provides a more rapid separation ($\sim$ min per set of five samples), and the final product is a peroxide precipitate. The precipitate can then be washed with acetone and requires a drying time of only $\sim$ 5 min. However, it was found that care must be taken during the peroxide precipitation because of internal pressure buildup.

A possible critical variable in each of the three methods is the HCl concentration. All three methods would be fairly forgiving if the concentrations of the acids were varied within a ± 2.0 M range. Figures 13 and 14 show this to be the case.

Figure 13 is applicable to U-Sep-2 and column anion exchange⁸ which call for 8 M HCl and 10 M HCl, respectively. The HCl concentration can be varied with no major loss of uranium. Figure 14 applies to liquid anion exchange. It indicates that a high acid concentration (8-10 M) would be ideal. However, since TIOA has a high affinity for zirconium at > 6 M HCl, 4 M is used in the method with no appreciable losses.

All samples prepared by the three methods (10 samples by each method) ran well in the mass spectrometer and produced good ion beam characteristics. Strong, steady beams and low standard deviations for the major mass peaks were common to all samples. A great deal more data is needed to make a more definitive comparison.

Thus, it was found that all three methods are workable for IDMS. Liquid anion exchange offers a faster method of separation for process uranium samples with somewhat higher yields. Column anion exchange offers possibly cleaner samples but requires much more time. Lastly, U-Sep-2 (tentative) produced the lowest yield in a moderate amount of time. U-Sep-2 (tentative) has practical merit in that it is the only method of the three that has been used in a process run at the ICPP.

⁸Kraus, K. A. and Nelson, F., "Anion Exchange Studies of the Fission Products", "Peaceful Uses of Atomic Energy", Proc. 1st Internat'l. Conf., Geneva, 1955, Vol II, p 113 (1956).

Figure 13. Extraction of Uranium from Hydrochloric Acid onto Anion Exchange Resin

Figure 14. Extraction of Uranium from Hydrochloric Acid into Tri(isooctyl)amine, TIOA, (5% in Xylene)

III. ADVANCED GRAPHITE FUELS REPROCESSING

(L. W. McClure)

The Rover processing equipment, currently being installed at the ICPP will serve as the headend process for recovering uranium from the Rover nuclear rocket fuels. In this process, the bulk of the graphite fuel matrix is converted to CO_2 in a primary burner. The residual graphite is combusted in a secondary burner to produce an ash consisting of U_3O_8 , $\text{Nb}_3\text{UO}_{10}$, and Nb_2O_5 . This ash is then dissolved, leaving 60% of the Nb_2O_5 as a solid residue. These undissolved solids are removed by a continuous solid bowl centrifuge, and the clarified solution is fed to the existing ICPP solvent extraction system. Current pilot-plant work provides verification of process designs which have been specified for the Rover facility and recommendations for rectifying design deficiencies. The major effort during this quarter was expended on erosion testing of solids transport systems and the centrifuge.

1. Solids Transport Systems Testing (H. S. Meyer)

1.1 Performance Tests with Model 23A Ejector

The transfer of solids from the secondary burner bed makeup pot to the secondary burner weigh pot in the Rover Plant is made by Penberthy Model 23A ejector. Tests were performed to verify the effectiveness of this jet for transferring Al_2O_3 .

A Model 23A ejector was installed in the pilot plant to compare its performance to a Model 63A ejector which is used elsewhere in the process. The comparison in performance is shown below in Table 10.

TABLE 10

COMPARISON OF PERFORMANCE OF MODEL 23A AND MODEL 63A EJECTORS

Operating Pressure (kPa)	Model 23A Ejector		Model 63A Ejector	
	Air Flow (m^3/s)	Al_2O_3 Transfer Rate (g/s)	Air Flow (m^3/s)	Al_2O_3 Transfer Rate (g/s)
550	16×10^{-3}	32	23×10^{-3}	20
415	11×10^{-3}	29	18×10^{-3}	22
275	8×10^{-3}	24	12×10^{-3}	20

These tests verified that the Model 23A ejector will accomplish the transfer of Al_2O_3 between the two vessels.

1.2 Erosion by Simulated Primary Burner Ash

A simulated primary burner ash erosion test, completed previously using a mixture containing 2.2% Al_2O_3 , showed an erosion rate of about 20 $\mu\text{m/h}$. The test for this quarter was performed with a 4.4% Al_2O_3 mixture transferred at an operating pressure of 550 kPa through a Model 63A ejector. The results showed an erosion rate of 55 $\mu\text{m/h}$.

The apparatus was assembled as shown in Figure 15. The simulated ash was composed of:

<u>Component</u>	<u>%</u>
Al_2O_3	4.4
Graphite	41.4
Iron Powder	24.6
Soda Ash	29.6

The results of the test and the previous erosion tests are shown in Figure 16 and summarized in Table 11. These tests showed that the erosion rate ($\mu\text{m/h}$) is roughly 8 to 12 times the percentage of Al_2O_3 for a 1 1/2-inch welded elbow located 20 cm from the jet and for a 1 1/2-inch screwed elbow located 22 cm from the jet. The erosion on the 1 1/2-inch screwed elbow located 79 cm from the first elbow occurred probably as a polishing effect during the first exposure. Most of the kinetic energy was expended on the first elbow resulting in slower moving particles at the second elbow. The erosion rate on the 1-inch welded elbow does not appear to be as strong a function of Al_2O_3 content as it is with the 1 1/2-inch welded elbow.

1.3 Erosion in Capped Tee

One means of preventing high erosion rates on solids transport line elbows is by use of a capped tee. A welded 1 1/2-inch Type 304 Stainless Steel Schedule 40 tee was used to replace the first elbow shown in Figure 15, and a welded 1 1/2-inch elbow was installed as the second elbow. The tee was oriented so that flow entered one straight run and exited the branch (see Figure 17). The other straight run had a removable plug. The solids being transported built up in the tee thus protecting the walls. Al_2O_3 was transported through a Model 163A ejector with an operating pressure of 550 kPa.

During the test, the following were observed:

- (1) After 2.3 h, the 1-inch welded elbow failed. The total operating time until failure of this elbow was 24.8 h comprised of 6.3 h of Al_2O_3 transfer and 18.5 h of ash transfer. The elbow was replaced with a cast iron 1 1/2-inch screwed elbow.
- (2) After 7.8 h, an additional 5.5 kg of Al_2O_3 was charged to the filter vessel.

ACC-A-2715

Figure 15. Rover Solids Transport Test Apparatus

TABLE 11

RESULTS OF EROSION TESTS ON ROVER PROCESS ELBOWS

Region on Figure 16	Erosion Test	Duration of Test (h)	Elbow ^(a)							
			First				Second			
			1 1/2-Inch Screwed		1 1/2-Inch Welded		1 1/2-Inch Welded		1-Inch Welded	
			Thickness Lost, μm	Average Rate, $\mu\text{m/h}$	Thickness Lost, μm	Average Rate, $\mu\text{m/h}$	Thickness Lost, μm	Average Rate, $\mu\text{m/h}$	Thickness Lost, $\mu\text{m/h}$	Average Rate, $\mu\text{m/h}$
I	Al_2O_3 attrition	1	1000	1000	-- ^(c)	---	300	300	---	---
II	Al_2O_3 erosion	4	--	--	>3350 ^(d)	850	N ^(e)	N	1100	275
III	2.2% Al_2O_3 Primary Burner Ash	8	--	--	152	30	N	N	178	22
IV	4.4% Al_2O_3 Primary Burner Ash	10.5	--	--	560	55	N	N	203	20

(a) Refer to Figure 15 for location of elbows for tests II-IV. For Test I the first screwed elbow was 22 cm from the jet, the second elbow was 15 cm from the the first elbow.

(b) The average erosion rates are thickness loss/total time of test (instantaneous rates may be higher).

(c) -- Indicates elbow was not used in the test.

(d) Failure of the elbow wall occurred. The 1 1/2-inch Sch 40 pipe has a 3700 μm thickness while the Sch 80 pipe has a 5100 μm wall thickness.

(e) N indicates negligible loss.

Figure 16. Erosion of Elbows

Figure 17. Amount of Erosion on Capped Tee During 84 H Test
(All measurements in micrometers. N = Negligible)

ACC-A-2780

- (3) After 73.1 h, the filter vessel was emptied and 5 kg of fresh Al_2O_3 was charged.
- (4) After 84 h, the ejector failed; a hole formed through the throat section of the body.
- (5) The plug was periodically removed and inspected. About 50-60 g of material was found packed in the tee each time. This material was removed during each inspection.

The results of this test were as follows:

- (1) 500 μm were lost on the wall of the tee directly across from the branch. Negligible losses occurred in the capped straight run (see Figure 17). The average erosion rate was 6 $\mu\text{m}/\text{h}$.
- (2) The plug in the tee lost about 10 mg during the test. This was probably due to some contact of the material on it after each inspection but before the solids built back up in the tee.
- (3) 500 μm were lost on the 1 1/2-inch welded elbow. The average erosion rate was 6 $\mu\text{m}/\text{h}$.
- (4) Erosion losses on the ejector were:

	<u>New Ejector</u>	<u>Failed Ejector</u>	<u>Change</u>
Weight (g)	450	370	-80 g
Throat dia. (mm)	12.5	16	+ 3.5 mm
Discharge dia. (mm)	20.5	23	+ 2.5 mm

- (5) 1300 μm were lost on the 1-inch welded elbow. The average erosion rate was 550 $\mu\text{m}/\text{h}$.
- (6) A 1.6 mm thick rubber gasket, placed on the deflector plate was worn at the place of contact with the incoming solids.

These tests showed that the capped tee is a viable solution to mitigate the high erosion rates for the elbow closest to the jet. Erosion rates are about 150 times lower for the capped tees than for the long radius elbows. The erosion rate on the welded elbow is low, 6 $\mu\text{m}/\text{h}$, similar to the rate on the second screwed elbow from the previous tests.

1.4 Erosion as a Function of Distance from the First Elbow

To test the effect of distance from the ejector to the elbow on erosion, the system (Figure 15) was changed to allow 0.6 m between the ejector and the first 1 1/2-inch welded elbow. Al_2O_3 was transferred at 550 kPa motive pressure through a Model 63A ejector.

During the test, the following was observed:

- (1) After 5 hours, the ejector failed; a hole formed through the

throat section of the body. About 380 μm were lost on the welded elbow. The erosion rate was about 75 $\mu\text{m}/\text{h}$. The ejector was replaced with a Type 316 stainless steel Penberthy Model LL-1 ejector; the manufacturer's replacement for the Model 63A is no longer manufactured. Due to a smaller throat, the air flow rate through the Model LL-1 ejector is lower than through the Model 63A.

- (2) After 12 hours, a new charge of Al_2O_3 was made to the filter vessel.
- (3) After 12.75 hours, the stainless steel ejector failed. It was replaced with a Model LL-1 cast iron ejector.
- (4) After 17.25 hours, the cast iron ejector failed.

The results from this test are:

- (1) 2160 μm were lost from the welded elbow wall for an average erosion rate of 125 $\mu\text{m}/\text{h}$.
- (2) Erosion rates during the test were 75 $\mu\text{m}/\text{h}$ and 145 $\mu\text{m}/\text{h}$ for the Model 63A ejector and the Model LL-1 ejector, respectively.
- (3) The Type 316 stainless steel Model LL-1 ejector failed after 7.75 h of transferring. The cast iron ejector failed after 4.5 h.

This test showed that the erosion rate is dependent on the distance from the ejector to the first elbow. At 60 cm between the jet and elbow, the erosion rate was 125 $\mu\text{m}/\text{h}$, while at 20 cm, the rate was 850 $\mu\text{m}/\text{h}$. Erosion of ejector continues to be a problem during elbow erosion testing.

2. Erosion of Tribaloy 700 in the Rover Pilot Plant Centrifuge (A. G. Westra)

Extended erosion testing of the Tribaloy 700 coating^a on the auger blades of the Rover pilot plant centrifuge was completed. The centrifuge was a Bird solid bowl centrifuge like the one shown in Figure 18. The centrifuge has been operated for 288 h using simulated Rover dissolver product. Maximum erosion occurred on the middle blades of the auger at the point where the feed stream enters the centrifuge (blades 5, 6, and 7 in Figure 18). The maximum erosion on the edges of the auger blades was 5.3 mm in 288 h of operation for an erosion rate of 18.4 micrometers/h. The erosion was readily visible when the centrifuge auger was examined.

The simulated dissolver product used for the tests was a slurry consisting of 0.62 g/L graphite, 2.45 g/L Al_2O_3 , and 6.93 g/L Nb_2O_5 for a total solids loading of 10 g/L. This is approximately the solids composition expected in the Rover plant dissolver product. In these tests, water was used in the slurry instead of the HNO_3 and complexed HF that will be present in the Rover plant. Substituting water for the acid mixture should not

^aDupont trademark

Figure 18. Schematic Diagram of Centrifuge Bowl Section

significantly alter the erosion rate. The slurry was gravity fed to the centrifuge at the rate of 3 L/min. The centrifuge was rotated at 250 rad/s (2400 rpm). This rotation rate was found to give good solids-liquids separation in the previous tests. The solids from the centrifuge were reslurried with the supernate and pumped back to the feed tank for recycling through the centrifuge. Since the suspended solid particles were ground smaller by the centrifuge as they were recycled, the slurry was dumped and fresh slurry was made up about every 25 hours. Separation efficiency of the centrifuge became poorer as the solid particles became smaller.

The solids concentration in the slurry did not remain constant at 10 g/L. Solids accumulated against the inside wall of the centrifuge bowl and were held up at times in the solids discharge line.

Erosion measurements were made from the top of the blade to the point where the blade attaches to the auger body. The measurements and the erosion rates on the individual blades are presented in Table 12, along with the erosion rates of the chromium oxide coating tested earlier. Auger blades 9 to 12 are on the end of the auger where only liquid is present so they were not eroded by the slurry. The erosion on the centrifuge auger had no noticeable affect on centrifuge performance. The erosion rate of the Tribaloy 700 was greater than the erosion rate for the chromium oxide coating tested earlier. The slurry composition used in these tests was approximately the same as that used in the chromium oxide erosion tests. However, replacing the slurry periodically in these tests may have affected the results.

For this application the wear properties of Tribaloy 700 appear to be inferior to those of chromium oxide. The Tribaloy 700 coating presents greater fabrication problems since it is a weld overlay, while the chromium oxide is a spray coating.

The Rover plant centrifuge will operate approximately 1200 h during the Rover reprocessing campaign assuming there are 100 processing days and the centrifuge operates 12 h per day. This is roughly 4 times as long as the pilot plant centrifuge was operated in this erosion test. It is very unlikely that the plant centrifuge would operate satisfactorily with 4 times the erosion suffered in this test. More than 70% of the auger blade would be eroded away in places. As the auger blade wears, solids will build up on the inside of the bowl. The reduced inside diameter of the centrifuge bowl will reduce the centrifugal force and consequently reduce the separation efficiency of the centrifuge. A spare auger with a chromium oxide coating will be available in case the auger on the Rover plant centrifuge wears out before the Rover fuel reprocessing campaign is completed.

3. Rover Process Support Dissolver (A. G. Westra)

A small scale dissolver system will be installed in the ICPP Low Bay Laboratory to provide process support to the Rover plant.

TABLE 12
EROSION MEASUREMENTS ON THE CENTRIFUGE AUGER

Blade No.	Before Measurement (mm)	After Measurement (mm)	Difference (mm $\pm$.25)	Erosion Rate of Tribaloy 700 ($\mu\text{m/h}$)	Erosion Rate of Chromium Oxide Coating ($\mu\text{m/h}$)
1	12.40	11.61	0.79	2.74	4.24
2	15.57	12.85	2.72	9.43	----
3	19.51	15.98	3.53	12.26	2.21
4	23.19	21.08	2.11	7.32	2.54
5	25.53	22.25	3.28	11.39	4.75
6	24.08	20.93	3.15	10.93	10.16
7	23.27	17.98	5.29	18.35	8.13
8	21.46	20.37	1.09	3.79	----
9	19.43	19.51	-0.08	nil	----
10	17.09	17.20	-0.11	nil	----
11	15.90	15.75	0.15	nil	----
12	15.06	14.94	0.17	nil	----

The materials which will be used for fabrication of the Rover support dissolver have been ordered, and receipt of all the material is expected by October 30, 1977. A maintenance work package is being prepared so that fabrication and installation can begin in November. The dissolver will not be an annular vessel like the Rover plant dissolver because of its small size. In other respects, the support dissolver will closely resemble the Rover plant dissolver, and it will have the capability to duplicate conditions that will be found in the Rover plant dissolver.

Plans for Next Quarter

Erosion testing of alternative transport systems will be completed and recommendations will be made for improvements to the Rover plant.

The Rover plant support dissolver and primary burner installation in the pilot plant will begin.

Long term sintered metal filter blowback for the secondary burner filters will be initiated to define the best blowback mode.

Further design verification studies will be performed as required.

IV. WASTE TRANSFER SYSTEMS

(B. E. Paige, L. W. McClure)

Underground transport of radioactive liquid and solid wastes via pipelines is common throughout the nuclear industry. Previously, little effort had been expended to standardize designs from one location to the next or to evaluate various pipeline design alternatives to maximize environmental safety while minimizing the total facility cost. The goal of this project is to evaluate various pipeline design alternatives and to publish those evaluations in the form of proposed guidelines to be used in the development of future underground piping standards for the nuclear industry. Included in this program are: (a) determination of soil corrosion resistance of pipeline materials, especially stainless steel, (b) laboratory and field evaluation of commercial pipeline coatings applied to stainless steel pipe, (c) evaluation of the use of cathodic protection to protect stainless steel piping from soil corrosion, and (d) studies of general secondary encasement and piping design including seismic stability.

1. Laboratory Disbonding Tests

(R. E. W. Birch)

Cathodic protection is used to slow or halt corrosion of metals, thereby decreasing the risk of failures which result in leaks to the environment. The amount of current needed to provide this corrosion inhibition is proportional to the metal surface exposed. Electrically resistant coatings decrease the amount of current needed. Due to the high current density which is required for the large amount of bare metal pipe being cathodically protected at ICPP, localized "hot spots" may be encountered. These "hot spots" or high potential areas may cause considerable amounts of hydrogen to be released at the cathodes (the pipes). The hydrogen evolution is known to cause disbonding (destruction of adhesion) of some pipe coatings from the pipes which allows corrosion and failure to occur in the pipe. Five commercial coatings are being tested at four voltages encountered at ICPP: 10 volts, 5 volts, 3 volts, and 1.5 volts. The five coatings are fusion bonded epoxy, hot applied coal tar tape, extruded polyethylene, coal tar epoxy and polyethylene tape. Tests are being performed in a liquid electrolyte in the laboratory and in soil in the field to evaluate relative disbonding resistance.

After two months of testing in the laboratory, visual inspection of the coated specimens reveals that the fusion bonded epoxy coating, both on sandblasted and unsandblasted pipe, have failed at 10 volts with respect to a Cu/CuSO_4 electrode. Large lumps or bubble-like areas mark the disbonding when hydrogen evolution has destroyed the coating's adherence. Also, the hot applied coal tar tape specimens have blistered and cracked. The other specimens appear to be intact.

At 5 volts, the fusion bonded epoxy on the sandblasted pipe has a large bubble in the coating. At 3 volts, tiny bubbles about one millimeter in diameter have erupted on the surface of the coal tar epoxy. All others appear intact at the voltages tested and were replaced in the tanks to continue the test.

2. Laboratory Corrosion Testing

(R. E. W. Birch)

Corrosometer probes have been placed in ICPP soil in the laboratory under monitored moisture and temperature conditions. The electrical conductivity of the probe decreases as corrosion progresses and the resistance increases allowing a direct readout of the metal lost. Readings have been taken over a two month period with the corrosion probes in ICPP soil. The soil has been moistened to accelerate corrosion and to simulate the moisture content found at a depth of five feet. Mild steel initially had a high rate of 175 $\mu\text{m}/\text{yr}$. The two month average is 75 $\mu\text{m}/\text{yr}$. Types 304L, 347, and 316 stainless steel show no visible corrosion after the two months exposure. All probes will be left in the soil to evaluate the rates at 6 and 12 months.

3. Field Test

(R. E. W. Birch)

Long-term bare metal testing in electrically insulated tanks of ICPP soil (alkaline) and Judkins soil^a (acid) are being monitored to check their natural corrosion (rest) potential. This testing is being done in the field to confirm the laboratory testing of Types 304L, 316, and 347 stainless steels.

Coated field specimens buried in the ICPP yard are being monitored to determine cathodic protection potentials and current requirements. This information will be correlated with laboratory disbonding tests. The current requirements of the coated samples showed little change. For this reason a scheduled three month retrieval for inspection was not made. Both bare metal and coated samples will continue to be monitored.

Plans for Next Quarter

- (1) Calibrate CPP soil and Judkins soil for water capacity measurements.
- (2) Complete chemical analyses of ICPP, Judkins, Savannah River, Barnwell, and Hanford area soils.
- (3) Initiate work with the rapid scanning potentiostat to determine corrosion characteristics of stainless steels in various soils.
- (4) Evaluate results of the 90-day laboratory and 6-month field disbonding tests.
- (5) Initiate duplicate disbonding test.

^aJudkins soil is a highly acidic (pH 5.2-5.8) soil found around pine trees. It is used in these tests to simulate typical soil found in the Eastern U. S.

V. ICPP WASTE MANAGEMENT DEVELOPMENT

1. Tank WM-183 Flowsheet Development

(J. T. Nichols)

Three 10-cm-dia calciner runs have been made with a feed blend of two volumes zirconium fluoride waste and one volume tank WM-183 waste (concentrated to 60% of its original volume). Concentrated WM-183 waste is approximately 0.4 M sodium which results in a low melting calcine. By blending this waste with zirconium fluoride waste, the melting point may be raised above the temperature used in calcining.

Run 183-4-14 was made with magnesium nitrate (rather than calcium nitrate). This run resulted in some formation of agglomerates and an unacceptable chloride carryover in the off gas. There were also some problems in controlling the particle size which was not anticipated with magnesium usually produces a softer product than calcium.

Run 183-4-15 was made to verify the results obtained from the last 35 hours of Run 183-4-13 during which no agglomerates were formed and the amount of chloride carryover was small. An error was made in the calcium addition to the feed for this run. This resulted in the formation of numerous agglomerates by calcine melting on the fuel nozzle. The chloride level in the scrub increased steadily, indicating a poor retention of chloride in the bed.

Run 183-4-16 was made with the addition of dissolved iron to tie up the sodium as NaFeO_2 (none was detected in the product) and also to help tie up the chloride. A 30-cm-dia calciner run indicated that chloride would be retained in the bed by iron; however, this did not happen in Run 183-4-16 with 0.15 M or 0.3 M iron. Run 183-4-16 also produced a great number of agglomerates which again formed on the fuel nozzle. The final bed contained approximately 3% agglomerates.

Plans for Next Quarter

During the next quarter Run 183-4-13 will be repeated (calcium addition of 0.75 mole Ca per mole F), and if there is low chloride carryover and little formation of agglomerates, this feed blend will be tested in the 30-cm calciner for 100 hours. Should these runs be unsuccessful, less concentrated blends of WM-183 waste will be tested in the 10-cm-dia calciner.

2. Sodium-Bearing Waste Flowsheet Development

(B. J. Newby)

The flowsheet proposed for calcination of ICPP sodium-bearing waste calls for blending 3 volumes of ICPP first-cycle zirconium waste with 1 volume of sodium-bearing waste and adding sufficient calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) to give a calcium to fluoride (Ca/F) mole ratio of 0.7. Flowsheets tried in the WCF using $3\frac{1}{2}$ or greater volumes of zirconium (Zr) waste blended with 1 volume sodium-bearing waste to which was added the appropriate

amount of $\text{Ca}(\text{NO}_3)_2$ resulted in some fluidized-bed particle roughness and release of chloride to the off-gas scrubbing system. Additional work is needed to: (a) modify the proposed flowsheet to prevent particle roughness, and excessive chloride volatility or (b) create a new flowsheet that will prevent any of these problems.

A series of scoping flowsheets were tested (results of the first three flowsheet tests are covered in the last Quarterly) by making runs of 14 hours or less in a 10-cm-diameter, fluidized-bed, in-bed combustion calciner to determine how the flowsheets affect calciner operability. Fluidized-bed calciner runs or differential thermal analyses have indicated that each of these flowsheets show some promise for preventing fluidized-bed agglomeration due to sodium.

Scoping flowsheets tested were:

- (1) Run SBW4-4: sodium-bearing waste plus 1.0 mole of CrO_3 per mole of sodium present.
- (2) Run SBW4-5: 10 volumes of sodium bearing waste blended with 1 volume of phosphoric acid.
- (3) Run SBW4-6: sodium-bearing waste plus 122 g of sugar for every mole of sodium.
- (4) Run SBW4-7: 1 volume Zr waste blended with 1 volume sodium-bearing waste having a Ca/F mole ratio of 0.1 plus sufficient powdered iron to give an iron to fluoride mole ratio of 0.1.

The first two flowsheets were terminated in less than 5 hours due to bed clinker formation. Fluidized-bed agglomeration did not occur in Runs SBW4-6 and -7. Run SBW4-6 experienced problems with continual plugging of off-gas lines and cyclones, above-bed burning, difficulty in controlling bed temperature, and sticky and agglomerating fines. Run SBW4-7 produced noduled calcine. Flowsheets containing some blend of Zr and sodium-bearing waste using $\text{Ca}(\text{NO}_3)_2$ seem to show the most promise (of the flowsheets scoped) for preventing fluidized-bed particle agglomeration.

Differential thermal analyses (DTA) -- X-ray examination of wastes containing sodium show that the sodium in commercial waste reacts with dissolved powdered iron to form sodium ferrate at temperatures (301 to 419°C) 200°C below the temperature where sodium ferrate is formed in ICPP sodium-bearing wastes (536 to 707°C). Sodium ferrate must form at temperatures below 500°C in these wastes to prevent fluidized-bed particle agglomeration during calcination of these wastes. Further DTA -- X-ray studies showed that the temperature at which sodium ferrate forms in ICPP sodium-bearing waste cannot be decreased by adding constituents to the ICPP wastes which are present in commercial waste but not in ICPP waste. Aluminum nitrate is present in the ICPP waste, but not usually in commercial wastes. The temperature at which sodium ferrate forms in commercial waste cannot be increased by adding aluminum nitrate to the waste prior to iron addition.

Plans for Next Quarter

Studies will be made in the 10-cm-dia. calciner to determine how the zirconium waste - sodium-bearing waste blend ratio affects fluoride and chloride volatility, calciner operability, and calcine properties.

3. Calciner Feed Flowmeter Testing

(J. T. Nichols)

The WCF uses an electromagnetic (EM) flowmeter on each of the three waste feed lines to the WCF. These flowmeters have a smaller diameter than the feed line and are further restricted by the EM electrodes which protrude into the waste stream. Precipitants or other solids in the feed can plug these flowmeters.

A search for flowmeters that do not have restrictions is being conducted. The flowmeters which seem the most promising for use with radioactive feed will be purchased and tested.

An ultrasonic cross-correlation flowmeter has been built by the ICPP Measurement Systems Group and is being tested. This type of flowmeter has no restrictions to flow. Preliminary tests with water and simulated zirconium waste have been successful.

Plans for Next Quarter

Complete flowmeter literature search and continue testing the cross-correlation flowmeter with simulated feed.

4. Transport System Moisture Monitor

(G. L. Cogburn)

A moisture monitoring system consisting of a moisture analyzer probe and a thermocouple will be installed on the transport air return line at the WCF to provide data which can be used to control the amount of moisture entering the solids transport system, thereby reducing the possibility of condensation and subsequent plugging in the line. The thermocouple has been installed on the transport air return line just as it enters the calciner cell. The moisture analyzer probe will be incorporated into the plug for the extended cleanout line downstream of the bin cyclone. Installation of the cleanout lines which extend from the three-inch transport line on either side of the bin cyclone up through the vault roof was included in the WCF turnaround package. However, because of lack of welder radiation exposure, the job was not completed. The core drilling in the vault roof has been completed and the cleanout lines, plugs, and moisture analyzer probe will be installed at the next available opportunity.

Plans for Next Quarter

Readings will be taken periodically, if the moisture analyzer probe is installed, using a portable dew point hygrometer. If the probe performs

satisfactorily during this test period, a dew point hygrometer will be purchased and permanently installed.

5. Waste Feed Chemistry Studies

(B. J. Newby)

Laboratory and 10-cm-dia., fluidized-bed, in-bed combustion calciner studies have shown that magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$) can be used to effectively suppress fluoride and chloride volatility during calcination of a blend of 3 vol first-cycle zirconium waste with 1 vol ICPP sodium-bearing (formerly called second-cycle) waste with minimum production of gelatinous solids in calciner feed. Studies using the 10-cm-dia. calciner were performed to determine the minimum magnesium to fluoride (Mg/F) mole ratio in the blend needed to produce calcine without nodules and effectively suppress fluoride and chloride volatility. A 64-hour, 10-cm-dia. calciner run using feed with a Mg/F mole ratio of 0.7 produced smooth calcine, allowed <0.6% of the fluoride to volatilize from the calciner, retained 74% of the chloride in the product and fines, and didn't allow the chloride concentration in the off-gas acid scrub to build-up excessively. Two 64-hour, 10-cm-dia. calciner runs were made using Mg/F mole ratios of 0.5 and 0.6. Both runs produced smooth calcine and allowed <0.6% of the fluoride to volatilize from the calciner. The run using a Mg/F ratio of 0.5 allowed the chloride in the scrubbing solution to gradually increase during the run, and retained only 38% of the chloride in the bed. The run using a Mg/F mole ratio of 0.6 reached an acceptable steady-state chloride level in the scrub and retained 59% of the chloride in the bed. Thus, an Mg/F mole ratio of at least 0.6 is required to effectively suppress chloride volatility.

Plans for Next Quarter

Determine in 10-cm-dia. calciner runs, using a blend of 3 vol zirconium waste - 1 vol sodium-bearing waste, if increasing the aluminum concentration of the calciner feed prior to adding $\text{Mg}(\text{NO}_3)_2$ will keep more chloride in the bed.

6. Alternate Sodium Waste Solidification Process

(S. S. Bodner)

Several problems have occurred during sodium waste calcination tests. Sodium nitrate does not decompose and is molten at normal calcination temperatures. This promotes agglomeration of the fluidized bed. Nodule formation on the calcine particles also occurs, thereby degrading fluidization. This has caused poor heat transfer, reduced product mobility and resulted in sintering at the fuel nozzle. The greater particle hardness increases transfer line erosion. Chloride volatility in the calciner results in chloride buildup in the scrubbing system in excess of 500 ppm and is a potential corrosion problem.

Approximately 3780 m³ of sodium bearing wastes are currently stored at ICPP. Annual sodium waste generation is approximately 190 m³.

The largest sources of sodium wastes are the fuel storage basin ion-exchanger, the second mixer-settler (H-116) of the first-cycle extraction system, and the Rare Gas Plant. Plant decontamination solutions are also a source of sodium wastes. The composition of a typical ICPP sodium waste is shown in Table 13. Sodium waste storage tanks could be full in FY-1981 if the waste is not calcined in the WCF or solidified by some other method.

TABLE 13
ICPP SODIUM WASTE COMPOSITION

	<u>Molarity</u>
NaNO_3	1.60
HNO_3	1.40
$\text{Fe}(\text{NO}_3)_3$	0.01
KNO_3	0.24
$\text{Al}(\text{NO}_3)_3$	0.56
HCl	0.03
AlF_3	0.0016

The only alternate solidification processes currently used in production facilities are the bent-tube evaporator and the vacuum evaporator-crystallizer. Both processes require a cooled settling tank for wet salt cake storage. Retrieval of the cake from the tank would be difficult; use of either of these systems at ICPP would require a new tank for product storage and would be contradictory to the waste management philosophy at ICPP.

Testing of full-scale wiped film evaporators at Savannah River has been delayed until mid or late FY-1978. Again, construction of a tank for interim storage of the salt cake would be necessary if this process were used at ICPP. Retrievability of the stored salt cake has not been demonstrated.

Development of the spray calcination/in-can melting process is essentially complete according to BNWL reports. Full-scale testing during FY-1978 will provide the additional information needed for production facility design. However, sodium waste processing experience is limited (41 hours operating time), and a flowsheet for ICPP sodium waste would have to be verified by long-term pilot-plant testing prior to construction of a plant-scale facility.

Preliminary test results at Battelle indicate that evaporation or calcination of feed prior to vitrification may not be necessary. High level wastes have been evaporated, calcinated, and vitrified in one step in a continuous melter. Further development is necessary on this process

before it could be considered for a plant-scale facility at ICPP.

None of the solidification processes discussed have data on equipment corrosion from wastes containing chloride and fluoride ion. Corrosion rates could be excessive at elevated temperatures, especially at those temperatures required for glass formation.

Plans for Next Quarter

A detailed evaluation of alternate solidification processes for sodium-bearing wastes will be prepared as a basis for selection of the most promising candidate process for further pilot-plant development.

7. Alternate Calciner Startup Bed Material

(D. H. Munger)

Several alternatives to dolomite have been investigated for their applicability as a startup-bed material for the WCF. These materials include: magnorite (fused MgO), fluorapatite (phosphate pebble $Ca_5(PO_4)_3F$ - mined in central Florida), and sodium silico-aluminate (a cold-rolled sphere using a clay binder). Preliminary test results have shown the fluorapatite to be superior to dolomite, magnorite, and sodium silico-aluminate in the areas of attrition resistance and erosion potential. Sodium silico-aluminate was eliminated due to insolubility in 2-3 M HNO_3 . The low erosion potential of fluorapatite is particularly important, since lost production time in the WCF has been traced to the abrasive qualities of dolomite and pipeline failure.

The question as to whether or not the fluorapatite particles are suitable as seed material for the aluminum nitrate solution (2.2 M) used as cold feed to the WCF was successfully answered in 10-cm calciner Run ASB-4-1. Cross-sectional photographs of the coated fluorapatite particles from the 18-hour run have shown the layers of aluminum oxide to be very even; the particles were approaching a spherical shape. No undesirable reactions were noted.

Plans for Next Quarter

Testing of additional materials will continue. The producers of the fluorapatite material will be visited to answer questions on availability and size and purity quality control.

VI. EFFLUENT MONITORING METHODS EVALUATION AND DEVELOPMENT

(R. C. Girton, M. A. Wong, S. J. Fernandez)

1. Evaluate In-Place Test Methods for Determining HEPA Filter Efficiencies

A test system has been fabricated for the laboratory evaluation of the dioctylphthalate (DOP) method used for testing the efficiency of HEPA filters used in corrosive off-gas environments, particularly off-gas systems from radioactive waste solidification facilities. A corrosive environment consisting of high temperature, high humidity and containing NO_x , will be used to test the interactions of these parameters with DOP. The off-gas environment will simulate the Waste Calciner Facility. Testing will begin immediately after the system is installed and the instrumentation and equipment has been checked out.

Plans for Next Quarter

Throughout the quarter testing will be conducted to determine the effect of each parameter on filtering efficiency. Both polydispersed and mono-dispersed DOP generators will be used, and concentrations will be compared by light-scattering photometers and a laser spectrometer.

2. Methods Evaluation for Monitoring of Radionuclides with Low-Energy Emissions

The purpose of this project is to investigate and evaluate stack monitoring techniques for low-energy emitting nuclides released in the off-gas from fuel reprocessing facilities. The present work has concentrated on the low-energy beta emitters ^{99}Tc ($\beta_{\text{max}} = 0.292$ Mev with secondary emphasis on ^{79}Se ($\beta_{\text{max}} = 0.14$ Mev) and ^{125m}Te ($\gamma = 0.035$ Mev). A literature search of current technology and analytical methods was completed. A technique for collecting a grab sample and a continuous monitoring method for each nuclide was selected for further study.

The most important aspect of technetium chemistry is that it is easily oxidized. Since both nitric acid and atmospheric oxygen oxidize Tc(IV) to Tc(VII)^8 , the technetium in the +7 oxidation state is likely to occur in stack gases. Technetium rapidly forms the volatile heptoxide (vapor pressure $\sim 10^{-1}$ mm Hg at 100°C)⁹ under stack gas conditions. It can be anticipated, therefore, that Tc_2O_7 is the chemical form of ^{99}Tc .

To date, experimental work has included tracer studies for the gaseous ^{99}Tc . Motojima and Tanase¹⁰ observed that during the sublimation of fission product ^{99}Mo , the volatilized ^{99m}Tc was collected almost quantitatively by a silver trap, probably forming silver pertechnetate. This

⁸Anders, E., The Radiochemistry of Technetium, p 11, (1960).

⁹Smith, W. T., Cobble, J. W., and Boyd, G. E., J. Am. Chem Soc., 75, 5773 (1953).

¹⁰Motojima, K. and Tanase, M., Int. J Appl. Radiat. Isotopes, 28, 485 (1977).

information was used to design a grab sampling technique using silver zeolite to collect gaseous ^{99}Tc . The ^{99}Tc is stripped from the silver zeolite with 10% perchloric acid and purified by distillation as the heptoxide. The technetium in the sample is measured using a liquid scintillation counting method. Tracer experiments indicate the chemical yield for this procedure is about 44%. The hypothesis that the collection efficiency of silver zeolite for ^{99}Tc is close to 100% is presently being tested with ^{99}Tc tracer experiments.

The applicability of the silver zeolite method is fortuitous since silver zeolite is presently used to sample the ICPP stack for gaseous ^{125}Sb . Analysis of archived silver zeolite samples, therefore, would indicate both the prevalent stack concentrations of ^{99}Tc and the required sensitivity for a continuous ^{99}Tc monitor. The results of several such analyses are shown in Table 14.

TABLE 14
 ^{99}Tc CONTENT OF ICPP STACK GAS

<u>Sample Dates (1977)</u>	<u>$\mu\text{Ci } ^{99}\text{Tc/cc}$ Stack Gas</u>
2/25 - 3/4	5×10^{-12}
5/23 - 5/30	4×10^{-12}
5/30 - 6/6	2×10^{-12}
6/13 - 6/20	14×10^{-12}

These concentrations are many times the estimated detection limit of $0.8 \times 10^{-12} \mu\text{Ci/cc}$. This indicates that a time integrated sampling technique has sufficient sensitivity for routine use.

The continuous monitoring method being studied is a modification of the described time integrated sampling technique. The stack gases are scrubbed by a 10% perchloric acid solution from which the ^{99}Tc is revolatilized, leaving possible interferences in the scrub solution. The scrub solution is circulated to prevent the organic concentration from exceeding 0.5 ppm in the scrub solution to assure safe experimental operations. The revolatilized ^{99}Tc gas stream is then dried using a permeation distillation dryer. The dried gas is counted on-line using a flow-through proportional counter or a surface barrier detector. Preliminary results indicate 50% of the incident ^{99}Tc is revolatilized from the perchloric acid scrub solution and 50-80% of the ^{99}Tc in the gas stream is passed by the dryer.

Plans for Next Quarter

The efficiencies determined for both the grab sampling method and the continuous monitoring technique are preliminary and will be refined in the next quarter. The collection efficiency of silver zeolite for Tc_2O_7 will also be determined. The instrumentation for ^{79}Se tracer experiments as well as the counting equipment for the continuous ^{99}Tc method will be obtained and installed.

RESULTS

OTHER PROJECTS SUPPORTING ENERGY DEVELOPMENT

I. NUCLEAR MATERIALS SECURITY

1. Development of Monitoring Systems for Chemical Plants

1.1 In-Plant Monitoring System Demonstration (W. J. Harris, H. R. Deveraux)

Development, testing, and evaluation of an in-plant safeguards monitoring system during this period included successful demonstration of the remote monitoring capabilities with a telephone link to ERDA Headquarters in Germantown. The status of the plant input tank section of the monitoring system was transmitted directly to Germantown. Control signals were transmitted back to the ICPP to demonstrate remote inspection capabilities which can be implemented in immediate response to indicated plant anomalies or as an inspection audit function, separate from the plant operator's safeguards systems.

This rather elementary demonstration supports the basic soundness of the theft detection system concept based on monitoring process operations with essentially standard commercial electronic devices.

Significant improvements were made in the plant data acquisition and display capability. The model system now has two small computers sharing a common magnetic disc memory with a capacity of five million words. One computer is dedicated to data collection and formatting for storing the disc, while the second computer is dedicated to data analysis, i.e., comparison of plant status data as it is recorded on the disc memory with alarm conditions. At the present stage of implementation, the data analysis program is set up for "quick look" analysis, i.e., it is limited to detection of changes in switch closures, with immediate flashing display on the CRT screen, and to selection of data from the disc file for display. Any recorded variable can be displayed within any selected time interval. The data collection is done on a time schedule which may be selected over a range of about 30 seconds to hours. Also data is automatically collected when any switch status change is detected to permit checking by the data analysis program for possible diversionary indications.

Functions performed by the plant monitoring, theft detection system include the accurate measurement of input tank levels automatically, eliminating manual reading of manometers, and providing timely measurements. The addition of the sensors on samplers and on transfer lines attached to the input tanks allows the remote computer system to verify directly without depending on administrative controls: (a) that the input tank was properly mixed before measurements and sampling were started, (b) that a sample was taken from the proper tank at the proper times, and (c) that the proper transfer lines to and from the tank and only the proper lines were in use.

The elementary installation at the ICPP gives up the opportunity to demonstrate the concept of an on-line computer for basic accountability information and for diversion detection. It also provides the test arrangement needed to test various types of sensors and level detectors without interfering with plant production activities.

1.2 Computer Programming Requirements for Plant Monitoring (G. L. Booman)

Based on the ICPP development work, general computer requirements for monitoring the safeguards activity in a chemical processing plant have been identified. The monitoring system requires attaching the computer addressable detection elements, (in many cases simple switches) to all valves, pumps and transfer devices in the plant which constitutes a potential change in path for the nuclear material being processed in the plant. These "valves" then serve as the focal points for monitoring the processing activity in the plant, especially with respect to monitoring the loss or substitution of any material being processed. The computing activity centers around comparing on a timely basis, the actual condition of the valves and other sensors in the plant with expected values for these devices as stored on a computer file.

From a computing point of view, the storage of all the sensor information will be in terms of:

- (1) The chemical process in progress which is defined as a task. The details of the task to be contained in a file called the "task file".
- (2) The subdivisions of the task, usually with respect to time, which is described in terms of the status of all the valves in the plant. This "snapshot" of the process is a "sample record" of the task file.
- (3) The subdivision of the sampling record is a "valve vector" which contains information on all the tests to be carried out concerning a given valve in the process defined by the sampling record.
- (4) The subdivision of the valve vector is a "probe component" of the valve vector, which consists of four quantities:
 - a. The logical address of the probe device.
 - b. The current value of the probe device.
 - c. The expected value of the probe device.
 - d. The standard deviation of the expected value of the probe device.

The "sampling computer" will be driven by a given task file, record by record, for the whole process being monitored. Each record will cause

all valves to be cyclicly probed to check its position and other sensor data against the file parameters. As each valve is checked by the supervisory computer a record will be post processed by a second computer, the archival computer, in order to monitor slow drifts and also to help establish the standard deviation values which are appropriate for the given task. Thus the overall process will be carried out by three computers; one to set up the task file, another to supervise the valves and probes, the last to do statistics on data produced by the second and produce an archive of this data to be used to monitor future plant runs. It is possible that the first and third computers will be the same machine. Valves (fuel element transfer devices, pumps, steam jets, and air lifts, are special kinds of "valves") serve as the focus of the checking system. Each valve has associated with it a vector of "probe" quantities. These are measurements of the status of the probes. They consist of four quantities: the address of the probe, the value of the probe as of the latest reading, the mean value of the probe for the same valve settings and time since the checked valve came to current setting, and the standard deviation of the mean at the current setting. By "setting" is meant the open/closed status of the valve.

A "probe" quantity is any parameter which may be convenient in defining a set of check quantities for the status of a given valve. One class of these quantities will be supervisor pass words, worker "signatures", current task codes, adjacent valve positions, or any other absolute checks. This class of parameters will usually have standard deviations of zero. However, they can be considered at times to have standard deviation of infinity, if the particular parameter is momentarily non-relevant. The other class of parameters will come from sensors attached to the vessels and piping connected to the valve in question. These will be actual measurements of temperature, pressure, count rate, conductivity, depth, density, or any other useful and measureable quantity. This class of probe values would, in general, have a standard deviation associated with the mean value. The statistics of these values may either be estimated ab initio or else developed over a number of carefully supervised runs by means of the archival computer.

All switches and other probes must be addressable by the supervisory computer, so that for each task a "task file" may be formed consisting of a collection of "sampling records" which have "valve vectors". These "valve vectors" contain the directives for the valves to be read and the probes to be tested in order to monitor the plant usage. When the sampling turn of a given valve arrives, the valve vector for the given task is moved from mass storage file (buffered I/O) to immediate access storage as a function of time from the start. The current probe values are updated by calling a subrouting giving as arguments the device address and the core address of where the reading should be stored. Since the total number of probes is known as a function of the vector length, we may characterize the process of reading the probes as being "driven by the valve vector file". This means that the probes associated with a given task for a given value for a given time from the start of the task are sequentially checked. The file may be written out as the task proceeds and will serve as the basis for statistical calculations by the second computer.

The file itself will have to be created or updated by an editor program which will add, correct or delete probe readings as experience is gained with the monitoring procedure.

The method of decisions based upon the tests will be the comparison of each "probe" actual value with the archival values given in the valve vector. If the actual readings are within two standard deviations of the average expected value, the new reading will simply be put into the output file. If on the other hand the reading is between two and three standard deviations of the expected value, a warning will be issued on that parameter. For values over three standard deviations from the expected values, an alarm will be given.

The output file of the supervisory computer will contain the values of all components of the input file left unchanged by the probe reading process. This file may be used by the archival computer to analyze for long-term trends by composing values of components from a number of previous files with that of the latest task and analyzing for trends. This process should protect against "leakage" as contrasted to the supervisory computers protection against sudden large losses.

The output files and the statistical procedures of the archival computer programs will serve another major purpose. When the task file is created, it will be necessary to estimate the means and standard deviations of many of the "probes". However, if several runs are made under the strictest security possible, then data can be accumulated against which future runs may be judged. Thus the task file will be improved by the analysis of the archival data.

There will be three major programs required for the implementation of a plant monitoring system based upon the method described above. The first will be a program to create task files for the various plant processes. This program will have to accept the command language of safeguards monitoring system engineers which will command the checking of the various probes. Each probe should be given a "logical unit designation" consistent with the designations already in use in the plant.

The safeguards monitoring system engineer-programmer will use terms already familiar to him in setting out the test conditions. The task compiler in addition to being able to create task files will need to be able to copy and edit them as well. This will make possible modifications of task descriptions as conditions change or new materials are processed in the plant. The output of the task compiler will be a task file ready to direct the operation of the sampling computer.

The second major programming effort concerns the sampling computer. This program should be as short and compact as possible since the compiler which formed the task file should have reduced all the commands which run the monitoring operation to the compact form set out earlier. The most difficult matter will be the optimization of probe reading

in order that the computer will not become so I/O bound by the slowest probes that it will not be able to keep up the sampling schedule set out in the task being monitored.

The third program is for the implementation of the archival computer. This machine will also require a compiler for commands for interpreting the output task files. This compiler will also need to be able to provide capability to generate updated task files new limits or error set by the compiler language or at least to communicate these values back to the task compiler.

2. In-Line Density Measurement (W. J. Harris, H. R. Deveraux, F. O. Cartan)

A rugged design gamma absorbtimeter is being installed in the ICPP pilot-plant facility for flow loop tests (including calibration with various uranium and nitric acid concentrations) and mass flow measurement tests with the bubble transit-time flowmeter. On completion of pilot-plant tests, the gamma absorbtimeter-flowmeter system will be installed in the plant to provide on-line measurement of the quantity of uranium entering the loadout storage banks. Engineering drawings, procedures, and schedules for plant installation are being prepared by ICPP Plant Engineering personnel.

3. Transit Time Flowmeter (W. J. Harris, H. R. Deveraux)

The bubble transit-time flowmeter is a special purpose instrument for accurate flow measurements in certain low-flow plant lines. This flowmeter uses spaced ultrasonic sensors to check the passage of an injected bubble, or to measure the transit time of random bubble, or to measure the transit time of random bubbles or particulate material by fast reponse correlation techniques. Plutonium and uranium product lines in a plant are of special interest because the nuclear material is in an attractive form for diversion. The flow measurement problem in these lines is severe because of the low flow rates, reliability and prevision requirements, and the need to withstand corrosive decontamination solutions during cleanout or maintenance turnaround cycles. During this period, the bubble flowmeter electronic was modified for remote operation. Successful remote operation both for data collection and system control was verified. The newly designed sealed sensors were completed and their qualification tests have been partially completed. A special sensor designed for correlation measurements without bubble injection was fabricated. This sensor has advantages for high reliability for in-cell applications, but does require small processor capabilities to reduce the sensor signals to flow information. Initial tests results indicate the deisgn will meet plant measurement needs. Metallic bonding techniques for the ultrasonic crystals will be applied to provide a radiation resistant device.

Plans for Next Quarter

The proposed schedule for the next quarter include:

- (1) Preparation for pilot-plant testing of the bubble transit-time flowmeter and gamma absorbtimeter.
- (2) Continuation of plant demonstration of the dual computer, on-line SNM theft detection, process surveillance system.
- (3) Continuation of development of model computer alogarithms for realistic tests of the Inspector function in a plant monitoring, theft detection system.
- (4) Preparation of specifications and Expenditure Authorization for a special lightweight magnetic focusing mass spectrometer for evaluation as an inspection device for rapid analysis and simple operation.

II. LIQUID-FLUIDIZED-BED HEAT EXCHANGER FOR GEOTHERMAL APPLICATIONS

(C. A. Allen, L. T. Cole, and R. E. McAtee)

Scale formation on heat transfer surfaces reduces the efficiency of the production of power from hydrothermal resources. Because of the abundance of low temperature resources, binary systems are attractive, but scale buildup must be controlled. Allied Chemical Corporation-Idaho Chemical Programs is responsible for the development of dense phase liquid fluidized-bed heat exchangers which show promise of controlling scale buildup.

1. Scale Control Test

Liquid-fluidized-bed scale-control testing was completed at the Geothermal Component Test Facility (GCTF), an ERDA facility at the East Mesa Geothermal site in the Imperial Valley, California. This site was selected because the geothermal water in the Imperial Valley has a greater scaling potential than is found at Raft River.

A horizontal tube and shell heat exchanger was used for this experiment. The shell was constructed of carbon steel with a 20 cm I.D. The tube bundle was constructed of Type 316 stainless steel. The bundle contained 57 tubes, 35 cm long, having a 0.95 cm O.D. The distributor-support plate was a bubble cap type. The vessel was equipped with thermocouples, located to obtain a heat balance and to measure bed temperature gradients. Turbine flowmeters were used to measure flow rates.

Pretesting was performed and vessel modifications made to improve the distribution of the fluidizing geothermal water. Following the modifications and hydrostatic testing, heat transfer was measured as functions of geothermal and cooling water flow rates. Three bed particle sizes, 0.6, 1.0, and 2.0 mm mean particle diameter (MPD), were used during the preliminary heat transfer tests.

The 90-day scale control test had a total operating time of 2100 hours. Near the mid-point of the test, the secondary coolant system was cleaned. A large amount of scale had formed on the inside of the tubes due to the hardness of the cooling water. The outside of the tubes, on the bed side, remained clean throughout the test. Operating conditions during the scale control test are shown in Table 1.

TABLE 1
OPERATING CONDITIONS DURING THE SCALE CONTROL TEST AT EAST MESA

<u>Variable</u>	<u>Operating Range</u>
Fluidizing velocity (m/sec)	0.041-0.061
Secondary fluid flow rate (L/sec)	2.67
Secondary fluid inlet temperature (°C)	15-32
Secondary fluid outlet temperature (°C)	29-48
Fluidized-bed temperature (°C)	138-156
Primary fluid inlet temperature (°C)	162
Bed particles	1.0 mm MPD silica sand

Figure 1 shows the bed-side heat transfer coefficient (h_o) and the overall heat transfer coefficient (U) as functions of time. ^oThe decrease in h_o after 90 days may be due to minor scaling on top of the tubes, where fluidization is minimal. The fouling resistance corresponds to $1.5 \times 10^{-5} \text{ m}^2 \cdot \text{K/W}$ ($8.6 \times 10^{-5} \text{ hr} \cdot \text{ft}^2 \cdot ^\circ\text{F/Btu}$) which is not significant. Decrease of the overall heat transfer coefficient from the beginning and mid-point of the test is due to fouling on the inside of the tubes. Fouling resistance on the inside of the tubes was near $1 \times 10^{-4} \text{ m}^2 \cdot \text{K/W}$ ($7 \times 10^{-4} \text{ hr} \cdot \text{ft}^2 \cdot ^\circ\text{F/Btu}$), which exceeds the outside fouling resistance by a factor of ten.

The inside fouling observed at the mid-point and end of the experiment typifies a problem frequently encountered in geothermal areas. The ground water tends to be of low quality, possibly because of leakage of hot water into the surface aquifers. The low quality cooling water will create problems in the condenser; liquid fluidized-bed technology may be required to minimize its effect.

- (1) The experimental equipment operated for 90 days. The only interruptions were caused by shutdown of the well for short periods and the scheduled mid-point examination.

ACC-A-2865

Figure 1. Bed Side and Overall Heat Transfer Coefficient during 80 Days of the East Mesa Scale Control Test

- (2) Heat transfer surfaces in the fluidized bed remained clean throughout the test.
- (3) Excessive scale on the cooling water side of the tubes reduced the overall heat transfer coefficient.

2. 60-kW Preheater

Power will be produced at Raft River by February in this country's first geothermal binary cycle power plant, which will be a 60-kW unit using isobutane as the working fluid. A six-stage liquid-fluidized-bed preheater will be installed as second generation equipment during FY-1978.

This will be the first test of a multistage liquid-fluidized-bed heat exchanger. The six stages will consist of three vertical shells and three horizontal shells. Two horizontal configurations will be tested. This will allow a direct comparison between the horizontal and vertical exchangers. Cost and performance will be closely monitored, since this will be the basis for choosing a configuration for the demonstration-scale heat exchangers. The preheater system will include a solids storage system and a solids transport system for filling and emptying the beds.

Specifications have been prepared for manufacture of the vessels and tube bundles. These will be fabricated by a heat exchanger vendor. The intention is to identify manufacturing problems imposed by the fluidized-bed design.

Following installation at Raft River, the system will be tested with cold water as the working fluid.

A boiler for the 60-kW plant will be designed during FY-1978 to replace the original boiler. The liquid-fluidized-bed boiler will be fabricated and installed during FY-1979.

3. Fluidized-bed Dryer

ACC-ICP is working with EG&G in design and operation of a gas-fluidized-bed geothermal dryer for industrial drying. It will be designed to handle a variety of feed materials. The proposed first test will be sludge from the secondary treatment of potato waste from a potato processing plant. Such waste contains 60 percent protein; attempts to dry the sludge in a rotary kiln was unsuccessful.

The heat exchanger shell will be square, 25 cm on each side. Two horizontal tube bundles will be installed. Drying capacity using 147°C geothermal water on the tube side will be about 10 kg/h. The heat exchanger will be equipped to measure temperature, pressure, differential pressure, and flow rate of the geothermal fluid and fluidizing air.

Plans for Next Quarter

- (1) Mechanical design of 60-kW preheater will be completed. The vessels and tube bundles will be put up for bid and a vendor will be selected.
- (2) The vertical plexiglass flow distribution vessel will be fabricated and tested. Heat transfer in vertical and horizontal configurations will be compared in the two plexiglass units.
- (3) Design and fabrication of the gas fluidized-bed dryer for industrial products will be completed.
- (4) The report on the scale control test at East Mesa will be completed.

III. IN-PLANT SOURCE TERM MEASUREMENT PROGRAM

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

The measurement program at the Zion Nuclear Generating Station was suspended. Operational problems in the ventilation system were discovered, and the plant initiated repair during this period. The present schedule date for completing the repair and rebalancing of the ventilation system is October 15, 1977. Plans currently call for an additional round of measurements of airborne activity as soon as the repairs are complete.

Several draft reports were sent to the NRC for review and comment. Included were:

- (1) Second Zion Data Report, January to June 1977.
- (2) ^3H and ^{14}C sampler-development and testing.
- (3) Final Report on Fort Calhoun Station.

Plans and schedules for the in-plant source-term survey were discussed with operating staff at Rancho Seco and Turkey Point stations. Measurements are presently scheduled to begin at Rancho Seco in the second calendar quarter of 1978. Final plans have not as yet been developed for measurements at Turkey Point; however, tentatively, the program will begin early in the fourth calendar quarter of 1977.

IV. BURNUP METHODS FOR FAST BREEDER REACTOR FUELS

(W. J. Maeck, R. L. Tromp, J. E. Delmore, A. L. Erikson, J. W. Meter, W. A. Emel)

The purpose of this program is to measure absolute fast reactor fission yields and to develop methods for the determination of burnup on Fast

Breeder Reactor (FBR) fuels. During this quarter, the analyses were finished on the two ^{241}Am samples. The analyses are showing extensive contamination of the fission products with the natural elements. Indications are that the original material was impure. This, coupled with the extremely low burnup, gives a high ratio of the natural elements to the corresponding fission product elements. The fission yields will be less accurate as a result, although they will adequately meet the programmatic needs. All of the other yield measurements have exceeded the published programmatic requirements.

Analyses for La and Ce were rerun on the Pu and Np capsules using newly developed techniques which allow the measurement of minor nuclides present in the natural element but not in the fission product element. This allows the differentiation of the two components, natural and fission product, allowing the analyses to be corrected for contamination. This technique is now being applied to the uranium capsules.

The major part of the experimental program for FY-1978 will be the analysis of 4 capsules (1 each of ^{233}U , ^{235}U , ^{239}Pu and ^{241}Pu) fabricated by ANL and irradiated for 4 years in EBR-II. These capsules were received the first week in September. The ^{233}U capsule is dissolved, and Kr and Xe gases have been analyzed. The other three capsules will be dissolved at about one-week intervals. The major part of the analytical work will start in October.

Two reports were published during this quarter, ICP-1050-II entitled, "Fast Reactor Fission Yields for ^{239}Pu and ^{241}Pu ", and ICP-1050-III entitled, "Fast Reactor Fission Yields for ^{237}Np ". These reports were delayed slightly in order to include the results of the La and Ce reruns using the new analytical procedure.

V. ABSOLUTE THERMAL FISSION YIELD MEASUREMENTS

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

All analyses (including reruns) are finished on the six ^{235}U capsules. The data appears to be good in all cases, although the final data evaluation will not be finished for several months. The evaluation of the six ^{239}Pu capsules is scheduled to begin this month.

A preliminary report was made in the previous quarterly¹ report of plans to initiate the analysis of 14 ATR fuel punchings. Since then, the plans have been expanded and the analyses begun. The additional analyses are Pu, Np, Kr, Xe, and several radionuclide ratios. This is in addition to the U, Nd and Cs IDMS analyses. All 14 of the punchings are dissolved with Kr and Xe measured. The basic U, Nd and Cs analyses are finished on the first two, with the other analyses under way. This work will overlap the start of the Pu capsule analyses.

¹Technical Division Quarterly Progress Report, April 1 - June 30, 1977, ICPP-1123.

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

(D. E. Adams, D. H. Meikrantz, G. W. Webb, E. E. Filby, W. A. Emel)

Uranium depletion and fluence analyses have been completed on 16 high-priority LWBR fuel segments. Preliminary reports of the data from these analyses have been made to Bettis Atomic Power Laboratory. Scheduled commitments for reporting the results for this program should be met. A preliminary analysis of the data indicates that the results for uranium concentration in a pellet have a relative standard deviation of about 0.08%, while the isotopic data for the major peak in a sample show about 0.04% relative standard deviation. The uncertainties in the preliminary gamma-ray analysis data have been estimated conservatively high, being estimated at around 6% for the ^{137}Cs , about 10% for ^{144}Ce , and 6-13% for ^{95}Zr . A complete error analysis for this set of measurements is in progress, and the results of this study will be included in the final report for these fuel segments.

Relatively few problems were encountered in completing these analyses. The fuel pellets dissolved during this quarter ranged in weight from about 36 grams down to about 0.64 gram. These dissolutions proceeded without serious difficulties. For two of these segments, the activities for ^{144}Ce and ^{95}Zr were found to be inconsistent with the reported final irradiation dates, so these results were exhaustively rechecked. However, new information from Bettis indicated that the actual radiation histories differed from those initially reported to us. The measured activities were found to be in agreement with this new information. In related work, a method for analyzing thorium by isotope dilution mass spectrometry have been developed. This included preparation and standardization of a ^{230}Th spike, establishment of workable analytical conditions for the mass spectrometer² and preparation of a thorium chemistry procedure. In other related work, a procedure for separating manganese from the Zircaloy cladding solutions has been developed and used.

VII. RESEARCH ON ANALYTICAL METHODS

1. Evaluation of Ion Chromatography as a Technique for Analysis of Geothermal Effluent Brines (R. P. Lash, C. J. Hill)

To evaluate analytical methods for the determination of various elements in geothermal effluents, Battelle Northwest Laboratory is currently conducting a round-robin analysis program. Two wells were sampled for this program: The East Mesa Well 6-2 and the Woolsey Well No. 1. Samples from these wells were distributed to the various participating laboratories. As part of our participation in this program, ion chromatography (IC)^a is to be evaluated as a technique for the determination of selected anions and cations in these samples. The ions selected for investigation by this technique are:

^aDionics Incorporated, Sunnyvale, California

²Webb, G. W., et al., This report, p 149

<u>Anions</u>	<u>Cations</u>
Fluoride	Lithium
Chloride	Sodium
Bromide	Potassium
Iodide	Calcium
Phosphate	Magnesium
Sulfate	Strontium
Sulfide	Ammonium
Nitrate	Rubidium
Nitrite	Cesium

1.1 Anion Analysis

A sample of the water was injected into the IC and an anion profile was obtained. This was compared with a standard anion mixture. Chromatographic conditions were:

Anion separator column :	3 x 500 mm
Anion precolumn :	3 x 150 mm
Anion suppressor column:	6 x 250 mm
Eluent :	0.003 M NaHCO_3
	0.004 M Na_2CO_3
Flow rate :	138 mL/h
Sample size :	100 μL fixed sample loop

Through a comparison of retention times, fluoride, chloride, bromide, and sulfate were identified. Nitrate was not resolved from sulfate under these conditions. However, adjustment of the eluent concentration to 0.002 M NaHCO_3 /0.0016 M Na_2CO_3 and flow rate to 115 mL/h resulted in complete resolution of the peaks. Under these conditions it was possible to determine fluoride, bromide, nitrate, and sulfate in a single sample aliquot (Figure 2) by simply changing detector sensitivity settings between the chloride and bromide peaks and, again, between the nitrate and sulfate peaks. Results are shown in Table 2. Chloride could not be determined simultaneously for two reasons: (a) the resolution of the fluoride and chloride peaks did not allow sufficient time to make a sensitivity change between peaks, and (b) the chloride concentration was extremely high so that its peak was off scale on the least sensitive detector setting of the IC at the dilution used for the other anions. The required resolution could have been obtained through further eluent and flow rate changes. However, these changes would have increased the retention time for the sulfate peak at at least a factor of two (to greater than 30 min). Therefore, chloride was determined alone (Table 2) on a separate dilution of the samples. The total analysis time for

TABLE 2

ANION AND CATION DETERMINATIONS IN GEOTHERMAL EFFLUENT BRINES

Sample Description ^a	Ions (mg/L)								
	<u>F⁻</u>	<u>Cl⁻</u>	<u>Br⁻</u>	<u>NO₃⁻</u>	<u>SO₄⁼</u>	<u>Na⁺</u>	<u>K⁺</u>	<u>Li⁺</u>	<u>NH₄⁺</u>
GRR-1 RU	5.6	1970	1.6	3.3	159	1480	130	4.5	17.3
GRR-1 FU	5.5	1980	1.6	0.3	159	1470	130	4.6	17.0
GRR-1 FA ^b	---	---	---	---	---	1420	127	4.2	16.1
GRR-1 FA Control ^b	---	---	---	---	---	1510	182	3.8	13.0
GRR-2 RU	13.8	132,000	94.5	3.8	33.4	48,900	11,300	167	371
GRR-2 RA ^b	---	---	---	---	---	48,700	11,200	167	346
GRR-2 RA Control ^b	---	---	---	---	---	17,700	7,150	93.7	480

^aThe GRR-1 sample prefix denotes samples or controls from the East Mesa Well, and the GRR-2 prefix denotes samples or controls from the Woolsey Well No. 1.

^bAnions could not be determined because of the large amount of Cl⁻ contributed by the hydrochloric acid used to acidify the samples.

Figure 2. Ion Chromatogram of Anions in Geothermal Water. Recorder Sensitivity: 10 μmho F^- , 3 μmho Br^- and NO_3^- , 30 μmho $\text{SO}_4^{=}$

determination of fluoride, bromide, nitrate, and sulfate was 2¼ hours and that for chloride was 1 hour. Precision and accuracy studies were performed using a control prepared to simulate an East Mesa well water sample. Results obtained to date are presented in Table 3. All anion analyses performed on the control were accurate to within ± 5% of the makeup values.

TABLE 3
BIAS AND PRECISION DATA FOR THE
DETERMINATION OF IONS IN GEOTHERMAL EFFLUENT BRINES.

<u>Ion</u>	<u>Bias, %</u>	<u>Rel. Std Deviation, %</u>
Na ⁺	+0.06	0.400 ^a
K ⁺	-1.25	1.24 ^a
Li ⁺	+1.86	1.35 ^a
NH ₄ ⁺	-2.80	1.83 ^a
F ⁻	+4.77	0.55 ^b
Br ⁻	-2.17	2.06 ^b
SO ₄ ⁼	-1.37	0.06 ^b

a - based on 10 determinations.

b - based on 3 determinations.

Attempts were also made to determine nitrite, phosphate, and iodine in the geothermal samples. Nitrite could not be determined by IC because of interference from a large, unknown peak with a similar retention time. Phosphate and iodine also could not be determined by IC because of the high chloride concentrations in the samples. The minimum dilution which could be made to avoid exceeding the capacity of the separator column with chloride ion resulted in concentrations of phosphate and iodine that were too low to be determined.

1.2 Cation Analysis

A cation profile of the water samples was also obtained and compared with a standard cation mixture. Chromatographic conditions were:

Cation Separator Column : 6 x 250 mm

Cation Suppressor Column: 9 x 250 mm

Eluent : 0.005 M HNO₃

Flow Rate : 184 mL/h

Sample Size : 100 μ L fixed sample loop

Lithium, sodium, ammonium, and potassium were identified by a comparison of retention times. Under these conditions, however, resolution of lithium from sodium and ammonium from potassium was poor. Adjustment of the eluent concentration to 0.003 M HNO_3 gave a resolution of all four peaks, cf., Figure 3. Using these conditions, lithium and ammonium were determined in a single sample aliquot by changing detector sensitivity between the two peaks. Sodium and potassium were also determined in a single sample aliquot again by changing detector sensitivity between peaks. Results are presented in Table 2. All four of these ions could be determined in a single dilution of the samples. However, because of the large sodium/ammonium ratio, there would be a loss of accuracy for the ammonium ion. The total analysis time for either the sodium-potassium pair or the lithium-ammonium pair was 1 hour. Precision and accuracy studies were performed for all four ions using the control described above for the anions. Results are shown in Table 3. All cation analyses were accurate to within $\pm 5\%$.

Attempts were made to determine rubidium and cesium in the samples. Rubidium could not be determined because: (a) the resolution of the potassium and rubidium peaks was inadequate, and (b) the concentration ratio of potassium to rubidium was too large. Cesium could not be determined because a large, unknown peak appears at the retention time expected for cesium.

An attempt was also made to determine the conductivity of the water samples using the conductivity detector incorporated in the ion chromatography unit. Such large dilutions of the samples had to be made in order to measure the conductivity on the IC unit that the conductance was not proportional to salt concentration.

Plans for Next Quarter

Additional work will be performed to determine sulfide, magnesium, calcium, strontium, borate, and carbonate in these geothermal water samples.

2. Gas Chromatographic Determination of Freon 113 in Geothermal Effluent Brines (R. P. Lash)

In support of the geothermal energy research program being conducted by EG&G, a method was developed for the determination of Freon 113 in geothermal effluent brines. Freon 113 is used as a direct-contact heat exchanger fluid, and it is necessary to determine the quantity of this material which is transferred to the brine during the process.

A gas chromatographic technique using the very sensitive electron capture detector appeared to be the best approach. However, due to the inherent problems associated with this detector, a hydrogen flame ionization

Figure 3. Ion Chromatogram of Cations in Geothermal Water. Recorder Sensitivity 3 μmho Li⁺ and Na⁺, 1 μmho NH₄⁺ and K⁺.

detector was used instead. Blades³ studied the response of the flame ionization detector to fluoro-alkanes and found it to have a good sensitivity for this class of compounds. He used a column packed with the porous polymer packing, Porapak Q.^a This packing material, in addition to being able to separate fluoro-alkanes, also has the desirable characteristics of being unaffected by the presence of water in a sample. Therefore, it was chosen as the packing material for this work. Calibration of the method was performed by means of internal standardization.

Development work was begun by packing a 4 ft x 1/8 in. stainless steel column with 80-100 mesh Porapak Q and conditioning it in the chromatograph at 175°C for 16 hours with helium flowing through the column. Initial chromatographic conditions for this work were:

Temperatures, °C

Column - 145

Injector - 150

Detector - 150

Flow rates, mL/min

Helium - 40 [380 kPa (55 psi) head pressure]

Hydrogen - 25

Air - 350

Range - 1×10^{-11} Ampere full scale

Attenuation - 8X

Sample size - 1 μ l

Two working standards of Freon 113 in 95% ethanol were prepared containing 1.17% wt/vol and 0.117% wt/vol Freon 113. One microlitre injections of these standards indicated that Freon 113 was eluted in approximately 3 min and solvent-related peaks were eluted in 1 to 2 min. Better resolution of the peaks was obtained by reducing the helium flow rate to 25 mL/min.

Since there was some doubt that the flame ionization detector had sufficient sensitivity for performing the analysis, one microlitre of a typical geothermal effluent brine was injected onto the chromatograph. A Freon 113 peak of approximately 13% of full scale was observed, indicating that there was sufficient sensitivity.

Internal standardization was selected as the means of calibrating the method. To do this, a compound had to be found which met the following requirements:

³Blades, A. T., "Response of the Flame Ionization Detector to Fluoro-Alkanes," J. Chrom. Sci., 11, 267 (1973).

^aTrademark of Waters Associates, Inc.

- (1) Be well resolved from other peaks
- (2) Elute close to the Freon 113 peak
- (3) Approximate the concentration of Freon 113
- (4) Be structurally similar to Freon 113
- (5) Must not react with Freon 113

1,2 dichloroethane met requirement (3) and (4). A solution of dichloroethane was prepared and injected onto the chromatograph under the conditions described above. The chromatogram showed that requirements (1) and (2) were also met by the 1,2-dichloroethane. In order to evaluate requirements (5), a solution containing both Freon 113 and 1,2-dichloroethane was prepared and injected onto the chromatograph twice over a period of 1 hour. Relative response factors were calculated from each of the chromatograms according to equation (1):

$$RR_x = \frac{H_x C_s}{H_s C_x} \quad (1)$$

where RR_x = Relative response of Freon 113 to that of 1,2-dichloroethane

H_x, H_s = Peak heights of Freon 113 and 1,2-dichloroethane, respectively

C_x, C_s = Concentrations of Freon 113 and 1,2-dichloroethane, respectively

The two factors remained essentially constant, indicating that requirement (5) was also met by 1,2-dichloroethane.

The geothermal water samples were analyzed by adding a known amount of 1,2-dichloroethane in ethanol to a known quantity of the water and injecting these solutions onto the chromatograph under the following conditions:

Temperatures, °C

Column - 145

Injector - 150

Detector - 150

Flow rates, mL/min

Helium - 25 [276 k Pa (40 psi) head pressure]

Hydrogen - 25

Air - 350

Range - 1×10^{-12} Ampere full scale

Attenuation - 2X

Sample size - 1 μ L

A typical chromatogram is shown in Figure 4. Samples of geothermal brines show 0.01 to 0.1 g Freon 113 per 100 mL brine.

3. Installation of Electron Spectrometer System

(D. A. Pavlica and W. A. Ryder)

A Physical Electronics Industries Model 549 ESCA/SAM System has been received and installed in the Spectrochemical Laboratory. The system is a combination of two instruments, the ESCA/Auger Electron Spectrometer and the Scanning Auger Microprobe (SAM). SAM and Electron Spectroscopy for Chemical Analysis (ESCA) are nondestructive techniques and are used to obtain information concerning surface elemental composition, in-depth variations in elemental composition, surface elemental distribution, and chemical bonding. Specific areas where the system is expected to be an invaluable tool include studies of the temperature embrittlement of metals due to microsegregation; the fracture properties of metallurgy parts; materials contamination; and the corrosion and oxidation resistance of various coatings.

To date, the system has been used to determine the composition of a selected point on the surface of conductive specimens and/or to determine the distribution of elements on the surface. Elemental composition as a function of depth into conductive specimens has been performed. Currently, methods are being investigated and refined to permit future analysis of semiconductors and non-conductors.

4. Installation of Automatic Titration System in the Remote Analytical Facility

(D. N. LeMaire and J. P. Henscheid)

An Automatic Titration system was installed in the Remote Analytical Facility (RAF) to facilitate the titration for acid. Previously acid titrations were made using a 10 mL buret and a pH meter. Two sources of errors in this method were: misreading the buret and not titrating to the correct pH.

The Automatic Titration system consists of a: Mettler DK-10 (Electrode Potential Amplifier), Mettler KD-15 (Equilibrium Titration Control), and a Mettler DV 11 (Buret Drive). The DV 11 Buret Drive will eliminate misreading the buret as it uses a Digital Display of titrant delivered. The DK-15 rate and end point control is used to stop the automatic titration procedure when a preset end point has been reached. It also automatically controls the rate of titrant delivery as a function of the rate at potential change. This will eliminate misreading the pH meter and over-titrating the end-point.

This system will make acid titration in the RAF easier and more precise. Once the titration is started, the system can be left unattended.

Figure 4. Chromatogram of Freon 113 Determination Sensitivity:
 1×10^{-12} Ampere Full Scale

Quality control data are being collected, and a comparison between the automatic system and the old system will be made when the quality control information is available.

5. The Determination of Manganese in Solutions Used as Neutron Detectors

(S. D. Reeder)

In previous reports⁴ the use of a large bath of manganous sulfate solution to capture and measure neutrons in certain nuclear physics experiments conducted at INEL and elsewhere was discussed. Since the accurate determination of manganese in these solutions is a vital part of the experiment, analytical support in the form of methods development and experimental participation from the Analytical Methods Development Group has been frequently provided. Recent participation in this work has apparently solved an approximately one percent discrepancy that has existed between an American and a British laboratory in the absolute calibration of neutron sources and the measurement of $\bar{\nu}$ (nu-bar) of ²⁵²Cf. In addition, a method for determining manganese by redox titrimetry has been studied and found to be highly suitable for "manganese bath" solutions.

As part of an effort to account for an approximately one percent discrepancy in the results of separate experiments involving the use of a "manganese bath" as a neutron detector, the experimentors involved were questioned on their methods for determining the concentration of manganous sulfate in their bath solutions. One had carefully prepared a density-concentration relationship (according to a method developed at INEL) using very pure manganous sulfate powder and then used a slightly lower grade of reagent for his experiment. His solution was discarded after use. The other experimenter in England used a pharmaceutical grade of manganous sulfate and determined solution concentration by evaporating an aliquot to dryness, heating to constant weight at 300°C and weighing the product as MnSO₄. The English researcher used the same bath for over 10 years. He reported that emission spectroscopy indicated negligible impurities. He was requested to provide a sample of his solution for analysis at INEL.

Volumetric analysis by EDTA titrimetry gave a very diffuse end point with the English solution indicating the presence of impurities. Since this method and the gravimetric weighing of solids after the evaporation of water from the solution are not specific for manganese, the identification and determination of the major impurities was undertaken. Atomic absorption and spark source mass spectrometry were used to determine several elements. Quantitative results were obtained for Al, Ca, Fe, Mg, Co, Ni, Cr, Na, and Zn. The EDTA titratable metals magnesium and calcium were the most abundant impurities. Considering all of the above impurities as sulfates, they constituted slightly more than 1% of the weight of the solute in solution. Although the 1% discrepancy was apparently accounted for, a simple selective method to determine manganese concentration in such solutions is required. EDTA titrimetry has been satisfactory for INEL solutions because the total impurity level is less than 0.02% and the total impurities is insignificant.

⁴ICPP Analytical Chemistry Monthly Progress Reports, January 1975, November 1975, and September 1976. Reeder, S. D.

An accurate and selective method developed by Lingane and Karplus⁵ for manganese has been studied and found to be highly acceptable for "manganese bath" solutions. Manganous ion, Mn^{+2} , is titrated in a neutral pyrophosphate solution with standard potassium permanganate with the reaction proceeding as follows:

The titration is performed potentiometrically using a platinum-calomel electrode pair. The method is virtually free of interferences.^{5,6} Large amounts of iron(III), cobalt, nickel, copper, zinc, cadmium, aluminum, calcium, magnesium, tin, antimony, lead, chromium(III), vanadium (VI), molybdenum(VI), tungsten(VI), uranium(VI), chloride, sulfate, nitrate, chlorate, perchlorate, and arsenate do not interfere. Oxidants such as hydrogen peroxide, chromate, and chlorine, and reducing agents such as nitrogen oxides and hydroxylamine interfere.

The method as originally reported was scaled down by a factor of approximately four for this work to cover a range of about 10 to 40 mg of manganese. The titration is conveniently performed using a 10 mL Mettler buret interfaced to an HP 9830 calculator for manual or automatic titrations, computation of results and plotting of data. The method has been applied to the manganese bath solutions from INEL and England. The results are in agreement with the EDTA titration for the INEL solution and confirm the results of the impurity analysis on the English solution. The ratio of the results between the simple gravimetric and the potentiometric method for the English solution is 1.0109.

The potentiometric method is simple and accurate. An accuracy and precision of less than 0.05% has been obtained with the method.

6. Induction-Coupled Plasma Source

(R. W. Stone)

An argon-supported induction-coupled plasma-optical emission spectrometer system (ICP-OES) is being investigated for the determination of elemental concentrations in liquid samples. The system consists of a radiofrequency generator, a monochromator and accessory optics, and an amplifier and readout system. The readout system is interfaced to an HP-9825 computer, which is programmed for data acquisition and reduction.

Detection limits and calibration curves have been obtained for several

⁵Lingane, J. J. and Karplus, R., Ind. Eng. Chem., Anal. Ed., 18, (1946).

⁶Scribner, W. G. and Anduze, R. A., Anal. Chem. 33, 770 (1961).

elements. Figure 5 shows a computer plot of the relative emission intensity of the aluminum 396.15 nm analytical line as a function of concentration. Repeat analysis of aluminum solutions of known concentrations gave relative standard deviations of 3.3, 1.7, and 2.0% at 50, 2,500, and 10,000 times the detection limit, respectively.

Detection limits for the elements investigated are given in Table 4. Calibration curves for all the listed elements were linear over at least four orders of magnitude.

The above work represents the first stage of a more thorough investigation of the applications of the ICP-OES system to single- and multi-element analysis of solutions.

TABLE 4
ICP DETECTION LIMITS IN 0.05N HNO₃ SOLUTIONS

Element	Line (nm)	$\mu\text{g/mL}$
Al	396.15(I)	0.02
B	249.67(I)	0.01
Be	234.86(II)	0.006
Ca	393.37(II)	0.003
Cr	357.87(I)	0.01
Nb	309.42(II)	0.05
Nb	313.08(II)	0.08

7. Determination of Sulfate in Synthetic Waste Calcination Feed Solutions by Ion Chromatography

(R. P. Lash and C. J. Hill)

Synthetic second cycle waste was received for analysis for the waste calcination program. Two methods were applied to determine sulfate in these samples: (a) a barium sulfate precipitation and (b) a Leco furnace method to determine total sulfur. Interference by the sample matrix prevented the precipitation of barium sulfate. The Leco furnace method involves conversion of sulfate to sulfur dioxide, which is trapped in an iodine titrant. The high nitrate concentration of the samples interfered with this method. Since neither of these commonly used methods could be applied to these samples, an investigation and subsequent development of a sulfate analysis method by means of ion chromatography was undertaken.

Ion chromatography combines the powerful separations capability of ion exchange with the sensitivity and universality of conductance detection.

Figure 5. Aluminum Calibration Curve

The sensitivity of the ion chromatograph is accomplished by use of a unique suppressor column, which strips out or neutralizes the ions of the eluent leaving only the species of interest as the major conducting species of the effluent. Using this technique, parts per million levels of most common anions can be determined.

The feed solutions have a complex matrix consisting of the following diverse ions:

<u>Ions</u>	<u>Molarity</u>
Al^{+3}	1.1
Na^{+}	1.1
K^{+}	0.16
Ni^{+2}	0.006
Ca^{+2}	0.12
Cr^{+3}	0.014
Cu^{+2}	0.0012
Fe^{+3}	0.066
Mg^{+2}	0.034
B^{+3}	0.005
H^{+}	2.3
F^{-}	0.012
Cl^{-}	0.012
PO_4^{-3}	0.0012
NO_3^{-}	7.3

When sulfate was determined by ion chromatography in this complex matrix, difficulties were encountered due to the high ratio of nitrate to sulfate (36:1 or greater), which prevented complete resolution of the peaks. Separation of these anions was obtained by adjusting the eluent concentration and the flow rate. The final conditions used for the determination of sulfate were:

Mode : Linear
 Columns : 3 x 500 mm anion separator column
 6 x 250 mm suppressor column
 Eluent : 0.003 M $NaHCO_3$ /0.0024 M Na_2CO_3
 Sensitivity: 10 μ mho full scale
 Flow rate : 138 mL/h

A precision and accuracy study was performed using a control which simulated the feed solution. The study showed that a relative standard

deviation of 0.6% (based on six determinations) and a positive bias of 3.8% can be expected for these samples. The SO_4^{2-} concentration ranged from 0.04 to 0.16M. The average total time for the analysis of a sample by ion chromatography was 30 min, which is a considerable time savings as compared to an hour for either the barium precipitation or Leco furnace method.

The procedure was checked by analyzing fluoride containing salts and a calciner sample that had been analyzed by volumetric analysis. A comparison of these data are shown in Table 5.

8. Analysis of Solid Samples for Fluoride by Fluoride Specific Ion Electrode

(D. R. Trammell and R. W. Anselmo)

The Analytical Laboratory recently received samples of calcined waste product and fines which could not be analyzed for fluoride in the usual method. Samples of this general type are usually analyzed for fluoride using a pyrohydrolysis technique to separate the fluoride followed by precipitation with an excess of Ce^{+3} and then titrating the excess Ce^{+3} with EDTA. The sample is mixed with tungsten anhydride, aluminum nitrate, and heated to 950°C with moist air flowing through the tube. The fluoride is trapped in 3.6 N NaOH. The recent samples were found to contain 11 to 14% magnesium instead of the usual calcium additive. During the pyrolysis of these samples a deposit formed in the exit tube of the apparatus and it was not possible to drive off and collect the fluoride. Therefore, it was necessary to develop a new method for analyzing these samples.

The nature of the sample and the required fluoride analysis eliminates acid dissolution of the sample. A basic fusion was selected, using sodium-hydroxide in a nickel crucible. The sodium hydroxide fusion was performed at a low temperature to reduce the possibility of loss of fluoride. These samples also contained boron; a successful analysis for the hydroxide fusion must break the boron-fluoride complex. The fusion does not give total dissolution of calcined samples. The melt is leached with the matrix 1 M citrate, 2 M chloride, 0.1 M TEA (tri-ethanolamine) used in the determination of fluoride by specific ion electrode. The solution is then taken to volume without filtering and analyzed by specific ion electrode. A water leach cannot be used because of insoluble fluoride. These insoluble fluorides dissolve in the citrate matrix.

These data show excellent recovery of the fluoride demonstrating the applicability of the new method. The standard deviations listed are for a single analysis derived from the quality control program for the potentiometric procedure.

The new method was also used to analyze another series of 8 more samples and the results were compared with volumetric data. These data are summarized in Table 6.

TABLE 5
ANALYSIS OF FLUORIDE-CONTAINING SOLIDS BY MODIFIED PROCEDURE

<u>Sample</u>	<u>Composition %</u>	<u>F⁻, %</u>
NaF	F = 45.25 ^a	44.0 ± 2 45.2 ± 2.6 42.9 ± 2 32.4 ± 1.8
CaF ₂	F = 48.67 ^a	48.7 ± 2.2 47.5 ± 2.0
3.2 CaF ₂ ·ZrO ₂	F = 32.59 ^a	32.1 ± 1.7 32.5 ± 1.7
Calcine	F = 18.1 ^b B = 1.7 Zr = 11.6 Al = 5.0 Ca = 26.2 Zn = 7.0 Cs = 0.16 Sr = 0.46 Ce = 0.1	18.1 ± 0.8 18.1 ± 0.8 17.8 ± 0.7 18.2 ± 0.8

^aTheoretical value

^bDetermined by volumetric analyses

These results verify results shown in Table 5. The fusion technique has an advantage over the volumetric procedure in that more than one sample may be processed at a time. If two samples are to be analyzed both procedures take about the same amount of time, but for each analysis after that an hour will be saved by the fusion method. Another advantage of the fusion technique is that it will break up or prevent the formation of boron-fluoride complexes, thereby allowing the use of the fluoride electrode for direct measurement of fluoride without using aluminum to break the complexes. Another advantage of this method is when an aliquot is used in which the fluoride is high and out of limits for the volumetric methods, the whole analysis has to be repeated; but for the potentiometric method all that is required is to take a smaller aliquot for the second dilution.

The lower limit has not been determined; this will depend upon the maximum sample size that can be fused and the maximum amount of flux that can be tolerated by the potentiometric matrix.

TABLE 6

COMPARISON OF POTENTIOMETRIC TO VOLUMETRIC PROCEDURES
FOR ANALYSIS OF FLUORIDE IN SOLID CALCINED SAMPLE

<u>Sample</u>	<u>Volumetric</u>	<u>Potentiometric</u>
77-5599-1	18.3 $\pm$ 2.2	18.2 $\pm$ 0.8
-2	18.0 $\pm$ 2.2	18.8 $\pm$ 0.8
-3	11.3 $\pm$ 2.2	11.4 $\pm$ 0.5
-4	12.4 $\pm$ 2.1	12.9 $\pm$ 0.6
77-6207-1	20.0 $\pm$ 2.1	19.8 $\pm$ 1.1
-2	19.0 $\pm$ 2.0	18.7 $\pm$ 0.9
-3	12.4 $\pm$ 2.3	12.2 $\pm$ 0.5
-4	11.6 $\pm$ 2.9	12.3 $\pm$ 0.5

9. The Determination of Uranium by Redox Titrimetry

(S. D. Reeder)

The development of a precise and selective method to determine milligram quantities of uranium by redox titrimetry was reported earlier. The method which is essentially a scaled-down and modified Davies-Gray titrimetric method requires only 5 to 25 mg of uranium in the titration volume (instead of 100 to 300 mg) without any significant reduction in accuracy or precision. The "miniaturized" procedure features a manual or automatic titration performed under computer control by an HP 9830 interfaced to a 10 mL Mettler buret. Recent experience with this method has resulted in a procedural change to achieve better temperature control in pretitration reactions and improvements in the calculator control programs. The method has been used to check uranium standards and to verify uranium concentration measurements performed by isotope dilution mass spectrometry.

Careful control of temperature during pretitration reactions is essential to obtain satisfactory results. The reduction of uranium by ferrous sulfate and the selective oxidation of excess ferrous ion requires a temperature of about 35°C. This condition is achieved naturally with the large volumes of reagents used in the original method but in the scaled-down version additional heat is required. In the previous scaled-down procedure, this was accomplished by warming the reagents

in a water bath. With wide fluctuations in ambient temperature, this practice was found to be inadequate so a small constant temperature bath heated by an electrical tape is now used to maintain the sample at 35°C throughout the entire procedure.

The computer program, originally written for automatic titration, was based upon electrode potentials and potential changes expected near the equivalence point of the titration. Since the potentials are affected by the amount of uranium in the sample and the past history of the platinum indicating electrode, the fully automatic titration has not always been satisfactory. To achieve the best results the titration must be completed in a few minutes and the end point approached at a systematic rate. A new program has been written to accomplish this task. It requires a close estimate of the volume of titrant required for a sample. Since samples are usually run in duplicate or triplicate for statistical evaluation of results, a manual titration of the first samples provides the information required to calculate titrant volumes. Duplicate samples can then be run in the automatic mode. The titrant is added automatically in decreasing increments to within about 0.02 mL of the estimated end point then increments of 0.005 mL are added until potential changes indicate that the end point has been passed. The volumes of titrant are then systematically increased to complete the data set.

This program is quite versatile and can be used to perform other potentiometric titrations with only minor program changes.

The entire titration program has been converted for operation on the HP 9830 function keys. This gives rapid access to manual or automatic modes, end point and concentration calculations, data storage, and data plotting.

10. Dissolution of Stainless Steel Containing CrB

(D. R. Trammell and T. R. Lyon)

The procedure that is typically used to dissolve boron-containing steels will not dissolve the boron when it is present as CrB. Boron is usually present as boron carbide which is dissolved by a carbonate fusion after acid dissolution of the steel. However, a carbonate fusion will not dissolve CrB.

CrB will dissolve in sulfuric acid, but in the process the chromium and other constituents of the stainless steel form insoluble sulfates that are difficult to dissolve. The following procedure was found to give the most rapid dissolution with the minimum problem with sulfates.

- (1) The sample was dissolved in quartz (Figure 6) under reflux with aqua regia.
- (2) The liquid was decanted through a Millipore filter, leaving as much of the CrB solids in the flask as possible. The solids were washed with water.

Figure 6. Digestion Apparatus

This step removed almost all of the stainless steel components.

- (3) The filter was returned to the flask and 2 mL of concentrated H_2SO_4 and 5 mL of concentrated HNO_3 were added. The HNO_3 destroyed the filter. The nitric acid was boiled off and caught in the trap shown in Figure 6.

As long as nitric acid was present there was no apparent reaction of the CrB.

- (4) After all of the HNO_3 was driven off, the flask was heated gently to get a reaction between the H_2SO_4 and CrB. The heat was kept low because excessive heat caused chromium sulfates to form that were difficult to dissolve. However, it was impossible to completely prevent some insoluble sulfates from forming. The reaction was stopped by adding back the HNO_3 from the trap when the vigorous reaction of the CrB was completed. HCl and water were also added because the sulfates are more soluble in HCl . The solution was digested under reflux until all the sulfates dissolved; this was indicated by a clear solution.
- (5) The solution was filtered, the solids were washed, and step (4) was repeated. This time the H_2SO_4 fuming gave total dissolution of the sample.
- (6) All fractions were combined for the boron analysis.

11. Investigation of Ion Chromatography for Determination of Dibutylphosphoric Acid

(R. P. Lash, J. R. Delmastro, C. J. Hill)

Dibutylphosphoric acid (DBP) is produced in ICPP uranium processing streams chiefly by the radiolytic decomposition of the tributylphosphate (TBP) extractant. A build-up of DBP is undesirable because it also complexes uranium and thereby increases losses of uranium to waste streams. A colorimetric method is currently used for the determination of DBP in ICPP process streams. This method is tedious and lengthy requiring up to 8 h/analysis, and uses a potentially hazardous perchloric acid fuming step. Development of a method which improves reliability, eliminates the hazards of perchloric acid, and reduces the analysis time would be extremely beneficial. A colorimetric determination of DBP using Rhodamine B through ion-pairing was investigated earlier, and conformance to Beer's law was demonstrated. However, subsequent application of this method to the determination of DBP in TBP process samples containing uranium failed due to matrix effects. Therefore, an investigation into the use of ion chromatography was performed. Promising results have been obtained for the determination of DBP after stripping it from TBP-kerosene mixtures.

Ion chromatography combines the separation capabilities of ion exchange

and the use of conductance detection with a unique system, which suppresses eluent conductance, leaving only the ions of interest as the major conducting species. Development of a chromatographic method for DBP involves finding an eluent capable of giving: (a) good separations from monobutylphosphoric acid, inorganic phosphate, and impurities derived from the kerosene diluent, (b) reasonable retention times (5-10 min), (c) a low background conductance, and (d) good recoveries of DBP in stripping it from the TBP-kerosene matrix.

Aqueous solutions of sodium bicarbonate and/or sodium carbonate and sodium phenate at various concentrations were investigated. Sodium phenate had a considerably lower background conductance as well as the ability of giving good separation and reasonable retention times. Since ion chromatography is based on an aqueous system, direct injection of the TBP-kerosene matrix was impossible. Therefore, stripping of the DBP into aqueous solution as a sodium salt by a base must be performed prior to injection. Sodium phenate proved to be as suitable a base for stripping as sodium hydroxide, which is currently used in the colorimetric method.

The procedure for preparing the DBP for injection involves shaking 5 mL of the TBP-kerosene matrix with 10 mL 0.001 M sodium phenate for one min, centrifuging at high speed for 2-3 min, removing the top organic layer with an eye dropper and removing the remaining kerosene under vacuum with a transfer pipet.

The sodium phenate-DBP strip was then injected into the ion chromatograph under the following conditions:

Mode	: Linear
Columns	: 3 x 500 mm anion separator column 3 x 150 mm anion precolumn 6 x 250 mm suppressor column
Eluent	: 0.001 M sodium phenate
Sensitivity	: 3 mho full scale
Flow rate	: 92 mL/h

A typical chromatogram of DBP is present in Figure 7.

Precision and accuracy studies were performed on a TBP-kerosene matrix prepared to simulate a first cycle "C" column raffinate from processing zirconium-uranium fuel. The results for eight determinations at both the 20 ppm and 50 ppm levels showed negative biases of 0.1% and 0.7%, respectively. Based upon a t-test with seven degrees of freedom, these biases are not significant at the 95% confidence interval. The relative standard deviations are 2.69% at the 20 ppm level and 2.83% at the 50 ppm level.

Recent developments have shown that sodium phenate contains impurities

Figure 7. Typical Chromatogram of 50 ppm Solution and Dibutylphosphate

which can poison the separator column. Therefore, further investigation into other eluents such as sodium hydroxide will be performed.

12. Mass Spectrometric Analysis of Thorium

(G. W. Webb, G. L. Peterson, P. L. Jorgenson)

An effort has been made to scope the Mass Laboratory's capabilities for routinely running thorium on our presently available mass spectrometers.

A solution of natural thorium was run ($\sim 1 \mu\text{g}$ loading) with five different loading techniques: (a) loaded on a side filament as is done with uranium, (b) loaded on a rhenium center filament, (c) loaded on a rhenium center filament and heated with a sugar solution, (d) loaded on a rhenium center filament and heated to dull red in air, and (e) loaded on a tantalum center filament and the filament heated to a dull red color in air.

Loadings (a), (b), and (c) gave a very small thorium beam and the beam died within seconds. Loading (d) gave a 30-mV thorium oxide beam which lasted for a few minutes. Loading (e) gave a 300-mV beam which lasted for 15 minutes but died when the current was increased.

Continued work on tantalum filaments has shown that $1 \mu\text{g}$ samples can be run with a 1 V beam if the current is brought up slowly and doesn't exceed ~ 3.1 amps. The procedure which has resulted from this study will be adequate for the analysis requested by the LWBR analytical support program. The Mass Laboratory is now in the process of running calibrations and the samples from this program. The method which is being used is preliminary, and further work would be required for programs with stringent precision requirements or for a rapid throughput of samples.

VIII. ENVIRONMENTAL IODINE SPECIES BEHAVIOR

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

Field measurements were initiated at the Quad Cities Nuclear Power Station. Source-term measurements are being made at the two release points in-plant, and environmental measurements are being made at several sites. As reported last quarter, this program is a cooperative effort between NRC and the Electric Power Research Institute (EPRI). The Allied Chemical Corporation-Idaho Chemical Programs responsibility in the plant is for Xe, ^{14}C , and ^3H measurements while the EPRI contractor is measuring the ^{131}I release rate and species. In the environment, EPRI is maintaining airborne iodine samplers at five sites. Allied Chemical is collecting Xe, ^{14}C , ^3H , milk, grass, and deposition (rain) samples at two of these sites. Wind speed and direction are being recorded at both sites.

Preliminary analysis of the data to date shows that iodine in milk is observed only after rainfall. That is, wet deposition appears to be a controlling factor in the transfer of iodine from air to the cow and then milk.

REPORTS AND PUBLICATIONS ISSUED DURING THE QUARTER

1. IDAHO CHEMICAL PROGRAMS REPORTS

1. D. W. Rhodes and J. L. Lee, Leak Testing Fuel Stored in the ICPP Fuel Storage Basin, ICP-1118 (June 1977).
2. T. R. Thomas, et al., Airborne Elemental Iodine Loading Capacities of Metal Zeolites and a Method for Recycling Silver Zeolite, ICP-1119, Idaho National Engineering Laboratory, Idaho Falls, ID, (July 1977).
3. C. M. Young, Factors Affecting the Atomization of Cobalt in a Graphite Furnace, ICP-1120, Idaho National Engineering Laboratory, Idaho Falls, ID, (June 1977).
4. C. M. Slansky, et al., Alternative Fuel Cycle Technology Progress Report for April 1-June 30, 1977, ICP-1122, (July 1977).
5. C. M. Slansky, et al., Technical Division Quarterly Progress Report for April 1-June 30, 1977, ICP-1123, (July 1977).
6. D. A. Knecht, Evaluation of Methods for Immobilizing Krypton-85, ICP-1125, (July 1977).
7. R. W. Benedict, An Evaluation of Methods for Immobilizing Solids Loaded with Krypton-85, ICP-1130, (August 1977).
8. W. J. Maeck, ed., Fast Reactor Fission Yields for ^{239}Pu and ^{241}Pu , ICP-1050-II, (August 1977).
9. W. J. Maeck, W. A. Emel, et al., Fast Reactor Fission Yields for ^{237}Np , ICP-1050-III, (September 1977).

2. PAPERS PRESENTED AT TECHNICAL SOCIETY MEETINGS

1. Institute of Nuclear Materials Management, Arlington, VA, June 29-July 1, 1977
 - a. J. A. Wielang, "An Expanded Approach to Certification".
2. Annual Meeting of the Geothermal Resources Council, San Diego, CA, May 9-12, 1977
 - a. C. A. Allen, A. F. Fanous, E. S. Grimmett, R. E. McAtee, "Report on the Development of Liquid Fluidized-Bed Heat Exchangers".
3. 12th Intersociety Energy Conversion Engineering Conference, Wash., D.C., September 12, 1977
 - a. C. A. Allen, et al., "Liquid Fluidized-Bed Heat Exchanger-Horizontal Configuration Experiments and Data Correlations".

4. 1976 Pacific Conference on Chemistry and Spectroscopy, Phoenix, AZ, November 8-10, 1976
 - a. C. A. Allen, J. M. Baldwin, and R. E. McAtee, "Well Sampling and Water Analysis Methods used by Allied Chemical Corporation for the Geothermal Well at Malta, Idaho".
5. Second Workshop on Sampling and Analysis of Geothermal Effluents, U.S. Environmental Protection Agency, Las Vegas, NV, February 15-17, 1977.
6. International Solvent Extraction Conference, Toronto, Canada, September 9-16, 1977.
 - a. W. W. Schulz and L. D. McIsaac, "Bidentate Organophosphorous Extractants: Purification, Properties and Applications to Removal of Actinides from Acidic Waste Solutions".
7. AIChE-ASME Heat Transfer Conference, Salt Lake City, UT, August 15-17, 1977.
 - a. E. S. Grimmer, A. F. Fanous, and C. A. Allen, "Advances in Liquid Fluidized-Bed Heat Exchanger Development".
8. IAEA Second Advisory Group Meeting on Fission Product Nuclear Data, September 5-9, 1977, Petten, Netherlands.
 - a. W. J. Maeck, "Fission Product Nuclear Data Requirements for Investigation of Irradiated Nuclear Fuel: Burnup Measurements, Neutron Dosimetry, Nuclear Safeguards".

DISTRIBUTION RECORD FOR ICP-1132

Internal Distribution

- 1 - Chicago Patent Group-DOE
9800 South Cass Avenue
Argonne, Illinois 60439
- 1 - C. A. Benson
Idaho Operations Office-DOE
Idaho Falls, ID 83401
- 1 - H. P. Pearson, Supervisor
Information Management
- 10 - INEL Technical Library
- 20 - Authors
- 84 - Special Internal

External Distribution

- 335 - UC-02 - General, Miscellaneous, & Progress Reports (Nuclear)
UC-10 - Chemical Separations Processes for Pu and U, Tid-4500, R66
- 61 - Special External

Total Copies Printed - 513