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TECHNICAL DIVISION QUARTERLY PROGRESS REPORT JANUARY 1 — MARCH 31, 1978

July 1978

MASTER

**Allied
Chemical**

IDAHO CHEMICAL PROGRAMS

IDAHO NATIONAL ENGINEERING LABORATORY

DEPARTMENT OF ENERGY

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

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TECHNICAL DIVISION QUARTERLY PROGRESS REPORT

January 1 - March 31, 1978

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July 1978

ALLIED CHEMICAL CORPORATION
IDAHO CHEMICAL PROGRAMS - OPERATIONS OFFICE

PREPARED FOR THE
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ABSTRACT

Progress for the first quarter of 1978 is reported on DOE - budgeted activities contracted to Allied Chemical Corporation - Idaho Chemical Programs 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 waste from the reprocessing of spent commercial nuclear fuel, on the post-treatment of the resultant calcine, and on the use of bidentate extractants for the separation of actinide elements from the high-level waste prior to calcination. In addition, the development of storage technology for krypton-85 waste, and the behavior of RuO₂ in fluidized-bed combustion of HTGR fuel are reported.

Special Materials Production

Reported are the long-term management of defense waste from the ICPP, the chemistry and pilot plant studies on the removal of actinides and mercury from ICPP first cycle raffinate, the calcined solids retrieval and handling of ICPP waste stored in vaults, and the preparation of environmental impact statements on options given the Defense Waste Document Process improvements are given on the Fluorinel headend process for zircaloy-clad fuel) and on methods for uranium accountability.

Other development results reported are on the Rover process for graphite based fuels, on the calcination of sodium-bearing waste, Fluorinel waste, tank WM-183 waste, and electrolytic process waste. Assistance to the Waste Calcination Process Plant is reported as well as support to the New Waste Calcination Process and methods for the monitoring of gaseous effluents.

Other Projects Supporting Energy Developments

Results are reported on nuclear materials security, the behavior of liquid-solid fluidized-bed heat exchangers, in-plant reactor source term measurements, burnup methods for fast breeder reactor fuels, absolute thermal fission yields, analytical support to light water breeder reactor development, and species of iodine in the environment. Research on analytical methods cover iodine-129 in calciner feed, computing room improvements, stack gas sampling for particulates, analysis of glassified calcined waste, and specific components in various materials.

SUMMARY

FUEL CYCLE RESEARCH AND DEVELOPMENT

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

1. Application of Microwave Energy to Processing of High-Level Wastes

A report on the potential applications of microwave energy to high-level waste treatment processes was issued. Two microwave applications, vitrification and rapid and uniform drying of pelleted calcine, have potential advantages over conventional methods. Microwaves provide uniform spacial heating, eliminate electrodes, and can be used to start the melting process. A microwave heater for drying pelleted high-level waste calcine was designed.

2. Study of Bidentate Compounds for Separation of Actinides From Power Reactor Reprocessing Waste

Distribution coefficients for elements between cadmium modified synthetic HAW solution and 30% dihexyl-N,N-diethylcarbamyldimethylenephosphonate (DHDECMP) in diisopropylbenzene (DIPB) were measured. Chemical and physical properties such as toxicity, viscosity, IR and UV spectra of purified DHDECMP are being obtained. Litre quantities of relatively pure (~85%) DHDECMP were produced by vacuum distillation.

II. KRYPTON-85 STORAGE DEVELOPMENT

Definition of rubidium corrosion kinetics of Type 304 stainless steel at 793, 843, and 893 K is 90% complete. Significant corrosion observed on the surface consisted of three distinct layers and an intergranular region. Both regions exhibit evidence of leaching of Fe by Rb, followed by transport of Fe away from the leading edge of the attack. Baseline tensile tests of hollow specimens and solid, notched samples are complete; tensile tests of exposed samples were started. Calculated loadings of krypton-85 on sodalite using a model based on the integrated Fick's diffusion law were compared with experimental values. A sodalite sample loaded with $36 \text{ cm}^3 \text{ g}^{-1}$ krypton did not leak while in contact with water at 27°C for 16 h.

III. HTGR FUEL REPROCESSING

Vaporization and plateout characteristics of RuO_2 in a fluidized-bed burner were determined. The amount of ruthenium released from the burner is dependent on the oxygen concentration in the fluidizing ruthenium gas during the thermal soak period. Volatility decreased by an order of magnitude when the oxygen was decreased from 60 percent to 20 percent. In addition, the effect of I_2 on the CO oxidation catalyst was studied. Reversible and irreversible poisoning reaction effects were identified; reversible poisoning is dependent upon I_2 concentration.

SPECIAL MATERIALS PRODUCTION

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

1. Post-Calcination Treatment of ICPP High-Level Wastes

A systematic study was completed to determine the effect of frit components on the melt viscosity and acid leach resistance of glasses made with ICPP fluoride containing calcine. Frits containing CuO and/or P_2O_5 , in addition to SiO_2 , Na_2O , and B_2O_3 , produced the most leach-resistant glasses. A potentiometric method to determine fluoride content in glass was developed. Glasses examined to date indicate that little fluoride volatilizes during melting. Coupons of Inconels 690, 625, and 601 (materials being considered as potential glass melting electrodes) were tested for resistance to corrosion in a glass melt. Inconels 690 and 601 were found to be satisfactory electrode materials. Liquid binders consisting of colloidal SiO_2 , H_3PO_4 , or $AlPO_4$ were tested for ability to form a pelleted waste on a disc pelletizer. Leach resistance of pellets tested to date increases with increasing H_3PO_4 addition.

2. Pilot-Plant Studies on Actinide Removal from ICPP Wastes

Flooding tests were continued using the pilot-plant extraction columns and simulated dissolver solution and kerosene. Kerosene was used instead of DHDECMP system to prevent loss of expensive extractant during the checkout phase. Although consistent results were obtained in the non-flooding region, data were scattered in the flooding range and reproducible results were difficult to obtain. Pilot-plant changes required to provide flexibility in operation were identified and equipment was specified. New tanks and pumps planned for installation will allow both pulsed columns to be operated simultaneously in the extraction and stripping mode. A spectrochemical method for analyzing the cerium to be used as a simulant for actinides was developed. The method will be adequate to measure cerium concentrations following six or seven stages of cerium extraction.

3. Chemistry Studies on Actinide Removal from ICPP Wastes

Mercury, present in ICPP first-cycle waste, is strongly bound to DHDECMP during actinide extraction and is not removed during subsequent stripping. Since the buildup of Hg in the extractant would eventually reduce the extraction of actinides, a study was made to assess various Hg removal techniques. The options include electrolytic replacement, reduction by H_3PO_2 , reduction by lithium amalgam, and complexation with mercaptoacetic acid ($HSCH_2COOH$). Further study will be made when a process option is selected.

The rates of extraction of Ce(III), Am(III), and Pu(IV) in the DHDECMP in synthetic Zr-Al dissolver solution system were measured as a function

of time. The extraction curves are similar in shape and show that equilibrium for all three elements is reached within the same time interval. Cerium can be used as an Am(III) and Pu(IV) simulant in pilot plant studies to predict actinide behavior.

4. Calcined Solids Retrieval and Handling

Cold prototype testing of the drilling equipment received for the Calcine Bin Sampling and Analysis Project showed that a scoop in the side of each sample tube and a penetrometer point on the bottom of the sample train are necessary to obtain an adequate sample. The sample will now be obtained during withdrawal of the sample train from the bin. The remote flow factor tester was received from ORNL for use in the Multicurie Cell examination of the retrieved calcine.

The calcine sampling is now scheduled for June and calcine analysis in the Multicurie Cell was rescheduled for July. Issuance of a report on the above is still scheduled for September 1978.

Installation of the small-scale rotating nozzle system was completed and tested; calcine successfully flowed to the nozzle.

5. Idaho Programmatic Environmental Impact Statement

Nuclear Safety Associates was awarded a contract to evaluate the potential environmental impact of each option considered in the Draft Programmatic Environmental Impact Statement (DPEIS). The Ralph M. Parsons Company completed their contract for providing source terms for environmental analysis of all proposed options and preconceptual design for options not included in the Defense Waste Document (DWD).

6. Long-Term Defense Waste Conceptual Design

Scoping studies for conceptual design of a full-scale pelletizing plant began. Pelletizing capacity (180 kg/hr), a candidate process based on 240 d/yr, and power requirements (150 kw) were defined.

II. ICPP PLANT PROCESS IMPROVEMENT

1. Uranium Accountability Measurements

The (triiso-octylamine-xylene) chemical separation method was further tested. Its tolerance for higher levels of sulfate ion is fairly good, but the presence of sodium in some samples saturated in sodium sulfate can cause instability in the ion beam. The effect of chloride ion upon sample loading and running was also tested, and preliminary results indicate that the effect may be very small. During the course of these studies, criteria (such as maximum analysis time and the precision of the measurement of isotopic abundance) for defining "good" instrument running behavior were quantified. Studies continued on the filament temperature versus current dependence. Finally, the normal level of filament-to-filament variation for mass spectrometry data was derived.

2. Zirconium Fuel Recovery Process

Cyclic corrosion tests designed to provide data to estimate the usable lifetime of the Hastelloy C-4 Fluorinel dissolver were completed on the dissolution flowsheet for the reference Fluorinel fuel. Increasing fluoride concentrations in the zirconium dissolver product solution from ~7 M to ~11 M increased the corrosion rate from 90 $\mu\text{m}/\text{mo}$ to 125 $\mu\text{m}/\text{mo}$ and also caused increased pitting attack.

III. ADVANCED GRAPHITE FUELS REPROCESSING

Tests to measure erosion rates of the Rover Plant dry solids transfer systems were completed. Erosion rates in schedule 80 pipe bends were compared with rates in Schedule 40 bends. The results showed that the decreased cross-sectional area of the Schedule 80 piping had no significant effect on the erosion rate of piping bends near the ejector. A porcelain-lined ejector was tested for erosion. This ejector lasted slightly longer than the stainless steel ejector, but the difference was not enough to justify replacement of the plant ejectors.

Installation of the dissolver for Rover plant support was started and operating procedures are being prepared. Modifications to convert the pilot-plant secondary burner for optional use as either a primary or a secondary burner were made.

A literature search and laboratory tests on the reliability of Kynar piping were conducted. Test welds were made to verify the manufacturer's procedure. New Kynar piping was recommended to replace the faulty Kynar piping in the Rover Plant, but care must be taken during installation to ensure proper welds.

A study of the Rover Plant process was started to identify potential operating problems and contingency plans for their solution.

IV. ICPP WASTE MANAGEMENT DEVELOPMENT

1. Sodium-Bearing Waste Flowsheet Development

Blending zirconium waste with ICPP sodium-bearing waste was studied as a method for calcining sodium-bearing waste. Calciner feeds containing zirconium waste to sodium-bearing waste blend ratios between 2 and 8 (adding sufficient calcium nitrate to give a calcium to fluoride mole ratio of 0.7) were tested in 10- and 30-cm-diameter calciners. A blend ratio of 3 to 4 was selected for testing in the WCF.

2. Fluorinel Waste Flowsheet Development

Tests using a 10-cm-diameter calciner have shown that cadmium in the design basis Fluorinel waste causes significant particle agglomeration. Two attempts to calcine the simulated waste resulted in forced shutdowns after eight h operation because of the formation of agglomerates.

The cadmium was omitted from the waste for the next tests; these ran successfully for 24 h. The next test, again with cadmium, failed after 10 h due to agglomerate formation. Further tests using a 10-cm-diameter calciner will be made to evaluate alternate Fluorinel waste flowsheets and additives for preventing agglomeration.

3. Tank WM-183 Flowsheet Development

A 10-cm-diameter calciner run successfully demonstrated that a 2:1 blend of zirconium fluoride to WM-183 waste would adhere to and build on a zirconium fluoride waste starting bed.

Run 64 (a test of the 2:1 blend zirconium fluoride waste with unconcentrated and concentrated WM-183 waste) was completed during the last reporting period. Analytical data for the run were received which showed the chloride level in the scrubbing solution did not exceed 72 ppm. The sintering temperature of the calcine was determined to be 650°C.

4. Electrolytic Waste Flowsheet Development

Two 10-cm-diameter calciner runs were completed using an electrolytic waste feed. The feed used during Run EL-10-1 was electrolytic waste (WM-101) concentrated to 33% of its original volume; the feed during Run EL-10-2 was electrolytic waste concentrated to 25% of its original volume. Neither run resulted in agglomerate formation; a higher than normal, but acceptable, amount of fines were generated.

5. Alternate WCF Start-Up Bed Material Studies

Because of high erosion caused by dolomite and high elutriation rates of dolomite during WCF startup, other materials were investigated to replace dolomite as a startup bed material. Based on attrition resistance, low erosion potential, and solubility in nitric acid, fluorapatite was chosen and successfully tested in the pilot-plant calciners. Fluorapatite will be tested in the WCF.

V. WCF SUPPORT

1. WCF Scrubbing Solution Chloride Limit

Based on corrosion testing with simulated scrubbing solutions, the chloride concentration limit for the WCF scrubbing solution was raised from 1300 to 2600 ppm. A plant test to reduce the chloride concentration in the WCF scrubbing solution was unsuccessful; indications are that the presence of sodium, calcium, and aluminum are necessary to prevent excessive chloride volatility during calcination.

2. Calciner Product Removal Studies

A calciner product removal system similar to that used at the WCF has been installed on the 30-cm-diameter calciner in the High Bay Laboratory.

This system will be used to more precisely define the range of operating conditions for the WCF and for scoping alternate designs.

VI. NWCF SUPPORT

1. Sump Sampling System Test

A mockup of the sampling system proposed for the NWCF liquid-waste sump tank was tested successfully. The sampler pulled liquid with a density of 1200 kg/m^3 to a height of 10.8 m above the sump.

2. Resistance of Compressor Sealing Materials to Decontaminating Reagents

Potential sealing materials to be used in the NWCF off-gas compressors--a poly(amide-imide) resin, a poly(amide-imide)-Teflon resin, and a silicone rubber material--were tested for their ability to withstand ICPP decontaminating reagents. The silicone rubber material was more resistant to a greater variety of reagents (particularly alkaline solutions) than were the other two materials.

3. Dense-Phase Pneumatic Transport Tests

Conveyability tests with simulated zirconium fluoride calcine were completed at the pilot-plant facilities of three vendors of dense-phase pneumatic-transport systems. The system fabricated by Dynamic Air was selected for verification testing based on lowest transport velocity, lowest product attrition, and fewest valves in contact with solids.

VII. EFFLUENT MONITORING METHODS EVALUATION AND DEVELOPMENT

The laboratory apparatus for measuring high efficiency particulate air (HEPA) filter efficiencies in a corrosive off-gas environment was checked out, problems identified, and modifications and improvements completed. Experimental testing is planned for the next quarter.

A time integrated sampling technique was developed for the collection of the long-lived isotopes ^{99}Tc ($\beta_{\text{max}} = 0.292 \text{ MeV}$, $t_{1/2} = 2.12 \times 10^5 \text{ yr}$) and ^{79}Se ($\beta_{\text{max}} = 0.16 \text{ MeV}$, $t_{1/2} = 6.5 \times 10^4 \text{ yr}$). An analytical procedure for separating the selenium and technetium from the silver substituted zeolite sampler media was investigated. Attempts were made to develop a procedure that simultaneously separates technetium, iodine, and selenium in a manner compatible with liquid scintillation counting. A procedure using distillation and solvent extraction was developed. Chemical yields for selenium and iodine were 14 and 17%, respectively. The chemical yield for technetium will be determined in the next quarter and the procedure will be verified on actual stack samples.

OTHER PROJECTS SUPPORTING ENERGY DEVELOPMENTS

I. NUCLEAR MATERIALS SECURITY

A listing of sensors and instruments for the ICPP test and evaluation safeguards monitoring system for the plant product loadout area was completed and conceptual design for a plant installation is in progress. Preliminary requirements for the safeguards data acquisition system were established and preparation of detailed specifications is nearly complete. Laboratory testing of a coriolis force flowmeter and a transit-time bubble flowmeter confirmed the anticipated 0.5% accuracy. Installation of the pilot-plant gamma absorbtimeter system was completed and the system was checked out with water in the flow loop. Mechanical modification of the Extranuclear Quadrupole Mass Spectrometer is in progress.

II. GEOTHERMAL PROJECTS

Flow distribution and outside heat transfer coefficients were measured using horizontal and vertical fluidized-bed heat exchangers. Higher heat transfer coefficients were measured with the vertical exchanger than with the horizontal exchanger.

III. IN-PLANT SOURCE-TERM MEASUREMENT PROGRAM

The in-plant source-term program is designed to collect data on radioactive commercial pressurized water reactors. The data collected will be used to verify or modify existing predictive models concerning the source and transport of radionuclides and process equipment effectiveness for removing radionuclides. Measurements have continued at the Turkey Point Station with major emphasis on the behavior of radionuclides in the secondary system during periods of a primary to secondary leak.

IV. BURNUP METHODS FOR FBR FUELS

Efforts have continued in the precise measurement of fast fission yields. Analysis of stable and long-lived fission product nuclides of Kr, Rb, Sr, Zr, Mo, Ru, Xe, Cs, Ba, La, Ce, Nd, and Sm were completed for the ^{235}U sample irradiated in EBR-II by ANL and made available by ORNL. Analysis of the ^{233}U sample from the same irradiation is in progress.

V. ABSOLUTE THERMAL FISSION YIELDS

Data analysis for the absolute thermal fission yields of ^{235}U is complete and the error analysis is in progress. Mass spectrometric analyses of the three low burnup ^{239}Pu samples were completed and those for the high burnup samples are nearing completion. Analysis, data reduction, and isotopic correlations were completed for the 14 punchings from two ATR fuel plates.

VI. SPECIALIZED FUEL RESEARCH - ANALYTICAL SUPPORT

The Nuclear Measurements Section is currently performing analytical support work for the Light Water Breeder Reactor program (LWBR), for Knolls Atomic Power Laboratory (KAPL), the Power Burst Facility (PBF), and General Atomic Company (GA). The preliminary report of the results for the four remaining LWBR segments was sent to the sponsor; the final report with the statistical analysis will be sent in the near future. Dissolution procedures for the KAPL program are being checked using unirradiated test segments, and other related procedures are being reviewed. Analyses of two sets of irradiated fuel samples from PBF were completed and the results were reviewed in consultation with the sponsor. Analyses were also run on a set of unirradiated PBF fuel samples. These were required not only for the program itself, but for the receiver's accountability value. The results for all of the analyses on the GA fuel particles were sent to the sponsor.

VII. RESEARCH ON ANALYTICAL METHODS

1. Stack Gas Leaching Study

Stack Gas Particulate Filters are now leached within the counting vials used to gamma-scan the pelletized sample. This minimizes cross contamination between samples and reduces the volume of the sample.

2. Remote Iodine-129 Separation Procedure

A remote separation procedure was developed for the determination of iodine-129 in radioactive WCF feed solutions.

3. Counting Room Improvements: Installation of Magnetic Tape Subsystem

A magnetic tape subsystem which replaced a tape cassette unit was installed on the Data General Nova 1200 dedicated Computer in the Radiochemical Analysis counting room. The new system will permit long-term data storage, reduce the possibility of data loss, and improve the speed of data recovery.

4. Improved Method For Gamma-Scanning ICPP Daily Stack Gas Particulate Filter Samples

The method of preparing stack gas particulate filters for gamma-scanning was improved. The samples, previously counted in a wedge shape, are now compressed and counted in a disc shape. The source-to-detector distance was reduced from 10-cm to 5-cm.

5. Analysis of Glassified Calcliner Material For Fluoride

Three samples of non-radioactive glassified calcine materials were used to determine the applicability of existing methods for analyzing fluoride

in this type of material. The materials were analyzed by three different methods. Data show that a modification of an existing fluoride potentiometric method can be used.

6. Gas Chromatographic Determination of Residual Monomers Ethyl Acrylate and Acrylonitrile in Insulation Adhesive

In support of the EG&G industrial hygiene program, a gas chromatographic method was developed for the determination of residual monomers of ethyl acrylate and acrylonitrile in an insulation adhesive. The method uses a column and a hydrogen flame ionization detector. The method is calibrated using n-pentanol as an internal standard.

7. Calculator Sample Bracketing Program for Flame Spectrometry

A sample bracketing program was developed to acquire and reduce the data obtained in routine analyses by flame spectrometry. The program reduces calculation time and improves the accuracy of routine analysis.

8. Analysis of Cutting Oil Samples Using an ICAP-VIDICON System

An induction coupled argon plasma-vidicon (ICAP-V) system was investigated as a method for determining metal concentrations in cutting oil. It was found that six elements could be run simultaneously and only minimal sample preparation was necessary. Analysis time was shortened from 2-1/2 d to less than 4 h.

9. New Counting Equipment: Alpha Pulse Height Spectrometer and Low Energy Photon Spectrometer (LEPS)

Two new counting systems, an improved alpha pulse height spectrometer and a low energy photon spectrometer, are being set up and calibrated by the Radiochemical Analysis Group. These systems will determine low specific activity alpha emitters and low energy X-ray and/or gamma ray emitters.

VIII. ENVIRONMENTAL IODINE SPECIES BEHAVIOR

The environmental iodine species behavior program is an NRC-funded program for measuring the release of radioiodine from nuclear facilities and for defining its behavior in the environment. Data are being reduced from several months of measurements at the Quad Cities Nuclear Station.

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RESULTS

FUEL CYCLE RESEARCH AND DEVELOPMENT

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

1. Application of Microwave Energy to Processing of High-Level Wastes

(T. C. Piper)

A report on the potential applications of microwave energy to high-level waste treatment processes was completed.¹ As part of this study, a microwave applicator to dry pelleted waste was designed. The applicator box is 51 cm wide, 51 cm high, and 90 cm long with three inclined glass plates sloped at 2 degrees to route the pellets through the applicator. Design capacity of the unit is 23 kg/h, and pellet residence time will be 15 min at 200°C. A vibrator will be used to control the movement of the pellets through the applicator. A 6 kW microwave generator will provide the power.

A study is underway to determine if radiation from high-level waste causes microwave breakdown.

Plans for Next Quarter

Fabrication of the microwave applicator will be started. Effects of ionizing radiation on microwave breakdown will be defined.

2. Study of Bidentate Compounds for Separation of Actinides From Commercial LWR Reprocessing Wastes

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

Distribution coefficients for Tc, Mo, Pd and Zr between cadmium-modified synthetic HAW solution and 30% dihexyl-N,N-diethylcarbamylnmethylenephosphonate (DHDECMP) in diisopropylbenzene (DIPB) were measured. Synthetic cadmium-modified HAW solution was prepared from synthetic HAW used in previous experiments² by adjusting the acidity to 3.5 M HNO₃ and making the solution 0.156 M in Cd(NO₃)₂ and 0.0044 M in H₂C₂O₄.

¹ T. J. Piper and J. R. Berreth, The Potential Application of Microwave Energy in Solidifying High-Level Nuclear Wastes, Allied Chemical Corporation-ICP, ICP-1145, (March 1978).

² C. M. Slansky (ed.) et al., Technical Division Quarterly Progress Report for January 1-March 31, 1977, Allied Chemical Corporation-ICP, ICP-141 p 19.

Experimental procedures for extraction, scrub, and stripcontacts were the same as those reported for oxidized synthetic HAW³ except that the scrub solution was 3.5 M HNO₃-0.5 M H₂C₂O₄. In general, extraction values are lower for the cadmium modified system than for the oxidized system reported previously³.

Preparative liquid chromatography was used to obtain a small quantity of purified (>99%) DHDECMP. This material is being used to obtain various physical and chemical data on the compound including density, viscosity, and infrared, ultraviolet, and nuclear magnetic resonance spectra. In addition, a mutagenic study is being conducted by Microbiological Associates of Bethesda, Maryland. Results of these studies will be reported later.

A major effort was made to distill litre quantities of relatively pure (>85%) DHDECMP. Enough DHDECMP has been distilled to carry out laboratory experiments for the next few months and to fill requests from outside laboratories. Depending on starting purity, about 350-500 mL of >85% pure DHDECMP can be produced per day with the modified CVC-5 molecular distillation unit.

Plans for Next Quarter

Additional distribution coefficients for cadmium-modified HAW will be determined. Preparations for a semi-hot minimixer-settler run using synthetic cadmium modified HAW as the feed will be completed. A sample of LWR fuel will be dissolved and typical first-cycle wastes will be generated for mixer-settler studies.

II. KRYPTON-85 STORAGE DEVELOPMENT

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

1. Storage Alternatives

A draft of the revised Program Plan was completed. It reflects a redirection of the program to the development of krypton-85 storage technology for DOE sites and the evaluation of alternative disposal technologies which might be competitive with zeolite encapsulation.

2. Krypton-85 Process and Storage Materials Testing

2.1 C-Ring Tests

Corrosion tests with C-ring specimens in liquid rubidium at 491 and 672 K were started. Materials and procedures are similar to the tests at 400

³ C. M. Slansky (ed) et al., Technical Division Quarterly Progress Report for April 1-June 30, 1977, Allied Chemical Corporation-ICP, ICP-1123 p 2.

and 573 K in the previous quarterly report. The test temperatures cover potential conditions of processing and storing krypton-85.

2.2 Rb Corrosion Kinetics Tests

Corrosion kinetics of Type 304 stainless steel, Inconel 600, and A286 steel in liquid rubidium at 650-925 K are being measured at Colorado School of Mines. Testing of Type 304 stainless steel is 90% complete; testing of Inconel 600 was started.

2.2.1 Results of Type 304 Stainless Steel Corrosion Kinetics

Rectangular coupons were immersed in liquid rubidium for 550 h at 793, 843, and 893 K. After exposure, coupons were analyzed metallographically using optical and scanning electron microscopes (SEM). Corrosion products were further analyzed chemically with the SEM using an energy dispersive X-ray (KEVEX) unit.

2.2.1.1 Corrosion Kinetics Tests at 793 K

The Type 304 stainless steel coupons showed significant corrosion damage. Specimens developed a thick external scale (Figure 1) which was shown by KEVEX analysis to be mainly Rb and Fe, some Cr, and no Ni.

2.2.1.2 Corrosion Kinetics Tests at 843 K

Samples exhibited significant corrosion in the form of a brown scale (Figure 2). KEVEX analysis of the scale showed mainly Rb and Fe, some Cr, and no Ni. Polished metallographic sections revealed continuous intergranular corrosion. SEM examination of the polished section (Figure 3) reveals that the exterior corrosion product consists of three layers as well as regions of intergranular corrosion (spot 4 in Figure 3). Chemical analysis of the three layers are summarized graphically in Figure 4 in terms of the concentration of Fe, Cr, and Ni in each zone relative to the concentration in the base alloy. The inner layer, zone 3, is depleted in Fe, while the outer layers are depleted in Cr and Ni.

It appears that the processes active during corrosive attack of Type 304 stainless steel by Rb involve (1) leaching of Fe from the alloy, and (2) transport of Fe away from the leaching edge of attack.

KEVEX analysis of corroded grain boundary areas, such as spot 4 in Figure 3, showed high enrichment of Cr (see Figure 4). The observation of high Cr concentration along corroded grain boundary paths is consistent with grain boundary sensitization of the Type 304 stainless steel. Unstabilized austenitic alloys such as Type 304 will precipitate chromium carbides at grain boundaries at 673-1923 K.⁴ The resulting Cr

⁴ H. H. Uhlig, Corrosion and Corrosion Control, New York: Wiley, 1967.

Figure 1. SEM Photograph Showing External Corrosion Scale on Type 304 Stainless Steel Exposed to Rb at 793 K.

Figure 2. SEM Photograph Showing External Corrosion Scale on Type 304 Stainless Steel, Exposed to Rb at 843 K.

Figure 3. SEM Photograph of Polished Type 304 Stainless Steel Exposed to Rb at 843 K, Showing Three Layers Outer Scale (1, 2, 3,) and Intergranular Attack (4) Spot Analysis of Base Metal Was Made at Point (5).

Figure 4. Chemical Analysis of Corrosion on Type 304 Stainless Steel Exposed to Rb at 843 K. Zone Numbers Correspond to Regions Shown on Figure 3.

depletion of the metal in the vicinity of the carbides makes it susceptible to corrosion. In the current tests, accelerated corrosion along the grain boundaries appear to result from leaching of Fe by Rb in such Cr-depleted zones.

2.2.1.3 Corrosion Kinetics Tests at 893 K

Corrosion damage at 893 K was observed similar to that at 843 K. A three-layer exterior corrosion product with similar composition to that in Figure 4 and a limited amount of grain boundary corrosion was observed.

2.3 Tensile Tests

Baseline tensile tests of hollow specimens and solid, notched samples are complete. Specimens which had been gamma exposed in liquid rubidium were removed, cleaned, and unstressed. Tensile testing of these samples was begun at Colorado School of Mines. A sample of rubidium from the gamma exposure assembly was shipped to the Liquid Metal Engineering Center for chemical analysis of Mn, Cr, Co, Mo, Ni, Cu, Fe, Al, and Mg.

3.0 Zeolite Encapsulation

Encapsulation experiments were made until equilibrium loadings were achieved. The results are shown as individual points on Figure 5. The curves were calculated from the literature values measured at other temperatures and lower fugacities (pressures).⁵ The data will be combined to calculate overall equilibrium loading curves which will be used to simulate the encapsulation behavior.

Using Fick's law of diffusion to describe the encapsulation of krypton by extracted sodalite, loadings were calculated as a function of time at 400°C and 159 or 193 MPa (23000 or 28000 psi) and at 500°C and 124 or 193 MPa (18000 or 28000 psi) by allowing the diffusivity to be a fitting parameter. Figure 6 compares the calculated with experimental results. The value of D calculated from leakage measurements made by us and by Vaughan^{5,6} is lower than the values required to fit the data. At the conditions used for encapsulation, D is expected to vary with krypton concentration and agreement is not expected for D measured by encapsulation and by leakage.⁷

⁵ D. E. W. Vaughan, Encapsulation of Rare Gases, Ph.D. Thesis, Imperial College, London 1967.

⁶ R. M. Barrer and D. E. W. Vaughan, "Trapping of Inert Gases in Sodalite and Cancrinite Crystals," J. Phys. Chem. Solids, Vol. 32, pp 731-743, 1971.

⁷ J. Crank, The Mathematics of Diffusion, 2nd Edition, Oxford Press, Oxford, 1975.

Figure 5. Fractional Krypton Loading on Extracted Sodalite; Curves Calculated from Data of Vaughan²; Points Measured in ICPP Work.

Figure 6. Krypton Loading on Extracted Sodalite. Curves Calculated by Allowing Diffusivity to Vary; Points Measured in ICPP Work (1 psi = 6.89×10^{-3} MPa).

The procurement schedule for design and fabrication of a hot laboratory scale encapsulation system was modified due to a six-month delay in availability of the Multicurie Cell at the ICPP for FY 1979 hot operation of the system. The bid package will be submitted during the next quarter. The design options were reviewed; existing compressors will be used in the new hot system. Drafts of the Expenditure Authorization and Environmental Impact Assessment were prepared and the safety analysis and design criteria were started.

In order to test the effect of water on storage integrity, a sodalite sample loaded with ~ 36 STP cm^3 Kr/g solid was stirred in water at $\sim 27^\circ\text{C}$ for 16 h; no leakage was detected by subsequent mass spectrometric analysis. The pores in sodalite appear to be too small to allow krypton displacement by absorbed water.

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

A preliminary analysis of long-term leakage of Kr from zeolite at 150°C for one month was made, and long-term experiments were started at 50, 100, and 150°C . Results show that unleached sodalite had the least amount of leakage, $<0.2\%$, while zeolite 3A lost $<98\%$ of the encapsulated krypton. Tests with sodalite samples need to continue for approximately six months, before the low temperature leakage rates can be defined. The results of these tests are required to specify the conditions under which sodalite loaded with krypton-85 must be kept for safe disposal.

Loaded sodalite samples were prepared for further gamma-irradiation testing, and a thermal analysis was made. A letter was written describing the gamma tests, which will start in March and continue through June, with samples removed for analysis every month.

A letter describing the proposed Rare Gas Plant upgrade to provide krypton-85 for future testing was sent to DOE-ID.

Plans for Next Quarter

A revised Program Plan will be published. Rate constants and activation energies for Rb corrosion of Type 304 stainless steel at 650 and 925 K will be determined. Inconel 600 exposed to Rb and candidate materials exposed to RbOH will be analyzed. Rb corrosion tests of Inconel 600 will be completed and tests using A286 will be started. Low-rate tensile tests of solid, notched, precracked specimens will be completed. Preliminary RbOH screening tests will be completed. Encapsulation experiments using Kr-Xe will be started. Modeling of zeolite encapsulation will continue using digital-analog techniques. The bid package for the hot laboratory-scale encapsulation system will be issued. Long-term and short-term leakage experiments will continue using various sodalite powder and pellet samples. Gamma-irradiation tests of loaded sodalite samples will be started.

III. HTGR FUEL REPROCESSING

(H. S. Meyer)

High Temperature Gas-Cooled Reactor (HTGR) fuel blocks consist of fuel particles in a graphite matrix. During proposed reprocessing, the blocks are crushed, and the graphite is burned in a primary burner to expose the fuel particles. The fuel particles are crushed and burned in a secondary burner. During this step, fission products in the fuel may vaporize. Tests are being performed to quantify the amounts of fission products that will be released to the off-gas cleanup system, and to determine the feasibility of a removal device. Tests are also being performed for the development of a CO oxidation device to reduce the amount of CO in the off-gas cleanup system.

1. Semivolatile Removal Device

(R. N. Drake, H. S. Meyer, K. L. Wagner)

The semivolatile fission product treatment work at ACC-ICP was reviewed, and the criteria for the concluding experiments were established.^a ACC-ICP will design a semivolatile removal device to be compatible with the current General Atomics secondary burner design. The device will be designed to remove ruthenium from particulate free, 770 K gas stream. ACC-ICP believes that the majority of the other semivolatile fission products will be retained in the burner, and probably cause severe in-burner filter plugging. In order to verify this expected behavior, further volatilization and plate-out studies will be performed on simulated fission products individually and on several combinations of fission products.

2. Volatilization and Plate-Out Testing

(K. L. Wagner)

The study of ruthenium volatility in a laboratory scale secondary burner was completed during this quarter. In these experiments, powdered RuO₂ was added with graphite to the fluidized-bed burner, and the volatilization and deposition of the ruthenium was examined at three different oxygen concentrations. These tests confirmed that the quantity of ruthenium that vaporized and deposited in the burner off-gas system could be greatly reduced by decreasing the oxygen concentration during the high temperature thermal soak period that followed the burn portion of each experiment.

A schematic drawing of the experimental burner apparatus is shown in Figure 7. Preheated gas at a flow rate of approximately 0.2 L/s at STP (0.5 scfm) enters the 5-cm-O.D. section of the transparent quartz burner and passes through a quartz distributor plate. The gas fluidizes a bed

^a In accordance with the President's Budget Proposal, all HTGR work at ICPP will terminate at the end of FY-1978.

Figure 7. Volatilization and plate-out testing apparatus.

ACC-A-2840

of 60 mesh alumina which is heated by a vertical tube furnace. The off-gas is cleaned by a 3.8-cm-O.D. by 15-cm-long sintered, stainless steel, H porosity filter. After passing through the inburner filter, the off-gas passes through a second filter of glass fiber. The off-gas is scrubbed twice before being vented to a fume hood. The first scrub is a solution of 50% HCl and 50% ethyl alcohol. It is followed by a distilled water scrub.

Four groups of experiments were performed in this study of ruthenium volatility. In each of these tests, graphite (<20 mesh, >60 mesh) was added to an air-fluidized, alumina bed, and the bed was then heated in the vertical tube furnace until the graphite began to burn. The burning graphite raised the bed temperature to more than 1170 K. After most of the graphite was consumed, the bed was held at approximately 1070 K for three h. Following this high temperature thermal soak period, the furnace was turned off, and the apparatus was cooled. Throughout each of the runs, the sintered stainless steel filter was blown back at a frequency of twice per minute.

The relationship between the oxygen concentration of the fluidizing gas during the thermal soak portion of the run and the volatility of ruthenium was investigated by varying only the oxygen concentration during the 3 h thermal soaks. The other experimental conditions were held constant. Experimental conditions for these tests are summarized in Table 1.

It was previously reported that ruthenium appeared to be most volatile during the thermal soak period when a high concentration of oxygen was present.⁸ This was again observed in this study. Ruthenium vapors in the off-gas system were not noted during the high temperature portion of the run when graphite was burning. Also, decreasing the oxygen concentration during the thermal soaks apparently reduced the volatility of ruthenium. The reduction in the amount of ruthenium vapors is thought to be the result of less RuO₂ being converted to the highly volatile RuO₄ because of the limited oxygen.

The concentrations of ruthenium in the scrub solutions confirmed the visual observations of vaporization and deposition. Table 2 lists the results of the atomic absorption analyses of the scrub solutions. The average ruthenium concentrations from the 60% O₂ thermal soak runs were 3.8 mg Ru/100 mL of 50% HCl-50% ethyl alcohol scrub solutions and 1.5 mg Ru/100 mL of distilled water scrub solutions. The average ruthenium concentrations of the scrub solutions from the 20% O₂ thermal soak tests were more than an order of magnitude lower. The ruthenium concentrations of the scrubs from the runs where N₂ was the fluidizing gas during the thermal soak periods were all below the analytical detection limit of 1 µg Ru/mL.

⁸ C. M. Slansky, editor, Technical Division Quarterly Progress Report, July 1-September 30, 1977, Allied Chemical Corporation-ICP, report ICP-1132 (October 1977).

TABLE 1
CONDITIONS FOR RuO₂ VOLATILIZATION AND DEPOSITION EXPERIMENTS

<u>Run Group</u>	<u>RuO₂ Added to the Bed (g)</u>	<u>Oxygen/Nitrogen Ratio During Thermal Soak</u>
A	3.6	60/40
B	3.3	20/80
C	4.2	0/100
Blank	0	60/40

The average ruthenium concentrations from the blank runs, where no RuO₂ was added, were 0.5 mg Ru/100 mL of 50% HCl-50% ethyl alcohol scrub solutions and 0.2 mg Ru/100 mL of distilled water scrub solutions. The ruthenium collected during these blank runs was volatilized off the walls of the quartz burner during the high oxygen thermal soak period.

The lower section of the quartz burner suffered considerable degradation during the RuO₂ volatility tests (see Figure 8). With RuO₂ present, some areas of the quartz wall have been permanently blackened, and other areas of the wall appear etched. Without RuO₂ present, attack on the quartz was not observed.

Measurements of the system pressure and pressure drop across the inburner filter during the runs in which only RuO₂ was added to the combustion bed were compared with the same pressure measurements taken during similar experiments in which both MoO₃ and RuO₂ were added (see Figure 9).⁸ During the combined MoO₃ and RuO₂ runs where 10.6g MoO₃ and 3.5g RuO₂ were added in each of 5 runs, both the system pressure and pressure drop of the filter rapidly increased by approximately 6 kPa until the off-gas was vented through the pressure relief device. During the tests in which only RuO₂ was added, the system pressure varied less than 2 kPa, and the pressure drop across the filter varied less than 1 kPa. Since all of the pressure measurements were taken under the same flow rate and temperature conditions, the observed difference indicates that MoO₃ was responsible for the pressure buildup during the combined MoO₃ and RuO₂ experiments.

3. CO Oxidation

(J. A. DelDebbio)

The effect of iodine on catalyst activity has been studied at levels ranging from 0.01 to 20 ppm I₂. The test gas consisted of 1.0% CO and 0.5% O₂ in CO₂ reacted over a 5-cm (2-in.) catalyst bed. The results are summarized in Tables 3 and 4.

TABLE 2

RUTHENIUM CONCENTRATION IN SCRUB SOLUTIONS FROM RuO₂
VOLATILIZATION AND DEPOSITION EXPERIMENTS

Run Group ^a	Oxygen/Nitrogen Ratio During Thermal Soak	Run Number	Ruthenium Concentration in Scrub Solution (mg/100 mL)	
			50% HCl-50% Ethyl Alcohol	H ₂ O
Blank	60/40	IB	BDL ^b	BDL
A	60/40	I-III	3.8 ± 2.6 ^c	1.5 ± 1.4 ^c
Blank	60/40	IIB	1.6	0.7
B	20/80	IV ^d	0.7	0.4
Blank	e	IIIB	---	---
Blank	60/40	IVB	0.1	BDL
B	20/80	V-VII	BDL	BDL
Blank	e	VB	---	---
Blank	60/40	VIB	0.1	BDL
C	0/100	VIII-XII	BDL	BDL

^a See Table 1^b Below detection limits of 0.1 mg/100 mL^c Average at 95% confidence level.^d Bed sintered during burning period. Thermal soak was performed.^e Bed sintered during burning period. No thermal soak was performed.

Figure 8. Laboratory-Scale Secondary Burner (After RuO_2 Volatilization and Deposition Experiments).

Figure 9. Pressure change due to Plateout.

The data in Table 3 indicate that, between 0.01 and 0.5 ppm I_2 , the percent conversion of CO is about constant. Beyond 0.5 ppm, the percent conversion decreases with increasing I_2 concentration. We assume all activity on the catalyst is due to platinum sites, and deactivation in the presence of I_2 is due to the formation of platinum iodide compound(s). It appears that below 0.5% ppm I_2 , one type of platinum iodide species is formed or one type of platinum site is affected. Above 0.5 ppm I_2 , additional platinum compounds or platinum sites may be involved to cause concentration dependent deactivation.

Table 4 shows two runs using 0.5 and 2.0 ppm I_2 which were conducted about two months after Runs 4 and 5 of Table 3. In Table 4, Column A shows the percent CO conversion in the presence of I_2 , and Column B shows the percent CO conversion when the run was continued without iodine. Column B conversion values for both runs are nearly the same. This indicates that there is an irreversible poisoning effect which is independent of I_2 concentration. Conversion values in column A show a definite concentration dependence (reversible reaction).

The conversion values at 823 K for Runs 4 and 5 (iodine-2 present) of Table 3 vary greatly from Runs 1A and 2A of Table 4. This indicates, that through continual use or regeneration (exposure to O_2 at 870 K), the catalyst has become more susceptible to iodine poisoning.

The platinum sites on the catalyst may exist as Pt^0 , $Pt(OH)_2$, and PtO .

The thermodynamics and equilibria of the following reactions are being examined to explain our experimental observations:

Plans for Next Quarter

Plans for the next quarter include a series of burning experiments where only MoO_3 will be added to the fluidized bed. The filter plugging characteristics of MoO_3 will be studied in these tests. Volatilization, deposition, and corrosion experiments using Cs_2CO_3 and Rb_2CO_3 are also planned. Scoping tests for RuO_2 removal will be performed on the semi-volatile removal device. Further investigations will be made on the platinum iodide compounds formed on the surface of the CO oxidation catalyst. The effect of Br_2 and SO_2 on catalyst activity will be determined.

TABLE 3

EFFECT OF TEMPERATURE AND I_2 CONCENTRATION ON CO CONVERSION

Run #	1	2	3	4	5	6
Bed Temp (K)	% Conv.* (no I)	% Conv. (0.01 ppm I)	%Conv. (0.1 ppm I)	% Conv. (0.5 ppm I)	% Conv. (2.0 ppm I)	% Conv. (20.0 ppm I)
723	92.5	50.0	47.0	46.0	24.0	7.0
763	92.5	62.5	60.0	55.0	31.0	23.0
823	92.5	77.5	76.0	76.0	56.0	45.0
863	92.5	90.0	88.0	88.0	75.0	65.0

*Conv. = conversion.

TABLE 4
EFFECT OF REVERSIBLE AND IRREVERSIBLE REACTIONS BETWEEN Pt AND I₂
ON CO CONVERSION

Bed Temp	Run 1		Run 2	
	A	B	A	B
	% Conv. With 0.5 ppm I	% Conv. With no I	% Conv. With 2.0 ppm I	% Conv. With no I
823 K	47.4	82.0	32.5	85

RESULTS

SPECIAL MATERIALS PRODUCTION

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

1. Post-Calcination Treatment of High-Level ICPP Wastes

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

One method being considered for treatment of ICPP wastes is the conversion of calcined high-level waste to glass. A systematic study was made of the effect of glass frit components on melt viscosity and uniformity and on acid leach resistance (on a glass made from fluoride containing ICPP waste calcine.) For the experiments, Na_2O and B_2O_3 content was held constant at 24 and 14 wt%, respectively, and SiO_2 was varied; prescribed Li_2O , P_2O_5 , CaO , CuO , and ZnO components were used in all combinations. Frit combinations, the relative viscosity of the melt at 1100°C , and the resistance to leaching in acid (pH 3.5) are shown in Table 1. The methods used to determine viscosity and leach resistance were previously reported.¹ Replications on acid leach rates for certain of the glasses were made to verify precision of the data for a statistical analysis. The statistical analysis showed that at low (0.1-0.5 wt% loss in 19 h) leach rates, a factor of 2.7 difference in leach rate is required to be statistically significant. The analyses also showed that a frit containing (1) SiO_2 , Na_2O , and B_2O_3 , (2) a two-component frit including CuO , and/or P_2O_5 (except P_2O_5 and ZnO), or (3) a three-component frit including P_2O_5 , resulted in significantly lower leach rates than for any of the other combinations. Generally, a glass containing P_2O_5 (except P_2O_5 and ZnO) resulted in a significantly lower leach rate than a glass without P_2O_5 .

Glasses, where the concentrations of the frit components including Na_2O and B_2O_3 were varied, were reported previously.¹ From the collection of data, four glasses have been chosen to evaluate the effect of calcine content and melting temperature on melt viscosity and acid leach resistance. The four glasses are being varied in calcine content from 25 to 40 wt% and melted at temperatures of 1050, 1100, and 1200°C to determine melt viscosities and acid leach resistance. Additional tests will be made on the glasses to determine devitrification properties and ability to contain fluorides before final selection of a glass frit for vitrifying ICPP zirconia calcine.

Since ICPP calcine is high in fluoride content and glass melting occurs at temperatures of 1100°C , fluoride volatility data are needed. Analysis of the glass for fluoride content proved to be more practical than attempting to analyze the off-gas. Seven methods for determining

¹ C. M. Slansky (ed.) et al., Technical Division Quarterly Progress Report - October 1-December 31, 1977, Allied Chemical Corporation-ICP, ICP-1141 (February 1978).

TABLE I
EFFECT OF FRIT COMPOSITION ON MELT VISCOSITY
AND ACID LEACH RATE OF ICPP WASTE GLASSES

Frit No.	Component wt% ^a						Acid Leach Rate Wt%lost/19h	Relative Viscosity ^b
	SiO ₂	Li ₂ O	P ₂ O ₅	CaO	CuO	ZnO		
107	62						2.9	3
50	60				2		0.3	2
105	60		2				0.6	2
103	60					2	3.5	1
104	59			3			9.9	2
106	60	2					10.0	1
63	58		2		2		0.1	4
99	57		2	3			0.2	3
61	58				2	2	0.2	3
101	58	2	2				0.3	2
57	58	2			2		0.5	2
98	57			3	2		0.5	2
100	57			3		2	0.5	2
90	58	2				2	0.7	2
91	57	2		3			1.2	1
102	58		2			2	2.1	1
88	56		2		2	2	0.2	2
97	55		2	3		2	0.2	2
93	56	2	2			2	0.2	1
94	55		2	3	2		0.2	2
95	56	2	2		2		0.3	2
92	55	2	2	3			0.5	1
96	55			3	2	2	1.3	2
62	56	2			2	2	1.6	1
89	55	2		3	2		2.3	2
78	55	2		3		2	3.1	2
74	54	2	2		2	2	0.4	1
80	53	2	2	3		2	0.4	1
86	53		2	3	2	2	0.4	2
87	53	2	2	3	2		0.8	1
79	53	2		3	2	2	4.6	2
81	51	2	2	3	2	2	1.0	2

a All frits contained 24% Na₂O and 14% B₂O₃

b 1 = lowest viscosity 10-100 poise
5 = highest viscosity 500 poise

fluoride content in glass were compared (Table 2). Potentiometric analysis appears to be in fair agreement with the colorimetric tests and with fluoride content calculated for the calcine. Potentiometric analysis is the easier and preferred of the two methods. Agreement of fluoride analyses by these two independent methods with calculated fluoride contents is the basis for assuming the analytical methods are accurate and dependable.

The potentiometric test involves fusing about 0.5 g of the powdered glass sample with about 2 g of NaOH in a nickel crucible, dissolving the fused mass in a solution of sodium citrate, triethylamine and NaCl, and after dilution, analyzing with a fluoride specific ion electrode. Fluoride during analysis is not lost due to the extremely basic environment, and the test gives reproducible results. The pyrohydrolysis method involves heating about 1 g of the powdered glass with NO_3 and $\text{Al}(\text{NO}_3)_3$ at 900°C under moist air, driving off the fluoride which is then caught for analysis in a caustic bubbler system. This test has yielded rather low results, possibly caused by interference from other elements in the glass matrix. The colorimetric analysis uses either the solution from the potentiometric test or the solution or solid is heated in H_3PO_4 at 185°C to distill off the fluoride which is again caught in a caustic bubbler for analysis. Results from this procedure confirm the results found with the potentiometric test, but the colorimetric analysis is far more time consuming.

The nitric acid dissolution method consists of dissolving about 2 g of glass in 8 to 16 M HNO_3 at 80°C for 24 h and then analyzing the solutions for fluoride. Although this test was performed on only one glass, it was time consuming and gave low results due to loss of off-gas and too many variable experimental parameters. X-ray fluorescence was also tried, but results were poor due to insufficient standards and the fact that fluorine is not easily detected by this method. The weak fluorine signal produced is easily shadowed by the matrix effect of other constituents in the glass. The off-gas capture method consisted of melting the glass raw materials and calcine in an ammonia-ammonium sulphate atmosphere and trapping the released fluorine as NaF in a caustic bubbler. Results were inconsistent and there is some evidence that the ammonia atmosphere enhanced release of fluorine. The results from the potentiometric analysis indicate that there is little or no fluoride loss during melting of the glass since the fluoride content measured agrees within experimental error of the fluoride introduced to the melt. The fluoride is probably held well in the glass due to the basic nature of the glass. These results are encouraging, since fluoride volatility could be a potential corrosion and cleanup problem in the off-gas stream.

Tests on corrosion of Inconels 601, 625, and 690 during glass melting show that 625 cannot be used, but 601 and 690 are candidate electrode materials in the glass melter. The tests consisted of suspending the coupons in alumina crucibles containing molten glass (glass 13, Table 3). Frit and calcine were added twice a day for 10 d for the long-term test, and hourly for four h for the 6-h test. The samples were then cleaned

TABLE 2
COMPARISON OF DIFFERENT METHODS FOR DETERMINING
FLUORIDE CONTENT IN GLASS

<u>Method</u>	<u>Glass Number</u>	<u>13</u>	<u>61</u>	<u>75</u>	<u>75</u>
		<u>wt % F⁻</u>			
Potentiometric		5.5 $\pm$.3 --	7.3 $\pm$.3 7.1 $\pm$.3	7.6 $\pm$.3 7.2 $\pm$.3	7.5 $\pm$.3 --
Pyrohydrolysis		--	3.3 $\pm$.1	3.6 $\pm$.1	4.3 $\pm$.1 3.4 $\pm$.1
Colorimetric Solution		--	7.9 $\pm$.4	7.2 $\pm$.4	7.4 $\pm$.4
Colorimetric Solids		--	5.9 $\pm$.6 5.1 $\pm$.6	6.8 $\pm$.6 7.0 $\pm$.6	7.9 $\pm$.6 7.1 $\pm$.6
Nitric Acid Dissolution		4.3 $\pm$.6	--	--	--
X-ray fluorescence	Weak signals and interference from other elements.				
Off-gas capture	Inconsistent results.				
Calculated (based on calcine)		5.5 $\pm$.2	7.0 $\pm$.2	7.0 $\pm$.2	7.0 $\pm$.2

and measured for weight loss. As seen in Table 4 and Figures 1, 2, and 3, Inconels 601 and 690 show little corrosion and are comparable, but 625 was almost completely destroyed. Attack on the coupons seemed most severe above the glass interface in the short-term test, but the long-term test showed that the most severe corrosion was in the glass phase itself.

An off-gas system for the laboratory-scale glass melter is presently being designed to measure the amount of volatile fluorides produced during calcine vitrification. The off-gas system will consist of a sintered metal filter and a condenser followed by three bubblers in series; the off-gas will be motivated by a vacuum. The first bubbler will be empty and act as a trap. The other bubblers will each contain 2 M NaOH, which will be used to isolate the fluorides in the off-gas for measurement.

Plans for Next Quarter

Properties of four selected glass formulations to vitrify zirconia calcine will be determined. Fabrication of a laboratory-scale glass melter will be completed. Design of a pellet-forming pilot plant will be completed.

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

Nine experimental pellet forming runs were made to evaluate various solid and liquid binders during pellet formation. Compositions of the binders and pellets are shown in Table 5. Runs P-16a and P-17c were made to test the usefulness of colloidal silica as a liquid pellet binder. Run P-16a used DuPont Ludox HS 40% colloidal silica, diluted with water to 20 wt% SiO_2 . The colloidal silica solution did not properly wet the calcine. The product consisted of few wet lumps and many calcine particles which remain unagglomerated. To improve calcine agglomeration, phosphoric acid was mixed with the colloidal silica. Phosphoric acid greatly improved the wetting ability of the colloidal silica solution. For Run P-17c, a solution containing 16 wt% SiO_2 and 3 M H_3PO_4 was used as the liquid binder. Spherically shaped, rough-surfaced pellets formed readily. The pellets from this run are being tested for leach resistance.

Runs P-16b, P-16c, and P-16d were made to determine the effect of H_3PO_4 concentration in the liquid binder on the leach resistance of the pellets. The higher the concentration of the H_3PO_4 in the liquid binder, the lower the leach rate (Table 6). The highest concentration of phosphoric acid that will spray properly is about 9 M, due to its high viscosity. Pellet Runs P-17a, P-17b and P-17c were made to test the effect of bentonite and H_3BO_3 on pellet leach resistance. Leach rates on pellets from these runs are being measured. The use of small amounts of bentonite (3-5 wt%) may eliminate the need for using metakaolin. Both bentonite and metakaolin react with Cs to form inert, leach-resistant compounds, but bentonite may react more efficiently than metakaolin, thus reducing the amount of solid pellet binder required.

Runs P-15c and P-17b were made to determine the effect of using AlPO_4 as a liquid pellet binder on pellet properties. AlPO_4 reacts with metallic oxides to form ceramic-like compounds. This reaction could increase the leach resistance of the pellets by reacting better than H_3PO_4 with the oxides in the pellets, but Run P-15c pellets did not have significantly lower leach rates than pellets formed with different binders. This could be explained if the Al_2O_3 slurried with the H_3PO_4 was unreactive and did not form AlPO_4 . Powdered Al metal dissolved in H_3PO_4 gave a solution of AlPO_4 which was used in Run P-17b. Leach results from P-17b may confirm the benefit of using AlPO_4 as a liquid binder.

1.3 Rotating-Tray Pellet Heat Treater Development (B. D. Taki)

A rotating-tray heat treater will be used in the pellet pilot plant to heat pellets up to 800-850°C. Preliminary data on movement of the

TABLE 3

Glass 13 Composition

<u>Component</u>	<u>wt%</u>
SiO ₂	38.3
Na ₂ O	20.9
B ₂ O ₃	9.6
Li ₂ O	1.5
CaO	2.1
ZnO	<u>1.6</u>
	74

Calcine

Al ₂ O ₃	5.2
ZrO ₂	5.2
CaF ₂	14.3
Other	<u>1.3</u>
	26

TABLE 4

Inconel Compositions and Corrosion Losses

<u>Inconel</u>	<u>Composition, wt%</u>		
	<u>601</u>	<u>625</u>	<u>690</u>
Ni	60.5	61.0	60
Cr	23.0	21.5	30
Fe	14.1	2.5	9.5
C			.03
MO		9.0	
Nb+Ta		3.65	
Al	1.35		
		<u>Corrosion, Wt% Loss</u>	
6 h test	1.2	3.9	0.99
10 d test	4.0	54.0	4.3

Figure 1. Comparison of Inconel coupons before and after exposure to molten ICPP waste glass at 1100 °C for 6 hours.

CLEANED INCONEL SAMPLES
AFTER 10-DAY TEST

601

625

690

Figure 2. Inconel Coupons exposed to molten ICPP waste glass at 1100 C for 10 days and after removal of scale.

FTER 10 DAY TEST

Figure 3. Inconel Coupons exposed to molten ICPP waste glass prior to removal of scale.

TABLE 5
Pellet and Binder Compositions

	Calcine wt%		Solid Binders wt%			Liquid Binder Composition (M)						
Run No.	Bed	Fines	H ₃ BO ₃	Meta-Kaolin	Bentonite	H ₃ PO ₄	HNO ₃	AlPO ₄	Al ₂ O ₃ ^a	SiO ₂ ^b	Ratio Solids: Liquids	Pellet Properties
P-15c	54.5	27	10	5.5	3	7	2		14		2:3	smooth, oblong
P-16a	41	41	10	5	3					20	2	liquid did not properly wet solids
P-16b	41	41	10	5	3	7	2				2:5	odd shaped, rough surfaced
P-16c	41	41	10	5	3	9	2				2:5	odd shaped, rough surfaced
P-16d	41	41	10	5	3	5	2				2:1	poor agglomeration, mostly odd shapes
P-17a	42.5	42.5	5	5	5	7	2				2:3	smooth spherical
P-17b	42.5	42.5	5	5	5	5		2			1:5	flat, smooth
P-17c	42.5	42.5	5	5	5	3				16	2:6	rough surfaced, spherical
P-18a	45	45	5		5	7	2				2:5	small, odd shaped, rough surfaced

a = wt% Al₂O₃ slurried in liquid feed

b = wt% SiO₂ from 40% SiO₂ colloidal silica diluted with H₂O

TABLE 6

PELLET LEACH RATES AFTER HEATING TO 800°C FOR 2 HOURS

Pellet Run	Wt% Lost in 100 h Soxhlet Leach				Wt% P ₂ O ₅ in Pellets
	Bulk	Cs	Sr	B	
P-15c	1.38	4.46	1.2	4.22	16
P-16b	1.27	6.41	1.03	3.66	17
P-16c	0.33	NA	NA	NA	22
P-16d	1.92	NA	NA	NA	14

NA - Not Analyzed

pellets through the trays were obtained using a mockup of the heat treater. A drawing of the conceptual rotating-tray heat treater is shown in Figure 4. The mockup has rotating trays 30.5-cm-diameter; each tray contains 3 slots. The trays are separated by a distance of 5.7 cm. The paddles, used to transfer the pellets to the next tray, are angled 15 degrees away from perpendicular, opposite to the direction of rotation. The trays are rotated at a speed of approximately 1.3 rph. Based on an initial layer of one pellet (0.6-cm high) the following results were obtained. The pellets stack 1.9-cm high against the face of the paddle. As the pellets fall through the slots, they form mounds 2.5-cm high and 6.4-cm wide on the next tray. Essentially none of the pellets fall simultaneously through successive trays. The following results were obtained with an initial layer of two pellets (1.3-cm high); the pellets stack 3.8-cm high against the face of the paddle. Approximately 75% of the pellets formed a mound 3.8-cm high and 10-cm wide. The rest of the pellets fell either simultaneously through successive trays, or over the side of the tray. High walls around the periphery of the trays will be needed to prevent the pellets from falling off. A pellet-leveling device will also be needed.

The rotating-tray heat treater in the pilot plant will require about 8 trays, 61-cm-diameter, 5.1-cm apart, rotating at ~4 rph. Each tray will contain approximately 5.7 kg (12.5 lb) of pellets. Leveling will be needed to prevent the formation of mounds greater than 3-cm high, from which excessive scattering would result.

2. Actinide Removal From ICPP Wastes - Pilot Plant

2.1 Pilot-Plant Tests (R. L. Nebeker, H. R. Maxey, C. B. Chamberlain)

Checkout of pilot-plant pulsed extraction columns using a zirconium dissolver solution and kerosene continued. Although the organic phase is

ACC-A-3166

Figure 4. Rotating-Tray Pellet Heat Treater

not the one of primary interest, the \$200/L cost of purified DHDECMF extractant prohibits its use where solvent losses can be expected while testing a system and developing experimental procedures. The procedures presently being developed are flooding tests to determine the fluid capacity of the columns, and extraction tests to determine the height of a column required to give a particular solute concentration. A procedure to determine the flooding capacity of a column was given by Long et al.^{2,3} Efforts to duplicate these results were only partially successful. The principle underlying these tests is illustrated in Figure 5. The amount of discontinuous phase in a column (in this case the organic phase) is a function of the total flow rate. This holdup increases linearly until the onset of flooding, when holdup increases at an even greater rate because the column loses its capacity to pass flows. Lines corresponding to the holdup in each region are plotted, and intersection of two lines should give the holdup volume at flooding. This holdup is proposed to be constant at all frequencies for a given amplitude. Maximization of column flow is obtained by plotting the holdup/capacity curve for various frequencies and choosing the maximum frequency.

The results of runs made at different frequencies for a 0.01-metre amplitude are plotted in Figure 6. While the points are extremely well-ordered for the non-flooding (emulsion) region, data are usually scattered in the flooding region. This may be because the increase in holdup with the onset of flooding is so great per incremental flow rate increases that experimental uncertainties do not permit accurate plotting of the line in the flooding region.

Uncontrolled variables which seriously interfere with the holdup determination also are present. These include pressure fluctuations, instrumentation (e.g., control valve operation), presence of entrained organic in the aqueous phase, or other undetermined variables. The curves for the emulsion region (non-flooding) show that a maximum frequency occurs between 50 and 67.5 cycles per minute for a 0.01-m amplitude. While this is the frequency range which permits maximum column flow, it may not give the smallest height of a transfer unit. Thus, the next object of the program is to extract the HNO_3 from the zirconium dissolver solution so that sampling and analysis procedures can be tested and height of transfer units calculated.

An analytical chemical method for determining the concentration of cerium was developed. The spectrochemical method will be adequate to measure cerium concentration following six or seven stages of extraction of cerium. Verification of the actinide removal process using tracer cerium is planned.

² J. T. Long, Engineering for Nuclear Fuel Reprocessing, Gordon and Breech Science Publishers, Inc., New York, NY, p 571-572, (1967).

³ W. K. Eister (ed), "Monthly Progress Report, April 1956," Oak Ridge National Laboratory, Report CF-56-4-21, p 65-72.

Figure 5. Method of Determining Pulse-Column Flooding^{1, 2}

Figure 6. Experimental Flooding Results.

Pilot plant revisions to add flexibility to operations were identified. New tanks, pumps, and miscellaneous equipment were specified to allow both pulsed columns to be operated simultaneously in the extraction and stripping mode.

Processing engineering calculations are required to size the actinide removal process and to adequately compare the process with other waste management options. A list of about 25 calculations was prepared and calculations to determine the number of extraction stages for various conditions were started.

Plans for Next Quarter

Flooding tests will continue, and extraction tests using HNO_3 , TBP, and dissolver solution will be started; pilot-plant revisions will be made, and sampling procedures will be developed further.

3. Actinide Removal From ICPP Wastes - Chemistry

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

3.1 Mercury Removal Methods

Mercury is used in the catalytic dissolution of aluminum fuels and is present in first-cycle wastes. The Hg is strongly bound to dihexyldiethylcarbamylnmethylphosphonate (DHDECMP) during actinide extraction and is not removed during subsequent stripping. As the buildup of Hg in the extractant would eventually hinder the extraction of actinides, a study was made to identify various Hg removal techniques.

The following methods successfully removed Hg from DHDECMP. No detrimental effects on extraction or stripping of actinides were noted.

- 1) Electrolytic replacement: Cu, Sn, and Zn were used to test the electrolytic replacement of Hg from DHDECMP. Copper was chosen for column tests because replacement of Hg using Sn and Zn produced large quantities of amalgamated fines in the preliminary batch experiments. It was necessary to load DHDECMP with sufficient acidity to promote replacement of the Hg. Therefore, the extractant was washed with 0.4 M HNO_3 prior to all tests. Column studies showed Hg replacement to be directly proportional to the Cu surface area. In a column packed with Cu turnings, a contact time of 2.5 min resulted in 80% removal of the Hg. However, in one pass, 3 to 4 times more Cu is exchanged than Hg is replaced. Further Hg reduction is possible with longer residence times; however, it is felt that the Cu concentration in the extractant would also increase.
- 2) Reduction: Mercury was rapidly and quantitatively removed from DHDECMP by extraction with lithium amalgam Li(Hg) . This is a

direct replacement reduction of Hg, hence, one litre of saturated Li(Hg) is sufficient to remove the Hg from 220 L of extractant. (The expected concentration of Hg present in DHDECMP is 0.004 M.) Hypophosphorus acid (H_3PO_2) removes Hg from the extractant as the finely divided metal. One molar H_3PO_2 removed 95% of the extracted Hg in a 10-min equal volume batch extraction. Hypophosphorus acid is oxidized to orthophosphate (PO_4^{3-}); therefore, excess reductant is required to assure Hg removal. The oxidation parameters for H_3PO_2 are not established; hence, the resultant PO_4^{3-} concentration is unknown.

- 3) Complexation: Hg(II), the species present in DHDECMP, is strongly complexed by mercaptoacetic acid (HSCH_2COOH) with a $k_f=10^{44}$. Contacting the extractant for 10 min with an equal volume of 0.05 M HSCH_2COOH in 0.5 M Na_2CO_3 removed 99.8% of the Hg. Two moles of HSCH_2COOH are consumed for each mole of Hg partitioned.

3.2 Extractant Solubility

The solubility of 22% DHDECMP in 2:1 decalin-DIPB into 0.005 M HNO_3 has been experimentally determined. Equal volumes of this extractant and 0.005 M HNO_3 were contacted for one h at 23°C. After the phases were separated, the aqueous fraction was washed twice with equal volumes of CH_2Cl_2 . The washings were combined and spiked with a known amount of pure TBP. The TBP is employed as an internal standard for subsequent determination of DHDECMP by gas chromatography. The relative flame ionization detector response function of TBP versus 99+% DHDECMP is 1.44. After evaporation of the CH_2Cl_2 , the mixture was analyzed. The solubility of extractant was measured to be 0.13 g/L, comparable to the solubility of TBP under similar conditions.

3.3 Sodium-Bearing Waste

Distribution coefficients for actinides and key elements between synthetic ICPP sodium-bearing waste and 20% DHDECMP in 2:1 decalin-DIPB were determined. Experimental procedures are the same as reported in previous quarterlies.⁴ Extraction contacts were followed by two 1:5-vol 6 M HNO_3 scrubs and three equal volume 0.05 M HNO_3 -0.05 M $\text{NH}_2\text{OH}/\text{HNO}_3$ strips. When necessary, an acid strip of equal volumes of 0.005 M HNO_3 -0.05 M $\text{H}_2\text{C}_2\text{O}_4$ followed by a 0.05 M Na_2CO_3 strip were performed. The actinides Pu, Am, and U showed favorable extraction, scrub, and strip behavior. Mercury was the only other element that extracted.

An interfacial scum appeared after the scrub contacts. Scrubbing with 3 M HNO_3 instead of 6 M HNO_3 reduced the amount of scum. Analysis of the scum showed it to be Hg_2Cl_2 . Addition of CrO_3 at the level of 1 mg/mL to the waste solution prior to extraction prevented scum formation, but resulted in a serious scum occurring during the Na_2CO_3

⁴ C. M. Slansky (ed.) et al., Technical Division Quarterly Progress Report for January 1-March 31, 1977, Allied Chemical Corporation-ICP, report ICP-1117, p 52.

strip. Pretreatment of the DHDECMP extractant with a CrO_3 wash still results in scum formation during scrubbing. A tracer experiment showed that the scum, which is highly visible, represents only about 1% of the Hg. An investigation to eliminate the acid scrub and thereby eliminate scum is being planned.

3.4 Kinetic Study

A study was made to determine the relative chemical kinetics of ^{144}Ce versus ^{241}Am and ^{239}Pu when extracted into DHDECMP from synthetic Zr-Al dissolver solution. This study was necessary because nonradioactive Ce was chosen as an actinide simulant during cold pilot-plant pulsed column studies. For this experiment, 86% DHDECMP was diluted to 20 vol% in 2:1 decalin-DIPB, caustic scrubbed, and water washed. Tracers were purified, converted to the nitrate form, and subsequently dissolved in 58 mL of synthetic dissolver solution and added to a 120-mL h-glass-shaped vessel. The Pu(IV) valence state was assured by the addition of H_2O_2 during the nitrate conversion. An equal volume of extractant was carefully added and the stirrers were turned on. One-tenth millilitre samples of the extractant were removed at timed intervals and analyzed. Cerium-144 and ^{241}Am were analyzed simultaneously by gamma ray spectroscopy using a Ge(Li) detector. A second study was made to determine the kinetics of ^{239}Pu transfer. Plutonium was analyzed by liquid scintillation counting. The aqueous phase was stirred magnetically using a Teflon coated stir bar. The organic phase was mixed with a glass, double bladed stir rod driven by an overhead motor. Stirring rates were at a constant speed which thoroughly mixed each phase independently without disturbing the aqueous-organic interface. Initial interface size was 1.54 cm^2 but enlarged to 1.77 cm^2 in $\sim 20 \text{ h}$. This was caused by the slight solubility of the aqueous phase in the organic extractant. The temperature of the liquid phases was 23°C throughout the experiment. The results are presented in Figure 7. This semi-logarithmic plot exhibits similarly shaped curves and times at which equilibrium is reached. Therefore, cerium traced pulse column studies should predict actinide HTUs.

Plans for Next Quarter

Distribution coefficients for actinides and macro-constituents will be established for sodium-bearing wastes. The hot cell facility is being renovated for mini mixer-settler experiments on sodium-bearing wastes. Efforts will continue in the search for alternate sources of DHDECMP, preferably purified to $\sim 80\%$, as large quantities will be required for pilot plant studies.

4. Calcined Solids Retrieval and Handling

(J. A. Hendricks, B. A. Staples, E. L. Wade,
S. J. Horn, and J. S. Schofield)

4.1 Calcine Bin Sampling and Analysis Project

The last of the drilling equipment for taking bin samples was received from the manufacturer. Cold testing of the equipment with various types

Figure 7. Kinetic Study of Various Nuclides Into 20% DHDECMP In 2:1 Decalin-DIPB

KINETIC STUDY OF VARIOUS NUCLIDES
INTO 20% DHDECMP IN 2:1 DECALIN-DIPB

of drill shoes resulted in the material (mixture of dolomite and magnesium oxide) packing in the bottom samplers and not passing up to the higher tubes. Sample traps were developed using machined brass rings and 3-mil brass shim stock. In order to obtain adequate sample volume, it has proven necessary to machine a scoop in the upper side of each sample tube. Material is then retrieved on tube withdrawal rather than insertion. A penetrometer point will be used in place of a drive shoe and the whole sample train pounded into the bins. A schematic of the sample train is shown in Figure 8.

Fabrication of the wrench housing, uncoupling wrench, casks, building footings, storage pad, and miscellaneous equipment are complete. Work is continuing on the building structure, scaffolding, grappling tool, guide tube, sample modifications, and miscellaneous other tools.

Equipment design and fabrication is on schedule for the Multicurie Cell analysis project. A trip was made to Oak Ridge National Laboratory to observe operation of their remote flow factor tester. This unit was obtained for our use and should be on-site shortly.

The schedule for starting calcine sampling is mid April. Start of calcine analysis in the Multicurie Cell is now scheduled for July. Issuance of a report on calcine sampling is planned for September 1978.

4.2 Cold Prototype Retrieval Equipment

Approval for use of the MTR building for the prototype equipment was obtained in early February. The design bases for the equipment were revised and reissued. The bases are currently being reviewed by DOE-ID personnel. Allowing an estimated six weeks for review and contract approval, design will start at Kaiser April 1.

4.3 Nozzle Development

Funds for the nozzle development project were eliminated early in FY-78. However, the small-scale rotating nozzle system was installed and operated once using a 55-gal drum. Operation was satisfactory, although satisfactory scale-up of the system to a 12-ft-diameter bin with internal structures is uncertain.

Plans for Next Quarter

Start and complete calcine sampling operation. Begin Title I design for the cold prototype retrieval equipment with Kaiser Engineering.

5. Idaho Programmatic Environmental Impact Statement

(N. A. Chipman, W. B. Kerr, G. G. Simpson and M. J. Carr)

A contract was awarded to Nuclear Safety Associates, Bethesda, MD., for evaluating the potential environmental impact of the candidate Long-Term

FIGURE 8 SCHEMATIC DIAGRAM OF SAMPLE TRAIN

Waste Management plans considered in the PEIS. A preliminary schedule estimates this work to be completed early in the next quarter.

The Ralph M. Parsons Company completed its contract covering design and cost estimation of two waste management options as well as effluent estimations and commitment of resources for all management plans.

Rough drafts were written for several sections of the DPEIS. Some sections were revised after internal ACC-ICP review and are now ready for DOE-ID review.

6. Long-Term Defense Waste Conceptual Design

6.1 Conceptual Design for Full-Scale Pelletizing Plant (S. J. Priebe)

Scoping studies were started on the design requirements for a full-scale calcine pelletizing plant. In bench-scale experiments, pellets were shown to be a hard, leach-resistant waste form for ICPP waste and potentially suitable for on-site storage of an actinide-free waste.

Studies for the pelletizing facility are based on processing the output from the New Waste Calcining Facility (NWCF). Based on scheduled waste processing projections and assuming existing bin-stored calcine will be processed over a period of ten years, the pelletizing capacity should be 160 kg/h.

To maintain system flexibility, three or four pelletizers are proposed for the facility. A three-screen separator will be used, with fines being recycled to the feed system and oversize pellets being broken up and rescreened. Microwave energy will be used to dry the pellets and radiant energy will be used for heat treatment. The pellets will then be either pneumatically transferred to storage bins or put in canisters for off-site storage.

Drying and heat treating the pellets will require about 150 kW. Process motors (feed system, pelletizers, screen, heat treater, etc.) will require about 14 kW. Including building lighting, heating, and other miscellaneous power requirements, the total power requirement will be about 200-250 kW.

A process flowsheet and sketches of a facility are being prepared and will include equipment layout in the process cell, support and storage areas, and a shipping facility.

Plans for Next Quarter

A process flowsheet for the calcine pelletizing process will be completed. Sketches of the facility will be made showing the relationships of the equipment and various support areas. Where possible, utility needs of the pelletizing facility will be defined; these include power, air, steam, water, and drains.

II. ICPP PLANT PROCESS IMPROVEMENT

1. Uranium Accountability Measurements

1.1 Areas of Work

Areas of work during this Quarter included further study of the TIOA-xylene chemical separations method and of a variety of sample loading and running parameters such as interfering ions, filament temperature, etc.

1.2 Testing of TIOA-Xylene Method (S. Kelly, Jr., E. E. Filby)

Previous work has shown that a chemical separation method using the liquid anion exchange material triisooctylamine (TIOA) diluted with xylene is very effective for the kind of sample normally analyzed for uranium.^{5,6} However, the possible effects of high sulfate upon the performance of the method was studied and, during the course of that work, the possibility arose that high concentrations of sodium ion might have a detrimental effect on the performance of the method.

1.2.1 Effects of Sodium Ion

The sulfate studies reported in the next section include work on a set of controls saturated with sodium sulfate. Those samples ran quite well, but only after a long period of stabilization in the mass spectrometer (see also section 1.3.2). Other experience has shown that sodium ion in a solution to be loaded on a filament might create this sort of running problem. To test this possibility, the same control used for the sodium sulfate study was saturated with sodium nitrate instead. (The routine use of nitric acid sample solutions shows that nitrate ion is no problem.) Table 7 shows the mass spectrometric behavior observed for this sample set.

The "Figure of Merit" (discussed further in Section 1.3.1) has been established as an objective measure of "good" running behavior. The values shown are much smaller than the acceptable value of 0.050.⁷ The time required for the ion beam to stabilize to the point where good data could be collected was much greater than for the samples containing no sodium ion. The presence of sodium in samples processed by the TIOA-xylene does not appear to affect the final quality of the data obtained, but it may drastically extend the time required to obtain the data. Interfering-ion studies for other sample-preparation methods explored the effects on extraction efficiency but not on instrument behavior. Thus, we have no comparable data for other methods.

⁵ C. M. Slansky (ed.), et al., Technical Division Quarterly Progress Report, July-September 30, 1977, ICP-1132, p 87.

⁶ C. M. Slansky (ed.), et al., Technical Division Quarterly Progress Report, October 1-December 31, 1977, ICP-1141, (February 1978).

⁷ C. M. Slansky (ed.) et al., Technical Division Quarterly Progress Report, April 1-June 13, 1977, ICP-1123, p 62.

1.2.2 Effects of Sulfate Ion

The three types of samples used for this study have been described previously. They included a zirconium control saturated with sodium

TABLE 7
RUNNING BEHAVIOR FOR SODIUM-TYPE SAMPLES

Major Peak ^c & (Rel. Std. Dev.)	Number of Samples	Figure of Merit ^a	Average Stabilization Time (min.)
77.114(+0.073%)	6	0.0152	39
77.111(+0.077%)	2 ^b	0.0130	18

^a Discussed in Section 1.3.1, a value 0.05 or less indicates good running behavior.

^b These two contained no sodium in the original samples.

^c Weight percent, no bias significant at the .95 confidence interval.

sulfate, a composite prepared from the high-sulfate "Kinglet" fuel solution, and a sulfate-containing control prepared for the Kinglet-fuel processing run. Only the first of these contained high levels of sodium ion. Table 8 shows the observed results for these samples.

It seems probable that the long stabilization time required for the samples containing sodium sulfate are due more to the presence of sodium ion than sulfate. Certainly the behavior for the other two types of samples indicates that sulfate should not be a problem using the TIOA-xylene procedure.

1.3 Loading and Running Studies(E. E. Filby, S. Kelly, Jr., G. W. Webb, K. R. Arnold)

Four topics in the area of filament loading and instrument running behavior were studied: (1) the use of the beam stabilization time as a criteria for instrument behavior, (2) the effect of chloride ion on the loading and running behavior, (3) an extension of the filament temperature versus current work, and (4) the normal variation in the data from two filaments loaded with the same solution.

1.3.1 Running Criteria

Objective criteria defining "good" running behavior in the mass spectrometer were established in previous work.⁷ The criteria were based on the computer-derived standard deviations for the major peaks in the mass spectrum.

Because some confusion has arisen from the use of the term "mean standard deviation", or "average standard deviation", we have decided to change this terminology. Figure 9 shows an example of the initial printout seen by the mass spectrometer operator as a sample is being run. The underscored numbers are the standard deviations for the major peaks derived from the scan set data.

TABLE 8
RUNNING BEHAVIOR FOR SULFATE-TYPE SAMPLES

<u>Sample Type</u>	<u>Number of Samples</u>	<u>Major Peak^b & (Rel. Std. Dev.)</u>	<u>Figure of Merit</u>	<u>Average Stabilization Time (min.)</u>
Zr Controls ^a	3	77.073(<u>+0.032%</u>)	0.0189	41
Kinglet Controls	6	93.160(<u>+0.013%</u>)	0.0119	19
Kinglet Composite	6	93.107(<u>+0.020%</u>)	0.0126	21

^a Saturated with sodium sulfate. More were not run because of excessive stabilization time observed.

^b Weight percent, no bias significant at the .95 confidence interval.

	329	8 327	6 328	2583.MV
	328	9 326	6 328	2512.MV
	328	11 325	7 327	2439.MV
	328	10 325	7 328	2372.MV
	328	11 325	6 328	2309.MV
	327	12 324	6 328	2250.MV
33.4260	.0109	33.1500	.0070	33.4061
<u>.0236</u>	<u>.0016</u>	<u>.0305</u>	<u>.0002</u>	<u>.0348</u>

Figure 9. Example of Computer Printout

These are the printed values the operator uses to judge the quality of the scan set (by the 0.050 criteria). In addition, the mean value for the scan sets derived from a series of samples will give a good idea of how well that series ran in the instrument. The mean value for a series will now be referred to as the "Figure of Merit" (FOM) for the series. Table 9 further illustrates the correlation.

TABLE 9
BACKGROUND FOR THE "FIGURE OF MERIT"

<u>Plant Run</u>	<u>Rel. Std. Dev.^a</u>		<u>Figure of Merit (FOM)</u>	<u>Samples Used for FOM</u>
	<u>Conc.</u>	<u>235_U^b</u>		
Zirconium (1976)	0.60%	0.063%	0.069	51
Coprocess (1977)	0.52%	0.048%	0.045	108
Electrolytic (1977)	0.31%	0.060%	0.027	43

^a From QC reports.

^b Typical values are 65-80 atom percent.

The 1976 Zirconium and 1977 Coprocess runs are shown. "Good" running behavior is exemplified by the 1977 Electrolytic Process run. Note that the FOM correlates very well with the relative standard deviation for concentration, but not with the precision on the major-peak isotopic value.

In addition to this figure of merit, we have now quantified the stabilization time as an objective criteria for running behavior.

1.3.2 Stabilization Time

Obviously the time required for some types of samples to attain a stable ion beam in the mass spectrometer is an important criterion for running behavior. Samples which take twice as long to stabilize will be more expensive to run. Moreover, considering the strong time-dependence reported previously⁶ for the data output, the time required could easily bias the results relative to those for samples which stabilize rapidly. We have noted previously that samples containing high levels of sodium ion have long stabilization times. Table 10 shows comparative data for two sets of samples--one of which stabilized rapidly, the other slowly. The Figure of Merit can be used to identify acceptable data.

TABLE 10

FIGURE OF MERIT AS A FUNCTION OF TIME FOR TWO SAMPLE TYPES

Time After Initial Startup (min)	Figure of Merit	
	Standard	Samples with Na ^a
15	0.0502	0.2338
20	0.0370	0.2001
25	---	0.1649
30	0.0339	0.1139
35	0.0247	0.0856
40	0.0204	0.0461
45	0.0155	0.0391

^a Data from 4 time-dependent study samples.

On the basis of these and other observations, we have now established another running parameter for use by our mass spectrometer operators. Except for one-of-a-kind or other special-situation samples, we now limit the time to 45 minutes for obtaining the first set of major-peak standard deviations of less than 0.050. If reasonable stability is not reached by that time, they take the data they have and reload the sample. If the new filament gives poor data, a resample must be called for, or other means must be taken to obtain a pure uranyl nitrate solution to be loaded.

1.3.3 Possible Chloride Interference

It has been suggested, on the basis of minimal data collected a number of years ago, that the presence of chloride ions in a sample would make it difficult or impossible to run in the mass spectrometer. This assertion was tested systematically by loading a series of filaments with solutions which ranged from zero chloride up to 2.0 M chloride. The acidity of all the solutions was held constant at 2.0 M by adding appropriate amounts of nitric acid while the uranium concentration throughout was constant at 1 mg/mL. Table 11 shows the results obtained for these sets of samples. (All solutions loaded without difficulty.)

TABLE 11
RESULTS FOR CHLORIDE-CONTAINING SAMPLES

<u>Chloride Concentration</u>	<u>Number of Filaments</u>	<u>Wt% ²³⁸U (Rel. Std. Dev.)</u>	<u>Figure of Merit</u>	<u>Average Stabilization Time (min.)</u>
0.00 <u>M</u>	11	99.269(+0.019%)	0.0068	19
0.01 <u>M</u>	5	99.268(+0.006%)	0.0054	15
0.05 <u>M</u>	8	99.271(+0.009%)	0.0107	16
0.10 <u>M</u>	6	99.270(+0.007%)	0.0101	14
0.50 <u>M</u>	7	99.270(+0.011%)	0.0127	15
1.00 <u>M</u>	6	99.268(+0.010%)	0.0095	17
2.00 <u>M</u>	7	99.270(+0.010%)	0.0048	16

The presence of chloride ions in the solutions loaded appears to have no systematic effect on the results obtained. While a few of the filaments showed noisy or erratic behavior, all stabilized quite rapidly and the Figures of Merit for the major peaks are extremely low.

Two factors must be considered when drawing conclusions from these data. First, only about 40-50 g of U were loaded, whereas we normally load 80-120 g. This is probably not a serious problem. Second, the samples were not run immediately after they were loaded; many were aged for several days or more. We intend to support the results reported above by loading a few of the solutions and running them immediately.

1.3.4 Filament Temperature Studies

We have previously reported the results from one study of the dependence of the filament temperature upon the applied current during sample drying.⁶ It was shown that the 2 A current used to dry the solution would maintain the temperature at around 215°C, while the 2.2 A current used to convert the nitrate to the oxide would give a temperature of around 280°C. Literature studies indicate that these temperatures would leave much of the trioxide in the hydrated form.

We have now extended this work to cover some other variables in the system. The filaments used in the previous study (and for most of the other loading studies) had not been prebaked in our filament bakeout chamber.

We have now examined the effects of such a prebaking upon the temperatures attained during loading. These studies were carried out in air at normal pressure. We have also studied the temperature profile when the filaments (not prebaked) are heated in a vacuum.

Figure 10 shows the data generated during the three experiments. The normal-pressure data (solid and open circles) indicate that the prebaking has essentially no effect on the temperature vs. current profile. On the other hand, heating in a vacuum does cause a difference--the temperature curve rises much more steeply for a given applied current. This can be attributed to the lack of atmospheric convection to carry heat away from the filament.

The ionizing center filaments used in the mass spectrometer are made from rhenium rather than tantalum. We also sometimes load samples onto a rhenium side filament. Thus, we have also studied the temperature versus current profile for unbaked and prebaked rhenium. The results are shown in Figure 11. Again, prebaking the material has no apparent effect on the profile. However, the curve rises much more rapidly for rhenium than it does for tantalum. (The dashed line in Figure 11 shows the profile for tantalum as derived in Figure 10.) This is to be expected from the comparative resistivities of the two materials (19.3 $\mu\text{ohms/cm}$ for Re, 13 $\mu\text{ohms/cm}$ for Ta).

This information about filament temperature should help us rationalize the chemical transformations that might occur in a sample during processing. That information will in turn aid in selecting the optimum loading and running procedures to be used for various kinds of samples.

1.3.5 Filament-to-Filament Variation

To determine the various possible sources of analytical uncertainty in mass spectrometry data, the instrument behavior under ideal conditions must be known. The variation in data from sets of filaments loaded with the same solutions was determined. Statistical analysis of the resultant data gives a measure of the filament-to-filament variation under rigidly-controlled ideal conditions.

The eight uranium solutions used were prepared by the dissolution of several samples of uranium dioxide. Two aliquots were taken from each of these solutions, and two filaments were loaded and run from each of the aliquots. The instrument was calibrated before and after a series of filaments was run, using NBS SRM U-050, which is similar in isotopic composition to the samples. Table 12 shows a summary of the statistical analysis results.

The variation in the data attributable to differences in the aliquots taken is totally negligible for the major peaks, ^{235}U and ^{238}U (which are around 4.4 and 95.5 weight percent, respectively). The data for the extremely small minor peaks (0.023 percent ^{234}U , 0.054 percent ^{236}U) is meaningless in this context. Thus, we do have a good measure of what can be expected when two successive filaments are run under ideal conditions.

(○ FILAMENTS NOT PRE-BAKED; ● FILAMENTS PREBAKED,
△ HEATING DONE IN VACUUM).

ACC-A-3172

Figure 10. Temperature Profile for Tantalum Filaments

Figure 11. Temperature Profile for Rhenium Filaments

(○ NOT PREBAKED, ● PREBAKED; DASHED LINE IS FOR Ta DATA)

ACC-A-3171

As expected, the variations are dependent upon the isotopic abundance of the peaks being measured. Table 13 shows the relative standard deviations (filament-to-filament) as a function of uranium weight percent. Also listed are the values for comparable peaks derived from routine QC data. For the major peaks, the absolute standard deviation rises to a maximum at 50 weight percent as expected for a normalized, essentially two-peak system.

The trends in the data indicate that rigid control of operating conditions can improve the precision on isotopic measurements of major peaks by a factor of about three. (Interestingly enough, very little improvement in the minor peak data appears possible.) Any improvements to be made must be evaluated within the context that a three-fold improvement is the best available. Of course, such rigid control is not possible on routine samples--for instance, the time required for additional calibrations would raise the cost-per-analysis by over 30%.

2. Zirconium Fuel Recovery Process

(M. L. Gates)

During the reporting period, cyclic corrosion tests designed to provide usable lifetime data on the Hastelloy C-4 Fluorinel dissolver were completed for the dissolution flowsheet for the reference Fluorinel fuel.

TABLE 12

DATA VARIATION BETWEEN MASS SPECTROMETER FILAMENTS

<u>Isotope</u>	<u>Wt%</u>	<u>Relative Standard Deviations</u>		
		<u>Filament-to-Filament</u>	<u>Net-to-Net^a</u>	<u>Aliquot-to-Aliquot^b</u>
234U	0.023	6.48%	8.52%	5.43%
235U	4.4	0.065%	0.051%	-0-
236U	0.054	3.19%	5.44%	1.30%
238U	95.5	0.0052%	0.0052%	0.0003%

^a The net variation is a combination of the filament and aliquot differences.

^b Calculated from the filament-to-filament and net deviations.

TABLE 13

STANDARD DEVIATION AS A FUNCTION OF WEIGHT PERCENT

<u>Isotopic Abundance</u>	<u>Relative Standard Deviations (%)</u>	
	<u>From QC Data</u>	<u>This Work</u>
95	0.0181	0.0052
50	0.0730	
5	0.276	0.065
0.5	0.79	
0.05	3.81	3.20
0.025	7.62	5.20

2.1 Cyclic Corrosion Tests (A. Chidester)

Cyclic corrosion tests were run to provide data to estimate the usable lifetime of the Hastelloy C-4 Fluorinel dissolver. Previous tests have been run with solutions which simulate process streams from the PWR and TRIGA (stainless steel clad) fuel dissolution flowsheets. The series of tests reported here was made in solutions which simulate process streams from the reference Fluorinel fuel dissolution flowsheets. Three sets of tests were run. Tests 1 and 2 used a low fluoride (6.8 M F^-) solution which had the composition shown in Table 14. Test 3 was run in a high fluoride (11 M F^-) solution which had the composition shown in Table 15. As in previous tests, welded coupons of Hastelloy C-4 were weighed and placed in the test apparatus shown previously.⁶ Test solutions were changed at intervals which approximated actual process conditions. A list of test parameters for each test run is shown in Table 16. Following each stainless dissolution step, the weight losses of the coupons were determined and converted to corrosion rates. The coupons were then photographed and examined visually for specific corrosion effects.

TABLE 14

DISSOLUTION FLOWSHEET FOR REFERENCE FLUORINEL FUEL-LOW FLUORIDE

	<u>F⁻M</u>	<u>Zr⁺⁴M</u>	<u>H⁺M</u>	<u>Al⁺³M</u>	<u>NO⁻³M</u>	<u>SO₄⁻²M</u>	<u>Cd⁺²M</u>	<u>Cr⁺³M</u>	<u>Ni⁺²M</u>	<u>Fe⁺²M</u>	<u>Mn⁺²M</u>
Decladding	7.23	--	8.80	--	--	--	0.21	--	--	--	--
Dissolver Product	7.40	1.36	1.60	--	0.005	--	0.21	--	--	--	--
Complexed Dissolver Product	3.07	0.60	2.03	0.42	2.48	0.21	0.16	--	--	--	--
Stainless Steel Dissolution	0.012	0.002	0.008	0.002	0.01	6.21	0.21	0.40	0.20	1.50	0.03

TABLE 15

DISSOLUTION FLOWSHEET FOR REFERENCE FLUORINEL FUEL-HIGH FLUORIDE

	<u>F⁻M</u>	<u>Zr⁺⁴M</u>	<u>H⁺M</u>	<u>Al⁺³M</u>	<u>NO⁻³M</u>	<u>SO₄⁻²M</u>	<u>Cd⁺²M</u>	<u>Cr⁺³M</u>	<u>Ni⁺²M</u>	<u>Fe⁺²M</u>	<u>Mn⁺²M</u>
Decladding	7.23	--	6.8	--	--	--	0.21	--	--	--	--
Dissolver Product	11.2	1.52	1.60	--	0.005	--	0.21	--	--	--	--
Complexed Dissolver Product	3.07	0.60	2.03	0.42	2.48	0.21	0.16	--	--	--	--
Stainless Steel Dissolution	0.012	0.002	0.008	0.002	0.01	6.21	0.21	0.40	0.20	1.50	0.03

TABLE 16
PARAMETERS FOR CORROSION TESTS
(Reference Fluorinel Fuel Process Cycle)

Solution		Time, h	Temperature, °C
(1) Decladding	Dissolution Cycle	1	80
(2) Zr Dissolver Product		6.5	80
(3) Complexing		3	80
(4) Stainless Steel Dissolution		20	100

Test 1 ran for a total of 362 h (five process cycles of 72.5 h each). Attack of weld metal defects was especially noted here. The Test 1 coupon was welded locally from 7/8 in. plate, and the weld was of lower overall quality than the welds in the Test 2 and 3 coupons which were welded by an offsite fabricator from 5/8 in. plate. Figure 12 shows the Test 1 coupon at the termination of the experiment. Figure 13 is the corresponding close-up showing the preferential attack of the weld defects. This demonstrates the importance of having high quality welds to minimize pitting and accelerated weld corrosion in process vessels.

Table 17 lists the corrosion rates for Test 2 and 3 in m/month. The average corrosion rate was 70.9 m/month for the low fluoride Test 2, and 126.6 m/month for the high fluoride Test 3. Thus, the high fluoride flowsheet increases the corrosion rate by approximately 80%. Coupons from Test 2 and 3 both showed weld metal pitting despite the higher quality welds. The pitting was more prevalent in the high fluoride, Test 3, but was not as severe as in Test 1. Figures 14 and 16 are photographs of the coupons at the termination of the experiment. Figures 15 and 17 are the corresponding close-ups showing preferential attack of the weld and interdendritic pitting in coupons from Tests 2 and 3.

Plans for the Next Quarter

Full-scale Fluorinel dissolver mockup testing will be completed. Scoping studies will be carried out on the dissolution of soluble nuclear poisons such as Cd, B, Sm, and Gd in Fluorinel process solutions. Cyclic corrosion tests will be continued using coupons welded by the automatic gas tungsten arc process. The corrosion resistance of various etched-disc filter and plant pump materials in Fluorinel process solutions will be evaluated with the potentiostat. The corrosion resistance of Grafoil gasket material in Fluorinel process solutions will be determined.

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

TABLE 17
CORROSION RATES FOR HASTELLOY C-4^[a]
(Reference Fluorinel Fuel Flowsheet Conditions During Dissolution)

<u>LOW FLUORIDE</u>	
<u>No. of Complete Process Cycles</u>	<u>Corrosion Rate, $\mu\text{m}/\text{month}$</u>
1	17.7
2	78.6
3	93.0
4	83.1
5	98.6

<u>HIGH FLUORIDE</u>	
<u>No. of Complete Process Cycles</u>	<u>Corrosion Rate, $\mu\text{m}/\text{month}$</u>
1	58.2
2	154.6
3	124.8
4	99.4
5	114.6

^[a]Conditions for tests are shown in Tables 14, 15, and 16.

Figure 12. Corrosion coupon from Test 1 (Exposed to reference Fluorinel fuel flowsheet conditions. Actual size)

Figure 13. Preferential attack of weld defects in Test 1 (corrosion coupon exposed to reference Fluorinel fuel flowsheet conditions. 10x)

Figure 14. Corrosion coupon from Test 2 (Exposed to reference Fluorinel fuel flowsheet conditions. Actual size)

Figure 15. Interdentritic pits in Test 2 (corrosion coupon exposed to reference Fluorinel fuel flowsheet conditions. 10x)

Figure 16. Corrosion coupon from Test 3 (Exposed to reference Fluorinel fuel flowsheet conditions. Actual size)

Figure 17. Interdentritic pits in Test 3 (Corrosion coupon exposed to reference Fluorinel fuel flowsheet conditions. 10x)

matrix is converted to CO_2 in a primary burner. The residual graphite is combusted in a secondary burner producing 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 efforts this quarter were expended in (1) completion of dry solids transfer system erosion tests, (2) preparation for installation of the plant support primary burner and dissolver systems, (3) a Kynar piping evaluation, and (4) initial work on a Rover Plant reliability analysis.

1. Solid Transport System Testing (H. S. Meyer, R. L. Ring)

1.1 Comparison of Erosion in Schedule 40 and Schedule 80 Piping

Two tests were conducted to determine if erosion rates will differ due to the 13% decrease in cross-sectional area of bends in 1-1/2 in., Schedule 80 pipe compared to bends in 1-1/2 in., Schedule 40 pipe. Previous pilot plant testing was performed with Schedule 40 piping, while the plant piping is Schedule 80.^{5,6} For these tests, the first bend downstream of the ejector and contiguous piping were replaced with 1-1/2 in., Schedule 80 piping and fittings. The bends tested were (1) a long radius ($R/D = 1.5$), 90-degree, horizontal elbow, and (2) a wide-sweep ($R/D = 5$), 90-degree, horizontal-to-vertical bend. The bends began 0.6 m from the discharge of the ejector. Al_2O_3 was transferred by Penberthy Model LL1 Ejectors. Air was supplied to the ejectors at a rate of $16.5 \times 10^{-3} \text{ m}^3 \text{ s}^{-1}$ and a pressure of 620 kPa.

As shown in Table 18, the erosion rates experienced are not significantly different. Therefore, the results obtained and reported for Schedule 40 piping are applicable to the Schedule 80 piping in the plant. The distance from the bend to the ejector affects erosion more than the cross-sectional area of the piping for the configurations tested.

1.2 Erosion of a Porcelain-Lined Ejector

A porcelain-lined Model LL1 Ejector was tested for resistance to the erosion that occurs in ejectors during dry solid transfers. In the same service, a hole formed in the lined ejector after 8 h of transferring Al_2O_3 , while the unlined ejector similarly failed after 7.7 h. This test showed no significant difference between lifetimes of the ejectors; therefore, porcelain-lined ejectors are not recommended for use as replacements for the plant ejectors.

2. Rover Support Dissolver (A. G. Westra, R. L. Ring)

Unused equipment has been removed from the module where the Rover support dissolver will be installed. The module has been decontaminated and is ready for the dissolver equipment installation. Figure 18 is a

TABLE 18
COMPARISON OF EROSION IN SCHEDULES 80 AND 40 PIPING

Type of 1-1/2 inch Piping	Erosion Rates (nm/kg Al ₂ O ₃ Transported)	
	Long Radius Bends (R/D = 1.5)	Wide Sweep Bends (R/D = 5)
Sch. 40	330	75
Sch. 80	250	60

flow diagram for the Rover Plant Support Dissolver. Drain valves and bulkhead fittings for vent lines have been installed in the polyethylene reagent makeup tanks. Fabrication of the glass vessels to be used as HNO₃ and aluminum nitrate feed tanks and the Monel HF feed tank was completed. Work will begin shortly on assembling the dissolver and installing the equipment in the module. The support dissolver, like the Rover Plant Dissolver, will be lined with Kynar.^a Kynar (polyvinylidene fluoride) was chosen as a lining for the plant dissolver because of its excellent chemical resistance at high temperatures and good radiation resistance. The top flange of the Rover Plant Support Dissolver and the internal probes will be made of Teflon. Since irradiated fuel will not be used in the support dissolver, radiation damage to the Teflon will not be a problem.

Heat will be supplied to the dissolver by electrical heating tape wrapped around the lower part of the dissolver. The temperature of the heating tape will be controlled to avoid overheating the Kynar. During operation of the dissolver, Rover secondary burner ash will be dissolved sequentially in HNO₃ and HF solutions at 350 K. Acid vapors from the dissolver will be condensed in a Teflon-lined condenser and drained back to the dissolver. When uranium dissolution is complete, the fluoride in the dissolver solution will be complexed with the correct amount of aluminum nitrate to simulate the plant flowsheet.

Operating procedures for the Rover process support dissolver have been written in draft form.

3. Rover Plant Support Primary Burner Installation

(A. G. Westra, D. L. Hovis)

The Rover Plant Support Primary Burner will use the off-gas system, instrumentation, and lower section that are now part of the 10-cm-diameter

^a Trademark of Pennwalt Corporation.

ACC-A-3113

Figure 18. Flow diagram of the Rover process support dissolver.

Pilot Plant Secondary Burner. The pilot plant burner will be modified so it can be operated either as a primary burner or a secondary burner by quickly changing a few components.

4. Kynar Pipe Evaluation (L. W. McClure)

During cold testing of the Kynar piping installed in the Rover Plant, many leaks were found. The leaks were determined to be a result of faulty welds. Inspection of the leaky joints showed poor bonding of the pipe and fittings. The procedure for welding solid Kynar piping is to (1) heat the pipe and fitting with a special tool for a specific length of time depending on the pipe size, (2) insert the pipe into the fitting, and (3) maintain pressure for 15 seconds.

Laboratory testing of the weld procedure and a literature search were conducted to determine if the faulty piping should be replaced with Kynar or with some other material. Kynar was recommended as the replacement material because of its chemical resistance, radiation resistance, and low cost; reliable welds can be made if the manufacturer's procedure is followed carefully.

4.1 Laboratory Testing of Weld Procedure

Welds were made in the laboratory to determine if reliable joints could be made following the manufacturer's recommended procedure. Two welds were made with piping inserted into a 3/4 in. elbow and two with a 1-1/2 in. elbow and piping. The 3/4 in. joint was tested under a water pressure of 6890 kPa (1000 psig), and no leakage occurred. The 1-1/2 in. elbow failed at 5170 kPa (750 psig), but there was no leakage from the welds. Therefore, properly made welds were found to be very dependable.

4.2 Literature Search

A literature search was made to determine if an alternative material would provide a more reliable system than Kynar in the Rover Plant. Information was gathered on the chemical resistance to HF, HNO₃ and mixtures, radiation resistance, fabrication techniques, and cost of various systems. The results of the comparison are shown in Table 19.

Based on the superior chemical resistance, acceptable radiation resistance, and relative low cost, Kynar was recommended as the best overall choice. Rover fuel is low burnup, long cooled so the radiation levels are low enough for Kynar to be acceptable.

5. Reliability Analysis (D. L. Hovis, A. G. Westra)

A study is being made of the installed Rover Plant burners with the objective of simplifying operation and improving reliability. Recommendations for improving burner control based on experience with pilot plant burners will be made to Rover Project personnel. This work is the initial phase of a reliability analysis of the entire Rover plant.

TABLE 19
COMPARISON OF ALTERNATIVE PIPING MATERIALS

<u>Alternative Method of Materials Fabrication</u>	<u>Chemical ^a Resistance</u>	<u>Radiation ^a Resistance</u>	<u>Relative ^b Cost</u>	
Kynar (solid) Weld, and/ Flanged	E	A	1	Thermal Threaded or
PVC and/or	U	A	0.04	Glued Welded
Teflon or	E	U	1.6	Threaded Swaged
Polyethylene or	U-A	A	0.02	Glued, Swaged Welded
Polypropylene	U-A	A	0.1	Glued, swaged or welded
Hastelloy C-4	A	E	5	Welded
Inconel	U-A	E	5	Welded
Kynar-lined ductile iron	E	A	2	Flanged

^a E = excellent, minor or no attack
A = acceptable, some attack
U = unacceptable, major attack

^b Cost is for pipe only, fabrication cost differences are not included. (1 = \$5.00/ft) Basis: 1" Schedule 80 pipe for solid Kynar and other plastics, 1" Schedule 40 pipe for Hastelloy and Inconel.

Plans for Next Quarter

The installation and check-out of the Rover Plant Support Dissolver and the Rover Plant Support Primary Burner will be completed. The reliability analysis on the plant burners will be completed and work will be initiated to analyze other critical parts of the plant. Further process verification studies will be conducted as required.

IV. ICPP WASTE MANAGEMENT DEVELOPMENT

1. Sodium-Bearing Waste Flowsheet Development (B. J. Newby)

The previous flowsheet proposed for calcination of ICPP sodium-bearing waste uses a blend of 3 vol of ICPP first-cycle zirconium waste, 1 vol of sodium-bearing waste, and 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 1/2 or greater vol of zirconium waste blended with 1 vol 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 possible excessive release of chloride to the off-gas scrubbing system. Additional work was performed to modify the proposed flowsheet to prevent particle roughness and excessive chloride volatility.

Calciners feeds containing zirconium waste (Zr) to sodium-bearing (Na) waste blend ratios of 2, 3, 4 1/2, 6, and 8 (using a Ca/F mole ratio of 0.7) were calcined for 40 h using a 10-cm-diameter calciner. Calcine produced from all blend ratios were observed under microscopes at magnifications of 15X and 50X; all blends seemed to be about the same in surface roughness. The calcine was relatively smooth and contained only a few nodules. Calcination of blend ratios of 2, 6, and 8 produced wet fines; calcination of blends with ratios of 3, 4, and 4 1/2 produced dry fines. Calcine size (mass mean particle diameter-MMPD) was controlled by varying the nozzle-to-air ratio (NAR). The more important average calciner operating conditions, fluidized-bed characteristics, and characteristics of solids produced during the calciner runs are shown in Table 20; average chloride and fluoride volatilities are also shown. The only possible trends shown in the table are an increase of calcine hardness and product-to-fines ratio as the Zr waste to Na waste blend ratio is decreased. The undissolved solid content of the calciner feed (due to $\text{Ca}(\text{NO}_3)_2$ addition) increases as the Zr waste to Na waste blend ratio increases. No fluidized-bed particle agglomeration was noted in any of the runs.

A run was made using a 30-cm-diameter calciner and a feed containing a Zr waste to Na waste blend ratio of 3 (using a Ca/F mole ratio of 0.7). Only limited information is presently available from the run. Wet fines were not produced during the run. The calcine size could be controlled by varying a combination of the NAR and oxygen-to-fuel ratio. There was no fluidized-bed particle agglomeration during the run. The calcine produced by calcining the 3 vol Zr waste to 1 vol Na waste blend had a tendency to set-up into a very fragile agglomerate when allowed to cool. Agglomerates cooled to 20-150°C readily broke up when poured

once from one bucket to another (simulating transfer of solids to storage bins) and did not set-up again even when heated at 500°C for 2-1/2 d and then cooled to 20°C. Other information available from the run is shown in Table 21.

Blending 3-4 vol of Zr waste with 1 vol Na waste using a Ca/F mole ratio of 0.7 will again be tested in the WCF as a flowsheet for calcining Na waste. Use of these blend ratios provides: 1) a margin of safety (a blend ratio of 1 is not calcinable), 2) a relatively high calciner through-put of Na waste, and 3) lower amounts of undissolved solids in calciner feed than when processing zirconium waste.

Plans for Next Quarter

Runs will be made using a 10-cm-diameter calciner to determine if cold aluminum nitrate or silica blended with sodium-bearing wastes is practical.

2. Heat Transfer Properties of Future ICPP Calcines (S. S. Bodner)

Safe and economical design of future calcine storage facilities requires accurate calcine heat transfer data. A proposal to determine simulated WCF calcine thermal conductivity as a function of temperature, density, and product-to-fines ratio has been received from Battelle Pacific Northwest Laboratories. The tests will take approximately three months and cost \$8500.

The ORGIN code by Oak Ridge National Laboratories is being used to predict heat generation rates of future ICPP calcines.

Plans for Next Quarter

The heat generation rates of various liquid wastes will be compiled for use in planning calciner processing schedules.

Plans for Next Quarter

A sodium-bearing waste flowsheet will be tested in the WCF. A decision to purchase the spray calciner test will be made after the WCF test is completed.

3. Fluorinel Waste Flowsheet Development (J. H. Valentine)

Tests using a 10-cm calciner, Run EM-Fluor-2, have demonstrated that unmodified Fluorinel waste cannot be calcined because the cadmium in the waste causes agglomeration. Apparently cadmium, like sodium, forms a stable nitrate with a low melting point (cadmium nitrate has a melting point of 350°C).

The calciner feed composition was based on the expected composition of the first 1.1 ML (300,000 gal) of Fluorinel waste. The differences in composition between Fluorinel waste and the present zirconium fluoride waste are lower fluoride and aluminum concentrations, 0.17 M cadmium

TABLE 20

CALCINATION TEST RESULTS AS A FUNCTION OF
Zr WASTE TO Na WASTE BLEND RATIO IN A 10-CM-DIAMETER CALCINER

Zr Waste to Total Na Waste Blend Ratio	NAR	% Bed Turnover	MMPD (mm)	Attri- tion In- dex (%)	Product to Fines Ratio	% Total F- Volatilized from Bed	% Cl Re- maining in Bed
2	1034	88	0.6080	66	7.7	0.26	93
3	1020	88	0.5913	80	5.6	0.67	92
4	1038	90	0.5748	64	5.7	0.25	87
4-1/2	1020	84	0.5966	43	2.4	0.47	92
6	935	89	0.5875	52	2.7	0.25	86
8	962	90	0.6151	39	4.1	0.20	88

TABLE 21

CALCINATION OF A BLEND OF 3 VOL ZIRCONIUM WASTE
WITH 1 VOL SODIUM-BEARING WASTE USING A 30-CM CALCINER

NAR	Bed Turn over (%)	MMPD (mm)	Attrition In dex (Final Bed) (%)	Product- to-Fines Ratio
387	99.6	0.481	68	2.5

(rather than boron), 0.048 M sulfate, and approximately 2 g/L dissolved stainless steel in Fluorinel waste. The feed had a Ca/F mole ratio of 0.55.

The test results are as follows:

1. Two attempts to calcine the simulated Fluorinel waste were terminated (forced) after about 8 h by the formation of agglomerates. Severe melting occurred in one test, and a cake formed around the feed nozzle in the other test.

2. To identify cadmium as the primary cause of the agglomeration, zirconium fluoride waste was first calcined for 24 h without problems. Cadmium nitrate was then added to the same zirconium fluoride waste feed to give a 0.17 M concentration of cadmium. The run was ended after 10 h of operation because the bed temperatures had spread. Examination revealed extensive agglomeration and the formation of a bridge across the calciner from the feed nozzle to the opposite wall.

An earlier run in October (EM-Fluor-1) using a Fluorinel waste with a high sulfate concentration (0.39 M) resulted in excessive fines generation, but no significant bed agglomeration. The run was terminated after 80 h when an off-gas leak developed in a liquid cyclone. Apparently the cadmium was either being solidified as cadmium sulfate (melting point of 1000°C) or the cadmium-containing material was being blown overhead as fines and not enough was sticking to the starting bed particles to cause agglomeration.

Plans for Next Quarter

Fluorinel flowsheet development using the 10-cm enclosed calciner will continue. The next run will use a feed containing a minimum amount of cadmium (0.062 M); boron (0.672 M) would partially replace the cadmium as the neutron poison in the Fluorinel dissolution process if this waste were produced.

4. Tank WM-183 Flowsheet Development (J. T. Nichols)

A 10-cm-diameter calciner run to test the buildup of a 2:1 blend of zirconium fluoride waste and to WM-183 waste on a starting bed of zirconium fluoride calcine was completed. The product-to-fines weight ratio during Run 183-4-18 was 1.5, the final MMPD was 0.5 mm, and the final attrition index was 64.

Analytical data from 30-cm calciner Run 64 (2 vol zirconium fluoride and 1 vol WM-183 waste blend) were received. Chloride in the scrubbing solution reached a maximum of 72 µg/mL after 80 h. The sodium/aluminum mole ratio rose in the scrubbing solution from 0.42 to 0.6 indicating some sodium was volatilized during calcination.

The sintering temperatures of Run 64 calcine after 68 and 102 h of operation were determined. The sintering temperature for both calcines was 650°C; therefore, these calcines should not be stored at bin temperatures greater than 600°C. This should present no problem since bin temperatures are now well below 600°C, and because conservative bin design will probably be below 600°C in future bin sets.

Plans for Next Quarter

Run 183-4-18 calcine samples will be sectioned to determine the nature of the particle growth. Detailed mass balances will be completed on Run 64 analytical data to determine sodium and chloride carryover.

Table 22

COMPOSITIONS OF WASTES IN TANKS WM-100, 101, AND 102

Component	WM-100	WM-101	WM-102
Cl	<30 $\mu\text{g/ml}$	<30 $\mu\text{g/ml}$	<30 $\mu\text{g/ml}$
Na	586 $\mu\text{g/ml}$	510 $\mu\text{g/ml}$	508 $\mu\text{g/ml}$
H ⁺	0.66N ^a	1.26N ^a	1.05N ^a
SO ₄ ⁼	0.04M	0.04M	0.083M
Al	1.2M	0.51M	0.65M
NH ₄ ⁺	<0.51M	<0.51M	<0.51M
NO ₃ ⁻	5.25M	3.34M	3.68M
F	486 $\mu\text{g/ml}$	130 $\mu\text{g/ml}$	50 $\mu\text{g/ml}$
Gd	--	0.021M	0.0169M
Fe	0.0733M	0.0644M	0.0644M
Cr	0.0035M	0.0152M	0.0121M
Zr	0.0083M	--	--
Mo	--	0.0025M	0.0023M
Ni	0.0017M	0.0078M	0.0058M

5. Electrolytic Waste Flowsheet Development (S. A. Birrer)

A program was started to develop a flowsheet for calcination of wastes contained in tanks WM-100, WM-101, and WM-102. WM-100 waste is mostly second-cycle raffinate and WM-101 and WM-102 wastes are mostly first-cycle electrolytic process waste. The compositions are given in Table 22. The 10-cm calciner Run EL-10-1 used a feed simulating WM-101 waste concentrated to 33% of its original volume. The 92 h run yielded a product-to-fines weight ratio of 1.5, an MMPD of 0.49 mm, and an attrition index of 64. The initial MMPD was 0.54 mm and dropped to a low of 0.37 mm due to several calciner shutdowns and startups. Run EL-10-2 also was operated with a simulated WM-101 waste, but the feed was concentrated to 25% of its original volume. The product-to-fines weight ratio was 0.67, the final MMPD was 0.38mm, and the final attrition index was 46. The calciner run was not considered a good test since some of the aluminum nitrate precipitated out of the feed solution before it was fed to the calciner. Neither calciner run resulted in excessive agglomerate formation.

Plans for Next Quarter

Further tests will be conducted using the 10-cm calciner. When a successful flowsheet is developed, a test will be made using the 30-cm calciner.

6. Alternate WCF Startup-Bed Material Studies (D. H. Munger)

The search for an alternate WCF startup bed material has led to the selection of fluorapatite to replace dolomite. Fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) is a natural phosphate rock mined in central Florida. The rock, in the form of "concentrate", is being separated from the coarse phosphate rock (+14 mesh), slime, and sand during mining and washing operations. The final size range of the concentrate is -30 to +150 mesh. The mass mean particle diameter ranges from 0.30 to 0.35 mm.

The purpose of this project was to solve several problems associated with the dolomite startup bed material:

1. Dolomite has a very high capability for erosion of the pneumatic transport pipeline bends--approximately 100 times that of zirconium calcine. This high erosion potential is due to the angular shape of the dolomite particles.
2. Dolomite has a very wide range of particle sizes, causing a high elutriation rate during calciner startup.
3. Dolomite has a relatively low resistance to attrition in a fluidized bed. It is not uncommon during WCF startup to add up to 60% more dolomite to maintain the bed level. The extra dolomite added to the calciner during startup lengthens the starting time and uses expensive storage space in the bins.

A search was started to find an alternate startup bed material that would be chemically, physically, and economically compatible with our needs at ICPP. Materials such as magnorite, rolled silico-aluminate, hydrated alumina, calcium nitrate, etc., were discarded as possibilities due to one or more serious process incompatibilities.

Fluorapatite showed no process incompatibilities upon preliminary evaluation. The results of these preliminary tests showed that:

1. Fluorapatite has an erosion potential 20 to 50 times less than dolomite. This is due to the rounded particle shape of the concentrate.
2. Fluorapatite has a substantially higher resistance to particle attrition.
3. Fluorapatite has a much narrower particle size distribution.
4. Fluorapatite costs only 1/5 as much as dolomite, exclusive of shipping.
5. Fluorapatite has a melting point in excess of 1000°C.
6. Fluorapatite contains less than 5% insoluble material (mostly quartz).

On the basis of these preliminary evaluations, fluorapatite was chosen for testing in the 10-cm and 30-cm-diameter calciners. These calciner tests, ASB4-1 and 30-cm calciner Run 65, showed that the aluminum nitrate startup feed properly built up a layer of alumina on the fluorapatite particles. These tests were a simulation of actual WCF startup procedures.

There was some concern that phosphate carried over into the scrubbing system would cause excessive formation of precipitates when scrubbing solution is blended with zirconium fluoride feed. This should pose no problem, since approximately 500 ppm of phosphate is presently being added to zirconium fluoride feed during calcium nitrate addition with no apparent effects. The phosphate level in the scrub when changing from aluminum nitrate to zirconium fluoride feeds should result in phosphate concentrations less than 500 ppm. Tests were made to determine the amount of precipitate formed in the feed by the addition of a scrubbing solution containing 365 µg/mL phosphate, which was the maximum phosphate concentration during 30-cm calciner Run 65. A WCF feed batch made with this scrubbing solution would contain ~15% more phosphate than normal. Measurements of undissolved solids in a simulated feed indicated this additional phosphate would have a negligible effect on undissolved solids content of the feed.

Plans for Next Quarter

Enough fluorapatite has been procured for use as a startup bed for the continuation of WCF Campaign H-8 in April. This test will demonstrate the applicability of fluorapatite as a calciner startup bed material.

V. TECHNICAL SUPPORT TO THE WASTE CALCINING FACILITY (WCF)

1. WCF Scrubbing Solution Chloride Limit (A. P. Hoskins)

Extensive tests for the presence and effects of mercury chloride compounds in the WCF scrub solution were made to determine if all of the chloride is identified when total chloride is analyzed. The conclusion is that the chloride analysis is identifying the total chloride present; therefore, the chloride limit for the scrubbing solution was raised from 1300 to 2600 ppm based on corrosion tests of Type 304L stainless steel in simulated scrub solutions containing chloride.

A method to reduce the chloride level in the scrubbing solution was developed in the pilot-plant calciners for Zr:Na-bearing waste blends and tested in the WCF on straight Zr waste. The method uses extra calcium nitrate and aluminum nitrate in the feed solution to reduce chloride volatilization. The chloride level in the WCF scrubbing solution was not reduced; apparently the presence of sodium as well as the extra calcium and aluminum is necessary to minimize chloride volatility.

Plans for Next Quarter

A Zr:Na-bearing waste blend will be tested in the WCF in May, and chloride concentration will be carefully monitored.

2. Calcliner Product Removal Studies (G. L. Cogburn)

A calcliner product removal system similar to that used at the WCF was installed on the 30-cm-diameter calcliner in the High Bay laboratory. Tests will be made to determine conditions for operating the calcliner product removal system at the WCF. The variables being considered in these tests are: 1) fluidizing velocity, 2) system pressure drop, 3) dilution air rate, 4) blast air rate, and 5) product removal rate.

Further testing will determine the operability of alternate designs. Additional variables to be studied in these tests are: 1) the angle at which the dilution air line enters the product removal line, and 2) the distance from the calcliner vessel at which the dilution air line enters the product removal line.

Plans for Next Quarter

Testing of the product removal system will be completed and the system will be used on a five-day, 30-cm-diameter calcliner run during which simulated electrolytic process waste will be calcined. Recommendations will then be made to the Production Division on the operation of the WCF calcliner product removal system.

VI. TECHNICAL SUPPORT TO THE NEW WASTE CALCINING FACILITY (NWCF)

1. Sump Sampling System Test (G. W. Pelletier)

The liquid waste collected in the NWCF sump tank must be sampled and checked for fluoride concentration before the liquid is jetted to the

evaporators. The sampler proposed for the NWCF sump tank would use a combination of an air lift and air jet to pull the liquid sample to the sample station located 10.8 m above the sample tank.

The proposed sampler was mocked up as shown in Figure 19 and tested successfully with an aluminum nitrate solution with a density of 1200 kg/m³. The mockup differed from the NWCF design in the use of 3/8" ss tube ($D_i=7.75$ mm) and 3/8" Tygon tube ($D_i=6.35$ mm) instead of 1/4" pipe ($D_i=9.25$ mm) in the vertical-lift section of the sampler. The jet--Penberthy model GH1/2A, Series 300--when supplied with 590 kPa air, pulled a vacuum of 50 kPa and pulled the liquid column to a height of 6.3 m. Introduction of the purge air into the liquid column (essentially forming an air lift) allowed the liquid to rise to the sample station. The sample bottle was filled 5 to 10 seconds after introducing the purge air. Sample flow was intermittent with short periods of backflow. Purge-air flows of 12 to 100 standard litres per hour provided average sample flow rates of 2.1 to 2.7 litres per hour. A purge- air flow of 40 standard litres per hour provided the highest sample flow rate.

Plans for Next Quarter

The study was completed.

2. Resistance of Compressor Sealing Materials to Decontamination Reagents (B. J. Newby)

Amoco's Torlon 4103 or 8020 is proposed for the interstage seals, and GE's Silmate RTV 1473 for the case seals in the NWCF off-gas compressor.

These materials were tested to determine their ability to withstand possible decontamination reagents that could be flushed through the compressor to reduce its background radiation level. Torlon 4103 is a poly (amide-imide) resin, Torlon 8020 is 80% poly(amide-imide) resin - 20% Teflon, and RTV 1473 is a silicone rubber.

Coupons of the materials were submerged in the decontaminating reagents listed in Table 23 at 80°C for 10-12 d. Coupons submerged in reagents 8, 9, and 10 for 10-12 d were then submerged in reagent 5 for an additional 10 d because any surface decontaminated by reagents 8, 9, or 10 is subsequently decontaminated by reagent 5.

The Torlons behaved similarly towards the reagents; they showed poor resistance to alkaline decontamination reagents, fair resistance to 6 M nitric acid, and good resistance to other reagents. RTV 1473 showed unsatisfactory resistance to solutions containing greater than 0.1 M fluoride, fair resistance to solutions 0.05 to 0.1 M in fluoride and greater than 1 M in nitric acid, and good resistance to other reagents. A greater variety of normally used ICPP decontamination reagents could be used to decontaminate RTV 1473 than could be used to decontaminate the Torlon.

Figure 19. Mock-up of NWCF Sump Sampler

TABLE 23

POSSIBLE NWCF DECONTAMINATION REAGENTS

<u>Reagent</u>	<u>Reagent Composition</u>
1	5% solution of Turco 4324
2	1.5 <u>M</u> sodium hydroxide-0.15 tartaric acid
3	1.5 <u>M</u> sodium hydroxide-0.05 <u>M</u> EDTA
4	6 <u>M</u> nitric acid
5	10% solution of oxalic acid-2% solution of citric acid
6	0.4 <u>M</u> ammonium oxalate-0.16 <u>M</u> citric acid-0.34 <u>M</u> hydrogen peroxide
7	1 <u>M</u> nitric acid-6 <u>M</u> sulfuric acid
8	8% solution of Turco 4502 ^a
9	1 <u>M</u> nitric acid-0.3 <u>M</u> hydroxylamine sulfate
10	2 <u>M</u> nitric acid-0.05 <u>M</u> potassium permanganate
11	0.4 <u>M</u> oxalic acid-0.1 <u>M</u> hydrofluoric acid-0.05 <u>M</u> hydrogen peroxide
12	8 <u>M</u> nitric acid-2 <u>M</u> hydrofluoric acid
13	1 <u>M</u> sulfuric acid-0.05 <u>M</u> hydrofluoric acid

^a Trademark of Turco Products Inc.

Plans for Next Quarter

No further work on this problem is anticipated.

3. Pneumatic Transport Test Loop (D. H. Munger)

A pneumatic-transport test loop for calcined waste is being designed for 1) measuring erosion rates with different bend designs, pipe materials, solids type, and transport air velocities, 2) measuring particle attrition, and 3) evaluating the operability of transport system components-e.g., blinded-tee bends, the tall fines column, and valves. The transport loop will provide 54 m of 1-1/2 in. tubing with six replaceable bends. Mechanical design and the fabrication of major vessels are complete. The electrical and instrumentation design have started.

Plans for Next Quarter

The transport loop will be installed.

4. Dense-Phase Pneumatic Transport Tests (D. H. Munger)

Conveyability tests with simulated zirconium fluoride calcine were completed at the pilot-plant facilities of three vendors of "dense-phase" pneumatic transport systems: Dynamic Air, Ducon, and Consolidated Engineering. These three systems were selected for testing, because they represented a cross-section of available "dense-phase" pneumatic transport technology.

The test results are summarized in Table 24. The Dynamic Air system was the only system that was able to move the product by slug flow; the other two systems required stream flow (for the product) in which the solids move at a (higher) velocity sufficient to prevent deposition. As shown in Figure 20, the Dynamic Air system uses boosters along the line to break up and spread out slugs with booster air. Thus, slug length is limited to the distance between boosters. By achieving slug flow, the Dynamic Air system was able to operate with the lowest air velocity and thus have the lowest product attrition. The lower air velocity should also result in a lower wall-erosion rate. Based on the above and also the use of only one valve "wetted" with solids, the Dynamic Air system was selected for verification testing.

Plans for Next Quarter

An order will be placed for purchase of a Dynamic Air transport system for verification testing.

VII. EFFLUENT MONITORING METHODS EVALUATION AND DEVELOPMENT

1. Evaluation of In-Place Test Methods for Determining HEPA Filter Efficiencies (L. P. Murphy, R. C. Girton)

The laboratory apparatus for measuring HEPA filter efficiencies in a corrosive off-gas environment was checked out. Tests were made using

TABLE 24 COMPARISON OF PNEUMATIC TRANSPORT SYSTEMS

	Max. Press kPa	ΔP kPa	Solid-to-Air Weight Ratio	Rate, kg/h	Air Velocity, m/s @ pickup @ disch		Attrition % Reduct. MMPD/100 m	# Solids Wetted Valves	Type of Solids Flow
WCF	0	~ 9	~0.05:1	~68	16-23	16-23	not known	none	stream
DHM-4-77	0	not known	not known	not known	20	20	30	none	stream
Fuller, 100 m	0	10	0.05:1	124	20	20	12-20%	none	stream
Consolidated, 100 m									
Product	150	150	15.5:1	2536	12.5	31	8%	3	stream
Fines	200	200	16.6:1	10,145	5	12	N/A	3	extrusion
Ducon, 70 m									
Product	48	48	8.5:1	4090	19	26	not known	2	stream
Fines	35	35	7.2:1	2860	22	30	not known	2	extrusion
Dynamic Air									
Product, 30 m	140	120	10.6:1	4690	10.8	24	13%	1	slug
Product, 100 m	140	120	9.3:1	2435	6.5	14.5	6%	1	slug
Fines, 30 m w/boost	140	70	36:1	19,681	not known	not known	N/A	1	extrusion
Fines, 100 m w/o boost	140	70	22:1	14,761	11	18	N/A	1	extrusion

Figure 20. Dynamic Air Pneumatic Transport System

mixtures of oxides of nitrogen (NO_x), dioctylphthalate (DOP), and water vapor. Equipment for generating and measuring the NO_x and DOP concentrations performed satisfactorily. However, modifications were required to obtain better control of the delivery and collection of water vapor in the system. A larger pump will also be installed to provide higher flow capabilities. In-line mass flow transducers were ordered and will be used for accurate flow measurements.

Plans for Next Quarter

The combined effects of NO_x , temperature, and humidity on the DOP filter test efficiencies will be determined during the quarter. This phase of the program will be in the final stages and documentation of the experimental results started.

2. Methods Evaluation for Monitoring of Radionuclides with Low Energy Emissions (S. J. Fernandez, R. C. Girton)

The purpose of this project is to investigate and evaluate existing stack monitoring techniques for low energy semivolatiles released in the off-gas from fuel reprocessing facilities. The semivolatiles selected for study were technetium-99 ($\beta_{\text{max}} = 0.292 \text{ MeV}$) and selenium-79 ($\beta_{\text{max}} = 0.16 \text{ MeV}$). Both technetium-99 and selenium-79 have been investigated to assess the feasibility of continuous on-line monitoring. A continuous monitor for technetium-99 based on the volatility of technetium from perchloric acid was described in the last quarterly progress report. An evaluation of beta detectors indicated that on-line analysis of selenium-79 was not feasible due to insufficient detector sensitivity. Present stack concentrations for technetium-99 and selenium-79 are anticipated to be on the order of 10^{-12} Ci/cm^3 . These low stack levels require time integrated sampling followed by liquid scintillation counting for accurate analysis. Since as a time integrated sampling technique would increase the sensitivity of the technetium procedure and AgX has long been used to collect iodine-129, it was decided to develop a separation procedure to simultaneously determine selenium-79, technetium-99 and iodine-129. The most promising separation method was solvent extraction for the following reasons:

- 1) Organic solution carry over would cause minimum quenching in toluene or xylene based liquid scintillation cocktails,
- 2) Solvent extraction procedures for these nuclides have demonstrated high decontamination factors and high yields, and
- 3) The need to perform carrier-free separations (stable Se and I quench liquid scintillation pulses) virtually ruled out precipitation as a final separation step.

Therefore, modifications of three solvent extraction methods were developed into a single procedure. The technetium procedure was a modification of the tetrapropylammonium salt extraction from 3 M NaOH reported

by Foster, Maeck, and Rein.⁸ The selenium procedure was a modification of the extraction method of Byrne and Gorenc from 18 N H₂SO₄ into toluene.⁹ The iodine procedure was based on the method published by Flynn.¹⁰ Each modified procedure was tested to determine the chemical yield for tracer quantities of each nuclide. The results are shown in Table 25.

These yields are acceptable for the purpose of this procedure. A flow-sheet of the described procedure is shown in Figure 21. The chemical yields of the selenium and iodine fractions were 14 and 17%, respectively. The relative error in these yield measurements was 20%. Should yields need to be known with greater accuracy, iodine-131 and selenium-75 spikes may be used although the selenium-75 spike method suffers from the long half-life (100 d) of selenium-75. The major loss of selenium in the tandem procedure occurred in the separation of the AgCl precipitate. The zeolite was completely decomposed as evidenced by the complete dissolution of the AgCl precipitate in NH₄OH. All of the unextracted selenium was found in the NH₄OH solution. Quantitative extraction of the selenium into the toluene phase did not require the addition of iodide to form SeI₄ or SeI₆ as in the Byrne and Gorenc⁹ procedure. Apparently, SeCl₄, SeF₄ or both species were formed during the HCl-HF dissolution and thus extracted into the toluene.

TABLE 25
CHEMICAL YIELDS FOR INDIVIDUAL PROCEDURES (%)

Technetium	89
Selenium	100
Iodine	85

⁸ Foster, R. E., Maeck, W. J., and Rein, J. E., "Liquid-Liquid Extraction of Technetium as Tetrapropylammonium Salt and Spectrophotometric Determination as the Thiocyanate Complex", Anal. Chem., **39**, 563 (1967)

⁹ Byrne, A. R. and Gorenc, D., "The Toluene Extraction of Some Elements as Iodides from Sulfuric Acid-Potassium Iodide Media. Application to Neutron Activation Analysis." Anal. Chem. Acta, **59**, 81 (1972).

¹⁰ Flynn, W. W., "A Rapid Solvent Extraction Method for the Determination of Radioiodine in Seawater," Anal. Chem. Acta, **76**, 113 (1975)

Figure 21. Separation Procedure Flow Diagram.

The iodide tracer was not coadsorbed on the preformed AgCl precipitate. This may be due to the high chloride and/or fluoride concentration in the HCl-HF dissolution liquor acting as a holdback carrier. The primary iodine losses occur in the distillation step. Over 90% of the iodine that distills volatilizes under 130°C, but 50% of the iodine charged remains in the distillation bottoms. The remainder of the iodine losses are incremental losses in the various extraction procedures.

Plans for Next Quarter

The chemical yield for technetium will be determined and the suitability of the procedure will be verified on actual stack samples.

RESULTS - OTHER PROJECTS SUPPORTING ENERGY DEVELOPMENT

I. NUCLEAR MATERIALS SECURITY

A revised Schedule 189 (Iodine-142) and an Advanced Safeguards Systems Development plan were submitted to DOE for an accelerated program in response to DOE development objectives. The scope of program activities was expanded to encompass:

- . Chemical process sensor and instrument development in support of safeguards functions.
- . Isotope ratio instrument development.
- . Design, installation, and operation of a safeguards process monitoring test and evaluation system in the ICPP.

1. In-Plant Process Test and Evaluation System (F. O. Cartan, E. P. Wagner, F. L. Bentzen)

The concept being developed at ICPP uses computers to monitor process and equipment sensors and instruments, and compares them with a model of acceptable plant operation. The computer would detect deviations from "acceptable" operation and flag them for investigation of possible diversion attempts. Various commercially available process and equipment sensors are being evaluated and some are being developed at ICPP. A safeguards plant test and evaluation system will be installed in various parts of the ICPP (e.g., fuel dissolution, solvent extraction, product handling) for development and evaluation of this concept for process monitoring and evaluation of the individual sensors for their suitability in a safeguards system.

Previous sensor and instrument development studies at ACC-ICP have used the monitoring system installed at ICPP to remotely monitor the operations in a cell of the main plant from a nearby building. This safeguards support system was scheduled for upgrade this fiscal year to accommodate the addition of several more sensors.

1.1 Conceptual Design Objectives

In a limited sense, the test and evaluation system comprises part of an overall safeguards protection system. It has the capability of providing safeguards coverage over parts of the chemical processes and the capabilities to input data from other safeguards systems for test and evaluation. For this reason, the conceptual designs initiated this quarter will meet the the broader objectives for testing operational safeguards concepts. These objectives are:

1. The system should detect diversion attempts as they occur.
2. The system should generate appropriate alarms and provide monitoring groups with the needed information and backup to initiate a response.

3. The system should detect operations that would compromise materials control. Any operation, whether accidental or intentional, that prevents accurate SNM accountability should be detected.
4. The system should not interfere with the operation of the plant. If possible, it should detect any leaks, anomalous operations sequences, or equipment failures in time for correction.
5. The system should operate during all plant sequences (startup, run, equipment failure, shutdown, cleanout, or emergency evacuation). It should tolerate the normal variations in plant procedures.
6. The system should detect a failure of any sensor or component and continue to operate.
7. The system should eventually be capable of monitoring the work done to verify that plant operational procedures are followed.
8. The system should eventually provide data for on-line prediction of plant concentrations, volumes, and flows. This could lead to an on-line inventory capability of useful accuracy.

1.2 Product Loadout Area Conceptual Design

The product loadout area is crucial for safeguards coverage in a processing plant due to product purity, high concentration, and low radioactivity. Inspections of these areas and extensive reviews of plant drawings have identified candidate devices for application in ICPP for test and evaluation. Table 1 gives a summary of the class and quantity of sensors and instruments that have been tentatively identified in a detailed study of devices, functions, and placements for safeguards testing over much of the ICPP product loadout area. Surveys of current instrument and sensor technology were started to identify specific devices.

The candidate lists prepared for this and other areas of ICPP are used for forming the conceptual designs. The product loadout area conceptual design is underway. Selection of sensors and instruments for ICPP installation will depend on current studies being conducted on prototype and representative devices and plant experience and standards. (These studies are described under Section 2.0 "System Sensors Development.")

1.3 Data Acquisition System Conceptual Design

Preliminary data acquisition system requirements were established. The system will be configured as several levels of hardware application (see Figure 1). The first level will consist of process sensor and instruments at various locations within the plant process areas which will

TABLE 1
ICP PRODUCT LOADOUT AREA
CANDIDATE SENSORS SUMMARY LIST

<u>Type of Sensor</u>	<u>Number in Area</u>
1. Valve Switches	24
2. Thermocouples	4
3. Power Monitoring Relays	6
4. Vacuum Switches	8
5. Pressure Switches	12
6. Scannivalve or ΔP Transducers	14
7. Precision ΔP Transducers (level)	4
8. Precision ΔP Transducers (density)	3
9. Motion Detectors	5
10. Electronic Balance	1
11. Air Monitor, Alpha	1
12. Door I.D. Sensors	6
13. Ultrasonic Liquid-in-Line Detector	1
14. Gamma Absorptimeter	1
15. Flow Meter	1

Figure 1. Preliminary Data Acquisition System Diagram

convert equipment status and process variables to electronic signals. The second level will consist of scanners, multiplexers, and buffers which optimize and convert the sensor signals for compatibility with the data acquisition system. The third level consists of electronics necessary for control and communications between the sensor instrument and the data analysis system. In order to minimize impact on production personnel and minimize occupancy of relatively "expensive" plant cell space, most of the test and evaluation system hardware and activities are located outside plant cells. A possible scenerio for a safeguards system consists of plant monitoring from a remote location. This planned system dispersion with data link communications between facilities provides test and evaluation of this safeguards monitoring and support staff concept. System specifications are being written for the essential components of the data acquisition and communications system. These specifications are scheduled for completion next quarter to enable competitive bid procurement and initial checkout this fiscal year.

2. Sensor and Instrument Development Studies

(H. R. Deveraux, T. E. Piper, W. J. Harris)

The application of safeguards development functions at a chemical processing plant requires consideration of the latest in sensor and instrument technologies. Process instrumentation engineers with chemical process and nuclear industrial experience are surveying current technology for safeguards applications.

The candidate sensors list of Table 1 shows sensor and instrument requirements for the product loadout area. Table 2 lists the devices that have been selected for development activities this quarter.

2.1 Flowmeter Development Activities

Preliminary checkouts of a coriolis force flowmeter and a transit-time bubble flowmeter were completed this quarter. Preliminary results indicated 0.5% accuracy for each. Further testing is scheduled in the pilot-plant next quarter.

2.2 Multi-Transducer Test System

The multi-transducer equipment received from the vendors is being checked out and calibrated. When complete, this system will provide improved measurements of level and specific gravity for plant accountability tanks via the bubbler probe plant instrumentation. An intercomparison of measurement from various transducer outputs will provide an on-line indication of transducer performance. This will show in-plant performance of high precision differential pressure transducers from various manufacturers (Ruska, Mensor, Pneumatron, MKS, and Paroscientific).

2.3 Pilot Plant Test of Transit Time Flowmeter and Gamma Absorptimeter

The initial pilot-plant installation of the transit time flowmeter and gamma absorbtimeter systems, along with the associated instrumentation

TABLE 2
Sensor and Instruments Selected for Safeguards Development

<u>Sensor</u>	<u>Testing Methods</u>	<u>Use for Safeguards</u>	<u>Future Developments</u>
<u>Flow Service</u>			
Groscopic Coriolis flowmeter (Micromotion Inc.)	Being tested in flow loop at CPP with H ₂ O. Future tests with accurately determined concentrations of Uranyl Nitrate.	Accurately measure (<0.5%) the Product flow from Z-cell to denitrator.	Evaluation of electronic readout to determine density more accurately. Vendor discussions for higher precision flow rate measurement and larger diameter pipe compatibility.
Transit-time, bubble flowmeter (ultrasonic transducers)	Same as above.	Same as above.	Needs additional evaluation and application of correlation techniques for data processing.
Liquid-in-line device, non-penetrating (Envirotek) actuates on presence of liquid in a pipe. Limit of sensitivity to pipes 1/2" diameter or larger.	None, device has been ordered.	Highly desirable to determine if liquid is in a line designated for air or steam only.	An order was placed for 1/2" and 3/4" pipe diameter units.
(Controlotron useful on 1" and larger lines.)	None. Not ordered due to application in large pipes only.	Same as above.	Will consider this device for larger pipe application.
<u>Thermal Devices</u>			
Thermistors (Fenwal Electric) Large change in resistance with temperature.	None. Samples have been received.	Determine small changes in temperature ~0.10C or less resulting from movement of product or steam in a line.	Preliminary calculations indicate significant temperature changes with product flow. A heated detector, similar to a hot wire anemometer, will also be evaluated.
<u>Pressure Devices</u>			
Scanivalve (Device scans up to 64 3-15 psi signals).	The Druck pressure transducer in the scanivalve was calibrated and the unit was interfaced to a desk top HP-9825 computer.	Sixty-four signals from plant transducers can be monitored for operational sequences.	The scanivalve is scheduled for plant installation and test.

TABLE 2 (continued)
Sensor and Instruments Selected for Safeguards Development

Sensor

Pressure Devices (cont.)

Precision pressure transducers.	Several pressure transducers have been ordered for comparison testing (awaiting delivery).	Precision level and specific gravity measurements.	Individual devices have been calibrated and tested in laboratory facilities. The devices are scheduled for parallel (but selectable) installation in CPP-601 for G-cell measurements. Three each transducers are scheduled for local and specific gravity tests (6 total).
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Valve Motion Sensor

The opening of a valve is detected by use of an LVDT mounted on a S.S. valve stem with a hollow magnetic core on the stem.	The LVDT and computer readout detects the very beginning of valve opening.	Detection of unauthorized valve opening provides significant information regarding clandestine operations.	Preliminary tests have been concluded. Fabrication of a higher impedance LVDT will be considered.
Precision Transducer/Limit Switch (Magnetoelastic Devices Inc.) Similar to a microswitch with remote setting capability (.025 in range) actuation on upper and lower set points repeatable to .002 inches.	Preliminary tests indicate proper operation. Future tests to be performed with micrometer.	Provides a versatile motion detector for any device such as a valve position.	Applications for determination of precise positions associated with product transport and measurement.

Analytical Instrumentation

Gamma Absorptimeter	Pilot plant installation and checkout/testing using water and uranyl nitrate. Activities pending approval of safety procedures.	Heavy element concentration measurements for verification and measurement of uranium or plutonium solution concentrations.	Pilot plant module hook-up is continuing. Water and uranyl nitrate tests are scheduled for next quarter. Concurrent testing with the two flowmeters above is scheduled.
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and data collection system, was completed during this quarter. The test flow loop has been operated using water as the fluid, and much of the instrumentation has been exercised to check for proper operation.

The goals for this testing are to verify proper operation of the equipment and to collect test data at various environmental temperatures. The test data are to be collected while using uranyl nitrate as the working fluid in the test flow loop. Uranyl nitrate test solutions, having uranium concentration values known with high precision (0.1% accuracy), are being prepared at the ICPP.

3. Mass Spectrometer Evaluation (H. R. Deveraux, M. W. Echo)

Effective safeguarding or inspection of nuclear materials in a processing plant requires that the location and isotopic composition of the materials be capable of direct and timely measurement. Current laboratory mass spectrometers used for isotope ratio measurements are bulky, expensive, and must be located in controlled environments. Development of a cost effective, portable mass spectrometer for plant use by plant control and safeguards personnel and for inspector use by DOE, NRC, or IAEA inspectors was considered an effective method for rapid identification and analysis of materials in plants and for fast detection of attempts to conceal diversion of SNM by isotopic substitution. Independent verification is greatly enhanced with an instrument which is operated and controlled by the auditing agency. The principal competing technique for this measurement is gamma spectrometry. Compared to this alternative and complementary technique, mass spectrometry has the advantage of using a very small sample, one microgram or less, and does not require self absorption or matrix corrections or decay equilibrium corrections. The mass spectrometer responds directly to the number of atoms present rather than to their activities. The accuracy and cost are expected to be equivalent.

A quadrupole mass spectrometer and a magnetic deflection mass spectrometer are being purchased. These will be modified and tested for use as portable instruments.

4. Plans for Next Quarter

The proposed schedule for the next quarter includes:

1. Start pilot-plant testing of the gamma absorptimeter and flowmeters with uranyl nitrate.
2. Continue with conceptual and detailed designs for sensor and instrument installation in the ICPP product loadout area.
3. Start the conceptual design for installation in the ICPP dissolution areas (E-cell and G-cell).
4. Completion of the preliminary conceptual design and functional specifications for the data acquisition and processing system part of the ICPP Test Evaluation System.

II. GEOTHERMAL PROGRAMS

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

1. Results of Model Tests

Two plexiglass liquid-fluidized-bed heat exchangers were tested. The horizontal unit is a 0.9-m-diameter vessel, 0.3-m-wide with 1.9-cm-diameter plexiglass dummy heat exchanger tubes. The dummy heat exchanger tubes can be replaced by an instrumented heater rod to determine external heat transfer coefficients. Plexiglass construction allows visual observation of flow patterns.

The vertical unit is 1.2-m-high and 25.4-cm-diameter. It has 1.9-cm-diameter dummy vertical tubes which can be replaced with instrumented rods for measuring convective heat transfer coefficient.

Visual observations showed the vertical unit flow distribution to be more uniform than the horizontal unit. The vertical unit operates comparatively trouble free; the horizontal unit results in particulate piling on top of the tubes and in "dead" areas in the bed.

Results of the outside heat transfer coefficient tests are shown in Figure 2. The vertical unit with a fluidized bed has higher coefficients than the horizontal unit. This is due to more complete fluidization in the vertical unit. Heat transfer coefficients are reduced in the horizontal heat exchanger due to flow separation and bed particle piling on the top of the tubes.

Flow distribution presents a problem in the horizontal unit due to the continually changing cross-sectional area. Experiments with different distributor plates led to the conclusion that the "dead" areas created at the outer edges of the heat exchanger cannot be completely eliminated. Thus, the design shown in Figure 3, which maintains a constant cross-sectional area, is recommended. The blocked-off shell area can be used for geothermal water transport and decreases some of the external piping which would normally be required.

Development of both the vertical and horizontal units is desirable, since geometric considerations show that a horizontal unit can be made smaller and is more suited to the large flow rates expected in power plants. This is due to the narrow range of fluid velocities which must be maintained to properly fluidize the bed and maximize the heat transfer. Horizontal vessels offer more cross-sectional area for the same tube length.

2. Geothermal Dryer

A gas-fluidized-bed heat exchanger has been designed to use geothermal heat to dry industrial or agricultural products such as potato waste. The unit is similar to a calciner design, but uses geothermal water

INEL-S-9574

Figure 2. External Heat Transfer Coefficients Determined from Fluidized Bed Models

LIQUID FLUIDIZED BED HEAT EXCHANGER

Figure 3. Proposed Horizontal Fluidized-
Bed Heat Exchanger Design

passed through a tube bundle to heat the bed. The material to be dried is sprayed into the heated fluidized bed to evaporate moisture. The unit shown in Figure 4 has been designed, constructed, pressure tested, and is now being installed. The first series of tests, scheduled to begin in April, will convert waste products from potato processing to dry animal feed.

Plans for Next Quarter

1. The geothermal dryer will be installed and made operational. Tests will be conducted to determine the effect on the product of different operating conditions.
2. A report will be written on the liquid-fluidized-bed model work.
3. Production and injection geothermal water will be chemically monitored. Oxygen content, pH, conductivity, and oxidation-reduction potential will be measured.

III. IN-PLANT SOURCE-TERM MEASUREMENT PROGRAM

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

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

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

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

The measurement program at the Turkey Point Station has continued throughout the reporting period. The refueling of unit 3 was completed and the primary-to-secondary leak present prior to the refueling outage was repaired. Unit 4 developed a primary to secondary leak and is currently down for repair and safety testing.

GEOHERMAL DRYER ASSEMBLY

Figure.4. Geothermal Fluidized-Bed Dryer

Turkey Point is the first plant in which measurements have been made during periods of a primary to secondary leak. Since few data are available concerning the behavior of radionuclides in the secondary system during such periods, major emphasis was placed on the secondary system. The behavior of radioiodine has been of particular concern.

Gaseous measurements have continued in the auxiliary building ventilation system as well as grab sampling of waste gas decay tanks and containment atmosphere.

The tentative schedule for future measurements is to continue the measurements at Turkey Point until June 1, 1978. A meeting will be held early in April with the NRC to review the Turkey Point program and to make firm commitments for a future schedule.

A draft of the final report for the measurements at Fort Calhoun Station was sent to the NRC for comments prior to publication. A draft of the report on the ^3H and ^{14}C monitoring system was sent to the NRC. A report entitled "Procedures, Source Term Measurement Program" was issued as an NRC document NUREG-0384.

IV. BURNUP METHODS FOR FAST BREEDER REACTOR FUELS

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

Work has continued on the fission product analysis of the four samples (one each of ^{233}U , ^{235}U , ^{239}Pu , and ^{241}Pu) irradiated in row 2 of EBR-II by ANL in the late 1960's and received last fall from ORNL.

After dissolution and collection of the fission product gases, Kr and Xe, approximately one-half of each solution was retained for fission product analyses and the other half was evaporated and returned to ORNL for use in another program.

The data obtained from the ANL samples will supplement that obtained from the samples we irradiated in Row 8 of EBR-II. Significant differences in percent burnup (~ 10 to $\sim 12\%$ vs $\sim 1\%$) and in neutron energy spectrum (spectral index $^{238}\text{U}(n,f)/^{235}\text{U}(n,f)$ at ~ 0.06 vs ~ 0.02) for the ANL versus ACC samples will enable us (1) to identify significant capture cross sections associated with potential fast burnup monitors, and (2) to evaluate the effect of changing neutron spectra on various fission yields.

All chemical separations, mass spectrometry sample preparation, and mass analyses were completed for the uranium-235 sample, and the analysis of the uranium-233 sample is complete except for the alkaline earths and alkali metals. Data reduction for both capsules is in progress.

V. ABSOLUTE THERMAL FISSION YIELD MEASUREMENTS

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

1. Thermal Fission Yields

Preliminary data reduction, evaluation, and recalculation or modification of treatment of certain data for the six uranium-235 samples (3 at $\sim 2\%$ burnup and 3 at $\sim 40\%$ burnup) were completed. The final rigorous error analysis is in progress. Calculations of thermal fluxes, neutron spectra, and values for uranium-235 were made, based on pre and post-irradiation actinide analyses. Comparison of total element fission yields between the 2% burnup and 40% burnup samples shows excellent agreement, generally better than 1% relative.

The most significant source of error in the measurement of absolute fission yields is the value for the number of fissions. For many years, we have determined the number of fissions based on the summation technique. The basis for this technique is that the sum of the fission product atoms in the heavy mass peak is equal to the number of fissions. In this work, we measured $\sim 90\%$ of the atoms in the heavy mass peak, and estimated the remaining 10%. The propagated uncertainty in the number of fissions determined by this technique generally ranges from 0.4-0.7%, relative. This is the only technique applicable to samples which have experienced low burnup. Although the assumptions involved in the summation technique are quite basic (i.e., each fission produces one fission product atom in each peak of the mass yield curve) there has never been an extensive effort devoted to the measurement of the number of fissions on the same sample by a completely independent method. The three high burnup uranium-235 samples presented us with the opportunity to make such a comparison. In addition to obtaining the number of fissions by the summation technique, the number of fissions were also obtained by the heavy element difference technique. In this approach, the number of fissions are equal to the loss of uranium atoms during the irradiation. This requires an accurate knowledge of the initial number of uranium atoms in the irradiation capsule prior to irradiation, and an accurate measurement of the residual uranium atoms after irradiation. In addition, a knowledge of the loss of uranium-236 resulting from neutron capture to produce ^{237}Np is required. (Generally, this correction is small and can be calculated.) This method is only applicable to samples which have experienced high burnup, preferably greater than 25%, because small uncertainties in the pre and/or post uranium analyses propagate into large errors in the number of fissions determined by mass difference. The 40% burnup samples were initially fabricated such that we had an accurate knowledge of the pre-irradiation uranium content and the high burnup offered nearly the ideal case for use of the difference technique.

For the three uranium-235 high burnup samples, the average ratio of the number of fissions determined by the two techniques was 0.996 ± 0.007 (summation/difference). Initial data evaluations of the fission yields

measured on the number of fissions obtained by the summation technique show a significantly smaller random error than yields based on the number of fissions obtained by the heavy element difference technique. Although the summation technique requires more extensive measurement than the heavy element difference technique, the summation technique for establishing the number of fissions has wider applicability and seems to be more accurate.

A similar evaluation will be conducted on the high burnup ^{239}Pu samples.

2. ATR Fuel Plate Analysis

All mass spectrometric and gamma ray spectrometric analyses were completed for solutions from the 14 sample punchings from ATR fuel elements (seven each from two plates which had extended burnup). Relative composition of all isotopes of uranium, plutonium, neodymium, and cesium, and absolute concentrations per unit weight of the diluted working solution were determined using mass spectrometry. For 12 of the samples for dissolutions, only relative Kr and Xe isotopic data were obtained, while for two of the punchings, the absolute quantities of Kr and Xe were determined.

Aliquots from each solution were counted on the Ge(Li) detector gamma pulse height analyzer for these specific fission products and activation products: ^{103}Ru , ^{106}Ru , ^{134}Cs , ^{137}Cs , ^{141}Ce , ^{144}Ce , ^{154}Eu , A separate two-peak mass analysis for $^{137}\text{Cs}/^{134}\text{Cs}$ was also run on the same mass lab sample submitted for total Cs isotopes. There is an unexplained 7% bias for the $^{137}\text{Cs}/^{134}\text{Cs}$ ratio determined by the two methods. The mass spectrometric values are believed to be more accurate.

The method used to calculate the number of fissions in each punching was based on the sum of measured $^{145}\text{Nd} + ^{146}\text{Nd}$, which is preferred to the traditional method based on ^{148}Nd , because the ^{148}Nd value can be biased high as a result of significant neutron capture on ^{147}Nd at higher flux levels. To calculate atom percent fission, the post-irradiation concentrations of all actinide nuclides present plus all major heavy element capture product nuclides must be known. Of these, all except ^{237}Np and nuclides beyond ^{242}Pu (which can be disregarded because their concentration is insignificant) were measured. After obtaining precise pre-irradiation uranium isotopic values, an iterative reestimation of ^{237}Np to convergence (allowing pile cross-sections to float) was run to obtain for uranium-235 (or the equivalent "fraction of resonance flux"), thermal flux and fluence, and atom percent fission. The values of show some fluctuation, but no apparent trend with flux or burnup. Since this calculation is probably overly sensitive to small discrepancies in input data, it appears to be essentially constant for each set of punchings.

In Table 3, percent burnup, for uranium-235, and thermal neutron flux are listed for the vertical array of seven punchings from each fuel element plate. The spacing between centers of adjacent punchings was 10.16 cm. Reactor mid-plane was approximately equidistant between the first and second punching in plate X130A, and slightly below the sixth punching in plate X135A.

VI. SPECIALIZED FUEL RESEARCH - ANALYTICAL SUPPORT

(D. E. Adams, E. E. Filby, R. K. Hague, G. W. Webb)

1. Light Water Breeder Reactor (LWBR) Fuel Analyses

The preliminary report containing the analytical results for the determination of uranium (total U and isotopic composition), selected fission products, ^{232}U , and ^{54}Mn in the four remaining LWBR fuel segments was sent to NRF for transmittal to the sponsor, Bettis Atomic Power Laboratories.

The complete statistical analysis for the fifteen priority-one, and one duplex, fuel segments analyzed previously¹ is also ready to be sent. The precisions estimated for three principal measurements are shown in Table 4.

The stored samples from this set have been disposed of.

2. Other Westinghouse Fuel Work

Work has begun on the fuel analysis program for Knolls Atomic Power Laboratory samples designated as "Type I". Analyses requested include uranium concentration and isotopic content, fission products, and several others. We are checking our dissolution procedures on a number of unirradiated test segments, and further reviewing our chemistry and data processing procedures. Dissolution of irradiated samples should begin shortly.

3. Power Burst Facility (PBF) Samples

Specialized fuel analyses included both irradiated fuel samples and segments from unirradiated pellets.

3.1 Irradiated Fuel Samples

Two sets of irradiated fuel samples were submitted for analysis from PBF, both requiring the same type of measurements for burnup determination. Due to manpower and facilities limitations, and deadline restrictions, we arranged with Remote and Service Analysis Lab personnel

¹ C. M. Slansky (ed) et al, Technical Division Quarterly Progress Report, October-December 1977, Allied Chemical Corporation-Idaho Chemical Programs, ICP-1141.

TABLE 3

ATR FUEL PUNCHING SUMMARY

<u>Plate X130A</u>	<u>% Burnup</u>	<u>α ²³⁵U</u>	<u>n/cm²/s.</u>
	49.54	.213	1.46E14
	48.19	.217	1.38E14
	46.01	.218	1.27E14
	43.94	.213	1.20E14
	39.58	.211	1.03E14
	26.08	.217	5.82E13
	13.16	.216	2.65E13
 <u>Plate X135A</u>	 <u>% Burnup</u>	 <u>α ²³⁵U</u>	 <u>n/cm²/s.</u>
	19.35	.219	4.06E13
	31.27	.216	7.35E13
	41.28	.212	1.09E14
	44.73	.217	1.22E14
	48.74	.210	1.43E14
	51.05	.221	1.51E14
	49.10	.217	1.42E14

TABLE 4
PRECISION FOR LWBR MEASUREMENTS

Measurement	.95 Confidence Interval (Relative)	
	Total ^a	Random Only
U Concentration	0.53%	0.23%
U Isotopic ^b	0.07%	--
¹³⁷ Cs Activity	8.9%	0.84%

^a Includes the random and systematic contributions.

^b Major peak atom percent (intensity = 60-90%).

for them to do the initial dissolutions of the segments in the RAF. Nuclear Measurements Section personnel completed the remaining work.

The results for the two sets (one of 7 samples, the other of 8) have been sent to the requester. A bias was observed between the burnup results (fissions/g U) as derived from the ¹⁴⁴Ce analyses versus those from the ⁹⁵Zr; the ⁹⁵Zr results were consistently lower. A check of the results done previously for this program found a similar pattern. A reason for the bias has not been found, though a heterogeneous solid sampling problem is an obvious possibility. We have consulted with the sponsor on this behavior.

3.2 Unirradiated Fuel Samples

These samples were from a set of new fuel assemblies to be used in future work at PBF. The analyses were required for the program itself as well as for the determination of the "receiver's" accountability value for comparison with the shipper's value. Eight samples, consisting of essentially pure uranium dioxide, were dissolved and analyzed. To attain maximum precision on the concentration values, a modified Davis-Gray titration was used.^{2,3} For maximum performance on the isotopic results, an NBS Standard Reference Material having an isotopic composition very similar to that expected (and found) for the samples, was used to calibrate the mass spectrometer. The precisions attained (0.085% and 0.15% for concentration and uranium-235 isotopic, respectively, at the one-sigma level) appear to justify the extra effort. However, the overall cost was about 50% greater than we would expect using a regular isotope dilution mass spectrometry method.

² C. M. Slansky (ed.) et al., Technical Division Quarterly Progress Report, April 1-June 30, 1977, p 113, ICP-1123.

³ C. M. Slansky (ed.) et al., Technical Division Quarterly Progress Report, July 1-September 30, 1977, p 143, ICP-1132.

4. General Atomic Fuel Particles

As noted before,¹ this area of work encompassed some samples whose analyses had been partially completed during FY-77. The spiked and unspiked uranium analyses for some subdivisions of the original sample particles were all that remained to be done. These analyses have now been completed, the previous results have been compiled into a summary report, and the report has been sent to the sponsor.

General Atomic has requested a cost estimate and time schedule for a much larger set of similar samples. A cost estimate and the estimate of time to complete the analyses on a given subset of the samples has been sent to the requester.

VII. RESEARCH ON ANALYTICAL METHODS

1. Stack Gas Leaching Study

(R. W. Anselmo)

Pelletizing the stack gas filter in plastic vials for gamma scanning⁴ has permitted an improved process of leaching the filter prior to determining radioactive strontium and gross alpha. In the previous method, the filter was torn into small pieces and placed inside a flask. About 100 mL of concentrated nitric acid were added to the filter, the sample was shaken vigorously for about five minutes, and then filtered into a 250 mL poly bottle. The filter pieces were then transferred back to the flask and another 100 mL portion of concentrated acid was added. This was filtered into the poly bottle and diluted to 250 mL. This method was messy and had a high chance of cross contamination because the leaching and filter apparatus were reused.

In this new method, the leaching is done in the plastic vials used to gamma scan the filter. Nitric acid (15 mL) is added directly to the compressed filter.⁴ The filter is broken into very small particles during compression and forms a fine slurry when the acid is added. The slurry is shaken, then centrifuged for five minutes. The supernate is decanted into a new 50 mL disposable plastic vial. The leaching and centrifuging steps are repeated two more times and the final volume is diluted to 50 mL in the new plastic vial. This method uses less acid and eliminates the possibility of cross contamination and minimizes the possibility of exterior contamination.

In a study to determine the number of leaches required, known quantities of ⁹⁰Sr-⁹⁰Y solution were pipeted onto two 152 mm fiber glass filters, dried, and compressed into wafers inside 50 mL counting vials.

⁴ Improved Method for Gamma-scanning ICPP Daily Stack Gas Particulate Filter Samples, this report p 132.

⁵ Sample self adsorption makes it impossible to make an accurate alpha determination.

The wafers were leached three times with each leach being gross beta counted to determine recovery. From Table 5 it can be seen that three leaches are required for quantitative recovery of the ^{90}Sr - ^{90}Y .

The study was repeated with the addition of ^{240}Pu , and instead of measuring the separate leaches, all three were combined, diluted to 50 mL, and gross alpha and beta counted. The results showed that $\geq 90\%$ of the ^{240}Pu and 97.2% of the ^{90}Sr - ^{90}Y were recovered.

In 1972 the fiber glass filter was first used; previously a cellulose acetate type filter was the filter of choice. With the change in filter

TABLE 5
OPTIMUM LEACHES TO REMOVE ^{90}Sr - ^{90}Y FROM STACK GAS FILTERS^a

	<u>Known</u>	<u>First Leach</u>	<u>Second Leach</u>	<u>Third Leach</u>	<u>Total Leaches</u>
d/s/mL	480	338	84.4	14.9	487.3
% Recovery	---	80.8	17.6	3.1	101.5

^a Activity values shown are averages of duplicates.

material, it was found⁶ that the radionuclides could not be quantitatively leached from the new filter medium hence, the decision to gamma-scan the filter prior to chemical leaching with just ^{90}Sr and alpha activity being determined in the leach solution. To determine if the new leach procedure improved the recovery of gamma-emitting nuclides a stack gas filter, previously analysed in the pellet form, was taken through the new leach procedure and the combined leach solutions gamma scanned for comparison. The results are in Table 6.

TABLE 6
RECOVERY OF STACK GAS GAMMA EMITTING NUCLIDES THROUGH FILTER LEACHING

<u>Nuclide</u>	<u>% Recovery</u>
^{134}Cs	94.6
^{137}Cs	96.5
^{106}Ru	89.3
^{125}Sb	45.1

It appears that no great improvement has been made; hence, the stack gas filter will be gamma scanned prior to leaching.

⁶ Evaluation of Stack Gas Filter, A. C. Hill, C. M. Wilcox, Analytical Chemistry Branch Annual Report, Fiscal Year 1972, ICP-1017 (Oct 1972) p 32.

2. Remote Iodine-129 Separation Procedure (L. E. Trejo)

Because of a recent iodine-129 release from the calciner, it became necessary to determine the iodine-129 content of liquid waste before calcination. ICPP waste is highly radioactive with 5 mL samples reading 1-10 R/h. Thus, a remote procedure was needed to decontaminate the sample and separate the iodine-129 for counting. A column separation procedure currently in use on bench-top samples was found too cumbersome and time-consuming for remote handling. A classical CCl_4 extraction procedure was finally selected for the iodine separation. This procedure was adapted for remote handling and has been successfully employed on calciner feed solutions reading as high as 4 R/h.

The procedure is outlined as follows:

1. Ten mg of iodine carrier is added to a maximum of 15 mL of sample.
2. The iodine in the sample is first oxidized with 5 mL of a 5% solution of hypochlorite and then reduced to the extractable I_2 using 2 mL of a 1 M hydroxylamine hydrochloride solution. This oxidation-reduction ensures that the iodine carrier added in Step 1 is in the same oxidation state as the iodine-129 in the sample. The presence of Hg(II) in some samples inhibits the formation of the free iodine which is to be extracted in Step Three. In these samples, careful addition of either oxidant or reductant is needed to obtain extractable I_2 .
3. The I_2 is extracted into 10 mL of CCl_4 . The sample and extractant are mixed remotely using a magnetic stirrer. A 50 mL centrifuge tube containing a stirring bar is used as the extraction vessel. This set-up provides excellent mixing and allows the use of equipment already available.
4. The CCl_4 phase is then transferred to the warm laboratory and washed with 1N H_2SO_4 .
5. The iodine is stripped from the CCl_4 phase into a basic NaHSO_3 solution.
6. An aliquot of the strip is titrated with AgNO_3 to determine the iodine yield for the separation procedure.
7. The remaining solution is counted on a LEPS (Low Energy Photon System) using the iodine-129 X-ray peaks at 29.77 and 29.46 KeV.

This procedure has been successfully employed to analyze highly radioactive calciner feed solutions during the current calciner run with values of 10-20 d/s/mL iodine-129 being reported.

3. Counting Room Improvements: Installation of Magnetic Tape Subsystem (L. R. Hinckley)

The magnetic tape system installation was completed during the month of January 1978. This system replaces the tape cassette unit of the Data General Nova 1200 dedicated computer system used for analysis of gamma ray spectral data.

The magnetic tape system will increase the capability for long-term storage of spectral data of gamma scans. Before the installation of this system, long-term storage of data was limited to the number of computer disks available. The data from four computer disks can be stored on one magnetic tape, which is a considerable savings in storage space and cost.

An added feature of using this system is eliminating the possible loss of one to thirty day's data stored on the computer disk due to a system failure. This is accomplished by dumping all the data generated on the disk to a magnetic tape at the end of each working day.

The magnetic tape subsystem substantially improves the speed and ease of recovering data from the archive files because it is no longer necessary to shut the computer system down and load the disk that contains the desired data. This operation can now be accomplished by leaving the system up and only loading the magnetic tape that the data is stored on.

4. Improved Method For Gamma Scanning ICPP Daily Stack Gas Particulate Filter Samples

(R. W. Anselmo, L. R. Hinckley, B. R. Hunter)

Health Physics personnel daily sample the ICPP stack off-gas to measure the amount and kind of radioactive particles discharged to the environment. The sample is collected over a 24 h period onto a 152-mm-diameter fiber glass filter and submitted for analysis. The daily analyses required are a non-destructive gamma scan of the filter, and after leaching of the filter, a gross alpha and ⁹⁰Sr analysis of the leach solution.

The stack gas filter is removed from the sampler, folded once, and placed into a thin-walled plastic bag. Upon receipt of the sample in the laboratory, the plastic bag and filter were folded into a wedge shape, taped together to maintain the wedge shape and gamma scanned at a source-to-detector distance of 10-cm. The wedge shape was not ideal for good counting precision.

Because of the effectiveness of the Atmospheric Protection System (APS) and other improvements in the plant process off-gas clean up systems, the activity of the stack gas filter is now reading as low as 0.5 mR/h beta-gamma at contact. With the decrease in sample activity, a count time of 2000 s is necessary to accumulate enough counts for statistically reliable data; it was impossible to reduce the source-to-detector

distance because of the irregular shape of the sample. Hence, it was recognized that a method was needed to compact the sample uniformly which would permit a reduction in the source-to-detector distance and reduce the count time. The compacting should also improve counting accuracy by providing a more reproducible shaped sample.

This report describes the study made to accomplish the above objectives. A hand-operated hydraulic press is used to form powders into uniform size pellets prior to X-ray diffraction. This appeared to be a likely way to make a more desirable shaped sample for gamma scanning; hence, the press and accompanying dies were used in the study. It was found that the 152-mm-diameter fiber glass filter could be compressed into a 25.4-mm-diameter by 3-mm disk using 82.7 MPa (12,000 lb/in.²) pressure.

Further, to minimize cross contamination between samples the filters are compressed within a 25 mm x 100 mm, 50 mL disposable polyethylene vial set inside a specially fabricated steel cup. This permitted the sample to be compressed and gamma scanned in the same container, with only the press "ram" requiring decontamination.

The next part of the study consisted of determining the optimum source-to-detector distance at which to count the sample. The stack gas "pellet" is essentially a disk source with a potentially heterogeneous distribution of the radioactivity. The detector-sample distance must be optimized to eliminate effects of non-homogeneity and to obtain a reasonable count time. An NBS mixed gamma ray emitting point source^a was used to determine the best source-to-detector distance. The source (Sample 1, Table 7) was gamma scanned in duplicate in two horizontal positions at 3 and 5 cm source-to-detector distances. It was gamma scanned at the center of an imaginary 2.54 cm disk and then at the edge of the same imaginary disk, thus simulating the ideal point source and also the worst case, (i.e., all the radioactivity concentrated at one point at the edge of the sample). The data are summarized in Table 7. They show considerable improvement in edge vs center agreement at the 5 cm vs the 3 cm distances.

Following this, a ¹³⁷Cs NBS point source standard^b (Sample 2, Table 7) was gamma scanned in the edge position of a simulated 2.54 mm disk source at 5 cm and 10 cm source to detector distance. This shows that counting the sample at 10 cm would gain very little over counting the sample at 5 cm.

As a result of these studies the 5 cm source-to-detector distance was selected as the ideal distance. It should be noted that the counting system is calibrated for a 25.4 mm disk source at 0, 3, 5, and 10 cm. The 0 cm distance was not studied, as it would be too close to count a heterogeneous disk source sample.

^a National Bureau of Standards Source SRM-42-16-E, mixed radionuclide gamma ray point source standard.

^b National Bureau of Standards Source 4200-B, ¹³⁷Cs, ¹³⁷Ba radionuclide gamma ray point source standard.

TABLE 7

OPTIMUM SOURCE TO DETECTOR DISTANCE STUDY OF
SIMULATED PELLETIZED STACK GAS FILTER USING NBS POINT SOURCE

Sample Number	Radionuclide	Source to Detector Distance	D/S/Sample		% Difference
			Center	Edge	
1 ^a	Cd-109	3 cm	400.5	374.4	6.75
		5 cm	402.9	389.5	3.38
1	Ce-139	3 cm	304.3	288.3	5.40
		5 cm	305.0	300.0	1.65
1	Co-57	3 cm	651.9	614.2	5.95
		5 cm	678.0	643.9	5.16
1	Co-60	3 cm	4076	3933	3.56
		5 cm	4124	4021	2.53
1	Cs-137	3 cm	1815	1735	4.48
		5 cm	1816	1766	2.79
1	Hg-203	3 cm	160.7	154.4	4.00
		5 cm	154.0	158.5	2.88
1	Sn-113	3 cm	1178	1131	4.07
		5 cm	1155	1136	1.66
1	Sr-85	3 cm	553.5	538.2	2.80
		5 cm	565.9	554.1	2.11
1	Y-99	3 cm	3952	3819	3.42
		5 cm	3982	3873	2.77
2	Cs-137	5 cm	1.021E5	.9944E5	2.64
		10 cm	1.021E5	1.004E5	1.68

^aAll values shown are averages of duplicates.

TABLE 8

COMPARISON OF KNOWN STANDARD AGAINST TWO
LABORATORY CREATED STACK GAS FILTER PELLETS

<u>Radionuclides</u>	<u>D/S/Sample¹ at 5 cm</u>		
	<u>Known</u>	<u>Pellet Number 1</u>	<u>Pellet Number 2</u>
Cs-134	1.067E2 <u>+4.077E0</u>	1.110E2 <u>+4.941E0</u>	1.077E2 <u>+4.982E0</u>
Cs-137	2.144E3 <u>+1.640E1</u>	2.137E3 <u>+1.995E1</u>	2.117E3 <u>+1.989E1</u>
Ru-106	5.799E2 <u>+2.171E1</u>	5.609E2 <u>+2.609E1</u>	5.687E2 <u>+3.060E1</u>

¹The error shown is associated only with counting statistics and is at the 1 σ level.

The final portion of the study consisted of analyzing two synthetic stack gas particulate samples by the new method. Table 8 shows the results with good agreement between the known value and the determined values.

As a result of this study, stack gas particulate filters are being pel-
letized and gamma scanned at the 5 cm distance. The count time will
remain 2000 s to provide optimum counting statistics.

A spin-off to this study was the discovery that the stack gas filter
could be easily leached within the counting vial, resulting in an im-
provement in that portion of the stack gas particulate filter analyses.
This work is described on page 103 of this report.

5. Analysis Of Glassified Calciner Material For Fluoride

(D. R. Trammell)

Samples of cold glassified calcine material were analyzed for fluoride
to determine the applicability of our fluoride methods to this type of
material. The calcine is glassified by mixing with a "glass" matrix and
fusing at 1100°C. The composition of the matrix is given in Table 9.
The matrix is mixed with the calcine at a ratio of 2:1 before fusing.

Three methods were investigated for the fluoride analysis: 1) Method
F-Vol-1 which uses a pyrohydrolysis separation followed by precipitation
of the fluoride with an excess of cerium and titration of the excess
cerium with EDTA, 2) a modified F-Pot-1 procedure.³ In this procedure
the solid is fused with sodium hydroxide, the melt is leached with 1 M
citrate, 2 M chloride, and 0.1 M TEA, and the fluoride is measured po-
tentiometrically with a specific ion electrode, and 3) method F-Color-1
which uses a micro distillation from phosphoric acid followed by a spec-
trophotometric measurement of fluoride using lanthanum alizarin complex
one. Three samples were analyzed by these methods and the results are
summarized in Table 10. The dissolved melt from the F-Pot-1 method was
also analyzed by method F-Color-1 and these data are also presented in
Table 10.

These data show good agreement between methods F-Pot-1 and F-Color-1
with the exception of sample GF-61. Method F-Vol-1 gives considerably
lower results. The actual composition of fluoride in the three samples
is not known, but based on the analysis of the calcine prior to the
glassification, the fluoride should be about 7 percent.

The study shows that the modified F-Pot-1 procedure for fluoride can be
used for the determination of fluoride in glassified calcine. Only
"cold" material was used and the manipulations involved may prohibit its
use on "hot" samples.

³ Technical Division Quarterly Progress Report, July 1-September 30,
1977, ICPP-1132, p 141.

TABLE 9
COMPOSITION OF GLASS MATRIX (%)

	GF-61	GF-76	GF-75
SiO ₂	58	50	50
Na ₂ O	24	24	24
B ₂ O ₃	14	14	14
Li ₂ O	--	2	2
P ₂ O ₅	--	2	2
CuO	2	2	6
ZnO	2	6	2

TABLE 10
COMPARISON OF FLUORIDE RESULTS OBTAINED
BY DIFFERENT METHODS

Method	Results, %		
	GF-61	GF-75	GF-76
F-Vol-1	3.31 $\pm$.11	3.62 $\pm$.11	4.26 $\pm$.12 3.37 $\pm$.25
F-Pot-1	7.28 $\pm$.3 7.12 $\pm$.3	7.56 $\pm$.3 7.19 $\pm$.3	7.52 $\pm$.3
F-Color-1 (liquid) ^a	7.9 $\pm$.4	7.2 $\pm$.4	7.4 $\pm$.4
F-Color-1	5.9 $\pm$.7 5.1 $\pm$.6	6.8 $\pm$.2 7.0 $\pm$.6	7.9 $\pm$.5 7.1 $\pm$.7

^a The dissolved melt from the fusion in method F-Pot-1 were analyzed by method F-Color-1.

6. Gas Chromatographic Determination of Residual Monomers Acrylonitrile and Ethyl Acrylate in Insulation Adhesive

(R. P. Lash)

A method was developed for the determination of the residual monomers acrylonitrile and ethyl acrylate in insulation adhesive in support of the EG&G Industrial Hygiene Program. It is necessary to know the residual amounts of these volatile monomers in the adhesive so that air quality can be maintained during its spray application.

Bollini et al.⁷ reported a gas chromatographic analysis of a variety of residual monomers including acrylonitrile and ethyl acrylate using a column packed with 10% OS-138 (6-ring polyphenylether) on 80-100 mesh Chromosorb W. Calibration of their method was performed by the absolute calibration procedure in which exact amounts of pure sample are injected into the chromatograph and the peak areas or heights are then plotted against the known amount injected.

The 6-ring polyphenylether stationary phase described above was not readily available for our use. Therefore a 6 ft x 1/8 in. stainless steel column was packed with 10% Polysev (7-ring polyphenylether) on 80-100 mesh Chromosorb W. However, this packing material would not resolve the acrylonitrile and ethyl acrylate peaks. Another column packing material which is suited for this type of separation is the porous polymer, Chromosorb 104. A 5 ft x 1/8 in. stainless steel column was packed with this material and conditioned in the chromatograph overnight with helium flowing through the column. Standard samples of acrylonitrile and ethyl acrylate were injected into the chromatograph and initial resolution of the two peaks was poor. However, after several adjustments of column temperature and carrier gas flow rate, satisfactory resolution was obtained.

The final chromatographic conditions were:

Temperatures, °C	
Column	- 165
Injector	- 175
Detector	- 175
Flow Rates, mL/min	
Helium	- 20
Hydrogen	- 20
Air	- 350
Detector	- Hydrogen Flame Ionization
Range	- 1×10^{-12} Ampere full scale
Attenuation	- 1X for acrylonitrile 8X for ethyl acrylate

⁷ M. Bollini et al., "Determination of Free Monomers in Aqueous Emulsions of Synthetic Polymers and Copolymers", *Textilia* 51, No.3, 25-28 (1975).

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

1. Be well resolved from other peaks.
2. Elute close to the acrylonitrile and ethyl acrylate peaks.
3. Approximate the concentration of acrylonitrile and ethyl acrylate.
4. Be structurally similar to acrylonitrile and ethyl acrylate.
5. Must not react with acrylonitrile or ethyl acrylate.

It was readily apparent that requirements 3 and 4 could not be closely met by a single component because the concentration of ethyl acrylate in the sample is approximately 25 times greater than that of the acrylonitrile and the structure of these two monomers is not similar. A number of compounds were investigated as possible internal standards. Acetone was well separated from both ethyl acrylate and acrylonitrile. However, it was not separated at all from one of the unidentified adhesive components. Pentanol was found to satisfy requirements 1 and 2. To test the behavior of pentanol as an internal standard, a solution containing acrylonitrile, ethyl acrylate, and pentanol was prepared and injected into the chromatograph twice over a period of 1 h. Relative response factors were calculated from each of the chromatograms according to equation (1).

(1)

$$RR_x = \frac{H_x C_s}{H_s C_x}$$

where RR_x = Relative response of ethyl acrylate or acrylonitrile to that of n-pentanol

H_x, H_s = Peak heights of ethyl acrylate or acrylonitrile and n-pentanol, respectively

C_x, C_s = Concentrations of ethyl acrylate or acrylonitrile and n-pentanol respectively

The two factors for each monomer agreed within 2% indicating that requirement 5 was also met by the n-pentanol.

The adhesive sample was analyzed by adding a known amount of n-pentanol to a known quantity of the adhesive and injecting the solution into the chromatograph under the above conditions. A typical chromatogram is shown in Figure 5. Results calculated using equation (1) to solve for C_s showed that the adhesive contained 53 parts per million acrylonitrile and 1300 parts per million ethyl acrylate.

Figure 5. Gas Chromatogram of Acrylonitrile and Ethylacrylate in Insulation Adhesive.

Sensitivity: 1×10^{-12} Ampere Full Scale
Attenuation: 1X for Acrylonitrile
8X for Ethylacrylate and n-Pentanol

7. Calculator Sample Bracketing Program for Flame Spectrometry

(C. J. Hill, D. A. Pavlica, V. R. Olson)

In order to reduce the calculation time and increase the accuracy attainable in routine analyses by flame spectrometry, a sample bracketing program has been developed for the Hewlett Packard 9830A calculator. This program was developed for use with a Varian Model AA-5 flame spectrometer when operating in either the flame emission or absorbance mode, and may be used with any similar instrument with the proper interfacing. The data collection system consists of a Hewlett Packard 3437A System Voltmeter interfaced to the AA-5 and to a Hewlett Packard 9830A calculator, with a printer and plotter to complete the system.

Sample bracketing, a useful technique for determining the concentration of a substance in a sample, is based upon the assumption that an unknown concentration can be determined by measuring a specific property of the substance along with a high and a low standard of the substance. Excellent results can be obtained in the analysis of samples by this technique if the concentrations of the high and low standards are sufficiently close so that the calibration curve approximates linearity over this range and if the concentration of the sample lies between the standards.

The sample bracketing program for flame spectrometry reduces errors resulting from baseline drift since the high standard, low standard, and sample are scanned within 60 seconds of each other. All data are acquired and reduced by the calculator-controlled system. The program allows the analyst the option of scanning a 5-point calibration curve at the beginning of a series of analyses. This calibration curve provides the following valuable information: (1) it verifies the integrity of the standards employed, and (2) it shows whether the curve is linear, non-linear, or a combination of linear and non-linear over the calibration range. If the calibration curve is linear, or if the analyst is working in the linear region of a calibration curve, the concentrations of the high and low standards used in sample bracketing do not have to be close to that of the sample. However, if the calibration curve is nonlinear the concentration of the standards used in sample bracketing must be close to that of the sample so that the response is linear over the narrow calibration range. The program contains other optional features which free the operator from keying in repetitive information, such as the concentrations of frequently used standards. Standard curve plots, readings (%T or absorbance), and resulting concentration calculations for the samples are produced on hardcopy.

8. Analysis of Cutting Oil Samples Using an ICAP-VIDICON System

(R. W. Stone and R. A. Smith)

Cutting oil samples are received periodically for quality control analyses. The required analyses are for traces of arsenic, antimony, bismuth, cadmium, lead, magnesium, mercury, tin, and zinc. In order to

lower analysis costs and shorten the turnaround time, an induction coupled argon plasma-vidicon (ICAP-V) system was investigated as a means of analyzing these samples. The basic advantage of the vidicon system is that it combines the multi-element property of the photographic plate with the on-line property of individual photoelectric detectors, resulting in an immediate display of a spectrum on the screen of a monitor for visual inspection and intensity measurements.

Prior to the ICAP-V investigation, concentrations for eight of nine requested elements were determined by a conventional emission spectrographic method which required 2 d of sample preparation to remove a matrix interference. The remaining element was determined by atomic absorption spectrometry.

The spectrometer system displays 130Å of spectral information on the vidicon tube. Investigation of emission line intensities in the 2770Å to 2900Å wave length region revealed that line intensities of six elements were sufficient for the required analyses. This allowed the simultaneous determination of the concentrations of arsenic, antimony, bismuth, lead, magnesium, and tin in the oil samples. The remaining three elements, cadmium, mercury, and zinc, were determined with the ICAP-V system in a single element mode. The only sample preparation required was a 2.5:1 dilution of the cutting oil sample with distilled water. Regular aqueous standard solutions could be used for calibration and addition of known amounts of element to the cutting oil dilutions showed that there was no matrix interference for any of the nine elements. One oil sample gave a relatively high background emission. However, the space-resolving property of the vidicon permitted simultaneous access to a large number of adjacent wavelength positions and background corrections could be made easily.

Analysis time, including all time required for development and calibration, was approximately the same as required for the previous method. However, this time will be shortened considerably, from 2-1/2 d to less than 4 h, for subsequent samples submitted for analysis.

9. New Counting Equipment: Alpha Pulse Height Spectrometer and Low Energy Photon Spectrometer (LEPS)

(I. L. Doggett, B. R. Hunter, D. A. O'Lehy)

Two new counting systems were recently received which will provide improved capabilities in both alpha counting and identification with surface barrier detectors and in low energy photon counting and identification with a hyperpure germanium detector.

Eventually the LEPS will become part of a gamma ray spectrometry system with dedicated computer, but for the present the two systems have been assembled to share the same multi-channel analyzer (MCA) and hard-copy data output devices consisting of an X-Y plotter for spectra recording and a teletype for printing integrated spectral data.

The alpha pulse height system is a four-unit counting chamber for use with surface barrier detectors. The design of the chamber is that of R. P. Larson and R. F. Selman⁸ which permits planchet positioning at a high and reproducible geometry. When this system becomes operational, it will be used for alpha pulse height counting of such samples at ICPP and INEL Burial Ground contaminated soils.

The LEPS system will be used for measuring iodine-129 in ICPP waste streams, ⁵⁵Fe in Westinghouse NRF Expanded Core Facility corrosion samples, and ²⁴¹Am in ICPP and INEL Burial Ground soil and waste samples.

VIII. ENVIRONMENTAL IODINE SPECIES BEHAVIOR

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

The purpose of the Environmental Iodine Species Behavior Program is to:

- 1) collect data for evaluating the potential dose to an organ through the air-grass-milk portion of the food chain,
- 2) collect data for evaluating the dispersion models currently used by the NRC.

In the present models, the meteorological data are used to calculate χ/Q values. Therefore, for a given source term (Q), the corresponding environmental concentrations (χ) can be calculated. The calculated concentrations are then used to evaluate the potential organ dose.

In the Quad Cities study, source term, environmental (air-grass-milk), and meteorological measurements were made. In addition, ¹³³Xe samples were taken at both the source term and in the environment. The ¹³³Xe measurements were made to obtain empirical χ/Q values in an attempt to verify and/or modify the existing dispersion models.

The analysis of all samples from field measurements at the Quad Cities Nuclear Station is complete. Data reduction and interpretation of these results is in progress. The meteorological data are being processed by INEL-NOAA personnel. These data will be used to calculate χ/Q values from the NRC predictive model. As mentioned before, the predicted values will be compared to the measured χ/Q values obtained from the ¹³³Xe data.

⁸ R. P. Larson, R. F. Selman, Radionanal. Letters 30(4)247, (1977)

REPORTS AND PUBLICATIONS ISSUED DURING THE QUARTER

1. IDAHO CHEMICAL PROGRAMS REPORTS

1. T. R. Thomas and D. H. Munger, An Evaluation of NO_x Abatement by NH₃ over Hydrogen Mordenite for Nuclear Fuel Reprocessing Plants, ICP-1133, (January 1978).
2. C. M. Slansky (ed.) et al., Technical Division Quarterly Progress Report for October 1-December 31, 1977, ICP-1141, (February 1978).
3. K. M. Lamb, Development of a Metal Matrix for Incorporating High-Level Commercial Waste, ICP-1144.

2. PAPERS PRESENTED AT TECHNICAL SOCIETY MEETINGS

1. J. M. Baldwin and C. M. Young, "Decomposition and Atomization of Cobalt Species in the Carbon Rod Atomizer", 4th National Meeting, Federation of Analytical Chemistry and Spectroscopy Societies, Detroit, November 7-11, 1977.
2. G. J. Curtis, R. L. Hand, and N. R. Zack, "An Improved Preparation of a Uranium Spike for Mass Spectrometry", American Chemical Society, 175th National Meeting, Anaheim, California, March 12-17, 1978.
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3. PUBLICATIONS IN JOURNALS

1. C. M. Young and J. M. Baldwin, "Determination of Nanogram Quantities of Cobalt in Complex Matrices by Flameless Atomic Absorption Spectrometry", Microchemical Journal 22, 489-497 (1977).
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