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IDAHO CHEMICAL PROGRAMS ANNUAL TECHNICAL REPORT FISCAL YEAR 1974

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ALLIED CHEMICAL CORPORATION
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IDAHO CHEMICAL PROGRAMS ANNUAL TECHNICAL REPORT

FISCAL YEAR 1974

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IDAHO CHEMICAL PROGRAMS -- OPERATIONS OFFICE

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ABSTRACT

The operating experience in fuel processing, waste calcining, and other waste management activities at the ICPP for FY 1974 is summarized. A new zirconium fuel dissolver has performed well, and the first-cycle extraction system shows near-zero losses. Approximately 390,000 gallons of high-level wastes were calcined during the period. Technical support activities in the areas of current and proposed operations at the ICPP are also presented. These include: a flowsheet to reduce acid consumption and volume of liquid wastes in the electrolytic process; a new dissolution process for ternary oxide PWR fuel using zirconium-fluoride-nitric acid solvent; a study and recommendation for treatment of fuel storage basin water; progress in design and development of processes for Rover and HTGR fuels, including successful pilot-plant demonstration of burning, fissile- and fertile-particle separation, and particle crushing for the HTGR fuel; corrosion evaluation of bins containing calcined wastes showing corrosion rates indicative of a safe 500-year or greater storage life; demonstration on a pilot-plant scale of conditions for calcination of stainless steel and Rover fuel wastes as well as commercial wastes; evaluation of equipment alternatives for a new waste calcining facility; studies related to improvements in rare gas recovery and process-off-gas treatment; demonstration of stability, or lack of it, when various high-level waste solutions are mixed; a detailed discussion of progress on postcalcination treatment of calcined waste solids (ceramic formation, incorporation in metals, and calcine-concretes); studies on removal of actinides from ICPP wastes; a conceptual design for a proposed radioactive solid-waste repackaging facility for the INEL. Significant progress is reported on the program for determination of burnup for fast breeder reactor fuels; fast fission yield measurements are reported for ^{233}U , ^{235}U , and ^{238}U , and initial development of a system for correlation of fission yields with neutron energy is reported.

SUMMARY

During a three-month fuel processing campaign, a new zirconium fuel dissolver was used for the first time. In general, this replacement dissolver of a modified design has performed well, giving higher fuel dissolution rates than the old dissolver. However, the operating rate for the system was low because of apparent restrictions in ability to remove dissolver product as fast as it can be generated. The first-cycle extraction system has functioned very well with the modifications reported last year, and aqueous raffinate streams repeatedly contain less uranium than detectable by laboratory analyses. The operating crew has been expanded so that the fuel processing facilities and the waste calcining facility can be operated simultaneously.

In fuel processing support studies, mathematical calculations using laboratory data and theoretical considerations have resulted in equations useful in extraction-column criticality evaluation and prediction of uranium-TBP (tributyl phosphate) distributions. A new flowsheet, in which half of the extraction column raffinate is recycled to the feed stream, will significantly reduce acid consumption and the volume of liquid wastes accumulated in the processing of electrolytic dissolver product. A new dissolution process for PWR (pressurized water reactor) ternary oxide fuel has been demonstrated on a laboratory scale; the boiling zirconium dissolver product resulting from dissolution of the Zircaloy cladding with hydrofluoric acid can serve as a solvent for the sintered fuel wafers when low levels (0.1 to 0.5 M) of nitric acid are added. Preliminary plans for decontamination procedures and a proposed decontamination facility at the ICPP (Idaho Chemical Processing Plant) are described.

Quantitative results of corrosion inspections of certain fuel-processing, waste-storage, and fuel-storage installations are reported. Monitoring of corrosion specimens from the interim liquid-waste storage tanks showed corrosion rates of 0.0001 to 0.09 mil/yr after up to 19 years of use, depending on the type of raffinate stored in the tanks. Reference is made to two reports recently completed, covering literature searches and laboratory data on corrosion of stainless steel and high-nickel alloys in fuel reprocessing environments. Detailed data are given on the effects of decontamination solutions on stainless steels.

Problems involved in maintaining satisfactory conditions in the fuel storage basin water from the standpoint of corrosivity, control of microorganisms, and limitation of radioactivity are explored. Chlorine used to control growth of microorganisms in the closed-cycle system (no discharge or bleed-off of basin water is permitted) can lead to corrosive conditions when reduced to chloride. Ion-exchange columns and filters used to remove radioactively-contaminated sediments and suspended matter become incubators for microorganisms. A revised, integrated system for basin water control is proposed; this includes ion exchange, filtration, chemical adjustment, and ozonization. Sludge will be vacuumed from the fuel storage basin floor and transferred to a shielded tank; when leached with nitric acid, 99% of the uranium content and 50% of the remaining solids can be dissolved for recovery or other disposition. Radiation exposure from the "bathtub ring" around the basin walls can be minimized by cleaning the walls with a vacu-blast technique and applying a Fiber-glaze epoxy coating which can be easily decontaminated.

In the graphite fuels program, Title II design of the Rover Fuels Processing Facility was completed, and construction of the facility is under way. Laboratory and pilot-plant studies were made in support of the Title II design and to verify operability of the annular dissolver and related equipment. Solids-liquid contact, sparge nozzle design, and transport of dissolver effluent are reported in detail. For the HTGR (High-Temperature Gas-Cooled Reactor) Fuel Reprocessing Prototype Facility, conceptual design documentation has been prepared; and work has continued throughout the year on system design descriptions and equipment specifications. Supporting laboratory and pilot-plant work reported in detail include: (a) a conceptual flowsheet for processing 12 Ft. St. Vrain fuel blocks per day, (b) primary burner studies in a 4-inch-diameter fluidized-bed burner, demonstrating the desirability of using external filters and a CO/O₂ torch for burner startup, (c) demonstration of effective separation of fissile and fertile particles by air classification, and (d) comparison of methods for grinding or crushing the fuel particles.

The Waste Calcining Facility (WCF) processed approximately 390,000 gallons of zirconium, aluminum, and stainless steel wastes during the year, for an onstream factor of 64% at an average gross feed rate of 2,720 gallons per day. Downtime was primarily due to failures of bellows seals on valves and plugging in the off-gas system. Potentially improved decontamination techniques are identified, and HEPA filter sealants for use in WCF off-gas service are evaluated.

Supporting studies for WCF operation include a laboratory investigation of problems associated with coatings used on calcium nitrate (used as a fluoride complexer) to prevent agglomeration; calcium nitrate without a coating should be obtained if possible. Ruthenium contamination of the WCF equipment is a problem because of the difficulty of removal; a mechanism has been proposed to explain this contamination problem and is being explored. In addition, possible adsorbents for the volatile ruthenium were studied; and preliminary results are presented. Stability studies of various calcines at elevated temperatures reveal maximum storage temperatures which should not be exceeded if the calcine is to remain in a nonagglomerated, easily retrievable form. Corrosion evaluation of test specimens removed from the calcine storage bins reveals very low rates of corrosion, well under the allowance for 500-year storage in the present bins.

Exploratory tests on a number of wastes to be calcined in the future are discussed. A flowsheet for fluidized-bed calcination of stainless steel sulfate wastes has been demonstrated on a plant scale, and scoping runs in a pilot-plant calciner indicate favorable conditions for calcination of stainless steel electrolytic wastes. Other pilot-plant studies indicate that second-cycle wastes blended with zirconium-fluoride waste can be calcined under suitable conditions, as can Rover wastes blended with zirconium wastes.

Pilot-plant tests indicated the feasibility of fluidized-bed calcination of low-sodium, simulated commercial wastes. High-sodium commercial wastes were not calcinable under the same conditions because of agglomeration caused by the sodium compounds; however, differential thermal analysis results and preliminary pilot-plant tests indicate that these wastes may be calcinable with certain additives. Design criteria are summarized for a

fluidized-bed calciner for these commercial wastes. A program to determine suitable conditions for the fluidized-bed calcination of Purex wastes has not yet yielded a successful flowsheet.

Studies are reported on several aspects of a proposed New Waste Calcining Facility (NWCF) including: (a) configuration of the calciner vessel, (b) process heating alternatives, (c) evaluation of cyclones and alternate dry-fines collection systems, (d) evaluation of wet-scrubbing systems, and (e) evaluation of the feasibility of leaching radioactive material from off-gas filters before disposal. In addition, the impact of calcining high-heat-generating HTGR waste in the NWCF is explored; such wastes must be calcined in a limited-size calciner or as a blend with colder wastes.

Rare Gas Plant developments reported include: (a) tests for activity of the catalyst used to decompose nitrous oxide, (b) possible use of a hydrogen recombiner to permit recovery of krypton from hydrogen-rich zirconium fuel off-gas, (c) methods for decomposition of ozone which can be a hazard when concentrated with recovered krypton, and (d) methods for storage of fission-product noble gas to mitigate release hazards and accumulation in the atmosphere. Other process-off-gas studies have demonstrated conditions for catalytic reduction of 99% of the NO_x in simulated waste-calciner off-gas. Monitoring evaluations and measurements of ICPP gaseous effluents are reported.

Stability tests conducted on a number of possible blends of ICPP first-cycle zirconium waste with other wastes produced in smaller amounts indicate that (a) stainless steel sulfate wastes can be blended, (b) second-cycle aluminum wastes can be blended, (c) Rover wastes cannot be blended, and (d) second-cycle zirconium wastes cannot be blended without forming undesirable precipitates in the interim storage tanks.

In other waste management areas, construction of an Atmospheric Protection System (APS) at the ICPP to minimize the release of radioactive particulates to the atmosphere is in progress and is scheduled for completion early in FY 1976. A solar evaporation pond is being considered to eliminate discharge of nonradioactive chemical wastes to a disposal well.

A detailed discussion is presented of studies on the postcalcination treatment of nuclear fuel wastes to produce stable, inert products suitable for long-term storage. Subjects covered include ceramic formation, incorporation in metals, and formation of calcine-concretes. Progress on the removal of actinides from ICPP wastes to produce "alpha-free" calcine is also explored in detail. While solvent extraction, ion exchange, and coprecipitation all offer possibilities, only solvent extraction is reported here; potentially useful compounds are DBBP and DHDECMP. The conceptual design for a proposed radioactive solid-waste repackaging facility for the INEL (Idaho National Engineering Laboratory) is discussed briefly. It is proposed that boxes and drums buried at the INEL be exhumed, monitored, opened, sorted, treated, repackaged, and finally stored in new facilities for easy future removal.

Other significant work reported includes progress on the determination of burnup for fast breeder reactor fuels. Specific accomplishments include: (a) completion of fission product measurements on a sample of ^{235}U irradiated by ANL-Chicago in EBR-II for fast fission yield measurements, (b) the first comprehensive measurement of ^{233}U fast fission yields, (c) the measurement of ^{238}U fast fission yields, and (d) the initial development of a system for the correlation of fission yields with neutron energy.

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I. FUEL REPROCESSING

1. OPERATING EXPERIENCE WITH ICPP FUEL RECOVERY PROCESSES

1.1 1974 Zirconium and Coprocessing Campaign (R.D. Denney, G.F. Offutt, C.L. Bendixsen)

The third zirconium and coprocessing campaign began in February 1974 and lasted until early May when an operators' union strike forced a shutdown of fuel reprocessing. Zirconium fuel only was processed for the first two months, and coprocessing of aluminum and zirconium fuels began in mid-April when the Rare Gas Plant was started up to recover fission-product xenon and krypton from the off-gases of the aluminum fuel dissolver. Chemical material balances and schematic equipment flowsheets for the fuel reprocessing operations have been published earlier^[1].

In the coprocessing system, zirconium fuel is charged batchwise to a Monel dissolver, averaging 670 kg of zirconium per batch and dissolved with a continuous flow of 6.8 M hydrofluoric acid. Aluminum fuel is charged batchwise to a charging cave where the fuel is periodically added to the aluminum dissolver (constructed of stainless steel) for continuous dissolution with 6.4 M nitric acid. The zirconium dissolver product is complexed with the aluminum dissolver product to (a) provide for long-term solution stability, (b) provide excess nitrate ion for salting the $\text{UO}_2(\text{NO}_3)_2$ into the organic phase in the extraction column, and (c) complex excess fluoride to prevent corrosion of stainless steel extraction equipment. During reprocessing of zirconium fuel alone, cold aluminum nitrate must be added to complex the zirconium dissolver product. The complexed solution is centrifuged to remove any solids and is contacted with tributyl phosphate with a normal paraffin hydrocarbon (NPH) diluent in the first-cycle extraction system. First-cycle extraction system product is concentrated and sent to intercycle storage. When intercycle storage is near capacity, the concentrated product is sent through second- and third-cycle extraction steps and to the fluid-bed denitrator which converts the uranyl nitrate to a granular uranium oxide. The uranium then is packaged and shipped.

During this campaign, a replacement^[2] dissolver vessel for zirconium-uranium fuels was operated for the first time. A schematic of the replacement dissolver is shown in Figure 1. In general, this dissolver has performed well with respect to dissolution, giving a higher reaction rate than with the previous dissolver vessel. An exact measure of the increased dissolution rate has not been possible due to apparent flow restrictions in removing product from the dissolver. The flow restrictions are most likely caused by excessive foam formation during the rapid dissolution rates, followed by foam entering the product overflow lines and restricting the airlifts. A possible alternate cause of flow restrictions could be formation and settling of solids (ZrF_4) in the product airlifts. The overall effect of these difficulties was to give a lower fuel processing rate than previously achieved.

Fig. 1 Replacement zirconium fuel dissolver.

The aluminum fuel dissolution system performed satisfactorily without any significant problems. The first-cycle extraction system functioned very well throughout the campaign. Aqueous raffinate streams repeatedly contained less uranium than detectable by laboratory analysis. Process upsets were very infrequent and of minor extent.

1.2 Custom Processing of Miscellaneous Fuel Materials (M.E. Jacobsen, L.C. Lewis)

Custom processing of fuel-containing materials continued during FY-74 using laboratory equipment in the Multicurie Cell. Approximately ten kilograms of ^{235}U was recovered from materials unsuitable for recovery in any existing plant process. These included the Gulf General Atomics Thermionic reactor fuel, and glass scrap from fuel fabrication operations at Argonne National Laboratory (ANL).

1.3 Training of New Operating Personnel (L.G. Pearson)

To conduct simultaneous operation of the waste calcining and fuel processing facilities, it was necessary to increase the size of the ICPP operating crews. Approximately 15 additional process operator helpers were hired early in FY 1974 for this crew expansion. These helpers were obtained from the labor pool and outside sources and had no previous experience in a nuclear fuel reprocessing plant. A comprehensive training program was initiated to train the new helpers to perform and understand various plant operations in a minimum time. Training consisted of the following steps:

- (1) Three weeks of classroom instruction
- (2) Three weeks of supervised shift assignments
- (3) Two weeks of classroom instruction
- (4) Three weeks of supervised shift assignments
- (5) One week of classroom instruction
- (6) Assignment to an operating crew.

Classroom instruction consisted of lectures, discussions, tours, and demonstrations of plant processes. Assignment to shift work, under the direction of an experienced operator, enabled the helpers to perform operations discussed in the classroom and previously demonstrated. Following regular shift assignment, training continued with on-the-job check lists. The training program has proven to be very effective with satisfactory progress being demonstrated by the new helpers.

2. SUPPORT STUDIES FOR ICPP FUEL RECOVERY PROCESSES

2.1 Extraction Column Criticality Calculations (C.L. Bendixsen)

In conjunction with developing the safety limits and requirements for the FY 1974 coprocessing campaign for zirconium and aluminum fuels, an improved mathematical model was developed for calculating the criticality safety of the extraction column in the first-cycle extraction system. Using the improved mathematical model, calculations showed that the frequency, at which the organic extractant (IAX) rate must be checked to assure safety, could be halved from the frequency previously used.

With a nominal coprocessing flowsheet, the critical portion of the first-cycle extraction column is the upper cylindrical head, shown in Figure 2. Based on assumptions describing the worst credible accident, i.e., those conditions that could achieve critical conditions in the shortest time, the ^{235}U concentration in the variable-depth organic layer will increase according to the following time-dependent differential equation:

$$\frac{V_o}{d\theta} \frac{dU_{\text{IAF}}}{d\theta} = F_{\text{IAF}} (U_{\text{IAF}} - U_R) \quad (1)$$

where:

- F_{IAF} = Aqueous flow rate, 110% of nominal, 480 ℓ/hr
- U_{IAF} = ^{235}U concentration in aqueous feed, 93.5% of 3.3 g/ ℓ
- U_{IAP} = ^{235}U concentration in organic layer, g/ ℓ
- U_R = ^{235}U concentration in aqueous raffinate, g/ ℓ
- V_o = Volume of organic layer, $\pi r^2 h = 7.41$ h liters
- h = Height of organic layer, inches
- θ = Time period since organic flow halted, hours.

In previous criticality safety analyses, an assumption was made that uranium transfer to the organic layer was total, i.e., that the uranium concentration in the aqueous raffinate (U_R) was zero. With that assumption, Equation (1) reduced to a straight-line function with respect to time.

The straight-line function is ultraconservative since, in theory and in practice, the uranium concentration of the aqueous phase will decrease to an equilibrium value described by the following:

Fig. 2 Upper head of first-cycle extraction column.

$$E_a^O = U_{IAP} / U_R \quad (2)$$

where E_a^O is the extraction coefficient which will not exceed a value of 9 with the coprocessing flowsheet.

Substituting Equation (2) into Equation (1) resulted in the following equation upon integration:

$$\theta = - \left(\frac{V_o E_a^O}{F_{IAF}} \right) \ln \left(\frac{E_a^O U_{IAF} - U_{IAP}}{E_a^O U_{IAF} - U'_{IAP}} \right) \quad (3)$$

Upon substitution of numerical values, Equation (3) reduces to:

$$\theta = -0.126 \, h \, \ln (1.125 - 0.0404 \, U_{IAP}) \quad . \quad (4)$$

Thus, the minimum time required to achieve critical ^{235}U concentrations is 2.7 hours with an organic layer thickness varying from 18 to 19 inches, as shown in Figure 2.

The above equations have assumed a ^{235}U enrichment of 93.5%, whereas with nominal irradiated fuels the ^{235}U enrichment is 86%. If the lower value is utilized, Equation (4) becomes:

$$\theta = -0.126 \, h \, \ln (1.125 - 0.053 \, U_{IAP}) \quad . \quad (5)$$

The results of this equation also are shown in Figure 3, with the minimum time now becoming 5.8 hours with an organic layer thickness of 22 inches.

The assumption that the aqueous and organic phases have achieved equilibrium with respect to uranium concentrations also is very conservative. If the actual ratio of U_{IAP} to U_R is less than E_a^0 , then even greater time periods would be required to achieve critical uranium concentrations.

2.2 Uranium - TBP Extraction Coefficients (C.L. Bendixsen, L.W. McClure)

Data on uranium extraction coefficients between aqueous Zr-Al-F- HNO_3 solutions and tributyl phosphate have been somewhat limited^[3], and a comprehensive study involving approximately 250 extraction tests was made. The tests were made using both 5 and 10 vol% TBP in a normal paraffin hydrocarbon with metal salt concentrations varying as follows:

Zirconium, <u>M</u>	0.30 - 0.70
Aluminum, <u>M</u>	0.30 - 0.90
Total Fluoride, <u>M</u>	1.33 - 4.20
F/Zr mole ratio	4.44 - 6.67
Acidity, <u>N</u>	0.35 - 3.70
Nitrates, <u>M</u>	1.1 - 4.9
Uranium, g/l	0.005 - 20.0.

Fig. 3 Time periods required to achieve criticality in upper head of first-cycle extraction column as determined by thickness of the organic layer and the uranium enrichment.

The laboratory analytical results were subjected to regression analyses, yielding the complex equation shown below. Accuracy in fitting the extraction coefficient data is within 5%, a significant improvement over previous correlations. Due to the method of analyses, however, solutions with compositions outside the range tested must be used with caution in this equation.

$$E_a^O = 1.592 (\text{NO}_3^-)^{3.20} (\text{T}_f)^x (\text{H}^+)^{-0.603} (\psi_a \frac{\text{Al}}{\text{F}})^{-0.916} (\psi_z \frac{\text{Zr}}{\text{F}})^{-2.72}$$

where:

E_a^O = The uranium extraction coefficient

NO_3^- = Equilibrium aqueous nitrate (moles/liter)

H^+ = Equilibrium aqueous acidity (moles/liter)

T_f = TBP corrected for extracted NHO_3 and UO_2^{++} ,

$$\text{i.e., } \text{T}_f = \text{TBP} - \text{H}_\text{O} - 2\text{U}_\text{O}$$

x = $1.88 - 0.15(\text{H}^+)$

$\frac{\text{Al}}{\text{F}}$ = Ratio of aluminum to fluoride concentrations

$\frac{\text{Zr}}{\text{F}}$ = Same ratio for zirconium

ψ_a = Average value of "a" in AlF_a^{3-a}

ψ_z = Average value of "z" in ZrF_z^{4-z}

ψ_a and ψ_z are functions of the HF/H^+ ratio, the Al, Zr and F concentrations, and the fluoride complexity constants for H^+ , U, Al, and Zr.

2.3 Recycle of Raffinate in the Extraction Process for Electrolytic Dissolver Product (R.D. Denney)

Material flowsheets have been written for the electrolytic dissolution and first-cycle extraction processes to effect a recycle of about one-half of the extraction column raffinate to the feed stream. The necessary feed rate for smooth and critically safe operation of the extraction column is much greater than the electrolytic dissolver output, thus requiring addition of extra liquid to the feed stream. Recycling of column raffinate instead of addition of dilute nitric acid will reduce the usage of acid and reduce the volume of radioactive aqueous waste. The feed stream resulting from a recycling of the raffinate will be higher in metal nitrate concentrations and may give an increase in the uranium extraction coefficient, thus increasing the effectiveness of the extraction column. Schematics of the presently used first-cycle extraction feed system and the proposed first-cycle extraction feed system with raffinate recycle are shown in Figure 4. The raffinate recycling scheme will be implemented when necessary modifications can be made in the first-cycle extraction system.

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Fig. 4 Schematic diagrams of the present and proposed feed makeup systems for the first-cycle extraction of EBR-II fuel dissolver product.

2.4 Vessel Sparging Study (R.D. Denney)

A literature search was made to find improved methods for air agitation of radioactive liquids contained in ICPP cylindrical tanks. The present sparge ring system adequately agitates the radioactive liquid, but presents a problem of liquid entrainment into the vessel off-gas system (VOG) giving undesirable contamination of VOG filters. The literature indicated that the presently used air agitation systems are over-designed, and that the air flow rates can in some cases be reduced, thereby decreasing the liquid entrainment to the vessel off-gas system. More efficient sparge air headers have been identified and include air-induced liquid circulators which may be a significant improvement over the conventional sparge-air header designs.

Quantitative literature data on particulate suspension with the more efficient sparge-air header designs are inadequate, specifically for vessels with dished heads which are common to the ICPP. Thus, it was concluded that tests should be conducted to determine minimum air sparging rates for various slurry concentrations and solution densities.

2.5 Dissolution Studies of PWR Ternary Oxide Fuel (B.E. Paige, S. Wildman, P. McCray)

Dissolution processes have been reported previously^[1,4,5] for fuel from the second seed of the second core of the Pressurized Water Reactor. This fuel consists of sintered wafers of enriched uranium dioxide-zirconium oxide-calcium oxide clad in Zircaloy. The most successful dissolvent to date for these highly resistant wafers was concentrated hydrofluoric acid (18 M), with 0.1 M CrO_3 used either simultaneously or as a succeeding treatment. This fuel dissolution process was less than satisfactory, however, from the standpoint of dissolution time, waste volume, and corrosion; in addition, skeletons of the wafers which had been converted to calcium fluozirconate posed a problem in waste handling.

During the current reporting period, a new dissolution process has been developed using boiling zirconium dissolver product (which results from the dissolution of the Zircaloy cladding) as dissolvent, with low levels (0.1 M and 0.5 M) of HNO_3 added. The zirconium dissolver product contained 6.8 M total fluoride with either 1.0 or 1.3 M zirconium.

Initial dissolution studies were made using wafers from each of the three composition zones. Zone 1 contains approximately 55% UO_2 and 40% ZrO_2 ; Zone 2 contains approximately 40% UO_2 and 55% ZrO_2 ; Zone 3 contains approximately 27% UO_2 and 67% ZrO_2 . The remainder of each zone is calcium oxide which stabilizes the sintered wafer. Dissolution data showed that all fuel wafers could be completely dissolved in the mixed dissolvent; however, Zone 3 wafers were the most difficult to dissolve. Zone 1, which contains more UO_2 , dissolved faster at the higher nitric acid level, while the higher fluoride-to-zirconium mole ratio (F/Zr) aided the dissolution of Zone 3 which contains more ZrO_2 . In simultaneous dissolutions of all three zones in fuel element proportions, the uranium was completely dissolved in 24 hours at an F/Zr mole ratio of 6.0. Only about 40% of the uranium was dissolved in 24 hours at a mole ratio of 5.1, although the dissolution was complete within 48 hours.

During dissolution studies using unclad wafers, it was observed that the fuel had a slow initial dissolution rate until the wafers had lost their integrity. This effect is partially due to the graphite coating which was added to facilitate the fabrication of the fuel. Figures 5-a, -b, and -c are photomicrographs showing progressive dissolution of a Zone 1 wafer in zirconium dissolver product (F/Zr - 5.1) and 0.5 M HNO_3 at the boiling point. The original graphite coating had no visible openings or fissures at this magnification (30x), but visible fissures developed within two hours and increased in size until the coating collapsed at 8 to 10 hours due to the dissolution of the fuel oxide within the wafer. Figure 5-d shows that a Zone 3 wafer required 10 hours to develop fissures comparable to a Zone 1 wafer which had been dissolved only 6 hours; this is the result of the slower dissolution rate of the oxide fuel in the dissolvent. Dissolutions using clad wafers which were similar to Zone 2 indicated that the graphite coating may be less cohesive after the wafers have been clad and formed into fuel plates.

5-A ZONE I, 6 HOURS OF DISSOLUTION.

5-B ZONE I, 8 HOURS OF DISSOLUTION.

5-C ZONE I, 10 HOURS OF DISSOLUTION.

5-D ZONE 3, 10 HOURS OF DISSOLUTION.

Fig 5 Disintegration of PWR fuel wafer coating during dissolution

Due to the corrosivity of the dissolvents required for dissolution of the PWR, Core 2, Seed 2 fuel, a dissolver constructed of a high-nickel alloy will be required^[1]. Scoping studies of a number of high-nickel alloys have indicated that Inconel 625 and Hastelloy C-276 are prime candidates. Table I presents corrosion data obtained at the boiling point for welded and machined coupons of these two alloys in mixed zirconium dissolver product and nitric acid dissolvents. Data show that corrosion rates increased only about 50% as the nitric acid concentration was increased from 0.1 to 0.5 M. Rates tripled when the amount of free HF (hydrofluoric acid) was increased by decreasing the zirconium concentration at a constant total fluoride concentration, i.e., by increasing the F/Zr mole ratio. All coupons showed preferential weld attack, and all Hastelloy C-276 coupons exhibited some weld decay. At the higher F/Zr mole ratio, all coupons also exhibited some end grain attack. These data clearly show that dissolution should be performed at as low a F/Zr mole ratio as possible to limit corrosion when the oxidant is present. Rates at the lower ratio are acceptable since only two PWR cores will be processed with this dissolvent.

TABLE I
CORROSION RATES AT THE BOILING POINT IN PWR DISSOLVENTS

HNO ₃ Concentration (M)	F/Zr Mole Ratio of Zr Dissolver Product	Corrosion Rate (mils per month)	
		Inconel 625	Hastelloy C-276
0.1	5.1	7	13
0.1	6.0	22	36
0.5	5.1	10	18
0.5	6.0	35	57

Figure 6 presents the proposed process flowsheet for one fuel element from Core 2, Seed 2, of the PWR reactor. The Zircaloy cladding is first dissolved in hydrofluoric acid, then nitric acid is added to dissolve the fuel wafers. Based on laboratory data, the flowsheet assumes that only 80% of the uranium has been dissolved when the next fuel charge is made; however, on the sustained basis, the heel of undissolved fuel should be constant as indicated. The dissolution of the Zircaloy cladding produces a F/Zr mole ratio of 5.1. The addition of sufficient hydrofluoric acid to dissolve the ZrO₂ in the wafers is required to prevent reaching low F/Zr mole ratios which decrease the rate of dissolution and cause solution instability. The addition rate will necessarily be controlled to prevent excessive corrosion.

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Fig. 6 Proposed flowsheet for PWR fuel.

Residual stainless steel poison pins, intimately contained in the Zircaloy cladding, will be dissolved periodically using sulfuric acid^[6]. The thin Inconel X spacer rings will remain to slowly dissolve during successive dissolutions.

The dissolution flowsheet has been verified in the laboratory. Without the addition of hydrofluoric acid, the dissolution rate of the unclad wafers dropped off drastically between 12 and 16 hours, indicating that additional acid was needed at this point. Methods for following the free hydrofluoric acid concentration during dissolution are being investigated. The process will be further verified on a pilot-plant scale using clad fuel.

2.6 ICPP Decontamination Manual (A.G. Westra)

An ICPP Decontamination Manual is being written to provide technical support to the Operations Branch in plant decontamination work. The manual is being written in modular form so that it can be related easily to specific decontamination problems which exist in various areas of the plant. Additions and changes will be made as more data and decontamination knowledge become available. Since, however, the manual is directed toward specific ICPP applications, it is being prepared for internal distribution only.

The manual begins with an introduction which broadly defines the decontamination problem and describes the layout of the plant. The introduction is followed by a discussion of the theoretical aspects of decontamination including: radionuclide properties, contamination and decontamination mechanisms, corrosion by decontamination treatments, and monitoring of the effectiveness of decontamination treatments.

Three sections of the ICPP Decontamination Manual have been completed: (1) Waste Calcining Facility, (2) Headend Fuel Dissolution and Feed Adjustment, and (3) First-Cycle Extraction. Each section begins with a brief description of the process and equipment in a specific area with emphasis on factors affecting decontamination, such as materials of construction and process temperature. For example: (a) Monel equipment should not be decontaminated with some reagents commonly used in stainless steel equipment; (b) The high temperatures in the WCF calciner vessel and off-gas line (500°C) cause radionuclides to diffuse into the metal faster than they do in equipment where the temperature stays below 100°C.

Following the equipment and process description, the contamination history of the equipment is described. Radioactive contaminants and process streams which contact equipment are identified, and areas where decontamination problems occur from solids deposits are pointed out. In fuel dissolution, feed adjustment, and headend extraction equipment, solids deposits are the major decontamination problem; while in the Waste Calcining Facility, volatile fission products which plate out in the calciner vessel and off-gas line are considered the major decontamination problem.

Finally, specific decontamination techniques are prescribed for decontamination problems. Effective decontamination reagents are listed along with application conditions, corrosion rates, and estimated relative effectiveness.

2.7 Proposed ICPP Decontamination Facility (J.E. Johnson, C.A. Allen, A.G. Westra)

Construction of a Decontamination Facility at ICPP has been proposed. This facility will house various decontamination operations wherein radioactively-contaminated tools and equipment of widely varying sizes and contamination levels can be safely decontaminated prior to repair and reuse.

Currently, all such equipment decontamination at ICPP is performed in a decontamination room which has no shielded work areas for remote decontamination and no sizable enclosed work areas -- e.g., walk-in hoods -- for controlling the potential spread of airborne contamination during decontamination operations. A steady increase in ICPP processing activities in recent years has expanded the decontamination work load beyond the capabilities of the present decontamination room. Lack of remote decontamination capabilities and lack of adequate separation between simultaneous jobs being performed in the present decontamination room have led to accumulation of excessive radiation exposures by personnel working therein. Inadequate control over the potential spread of airborne contamination limits the decontamination techniques which can be employed, thereby reducing the efficiency and speed of decontamination and limiting the degree of decontamination which can be achieved. In order to perform the necessary functions of decontaminating, repairing, and reusing failed process equipment at ICPP in a safe manner, instead of burying and replacing these items with new equipment, a new Decontamination Facility is needed at the earliest possible time.

Preliminary design criteria, a conceptual design, and an engineering-type cost estimate were prepared for the proposed ICPP Decontamination Facility. A Construction Project Data Sheet (Schedule 44) and an Environmental Assessment were submitted to the AEC (Atomic Energy Commission) in anticipation of initial funding of the facility in FY 1976. The proposed facility (Figure 7) will house a remote decontamination cell equipped with lead-glass windows, remote-handling manipulators, portable radiation detectors, decontamination solution spray taps, a folding-panel roof, an air-lock entryway, and controlled ventilation and off-gas filtration systems.

The decontamination work areas at the facility will consist of two adjacent rooms: a high-activity-level room and a low-activity-level room. A remote cell, two contamination-control cubicles, two soaking tanks, and an alpha glovebox-hood combination will be in the high-level room. Sink-hoods, a dry buffing hood, a high-pressure spray cabinet, a large ultrasonic cleaner tank, a master-slave manipulator repair/storage area, and a lightly-shielded storage cubicle will be located in the low-level room. The high-level room will be a high-bay area serviced by a 30-ton bridge crane; the low-level room will have less vertical clearance and will be serviced by a one-ton hoist suspended from an overhead monorail. Two liquid-waste sump tanks and two decontamination solution surge tanks will be located in shielded cells below the main floor.

Benefits that will be realized by construction and operation of the proposed facility include:

- (1) Reduced personnel radiation exposures
- (2) Reduced burial of contaminated equipment
- (3) Better control over airborne contamination during decontamination operations

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Fig. 7 Proposed ICPP decontamination facility.

- (4) More efficient and rapid decontamination of equipment
- (5) High degree of decontamination achievable
- (6) Capability for remote examination of nonrepairable process equipment to determine causes of failure.

3. CORROSION EXPERIENCE AND STUDIES

3.1 Corrosion in Headend Process Vessels (T.L. Hoffman)

Corrosion control of the ICPP process equipment is maintained by periodic inspections. Following decontamination at the end of the last zirconium fuel processing campaign, the wall thickness of the Carpenter-20-stainless-steel product-complexing tank was measured by ultrasonic techniques. The upper and lower 3/8-inch-thick heads and the 5/8-inch vessel wall averaged 0.337, 0.327, and 0.605 inch, respectively. These measurements indicate that during 28,600 service hours, the respective corrosion losses were 38, 48, and 20 mils, or corrosion rates of 1.0, 1.2, and 0.5 mpm. These losses are well below the 1/8-inch corrosion allowance that was designed into this vessel.

Prior to the FY-74 coprocessing campaign, ultrasonic-thickness measurements were made on the walls of the aluminum fuel dissolver-product-input-measuring tanks, the complexing solution feed tank, the spare waste collection tank, and the HF acid storage tank. Thinning was observed at three spots on the upper portion of the right cylinder of the complexing tank, in excess of the 125-mil corrosion allowance for this vessel. However, because the thin spots were in the vapor space above the liquid level, this vessel was placed in service until repair can take place. All other vessels were judged to be adequate for this processing campaign. These tanks are all constructed of Type 347 stainless steel, except for the HF storage tank which is constructed of flange-quality carbon steel, Grade 1020.

3.2 Corrosion in Liquid-Waste Storage Tanks (T.L. Hoffman)

At ICPP, stainless steel tanks in underground concrete vaults are used for interim storage of acidic radiochemical wastes prior to their conversion to a solid by fluidized-bed calcination. The condition of these tanks is periodically monitored by observing the condition of corrosion coupons immersed in the tanks. Some of the older tanks, in service for 19 years, have been monitored for corrosion damage at five different times. During this year, coupons were again withdrawn from the tanks and evaluated. For the ten 300,000-gallon tanks with service times of 7 to 19 years, the measured corrosion rates ranged from 0.09 to 0.0001 mil per year, depending primarily on the type of raffinate stored in each tank.

In addition, an inspection by remote television of limited external areas of two of the tanks, made in August 1973, showed the steel plates and welds to be in the original condition with some machine marks still visible. A comprehensive report is being prepared on the results of this corrosion evaluation.

3.3 Corrosion Monitoring in the Fuel Storage Area (C.A. Zimmerman)

Routine periodic corrosion surveillance of certain types of materials currently stored in the ICPP basin is undertaken to ensure that there is no deterioration which could lead to problems in handling the fuel or which could lead to fission product leakage into the basin water. Two such fuels are the EBR-I, Mark IV fuel which is destined to be shipped to Savannah River Plant because of the plutonium it contains and the TORY-IIA fuel which contains beryllium. The TORY-IIA fuel is to be processed in the early 1980's.

Inspection of EBR-I, Mark IV Fuel Containers. EBR-I, Mark IV fuel materials have been stored in the ICPP storage basin since 1964 in two-inch-diameter galvanized pipe containers having screwed end caps. Inspection of two of these containers revealed considerable rusting in the thread area, a loss of zinc galvanizing material, and indications that pitting could be occurring. The containers were found to have a $\beta + \gamma$ reading of ~ 5 R at six inches. Removal of these containers from aqueous storage was recommended, and the containers are currently being held in a dry storage area.

Inspection of TORY-IIA Fuel Cans. Visual inspection of several aluminum cans containing TORY-IIA fuel showed the cans to be in satisfactory condition after eleven years in the ICPP basin. The cans inspected showed a darkening of the metal surface with spots of white scale or crust-like material. Some pitting was observed; however, the pits appear to be shallow. Radiation readings on one can show a $\beta + \gamma$ reading of 400 mR/hr and a γ reading of 125 mR/hr at contact.

3.4 Corrosion of Austenitic Stainless Steel Alloys Due to Nitric-Hydrofluoric Acid Mixtures (H.S. Cole)

Both present and future processes at the ICPP require the use of corrosive solutions containing nitrates and fluorides for the processing of spent nuclear fuel elements to recover unfissioned ^{235}U . By far the most prevalent materials used for process vessels and piping to contain the process solutions have been the austenitic stainless steels. A report summarizing information available in the literature, both experimental and operational (including some locally-obtained experimental results), on the various parameters surrounding the corrosion of austenitic stainless steels by HNO_3 -HF mixtures has been prepared^[7]. A summary of the principal disclosures indicates that:

- (1) Type 304L stainless steel is a suitable choice for service at the ICPP with fully complexed nitrate-fluoride-bearing solutions.
- (2) Annealing of stainless steels will improve their corrosion resistance.

- (3) Stabilizing the stainless steels with columbium (niobium) or titanium will improve their corrosion resistance.
- (4) Stainless steels with low carbon content have increased corrosion resistance.
- (5) Where it is necessary to alloy neutron-absorbing elements in the metal for criticality control purposes, their percentage should be kept to a minimum, as the corrosion rate increases with the increasing addition.
- (6) Complexing nitrate-fluoride-containing solutions with aluminum, zirconium, or thorium will also mitigate corrosive effects.
- (7) The corrosion of several stainless steel alloys appears to vary directly with the quantity of uncomplexed hydrofluoric acid present.

3.5 Corrosion of High-Nickel Alloys in Combined-Fluoride Solutions (B.E. Paige, N.A. DePue)

The processing of the PWR fuel (Section I-2.5) will require a dissolver and possibly other equipment which can resist a variety of fluoride-containing solutions. An extensive study of the corrosion of welded high-nickel alloys in combined-fluoride solutions has been made and is reported in detail in ICP-1053^[8]. Tests were made in simulated process solutions using both welded and unwelded coupons as well as fabricated vessels; specimens included both machined and unmachined surfaces. Solutions studied individually and in combination included hydrofluoric acid, zirconium dissolver product, nitric acid, aluminum nitrate, and sulfuric acid. Effects of solution composition were investigated for variables such as total fluoride concentration, fluoride-to-zirconium mole ratio, oxidant concentration, degree of fluoride complexing with aluminum, and fluoride level in sulfuric acid. Alloys included in scoping tests were Hastelloy C-276, Hastelloy C-4, Hastelloy G, Hastelloy S, Stellite 50% Nickel-50% Chromium alloy, Incoloy 825, Inconel 625, and Uniloy LR-HC (similar to Hastelloy C-276). The majority of the tests were performed with Hastelloy C-276. A comparison between alloy analysis and performance is presented for different manufacturers and heats. Weld effects, corrosion rates, and metallurgical evaluations are given for long-term exposures of two fabricated vessels at process conditions. Corrosion values for designing wall thickness of process equipment are presented for expected process solutions and operating temperatures.

The test program showed that Hastelloy C-276 can be used for the PWR dissolver, but the vessel should be fabricated to minimize the effect of preferential weld attack. A limited number of tests indicate that the newer alloy, Hastelloy C-4, will be superior because it eliminated the weld decay which occurred with Hastelloy C-276 in some process solutions.

3.6 Corrosion of Stainless Steels by Decontaminating Solutions (C.A. Zimmerman)

It is essential to decontaminate various sections or areas in the ICPP and WCF at intervals in order to permit maintenance or modification of process equipment. Corrosion tests have been run on various decontaminating reagents and decontamination systems as part of a continuing study to improve decontamination procedures and develop decontamination systems for treating specific areas or contaminants.

Three series of cyclic laboratory scoping tests have been run to evaluate the corrosion resulting from use of various decontamination reagents and systems. It should be noted that the results reported are cumulative results, and that they reflect the fact that the coupons used were in the "as-welded, as-machined" condition with no passivating treatment prior to the first cycle of the decontamination test.

In the first series of tests, eight decontamination systems were checked for corrosion of Type 304L and 347 stainless steels. The cumulative results of the five-cycle procedures used in testing these reagents are presented in Table II and indicate that most of these reagent systems can be used in a cyclic manner without excessive corrosion of these two alloys.

TABLE II
CUMULATIVE CORROSION RATES^[a] IN VARIOUS DECONTAMINATION SOLUTIONS

	Type 304L SS (mils/month)	Type 347 SS (mils/month)
<u>Test 1</u>		
5 M Nitric Acid		
1 M Sulfuric Acid	0.02	0.03
80°C 4 hr/cycle		
<u>Test 2</u>		
1 M Nitric Acid		
6 M Sulfuric Acid	0.20	0.14
80°C 4 hr/cycle		
<u>Test 3</u>		
1 M Nitric Acid		
6 M Sulfuric Acid	0.01	0.03
50°C 4 hr/cycle		
<u>Test 4</u>		
0.4 M Ammonium Oxalate		
0.16 M Citric Acid		
0.34 M Hydrogen Peroxide	0.01	0.01
90°C 24 hr/cycle		

TABLE II (contd.)

	Type 304L SS (mils/month)	Type 347 SS (mils/month)
<u>Test 5</u>		
0.4 M Oxalic Acid		
0.1 M Hydrofluoric Acid		
0.05 M Hydrogen Peroxide	19.4	16.7
90°C 6 hr/cycle		
<u>Test 6</u>		
<u>Step A</u>		
Turco 4502 1 lb/gal		
85°C 4 hr/cycle	0.03	0.12
<u>Step B</u>		
1 M Oxalic Acid		
85°C 1 hr/cycle	2.7 ^[b]	3.6 ^[b]
<u>Step C</u>		
4 M Nitric Acid		
85°C 1 hr/cycle	0.14	Wt. Gain
<u>Test 7</u>		
<u>Step A</u>		
1.3 M Sodium Hydroxide		
0.1 M Potassium Permanganate	0.18	0.16
85°C 6 hr/cycle		
<u>Step B</u>		
0.8 M Nitric Acid		
0.3 M Hydroxylamine Sulfate	31.1 ^[c]	40.5 ^[c]
85°C 6 hr/cycle		

[a] Coupons were exposed to five consecutive cycles under the conditions noted with the coupons being cleaned and weighed after each cycle.

[b] The corrosion rate in the first cycle of this five-cycle test was considerably higher than in the following cycles. This may reflect the effect of welding temperature and/or mechanical working of the metal during coupon preparation. If the results of this first cycle are omitted, and only the results of the last four cycles averaged, the 304L shows a corrosion rate of 0.16 and the 347 a rate of 0.34 mil per month.

TABLE II (contd.)

[c] These results reflect an unusually high corrosion rate experienced during the first cycle of the five-cycle test. The high attack may be a reflection of the coupon being in the "as-welded and machined" condition without any acid cleaning or passivating treatment. The average corrosion experienced in this solution during the following four cycles was 0.23 mil/month for the Type 304L stainless steel coupon and 0.1 mil per month for the Type 347 stainless steel coupon.

The second series of decontamination tests was made to check the effectiveness of hydrofluoric acid - sulfuric acid as a decontamination system for severe decontamination such as in decommissioning or removal of equipment from service. The results of this series of tests are shown in Table III. Results are presented at room temperature and at elevated temperatures. These results indicate that the hydrofluoric acid - sulfuric acid decontamination system can be formulated to give a metal removal rate (from Type 304L or 347 stainless steels) which would be practical for decommissioning of equipment. It should be noted, however, that the use of this system requires the complexing of the decontaminating reagent prior to a subsequent processing of the waste solutions.

TABLE III

CUMULATIVE CORROSION RATES^[a] IN SULFURIC ACID - HYDROFLUORIC ACID
DECONTAMINATION SOLUTIONS

	Type 304L SS (mils/month)	Type 347 SS (mils/month)
<u>Test 1</u>		
1 M Sulfuric Acid		
0.05 M Hydrofluoric Acid	549	752
85°C 4 hr/cycle		
Room Temperature 4 hr/cycle	0.02	0.03
<u>Test 2</u>		
1 M Sulfuric Acid		
0.005 M Hydrofluoric Acid	161	124
85°C 4 hr/cycle		
Room Temperature 4 hr/cycle	0.05	0.19

TABLE III (contd.)

	Type 304L SS (mils/month)	Type 347 SS (mils/month)
<u>Test 3</u>		
2 M Sulfuric Acid 0.005 M Hydrofluoric Acid 85°C 4 hr/cycle	1663 ^[b]	1092 ^[b]
Room Temperature, 4 hr/cycle	5.1	3.6
<u>Test 4</u>		
2 M Sulfuric Acid 0.05 M Hydrofluoric Acid Room Temperature, 4 hr/cycle	4.1	2.8
<u>Test 5</u>		
<u>Step A</u>		
1 M Sulfuric Acid 0.05 M Hydrofluoric Acid 55°C, 4 hr/cycle	---	---
<u>Step B</u>		
5 M Nitric Acid 55°C, 4 hr/cycle	5.5	4.2
[a] Coupons were exposed to five consecutive cycles under the conditions noted with the coupons being cleaned and weighed after each cycle.		
[b] Three cycles only due to excessive corrosion.		

Results of the third series of tests of decontaminating solutions are shown in Table IV. This was a series of two-step tests where exposure to nitric acid - potassium permanganate solution was followed by an oxalic acid treatment. The results indicate that varying the concentration of the ingredients in Step A apparently does not exert much influence on the corrosion rates for Types 304L and 347 stainless steels, and that this system will remove appreciable metal and thus should be used with care.

TABLE IV
CUMULATIVE CORROSION RATES^[a] IN ACID - PERMANGANATE
DECONTAMINATION SOLUTIONS

	Type 304L SS (mils/month)	Type 347 SS (mils/month)
<u>Test 1</u>		
<u>Step A</u>		
0.5 M Nitric Acid		
0.05 M Potassium Permanganate		
50°C, 5 hr/cycle		
<u>Step B</u>		
1.1 M Oxalic Acid		
50°C, 1 hr/cycle	11.4	12.8
<u>Test 2</u>		
<u>Step A</u>		
0.5 M Nitric Acid		
0.1 M Potassium Permanganate		
50°C, 5 hr/cycle		
<u>Step B</u>		
1.1 M Oxalic Acid		
50°C, 1 hr/cycle	12.1	12.9
<u>Test 3</u>		
<u>Step A</u>		
2.0 M Nitric Acid		
0.5 M Potassium Permanganate		
50°C, 5 hr/cycle		
<u>Step B</u>		
1.1 M Oxalic Acid		
50°C, 1 hr/cycle	10.1	9.5
<u>Test 4</u>		
<u>Step A</u>		
2.0 M Nitric Acid		
0.05 M Potassium Permanganate ^[b]		
50°C		

TABLE IV (contd.)

	<u>Type 304L SS</u>	<u>Type 347 SS</u>
	<u>(mils/month)</u>	<u>(mils/month)</u>
<u>Step B</u>		
1.1 M Oxalic Acid		
50°C 1 hr/cycle	1.4	3.4
[a] Coupons were exposed to five consecutive cycles with the coupons cleaned and weighed after each cycle.		
[b] Potassium permanganate additions were made every four hours with the total exposure period being 18 hours.		

4. INSTRUMENTATION AND SAFEGUARDS

The ICPP is engaged in a program of instrument development and modernization, including electronic data processing, for process surveillance, data acquisition, operator guidance, and plant protection. The following topics, in brief outline form, note developments and results of the past year, sufficient for interested persons to inquire for technical details. The actual details are voluminous, and it is not felt that the present report is an appropriate vehicle for their transmittal.

4.1 ICPP Accountability Instrumentation (F.O. Cartan, J.P. Morgan, R. Salverson)

A computer model of uranium flow in the first cycle of the ICPP was written. The model will be used as a design tool for a computer-operated Safeguards/Accountability system.

The dual-energy gamma absorptimeter^[2] was tested and interfaced with the Nova 1200 minicomputer^[1]. Modifications were made to the high energy source shield, the low energy source, and to the pulse amplifiers. The computer interface, the software drivers, and the BASIC interpreter show the required performance.

A sonic flowmeter is being investigated for measurement of ICPP product volumes. The transducer and electronics, after repairs and modifications, operated successfully in water, solutions of aluminum and uranyl nitrate, TBP in kerosene, and a fluozirconate slurry approximating the expected WCF feed. Gas bubbles, very heavy slurry, and unmixed solutions caused signal losses. The instrument was calibrated with water at the Standards Laboratory using the gasketed transducer. Standard deviations of 0.5% or less were observed at flows of 1, 2, and 3 liters/minute. Excessive time dependent shifts in calibration and zero point were corrected by circuit changes by the manufacturer. A nongasketed transducer has been designed.

Specifications were prepared for a mass spectrometer for low-cost uranium-plutonium isotope ratio measurements.

4.2 A Loadout Area Monitoring System for the General Electric Midwest Fuel Reprocessing Plant (MFRP)
(F.O. Cartan)

Completion of calibration and evaluation of the minicomputer-operated loadout area monitor at the MFRP have been indefinitely delayed due to changes in plans for operation of the plant. Descriptive information and laboratory test data will be published, supporting this approach to in-line monitoring of fissionable material.

4.3 Conductivity Meter for the Electrolytic Dissolver
(F.R. Phelps)

A new electrical conductivity meter for determining solution concentrations in the electrolytic dissolver effluent has been designed, fabricated, and calibrated and is being installed in Cell 5 of the Hot Pilot Plant. This instrument must meet the criterion of long life in a high-temperature, highly-radioactive stream. Calibration results look very good and indicate that the accuracy of the instrument will be well within the desired $\pm 5\%$.

4.4 Level System for the Waste Tank Farm Vessels
(F.R. Phelps)

A RF level-sensing system for the tank farm is being developed with continuing good results, which support the high-frequency (10 to >500 MHz) resonant chamber design. A prototype probe is being designed for installation in a large radioactive waste tank. Experimental results indicate that the resolution of ± 0.050 inch at 50 feet can be achieved.

4.5 Computer Applications
(J.W. Brothers, F.M. Groth, J.P. Morgan, R.D. Salverson, D.G. Headington)

Real-time data acquisition and analysis activities including planning, equipment acquisition, interface design and construction, and programming were performed in the areas described in the following listing.

FY-74 ICPP COMPUTER ACTIVITIES - COMPUTER APPLICATIONS GROUP

Pilot-plant
computer system

Data acquisition and display for the aqueous halide pilot plant were completed.

Counting facility
computer system

Data acquisition and analysis of Ge(Li) and NaI(Tl) gamma-ray spectra were adapted to the Nova computer system.

Demonstration plant panel display	Color graphics for pilot-plant processes were specified.
ICPP safeguards system	Implementation of BASIC-based data acquisition and analysis was achieved.
Stack microprocessor	Microprocessor/display system was designed for real-time radioactivity effluent monitoring.
Health and safety computer system	Automation of ICPP safety functions was specified and documented for computer purchase.
Mass spectrometer computer system	Computer functions were upgraded with a new core memory.
Plant automation	Studies of functional areas were documented and published with a report by Profimaties.

5. FUEL STORAGE BASIN STUDIES

5.1 Fuel Storage Basin Water Quality Study (B.J. Grady, D.W. Rhodes)

Nuclear reactor fuel is received and stored at the ICPP Fuel Storage Basin prior to processing at the Idaho Chemical Processing Plant. The fuel is stored in one of three interconnected basins under approximately 20 feet of water. The total dissolved solids in the basin water, especially chloride which results from the use of chlorine for microbiological control, have been increasing steadily since 1966 when the discharge of basin water to a local dry well was terminated. A study was conducted by J.M. Montgomery, Consulting Engineers, to evaluate the problems associated with the quality of the basin water and to recommend solutions. The primary problems are: (a) poor water clarity due to suspended solids and periodic "bloom" of microorganisms which increases the difficulty of handling fuel elements under 20 feet of water, and (b) the increasing chloride concentration which creates a potential for corrosion of the aluminum-clad fuel elements.

The Fuel Storage Basin Water Quality Study covered the following areas: a comprehensive review of existing and projected basin water quality, including determining the need for treatment; the establishment of optimum water quality criteria to prevent corrosion, improve clarity, and control biological factors; the establishment of a practical (achievable) water composition; a review of available processes to achieve the desired water composition; an investigation of methods to minimize waste volumes and disposal problems; recommendations for the most practical and economical process for further study; preparation of a conceptual design criteria report on the recommended process; and preparation of an estimate of the capital costs for the recommended process.

The consultants recommended several alternatives for reducing the chloride concentration in the fuel storage basin. The process being considered is an ion-exchange demineralization process using strong-acid cation and weak-base anion resins. This process can be installed with only minor modifications to the existing ion-exchange facilities. The cation resin will be regenerated with nitric acid and the waste will be discharged to the process equipment waste (PEW) evaporator. Upon being exhausted, the anion resin will be replaced by new resin. The exhausted resin will be discharged to a new spent resin tank designed for removal to the burial ground when full. A schematic of this alternative is shown in Figure 8.

Once the chlorides are reduced, the mineral quality of the basin should be adjusted to that shown in Table V. Generally, the water would have a pH of 7.0; a nitrate/chloride relationship governed by the Uhlig equation; a Langelier Index near zero; and a turbidity of less than 0.5 FTU.

The basin water conditioning system will be designed to maintain the water quality recommended in Table V and will consist of two process loops: (1) a low-capacity basin decontamination loop, and (2) a high-capacity clarification loop. The decontamination loop will consist of the existing diatomaceous earth filter, the existing ion-exchange system (with the Amberlite-200 in acid form), and a mixing tank where lime can be used to adjust the effluent pH to near neutral. The clarification loop (1,000 gpm) will consist of a dual-media filter, an ozonation column and a carbon dioxide column for pH adjustment. Ozone will be produced on site from air, and carbon dioxide will be drawn from an insulated, refrigerated receiver located outside the fuel storage building.

An effort will be made to reduce or eliminate all basin inputs which might degrade the mineral quality of the basin water. A small demineralizer will be used to process all basin makeup water or collected steam condensate. Facilities also will be provided to permit intermittent shock-dosing of the basin water with ozone.

5.2 Treatment of Basin Water With Chlorine to Inhibit Growth of Microorganisms (M.W. Wilding)

To maintain good clarity in the fuel storage basin water, the growth of microorganism must be prevented. Whenever a "bloom" of microorganisms occurs in the water, visual handling of the fuel underwater becomes difficult. Chlorine has been used to inhibit the microbiological growth in the water ever since recycle was started in 1966. Chlorine is colorless and an effective biocide that does not reduce the clarity of the water as do many other biocides. Chlorine is relatively stable and has a residual biocidal effect for several days. On the other hand, chlorine eventually reduces to chloride, which has no biocidal effects. In fact, chloride is corrosive to aluminum fuel elements and the carbon steel super structure in the basin; consequently, the chloride should be kept as low as practical (below 50 ppm is optimum).

Fig. 8 Proposed fuel storage basin water demineralization system.

TABLE V
PRACTICAL FUEL STORAGE BASIN WATER COMPOSITION

<u>General Criteria</u>					
pH = 7.0					
$\text{Log (Cl}^-\text{)} = 0.65 \text{ Log (NO}_3^-\text{)} - 0.78$					
Langlier Index = 0					
Buffer capacity approximately 2.0					
O ₃ residual 0.005 to 0.01 mg/l					
Turbidity less than 0.5 FTU					
<u>Mineral Composition of Practical Water</u>					
<u>Cations</u>	<u>meq/l</u>	<u>mg/l</u>	<u>Anions</u>	<u>meq/l</u>	<u>mg/l</u>
Ca	5.00	1.00	Cl	1.41	50
Mg	Trace	Trace	HCO ₃	4.75	290
Na	1.96	45	NO ₃	0.73	45
K	Trace	Trace	SO ₄	Trace	Trace
Total	6.96			6.89	
Total dissolved solids approximately 380 mg/l.					

Chlorine has been added as calcium hypochlorite and as gaseous chlorine. Calcium hypochlorite adds calcium to the system, which is undesirable because it competes with Strontium-90 in the ion-exchange system. The calcium hypochlorite also contains calcium carbonate as an impurity which causes temporary cloudiness in the basin water. The addition of gaseous chlorine forms some hydrochloric acid in water which decreases the pH and requires the periodic addition of sodium hydroxide to adjust the pH to approximately 7.0.

Microbiological growth has been inhibited in the basin water by maintaining a residual chlorine level of approximately 0.2 ppm with a periodic shock treatment, where the chlorine level is increased to 1.0 or more, to kill any resistant strains of organisms. Approximately 150 lbs of chlorine is added to the 1,500,000 gallons of basin water each month to maintain a chlorine residual of >0.2 ppm. Methods to eliminate or reduce the amount of chlorine needed are being studied.

5.3 Use of Ultraviolet Light for Inhibiting Growth of Microorganisms (M.W. Wilding)

An ultraviolet light sterilizer has been installed as a test unit at the fuel storage basin to evaluate its efficiency in killing microorganisms in this environment. Microorganisms grow profusely in the water if no control measures are used. As the microbial population increases the water clarity decreases, making it difficult to see the fuel which is stored under 20 feet of water.

Ultraviolet-energy radiation is produced by a low-pressure mercury lamp which has a special glass formula to allow the passage of the 2,537 Angstrom ($\text{\AA}$) light rays. This radiation energy breaks the outer membrane of the microorganisms, reaching the DNA (desoxyribonucleic acid) causing modification or impairment of the DNA (considered the heart) which destroys the microorganisms^[9].

Water enters the sterilizer chamber containing twelve high-intensity ultraviolet lamps equally spaced throughout the chamber. Each lamp is housed in a fused quartz sleeve that acts as a temperature buffer, maintaining an operating lamp temperature of about 41°C . The quartz sleeves are sealed and keep the lamps from coming in contact with the water. Baffles are arranged such that the water is agitated and forced to travel tangentially through the chamber, bringing the microorganisms close to the ultraviolet source. Approximately 6,000 to 13,000 microwatt-seconds of 2,537 Angstrom light are required for complete destruction of organisms^[9]. The unit installed is designed to provide in excess of 25,000 microwatt-seconds of 2,537 Angstrom light. The life of these tubes is about 8,000 hours of continuous operation.

Plant operating tests on the ultraviolet light sterilizer were made using effluent from the Zeolon-900 and Amberlite-200 ion-exchange columns. These tests indicated that 99.5 to 99.9% of the bacterial organisms were killed by the ultraviolet rays in water originally containing 8,000 to 10,000 organisms per milliliter.

5.4 Quantitative Analysis of Microbiological Population in the Fuel Storage Basin (V.H. Barnes)

Microbiological growth in the fuel storage basin at the ICPP can impair visibility; poor visibility inhibits normal unloading and transferring of fuel. The long residence time of water in the pipes that provide fresh water to the basin, the low filtration rates, and the presence of copious quantities of sediment provide favorable conditions for growth of microorganisms. The principal sources of microbial contamination are believed to be raw water, airborne contamination, and contamination by fuel casks and other equipment. Also, the resin columns used for the removal of strontium and cesium serve as an incubator for microorganisms; hence, the discharge from these columns into the basin is often highly contaminated.

Quantitative analysis of the basin microbiological population is accomplished by use of the "membrane filter" method. A water sample aliquot is filtered through a 0.45- μ millipore membrane filter, and the filter is then aseptically placed on a broth-saturated pad in a petri dish and incubated at 35°C for 48 hours. All equipment and materials used are either purchased as sterile prepackaged goods or are sterilized in an autoclave at 121°C and 15 psi for 30 minutes. The filter paper is then examined under 10-20x magnification and the number of colonies counted. It is assumed that each colony originates from an individual microorganism. The approximate microbiological population can then be tabulated from this number and the sample aliquot volume.

The membrane filtration method was chosen because of its high degree of reproducibility, the ability to test larger volumes of sample, and ability to obtain results more rapidly than standard tube procedures, with minimum requirements for laboratory space, equipment, and supplies.

Studies to date indicate that a microbiological population of less than 200 organisms/ml is desirable to provide good visibility in the basin. At present, chlorine is being used as the disinfectant in the basin and a concentration of not less than 0.2 ppm free chlorine is needed to maintain a low microbiological population. Results have shown that when the chlorine was less than 0.2 ppm the microbiological population can be greater than 1,000 organisms/ml. When the chlorine was 1 ppm or greater, the microbiological population was less than 10 organisms/ml. During a ten month study, there has been a direct relationship between the amount of chlorine in the water and the microbiological population.

5.5 Ion-Exchange Studies with Fuel Storage Basin Water (M.W. Wilding)

The fuel storage basin is used to store irradiated fuel elements underwater (as shielding) until they are reprocessed. This water is contaminated with Cesium-137 and Strontium-90 that has leaked from stored fuel.

Laboratory experiments and plant operating data at ICPP indicate that Cesium-137 and Strontium-90 can be removed from the basin water by ion exchange even though the water contains competing cations. Zeolitic ion-exchange materials are more selective for cesium than are the organic cation resins. Zeolon-900 proved to be more selective for cesium adsorption than either of two other zeolites (clinoptilolite or AW-500) in this particular system, even though the AW-500 is reported to have a higher cation-exchange capacity than the Zeolon^[10].

Strontium-90 was removed from basin water by several ion-exchange resins; however, none were as selective for strontium as the zeolites were for cesium. The resin capacity for strontium was low because of competition for sites from other cations in the basin water; however, Amberlite-200 appeared to have the highest capacity of any of the resins tested. Amberlite-200 was selected for use in the plant-scale ion-exchange column because (a) a

large volume was processed (1,200 column volumes) before 1% breakthrough occurred, (b) it is a macroreticular resin that is resistant to physical degradation, and thus provides high flow rates, and (c) it is readily available at a reasonable cost.

Laboratory studies indicate that Zeolon-900 loaded with Cesium-137 was partially regenerated with several reagents, including ammonium sulfate, ammonium nitrate, and potassium and sodium nitrates; however, regeneration of a plant-scale column was apparently unsuccessful, i.e., the concentration of Cesium-137 in the effluent was approximately the same before and after regeneration. After approximately 50% breakthrough of the plant-scale column, the zeolite was removed and replaced with new Zeolon-900 instead of trying to regenerate the column.

Amberlite-200 resin loaded with Strontium-90 was regenerated successfully both in the laboratory and in a plant-scale column using 5 M Na NO₃; approximately 90% of the strontium was removed using two column volumes of regenerant. Fifty successive regenerations have not reduced the exchange capacity of the resin.

5.6 Leachability of Sludge From the Fuel Storage Basin (M.W. Wilding)

The fuel storage basin contains sludge which has been accumulating on the bottom since the basin was put into operation. The sludge is primarily wind-blown dust, corrosion products, saw filings, and other debris that has entered the water. In the near future, the sludge is to be removed from the basin floor using a vacuum technique, which will transfer it to a 25,000-gal underground tank. If, in the future, recovery of the uranium or any other constituent appears to be desirable, leaching data will be necessary in designing leaching facilities. The results of this study indicate that sludge from the fuel storage basin floor can be leached with nitric acid to remove uranium and other radioisotopes from the sludge. Cobalt-60 and Niobium-95 appear to be the principal radioisotopes that are not readily leached with nitric acid.

The principal chemical and radiochemical elements in the basin sludge are shown in Tables VI and VII.

The sludge sample used for analysis from each basin was a composite of approximately 100 samplings taken randomly through each basin. Each composite sample (identified as north, center, and south) was thoroughly mixed and a sample taken from each for analysis.

Uranium and fission products were leached from sludge in the following manner: Each sample was dried by a heat lamp at approximately 100°C, weighed, and leached with 4 M nitric acid at ambient temperature in a batch-type leaching apparatus. A second contact was

TABLE VI
CHEMICAL ELEMENTS IN BASIN SLUDGE

<u>Component</u>	<u>Center Basin</u>	<u>North Basin</u>	<u>South Basin</u>	<u>South Basin (wt%)</u>
Al	M-m	m	M	10.0
B	T	T	T	0.005
Ca	m	m	m	0.1
Cr	T	T	T	0.02
Cu	T	T	T	0.02
Fe	M	M	M	5.0
Mg	m-T	m-T	m-T	3.0
Mn	T	T	T	0.1
Ni	T	T	T	0.03
Pb	m	m	m-T	0.2
Si	M	M	M	20.0
Ti	m-T	T	T	0.1
Zn	m	m	m	3.0
Zr	-	T	-	0.001

M = Major ≥ 5 wt%

m = Minor $< 5 > 0.1$ wt%

T = Trace < 0.1 wt%

made on the same solid to determine the effect of a second leach on uranium recovery. The percentage of radioisotopes leached from the sludge with the nitric acid was determined by the analysis of the sludge before and after leaching and by analysis of the leachate from the first and second leaching steps.

The results indicated that at least 50 wt% of the sludge dissolved. The highest amount was 77% for sludge from the south basin. This higher weight loss in the south basin probably can be accounted for by the greater amounts of calcium compounds added to that basin. The main source was calcium hypochlorite, containing about 30% calcium carbonate. The hypochlorite was added periodically to provide chlorine to inhibit microbiological activity in the south basin.

TABLE VII

CONCENTRATION OF RADIOISOTOPES IN FUEL STORAGE BASIN SLUDGE

	Fission Products, μ Ci/g Sludge		
	North	Center	South
Cerium-141	0.07	0.02	0.07
Cerium-144	22.68	17.0	30.8
Cobalt-60	15.2	3.38	1.45
Cesium-134	0.15	0.19	0.29
Cesium-137	7.81	9.14	14.2
Europium-154	0.28	0.31	0.42
Manganese-54	0.15	0.06	0.33
Niobium-95	1.46	0.16	0.74
Ruthenium-106	0.58	0.28	1.34
Strontium-90	5.14	6.02	24.0
Zirconium-95	0.90	0.11	0.37
Total Beta	76.2	54.3	128
Uranium (Total) (wt %)	0.027	0.038	0.090

Table VIII shows the percent of the radioisotopes leached from basin sludge with 4 M nitric acid.

Approximately 90% of the leachable radioisotopes were removed during the first nitric acid leach. The volume of gas generated by the nitric acid treatment was measured and analyzed. The results are shown in Table IX.

5.7 Testing of Fiber-Glaze Epoxy for Coating of Fuel Storage Basin Concrete Walls (M.W. Wilding)

Suspended solids in the water in the fuel storage basin have contaminated the concrete basin walls to form a "bathtub ring", which is a significant source of radiation exposure to personnel. A possible approach to reduction in the amount of radiation from this source is to lower the water level in the basin three to five feet, clean the concrete wall by a vacu-blast technique, then paint the cleaned area with a special epoxy coating that will not adsorb appreciable amounts of radionuclides and that can be decontaminated easily.

Tests were made to evaluate the stability and decontaminability of a candidate epoxy as follows. Concrete blocks 6 x 6 x 2 inches were cut and painted with a material called

TABLE VIII

RADIOISOTOPES LEACHED FROM SLUDGE WITH 4 M NITRIC ACID

	Percent Leached		
	North	Center	South
Cerium-141	100	100	100
Cerium-144	100	100	100
Cobalt-60	5	5	<1
Cesium-134	100	100	70-100
Cesium-137	100	100	100
Europium-154	100	100	100
Manganese-54	75-100	100	30-100
Niobium-95	27	16	62
Ruthenium-106	42	75	65
Strontium-90	99	95	98
Zirconium-95	50	90	65
Total Beta	73	79	98
Uranium (Total)	99	99	99

TABLE IX

GAS ANALYSIS FOR SLUDGE SAMPLES TREATED WITH NITRIC ACID

(11.5 ml gas/g of sludge treated)

Gas	Volume Percent	
	Sample 1	Sample 2
H ₂	0.01	0.04
CO ₂	6.7	1.9
N ₂	72.6	73.3
O ₂	19.6	20.8
Ar ₂	1.15	0.95

"Fiber-glaze", which is a fiberglass epoxy paint; the blocks were primed and painted according to factory specifications and placed in the basin under various test conditions. One block was located next to an irradiated fuel element to test the effect of radiation on the coating. Other blocks were placed either under water or at the surface, with part of the block exposed to air.

After a 150-day test period, there was no radiation damage to the coating, and the coating still adhered firmly to the concrete. Contaminated blocks were decontaminated by washing with a water spray and by wiping the painted surface with a clean damp cloth. Smear counts were taken before and after each step. The average results of smears taken across the blocks after 30 and 150 days are shown in Table X.

TABLE X
DECONTAMINATION OF CEMENT BLOCKS COATED WITH FIBER-GLAZE

<u>Days Contact</u>	<u>Block No.</u>	<u>Average Counts/m/Smear</u>			<u>DF</u>
		<u>Original</u>	<u>Spray Wash</u>	<u>Cloth Wash</u>	
30	1	33,000	19,000	32	1031
150	1	42,000	6,500	400	106
150	2	73,500	17,400	200	367
150	3	73,000	11,600	450	182

Based on the results of this experiment, painting the cleaned basin walls with the Fiber-glaze will reduce penetration of radionuclides into the walls. In addition, the coating can be decontaminated periodically to significantly reduce radiation exposure. Long-term radiation effects on the epoxy, at the low dose rate the walls receive, appear to be negligible.

6. GRAPHITE FUELS PROGRAMS

6.1 Rover Fuels Processing Facility (RFPF) (R.D. Modrow)

Title II Design of the Rover Fuels Processing Facility was completed. Construction of the facility is under way and is scheduled to be completed in December 1976. Contracts have been awarded for almost all Schedule X (Government-furnished) equipment, and procurement of these items is progressing satisfactorily.

The facility design remains as described in the previous annual report^[2]. This design provides for a semicontinuous burn-leach headend for recovery of about 2,600 kg of 93% enriched uranium from graphite matrix Rover fuels. A nominal throughput of 30 kg of uranium per day is anticipated. The Rover Fuels Processing Facility will provide suitable feed for the existing ICPP solvent extraction systems.

6.2 High-Temperature Gas-Cooled Reactor Fuel Reprocessing Program (A.P. Roeh, J. Dugone, J.D. Hammond, E.H. Smith)

6.21 General. ACC (Allied Chemical Corporation) - ICP intensified its efforts as a participant in the development of fuel reprocessing technology under the National Thorium Utilization Program being promoted by the United States Atomic Energy Commission. This program is associated with the development of the high-temperature gas-cooled reactor in the United States by General Atomic Company (GAC).

The HTGRs are based on the thorium fuel cycle, using helium as a coolant and graphite as moderator and core structural material. Since no commercial facilities presently exist for reprocessing the HTGR fuel, GAC, Oak Ridge National Laboratory (ORNL), and ACC are cooperating in an AEC-sponsored program to perform a "hot" reprocessing demonstration to develop the fuel recycle technology required for commercial HTGR fuel reprocessing.

The fuel reprocessing demonstration is proposed for FY 1975 funding, with operation of the facilities beginning as early as FY 1982. Irradiated Fort St. Vrain Reactor (FSVR) fuel will be reprocessed during the demonstration. The FSVR fuel is the only HTGR-type fuel available that is similar in size and composition to commercial HTGR fuel. This fuel will be received at ICPP and stored in a storage facility that was recently completed^[2,11].

As presently proposed, the demonstration facility will be modified to increase the capacity and will be operated for a number of years to reprocess HTGR fuel which the AEC may be committed to receive. Although improving the process and providing increased capacity for interim processing would require additional capital expenditures, the added expense would be far exceeded by the cost of additional facilities for storing spent fuel pending completion of a commercial facility in FY 1987^[11].

6.22 Conceptual Design of HTGR Fuel Reprocessing Facility. ACC, as prime contractor to the AEC, is responsible for providing a facility for reprocessing irradiated commercial HTGR fuel -- a graphite matrix containing uranium fissile and thorium fertile particles -- to recover uranium.

As developed through laboratory and pilot-plant studies at ICPP, ORNL, and GAC, the process -- together with the required ancillary services -- consists of (a) crushing, burning, and leaching in the headend system; (b) separating the thorium, uranium, and fission products in the solvent extraction system; (c) packaging and shipping the uranyl nitrate solution; and (d) separating the iodine, tritium, radon, and krypton from the headend off-gases in the off-gas cleanup system.

The **original design** (hereinafter called "base facility") assumed installation of the facility at the ICPP in new and modified existing buildings as follows:

- (1) Install the headend process, having a nominal throughput of 12 fuel elements a day, in Cells 1, 2, 3, and 4 of Building CPP-640.
- (2) Install the solvent extraction process in Cells A, B, C, and D of Building CPP-601.
- (3) Install the off-gas cleanup process in the middle cell on the west side of Building CPP-604.
- (4) Install the liquid product loadout system in a portion of a new building to be built adjacent to Building CPP-640. Use the remainder of this new building to house a product storage vault and the ventilation, filtration, and exhaust systems.
- (5) Conduct the required process analyses in the existing Building CPP-627 (the Remote Analytical Facility).
- (6) With the exception of the off-gas cleanup system, conduct the processing within an envelope established to preserve isolation of the ^{233}U systems and confinement of the ^{233}U .

The **design criteria for the base facility** are incorporated in Section 1 of the following system design descriptions (SDDs):

- (1) SDD 1.1, "Headend Processing System"
- (2) SDD 1.2, "Solvent Extraction Processing System"
- (3) SDD 1.3, "Off-Gas Cleanup System"
- (4) SDD 1.4, "Liquid Product Loadout and Shipping"
- (5) SDD 1.5, "Facilities".

The overall description of the demonstration facility is presented in the Overall Plant Design Description (OPDD 1.0).

Preliminary drafts of these documents were prepared and disseminated for review. When review comments are resolved, a complete issue of OPDD 1.0 and each SDD will be updated and submitted to the AEC for approval late in the first quarter of FY 1975 (except SDD 1.3).

A subcontract for architect-engineer services was negotiated with the Ralph M. Parsons Company (RMP) covering conceptual design of the HTGR Fuel Reprocessing Facility. The subcontract stipulated the following scope of work:

- (1) Consult and collaborate with the AEC or its designees to determine the requirements which will govern the project design and to confirm architectural and engineering criteria, codes, and design standards. The basic criteria for the design are defined in Section 1 of SDDs 1.1 through 1.5, but the architect-engineer is expected to apply to the design criteria its industrial experience and knowledge from similar projects. Applicable RDT standards are to be used.
- (2) Prepare design of an isolation envelope to prevent cross-contamination of the ^{233}U systems of the demonstration with the existing ICPP ^{235}U systems. This envelope may consist of physical barriers as well as filters and a separate ventilation and exhaust system.
- (3) Prepare a preliminary conceptual design of each of the systems and the facilities of the HTGR demonstration.
- (4) Prepare equipment layouts of the systems.

The scope of work was subsequently modified as follows:

- (1) In February 1974, RMP was instructed to expand its services to include the following:
 - (a) Prepare a management plan to identify means of expediting the project at ICPP to shorten the time to completion of construction.
 - (b) Prepare a model of the Hot Pilot Plant (Building CPP-640) and Cells A, B, C, and D of Building CPP-601 to be used for evaluation of the proposed headend layout and facility modification to achieve the required ^{233}U isolation.
 - (c) Make preliminary shielding calculations as the need is identified and agreed to by ACC, using shielding methods and codes resolved in advance with ACC.
 - (d) Prepare an updated cost estimate.
- (2) In Revision 1 to the subcontract, issued in April 1974, RMP was instructed to perform additional services as follows:

- (a) Expand the extent of the model of Buildings CPP-640 and CPP-601 (Cells A, B, C, and D) to include the analytical facility to be located in CPP-627 and the new ventilation and exhaust building. The model is to show the major equipment and the waste storage tanks, but not the piping or electrical equipment, and be so constructed that later additions can be made when the design is more complete.
 - (b) Replace the product denitration, loadout, storage, and shipping with liquid loadout, storage, and shipping in the design, preceding the replacement with a cost tradeoff study between ^{233}U liquid loadout and solid UO_3 loadout systems.
 - (c) Perform other minor services related to schedules, costs, and technical studies and design work.
- (3) In Revision 2 to the subcontract, issued in May 1974, RMP was instructed to prepare a cost estimate for an HTGR Fuel Reprocessing Facility utilizing a new building (hereinafter called "single facility") rather than the base facility. The single facility estimate, to be completed by June 1, is to be based on the assumption that the ICPP Atmospheric Protection System, the Waste Calcining Facility, and existing utilities that are adequate are used.
- (4) In June 1974, RMP was instructed to perform the following additional services:
- (a) Update the management plan to reflect current facility design, manpower effectiveness estimates, and interfacing with the Rover projects; to describe and relate the significant management efforts required to complete the HTGR demonstration facility in a timely and cost-effective manner; and to describe the relationship and effort required of the organizations participating in this project.
 - (b) Prepare a realistic schedule based on the single facility concept.

ACC received conceptual design documentation and a 60% cost estimate from RMP and transmitted the information to the AEC. The AEC incorporated the information into a request for proposal (RFP) that was distributed to qualified architect-engineer firms on May 9 for proposals on the advanced conceptual design.

6.23 Remote Handling Concepts. Negotiations were conducted to obtain an outside consultant to evaluate methods and propose a concept for the remote operation and maintenance systems of the demonstration project. RFPs were sent to 13 companies; 4 companies submitted proposals, but the other 9 declined to submit.

All work related to standard, fixed types of devices was awarded to Programmed and Remote Systems Corporation. All work related to mobile, advanced concept types of devices was awarded to MB Associates. Both companies initiated work in May.

6.24 Material Safeguards. The Brookhaven National Laboratory Technical Support Organization will provide assistance to ACC in evaluating the HTGR Fuel Reprocessing Facility for material safeguards and accountability.

6.25 Safety Evaluations. Final revisions to the draft of the Environmental Statement, HTGR Fuels Reprocessing Facilities, were completed. AEC-RRD (Reactor Research and Development) is obtaining final approval for publication of this statement as WASH-1534. Work is under way on the Preliminary Safety Analysis Report.

The feasibility of shipping liquid uranyl nitrate rather than uranium trioxide to ORNL was investigated by comparing process systems and costs of construction. As a result of this comparison, ACC recommended shipping product in the liquid form in a meeting of RRD, ID (Idaho Operations Office), GAC, ORNL, and ACC representatives in Idaho Falls on March 27. The recommendation, which was documented in Reference 12, was based on significantly reduced cost and reduced radiation exposure for personnel. AEC-RRD, AEC-ID, ORNL, and GAC agreed with this recommendation.

Preliminary shielding calculations for the liquid product shipping containers were completed. Criticality calculations are being made for the primary burner. Calculations were initiated to obtain a more accurate estimate for the fission product inventory in the FSVR fuel elements to be processed at ICPP.

Graphite Fuels Process Development

Development of combustion-dissolution headend processes for reprocessing graphite fuels at ICPP is continuing. Anticipated development effort necessary for eventual successful hot operation of the Rover fuels process being constructed at ICPP was completed. Small scale pilot-plant equipment was tested to verify the design of headend equipment for reprocessing Ft. St. Vrain fuel.

6.3 Rover Fuels Reprocessing

(G.W. Hogg, J.A. Rindfleisch, W.B. Palmer, D.L. Anderson, M.K. Valentine)

In the combustion-dissolution process for Rover fuels, graphite fuel is burned in a primary burner containing an inert bed of alumina fluidized with oxygen; primary ash (U_3O_8 , Nb_3UO_{10} and graphite) is separated from the fluidized-bed by elutriation. Excessive carbon (15-25 wt%) in the primary ash is reduced to less than 2 wt% in a secondary, batch, fluidized-bed burner to eliminate frothing during subsequent dissolution. The elutriated ash

from the secondary burner is dissolved using a sequential HF-HNO₃ dissolution process; HF dissolution is necessary to recover uranium from the Nb₃UO₁₀ formed during primary combustion. The dissolver effluent is complexed with aluminum nitrate to reduce its corrosion potential and passed through a continuous centrifuge for solids removal (undissolved Nb₂O₅, minor amounts of Al₂O₃) before being fed to the first-cycle solvent extraction system.

Residual development studies were made in support of Title II design and to verify operational safety and uranium accountability in the Rover fuels processing plant. Additional laboratory and pilot-plant studies were conducted to verify the operability of the annular Rover dissolver. Solids-liquid contact, the most effective sparge nozzles, and transport of dissolver effluent from a simulated annular dissolver were studied, and design criteria for the annular plant dissolver were recommended. The studies showed that solids-liquid contact in the annular dissolver was equal to that in the previously studied cylindrical dissolver. A sparge nozzle directed upward from the apex of an inverted cone was found to be most effective in promoting solids-liquid contact. It was determined that a steam jet was very satisfactory for transporting simulated Rover dissolver effluent.

Tests were made to establish erosion rates of Rover dissolver solution on plastic dissolver linings (Kynar and Teflon). The test results showed that the maximum erosion rate under the most severe anticipated simulated conditions was less than 3 mils per month.

A brief study was conducted to verify the compatibility of the Rover dissolution flowsheet with the existing TBP extraction system. The study showed that higher than anticipated acid concentrations in the feed to the extraction system would be required.

A neutron interrogator for nondestructive assay of irradiated nuclear fuel was tested as a means of measuring the uranium content of Rover fuel elements and of the centrifuged undissolved solids. The tests showed the instrument was effective in measuring uranium content of Rover fuel to within a 5% error, and could be used in fields with a gamma activity of up to 5 R/hr. No other device is available that performs satisfactorily in radiation fields greater than 200 mR/hr.

6.31 Annular Rover Dissolver Studies. Annular Rover dissolver studies consisted of sparging, sparge nozzle design, slurry transport, and abrasion studies.

(1) Annular Rover Dissolver Sparging. Cell-space limitations and the desirability of operating the Rover process equipment without mass limits necessitated changing the Rover dissolver design from simple-cylindrical to a cylindrical-annular geometry. To determine sparging efficiency of the new annular design, tests were made using simulated plant dissolvers constructed of glass.

Several means of comparison were devised to study the effectiveness of sparging with and without an inner vessel. These methods were: (a) measuring the rate of particle mixing,

(b) measuring the time required to achieve complete mixing following the addition of simulated acid to the simulated ash, and (c) determining the lowest sparge rate (less than the design rate) at which "effective" mixing occurred.

Experimental Equipment: The simulated dissolver (Figure 9) consisted of an outer vessel fabricated from a 2-foot length of 3-inch OD (outside diameter) glass tubing fitted with a 60° conical bottom. Sparge air entered through the bottom of the cone and was dispersed to the vessel through a distributor plate located about 1/2 inch above the bottom of the outer cone. Several holes were drilled around the outside edge of the distributor plate to improve air distribution. A slurry removal line was located just above the distributor plate and was sloped at a 45° angle to permit slurry removal by gravity.

The inner vessel was a 1.5-inch-OD, 2-foot-long glass tube fitted with a 60° conical bottom. The outer vessel was supported on a test stand, and the inner vessel rested on the distributor plate (spacers were welded to the inner vessel).

Testing Methods: The methods used to quantify sparging effectiveness were:

- (1) Measuring the rate of mixing by timing the movement of sparged particles as they migrated down the transparent dissolver-cone wall.
- (2) Measuring the length of time required to achieve full and complete mixing after the simulated acid was added to the dry simulated ash.
- (3) Measuring the percentage decrease in sparge rate before incomplete or ineffective mixing was observed. In this method, the sparge rate was incrementally decreased about 10% each time; 2 minutes were allowed at each sparge rate before the effectiveness of mixing was observed.

All the methods used required some judgement. To minimize bias and to keep the judgement as objective as possible, the experiments were repeated with different people observing and measuring results.

Experimental Results: All tests were made using a simulated Rover dissolver with and without the inner vessel. Thus, the quantitative results of each test are not as important as the comparison of the results with and without the inner vessel. For the sake of clarity, only results obtained during tests using calcine material of the size distribution expected in the Rover ash are reported in detail. Results of the other tests did not contradict the results obtained during tests with calcine. All tests were conducted using a simulated full batch charge.

The comparative results of the sparging tests analyzed by the three methods are listed in Table XI.

Fig. 9 Bench-scale Rover annular dissolver.

TABLE XI
COMPARATIVE RESULTS OF SPARGING TESTS

Test Method	Without Inner Vessel		With Inner Vessel	
	Range	Average	Range	Average
1. Rate of particle mixing in dissolver cone, turnover/minute ^[a] .	15-24	20	18-25	20
2. Time required to achieve complete mixing, seconds.	60-120	90	60-90	80
3. Sparge rate at which "ineffective" mixing occurs, scfm/ft ² (1.2 scfm/ft ² is the design sparge rate).	0.6-1.0	0.8 (33-1/3% decrease from design rate)	0.6-1.0	0.8 (33-1/3% decrease from design rate)

[a] The length of time required for particles to move from the top to the bottom of the cone constitutes one turnover.

Essentially no difference in the effectiveness of sparging was noted between the annular and the cylindrical designs. The study confirmed that sparging effectiveness was a strong function of particle size; the larger the particles, the less effective the sparging. For the large material, 60-mesh Al_2O_3 , the design sparge rate had to be nearly tripled before adequate mixing was observed. Al_2O_3 solids of the 100-mesh size were sparged much more effectively at the design rate than 60-mesh particles, but mixing was still less than desirable. Powdered material such as 325-mesh Nb_2O_5 , became quickly suspended and was very effectively sparged. The simulated Rover ash was also very effectively sparged at the design rate.

(2) Annular Rover Dissolver Sparge Nozzle Design. Sparge nozzle design studies were made in conjunction with the sparging efficiency studies. Although the sparging efficiency at the design sparge rate (1.2 scfm/ft^2 cross-sectional area) was considered adequate, this efficiency was found to be dependent on the design of the sparge nozzle. Several different designs were investigated in the same glass apparatus used for the previous study. These designs included "swirling" type nozzles, sparge rings, tubes opening at the bottom, and "side-opening" tubes shown in Figure 10.

The relative efficiencies of each design were measured by the same methods used in the previous study: (a) measuring the rate of particle mixing, (b) measuring the time required to achieve complete mixing following the addition of simulated acid to the simulated ash, and (c) measuring the lowest sparge rate at which "effective" mixing was judged to occur.

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Fig. 10 Sparger designs for new Rover annular dissolver.

The results of the study showed that sparge-mixing in a simulated annular Rover dissolver was most effectively accomplished by discharging air directly into or from the bottom of the dissolver cone; this maximized particle movement (mixing) along the cone.

(3) Slurry Transport by Steam Jet. The Rover design criteria document specifies using a steam jet located at the top of the dissolver with a suction leg extending to the bottom of the dissolver as the primary method of transferring the slurry from the dissolver. This requires the steam jet to lift the dissolver slurry by induced flow to a height of 12 feet. Two proposed alternate methods for the transfer utilize steam jets located below the dissolver. These jets are gravity fed and transfer the slurry by forced rather than induced flow.

Some questions were unresolved as to the operability of a steam jet at the solid loadings expected in the Rover dissolver solutions. Therefore, the operability of the three different proposed steam-jet feed arrangements were investigated using experimental apparatus installed in the Low-Bay Laboratory. Figure 11 shows the arrangements evaluated. Two different types of steam jets were also evaluated. Both jets were 3/4 inch OD; one was the venturi type (Figure 12); the other was cylindrical (Figure 13). The induced feed arrangement is less desirable than the gravity feed arrangement for three reasons: (1) the maximum operating temperature of the feed solution with solids present using induced feed is 46°C, compared to 70°C for the gravity type, (2) the solids loading can be almost ten times greater for the gravity feed arrangement than for the induced feed arrangement, and (3) slurry flow is easier to initiate with the gravity feed arrangement.

Fig. 11 Possible slurry-transfer arrangements.

Fig. 12 Design of venturi steam jet.

Fig. 13 Design of cylindrical steam jet.

Both induced and gravity feed systems appear to be satisfactory for the solid loadings and temperatures expected in the Rover dissolution system. It is unlikely that a jet will plug as long as the solids are suspended before and during the slurry transfer. If the sparge is inoperable, the transfer should not be attempted.

Horizontal gravity feeding was slightly superior to vertical gravity feeding. Both systems could be readily unplugged with purge water.

(4) Annular Rover Dissolver -- Kynar Abrasion Study. Two metal coupons coated with vinylidene fluoride (Kynar) were subjected to abrasion tests in the 3-inch glass annular Rover dissolver used in previously reported sparging studies. Neither coupon showed measurable weight loss (to the nearest 0.0005 gram -- the accuracy of the scale) after testing, and no evidence of pitting, scarring, or flaking was observed in microscopic observations.

The coupons used in the abrasion tests were a small nail head and a round-head wood screw which were coated with Kynar according to the manufacturer's recommended procedure. Each coupon was placed in the dissolver vessel at a point where maximum erosion was expected to occur as determined from the previous sparge studies.

The nail head was subjected to a 7-day test using the perforated-bottom sparge tube (Figure 14) and an air rate of 1.2 scfm/ft². The wood screw was used with the open-bottom sparge tube (Figure 14) and was subjected to a 7-day test at an air rate of 1.2 scfm/ft² followed by an additional 6 days at an air sparge rate of approximately 2.4 scfm/ft². These sparge designs are believed to present the greatest potential for abrasion to the dissolver

Fig. 14 Apparatus for testing abrasion resistance.

coating. The results of the study confirmed that abrasion should not be a crucial consideration in the design of the sparge system required for most effective mixing of Rover ash and acid during dissolution.

6.32 Neutron Interrogation Analysis of Irradiated Rover Fuels. The uranium content of the Rover fuel elements to be reprocessed in the ICPP plant facility is not well defined. In order to maintain accountability of the uranium in the process, it is necessary to have some knowledge of the quantity of uranium being charged to the system. Since 30,000 irradiated Rover fuel rods will be charged to the system, a fast and accurate method for the uranium determination is desirable. A demonstration of the neutron interrogator performance in assaying irradiated Rover fuel rods was conducted at ICPP.

Fuel Rod Unit and Testing Procedure: The fuel rod unit tested consisted of a 10-inch diameter cylinder, five feet in length; two parallel 1-inch holes were drilled through the diameter of the cylinder: one for the neutron source, the other for the fuel rod. The detector, mounted at the top of the cylinder, was a fast-neutron type, very insensitive to gamma radiation. It was connected to a small electronic digital output unit by a pair of coaxial cables. Two inches of lead was positioned between the fuel rod and the detector to provide the necessary gamma shielding for irradiated samples. The samples were interrogated by an isotopic neutron source of 8×10^5 neutrons/sec which cause the ^{235}U to fission, thus producing an increase in neutrons and gamma rays. Since the detector was insensitive to gamma radiation, only the neutrons were detected and the neutron counts were proportional to the ^{235}U content.

The neutron interrogation system appeared satisfactory for nondestructive uranium analysis of irradiated Rover fuels. The uranium content of all rods and ash standards was based on the best available data. The tests were directed toward determining the feasibility of analyzing irradiated uranium fuel rather than obtaining high precision and accuracy. However, the accuracy of the measurements was within $\pm 5\%$ error. Future testing is required to obtain overall proficiency.

It appeared that the detector was insensitive to as high as 5 R/hr gamma radiation with no shielding. If shielding can be provided to reduce the gamma activity of samples to below 5 R/hr, then any sample can probably be analyzed if representative standards are available. The results should be independent of the radiation level as long as the level is below 5 R/hr at the detector window.

6.4 Ft. St. Vrain Fuel Reprocessing

(G.W. Hogg, J.Z. Rindfleisch, W.B. Palmer, D.L. Anderson, M.K. Valentine)

The graphite in the Ft. St. Vrain fuel will be burned in a primary fluidized-bed burner to expose the SiC-coated fissile and fertile particles. The fluidized-bed solids will be removed from the burner, and the fissile and fertile particles will be classified (separated). The fertile particles, containing ^{233}U , will be crushed to break the SiC coating and burned in a secondary burner to convert the carbon, thorium, and uranium to their respective oxides. Thorium and uranium oxides will be dissolved in a HF-catalyzed HNO_3 solution; undissolved solids (mainly SiC hulls) will be separated in a continuous bowl centrifuge

before the solution is passed to the solvent extraction system for ^{233}U recovery. Krypton and other volatile fission products will be recovered using a low-temperature, high-pressure absorption process. The thorium may be recovered and stored, or discarded with the aqueous waste. The fissile particles may be stored as solid waste or processed in a similar manner (but separately) to the fertile particles.

A conceptual materials flowsheet for the headend processing of 12 Ft. St. Vrain fuel blocks per day was developed. The flowsheet showed the quantities of fission products, ^{233}U , and other processing materials for two different reactor irradiation periods (one year and six years) with a six-month cooling period in each case.

A 4-inch-diameter primary fluidized-bed burner was used to establish the effects of fluidizing velocity, bed temperature, feed rate, and bed depth on burning rates and fines generation using a fluidized bed of fissile and fertile particles and a grid plate to support the fluidized bed.

A series of tests using in-vessel, above-bed filters showed that internal fines recycle was impractical, because fines could not be effectively returned to the bed from the disengaging section; burn-through of the in-vessel filters occurred during three consecutive tests.

A series of 15 consecutive tests was successfully completed to obtain parametric operating data using filters located in an external gas-solids disengaging pot without fines recycle. The tests showed that 25 to 30% of the feed to the primary burner is elutriated as unburned graphite fines. The tests also showed that the minimum acceptable bed temperature to maintain stable burning was 875°C .

Preliminary tests in which fines were pneumatically recycled to the primary burner showed that less than 20% of the fines charged to the burner are burned on each pass. Due to the discouraging internal-filter tests which suggest large amounts of fines cannot be burned in the secondary burner, and since total fines recycle to the primary burner may not be practical, it is possible that the bulk of the fines from the primary burner should be burned in a separate fines burner (yet to be defined).

A primary burner startup heating method was developed. The heating method which employs in-bed combustion of CO with pure O_2 is routinely used to reliably heat the 4-inch-diameter pilot-plant burner bed from ambient to 700°C in 30 minutes. The heater also allows idling of the burner at any desired temperature with a full fluidized bed.

The efficiency of separating Ft. St. Vrain fissile and fertile particles containing unburned graphite from the primary burner bed was tested using a pilot-plant air classifier and a commercially available "zigzag" air classifier. Purities greater than 99% pure fissile and 95% pure fertile fractions were obtained simultaneously with both classifiers. The presence of the unburned graphite did not significantly affect the separation efficiency of the classifiers. Parametric data were obtained for 30 tests in which fluidizing gas and feed rates were varied. Mechanical, pneumatic, and gravity feed systems were tested. Pneumatic systems appear most attractive because they require little maintenance and result in steady-state feeding; however, some plugging problems in the pneumatic feeder remain to be solved.

Jet grinding, fluid-energy milling, and roll crushing were studied to determine the most practical means of breaking TRISO particles. Data show that jet grinding breaks the silicon carbide hull in half (leaving whole kernels), is simple and relatively maintenance-free, and results in moderate gas usage. The maximum efficiency with respect to minimum gas usage is yet to be determined. Fluid-energy milling was unsatisfactory from the product drawoff standpoint. It was necessary to pulverize the product (undesirable from the solids transport standpoint and for subsequent secondary burning) to allow product drawoff from the fluid-energy mill product removal cyclone. Parametric data were obtained for various feed rates, roll speeds, and gap settings in a roll crusher. The roll crusher was very satisfactory for crushing particles, but is potentially unacceptable for remote operations due to possible roll-wear and the need for maintaining roll-gap tolerances on the order of ± 0.002 inch.

A 2-inch-diameter dissolver has been fabricated and is being installed in the Low-Bay Laboratory at ICPP. The dissolver will be used to verify slurry handling and dissolution rates. The 2-inch-diameter Rover secondary burner was disassembled, decontaminated, and relocated in the Low-Bay Laboratory. The burner will be used to establish the operating mode of the Ft. St. Vrain secondary burner.

A bench-scale study of extraction distribution coefficients and feed adjustment requirements was completed. The tests showed that the U and Th decontamination was less than previously anticipated for acidic extraction feed.

A bench-scale study of potentially volatile fission products that could cause processing problems such as line plugging due to plate-out is in progress. A bench-scale glass fluidized-bed burner has been constructed and used to trace the flow path of Ru in a simulated off-gas train. The equipment will subsequently be used for testing the flow path of other anticipated fission products such as Cs and Ce.

6.41 Definition of Materials Flowsheet. A conceptual material flowsheet for the headend processing of Ft. St. Vrain fuel was developed as shown in Figure 15. The flowsheet is compatible with the following Ft. St. Vrain fuel reprocessing steps and requirements:

- (1) Crushing and burning of the graphite-based fuel blocks
- (2) Separation of TRISO/TRISO fissile and fertile particles
- (3) Crushing and burning of the particles before dissolution
- (4) Handling large quantities of fission products
- (5) Operating at extremely high radiation levels
- (6) Evaporation and acid stripping of dissolver solution for feed adjustment to the extraction columns.

DESCRIPTION	STREAM	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
		FUEL CHARGE	PRIMARY CRUSHER PROD.	SECONDARY CRUSHER PRODUCT	TERTIARY CRUSHER PROD.	PRIMARY BURNER PROD.	PRIMARY BURNER OFF - GAS	FISSILE FRACTION FROM CLASSIFIER	FERTILE FRACTION FROM CLASSIFIER	FERTILE CRUSHER PRODUCT	FISSILE CRUSHER PRODUCT	FERTILE SECONDARY BURN PRODUCT	FISSILE SECONDARY BURN PRODUCT	FERTILE SECONDARY BURN OFF - GAS	FISSILE SECONDARY BURN OFF - GAS		
RATE, BLKS/d	12																
C, Kg/d	1152	1152	1152	1152	115 (A)	1037	115	0	16.2	148	0.3 (B)	3.0 (B)	23.6 (C)	187 (C)			
UC ₂ , Kg/d	6.3-69	6.3-69	6.3-69	6.3-69	6.3-69		5.2-4.6	1.2-2.3	1.2-2.3	5.2-4.6							
ThC ₂ , Kg/d	129-118	129-118	129-118	129-118	129-118		51-46	78-72	78-72	51-46							
SiC, Kg/d	54.4	54.4	54.4	54.4	54.4		40.4	14.0	14.0	40.4	14.0	40.4					
CO ₂ , SCFM						60							1.2	9.2			
O ₂ , SCFM						4							4.4	35			
Kr, g/d									(D) 4.3-26.2	(D) 6.7-17.3			17.3-69.1	26.9-105			
H ³ , mg/d						3.9-12			(D) 0.31-2.4	(D) 0.67-1.2			1.3-4.8	2.6-9.6			
TOTAL SOLID, Kg/d	1395	1395	1395	1395	358		248	110	110	248	96.7	105					
FERTILE, Kg/d	131	131	131	131	110		0	110	0	0	0	0					
FISSILE, Kg/d	149	149	149	149	133		133	0	0	0	0	0					
SIZE, INCH	1/4 x 3/12	< 6	< 2	< 3/16	< .028		< .016	< .028	< .010	< .010	< .010	< .010					
B, g/d	176	176	176	176	176		176	0	0	176	0	176					
FISSION PRODUCT, Kg/d	3.4-14	3.4-14	3.4-14	3.4-14	3.4-14		2.1-8.8	1.3-5.2	1.3-5.2	2.1-8.8	0.87-3.5	1.4-5.6	(E) 0.41-1.7	(E) 0.78-3.2			
U, Kg/d	5.7-6.3	5.7-6.3	5.7-6.3	5.7-6.3	5.7-6.3		4.7-4.2	1.1-2.1	1.1-2.1	4.7-4.2	1.1-2.1	4.7-4.2					
U-233, Kg/d	1.6-2.8	1.6-2.8	1.6-2.8	1.6-2.8	1.6-2.8		0.59-1.1	0.97-1.8	0.97-1.8	0.59-1.1	0.97-1.8	0.59-1.1					
U ₃ O ₈ , Kg/d											1.3-2.5	5.5-5.0					
ThO ₂ , Kg/d											80.6-77	52.7-48					
Xe, g/d													127-527	196-790			
U-235, Kg/d	3.3-1.1	3.3-1.1	3.3-1.1	3.3-1.1	3.3-1.1		3.3-1.1			3.3-1.1		3.3-1.1					

(A) 10% C ASSUMED UNBURNED
(B) 2% C ASSUMED UNBURNED

(C) INCLUDED CARBIDES
(D) 20% Kr AND H³ ASSUMED RELEASED

(E) ALL VOLATILE FISSION PRODUCTS RELEASED INCLUDE
Xe, Kr, I, H³, Ru, Rh, Tc, Te, AND Cr

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Fig. 15 Conceptual Ft. St. Vrain flowsheet.

DESCRIPTION	STREAM	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
	THOREX DISSOLVENT																
	FERTILE DISSOLVER PRODUCT																
	FISSILE DISSOLVER PRODUCT																
	WATER WASH IN CENTRIFUGE																
	CENTRIFUGED FERTILE DISSOLVER PRODUCT																
	CENTRIFUGED FERTILE SOLIDS																
	CENTRIFUGED FISSILE DISSOLVER PRODUCT																
	CENTRIFUGED FISSILE SOLIDS																
	FERTILE FEED EVAPORATED SOL																
	FISSILE FEED EVAPORATED SOL																
	FERTILE CONDENSATE																
	FISSILE CONDENSATE																
	FERTILE DILUTION WATER																
	FISSILE DILUTION WATER																
	FERTILE IAF																
	FISSILE IAF																
FLOW, l/d	347	382 (A)	382 (A)	190	572		572		72	48	500	524	235	157	307	205	
FLOW, l/hr	14.5	15.9	15.9	7.9	23.8		23.8		3.0	2.0	20.8	21.8	9.8	6.5	12.8	8.5	
C, Kg/d		0.3	3.0		0	0.3	0	3.0									
SiC, Kg/d		14.0	40.4			14.0		40.4									
TOTAL SOLIDS Kg/d		(B) 15-16	(B) 47-46		0.006		0.006										
FISSION PROD, Kg/d		0.87-35	1.4-5.6		(B) 0.43-1.8	(B) 0.43-1.8	(B) 0.7-2.8	(B) 0.7-2.8	2.43-1.8	0.7-2.8					2.43-1.8	0.7-2.8	
U, g/l		2.9-5.5	12-11		1.9-3.7		8.2-7.3		15-29	98-88					3.6-6.8	23-20	
Th, g/l		186-177	120-113		124-119		80-75		985-945	953-894	231-219	230-215			231-223	223-209	
U-233, g/l		2.5-4.7	1.5-2.9		1.7-3.1		10-1.9		13-25	12-23					3.1-5.9	2.9-5.4	
B, g/l	1.0	0.91	1.37		0.61		0.91		4.8	10.8					1.1	2.5	
H, M	13	8.7	8.7		5.8		5.8		(D) -0.62	(D) -0.61	6.7	6.4			-0.15	-0.15	
NO ₂ , M	13.3	12.1	12.1		8.1		8.1		15.4	23.1	6.7	6.4			3.6	5.4	
Al, M	0.10	0.09	0.09		0.06		0.06		0.47	0.72					0.11	0.17	
F, M	0.05	0.003	0.003		0.002		0.002		0.02	0.02					0.005	0.005	
SOLIDS, g/l		3.9-4.6	11.5-12.0		0.01		0.01		0.08	0.12					0.02	0.03	
Th, Kg/d		71-68	46-43		71-68		46-43	0.06(C)	71-68	46-43					71-68	46-43	
U, Kg/d		1.1-2.1	1.7-4.2		1.1-2.1		4.7-4.2		1.1-2.1	4.7-4.2					1.1-2.1	4.7-4.2	
U-233, Kg/d		0.97-1.8	0.57-1.1		0.97-1.8		0.59-1.1		0.97-1.8	0.59-1.1					0.97-1.8	0.59-1.1	
U-235, Kg/d			3.3-1.1				3.3-1.1			2.3-1.1						3.3-1.1	

(A) 10% INCREASE IN VOLUME FROM SOLIDS
 (B) 50% FISSION PRODUCT ASSUMED DISSOLVED

(C) ASSUMES 99.9% RECOVERY
 (D) BY STEAM STRIPPING OR EVAPORATION

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Fig 15 Conceptual Ft. St. Vrain flowsheet (contd.).

The flowsheet is based on the process presently envisioned for the Ft. St. Vrain fuel reprocessing plant and a processing rate of 12 fuel blocks per day. The flowsheet shows the quantities of anticipated fission products and ^{233}U to be processed.

The Ft. St. Vrain flowsheet is calculated for two different irradiation periods (one year and six years) with a cooling period of six months. The first value in the flowsheet corresponds to the one-year irradiation time period and the second value to a six-year irradiation period. For example, Stream 1 in Figure 15 shows ThC_2 as 129-118 kg/d. The 129 kg/d is for the one-year irradiation period and the 118 kg/d is for the six-year period.

Uranium: The uranium content of the fuel is a function of the time the fuel is in the reactor. For respective one- and six-year irradiation periods, the uranium throughput for fertile particles in Ft. St. Vrain fuel is 1.1 and 2.1 kg/d of which 98% and 90% is ^{233}U , respectively. For processing of the fissile particles, Ft. St. Vrain fuel generates 4.7 and 4.2 kg of uranium per day of which 13% and 26% is ^{233}U , respectively. The ^{235}U is found only in the fissile fraction and is 3.3 and 1.1 kg/day, which is 70% and 26%, respectively, of the total uranium.

Fission Products: The quantity of fission products contained within the fuel blocks is also dependent on the time the fuel is in the reactor. Any nuclide with a boiling point below 800°C will be expected to volatilize and be included in the off-gas from the secondary burner. These volatile elements include Kr, He, I, H^3 , Ru, Rb, Te, Tc, and Cs. The fissile fraction contains 63% of the fission products while the fertile portion contains only 37%. One-year-irradiated, 6-month-cooled fuel contains 287 g of fission products per element while 6-year-irradiated, 6-month-cooled fuel contains 1,171 g per element.

6.42 Primary Burner Studies. Primary burner studies included burner operations with external filters, burner operations with in-vessel filters, and application testing of a full-bed CO/O_2 startup torch.

External Filter Testing: A series of tests to establish the operability of the 4-inch pilot-plant primary burner when using filters located in an external filter pot has been completed. The effect of fluidizing velocity, feed rate, bed temperature, and bed depth on combustion efficiency, fines generation, and heat transfer rates was studied during the tests. The external filters performed satisfactorily during the testing; no burn-through of the filters or filter plugging occurred.

A flow diagram of the 4-inch-diameter primary graphite burner is shown in Figure 16. The crushed feed (-3/16 inch size, 16.5 wt% fuel particles and 83.5% graphite, 8,000 grams/run) was metered to the feed line by a variable speed auger; feed flowed by gravity into the hot fluidized bed of fissile and fertile particles and unburned graphite fluidized by oxygen. The off-gas passed from the burner to the filter chamber, through the sintered-metal filters, through a HEPA filter, and then to the atmosphere. The two sintered-metal filters were 2-3/4-inch OD, 18-inches long, 5- μ porosity, and constructed of 316L stainless steel. The fine graphite particles elutriated from the bed were collected on

Fig. 16 Primary burner pilot plant.

the surface of the sintered-metal filters and periodically displaced from the filter surface by a pulsed blowback system.

The blowback was controlled by an automatic timer giving an approximate 0.1 second pulse every 15 minutes to each of the filters. The blowback air pressure was 75 psig. The fines were collected continuously and were weighed following the run.

Burner startup and supplemental heat was provided by a CO/O₂ combustion torch located in the fluidized bed. Bed temperature was controlled at the specified level by passing cooling air through the vessel shroud and/or by adding air to the fluidizing oxygen. The burner was operated semicontinuously; feed was added to the burner continuously, but the product (fissile and fertile particles) was removed after nearly all the graphite was burned from the bed. The final fluidized-bed depth was approximately 18 inches except in the last two runs in which the starting bed depth was greater than for the previous runs.

Fifteen runs were made to test burner operability using the external filters. The run plan was to test the effect of fluidizing velocity, feed rate, bed temperature, and bed depth on combustion efficiency, fines generation, heat transfer, and general burner operability. Fourteen of the runs were successfully completed; one run at low bed temperature (~800°C) resulted in the bed being extinguished early; the bed temperature could not be reinstated because of torch ignition problems. (The torch was repaired and has since functioned reliably.)

The test results showed that for best burner operation, (a) the fluidizing velocity should be as low as the required throughput will allow, (b) the feed rate should be as high as possible but consistent with good fluidization of the large graphite pieces, and (c) the bed should be as deep as possible without excessive slugging.

In-Vessel Filter Testing: In-vessel filter testing using the 4-inch-diameter primary graphite burner was completed. The results of 9 runs show that in-vessel filters in the vapor space of the primary burner are impractical because of filter burning and the inefficient burning of fines blown off the filters.

The 4-inch-diameter primary graphite burner with the sintered-metal filter installed in the vapor space was used for the experimental testing. The crushed feed (-3/16 inch size, 16.5 wt% fuel particles and 83.5% carbon) was metered to the burner by a variable speed auger. The feed flowed by gravity into a hot (875°C) fluidized bed of fissile and fertile particles and unburned graphite; oxygen was the fluidizing medium. Off-gas passed through the in-vessel filter, the secondary filter pot, and a HEPA filter. Fine graphite particles, elutriated from the bed, were collected on the surface of the in-vessel filter. The fine particles were periodically displaced from the filter surface by a pulsed blowback system.

Burner startup and supplemental heat was provided by a CO/O₂ combustion torch located in the fluidized bed. Bed temperature was controlled at the specified level by passing cooling air through the vessel shroud or by adding air to the fluidizing oxygen. The burner was operated semicontinuously; feed was added to the burner continuously, but the product (fissile and fertile particles) was removed after nearly all the graphite was burned from the bed. The final fluidized-bed depth was approximately 18 inches.

Nine runs were made to test burner operability using the in-vessel filters. The run plan was to test the effect of feed rate, fluidizing velocity, and bed temperature on burning rate and filter performance. Completion of all runs was not possible because of high filter pressure drop, inability to remove heat at the required rate from the burner, and filter burn-through.

Based on the results of the nine experimental runs, in-vessel filters in the primary burner are not recommended. The test results show that the fines do not mix back into the bed to any significant degree after blowback, even though fines are dislodged from the filter. An expanded top section would allow more effective blowback and lower gas velocities around the filter, but the gas velocity at the top of the bed would not be reduced. In addition, in-vessel filters in the primary burner are subject to burning. Graphite fines, oxygen, and high temperatures in the vicinity of the filter are always possible in the primary burner. The hazard of ignition of graphite fines on the filters could be minimized by increasing the disengaging height, installing a filter cooler, lowering gas velocities, etc., but the reliability of the system would remain questionable.

Application of the CO Combustion Torch: In-bed combustion of CO gas is potentially the simplest and most rapid method yet considered for startup heating of the proposed HTGR primary graphite burner. A simple combustion torch has been tested in the 4-inch-diameter primary graphite burner during 29 runs using beds of fissile and fertile particles. The torch has proven to be a rapid and reliable heating method.

The data obtained during 2 of the runs were used to estimate the number of torches needed to provide startup heat for 16-inch-diameter burner. The results indicate that 3 to 6 torches are required, depending on bed depth and the desired startup heating time.

6.43 Air Classification Studies. The classification of Ft. St. Vrain fissile and fertile particles was successfully demonstrated using the Air Classifier Pilot Plant (ACPP). Product purities of >95% pure fissile particles and >85% pure fertile particles were attained over a wide range of particle feed rates.

The success of these tests provided a basis for acceptance of air classification as a process step during processing of Ft. St. Vrain fuel. However, the confidence in extending these data to irradiated fuel particles, especially from the particle-breakage standpoint, is unknown.

6.44 Particle-Breaking Studies. Particle-breaking studies included tests using jet grinders, roll crushers, and fluid-energy mills:

Jet-Grinding Studies: The feasibility of using jet grinders to crush Ft. St. Vrain fertile particles was tested. The experimental results show that jet grinding produces a more desirable product than other crushing methods, and it could eliminate a high-maintenance process step such as roll crushing.

A sketch of the equipment used for the jet-grinding experiments is shown in Figure 17. The column and cyclone are glass, and the jet grinders are 1/8-inch OD stainless steel tubing with one end welded closed and a single small hole drilled through the wall.

Fig. 17 Experimental jet-grinding apparatus.

The fertile particles used for these tests were obtained by burning the graphite matrix from scrap fuel compacts and then screening the particles into +35 U.S. mesh (fertile) and -35 U.S. mesh (fissile) fractions. The starting bed was 10 grams of fertile particles; the run length was one hour, and the total air flow (jet air plus fluidizing air) through the column was constant at 1.4 scfm for all of the runs. The variables tested were jet size, jet orientation, air pressure to the jet, and the effect of graphite particles in the bed. Jet and impact plate separation distance is an important variable which was not thoroughly investigated.

The most surprising result of the experiments was in the way the fertile particles were crushed. Unlike a roll crusher which crushes the hull, buffer layers, and kernel, the jet grinder cracks the silicon carbide hull and buffer layers in half; and the kernel separates from the hulls and remains whole.

Almost 100% of the particles are broken in half and few fines are generated. Immediately upon cracking, the hulls are elutriated from the bed. The ThC_2 kernel, which is very tough, remains unbroken in the bed. Microscopic examination of the bed following each run has failed to show any broken kernels. When the kernel is released from the hull, very little carbon is left on the kernel; and very little thorium remains with the carbon buffer layer. Analytical results show that less than 0.10 wt% of the overhead product is thorium, which means that greater than 99.96% of the thorium remains in the bed. Conditions and results of 13 experimental runs are summarized in Table XII.

Roll-Crushing Studies: Preliminary testing of a 4-inch double roll particle crusher was completed. The effect of feed rate, roll speed, roll clearance, and carbon particle interference on crushing efficiency and size distribution was determined.

The test results showed that:

- (1) The 4-inch roll crusher has enough capacity for plant-scale processing
- (2) The crusher was able to crush graphite as large as 0.050 inch in diameter
- (3) The optimum roll clearance is between 0.012 and 0.018 inch
- (4) The roll speed should be as slow as required throughput will allow
- (5) The feed rate has no appreciable effect on crushed product character.

A roll crusher was used for the experimental roll-crushing tests. The two rolls are both 4 inches in diameter and 1.5 inches long. The clearance between the rolls can be adjusted from 0.00 to 0.25 inch within an accuracy of ± 0.001 inch by using a thickness gauge. The crusher is driven by an electric motor coupled to a worm-gear speed reducer. The roll speed can be varied from 0 to 200 rpm. The feed system consists of a hopper, which feeds the crusher by gravity, and a stopcock-type valve which controls the feed rate. To obtain a different feed rate, a stopcock with a different size port is used.

Two series of experiments were completed. Series I consisted of 12 runs which were used to calibrate the crusher equipment, determine the range of parameters to be studied in the Series II runs, determine the maximum crushing rate, and determine the maximum size of graphite the crusher would accept as a function of roll clearance. The results of the Series I runs are summarized in Table XIII.

Series II tests consisted of 22 parametric runs to determine the effect of roll clearance, roll speed, and feed rate on the size distribution of the crushed particles. A summary of the conditions and results of the Series II runs is shown in Table XIV. The results are shown as wt% +35 mesh and MMPD. Since all of the feed particles were +35 mesh, the values would be the upper possible limit of uncrushed particles, although in most cases the +35 mesh material is probably also crushed, but still too large to drop through the screen.

TABLE XII

SUMMARY OF JET RUN CONDITIONS AND RESULTS

Run No.	Orifice Size (in. dia.)	No. Jets	Jet Configuration	Jet Pressure (psig)	Jet Air (scfm)	Fluidizing Air (scfm)	Graphite Added to Bed	Final Overhead Volume (cc)	CC Overhead Scf Jet Air	Bed <35 Mesh (%)
6	0.0135	2	Up	50	0.25	1.04	No	4.50-2.40 ^[a]	0.160	54.6
7	0.0135	2	Opposed	50	0.25	1.04	No	2.1	0.140	45.6
8	0.0135	2	Plate	50	0.25	1.04	No	1.77	0.118	39.5
9	0.0135	1	Plate	50	0.125	1.17	No	1.80	0.240	41.4
10	0.0210	1	Plate	50	0.40	0.89	No	3.40	0.142	86.1
11	0.0280	1	Plate	50	0.53	0.32	No	3.10	0.097	82.0
12	0.0135	1	Plate	35	0.09	1.20	No	0.78	0.144	16.7
13	0.0135	1	Plate	20	0.05	1.25	No	0.20	0.067	2.0
14	0.0135	1	Plate	50	0.125	1.17	Yes	0.95	0.127	9.0
15	0.0350	1	Plate	50	0.88	0.02	No	3.07	0.058	74.4
16	0.0135	1	Plate	50	0.125	1.17	No	1.90	0.253	43.0
17	0.0135	1	Plate	50	0.125	1.17	Yes	2.00	0.267	39.0
18	0.0135	1	Up	50	0.125	1.17	No	0.22	0.029	3.5

[a] The first number is the volume actually elutriated and the second number is the volume that would have elutriated under normal conditions.

TABLE XIII

RESULTS OF SERIES I ROLL-CRUSHER TESTS

-
- A. Range of parameters to be studied in Series II runs:
Roll clearance: 0.002 to 0.024 in.
Roll speed: 20 to 180 rpm
Feed rate: 40 to 225 g/min
- B. Maximum crushing rate:
@ 100 rpm = 1000 g/min
@ 200 rpm = 1300 g/min
- C. Maximum graphite particle size accepted by crusher:
100% of -14 U. S. Mesh (0.039 in.)
Part of -12 + 14 U. S. Mesh (0.046 to 0.055 in.)^[a]

[a] Increasing the roll clearance from 0.002 to 0.024 inch did not cause a significant increase in the amount of graphite crushed in this size range.

Fluid-Energy Mill Studies: The crushing of Ft. St. Vrain fertile particles was studied using a commercially available fluid-energy mill. Pulverizing the particles to a fine powder is feasible, but results indicate that other methods of crushing yield a more desirable product.

An air impact pulverizer, Figure 18 was used for the tests. Particles impinge on each other in opposing sonic-velocity air streams. The particles were then discharged from the classification chamber or recycled to the opposing air streams until they attained a size sufficiently small to be discharged. The cyclone effect in the classification chamber was maintained with a higher air supply pressure to the "O" jet (100 psig) than to the "P" jet (70 psig). Off-gas from the discharge port passed through a cyclone for collection of pulverized particles and through a filter to the laboratory off-gas system.

Particles were fed to the "P" jet by gravity flow through a stopcock. Steady-state operation was attained by establishing and maintaining an arbitrary level of particles in the downstack while feeding particles. Material from the cyclone was collected and the size distribution determined.

The size of the "O" and "P" jets was varied to study the effect of jet velocity on pulverizing rate. Total air flow rate to the pulverizer was measured with a flowmeter upstream of the jet pressure control valves and was governed by jet orifice size.

A run consisted of initially feeding a known weight of particles to the mill until steady state was attained, noting the time elapsed while feeding another known weight of particles, and simultaneously maintaining a constant level in the downstack.

TABLE XIV
RESULTS OF SERIES II ROLL-CRUSHER TESTS

Run	Roll Clearance (inch)	Roll Speed (rpm)	Feed Rate (g/min)	Product Size	
				wt% + 35 U.S. Mesh	MMPD (in.)
1	0.002	100	130	0.63	0.00639
2	0.008	100	130	0.74	0.00813
3	0.012	100	130	0.37	0.01049
4	0.018	100	130	14.68	0.01530
5	0.024	100	130	90.61	0.02054
6	0.0012	20	130	--[a]	--[a]
7	0.0012	40	130	0.12	0.01027
8	0.0012	80	130	0.13	0.00958
9	0.0012	120	130	0.00	0.00899
10	0.0012	140	130	0.00	0.00873
11	0.0012	180	130	0.00	0.00837
12	0.0012	100	50	0.10	0.00959
13	0.0012	100	80	0.13	0.00943
14	0.0012	100	160	0.12	0.00886
15	0.0012	100	190	0.25	0.00908
16	0.0012	100	225	0.38	0.00912
17	0.0012	100	130	0.10	0.00821
18	0.0012	100	50	0.00	0.00923
19	0.0012	100	80	0.00	0.00853
20	0.0012	100	160	0.00	0.00866
21	0.0012	100	190	0.00	0.00845
22	0.0012	100	225	0.13	0.01053

[a] The crusher drive did not have sufficient power at 20 rpm and the crusher stalled.

Fig. 18 Air-impact pulverizer and collection system.

The results in Table XV show a maximum grinding rate of 3.2 g fertile particles/min and a maximum air usage efficiency of 0.57 g fertile particles/scf. The grinding rate could be

TABLE XV

SUMMARY OF RESULTS OBTAINED USING THE TROST PULVERIZER

"P" Jet Orifice Diameter (in.)	"O" Jet Orifice Diameter (in.)	Grinding Rate (g/min)	Air Rate (scfm)	Air Usage (g/scf)
0.055	0.0465	2.03	5.51	0.369
0.055	0.0465	3.17	5.60	0.566
0.046	0.040	1.13	3.87	0.293
0.033	0.028	0.456	1.73	0.264
0.016	0.0135	[a]	0.43	--

[a] Air flow was too low for proper operation. The material circulated in slugs and little or no pulverizing occurred. The total weight of material collected was 0.85 g.

improved simply with a larger pulverizer. The air-usage efficiency is quite low; a number of previous crushing tests using jet grinders had air-usage efficiencies as much as 15 times higher.

It was concluded that the low air-usage efficiencies obtained during the experimental tests and the undesirable fine product generated clearly suggest that development efforts for crushing Ft. St. Vrain fertile particles should be concentrated on methods other than the fluid-energy mill.

6.45 Burner Heat Transfer Calculations. Calculations were made to determine heat transfer rates through the wall of a shrouded 16-inch-diameter primary burner. Heat transfer rates were calculated for both finned and unfinned vessel walls. Fourteen blocks per day (57 kilograms of carbon per hour) can be processed using a 16-inch-diameter burner having a 6-foot fluidized-bed height and fins on both inside and outside of the vessel wall. A processing rate of 13 blocks per day (53 kilograms of carbon per hour) can also be achieved without internal fins if a 9-foot fluidized-bed height is used. A 16-inch-diameter burner having a 6-foot fluidized-bed height and no internal fins can process 13 blocks per day if fines are not burned in the primary burner.

6.46 Off-Gas Decontamination Studies. A 2-inch-diameter quartz fluidizing vessel was assembled. Graphite was burned at fluidized-bed temperatures as high as 930°C in the vessel. The vessel will be used to define the flow path of ruthenium in the off-gas equipment.

6.47 Solids Transport Studies. A literature study of solids transport devices applicable to headend processing of Ft. St. Vrain fuel was completed. Based on the survey, the most attractive pneumatic transport devices for each application were defined; and a program plan was outlined to obtain critical solids transport data such as flowability, erosion, and line sizes.

6.48 Secondary Burner Studies. The 2-inch-diameter Rover secondary burner was relocated in the Low-Bay Laboratory. A program plan for defining secondary burning requirements was developed, and secondary burner testing is in progress.

6.5 Effect of Loss of Cooling Air on Stored HTGR Fuel (B J. Newby)

The HTGR fuel will be stored in steel canisters having a lid with a metal-to-metal seal. The canisters will be cooled continuously with air to remove heat produced by fission product decay. Should the cooling air be shut off completely, the temperature of the fuel is expected to rise to about 1,100°F in two days and possibly higher over a longer period.

A study was carried out in the laboratory to determine the manner in which HTGR fuel stored in open containers would burn when subjected to various temperatures. Cylindrical pieces of reactor-grade graphite (approximately 1-inch diameter by 3-inches

long, weighing 70g) were used to simulate fuel. The graphite burned at a rate of 0.050 g/hr at 1,100°F, 0.51 g/hr at 1,200°F, 1.90 g/hr at 1,300°F, and a rate of 2.42 g/hr at 1,400°F. In closed containers, graphite will not burn at 1,400°F.

7. ICPP SAFETY REVIEW DOCUMENT

(D.E. Black, H.V. Chamberlain, W.R. Carpenter, G.K. Cederberg,
W.G. Morrison, R.L. Nebeker, C.W. Nielsen, W.L. Slagle,
A.D. Summers, M.K. Valentine, D.R. Wenzel)

Preparation of an ICPP Safety Review Document (SRD), a comprehensive safety review of ICPP systems and facilities, is in progress. This review is part of the AEC's "Fire, Safety, and Operating Continuity" effort, and its purpose is to determine if operations conducted at the ICPP result in hazards to (a) individuals working at the plant, (b) other persons at the INEL, or (c) populations beyond the perimeter of the INEL.

Two project milestones were fulfilled during FY-74. These were (1) issuing of Volume I of the SRD, which includes an introduction, INEL site description, and ICPP plant facilities, and (2) completion of a study on the flooding potential at the ICPP. The results of this flood study are summarized in Section I-7.1, following.

Work continued on the technical description of facilities and processes, effects of natural calamities (such as earthquakes, tornadoes, and volcanic actions), criticalities, and radiation exposures and shielding. The safety evaluation of two major systems -- "Semicontinuous Zirconium-Alloyed Fuel Dissolution" and "TBP Extraction" -- are essentially complete and will be issued early next fiscal year.

7.1 Flooding Potential at the Idaho Chemical Processing Plant

Flood evaluation studies are usually made by one of two methods. The water flow and flood crest records can be evaluated statistically and projected into the future to show flood crests and return periods for given time intervals^[13], or the maximum storm occurring under the worst conditions can be used to estimate the volume of water that falls as precipitation. The first method is most frequently used for zoning flood plains, planning water use, and evaluating flood hazards.

The current study considered both methods. Determining the maximum potential flood requires that a drainage basin be divided into subbasins. Then, infiltration and runoff is computed to make a flood hydrograph for each subbasin; then the discharge shown for each subbasin is routed into the main basin stream. Flood routing calculations (which consider infiltration, bank storage, channel storage, velocity, and distance) are made for the main stream. Thus, the maximum crest can be predicted for points downstream.

The Predicted Maximum Precipitation (PMP) storm refers to the maximum precipitation that could occur in an area in a given time span. This is based on the maximum amount of moisture that can be transported into a basin to be released as precipitation by natural atmospheric processes.

PMP storms were considered in this study, but specific flood routing calculations for the Pioneer Basin have not been made because of the limited time and funding available. Use of the geologic record and PMP studies for other Idaho basins allows an estimate of the maximum flood to be made, and the results are considered satisfactory.

On the basis of the comparative studies and on geologic evidence, the maximum Lost River flood crest at ICPP appears to have been between 20,000 and 30,000 cfs. On the basis of geologic and paleoclimate data, it appears that the last maximum flood occurred several thousand years ago in a wetter climate cycle, probably associated with one of the late glacial periods. Thus, a 30,000 cfs flood could also be considered to be the maximum Lost River flood which could occur, even with adverse changes in local climate, over periods of hundreds or thousands of years.

7.11 An Estimate of the Maximum (PMP) Thunderstorm. PMP calculations were made for a maximum thunderstorm in the Pioneer Basin for various summer months. The maximum storm would occur in the month of August and would cover about 539 square miles. The maximum rainfall -- 9.2 inches in one hour (normal annual rainfall is 8 inches) -- would cover about one square mile in the center of the storm. The rainfall would decrease to zero at the edge of the storm. An area about 23 by 28 miles would be covered; the general shape of the storm would be ellipsoidal. The total rainfall volume from this storm would be nearly 90,000 acre-feet. The average rainfall deposition would be about 3.1 inches over the storm coverage of 539 square miles.

It appears that more data on permeability, drainage patterns, and local storage in many small topographic depressions would have to be developed before meaningful subbasin hydrographs could be developed; therefore, no subbasin hydrographs or flood routing computations were made. However, the storm was placed at three locations in the Pioneer Basin to determine the worst threat to ICPP. The general knowledge of past runoff patterns coupled with a general knowledge of geology and topography were used to evaluate potential hazards.

Case 1. Storm Centered Over ICPP: About 3/8 of the available rain could drain past ICPP, while the rest will follow other local drainages to join the Lost River downstream of ICPP. The worst effect of a storm located here would be a sheet flood 6 to 8 inches deep. This would result from the rainfall east of Lincoln Boulevard moving to local drainages (as a sheet of water over the surface) and then to the Lost River.

Case 2. Storm Centered Upstream of the Lost River Flood Diversion Facilities within Pioneer Basin: About one inch of rain will fall at ICPP; thus sheet flooding should be negligible.

Case 3. Storm Centered Between the Lost River Flood Diversion Facilities and ICPP: This condition provides the maximum potential flooding at ICPP due to a PMP thunderstorm. When the isohyets with near maximum rainfall occur over ICPP, a general sheet flooding

estimated at between 2 and 3 inches in depth results. This sheet flood would last about an hour before subsiding. The main body of water would flow to the Lost River and could be evaluated as a Lost River flood. Assuming 90% runoff for the 2 hours of greatest rainfall, the projected flood crest would be about 35,000 cfs.

7.12 Effect of Man-Made Structures. Man-made structures upstream from ICPP were examined for possible flood threats to ICPP. A failure of Mackay Dam would result in a flood somewhat smaller than the estimated maximum Lost River flood. A failure of Dike 2, INEL Flood Diversion Facility, would result in a flood slightly less than the worst postulated PMP thunderstorm flood.

7.13 Flood Effects at ICPP. A stage-discharge curve, computed for the ICPP area, shows that during the maximum predicted flood, 35,000 cfs, water would be only a foot deep at the CPP-601/602 building complex. The building construction is amenable to sandbagging to protect against a 35,000 cfs flood. The water velocity around the buildings would be on the order of 3 to 6 miles per hour. This velocity would not be sufficient to cause serious erosion damage to roads, backfill around the buildings, or sandbag dams. The shallow water would preclude damage by floating objects (trees, timber, etc.).

7.14 Flood Return Periods. The primary objective of frequency analysis is to determine the recurrence interval of floods of a given magnitude. The average interval of time within which the magnitude of a given event will be equaled or exceeded is known as the recurrence interval, return period, or frequency.

Carrigan^[14] computed the flood crest and return periods of Lost River floods up to 5,400 cfs that had a return period of 300 years; his work is shown as the solid line on the flood-frequency graph (Figure 19). The maximum probable Lost River flood, 30,000 cfs, is

Fig. 19 Flood frequency at the INEL.

also plotted on the graph with a return period of 10,000 years. The frequency and crest of floods between these two points can be interpolated by the dashed line connecting Carrigan's curve with the maximum probable flood.

7.15 Flood Probability and Risk Analysis. The probability of a flood of a given magnitude occurring in any given year is an inverse function of its frequency. This relationship is shown by the equation

$$P = \frac{1}{T}$$

where P is the probability and T is the return period^[15]. Thus, the probability of a 35,000 cfs flood occurring (Figure 19) in any given year is:

$$P = \frac{1}{10,000} \text{ or } 0.0001 .$$

Most structures at ICPP are designed to be used for production or storage for many years. The simple one year probability must be modified to assess the flood risk over the design life of the structure. The probability of a flood of a given period occurring in the design life of a particular structure is given by the formula:

$$P' = 1 - p^N$$

where p is equal to the probability of a flood not occurring in a given year ($p = 1 - P$) and N is the design or expected life of a structure.

For example, consider a hypothetical shed to be used 10 years on the flood plain near ICPP. Assume it would be damaged by a 35,000 cfs flood. The return period of this flood is 10,000 years; therefore, the probability of damage in any one year (P) is 1/10,000 or 0.0001. The probability of its not being damaged in any one year (p) is: $1 - 0.0001 = 0.9999$, while the probability of its being damaged in its 10-year design life is:

$$P' = 1 - (0.9999)^{10} \text{ or } 0.0009996 .$$

II. WASTE MANAGEMENT

1. OPERATING EXPERIENCE IN THE LIQUID WASTE TANK FARM

1.1 Water Accumulation in Waste Storage Tank Vaults (M.D. Staiger)

The stainless steel waste tanks used for interim storage of radioactive plant wastes awaiting calcination are, in turn, contained in concrete vaults buried in the ground. These vaults are monitored for accumulation of liquid to give indication of possible tank leakage. Periodically, liquid has been found in the vaults, but analysis has shown it to be water which is jetted out and disposed of through the process equipment waste evaporator system. An investigation was made to determine the probable source of the water accumulation.

In the fall of 1973, ten monitoring wells were drilled in the tank farm area. These wells were drilled to lava rock (approximately 40 feet). The wells have been sampled semimonthly, and to date, water has been detected in only one well on two different samplings. Lack of water in the wells indicated that the water accumulation in various tank vaults did not result from underground water.

The manway to WM-190 tank vault (spare tank, not radioactive) was opened, and visual inspection of the vault interior was made. It was determined by this inspection that water entered WM-190 vault through a leaking roof. It was postulated that water was entering other vaults by a similar route. To confirm this, a test was conducted in which fluorescein dye was spread on the ground above several vaults. Fluorescein has appeared in WM-189 vault samples, thus confirming that water could have entered through the roof.

1.2 Leakage From Valves in the Waste Tank Farm Area (M.D. Staiger)

Radioactive liquid was found in the concrete vault which contains waste tank WM-185. This was jetted back to waste storage and an investigation was undertaken. Maintenance activities in several tank farm diversion boxes, containing valves which control the routing of waste solutions, uncovered failed gasket material. All of the deteriorated gaskets were made from "Teflon" gasket material. Asbestos fiber gaskets in the same service were found to be in satisfactory condition.

Failed gaskets allowed solution to leak from process piping into the diversion boxes. The diversion boxes drain to the tank vaults. It was from such a source that activity gained entrance to WM-185 vault.

2. OPERATING EXPERIENCE WITH THE IDAHO WASTE CALCINING FACILITY

2.1 The Sixth WCF Processing Campaign (S.S. Bodner)

At the ICPP, high-level radioactive aqueous wastes are produced during the reprocessing of spent nuclear fuel elements. After a short decaying period in stainless steel tanks, these wastes are converted to granular solids in the Waste Calcining Facility and stored in three, engineered, surface-storage facilities located near the WCF. The conversion of high-level radioactive aqueous wastes into the granular solid form presents several advantages: high volume reduction, reduced mobility (should leakage occur), reduced corrosion, and ease of retrievability. Since 1963, in six separate campaigns (as shown in Table XVI), over 2.7 million gallons of aluminum, zirconium, and stainless steel wastes have been converted to approximately 44,000 ft³ of solids. The sixth processing campaign in the WCF began on May 25, 1973, and terminated May 8, 1974.

TABLE XVI
HISTORICAL PRODUCTION SUMMARY OF THE WCF

<u>Period</u>	<u>Waste Processed (gal)</u>	<u>Solids Produced^[a] (ft³)</u>
12/8/63 to 10/15/64	511,000	7,600
4/1/66 to 3/24/68	989,000	14,600
8/14/68 to 6/3/69	329,000	5,600
8/3/70 to 1/5/71	225,000	4,600
9/23/71 to 5/11/72	300,000	5,300
5/25/73 to 5/8/74	386,000	6,500
Totals	2,740,000	44,200

[a] Includes solids produced during periods of processing nonradioactive waste.

The sixth WCF processing campaign followed a one-year period in which the facility was decontaminated, repaired, and modified. The production summary for the campaign is shown in Table XVII. Approximately 390,000 gallons of zirconium, aluminum, and stainless steel wastes were converted to about 6,500 ft³ of solids (including solids produced during periods of processing nonradioactive waste). The campaign consisted of 8,357 hours (349 days) which included 2,336 hours (98 days) of unscheduled downtime and 681 hours of

TABLE XVII

WCF PRODUCTION SUMMARY FOR RUN H-6

<u>I. Liquid Waste Origin</u>	<u>Volume (gal)</u>	<u>Type</u>
WM-189	159,300	Zr
WM-188	113,100	Zr
WM-183	109,600	Al
WM-106	4,200	SS
Total	386,200	
<u>II. Time Distribution</u>		
Date WCF Radioactive Processing commenced - May 25, 1973		
Date WCF Radioactive Processing terminated - May 8, 1974		
Total hours Radioactive Processing Time - 5339.5		
Total hours down time and Nonradioactive Waste - 3017.5		
On stream efficiency - 64%		
<u>III. Chemical Utilized</u>	<u>Total</u>	
Gaseous Oxygen	24,300,000 scf	
Calcium Nitrate	402 tons	
Kerosene	160,750 gal	
Nitric Acid	366,800 lb	
Aluminum Nitrate	522,000 lb	
Boric Acid	4,600 lb	
<u>IV. Feed Data - Radioactive Operation</u>	<u>Total (gal)</u>	<u>Rate (gpd)</u>
Net feed to WCF	386,200	1730
Additives to feed	117,300	530
Recycle	101,400	460
Gross feed to calciner	604,900	2720
<u>V. Solids Storage</u>		
Volume of Solids Produced - 6500 ft ³		
Volume reduction factor, radioactive Run H-6 - 7.9		

operation on nonradioactive waste. This resulted in an on-stream factor of 64%. The average gross feed rate to the calciner was 2,720 gpd during periods of radioactive waste processing; the net tank farm depletion rate averaged 1,620 gpd for the zirconium waste, 2,110 gpd for the aluminum waste, and 1,680 gpd for the stainless steel waste. The difference between the gross and net feed rates is a result of jet dilution during transfers, recycled scrub solution, and chemical additives.

Failure of the bellows seals on feed control valves caused two shutdowns for a total of approximately seven weeks downtime. Plugging of the primary cyclone and equipment vent condenser caused a third shutdown which lasted another seven weeks. Feed valves and feed and fuel nozzles were replaced during two of the shutdowns. The calciner operated at about 2/3 normal feed rate for approximately two months due to failure of the bellows on one feed line. During the last six weeks of the campaign, the calciner operated at about 1/2 normal feed rate due to air leakage into the calciner system, plugging in the air transport system, and high pressure drop across the filters.

2.2 Decontamination Experience in the WCF (A.G. Westra, J.E. Johnson)

Waste Calcining Facility decontamination efforts during FY 1974 were evaluated to determine which methods were most effective, and how decontamination could be improved in the future. During February 1974, the calciner cell was decontaminated to repair the calciner feed-control valves. At that time, several of the most promising decontamination techniques were used and evaluated.

First, a dolomite startup bed was fluidized in the calciner vessel to remove radioactive contaminants by abrasive action. This method was found to be a moderately effective initial step for decontaminating the calciner vessel. Then, hot 5 M HNO_3 /0.3 M ANN solution was used to dissolve the residual calcine in the calciner vessel, the dry cyclone, and the product takeoff and transport air lines. This was also successful. Finally, a sequence of 5 wt% Turco 4502, 5 wt% oxalic acid, and 5 M HNO_3 was used in the calciner vessel in an attempt to further reduce radiation fields in the calciner cell. Each solution was heated in the makeup tanks before being transferred to the calciner vessel and was maintained at boiling temperature by steam sparging. The sequence was repeated seven times, with only a small reduction in the radiation fields per cycle.

As a result of the evaluation of this and prior WCF decontamination experience, it was concluded that: (a) more effort should be spent monitoring the effectiveness of chemical treatments employed, so that ineffective treatments can be abandoned earlier in favor of potentially more effective treatments; (b) spent decontamination solutions should be sampled and analyzed more frequently to determine the progress of decontamination and to identify the radionuclides which are being removed; and (c) more uniformity should be obtained in radiation survey methods.

Three decontamination treatments which are potentially more effective than the ones used in the past are:

- (1) 6% Turco 4502 followed by a water rinse and then by 1 M HNO_3 /0.3 M hydroxylamine sulfate
- (2) 2 M HNO_3 /0.05 M KMnO_4 followed by either 0.9 M oxalic acid or 1 M HNO_3 /0.3 M hydroxylamine sulfate
- (3) 0.4 M oxalic acid/0.1 M HF /0.05 M H_2O_2 .

These will be tested in future WCF decontamination programs.

2.3 Sealants for WCF HEPA Filters (B.J. Newby)

During startup of the WCF in the sixth processing campaign, HEPA filter material tore loose from the filter frame after being subjected to WCF off-gas for about 10 days. The polyurethane material used to seal the filter material to the frame had deteriorated badly. Prior to exposure to the WCF off-gas, the sealant was pliable (similar to foam rubber or cork) and could be torn apart, but did not disintegrate when squeezed with tweezers. After exposure to WCF off-gas, the sealant was so brittle that it disintegrated when a "squeezing" pressure was applied.

The WCF off-gas operating conditions during the ten-day exposure of the filters were as follows: (a) water condensed on the filters, (b) the filters were operated at about 60°C, and (c) the maximum nitrogen dioxide content of the gas was about 2% by volume (2 mole%). Using nitric acid vapor-liquid curves, calculations indicated that the water condensed on the filter could be as high as 12.4 M in nitric acid after equilibrium was reached with the nitrogen dioxide in the off-gas.

Laboratory tests were made under simulated WCF off-gas conditions on the polyurethane sealant and on two materials that the manufacturer was considering as possible sealant on HEPA filters – a silicone sealer and a rubber base adhesive, Z-743. The three different materials were exposed to 4 M nitric acid and to dry air containing 2% by volume nitrogen dioxide at 60°C. After exposure to the nitric acid: (a) the polyurethane sealant, after 2 days, became so brittle that it disintegrated when squeezed with tweezers; (b) the rubber base adhesive became equally brittle after 6 days; and (c) the silicone sealer contained a few small blisters and had decreased elasticity after 14 days. After exposure to nitrogen dioxide: (a) the surface of the polyurethane sealant became powdery but the interior of the sealant had not deteriorated after 10 days, (b) the rubber base adhesive turned black and had decreased elasticity after 14 days, and (c) the silicone sealer was unaffected after 14 days. Based on these results, the silicone sealer is considered to be superior to the other two materials for use on HEPA filters in the WCF.

3. SUPPORT STUDIES FOR WCF OPERATIONS

3.1 Problems with Calcium Nitrate as an Additive to Zirconium Waste (B.J. Newby)

Calcium nitrate is added to ICPP zirconium waste prior to calcination in the WCF to prevent fluoride volatilization. The vendor of the calcium nitrate $[\text{Ca}(\text{NO}_3)_2]$ used at the ICPP currently adds an organic material to the product to make it less prone to agglomeration. The calcium nitrate is used at the ICPP as a saturated aqueous solution, prepared by dissolving in an agitated solution at 60 to 80°C, transferring to a hold tank, and

allowing to cool to ambient temperature. The organic material forms a floating scum or grease (in the nonagitated hold tank) that coats the sides and heating coils as the tank is drained. Studies were performed: (a) to find a $\text{Ca}(\text{NO}_3)_2$ without an organic coating that could be used at the ICPP, (b) to find a calcium-containing substitute for $\text{Ca}(\text{NO}_3)_2$, and (c) to examine the properties of the organic material on the $\text{Ca}(\text{NO}_3)_2$ now used at ICPP in order to cope with problems that its presence in equipment might cause.

3.11 Search for Calcium Nitrate Without a Coating. Two samples of $\text{Ca}(\text{NO}_3)_2$, reportedly free from hydrocarbon, were tested to see if they could be substituted for $\text{Ca}(\text{NO}_3)_2$ now used at ICPP. Saturated aqueous solutions of the two samples were prepared. The saturated aqueous solution of the first sample (A) contained about as much visible, water-insoluble material as similar solutions prepared from the $\text{Ca}(\text{NO}_3)_2$ now used at the ICPP; the solution of the second sample (B) contained just enough insoluble material to color the solution brown and amounted to only 0.009% of the total weight of $\text{Ca}(\text{NO}_3)_2$. Table XVIII shows that Sample B of $\text{Ca}(\text{NO}_3)_2$ contains the same amount of calcium, slightly more chloride, and much less carbon than either sample A or the $\text{Ca}(\text{NO}_3)_2$ now used at the ICPP. It was recommended that the $\text{Ca}(\text{NO}_3)_2$ represented by Sample B replace the $\text{Ca}(\text{NO}_3)_2$ now used at the ICPP. However, the fact that both Samples A and B were supposed to represent $\text{Ca}(\text{NO}_3)_2$ free from hydrocarbon, yet only one was acceptable, demonstrates how easy it might be to receive $\text{Ca}(\text{NO}_3)_2$ that is undesirable. If possible, random samples from each shipment should be analyzed for carbon before acceptance and should be required to contain <0.001 wt% carbon.

TABLE XVIII

CHEMICAL ANALYSES OF CALCIUM NITRATE SPECIMENS

$\text{Ca}(\text{NO}_3)_2$ Source	Ca (wt%)	Cl (ppm)	C (wt%)
$\text{Ca}(\text{NO}_3)_2$ used at ICPP	18.8	4.6	0.034-0.074
Sample A $\text{Ca}(\text{NO}_3)_2$	18.9	6.8	0.031
Sample B $\text{Ca}(\text{NO}_3)_2$	18.9	8.0	<0.001

3.12 Possible Calcium Nitrate Substitutes. Calcium oxide (CaO) was examined as a substitute for $\text{Ca}(\text{NO}_3)_2$. Addition of solid CaO directly to zirconium waste is not recommended because the volume of precipitate is three times greater (extra precipitate caused by hydroxide formation) than when solid $\text{Ca}(\text{NO}_3)_2$ is added. Calcium oxide can be added to nitric acid solution which can then be added to zirconium waste to give satisfactory results. The reaction of CaO with nitric acid is vigorous, but a clear solution results; both chemicals are readily available, and the cost is comparable to the cost of $\text{Ca}(\text{NO}_3)_2$. Additional laboratory work was not done to define conditions for preparation of $\text{Ca}(\text{NO}_3)_2$ solution from CaO because a source of $\text{Ca}(\text{NO}_3)_2$ free from hydrocarbons was located.

3.13 Properties of Organic Coating Material on Calcium Nitrate. Infrared examination of the organic material (grease) obtained from the dissolution of $\text{Ca}(\text{NO}_3)_2$ in water showed that the grease is a long-chain hydrocarbon containing some silicon-to-carbon bonds; a spectrochemical analysis showed silicon to be the only element (besides carbon) present in greater than trace quantities. The melting point of the grease is 33 to 35°C. Calcium nitrate stored at the ICPP is contained in either paper or plastic bags, representing different batches; samples from 5 paper bags and from 5 plastic bags were analyzed for carbon (Table XIX). Grease obtained from deposits in the plant about 8/9/73 analyzed 58 wt% carbon while grease obtained on 9/11/73 analyzed 81% carbon. This may indicate difficulty in obtaining a representative analytical sample rather than a variation of grease composition.

TABLE XIX
CARBON CONTENT OF ICPP CALCIUM NITRATE SAMPLES

<u>Sample No.</u>	<u>Source of Sample</u>	<u>Wt% Carbon</u>
1	Plastic Bag	0.041
2	Plastic Bag	0.034
3	Plastic Bag	0.036
4	Plastic Bag	0.074
5	Plastic Bag	0.061
6	Paper Bag	0.060
7	Paper Bag	0.044
8	Paper Bag	0.057
9	Paper Bag	0.048
10	Paper Bag	<u>0.039</u>
Average		0.049

Organic material was observed in solutions prepared on a laboratory scale by dissolving plant $\text{Ca}(\text{NO}_3)_2$ in water (saturated solutions being 3.94 M calcium). Plant $\text{Ca}(\text{NO}_3)_2$ was added to zirconium waste (to give a Ca-to-F mole ratio of 0.55) as a 3.94 M aqueous solution and as a solid, at 24°C and 60°C. No differences in properties were observed between the calcium fluozirconate precipitates formed by the different procedures, nor were any differences observed in calcium fluozirconate precipitates formed from $\text{Ca}(\text{NO}_3)_2$ with and without organic material. Organic material was not observed in the precipitates or the supernatant liquid. Small quantities (several pea-sized globules) of grease have been observed floating in the unheated 350-liter feed hold tank on a 12-inch pilot-plant calciner after several days of operation. These small grease globules have not caused any problems in the pilot plant and would be dispersed if the feed were heated to 50°C. Long-term buildup and possible decontamination problems cannot be duplicated in the laboratory or pilot plant.

The solubility of organic material obtained from the dissolution of $\text{Ca}(\text{NO}_3)_2$ in water at the ICPP was measured in various solvents for possible use in the event the material caused plugs in lines or valves. Solvents tried were: benzene, 17.8 M sulfuric acid, 14.7 M ortho phosphoric acid, 17.4 M acetic acid, 15.7 M nitric acid, kerosene, 5.9 M sulfuric acid, 8.9 M sulfuric acid, 1 vol 17.8 M sulfuric acid - 1 vol 15.7 M nitric acid, 6 M sodium hydroxide, 14.3 M ammonium hydroxide, and zirconium waste solution. Of the solvents tried, the organic material is most soluble in benzene, followed by 17.8 M sulfuric acid, 14.7 M phosphoric acid, and 17.4 M acetic acid, respectively. Of these solvents, acetic acid would be preferred. The acetic acid would mix with the waste, would not pose calcination problems (from past experience, waste containing phosphate or sulfate is difficult to calcine), and could be burned off during calcination.

An estimate of the solubility of the $\text{Ca}(\text{NO}_3)_2$ grease in zirconium waste solution was obtained by carbon analysis of a simulated zirconium waste solution which had been contacted with a large quantity of grease [obtained from the WCF $\text{Ca}(\text{NO}_3)_2$ hold tank] for 2 days at 50°C. The solubility of the grease in the waste is approximately 0.1 g/l. On this basis, if solid $\text{Ca}(\text{NO}_3)_2$ containing 0.07 wt% organic material (grease) is added to the waste, only 40 to 60% of the grease will actually dissolve. The remaining undissolved grease will be dispersed as an emulsion in the calcium-fluozirconate solution.

Kerosene was ineffective in removing the organic layer. Scoping studies to see if the organic material could be removed from $\text{Ca}(\text{NO}_3)_2$ by burning were not promising. The grease partially burns in a flame but will not support combustion; the ash remaining is partially soluble in 2 M nitric acid. Calcium nitrate loses its pellet form and is converted into a hard solid mass when heated at 200°C or above. Thus, if organic material was burned from $\text{Ca}(\text{NO}_3)_2$, the latter would have to be dissolved in water to be transported, or scraped from the vessel in which the organic material was burned, and then crushed. A 3.94 M calcium aqueous solution (concentration used in the plant) can be prepared by dissolving $\text{Ca}(\text{NO}_3)_2$ that has been heated at 450°C for 2 hours, or the fused calcium nitrate can be dissolved in zirconium waste to give the desired calcium-to-fluoride mole ratio of 0.55.

The grease obtained from $\text{Ca}(\text{NO}_3)_2$ dissolution in water burns in a flame but stops burning when the flame is removed. Some of the grease was heated with an external source in a stainless steel batch calciner between 24 and 500°C and then held at the latter temperature for about an hour with air being used as a sweep gas at all times. Observation of the glass off-gas line immediately above the calciner indicated that the grease melted, boiled to dryness, and the residue charred. No particulate deposits were observed in the glass off-gas line, on a sintered-glass filter in the off-gas line (porosity of 40 to 60 microns), or in a water scrubber at the end of the off-gas line. Off-gas samples were collected while the grease was being heated between 24 and 500°C; and at 500°C, the carbon-containing gases (other than CO and CO_2) were essentially one- or two-carbon chain fragments; but 3-to-8 carbon chain fragments were also found. The ash remaining after the calcination of $\text{Ca}(\text{NO}_3)_2$ grease at 500°C is partially soluble in 2 M nitric acid; much of the remaining ash settles out of solution and is readily dispersed. Thus, suspended ash in WCF off-gas scrubbers can be recycled easily to the hold tanks.

3.14 Effect of Detergent. A 3.94 M $\text{Ca}(\text{NO}_3)_2$ solution was prepared, containing 2g of Chemical Rubber Company's "New Formula Washermix" per 100 ml of water. Without the detergent, the organic material would have settled out within several hours; with the detergent present, the organic material remained in suspension.

An aqueous solution of Tide has been used to remove grease from the walls of the vessel in which saturated solutions of calcium nitrate are stored and could possibly be used in case plugs occurred within the system piping. A laboratory study was made to determine the effect of Tide on the stability of zirconium waste, with and without $\text{Ca}(\text{NO}_3)_2$ added.

The stability of simulated zirconium waste solutions containing 2-1/2 g/l of Tide [with and without $\text{Ca}(\text{NO}_3)_2$ added to give a calcium-to-fluoride mole ratio of 0.55] was observed for one week at 24°C. Solutions without $\text{Ca}(\text{NO}_3)_2$ were stable for 5 to 24 hours after Tide addition. Once solids formed, the quantity did not seem to increase between 1 and 7 days. The quantity of solids found in waste without $\text{Ca}(\text{NO}_3)_2$ was 12 cc/l (1.1 g/l); in waste containing $\text{Ca}(\text{NO}_3)_2$, the quantity of solids was about 1.5 times greater. The limit of solubility for Tide in zirconium waste is about 2-1/2 g/l. The solids in solutions without $\text{Ca}(\text{NO}_3)_2$ were high in zirconium, tin, and phosphorus (probably phosphate supplied by the Tide). Phosphate solids were also present in wastes to which $\text{Ca}(\text{NO}_3)_2$ was added.

3.2 Mechanism of Ruthenium Contamination in the WCF (C.A. Allen)

Volatile species of fission product ruthenium deposit in the upper part of the calciner vessel and in the high-temperature off-gas line in the WCF. Removing these deposits during decontamination has become increasingly difficult, causing increased personnel radiation exposure and equipment downtime. This problem requires special attention now because (a) the new WCF should incorporate features to reduce the problem, and (b) the HTGR fuel raffinate will contain higher ruthenium concentrations.

Parallel programs aimed at reducing decontamination time have begun. These include determination of the contamination mechanism and use of this to generate improved decontamination techniques.

A literature search covering the period from 1935-1973 was conducted on ruthenium behavior as it applies to waste calcination. Over 300 abstracts were collected and indexed by subject, and this file is available for local use.

This literature, the WCF decontamination log books, and conversations with individuals directly involved in calciner decontamination led to a theory of the contamination mechanism. The proposed mechanism consists of an accelerating cycle of deposition, diffusion, and corrosion. It is assumed that volatile ruthenium species formed during in-bed combustion at 500°C and deposited on stainless steel walls in the range between 450°C and 500°C for several months will penetrate the surface below the passive oxide layer by grain boundary diffusion. Only corrosive reagents capable of widening the grain boundaries would be effective decontaminants. The pitted surface then allows more

deposition and deeper penetration during the next processing period. If this correctly describes the mechanism, either substantial decontamination corrosion must be accepted; or major process changes in the WCF must be instituted to reduce deposition. The extent of this mechanism will be investigated in the laboratory.

Baffle-plate samples removed from the calciner vessel will be examined to detect ^{106}Ru penetration. These samples have been extensively decontaminated, subjected to serious corrosion and abrasion, and are two years old, but may provide qualitative information concerning the credibility of the diffusion mechanism.

Coupons of Type 304L, 347 and 310 stainless steels, which represent the materials in the current and planned calciner vessels and hot off-gas lines, will be put through a series of one to ten simulated decontaminations with three reagent systems. Corrosion will be measured by weight loss and microscopy. Ruthenium-103 will be deposited on the coupons in a specially fabricated vessel simulating a calciner. Half of the samples will be held for 90 days at 550°C , and the relative effects of deposition and diffusion will be determined. Scanning-electron microscope analysis will show if ruthenium accumulates in the grain boundaries. Diffusion coefficients and deposition quantities will be correlated with corrosion due to type and number of simulated decontamination treatments.

If these experiments verify the deposition-diffusion-corrosion mechanism, effort can be focused on process variables which will prevent ruthenium volatility or control deposition to specified removable areas.

3.3 Removal of Ruthenium from Scrubbed Calciner Off-Gas with Solid Sorbents (B.J. Newby)

Volatile ruthenium is currently removed from scrubbed calciner off-gas in the WCF with Davison Chemical's Grade 40 silica gel. A new fluidized-bed calciner being proposed will process wastes with higher ruthenium concentrations and at higher rates, presumably producing more volatile ruthenium to be trapped. Studies are underway to obtain improved ruthenium sorption from calciner off-gas using solid sorbents. In addition to sorbing ruthenium, sorbents must be resistant to calciner off-gas. All sorbents tested were either described in the literature as being nitric-acid resistant and effective in removing ruthenium from media different from calciner off-gas or were recommended by leading vendors of exchange and adsorption resins as possible solutions to the problem.

3.31 Procedures and Equipment. Simulated calciner off-gas was generated in the laboratory by continuously vaporizing a ruthenium-containing simulated waste in a small static calciner. Evaporation of the simulated waste, which was injected into the calciner by means of a syringe pump, was essentially instantaneous and took place on a perforated stainless steel surface at 400°C . The simulated waste fed to the calciner was 6.6 M nitric acid, 0.02 g/l ruthenium as the trichloride, and 1 to 7×10^{-3} m Ci/ml of Ruthenium-103 trichloride tracer. Concurrent with injection and evaporation of the simulated waste, preheated air was metered into the calciner, sweeping the waste vapors out of the calciner and through a column of the adsorbent. Ruthenium removal efficiency of an adsorbent column was determined by measuring the concentration of radio-ruthenium in the calciner

off-gas before and after the resin column. An attempt was made to maintain the resin at 80°C (slightly above the dew point of the calciner off-gas); however, in some cases, reaction of the off-gas with the resin made it impossible to maintain a steady-state temperature of 80°C. The depth of the resin in the column was 26 inches; the superficial vapor velocity of calciner off-gas through the resin column was 0.4 or 0.7 ft/sec. Composition of the calciner off-gas as it left the calciner (at 400°C) was approximately (mole fraction): 0.59 N₂, 0.21 H₂O, 0.17 O₂, 0.010 NO, and 0.018 NO₂. Ruthenium removal from off-gas was determined for each hour during 3 hours of column operation, unless the operation was for less than an hour, in which case ruthenium removal was determined over the entire period.

3.32 Adsorption-Desorption Results.

Silica Gels: The ICPP purchased Grade 40 silica gel from Davison Chemical Division of W.R. Grace and Company for the initial charge used in the WCF. Since this initial purchase, Davison has modified their methods for manufacturing Grade 40 silica gel to give improved water and hydrocarbon removal characteristics. Table XX shows that these modifications have resulted in a Grade 40 silica gel that gives lower ruthenium decontamination from calciner off-gas and does not sorb ruthenium effectively at as high a vapor velocity as did the original Grade 40 silica gel. Grade 407 gives about the same ruthenium sorption characteristics as Grade 40; Grade 81 is a less effective ruthenium sorber. Other experiments showed that Grade 40 silica gel, as received, must be heated to 180°C before it will produce ruthenium decontamination factors greater than 100, but that ruthenium removal is not improved by treating the gel with hot water or nitric acid before heating. About 47% of the ruthenium sorbed on Grade 40 silica gel can be removed by washing with hot water. The silica gels were resistant to calciner off-gas.

TABLE XX

RUTHENIUM REMOVAL FROM CALCINER OFF-GAS WITH DAVISON'S SILICA GELS

<u>Silica Gel</u>	<u>Superficial Vapor Velocity (ft/sec)</u>	<u>Typical Ruthenium Decontamination Factors</u>
Old Grade 40	0.4	100-1500
	0.7	1000-3000
Current Grade 40	0.4	110-300
	0.7	2-90
Grade 407	0.4	120-300
	0.7	16-200
Grade 81	0.4	16-48

Acid Resistant Molecular Sieves (Zeolites): Acid resistant zeolites (mordenites and chabazites) were subjected to calciner off-gas for 3 hours. All of the zeolites were resistant to off-gas but gave poor decontamination factors (see Table XXI). By successively treating Zeolon-200 with hot water, nitric acid, acetic acid, sulfuric acid, sodium nitrate, and sodium hydroxide, 32% of the ruthenium sorbed on the exchanger from off-gas was removed.

Organic Ion Exchangers: The currently most popular organic ion exchangers [phenolic-based and styrene-divinylbenzene (DVB) exchangers], as well as an organic exchanger converted to a copper sulfide exchanger, were scoped to determine their ruthenium sorption characteristics and resistance to off-gas. None of the exchangers were sufficiently resistant to calciner off-gas to be used. Table XXII lists the exchangers scoped as well as ruthenium removal obtained. Lack of resistance to test conditions and/or reaction of exchangers caused some of the tests to be terminated in less than 3 hours.

Miscellaneous: A hydrous zirconium oxide gel gave excellent ruthenium removal from off-gas and was resistant to off-gas (see Table XXIII). However, treating this gel successively with hot water, nitric acid, acetic acid, sulfuric acid, sodium nitrate, and sodium hydroxide removed only 22% of the ruthenium sorbed on the gel. The gel costs approximately 40 times more than Grade 40 silica gel. An impregnated alumina showed promise as a ruthenium sorber giving ruthenium decontamination factors of slightly greater than 100 over a superficial vapor velocity range of 0.4 to 0.7 ft/sec. Treating the ruthenium contaminated alumina successively with hot water, nitric acid, acetic acid, sulfuric acid, sodium nitrate, and sodium hydroxide removed 91% of the ruthenium. Porous Glass Code 7930 gave low ruthenium decontamination from off-gas.

3.33 Conclusions. A number of sorbents were scoped to determine their ruthenium sorption efficiency from simulated calciner off-gas and their resistance to the off-gas. Of the sorbents scoped, Bio-Rad HZO-1 (a hydrated zirconium oxide gel), Nusorb 1511 (an impregnated alumina), and Davison's silica gels Grade 40 and 407 showed the most promise. Some of these sorbents will be studied in more detail to determine their potential as a sorbent of ruthenium from scrubbed calciner off-gas in the new ICPP calciner.

TABLE XXI

RUTHENIUM REMOVAL FROM CALCINER OFF-GAS WITH ACID-RESISTANT
MOLECULAR SIEVES

Molecular Sieve	Vendor	Superficial Vapor Velocity (ft/sec)	Ruthenium Decontamination Factors
Zeolon-900 (Na ⁺ form)	Norton Co.	0.7	6-63
Zeolon-900 (H ⁺ form)	Norton Co.	0.7	10-70
Zeolon-200 (H ⁺ form)	Norton Co.	0.7	3-170
		0.4	12-103
AW-300	Union Carbide	0.7	2-19
AW-500	Union Carbide	0.7	5-150

TABLE XXII

RUTHENIUM REMOVAL FROM CALCINER OFF-GAS WITH ORGANIC ION EXCHANGERS

(Superficial Vapor Velocity-0.7 ft/sec)

Exchanger	Vendor	Exchanger Description	Off-Gas Time Through Exchanger	Ruthenium Decontamination Factors
Duolite A-6	Diamond Shamrock Chemical Co.	Phenolic-based, weakly basic, anion exchanger	20 min	3.2
Duolite C-3	Diamond Shamrock Chemical Co.	Phenolic-based, strongly acidic, cation exchanger	2 hr	4,000-19,000
Duolite CS-100	Diamond Shamrock Chemical Co.	Phenolic-based, weakly acidic, cation exchanger	2 hr	2-17,000
Duolite S-30	Diamond Shamrock Chemical Co.	Phenolic-based limited ion-exchange capacity	30 min	650
Copper Sul- fide Ex- changer	Organic Exchanger used to prepare Copper Sulfide Ex- changer from Rohm & Haas	Organic starting exchanger was styrene-dvb, 1 hr strongly basic, anion exchanger	1 hr	>2,500
MB-1	Rohm & Haas	Styrene-dvb, mixture of strongly acidic- basic, cation-anion exchanger	1 hr 36 min	>2,100
Desiccant Resin 810	Dow Chemical Co.	Styrene-dvb, strongly acidic, cation exchanger	3 hr	520-1,100

TABLE XXIII

RUTHENIUM REMOVAL FROM CALCINER OFF-GAS WITH MISCELLANEOUS MATERIALS

<u>Material</u>	<u>Vendor</u>	<u>Material Description</u>	<u>Superficial Vapor Velocity (ft/sec)</u>	<u>Ruthenium Decontamination Factors</u>
Bio-Rad HZO-1	Bio-Rad Laboratories	Hydrous zirconium oxide gel	0.7	3,500-11,500
Nusorb 1511	Nuclear Consulting Services Inc.	Impregnated alumina	0.4	99-112
			0.7	107-140
Porous Glass Code 7930	Corning Glass Works	Porous glass	0.4	24-60

3.4 Stability Testing of Calcines for Storage (M.W. Wilding)

Calcine produced at the ICPP is stored in stainless steel bins. To assure that this calcine can be removed at some future date, if desired, the temperature resulting from the heat of radioactive decay must be low enough to avoid agglomeration of the particles by sintering. Thus, it is necessary that the sintering temperature be known for each type of calcine so that proper storage conditions can be specified.

To determine the sintering temperature, synthetic calcine (approximately 200 g) is placed in a quartz combustion tube furnace and heated at constant temperature. If significant agglomeration occurs because of sintering, the temperature is lowered; and the experiment is rerun with a fresh sample of calcine. This procedure is repeated until only mild agglomeration occurs. Mild agglomeration is considered to be when the agglomerated particles fall apart and flow freely as the combustion tube containing the sample is tapped slightly. The results of experiments using five different calcine samples are shown in Table XXIV.

TABLE XXIV
SINTERING TESTS OF VARIOUS CALCINES

<u>Types</u>	<u>Results</u>
Unblended zirconium	700°C - No agglomeration in 15 days Mild agglomeration in 95 days
7 volumes zirconium- 1 volume stainless steel sulfate	800°C - No agglomeration in 3 days Agglomeration in 30 days 700°C - Mild agglomeration in 30 days
10 volumes zirconium- 1 volume stainless steel sulfate	800°C - No agglomeration in 3 days Agglomeration in 30 days 700°C - Mild agglomeration in 60 days
3 volumes zirconium- 1 volume second-cycle (Ca/F mole ratio - 0.55)	700°C - No agglomeration in 30 days
3 volumes zirconium- 1 volume second-cycle (Ca/F mile ratio - 0.7)	700°C - Agglomeration in 30 days 550°C - Mild agglomeration in 30 days 500°C - No agglomeration in 30 days

Based on the results of these studies, the calcines tested can be stored in a retrievable condition at the following temperatures:

- (1) Zirconium calcine (unblended), at slightly below 700°C
- (2) Zirconium - stainless steel sulfate (blended 7:1 and 10:1), at slightly less than 700°C
- (3) Zirconium - second-cycle (with a Ca/F mole ratio of 0.55), at 700°C
- (4) Zirconium - second-cycle (with a Ca/F mole ratio of 0.7), at slightly less than 550°C.

3.5 Corrosion Monitoring in the Solid Waste Storage Bins (T.L. Hoffman)

High-level radioactive aqueous wastes resulting from the solvent extraction of uranium from nuclear fuel elements are calcined to granular solids in the Waste Calcining Facility at the ICPP. The granular solids are stored in stainless steel bins which in turn are contained inside buried concrete vaults. This arrangement provides double containment and enables detection of failure of the primary containers or seepage of surface or ground water through a fissure in the concrete vault.

The primary bases for selection of materials for bin construction were lifetime requirements and overall cost. Due to the long-lived fission products (particularly Strontium-90 and Cesium-137), a bin lifetime of at least 500 years was considered desirable before release of the solids from storage to the open environment could be considered.

The second solids-storage facility consists of a circular concrete vault holding seven vertically-arranged cylindrical metal bins. Each is 12 feet in diameter and 42 feet high. The bins, which are constructed of ASTM-SA-240-61T Type 304 stainless steel, have 1/4-inch-thick walls, including a 1/8-inch allowance for corrosion protection.

A long-term corrosion testing program has been instituted for monitoring these storage bins. Existing corrosion information on metal alloys suitable as possible construction material for calcined-solids storage bins has been obtained from laboratory tests lasting only 10 years or less. To obtain actual "in-service" results, 160 plant-test coupons were hung on ten cables in two of the storage bins. Each cable had 16 sample coupons, four each of four different alloys – Types 405, 304, and 304L stainless steels and Type 1025 carbon steel. It was planned that one cable from each bin be withdrawn on the 5th, 10th, 20th, 40th, and 80th year of solids storage, and that the samples would be examined and measured for corrosion effects. The test results would be used for more accurate determination of the expected lifetime of the bins and for the design of future solids-storage bins.

During October 1973, the first sets of corrosion coupons were removed from two bins in the second solids-storage facility. One bin contained alumina calcine solids and the other zirconium calcine solids. In both the alumina and zirconium calcine bins, Type 1025 carbon steel suffered the most corrosion, with progressively decreasing amounts on Types 405, 304, and 304L stainless steels. The corrosion data, extrapolated to forecast the 500-year corrosion losses in alumina calcine, showed thickness losses of 36, 26, 5, and 4 mils, respectively. Similarly, in zirconium calcine storage service, the 500-year forecast corrosion losses are 12, 7, 1, and 2 mils for Types 1025, 405, 304, and 304L steels, respectively.

Of general significance is the fact that the corrosion coupons were free of adherent calcine and salt-caking. Further, the expected high frictional forces between the coupons and the calcine solids, upon withdrawal of the coupon cable, were not experienced; the coupons were withdrawn easily. These observations indicate that the stored calcine is free flowing and retrievable.

3.6 Storage Requirements for Future Calcines (R.E. Schindler)

The decay-heat generation rate of calcines solids from future fuel reprocessing wastes at the ICPP is expected to increase for three reasons: (1) the ATR recycle program will nearly double the burnup of the aluminum fuel reprocessed at ICPP, (2) the fuel reprocessing schedule proposed for the early 80's contains nearly all coprocessing runs; coprocessing wastes have higher fission-product concentrations than most of the current ICPP wastes, (3) the increased calcining capacity of the New Waste Calcining Facility will allow a reduction in liquid-waste and fuel inventories, leading to the calcination of shorter-cooled wastes. The storage of calcined solids with increased decay-heat generation rates will require either bins of smaller diameter or alternative designs with increased decay-heat dissipation capacity. Annular bins are a promising alternative. A program is being initiated to evaluate design alternatives for future calcined-solids storage facilities.

4. SUPPORT STUDIES FOR FUTURE FLUIDIZED-BED CALCINING OPERATIONS

4.1 Calcination of Stainless Steel Sulfate Waste (A.S. Neuls)

A flowsheet for the calcination of stainless steel sulfate waste (SS-SO_4) was successfully developed in the pilot plant and demonstrated in the WCF. The flowsheet consists of blending one unit volume of SS-SO_4 waste with 6.7 volumes of first-cycle zirconium fluoride waste (ZFW). This blend ratio would result if 37,000 gallons of SS-SO_4 waste (the total inventory on January 1) were blended with 248,000 gallons of ZFW waste in a single liquid waste storage tank. Between January 16 and February 6, 5,000 gallons of SS-SO_4 waste were calcined in the WCF using the flowsheet.

4.2 Calcination of Stainless Steel Electrolytic Waste (D.G. Swink)

Scoping runs in the 4-inch pilot-plant calciner, using in-bed combustion heating, demonstrated the feasibility of calcining stainless steel electrolytic waste when blended with 3, 5, and 10 parts of first-cycle zirconium fluoride waste. Calcination of a 1:1 blend of electrolytic and zirconium wastes and of straight electrolytic waste were unsuccessful because of excessive fines carry-over caused by the attrition of the soft product. Calcination of the 1:3 blend of electrolytic-to-zirconium wastes gave a product-to-fines ratio of 3.95 over a 16-hour run, which achieved a 55% bed turnover. The 1:10 electrolytic-to-zirconium blend gave a product-to-fines ratio of 2.7 over a 40-hour run (84% bed turnover). Both these blend ratios appear practical for WCF operation.

4.3 Calcination of Second-Cycle Waste (A. S. Neuls)

Approximately 850,000 gallons of second-cycle waste are stored in three waste storage tanks at ICPP. Direct calcination of this waste is not possible because of NaNO_3 , which can be molten between 300 and 800°C and causes agglomeration. Further, the chloride ion present in second-cycle waste volatilizes during calcination and can accumulate in the off-gas wet-scrubbing system, leading to excessive corrosion.

Calcination of mixtures of second-cycle waste and zirconium fluoride waste has been shown to be feasible. A process was developed in FY 1973^[2] that retains the chloride in the solid calcine as a nonvolatile species. The process consists of blending 1 volume of second-cycle waste with 3 volumes of zirconium fluoride waste and adding 0.5 mole of calcium nitrate per mole of fluoride prior to calcination at 500°C; however, the product from this process has a rough, nodule surface. The high interparticle friction caused by the nodules results in poor fluidization quality, which contributed to the formation of fuel nozzle clinkers during pilot-plant tests.

Although efforts to determine the chemical structure of the nodules were unsuccessful, a similar flowsheet (1:3 blend) using 0.6 to 0.7 mole of calcium nitrate per mole of fluoride produced a calcine without nodules. A 130-hour test in the 12-inch-diameter pilot-plant calciner was completed using a 1:3 blend with 0.7 mole of calcium nitrate per mole of fluoride. No surface nodules were formed during the run; however, the product was very attrition resistant; and particle size was not controlled.

Studies in the 4-inch-diameter calciner show that surface nodules will not develop if 0.6 mole of calcium nitrate per mole of fluoride are added prior to calcination. During the next WCF campaign, the flowsheet consisting of a 1:3 blend with 0.6 mole of calcium nitrate per mole of fluoride will be tested to determine if particle size control is a problem in the WCF. Because the energy input at the feed nozzles in the WCF is greater than the energy input at the feed nozzle in the 12-inch calciner, particle size might be more easily controlled in the WCF. If particle growth is a problem in the WCF, pilot-plant jet-grinding studies will be initiated.

4.4 Calcination and Storage of Rover Waste (B.J. Grady)

Development work in the 4-inch pilot-plant calciner using in-bed combustion heating has demonstrated that Rover waste can be calcined successfully when blended with two or more parts of first-cycle zirconium waste. Calcination of pure Rover waste was unsuccessful because of excessive fines generation produced by the attrition of the soft product. Development of a flowsheet with additives to harden the product is being considered for calcining the pure Rover waste.

Rover fuel processing is currently scheduled to start at ICPP during the third quarter of FY-76. Calcination of the waste will probably occur within a year or two after generation. Approximately 115,000 gallons of first-cycle waste (0.16 Ci/gal) and 29,000 gallons of second-cycle waste (0.034 Ci/gal) will be generated. The storage of the first-cycle Rover waste during generation, and prior to calcination, is a significant problem that is being investigated.

The major problem which complicates the storage of Rover first-cycle waste is the instability (precipitation) that results when blended with either fluoride or aluminum wastes. Rover waste must be stored unblended to prevent significant quantities of Nb_2O_5 and AlF_3 from precipitation during long-term storage. Complexed Rover feed (waste) has a stability range that varies from 0 to 10% with respect to Al^{+3} concentration; if over complexed, Nb_2O_5 will precipitate; and when under complexed, AlF_3 precipitates. Laboratory studies indicate that blending Rover waste with any other waste containing a significant amount of aluminum will cause the Nb to precipitate. Fluoride (zirconium), intermediate-level, and electrolytic wastes all contain more than 0.2 $\underline{\text{M}}$ Al^{+3} . Additional studies indicate that blends of one part Rover waste with 1 to 10 parts of zirconium waste would result in collection of ~ 1 inch of precipitate on the tank bottom. Similar stability tests with unblended Rover waste indicate that it is probably suitable for long-term storage (very little precipitation after 6 months). The Rover second-cycle waste should not present any problems and can be mixed with other first- or second-cycle wastes.

4.5 Decomposition Characteristics of Simulated PW-6 Commercial Waste (WMT Funded) (B.J. Newby)

Differential thermal analyses (DTA) and X-ray diffraction techniques were used to study the calcination chemistry of a simulated, high-sodium waste (PW-6) that represents a waste to be produced from the commercial reprocessing of spent nuclear reactor fuel. The composition of the PW-6 commercial waste is shown in Table XXV. A typical analysis of the rare earth mixture contained in the waste is shown in Table XXVI.

One of the major constituents of PW-6 waste is sodium nitrate. The fluidized-bed calcination of wastes containing sodium nitrate poses special problems; the large temperature range over which sodium nitrate exists in the molten, undecomposed state makes the fluidized-bed particles prone to agglomeration. Substances may be added to lower the decomposition temperature of the nitrate, either by acting as a catalyst or by forming a

TABLE XXV

COMPOSITION OF PW-6 COMMERCIAL WASTE

<u>Constituent</u>	<u>Concentration (Molar)</u>
$\text{Sr}(\text{NO}_3)_2$	0.027
$\text{Ba}(\text{NO}_3)_2$	0.027
MoO_3	0.12
KNO_3	0.064
$\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	0.13
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.010
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.052
TeO_2	0.012
AgNO_3	0.0020
$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	0.0020
CrO_3	0.045
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	0.56
HNO_3	3.39
H_3PO_4	0.042
NaNO_3	2.0
Rare earth mixture	80 g/l

TABLE XXVI

TYPICAL ANALYSIS OF RARE EARTH MIXTURE

<u>Analyzed as:</u>	<u>Concentration (wt%)</u>
CeO_2	22.0
La_2O_3	11.0
Nd_2O_3	7.8
Pr_6O_{11}	2.3
Sm_2O_3	1.4
Gd_2O_3	1.0
Y_2O_3	0.1
Other rare earth oxides	0.4

stable compound with sodium nitrate. The effects of these materials were studied by the DTA techniques to avoid making pilot-plant calciner runs on materials which could be eliminated from consideration.

A schematic sketch of the differential thermal analyzer used is shown in Figure 20. The components of the analyzer are stock items from various companies. The techniques used are the same as those for DTA studies described in ICP-1008^[16], except that the analyzer used did not use gas dispersal of the atmosphere surrounding waste samples being heated. The abscissas of all DTA curves represent the temperature to which the sample is being heated; the ordinates represent the temperature differences (ΔT) between the sample and a reference material (Al_2O_3) stable over the temperature range being studied. In addition to examination by DTA, wastes heated to appropriate temperatures between 105 and 1000°C were examined by X-ray diffraction to more accurately interpret DTA curves. Information obtained from the literature was also used to interpret DTA curves.

Fig. 20 Schematic diagram of differential thermal analyzer.

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Sodium nitrate has been converted to a ferrate by heating with ferric oxides^[16]. Although iron is a major constituent of PW-6 waste, there is not enough present to stoichiometrically convert the sodium nitrate to a ferrate. Attempts were made to convert sodium nitrate to a ferrate at temperatures low enough to prevent bed agglomeration by adding the following to PW-6 waste: (a) iron and nitric acid to give 1.3 moles of iron and 1.3 moles of nitric acid for every mole of sodium nitrate, (b) ferric oxide to give an iron-to-sodium nitrate mole ratio of 0.83 in the waste, and (c) ferric nitrate to give an iron-to-sodium nitrate mole ratio of 1.3. Since iron decomposed the nitric acid present in the waste, additional nitric acid must be added to prevent hydroxide precipitation, as the waste tends to become basic. Iron added to the waste reduces nitrates present and is oxidized to ferric oxide, which in turn reacts with sodium nitrate to form NaFeO_2 between 301 and 419°C (see Figure 21). Ferric oxide added to PW-6 waste converts sodium nitrate to a ferrate at 594-719°C (see Figure 22) while ferric nitrate converts sodium nitrate to a ferrate at 481-666°C (see Figure 23). Thus, addition of iron and nitric acid to PW-6 waste shows promise as a method to prevent sodium nitrate agglomeration; on the other hand, ferric oxide or nitrate converts the sodium nitrate to a ferrate at a temperature range too high to prevent agglomeration during calcination.

Sodium nitrate might be converted to sodium carbonate by either formic or acetic acid according to the reactions^[17]:

Sodium carbonate has a melting point of 851°C. Thus, addition of formic or acetic acids to PW-6 waste might eliminate particle agglomeration. Figure 24 shows that the addition of formic acid to the waste to give a formic acid-to-sodium nitrate mole ratio of 3.2 did not convert sodium nitrate to the carbonate. Further, Figure 25 shows that the addition of acetic acid to PW-6 waste to give an acetic acid-to-sodium nitrate mole ratio of 1.2 did not convert sodium nitrate to the carbonate.

Chromic oxide might convert sodium nitrate to the chromate according to the reaction $4\text{NaNO}_3 + \text{Cr}_2\text{O}_3 + \frac{1}{2}\text{O}_2 \longrightarrow 2\text{Na}_2\text{CrO}_4 + 4\text{NO}_2$ ^[18]. Figure 26 shows that the addition of chromic oxide to waste to give a chromic oxide-to-sodium nitrate mole ratio of 1.3 did convert the sodium nitrate to a chromate between 223 and 361°C. Thus, addition of chromic oxide to PW-6 waste shows promise as a method to prevent sodium nitrate agglomeration of the waste during its calcination.

In conclusion, DTA - X-ray diffraction techniques show that the addition of iron and nitric acid or chromic oxide to PW-6 waste are possible methods to prevent sodium nitrate agglomeration of the waste during calcination while ferric oxide, ferric nitrate, formic acid, or acetic acid did not appear to be useful for this purpose.

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Fig. 21 Thermal chemistry of PW-6 waste to which iron and nitric acid are added to give 1.3 moles of iron and 1.3 moles of acid for each mole of sodium nitrate present.

ACC-A-1611

Fig. 22 Thermal chemistry of PW-6 waste to which ferric oxide has been added to give an iron-to-sodium nitrate mole ratio of 0.83.

Fig. 23 Thermal chemistry of PW-6 waste to which ferric nitrate has been added to give an iron-to-sodium nitrate mole ratio of 1.3.

ACC-A-1612

Fig. 24 Thermal chemistry of PW-6 waste to which formic acid has been added to give a formic acid-to-sodium nitrate mole ratio of 3.2.

ACC-A-1610

Fig. 25 Thermal chemistry of PW-6 waste to which acetic acid has been added to give an acetic acid-to-sodium nitrate mole ratio of 1.2.

ACC - A - 1613

Fig. 26 Thermal chemistry of PW-6 waste to which Cr_2O_3 has been added to give a Cr_2O_3 -to-sodium nitrate mole ratio of 1.3.

4.6 Calcination of Simulated Commercial Wastes (WMT Funded)
(L.L. Taylor, W.A. Freeby)

Development of waste calcination flowsheets for fluid-bed calcination of simulated commercial wastes is continuing. The objectives of the program are to: (a) develop a fluid-bed calcination process for each of three types of simulated commercial wastes (PW-4b, PW-4c, and PW-6)(Table XXVII), (b) provide process and equipment design criteria for a pilot-plant fluid-bed calciner for the Waste Fixation Program at Pacific Northwest Laboratories, and (c) provide flowsheet development and calcine for postcalcination treatment studies at ICPP. Results to date indicate that fluid-bed calcination of the PW-4b,

TABLE XXVII
COMPOSITION OF SIMULATED COMMERCIAL WASTES

Constituent	Concentration		
	PW-4b Waste	PW-4c Waste	PW-6 Waste
$\text{Sr}(\text{NO}_3)_2$, g/l	5.71	5.71	5.71
$\text{Ba}(\text{NO}_3)_2$, g/l	7.05	7.05	7.05
MoO_3 , g/l	16.84	16.84	16.84
KNO_3 , g/l	6.47	6.47	6.47
$\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, g/l	34.9	34.9	34.9
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, g/l	2.91	2.91	2.91
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, g/l	10.75	10.75	15.21
TeO_2 , g/l	1.91	1.91	1.91
AgNO_3 , g/l	0.34	0.34	0.34
$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, g/l	0.62	0.62	0.62
CrO_3 , g/l	1.2	1.2	4.5
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, g/l	44.0	44.0	225.84
HNO_3 (15.7 M), cc/l	127	127	216
H_3PO_4 (14.7 M), cc/l	2.88	2.88	2.88
NaNO_3 , g/l	None	1.7	170
Rare Earth Mixture, g/l	~80	~80	~80

and PW-4c wastes is practical, but calcination of the PW-6 waste produces severe bed agglomeration due to the presence of a high concentration of sodium nitrate; use of additives can assist in the calcination of PW-6 waste.

4.61 Pilot-Plant Calcination of PW-4b and PW-4c Waste. Four pilot-plant runs in the 4-inch-diameter calciner with PW-4b and PW-4c (PW-4b waste with 0.02 M Na added) wastes were made to gain more operating experience and provide calcine for postcalcination treatment studies. A long-term (75 hr) run with PW-4b waste showed that bed particle size can be controlled.

The PW-4c runs were made on a batch basis. Operation of these runs consisted of coating PW-4c waste on a starting bed of alumina until the bed weight increased to 30 to 40% of the original bed weight, at which time the runs were terminated. No significant operating problems were experienced during any of the PW-4b or PW-4c runs.

4.62 Calcination of PW-6 Waste. Calcination of PW-6 waste is still plagued by nozzle agglomerates and clinker formation due to sodium nitrate. Seven scoping runs were made with several different additives that would potentially form stable sodium compounds. Blends of PW-6 waste with aluminum nitrate, aluminum nitrate and calcium nitrate, chromic oxide, and iron and chromic oxide were unsuccessful. Calcination of PW-6 waste with iron additive and with aluminum nitrate and chromic oxide additives both show promise. Short-term runs with these additives were successful; no significant operating problems were experienced, and no particle agglomerates were formed.

4.63 Design Criteria for the Fluid-Bed Calciner. Design criteria for a fluid-bed calciner rack were prepared in support of the Waste Fixation Program being conducted by Battelle at Hanford. The criteria are based largely on pilot-plant experience at the Idaho Chemical Processing Plant and process requirements for the PW-4b flowsheet. Continued development work on fluid-bed calcination of PW-6 waste will be directed toward establishing a flowsheet compatible with the recommended equipment design.

In-bed combustion was recommended as the primary heating method because the ratio of heat input/unit volume of bed material can be varied over wide ranges. High waste throughput is possible, and the need for large heat transfer surface areas is eliminated. An alternative method of process heating based on electrical cartridge heaters in the bed would result in a significant reduction in waste throughput.

The waste will be sprayed into the heated fluidized bed through pneumatic nozzles. Bed particle growth by waste deposition and evaporation is offset by particle attrition, elutriation, and bed withdrawal. The nitrate salts of the fission products and other cations decompose into oxides of nitrogen and solid oxides. The primary off-gas cleanup system consists of a bank of sintered-metal filter tubes in parallel and an air blowback system. Solids collected as both fine particulates from the off-gas system and granular solids from the fluid bed are transferred to a melter by gravity.

The feed system consists of a pneumatic atomizing nozzle and control instrumentation for both the liquid and gas streams. Waste feed will be pumped to the calciner; a feed recycle loop will provide a constant pressure. The fuel system requirements for instrumentation and control are similar to those of the feed system. The fuel system will be completely automated: a temperature recorder/controller will regulate the fuel requirements; oxygen for combustion will be ratioed to the fuel flow.

The proposed calciner vessel has a square cross section. The lower section containing the fluidized bed will be 6.75 inches on a side. Both the fuel and feed nozzles will be located in this section; a removable sidewall will permit access to the calciner for postrun cleanup and inspection. The disengaging space will be expanded to 9 inches on a side to reduce the superficial velocity and decrease the transport disengaging height required for deentrainment. The primary off-gas cleanup system will use a bank of sintered-metal filters in parallel.

Solids generated in the fluid-bed calciner will be gravity fed to the melter. Granular product will be removed continuously from the calciner but fed to the melter on an intermittent basis. Off-gas particulates collected on the sintered filters and removed by an air blowback system will be fed continuously to the melter.

4.7 Calcination of Simulated Neutralized Purex Waste (WMT Funded) (S.S. Bodner, W.A. Freeby)

The purpose of this work is to develop a process flowsheet for solidifying AEC neutralized Purex waste using the fluidized-bed calcination process and to develop suitable postcalcination techniques that could be used for decreasing the leachability of the calcined solids. Results from the development studies will form the basis for a conceptual process design and cost estimate.

A solidification process capable of the throughput rates required to solidify the wastes in a reasonable time does not exist. An extension of the fluid-bed technology currently used in the WCF at the ICPP is one logical approach to solidification. Though the basic technology exists, flowsheets for fluid-bed calcination of neutralized Purex waste (NPW) must be demonstrated.

The major problem in the calcination of NPW is the tendency for the NaNO_3 to cause particle agglomeration during calcination; this results because the NaNO_3 is molten over the range of calcination temperatures. In the present approach, chemical additives are being evaluated for ability to convert the sodium to stable compounds to eliminate the agglomeration.

Pilot-Plant Studies of Neutralized Purex Wastes: The composition of the simulated NPW is mainly NaNO_3 , NaNO_2 , and $\text{Fe}(\text{OH})_3$ precipitates, with minor amounts of other constituents. After preliminary scoping studies with a simulated Purex waste^[2], a revised feed makeup was developed to more closely simulate the neutralized Purex waste without fission products. The reactions of this simulated waste are now quite different, and additives thought to be successful in previous pilot-plant studies^[2] were found to be infeasible.

The chemical additives selected for study during FY 1974 were aluminum nitrate, calcium nitrate, ammonium sulfate, magnesium sulfate, and urea. Nine pilot-plant runs were made in the 4-inch-diameter calciner to evaluate potential fluidized-bed calcination flowsheets. None of the runs was considered successful as excessive fines production and/or the formation of sintered agglomerates forced shutdowns. Further studies on the program are planned for the coming year.

5. NEW WASTE CALCINING FACILITY DEVELOPMENT

5.1 NWCF Calciner Vessel Configuration (D.G. Swink)

Pilot-plant studies are currently underway to determine the NWCF calciner vessel configuration. The following areas are being investigated: vessel shape and diameter, baffle design and placement, and nozzle location. The objectives of these studies are to improve the quality of fluidization while minimizing the particle entrainment and carry-over.

Design Recommendations: The pilot-plant results to date indicate that the NWCF calciner should be designed with a five-foot-diameter bed section and a seven-foot-diameter expanded upper section containing a double venetian-blind baffle located near the top. In addition, the vessel deentrainment height should be as high as possible within the constraints of cell dimensions.

Equipment Description: The pilot-plant equipment consists of a small two-dimensional conical bed and a straight-sided cylindrical bed [11 inch inside diameter (ID)] that can be fitted with either a straight-sided cylindrical upper section (11 inch ID) or an expanded cylindrical upper section (19.5 inch ID). The expanded upper section contains a movable and removable baffle plate. In addition, a cyclone is located in the off-gas line from the upper section to determine particle carry-over. Steam coils can be placed in the 11-inch ID bed for heat transfer and fluidization studies. The straight-sided bed is constructed of transparent plastic to allow observation of the fluidized calcine.

Experimental Testing and Results: Testing was conducted in the 11-inch ID bed to determine quality of fluidization and particle entrainment and in the conical bed to determine quality of fluidization. The results from the conical bed indicated that poor fluidization resulted near the walls at normal operating velocities. The cylindrical bed was found to produce excellent fluidization (good mixing) as indicated by the low-temperature gradients over the bed. In addition, the location of the heat source (steam coils) within the bed had no apparent effect on the size of the temperature gradients.

The results of the particle deentrainment studies are shown in Table XXVIII. In all the tests a constant volume of alumina calcine was charged to the 11-inch ID cylindrical bed. The fluidizing velocity was kept approximately constant at 4.75 ft/sec. The quantity of fines carry-over was determined by collecting and weighing, each hour, the material caught in the off-gas cyclone. As can be seen in Table XXVIII, the expanded upper section produced a major reduction in the fines carry-over. The addition of a double venetian-blind baffle plate at the top of the expanded section further reduced the carry-over by approximately one-half.

Additional testing will be performed to determine if nozzle location has any effect on particle entrainment.

TABLE XXVIII

RESULTS OF PARTICLE DEENTRAINMENT TESTS IN A CYLINDRICAL BED

Configuration ^[a]	Quantity of Collected Material (g/hr)	Carryover Reduction Factor
Straight-sided cylindrical upper section (11-in. ID)	102	1
Expanded cylindrical upper section (19.5-in. ID)	13.1	7.8
Expanded upper section with double venetian blind baffle plate 9 in. above bed	7.3	14.0
Expanded upper section with double venetian blind baffle plate 40 in. above bed	7.0	14.6
Expanded upper section with single venetian blind baffle plate 40 in. above bed	10.0	10.2

[a] All tests were conducted in the 11-in. ID cylindrical bed.

5.2 NWCF Process Heating Alternatives (B.J. Grady)

During the past year, numerous indirect heating systems were evaluated for use in the NWCF calciner. Indirect heating as compared to direct heating (i.e., in-bed combustion) will minimize off-gas release and the potential for clinker formation during calcination; it will also eliminate the buildup of unburned hydrocarbons on ruthenium adsorbers and final filters. Electrical resistance heating was chosen as the most promising system for further study and verification. A pilot-plant facility to test the electrical heaters is being fabricated. If the electrical heaters prove feasible, they will serve as a potential backup heating system for the calciner. A blank backplate will be provided on the calciner vessel for insertion of electrical heaters at some future date.

Electrical resistance heating is the only alternative heating system that approaches in-bed combustion in thermal efficiency and simplicity of operation. Pilot-plant testing will be conducted on long-life, high-power-density, electrical resistance elements. The testing will be conducted primarily on elements that have an attached finned-surface area or on elements that are inserted in finned tubes.

The pilot-plant testing program will be divided into three major phases. The first phase will be conducted in a new fluidized-bed test unit which will simulate operating conditions without calcining any waste. The elements will be evaluated during short test runs to detect defects and to determine operating and heat transfer characteristics. The second phase will be conducted in the existing 12-inch pilot-plant calciner. These tests, increasing to one week's duration, will determine the effectiveness of the elements under actual calcining conditions. Reliability, efficiency, and operability will be evaluated as well as any differences in the calcine product. The third phase of the testing program will be conducted in the fluidized-bed test unit and will emphasize reliability for long periods of continuous operation. In these tests, the elements will be operated at design conditions in a fluidized bed for up to two months.

5.3 NWCF Cyclone Selection (R.E. Schindler)

The WCF uses a cyclone to collect fines carried from the calciner by the off-gas. A high collection efficiency is important because fines not collected by the cyclone are collected by the scrubber and recycled to the feed, thus reducing the net feed rate. As part of the NWCF development program, cyclone designs and alternative dry-fines-collection systems are being evaluated.

The basic strategy is to rely on and evaluate vendor designs, then purchase a fines collector on a performance specification. First, vendor data, recommendations, and performance estimates were collected. Tests were then conducted at vendor facilities to evaluate the efficiency of the dry-fines collectors with fines generated by the pilot-plant calciner.

Performance tests were conducted on three different fines collectors. In the first test, a 21-inch-diameter high-efficiency cyclone had a collection efficiency of 96% for a sample of fines from the pilot-plant calciner. A slightly better collection efficiency was provided by a multiple-cyclone system which used tangential jets of secondary air to provide the swirl. This system, which is still under development, promises to provide higher collection efficiencies when some reentrainment problems are eliminated. In a third test, an impactor-type collector gave rather poor collection efficiency.

The reevaluation of the cyclone discharge jet is a related study which is just beginning. The WCF cyclone discharges solids to the transport air system through a jet eductor. As a result of the small size of the eductor (0.86 inch diameter), the entrance to the eductor is easily plugged. The jet evaluation program proposed to investigate the possibility of enlarging the cyclone discharge jet.

5.4 NWCF Wet-Scrubbing System (B.J. Grady)

A number of advanced, high-efficiency, low-pressure-drop, wet-scrubbing systems were evaluated for possible use in the NWCF. An improved wet-scrubbing system is desirable to prolong the operating life of the final filters by increasing the particle removal efficiency and to reduce the size of the blowers by decreasing the overall pressure drop.

Several commercial scrubbing systems were chosen for further evaluation following a literature search. Each system was rejected for one or more of the following reasons: low efficiency under projected operating conditions in vendor pilot-plant tests, lack of vendor pilot-plant facilities to verify literature claims, unsound technical operating principles, and impractical design for use in a radioactive facility.

As an alternative, a high-energy venturi scrubber with an adjustable throat area (variable pressure drop) was to be evaluated as a possible improvement over the existing high-energy venturi scrubber. The adjustable design would be desirable to allow "fine tuning" of the scrubber in order to ensure the maximum scrubbing efficiency, to maintain constant pressure drop and scrubbing efficiency as the process varies, and to enable operation at a higher pressure drop (greater particle removal efficiency) to further reduce the outlet loading. The pilot-plant testing of the adjustable area venturi scrubber had to be canceled because a suitable unit could not be obtained in the small size required. Further discussions will be held with the vendor to determine if this type of unit is practical in our application. A performance specification for the recommended type of venturi scrubber will be provided for the NWCF Design Criteria.

5.5 NWCF Filter-Leaching and Handling System (D.G. Swink)

Pilot-plant studies have been conducted to determine the feasibility of a filter-leaching system for removal of radioactivity from the NWCF final off-gas filters before they are disposed of. A leaching system is recommended as tests indicate that a DF of >10 can be achieved. The facility would consist of: (a) a vessel with a removable hood and a removable screen to support the filter and catch any pieces of filter media that breakoff, (b) a pump to force the leachate (nitric acid) through nozzles located above and below the filter and to recirculate the solution, and (c) heaters to keep the leachate at approximately 70°C.

Experimental Testing and Results: Initial leaching tests were conducted on glass-fiber filter samples contaminated with radioactivity from the WCF off-gas. Gamma spectra and gross-beta measurements were used to evaluate various leaching solutions. Of the four solutions tested (nitric acid, sulfuric acid, sodium hydroxide, and potassium permanganate followed by oxalic acid), the nitric acid proved as good as, or better, than the others while being the most compatible with the rest of the system in case of recycle. A nitric acid leaching test was then run on a 6-inch-deep HEPA filter which had simulated zirconium fines blown onto it. The filter disintegrated under the high liquid pressure, and the test was rerun using fine spray nozzles. The acid strength was 9 M, and the test was run at 25°C. An

average DF, based on 3 filter samples, of 10.8 was achieved. DF in this test was based on the amount of zirconium removed from the filter since cold calcine was used, and most of our future wastes will contain zirconium. It was assumed that most of the fission products would be associated with the zirconium fines on the filter.

Additional tests will be run to determine the range of operating parameters.

5.6 Impact of Calcining HTGR Waste in the NWCF (B. J. Grady)

The projected reprocessing of HTGR fuel will generate liquid wastes with a much higher decay-heat generation rate than our current reprocessing wastes. A reprocessing demonstration program consisting of 2,000 blocks of Ft. St. Vrain fuel is scheduled to begin in FY-80. This will be followed by interim processing of at least 16,600 blocks of commercial HTGR fuel. Since the calcine generated from the HTGR waste will have a high decay-heat generation rate, special consideration must be given to the safe operation of the calciner during loss of fluidizing air.

The results of heat transfer calculations indicate that both types of HTGR waste must be calcined as either a blend with zirconium waste or in a smaller diameter vessel because of their high heat-generation potential. The calculations were based on a maximum calciner centerline temperature of 650°C and a collapsed bed (loss of fluidization). In addition, the blend ratio of zirconium to HTGR waste was calculated assuming a 75 Btu/hr-ft³ heat generation rate for zirconium waste and a 100 Btu/hr-ft³ maximum allowable heat generation rate for calcine solids in the five-foot-diameter NWCF calciner. The alternatives for calcining the two types of HTGR waste are presented in Table XXIX.

The blending ratios required for calcining the demonstration waste are considered feasible with the projected waste inventories. It is felt that a separate calciner vessel will not be required for this waste. Since the waste volume associated with the HTGR demonstration processing is about 60,000 gallons, the blending operation will require between 180,000 to 378,000 gallons of zirconium waste and 150 days of calciner operation.

The HTGR interim processing will generate up to 700,000 gallons (or more) of waste which will require calcination. If the waste is calcined as a blend, then over 11.5 million gallons of zirconium waste will be required. At the NWCF processing rate, over 4,000 days (14 yr) of calciner operation will be required to process this volume of waste. A separate calciner vessel with a 12-inch OD and a 450 gal/day capacity would require over 1,600 days (5.2 yr) of calciner operation to process the interim waste. The small diameter calciner would be located in the NWCF cell with the main calciner. The HTGR calciner would require a separate cyclone and product removal system, but would utilize the remainder of the NWCF off-gas system. There is some question as to whether both calciners could be operated at the same time. A trade-off study will be performed to decide which of these options to choose.

TABLE XXIX

ALTERNATIVES FOR CALCINING HTGR WASTE

	Average Decay- Heat Generation Rate (Btu/hr-ft ³)	HTGR: Zr Blend Ratio	Vessel Diameter for Nonblended Calcination (in.)
<u>HTGR Demonstration Processing</u>			
Maximum Case (1st-cycle fertile and fissile waste)	835	1:6.3	19
Minimum Case (1st- and 2nd-cycle fertile and fissile waste)	365	1:3.0	30
<u>HTGR Interim Processing</u>			
Maximum Case (1st-cycle fissile and fertile waste)	2020	1:16.5	11.5
Minimum Case (1st- and 2nd-cycle fertile waste)	650	1:8.4	21.8

6. RARE GAS PLANT AND PROCESS-OFF-GAS STUDIES

6.1 Tests of Rhodium Catalyst from the Rare Gas Plant (R.R. Hammer)

The regeneration of the rhodium catalyst used to decompose nitrous oxide in the Rare Gas Plant has been reported previously^[2,19]. During the past year, it was possible for the first time to determine the reactivity of catalysts in a wide range of conditions.

Prior to operation of the Rare Gas Plant (RGP), samples of the rhodium (Rh) catalyst were taken from the catalyst beds and examined in the laboratory for their effectiveness in decomposing N_2O . It was found that the catalyst had lost a considerable amount of its effectiveness at lower temperatures, but was still very effective for N_2O decomposition at temperatures of 400°C (725°F) and higher.

The effectiveness of a catalyst sample was determined by flowing a 4% N_2O -air mixture through a 2.2-cm-diameter column containing a 9.5-cm length of the catalyst (0.5 wt% Rh on an alumina base) at various temperatures. The space velocity of the gas through the catalyst was similar to that for the catalyst in the RGP. The N_2O in the gas mixture was analyzed by gas chromatography before and after passing through the catalyst bed. The percent of N_2O remaining after passing through the bed is given as a function of temperature in Figure 27, for:

- (1) New catalyst
- (2) Oxidized catalyst with unsatisfactory reactivity characteristics
- (3) Oxidized catalyst that had been regenerated by reduction with hydrogen (H_2)
- (4) A sample of catalyst recently taken from the RGP.

As shown in Figure 27, the sample of catalyst recently taken from the RGP appears to have lost its effectiveness at lower temperatures. From a private communication with a representative of Engelhard Corporation (manufacturer of the catalyst), this type of behavior is expected in an oxidizing atmosphere. The most active sites in the catalyst are rapidly oxidized, followed by a much slower rate of oxidation of the rest of the catalyst.

6.2 Hydrogen Recombiner for Dissolver Off-Gas (C.L. Bendixsen, M.W. Andrews)

Installation of a hydrogen recombinder on the hydrogen-rich off-gas stream from the zirconium fuel dissolver has been proposed. The installation is necessary if increased quantities of Krypton-85 are to be recovered at the ICPP. Because of the hydrogen content of zirconium fuel dissolver off-gas, the ICPP Rare Gas Plant is unable to recover the 30,000

Fig. 27 N_2O removal efficiency as a function of temperature and catalyst.

curies of Krypton-85 per year which is needed to meet the projected commercial demand. At present, the RGP can safely process only those gas streams with hydrogen concentrations of less than 4 vol%, the lower flammability of hydrogen with air. Installation of a hydrogen recombiner can more than double the recoverable quantities of Krypton-85 by removing hydrogen from hydrogen-rich off-gas streams. Installation cost (FY 1976) of the hydrogen recombiner has been estimated to be \$465,000.

Both thermal and catalytic hydrogen recombiners are commercially available, and each type has particular advantages relative to the ICPP, but selection of the preferred type awaits further evaluation. The hydrogen recombiner will be designed for a maximum gas flow rate of 50 scfm with an average flow rate of 15 to 20 scfm. Hydrogen concentration in the gas stream will vary from 0 to 60 vol%. The recombiner will be designed for safe, automatic operation at all process gas flow rates and concentrations. Appropriate gas analyzers will be installed to detect any changed in gas compositions which could lead to hazardous conditions.

6.3 Catalytic Decomposition of Ozone (R.R. Hammer)

Ozone is generated when oxygen is present in the concentrated krypton streams in a cryogenic plant for recovery of fission product noble gases. At higher concentrations, the ozone can decompose violently. In the ICPP Rare Gas Plant, it is not possible to separate the oxygen totally from the krypton before concentration of the krypton; therefore, other techniques must be used to prevent the formation of high concentrations of ozone.

The use of molecular sieves for decomposition of ozone has been reported^[20], and an acid-resistant zeolite, Zeolon-200H, is being considered for use in the RGP. It was reported that water adsorption decreases the effectiveness for O_3 decomposition, but the effectiveness of the specific acid-resistant zeolite, Zeolon-200H, was not given in the patent. Testing of Zeolon-200H for O_3 decomposition was necessary prior to possible use in the Rare Gas Plant, since other zeolites are attacked by traces of NO_x present in the RGP gas streams; and Zeolon-200H might be poisoned by the NO_x and water vapor.

In laboratory scoping experiments, a 2.4% O_3 - O_2 mixture was passed through 1-inch-thick beds of the molecular sieve samples at superficial space velocities of 24 cm/min. Table XXX summarizes the experimental conditions and results.

For Experiments 1 and 2, the bed was warmed to room temperature and purged with oxygen for 2 hours after exposure to the O_3 - O_2 mixture. In these experiments, no detectable amounts of O_3 were desorbed from the pellets. Several pellets from each experiment were ground up in a KI solution, and no detectable amounts of I_2 were liberated. It is likely, therefore, that most of the O_3 is decomposed after adsorption.

The exposure to the CO_2 - O_2 - N_2 atmosphere (Experiment 2) was sufficient to saturate the bed with CO_2 ; however, little or no loss of efficiency was observed. Although nearly all of the active sites were filled for the water-saturated molecular sieve (Experiment 3), some

TABLE XXX

OZONE REMOVAL BY ZEOLON-200H AT -86°C

Test Number	Zeolon Pretreatment	% O ₃ Removed
1	None (activated by heating to 250°C for 24 hours)	>99% ^[a]
2	35 minute exposure to a 12.3% CO ₂ -23.4% O ₂ -N ₂ atmosphere at 700 cc/min and -86°C	>99% ^[a]
3	Presoaked in water for 2 days and air dried at 20°C	40%

[a] Less than the detectable limit of O₃ passed through the Zeolon-200H bed.

O₃ was removed. This indicates that very few active sites are necessary for O₃ decomposition. It is expected that NO₂ would behave similarly to water with regard to loss of O₃ removal efficiency. To assure that O₃ removal efficiency is maintained for any Zeolon-200H adsorber placed in the RGP, it is recommended that the bed be heat-traced to facilitate regeneration.

6.4 Fission-Product Noble Gas Storage Development (B.A. Foster, D.T. Pence, B.A. Staples)

The development of a method for collection and long-term (100-year) storage of ⁸⁵Kr has been proposed to mitigate both local release hazards and global accumulation. The purpose of this program is the evaluation of possible collection and storage methods for the 10.8-year half-life isotope and the development of the most promising techniques. Three methods have so far been chosen for further study: (1) high-pressure steel cylinders, (2) clathrate inclusion compounds, and (3) a zeolite encapsulation process. The latter process will be studied on a laboratory scale for further evaluation. Topical reports on the first two methods are in preparation.

High-pressure steel cylinders have the favorable characteristics of a well established history of development and use in industry, good radiation and thermal resistance, high capacity, low cost, and ease of recovery. In contrast, there exists the possibility of a cylinder failing and releasing its contents if it is subjected to overheating, impact, or contact with corrosives. The high capacity of the cylinders will mean considerable quantities (~1000g) of rubidium will be present after a few half-lives. The presence of such large quantities of rubidium in the cylinders does not appear to pose any difficulties with regard to cylinder structural integrity but could present a fire hazard in the case of a cylinder failure.

Quinol clathrates are severely limited in capacity to contain ^{85}Kr due to poor thermal stability. The heat generated by the beta decay, even for low concentrations of ^{85}Kr , appears to be sufficient to raise the temperature of the clathrate enough to cause release of the ^{85}Kr . This low capacity makes the clathrates economically unfavorable.

The zeolite encapsulation process is a high-temperature, high-pressure process for trapping gases in a porous potassium-exchanged zeolite mineral. Optimum operating conditions and capacities need to be determined in the laboratory before this method can be properly evaluated. Capacities of up to 25 cc/g are anticipated with operating temperatures of around 350°C and pressures below 10,000 psi. Higher capacities, attainable at higher pressures, may not be tolerable due to heat generation from ^{85}Kr decay. While the zeolite capacity for a given volume is expected to be somewhat below that of high-pressure steel cylinders, encapsulated zeolites can be stored at ambient pressure, thus offering an advantage in safety over cylinders. A contract for procurement of the gas encapsulation equipment for the laboratory studies has been awarded. Pending arrival of this equipment, ion-exchange studies are being performed on zeolites to produce various Na/K cation ratios, which will be tested for effect on capacity.

Based on heat transfer calculations, a summary of the anticipated ^{85}Kr storage capacities of 50-liter gas cylinders or similar sized containers is given in Table XXXI for

TABLE XXXI
STORAGE CAPACITIES FOR ZEOLITES, CLATHRATES, AND
HIGH-PRESSURE CYLINDERS

	Temperature at Centerline of Container ($^{\circ}\text{C}$)	Curies of ^{85}Kr Contained per 50-l Container
Zeolites	100	77,400
Clathrates	55	32,300
Cylinders at 500 psi	60	128,000
Cylinders at 2000 psi	127	419,000

several methods as a function of temperature. The leakage rate from ^{85}Kr -encapsulated zeolite has not yet been determined; until this has been determined, a maximum temperature of 100°C has been chosen to represent the maximum allowable temperature for the zeolite.

6.5 Catalytic Reduction of NO_x with Ammonia Over Zeolites (T.R. Thomas)

Laboratory testing has been conducted to evaluate the abatement efficiencies obtainable by the catalytic reduction of NO_x with NH₃ in simulated WCF off-gas test atmospheres. Previously, it has been reported^[2,21] that greater than 99% of the NO₂ in a humid air stream could be abated by a catalyzed NO_x-NH₃ reaction. The WCF off-gas contains CO, CO₂, and considerably more water vapor and both NO and NO₂. Therefore, it is necessary to study the effects of these added constituents on the behavior of the abatement process which may have future application at the ICPP.

The experimental conditions of recent tests were: catalyst, hydrogen mordenite; bed depth, 8 inches, superficial face velocity, 100 ft/min; residence time, 0.4 second; exit bed temperatures, 300 to 500°C; NO and NO₂ concentrations, 0.5 to 1.5%; and test atmosphere, air + 31% H₂O + 5% CO₂ + 2% CO.

The experimental results indicate that:

- (1) Greater than 99% abatement efficiencies for both NO and NO₂ are obtainable in the temperature range 400 to 500°C. This can be achieved with near-stoichiometric quantities of NH₃ (i.e., $\pm 20\%$).
- (2) Between 300 and 380°C, there is a large temperature effect on reaction efficiency. The maximum obtainable removal efficiencies for NO are 45, 75, and 99% and for NO₂ are 78, 93, and 97% at exit bed temperatures of 300, 350, and 380°C, respectively.
- (3) There is no apparent effect due to the presence of CO and CO₂.
- (4) There is a pronounced water effect below 400°C. At 380°C, the maximum NO₂ abatement efficiencies are 97, 99.3, and 99.9% for a water vapor content of 31, 10, and 1%, respectively.
- (5) When the test atmosphere contains only nitric oxide (NO), no nitrous oxide (N₂O) by-product is produced in the temperature range 300 to 550°C. When it contains NO₂, about 20% of the influent NO₂ is converted to N₂O at 350°C. Above 400°C, the N₂O is not detected.
- (6) Throughout the entire temperature range tested, at least part of the unused NH₃ appears in the effluent.

More tests are being conducted to study the effect of variable bed depth and face velocity on the reaction efficiency.

6.6 Monitoring Evaluations and Measurements of ICPP Gaseous Effluents (R.C. Girtton)

Most of the gaseous effluents from the various plant systems at the Idaho Chemical Processing Plant are discharged from a 250-foot stack. A stack monitor samples the gas at the 90-foot level of the stack. A continuous program is conducted to evaluate and upgrade the stack monitor and to evaluate the various process and ventilation streams that contribute to the stack effluent. This includes efforts to obtain more accurate flow measurements, more detailed particulate information from the individual gas streams, evaluation of stack monitor filter media, and monitoring of radioactive gases in the stack. Specific areas covered are reported below:

- (1) A comparison study of flow measurement devices for the WCF off-gas effluents was performed to improve the accuracy of the gas velocity measurement. Measurements taken with the permanently installed orifice meter were compared with measurements taken with a Gentile flowmeter and with a pilot tube and manometer. A correction curve was prepared for the orifice meter. Corrected flow rates for the WCF off-gas were about 1,700 scfm.
- (2) A continuous air monitor was installed in the WCF eastside ventilation duct to assist in the identification of the source of radiation bursts registered on the stack monitor. It has detected nonroutine releases of activity which were not detected by the stack monitor, appearing to be more sensitive to releases from the WCF ventilation air than is the stack monitor. Operation of the transport-air has coincided with these releases.
- (3) A program to evaluate various filter materials was initiated in FY 1974. A significant improvement (up to 40%) in the accuracy of radiochemical analyses of deposits on off-gas monitor filters should be obtained by replacing the present asbestos/fiberglass filter with a soluble HEPA filter. A number of filter manufacturers were contacted for samples, and the filter characteristics are being tested in the laboratory to establish their efficiency.
- (4) An isokinetic probe was installed in the stack monitor sample line. This probe presently provides continuous and isokinetic sampling for particle size distribution studies, but it can also be used for future monitoring requirements.
- (5) A silver zeolite sampler for the total collection of radioantimony was installed in the stack monitor sample line. The data provided by this continuous sampler will be included in the ICPP gaseous release information.
- (6) A high-volume cascade impactor is routinely operated to collect ambient air particulate data within the ICPP perimeter. This is a new sampling program and conclusive information has not been obtained as yet.
- (7) A program to study the particle size distribution in individual gaseous discharge systems at the ICPP was continued. An Anderson cascade impactor with a backup HEPA filter was used to sample the particulates to determine particle

size distribution, chemical composition, total dust load, and radionuclide distribution by particle size. Gaseous effluent systems that were sampled include:

- (a) **Continuous-monitor line of the stack sampler:** This sampler is operating on a routine basis and is providing comparative quantitative information during plant and/or WCF shutdown, plant co-processing operations, and WCF operations. During all operating conditions, results indicate that about 60% of the particulate activity is associated with particles less than 0.5 micron in diameter (Figure 28). Cesium-ruthenium ratios have been calculated in an

Fig. 28 Relationship of radioactivity to particle size in off-gas particulates.

effort to relate the data to specific plant operating conditions. Autoradiography has been used to study relative radiation intensities of each particle-size fraction. A series of three impingers, containing caustic and water solutions, were placed immediately downstream of the HEPA backup filter. About 5% of the total radioactivity was collected in the impingers, indicating that significant radioactivity associated with particulates is penetrating the filter.

- (b) **Main exhaust air duct in CPP-605, containing ventilation air from CPP-601, -640, and -604, and the WCF ventilation air duct:** The main air duct was sampled during coprocessing and electrolytic dissolution operations, and the WCF air duct was sampled during both WCF shutdown and WCF operations. The purpose of this sampling has been to obtain data to predict the frequency of HEPA filter changeouts in the Atmospheric Protection System.

Analysis of the collected material from the main ventilation exhaust duct indicates that the average dust emission rate during either shutdown or plant operations is about 0.3 lb/day. The total gamma radioactivity released from the ventilation duct varied from about 0.3 mCi/day during plant shutdown to 52 mCi/day during an electrolytic run; about 21 mCi/day was released during the coprocessing sample period. The particulates during all sampling periods in this duct were smaller than 10 microns in diameter, and about 70% of the particles were found to be smaller than 1 micron in diameter. The amount of radioactivity associated with the particulates was directly proportional to the particle-size distribution.

The average dust emission from the WCF ventilation duct is only about 0.03 lb/day during both shutdown and operation. The total gamma radioactivity released during the sampling periods was 0.21 mCi/day during shutdown and about 2 mCi/day during WCF operation. The particle-size distribution and gamma radioactivity associated with each particle-size fraction is similar to that of the main exhaust duct.

- (c) **Immediately downstream of the cyclone on the 12-inch calciner:** Sampling was done during operations of this calciner when simulated wastes were calcined. Results indicate that over 95% of the particulate escaping the cyclone were less than 3 microns in diameter, and about 85% were less than 1 micron in diameter during the calciner operation.
- (d) **WCF Station 3, located between the scrubber and silica gel bed, and WCF Station 5, located downstream of the final process off-gas filters:** Station 3 sampling has indicated that all particulates are less than 3 microns in diameter, and about 93% are less than 1 micron in diameter. Station 5 results show that 100% of the particulates are less than 1 micron in diameter, and over 90% are less than 0.4 micron in diameter.

Recommendations: The following evaluation studies and improvements are recommended for the effluent sampling and monitoring systems:

- (1) Design and development of a total collection device for submicron particles. Sampling data have indicated that a significant amount of radioactivity is penetrating HEPA filters.
- (2) Development of a system for total collection and accurate analyses of all volatile species, particularly ^{85}Kr and ^{129}I .
- (3) Development of improved ruthenium monitoring capabilities for the WCF and stack.
- (4) Investigation of methods and instrumentation available to quantitatively collect and analyze alpha- and beta-emitting isotopes at the stack monitor.

7. STABILITY AND INTERIM STORAGE OF WASTE SOLUTIONS

7.1 Stability of ICPP First-Cycle Zirconium and Aluminum Wastes Blended with ICPP Second-Cycle Waste (B.J. Newby)

Waste storage tanks at the ICPP used for interim storage of second-cycle waste may be full in the near future; the waste may then have to be stored in tanks containing other wastes, with first-cycle zirconium waste being a logical choice. Since ICPP policy prohibits storing unstable waste solutions, stability studies were carried out to see if blends consisting of small volumes of second-cycle waste blended with large volumes of first-cycle zirconium waste were stable. At the time this stability study was initiated, a tank of first-cycle aluminum waste was available for blending; so stability studies were also made on blends of second-cycle waste and first-cycle aluminum waste. Since that time, stainless steel nitrate waste has been added to the tank of aluminum waste, making the studies to determine the stability of aluminum and second-cycle waste blends of academic interest only. The concentrations of the constituents in the simulated first-cycle zirconium, first-cycle aluminum, and second-cycle wastes used in the stability studies are shown in Table XXXII and are typical of actual wastes.

The stability of blends of 1 vol second-cycle with 10 to 100 vol first-cycle zirconium waste, 1 vol second-cycle with 1 to 10 vol first-cycle aluminum waste, and 1 vol first-cycle aluminum with 5 and 10 vol second-cycle waste were studied at 24 and 35°C for 6 months. Increasing the storage temperature from 24 to 35°C increased the rate of blend instability for second-cycle/zirconium waste blends, but decreased the rate for second-cycle/aluminum waste blends. Increasing the storage temperature from 24 to 35°C also increased the quantity of residue in second-cycle/zirconium waste blends after a 6-month storage period. At the end of 6 months, the blend of 1 vol first-cycle aluminum with 1 vol second-cycle waste stored at 35°C contained only 0.043 g/liter (0.4 cc/liter) of solids; all other blends of aluminum and second-cycle waste contained only trace amounts of residue. The blends of 1 vol second-cycle with 10 vol zirconium waste were stable for less than 5 hours; the other second-cycle/zirconium waste blends were stable for only 1 day. The rate at which solids

TABLE XXXII
COMPOSITION OF SIMULATED FIRST-CYCLE ZIRCONIUM,
FIRST-CYCLE ALUMINUM, AND SECOND-CYCLE WASTES

Constituent	Concentration (Molar)		
	1st-Cycle Zirconium Waste	1st-Cycle Aluminum Waste	2nd-Cycle Waste
Zr	0.41	---	---
Al	0.68	1.16	0.66
H ⁺	1.4	0.99	1.28
B	0.19	---	0.013
Na	---	---	2.59
Sn	0.0039	---	---
Cr	0.015	---	---
NH ₄ ⁺	0.02	---	0.035
K	---	---	0.25
Hg	0.002	---	0.0049
Fe	0.0076	---	0.022
Mn	---	---	0.025
NO ₃ ⁻	2.28	4.57	6.04
F ⁻	3.24	---	0.0065
PO ₄ ⁻³	---	---	0.028
SO ₄ ⁼	---	---	0.063
Cl	---	---	0.048

formed and the quantity of solids that had separated from solution at the end of 6 months both increased as the volume ratio of zirconium waste to volume of second-cycle waste decreased: A blend of 10 vol zirconium with 1 vol second-cycle waste at 24°C contained 1.8 g/liter of solids while a blend of 100 vol zirconium with 1 vol second-cycle waste contained 0.17 g/liter of solids. Solids separating from blends of 1 vol second-cycle with 10 vol zirconium waste were granular, but sufficiently small to be readily transported by slurring. Solids separating from all other blends were fine and easily dispersed. Solids separating from second-cycle/zirconium waste blends were essentially zirconium solids.

Storing 285,000 gallons of a blend of 1 vol second-cycle waste with 10 vol zirconium waste at 24°C in a single 300,000-gallon tank would produce 0.77 inch of solids on the bottom of the tank; while storing the same volume of a blend of 1 vol second-cycle waste with 100 vol zirconium waste at the same temperature would produce 0.40 inch of solids. The settled densities of the solids are considerably different.

In conclusion, all second-cycle/aluminum waste blends studied would be suitable for long-term storage with the possible exception of the 1-to-1 vol blend. All second-cycle/zirconium waste blends studied were unstable; a blend containing as little as 1 vol of second-cycle waste in 100 vol of zirconium waste stored at 24°C would produce 0.17 g/liter of solids after 6 months.

7.2 Stability of ICPP First-Cycle Zirconium Waste Blended with ICPP Stainless Steel Sulfate Waste (B.J. Newby)

Approximately 37,000 gallons of waste was generated by dissolution of stainless steel fuel in sulfuric acid and subsequent extraction of the uranium. An attempt was made to calcine this waste in the WCF two different times, but a rapid buildup of pressure drop across the final filters of the WCF off-gas system occurred both times. Because of the small amount of stainless steel sulfate waste relative to other wastes, it is being calcined by blending a small volume of stainless steel sulfate waste with a large volume of first-cycle zirconium waste (Section II-4.1).

The stainless steel sulfate waste may be blended and stored for an extended period of time in ICPP storage tanks prior to calcination. Studies were performed to determine the stability of blends containing 5-15 vol of zirconium waste to 1 vol of stainless steel sulfate waste stored at 24 and 35°C for 6 months. Wastes are routinely stored between 24 and 35°C in ICPP storage tanks. The concentration of the constituents in the simulated first-cycle zirconium waste and stainless steel sulfate waste, used in the stability studies, is shown in Table XXXIII and is typical of the actual wastes.

All blends contained a trace of solids within 30 minutes; no increase in solids content was noted after 8 days of storage. The solids were fine and easily dispersed. The solids content of the blends was independent of blend concentration between 5 to 15 vol of zirconium waste per volume of stainless steel sulfate waste and storage temperatures between 24 and 35°C. The weight of solids in the blends after 6 months of storage was 0.37 g/liter; the volume of packed solids was 0.24 cc solid/liter of waste. X-ray diffraction showed SnO_2 to be the only crystalline component of the solids. Spectrochemical analyses of the solids showed 32 wt% tin, 2.4% aluminum, and 1.8% zirconium. Solids resulting from blending 37,000 gallons of sulfate wastes with 248,000 gallons of zirconium wastes would amount to about 0.06 inch on the bottom of a 300,000-gallon storage tank.

Effect of Addition of Calcium Nitrate: An experiment was performed to compare the behavior of zirconium waste and a zirconium waste - stainless steel sulfate waste blend when plant $\text{Ca}(\text{NO}_3)_2$ was added. Sufficient saturated $\text{Ca}(\text{NO}_3)_2$ solution to give a calcium-to-

TABLE XXXIII
COMPOSITION OF SIMULATED FIRST-CYCLE ZIRCONIUM WASTE
AND STAINLESS STEEL SULFATE WASTE

<u>Constituent</u>	<u>Concentration (Molar)</u>	
	<u>1st-Cycle Zirconium Waste</u>	<u>Stainless Steel Sulfate Waste</u>
Zr	0.57	---
H ⁺	1.54	3.37
Al	0.74	---
Fe	---	0.069
Cr	0.015	0.016
Ni	---	0.010
B	0.23	---
Sn	0.0067	---
NH ₄ ⁺	0.03	---
NO ₃ ⁻	2.21	2.50
SO ₄ ⁼	---	0.62
F ⁻	4.12	---

fluoride mole ratio of 0.55 was added as follows: (a) to zirconium waste, (b) to zirconium waste after which sufficient stainless steel sulfate waste was added to give a blend of 5 vol zirconium waste - 1 vol stainless steel sulfate waste, and (c) to a blend of 5 vol zirconium waste - 1 vol stainless steel sulfate waste. The resulting wastes were stored for 72 hours and their appearances compared. No differences were observed in the characteristics of the calcium fluozirconate precipitates formed, except that the precipitates in the blends settled more rapidly, and occupied slightly less volume, than did the precipitate in the zirconium waste (probably due to viscosity differences of the waste solutions).

7.3 Stability Of Blended ICPP First-Cycle Zirconium and Rover Fuel Wastes (B.J. Newby)

The reprocessing of Rover fuel at the ICPP in the near future will produce an estimated 115,000 gallons of first-cycle waste. Sufficient tank storage is not available to devote an entire 300,000-gallon tank to storage of Rover first-cycle waste although it might

be stored in the 30,000-gallon tanks from which stainless steel sulfate is being removed and calcined. The alternative is to blend the Rover fuel waste in a tank with other wastes. Since first-cycle zirconium fuel waste is the most likely candidate for blending, studies were made to see if blends of zirconium and Rover fuel wastes were stable. The concentrations of the constituents in the simulated first-cycle zirconium and first-cycle Rover fuel wastes used in the stability studies are shown in Table XXXIV. The composition of the zirconium fuel waste is typical of the actual waste; the composition of first-cycle Rover fuel waste is that proposed at the time of this study.

TABLE XXXIV
COMPOSITION OF SIMULATED FIRST-CYCLE ZIRCONIUM FUEL
WASTE AND ROVER FUEL WASTE

Constituents	Concentration (Molar)	
	1st-Cycle Zirconium Fuel Waste	Rover Fuel Waste
Zr	0.41	---
Nb	---	0.041
Al	0.68	0.36
H ⁺	1.40	2.12
Fe	0.0076	---
B	0.19	0.073
NH ₄ ⁺	0.020	0.044
U	8 x 10 ⁻⁶	2.1 x 10 ⁻⁵
Sn	0.0047	---
Cr	0.015	---
Hg	0.002	---
F ⁻	3.24	1.14
NO ₃ ⁻	2.28	2.16

Studies were made on four solutions and blends:

- (1) Rover first-cycle waste stored at 24°C
- (2) One vol of first-cycle Rover fuel waste added to one through ten vol of first-cycle zirconium fuel waste stored at 24°C

- (3) One vol of first-cycle Rover fuel waste added to one through ten vol of first-cycle zirconium fuel waste stored at 35°C
- (4) One through ten vol of first-cycle zirconium fuel waste added to one vol of first-cycle Rover fuel waste stored at 35°C.

These solutions were stored for about six months at the designated temperatures; 35°C is the upper limit recommended for the storage of blends of zirconium waste with other wastes^[22]. All blends were stable for at least 7 hours, but for no longer than 20 days. Instability increased more rapidly at the higher temperature, but the quantity of solids was only slightly different after a 6-month storage period. At 24°C, stability of blends varied from 2 days for a 1-to-1 zirconium-Rover waste blend to 20 days for a 10-to-1 zirconium-Rover waste blend; at 35°C, these same blends were stable for 7 to 24 hours and 3 days, respectively. The rate at which solids formed and the quantity of solids separating from solution at the end of 6 months increased as the ratio of zirconium waste to Rover waste decreased; a 1-to-1 zirconium-Rover blend at 24°C formed 3 g/liter of solids while a 10-to-1 zirconium-Rover blend formed 0.39 g/liter of solids. Instability is independent of whether Rover waste is added to zirconium waste or vice versa; solids separating from the blends are fine and easily dispersed. The Rover fuel waste became slightly unstable after 108 days storage at 24°C; at the end of 186 days of storage, this waste was still only slightly unstable. Solids that sloughed-off the walls of the Rover waste container were in the form of small plates and might be difficult to disperse into solution. Niobium was the principal constituent of solids separating from all solutions.

Storing the unblended 115,000 gallons of first-cycle Rover fuel waste in a single 300,000-gallon tank would produce 0.07 inch of solids on the bottom of the tank; storing the Rover fuel waste in 3 different tanks, each containing 247,000 gallons of zirconium waste, would produce 1.6 inches of solids in the bottom of each of the 3 tanks. In conclusion, all blends studied are unsuitable for long-term storage; the unblended Rover waste is probably suitable for long-term storage if stored at 24°C.

7.4 Storage Requirements for HTGR Liquid Wastes (R.E. Schindler)

The proposed interim processing of commercial HTGR fuel is expected to generate from one to four tanks of liquid waste with a decay-heat generation rate much higher than that of current ICPP liquid wastes. Currently, liquid waste temperatures are easily maintained below a 35°C limit to maintain low corrosion rates. However, storage (in the existing storage tanks) of liquid waste from the proposed reprocessing of HTGR fuel will produce a calculated in-tank temperature of from 40 to 100°C; the temperature varies with the concentration and age of the waste.

8. OTHER WASTE MANAGEMENT ACTIVITIES

8.1 Atmospheric Protection System for Filtration of Ventilation Air and Off-Gas Streams (P.I. Nelson)

Construction of an Atmospheric Protection System (APS) at the ICPP to minimize the release of radioactive particulates to the atmosphere is in progress and is scheduled for completion in early FY-76. Existing off-gas cleanup systems for ICPP and WCF processes remove radioactive particulates to well below allowable limits for controlled areas before the gases are released to the plant stack. However, all ventilation air from process areas is discharged to the stack without treatment. The APS will provide continuous filtration of all building ventilation air from process areas and backup filtration of all process off-gases before they are released to the atmosphere.

The filter system for the ventilation air will consist of a seven-foot-deep fiberglass prefilter in series with separatorless HEPA filters. This system will be capable of filtering 150,000 cfm of ventilation air from the main fuel processing building, waste disposal building, and waste calcining building. The prefilter will be contained in an underground concrete vault and will include a system for washing the filter media. The HEPA filter system will be composed of 26 filter caissons installed in parallel, with each caisson containing four HEPA filters. Valving will permit isolating each caisson and replacing the filters without disrupting the system operation. Filter change-out will be accomplished by contact maintenance using bagging procedures. Three new fans, any two of which have adequate capacity for the system, will also be provided.

Separate filtration systems consisting of deep bed prefilters and HEPA filters will be included for both the 50-cfm hydrogen-rich and 4,000-cfm NO_x-containing process-off-gas streams. These streams must be contained in acid-resistant systems because of the high probability of forming acids which would be corrosive to standard materials of construction, such as carbon steel and concrete. The hydrogen-rich stream, because of its explosive nature, will be handled separately from NO_x-containing off-gas. The hydrogen-rich stream is mixed with the ventilation air upstream of the new ventilation fans for discharge to the stack. New blowers for the NO_x-containing off-gas will be provided along with a condenser, demister, superheater, and filters. The NO_x-containing off-gas will be discharged directly to the stack.

Provisions will be made for sampling and monitoring the ventilation air and process-off-gas streams in the fan building. Instrumentation for control and measurement of pressure drops and radiation levels within the system will also be provided.

8.2 Solar Evaporation Pond for ICPP Chemical Waste Disposal (R.R. Smith)

A conceptual design has been completed for a proposed solar evaporation pond to eliminate discharge of nonradioactive chemical waste from the ICPP through the presently used discharge well. Nonradioactive chemical waste totals approximately 485,000 gallons per month from various units in the service building, including ion-exchange units providing

either soft or demineralized water for various ICPP processing operations and the periodic sludge removal from the conventional boilers through boiler blowdown lines. The proposed waste disposal system consists of a collection system for the liquid wastes, a pumping station for transferring the waste to the solar evaporation pond, and a 13.4-acre pond lined with an impermeable membrane. Sizing of the evaporation pond is based on the criterion that the annual flow is equal to the net annual evaporation rate.

8.3 Posttreatment of Calcined Nuclear Fuel Wastes (WMT Funded) (J.R. Berreth, H.W. Cole, L.C. Lewis, J.M. Beeston)

Investigations of methods for treating calcined high-level nuclear fuel wastes with additives to form stable inert products suitable for long-term storage were initiated this year. The scope of these investigations includes treatment methods for wastes of AEC origin and projected wastes from reprocessing of commercial reactor fuels. Fixation of commercial reactor wastes in glasses is being extensively studied both in the United States and other countries^[23,24,25]. Therefore, the present program is investigating alternative treatment methods to that of glass formation and treatment methods for certain wastes which are not compatible with current glass formation processes. In the case of AEC-originated wastes, which are not as compatible to glass formation as commercial wastes due to their chemical nature, alternative treatment methods or special glasses are being investigated.

Calcined nuclear fuel wastes are, in general, a stable granular material. However, they do suffer from relatively poor leachability properties, in particular for cesium^[26]. To improve this and other properties, several methods of calcine posttreatment are proposed including: metal matrix formation; ceramic or glass-ceramic formation; calcine particle coating with either metal or ceramic coats; concrete incorporation (with lower-level wastes); and for certain wastes, graphite or carbide coatings. The addition of materials to the calcining step to improve the calcine product may also be possible.

In comparing a massive matrix and a coating process, there may be areas where a particulate coating process has an advantage over a massive matrix process. These are: ease of handling, retrievability from storage, greater volume reduction, and possibly lower treatment costs. Disadvantages may be lower thermal conductivity and potential for higher leach rates because of much larger surface area. To date, experiments have been conducted on metal-matrix formation and ceramic formation with both AEC calcines and proposed commercial calcines; in addition, concrete incorporation with some AEC calcines has been studied.

Types of Wastes: Nuclear fuel wastes processed at AEC plants originate from several types of fuels and therefore, vary in chemical composition. Major chemical components, relative fission product content, and heat generation rates for several wastes are given in Table XXXV. Most of the high-level AEC wastes do not lend themselves well to current glass forming processes because of the presence of high alumina, fluoride, sulphate, sodium, iron, and other components that are incompatible with glass formation. Several of the AEC wastes in the form of fluidized-bed calcines are produced at the ICPP. Most work, to date, has been with a zirconium-base calcine (Zr calcine), which is approximately 21 wt%

TABLE XXXV

TYPICAL CALCINED NUCLEAR FUEL WASTE COMPOSITIONS

AEC Wastes	Major Components (wt%)					Fission Product Content	Heat Output
	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	ZrO ₂	CaF ₂		
Aluminum	89	--	1.3	--	--	Low	Low
Zirconium	22	--	--	21	54	Low	Low
Stainless Steel	50	45	--	--	--	Low	Low
Neutralized Purex	10	6	65	--	--	Low	Intermediate
Commerical Wastes[a]							
PW-4b	--	3.7	--	--	--	High	High
PW-6	--	5	10	--	--	High	High

[a] Assumes no additives used to produce calcine.

zirconium oxide, 22 wt% aluminum oxide and 54 wt% calcium fluoride, and a blended calcine (Zr-2nd cycle) derived from approximately a 67 vol% zirconium raffinate and 33 vol% second-cycle raffinate. The second-cycle component may contain up to 65 wt% sodium oxide, and therefore, the Zr-2nd-cycle calcine has a high fluoride and sodium content.

Commercial nuclear fuel processors coming on stream may produce several types of fuel wastes; prevalent among these are a PW-4b (nonsodium-containing) and a PW-6 (sodium containing) waste^[27]. It is anticipated that a particulate calcined material will be an intermediate product in the total waste solidification process. A currently proposed solidifying route for a commercial waste is to fluid-bed calcine a PW-4b-type waste with high-fired alumina as a particle nucleous. A synthetic PW-4c fluidized-bed calcine composed of 52% high-fired alumina and 48% PW-4c has been prepared at ICPP for posttreatment studies. This particular calcine is identical to a PW-4b calcine with the exception that it has a 1% Na content. Experiments conducted to date have been with the PW-4c calcine.

Ceramic Formation: Much research has been previously performed on incorporating radioactive liquid wastes with clays, zeolites, and other similar materials^[28,29,30]. But since solid high-level wastes such as the fluidized-bed calcines were nonexistent, the process of interacting fluxing agents with the calcines at elevated temperatures to affect solid-state or semi-solid-state reactions has received only cursory investigation^[30,31].

Experiments have begun on incorporating calcines into final products of a ceramic form. There are several routes open to development in the area of ceramics; one is sintering of the fluidized-bed calcines with suitable fluxes to form an inert solid matrix, ideally, at temperatures below 1,000°C; another, is ceramic coating of sintered calcine; and a third is the stoichiometric reaction of calcine with suitable materials to form an inert material. Experiments to date show that the ICPP calcines may be sintered into a solid matrix below 1,000°C by compacting the calcines prior to heating. These sintered calcines have good strength and do not shatter on breaking, as glasses often do. Leachability does not appear to be greatly reduced by this process, but suitable ceramic coatings could make these solid matrices inert as a unit.

Calcines, when mixed with suitable additives (which act as fluxing agents) such as clays, borates, silicates, etc., form ceramic or glass-ceramic materials when heated to high temperatures. Three calcines, PW-4c, Zr, and Zr-2nd cycle, which have been prepared in ceramic forms by mixing a calcine and fluxing agent, then compacting and sintering, are being tested for leachability in water at 90°C to study the effect of percent makeup water, compacting pressure, and sintering temperature. Figure 29 shows the percent weight loss over a 150-hour period for a Zr-2nd-cycle calcine mixed in the ratio of 3 parts calcine to 1 part fluxing agent, indicating the effects of sintering temperatures of 800°C and 900°C and of percent makeup water used in mixing and compacting the sample. Temperatures of 800°C for the combination of this fluxing agent (a mix of B_2O_3 , SiO_2 , CaO , and clay) and calcine used, appears to be too low for good sintering, as is indicated from the leach rate, and also by the poor physical appearance. Compacting pressure appears to have minimal effect on leachability; for example, the lowest 900°C leach curve (Figure 29) is based on leach rates for compacting pressures ranging from 5,000 psi to 20,000 psi, but the range of total percent weight lost after 150 hours was only from 0.75 to 0.9%. Addition of makeup water for mixing and ease of compacting appears to have a beneficial effect on sintering properties (see Figure 29), probably because it aids in obtaining somewhat higher compacting densities, and therefore, better contact for sintering. The variation of density with compacting pressure is shown in Figure 30. There is an increase of density with pressure, approximating only 8%, over the range 5,000 psi to 10,000 psi, which suggests that the use of an extrusion process at pressures near or below 10^4 psi is feasible.

Ratios of calcine to fluxing agent of 4:1, 3.5:1, and 3:1 have been tried; and accelerated leach rates are very nearly the same for 900°C sintered samples using 6% makeup water. Loss of weight on sintering appears to be only a function of the sintering reactions and independent of compacting pressure or unfired density. Weight losses for the Zr and Zr-2nd-cycle ceramics are in the range of 5 to 7% during sintering at 900°C and probably are mostly due to loss of CO_2 from the fluxing agent; whereas volume loss during sintering varies somewhat more, from near 0% up to 8% for 900°C sintering.

Leach rates at 25°C using the Paige method^[32] are being measured for 3:1 calcine-to-fluxing agent ratios for both Zr and Zr-2nd-cycle calcines. Boron and calcium are the leachates determined for the Zr product, and sodium and chromium are the leach rates being determined for the Zr-2nd product. The leach rate for a Zr ceramic is 4×10^{-4}

Fig. 29 Leach rate for Zr/2nd-cycle ceramic.

Fig. 30 Variation of density with pressure, before and after sintering, for a Zr ceramic.

at 35 days. For these ceramics, greater analytical sensitivity for leachable elements present is needed. Data for the Zr-2nd-cycle leach tests are not complete.

A splitting tensile strength of 1,770 lb/cm² has been measured for the Zr ceramic. Since these calcines are very high in fluoride content (20%), which makes them noncompatible with present day glasses, the ceramic process may well provide a means for preparing an inert and stable fluoride-containing product.

The commercial calcine (PW-4c), when mixed in the same ratio (3 parts calcine - 1 part flux), compacted at 10⁴ psi, and heated to 900°C, sinters well. The PW-4c calcine is also a material of high density (1.9 g/cc³), and when sintered with the fluxing agent, results in a ceramic of density near 2.8 g/cc³, which approaches the density of a glass (3 to 3.5 g/cm³). The product appears to be quite hard and strong. It does have a low percentage of voids (exact amount not yet determined). A hardness test showed a value of 59 Rockwell B, which may be compared to mold steels. A splitting tensile strength test resulted in a value of 2,550 psi.

In order to obtain information quickly as to the quality of the sintered samples, accelerated leach tests were performed by soaking in 500 cc of distilled water at 90°C. The specimens were approximately 3/4 inch in diameter by 3/4 inch in height and weighed 12g each. Specimens were removed approximately every 20 hours, dried at 105°C, cooled and

weighed, then replaced in fresh water and the process repeated. Figure 31 shows the results on 3 different samples over a 250-hour leaching period: All have very low leach rates, with the 1,020°C sintered sample showing the lowest, less than 0.05% after 250 hours; the 1,020°C sample started to flow during sintering. Leach rate tests at 25 °C are underway: Only a 24-hour leach result is available; it has a value of 1.6×10^{-4} g/cm²/day based on sodium.

Seven percent was the amount of makeup water required to obtain the best compacting density with the PW-4c calcine. Loss of weight on sintering at 900°C appears to be constant at near 4%; and volume loss is near 11%, thereby resulting in a density increase of near 20%, to 2.8 g/cc, on sintering. Sintered (900°C) samples have been maintained at 700°C for 192 hours without any additional loss in weight, dimensional change, or deterioration of the sample.

Experiments on the treatment of high-sodium content wastes, such as neutralized Purex wastes, were started. For this experiment, a synthetic liquid neutralized Purex waste was chosen because of its high-sodium content (6 M). The goal of the experiments was to treat these wastes with the addition of suitable ceramic-forming compounds to bring about a stoichiometric ceramic reaction to produce an inert material, such as a sodium aluminum silicate. Treatment of this liquid with natural mineral additives at temperatures of 800 to 900°C has resulted in what appears to be an inert, ceramic-type material. The material is hard and not friable. Sufficient testing to evaluate the merits of this method have not been completed.

Metal Incorporation: Experiments studying the incorporation of calcines in metal are being conducted. Several ratios of metal to calcine have been studied as shown in Table XXXVI. All of these samples have been prepared by powder metallurgy methods. The method is based on mixing particulate calcine with a metal powder, compacting, and sintering at proper temperatures in an inert atmosphere. Mixes using 30 to 80 wt% calcine have been prepared. Resultant samples appear to have good strength and integrity. Sintered calcine-aluminum samples maintained in air at 400 to 500°C for six days showed no signs of deterioration. These samples, and similarly the high-calcine-content vacuum cast samples [22], appear to have suitable physical strength characteristics. Thermal conductivity measurements have not been performed to date. To scope the nature of the effects of powder compositions, two compositions were selected for testing. For one, the metal matrix would be continuous; and for the other, it would not. The purpose was to accentuate the effects of changes in the calcine composition, changes in metal composition, and the addition of titanium as a wetting agent for the oxides. Two metal powders were used as a matrix: aluminum and iron.

The density and compression strength of the calcine-metal composites measured to date are given in Table XXXVI. The calcines indicated in the table are zirconium (Zr), zirconium-2nd cycle (Zr-2nd), and PW-4c. The compact composition is given in wt%; therefore, the volume percentage of the metal matrix is less in the iron matrix compacts. The effect of calcine particle-size distribution on density and strength was examined with screened and unscreened calcines and was found to be minimal.

Fig. 31 Leach rate at 90°C for a high-fired-alumina-base PW-4c ceramic.

TABLE XXXVI

DENSITY AND STRENGTH OF CALCINE-METAL COMPOSITES

Number	Composition (wt%)	Density (g/cm ³)	Compression Strength (lb/in. ²)
1	50 Zr ^[a] -50Al	2.28	15,100
2	50 Zr-2nd ^[b] -50Al	2.31	13,340
3	80 Zr-20Al	2.19	7,460
4	80 Zr-2nd-13Al-7Ti	2.25	7,800
5	80 Zr-2nd-13Fe-7Ti	2.59	7,300
6	80 Zr-13Al-7Ti	2.15	7,460
7	80 Zr-13Fe-7Ti	2.5	5,580
8	50 Zr-50Fe	3.3	19,000
9	80 PW4c-13Al-7Ti	3.11	11,000
10	80 PW4c-13Fe-7Ti	2.7	580
11	50 PW4c-40Al-10Ti	2.84	19,250
12	50 PW4c-40Fe-10Ti	3.30	350
13	50 PW4c-50Fe	4.19	12,300
14	50 PW4c-50Al	2.82	22,700

[a] Zr calcine.

[b] Zr 2nd-cycle calcine.

The composition of the calcine appears to have an effect on the strength of the compact; for example, consider the pairs numbered 1 and 8 and 13 and 14. In the first pair, zirconium calcine with iron produces a stronger compact than with aluminum; while in the second pair, PW-4c calcine with aluminum produces a stronger compact than with iron. The magnitude of this effect would be expected to change with volume percentage of metal matrix and with optimum sintering temperatures.

The metallography (see Figures 32, 33, 34, 35) showed that sintering of the iron powder compacts was poor. The compacts were subject to particle pull-out during polishing. Even in the 50 wt% iron compacts, there is a sinterability problem, although the strength is as high as in the aluminum compacts (see Samples 1 and 8 and Samples 13 and 14 of Table

Fig 32 Iron matrix shows porosity and Zr calcine shows cracking, iron is not contiguous Sample 8, 50 Zr/50 Fe, polarized light, 100x.

Fig 33 Aluminum matrix and Zr calcine show cracking, aluminum matrix appears contiguous Sample 1, 50 Zr/50 Fe, bright field, 100x.

Fig. 34 Titanium present in aluminum matrix as second phase. Aluminum matrix is not contiguous. Sample 4, 80 Zr-2nd, 13 Al-7Ti, 100x.

Fig. 35 Angular shape of PW-4c calcine. Titanium distributed in aluminum matrix. Sample 11, 50 PW-4c, 40 Al-10Ti, polarized light, 100x.

XXXVI). The metallography also showed some cracking of the matrix during cooldown or mounting. Further work needs to be done before firm conclusions can be drawn.

Accelerated leach rate tests at 90°C on Zr calcines indicate that when the metal is 20 wt%, weight losses of approximately 0.1% per day are observed; and when the metal is 50 wt%, a weight gain of approximately 0.1% per day is observed.

Accelerated leach rate tests at 90°C for PW-4c calcines in a compacted 40% iron - 10% Ti matrix, show a weight gain of 0.2 to 0.1% per 20 hours of leaching. A 40% Al - 10% Ti compact shows a weight gain of 2% in the first 18 hours and a reduction in weight per 20-hour period from 0.4% to 0.01% over 11 20-hour leaches. A 13% Al - 7% Ti compact had an initial 6% weight gain with subsequent weight losses of approximately 0.2% per 20-hour period over 11 leaches. After the initial oxidation of the metal at 90°C, subsequent weight changes appear to be small. Leach rates based on sodium, at 25°C for a 40% Al - 10% Ti samples, were 7×10^{-2} g/cm²/day in the first 24 hours and 3×10^{-3} g/cm²/day after 95 hours. In both cases, leachability at 25°C for sodium is near 5% per day. Apparently, because particle-to-particle contact occurs, a continuous path for leaching is present. Metal coating of calcine particles or of the matrix are possible routes to reduce the leaching characteristics of these matrices.

Calcine-Concretes: This study was undertaken to determine the value of cement as an incorporating medium for fluidized-bed calcine. A high-alumina cement, in general, is superior to Portland cements on the basis of leachability, degradation in natural water systems, and strength characteristics. Thus, it was chosen for calcine incorporation studies.

The use of cements in any incorporation process may be limited, because the cured product is permeable to water. While this permeability might be prevented by coating or impregnating the finished product with bitumen or other material, bitumen materials are subject to radiation damage during prolonged exposure. Glaze materials, which could be sprayed on the surface, might be used to provide watertightness.

An unfavorable property of alumina cements is the breakdown of the hydraulic bond in the temperature range 225 to 270°C. The result of this breakdown is a loss of strength and structural integrity. However, with the proper fluxing agents present, the cement may be sinterable into a ceramic at elevated temperatures. Temperatures above 225°C are to be avoided unless the material is sintered.

Experiments were performed on incorporating calcines with high-alumina cement. These included varying the ratios of calcine to cement and the use of additives such as sand, bentonite, sodium silicate, and calcium chloride in varying fractions to determine effects on strength, sinterability, and leachability. The resulting calcine-concretes were strength-tested after curing 28 days.

A tabulation of representative specimens prepared with their compositions and strength tests is shown in Table XXXVII. Those specimens, which were leach tested, are also indicated. The use of bentonite as an additive considerably reduced the concrete strength.

TABLE XXXVII

Zr 2nd-CYCLE CALCINE-CONCRETE COMPRESSION STRENGTH TESTS

Material (wt%)							Break Point (psi)	Specimens Leach Tested
Calcine	Cement	Water	Bentonite	CaCl ₂	Na ₂ SiO ₃	Sand		
32.2	48.4	19.4					6590	✓
41.7	41.7	16.6					6015	✓
51.1	34.5	13.8					6110	✓
59.3	25.4	15.3					3820	
47.2	31.5	17.7	1.6				1525	✓
45.4	30.2	17.9	4.5				350	
47.6	33.1	16.6		0.7			7640	
49.0	32.1	16.3		2.0			3470	✓
49.5	33.0	16.5			1.0		3660	✓
46.9	31.3	15.6			6.2		41	
32.0	10	20				8	2705	
32.3	32.3	16.1				19.3	5285	✓
28.6	28.6	14.2				28.6	4710	

Two percent calcium chloride slightly decreases the strength. The addition of increasing quantities of sodium silicate progressively reduces the strength. Standard high-alumina concretes for construction normally have strengths of 5,000 to 9,000 psi; whereas, strengths of Portland Cement concretes are normally 3,000 to 4,000 psi. Many of the calcine concretes tested appear to fall in a favorable strength region of 2,500 to 6,000 psi. Concrete samples have been leach tested at 25°C by following the sodium and chromate removal -- the two most leachable ions present. Figure 36 shows the leachability of sodium and chromium for three different samples. The leach rate for sodium in concrete appears to be approximately 20 times greater than that for chromium. Figure 37 shows sodium leach rates for calcine-cement with the four additives bentonite, sodium silicate, calcium chloride, and sand; Figure 38 shows the chromium leach rates for the same four additives. The two figures indicate that there is a significant leach rate reduction from approximately 30% in 150 hours to 4 to 6% in 150 hours for sodium with the addition of calcium chloride or sand.

Attempts have been made to form a sintered concrete product by heating to 1,000°C. Sintering tests of calcine-concrete samples containing a few percent of the additives bentonite or sodium resulted in failures, in that the fired samples were easily crumbled.

Heat transfer calculations, assuming a maximum allowable centerline temperature of 200°C, an outside wall temperature of 50°C, and a 25 wt% ICPP-type calcine in concrete, which results in a heat source of 1.6×10^{-4} watt/cc, indicate only a 51°C temperature difference from centerline to outside wall for a 2-foot-diameter cylinder.

Incorporation of commercial high-level wastes into cement seems impractical due to the large heat output of these calcines and the low-thermal conductivity of the mixture. A commercial waste, such as PW-4b, that results from processing of a fuel with a burnup of 45,000 MWd/tonne and out of the reactor for one year, may have a heat generation rate of up to 0.242 watt/cc. The thermal gradients for a cylindrical specimen containing 10 wt% of high-level waste are enormous compared to ICPP calcine-cement mixes. If cement is to have application as a medium for incorporating high-level wastes, the thermal gradients must be lowered and the cement mix still contain a reasonable amount of waste. For example, an annular configuration can contain more waste per linear foot than a solid cylinder. A solid cylinder of radius 5.4 cm and infinite height, containing 1.6 lb of waste/ft of height, has a maximum thermal gradient of 28°C/cm. An annular configuration of inner radius (7.8 cm), outer radius (15.25 cm), and infinite height, can contain 9.6 lb of waste/ft of height and have the same maximum thermal gradient. It was assumed both the cylindrical solid and the annular solid were cooled under conditions of free air convection.

8.4 Actinide Removal from ICPP Wastes (WMT Funded) (L.D. McIsaac, J.D. Baker)

An important objective of the nuclear industry's waste management plan is the minimization of the quantities of wastes contaminated with very long-lived, alpha-emitting isotopes. The actinide elements: uranium, neptunium, plutonium, americium, and curium are the prime sources of alpha emission. Although the mass of these elements in the wastes

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Fig. 36 Leach rate for sodium and chromium from particulate calcine and a calcine-concrete.

Fig. 37 Percent sodium leached with time for various additives to a Zr 2nd-cycle calcine-concrete.

Fig. 38 Percent chromium leached with time for various additives to a Zr 2nd-cycle calcine-concrete.

is small compared with other components, such as bulk fission products, cladding materials, and salting agents, the net effect of their presence is that all wastes must be handled as alpha waste with the long periods ($>1,000$ yr) for decay.

The purpose of this program is to develop the technology for removal of actinide elements from ICPP wastes so that the calcined residual waste will contain less than 10 nCi/g of solids. This level of activity is presently defined as "alpha-free" and will allow the handling of the calcine in a less restrictive manner than that for alpha-contaminated material.

8.41 Characterization of ICPP Waste. The bulk of the wastes stored at ICPP has been generated from the processing of zircaloy- and aluminum-clad fuel elements. The uranium recovery process for zircaloy-clad elements requires the addition of aluminum nitrate as both a salting agent and a complexant for the free fluoride present in the dissolution process. When available, the dissolver solution from aluminum-clad elements is coprocessed with zircaloy-clad elements, thus serving the same purpose. Waste generated from these campaigns are, therefore, similar. The chemical analyses for three major waste storage tanks at ICPP are shown in Table XXXVIII. Actinide analyses are given in Table XXXIX. Any process for actinide removal at ICPP must necessarily be applicable to this type of waste.

TABLE XXXVIII

CHEMICAL ANALYSES OF ICPP FIRST-CYCLE WASTES

Analysis	Tank Number		
	WM-185	Wm-187	WM-188
H^+ , <u>M</u> (± 0.04)	1.51	1.62	1.72
Al, <u>M</u> (± 0.02)	0.68	0.64	0.69
Zr, <u>M</u> (± 0.01)	0.44	0.44	0.48
F^- , <u>M</u>	3.12	3.00	3.52
B, g/l	2.16	2.08	2.34
NO_3^- , <u>M</u> (± 0.16)	2.36	2.32	2.40
Fe, g/l (± 0.012)	0.257	0.225	0.298
Cl^- , mg/l	9	12	37
Na, Mg/l	29	60	74
specific gravity	1.192	1.185	1.203

TABLE XXXIX
ACTINIDE ANALYSES OF ICPP FIRST-CYCLE WASTE^[a]

<u>Isotope (g/l)</u>	<u>Tank Number</u>		
	<u>WM-185</u>	<u>WM-187</u>	<u>WM-188</u>
²³⁷ Np	1.19 x 10 ⁻⁵	1.57 x 10 ⁻⁵	0.97 x 10 ⁻⁵
²³⁹ Pu	1.39 x 10 ⁻³	0.80 x 10 ⁻³	1.08 x 10 ⁻³
²⁴⁰ Pu	3.40 x 10 ⁻⁴	2.44 x 10 ⁻⁴	2.91 x 10 ⁻⁴
²⁴¹ Pu	1.51 x 10 ⁻⁴	1.09 x 10 ⁻⁴	1.26 x 10 ⁻⁴
²⁴² Pu	4.78 x 10 ⁻⁵	4.05 x 10 ⁻⁵	4.16 x 10 ⁻⁵
²⁴¹ Am	4.4 x 10 ⁻⁵	2.7 x 10 ⁻⁵	3.5 x 10 ⁻⁵
²⁴³ Am	1.2 x 10 ⁻⁶	0.78 x 10 ⁻⁶	0.95 x 10 ⁻⁶
²⁴⁴ Cm	7.3 x 10 ⁻⁸	4.5 x 10 ⁻⁸	5.8 x 10 ⁻⁸

[a] Am and Cm values are calculated.

The wastes shown in Table XXXVIII typically calcine down to about 250 g of solids per liter of throughput. It is apparent from the actinide analyses that separation factors in excess of 100 must be attained for the Pu and Am to reach the desired 10 nCi of alpha emission per g of solids.

8.42 Potential Separation Procedures. A literature survey has been made for procedures or technical information that would be applicable to the alpha removal program at ICPP. Many separation procedures found in the literature appear promising, but their application to liquid waste peculiar to ICPP needs investigation. These procedures fall into three categories outlined below:

(1) Solvent Extraction.

Nonsynergistic: TBP, dibutylbutyl phosphonate (DBBP), and di(2-ethyl-hexyl) orthophosphoric acid (HEDHP) have been shown to be effective extractants of +3 and higher valence actinides from 5 - 7 M NO₃⁻, 0.1-0.5 M H⁺ aqueous media^[33,34,35]. Bidentate organophosphorus compounds, such as tetrabutyl-methylene diphosphonate (TBMDP), have been shown to have high affinity for actinides in greater than 1 M HNO₃^[36].

Synergistic: Trioctyl phosphine oxide (TOPO) and 1-phenyl-3 methyl-4 benzoylpyrazolone-5 (PhMBP) in cyclohexane extracts +3 Am and Cm quantitatively from unsalted 0.1 $\underline{\text{N}}$ HNO_3 ^[37]. TBP and PhMBP in cyclohexane exhibits similar extraction strength^[37]. HDEHP and P_2O_5 in cyclohexane extracts +3 Am quantitatively from 1 - 12 $\underline{\text{M}}$ HNO_3 ^[38]; up to 1.5 $\underline{\text{M}}$ $\text{Al}(\text{NO}_3)_3$ and 0.1 $\underline{\text{M}}$ F^- do not interfere.

(2) Ion Exchange. A chelating resin based on aminopolystyrene and Arsenazo I sorbs +3 Am and Cm from 1 $\underline{\text{M}}$ HNO_3 with a $K_d > 10^3$ ^[39]. Macro amounts ($\leq 1.5 \underline{\text{M}}$) of aluminum do not interfere. Anion exchange using Dowex 1 x 4 removes +4 Np and Pu ($K_d > 10^3$) from 7 $\underline{\text{N}}$ NO_3^- solutions^[40]. Fission products, corrosion products, and fuel-cladding metals do not interfere. The inorganic exchange resin, ammonium 12-molybdophosphate, has been suggested for the removal of +4 actinides from highly acidic media^[41].

(3) Coprecipitation. Oxalate precipitation of Ca^{+2} has been used for batch removal of actinides from dilute nitric acid solutions^[42].

Light fission product rare earth elements will accompany +3 actinides in whatever separation procedure is developed. Several procedures exist in the literature for separation of +3 Am and Cm from rare earths. Cation-resin separation using organic chelating agents are numerous. A solvent extraction method called "TALSPEAK" has been developed for partitioning +3 actinides from rare earths^[43]. Mixed TBP and HDEHP extractants remove light rare earth elements selectively from a complexing solution of lactic acid and pentasodium diethylene triamine pentaacetic acid.

8.43 Experimental Program.

Synergistic Extractants: A synergistic extractant composed of 0.3 $\underline{\text{M}}$ HDEHP - 0.1 $\underline{\text{M}}$ P_2O_5 in cyclohexane has been used with a synthetic Zr-Al dissolver solution tagged with ^{241}Am . A distribution coefficient, E_a^0 (organic concentration divided by aqueous concentration), greater than 40 was observed. However, once extracted, the Am was so strongly bound in the organic phase that all efforts to find a stripping agent have been unsuccessful. Other synergistic systems studied were TBP-PhMBP, DBBP-PhMBP, and TOPO-PhMBP. Each proved very effective in removing ^{241}Am from 0.1 $\underline{\text{N}}$ HNO_3 solution (i.e., $E_a^0 > 1,000$), but were totally ineffective in removing ^{241}Am from synthetic dissolver solution adjusted to 0.6 $\underline{\text{M}}$ H^+ with ammonia. Below 0.6 $\underline{\text{M}}$ H^+ , Zr-Al dissolver solution becomes unstable toward precipitation.

DBBP: An evaluation of DBBP as a possible extractant for actinides in ICPP wastes is in progress. Tracer amounts of ^{239}Np , ^{239}Pu , and ^{241}Am have been added to synthetic Zr-Al dissolver solution to study the extraction behavior of these elements. For the study of fission products and cladding elements, tracers of ^{95}Zr , ^{95}Nb , ^{106}Ru , ^{144}Ce , ^{155}Eu , ^{51}Cr , ^{203}Hg , and ^{59}Fe have been used. DBBP has been purified prior to use by successively scrubbing with 5% Na_2CO_3 and 0.6 $\underline{\text{M}}$ HNO_3 . $\text{NaI}(\text{Tl})$, $\text{Ge}(\text{Li})$ and liquid scintillation spectrometry have been used to determine trace activities in organic and aqueous phases. Kerosene and carbon tetrachloride have been used as a diluent for DBBP; kerosene proved superior for Am extraction and, therefore, has been used in all studies reported.

Tracers, usually added one at a time for each study, were taken down to near dryness several times with concentrated HNO_3 before adding to the dissolver solution. At least one hour was allowed for the tracers to equilibrate with the Zr-Al dissolver solution before extraction. Because of the poor +4 Pu extraction experienced in processing at ICPP with Zr-Al dissolver solution, two types of extraction studies with DBBP have been made. In one type, ferrous sulfamate was added, thus reducing Pu to +3, assuring a behavior similar to +3 Am and Cm. In the second, CrO_3 was added to oxidize Pu to +6. A one hour period was allowed for completion of these redox reactions before extraction studies were commenced. Tracer equilibrium and redox reaction times were combined.

Acidity adjustments of Zr-Al dissolver solutions have been made by additions of concentrated NH_3 . Solutions adjusted to 0.6 M H^+ have remained stable for 60 days thus far.

A kinetic study of the extraction of Am into DBBP indicated equilibrium is reached in two minutes or less; therefore, extraction times of two minutes have been used throughout this work. The results of extraction and back-extraction measurements made with 0.6 M H^+ Zr-Al dissolver solution are summarized in Tables XL and XLI. Only the extraction of Pu, Np, Hg, and Fe have been studied in the CrO_3 -oxidized dissolver solution.

An acid-dependence study has been made for Am extraction into DBBP. These data are shown in Table XLII. A log - log plot of E_a^0 versus M H^+ indicates the extraction to be inversely second-order, dependent on the acid strength.

To determine if any significant concentration effect occurs with DBBP, two synthetic Zr-Al dissolver solutions were neutralized to 0.6 M H^+ with NH_4OH ; one was tagged with $\sim 0.12 \text{ } \mu\text{g/ml}$ Americium-241 and the other with $\sim 0.12 \text{ } \mu\text{g/ml}$ Plutonium-239. Ferrous sulfamate was added to the plutonium sample and allowed to equilibrate for one hour. Both samples were extracted five successive times with equal volume amounts of 30% DBBP in kerosene. The distribution coefficients, E_a^0 (concentration in organic divided by concentration in aqueous), and the metal ion concentration for the successive extractions are shown in Table XLIII.

The concentrations, given as nanograms/ml, show the amount of metal ion present at the beginning of each batch extraction. The total decontamination factor for plutonium is 760 and for americium, 1,630. No significant change in the distribution coefficients as a function of concentration was observed.

Distribution coefficients for two Am extractions with DBBP from Zr-clad fuel 1st-cycle raffinate from a recent ICPP fuel reprocessing campaign have been measured. A newly developed analytical procedure, employing isotope-dilution mass spectrometry, was used to obtain the data shown in Table XLIV. Both extractions resulted in interfacial scum. Loss of Am to the interface cannot be excluded.

TABLE XL

EXTRACTION AND STRIPPING DISTRIBUTION RATIOS

Conditions:			
1. Zr-Al Dissolver Solution Adjusted to 0.06 <u>M</u> Ferrous Sulfamate and 0.6 <u>M</u> H^+ Before Extraction.			
2. 30% DBBP in Kerosene Used as Extractant.			
Element ^[a]	E_a^o (Extraction) ^[b]	E_a^o (H_2O Strip) ^[b]	E_a^o (6N HNO_3 Strip) ^[b]
Al	<0.005	---	---
Ru	0.45	2.5	0.045
Np	5.0	0.26	15
Pu	3.1	0.38	>100
Am	3.7	0.13	0.060
Ce	1.6	0.23	0.032
Eu	2.9	0.16	0.21
Zr	0.022	0.007	0.80
Nb	0.18	---	0.22
Fe	<0.01	---	---
Cr	0.025	---	---
Hg ^[c]	0.09	1.2	0.11

[a] Al analyzed chemically; all others analyzed radiometrically.

[b] All values have an estimated accuracy of $\pm 10\%$.

[c] Zr-Al dissolver solution made 0.002 M Hg^{++} before reduction.

TABLE XLI

EXTRACTION OF Np AND Pu FROM 0.6 M H⁺ ACID Zr-Al DISSOLVER SOLUTION

Conditions:		
1. Adjusted to 0.01 <u>M</u> and 0.1 <u>M</u> CrO ₃ .		
2. 30% DBBP in Kerosene Used as Extractant.		
Element	E_a^o (0.01M CrO ₃) ^[a]	E_a^o (0.1M CrO ₃) ^[b]
Np	1.6	9.9
Pu	13	33
Hg ^[b]	0.2	0.20
Fe	<0.01	---

[a] All values have an estimated accuracy of $\pm 10\%$.[b] Zr-Al dissolver solution made 0.002 M Hg⁺⁺.

TABLE XLII

DISTRIBUTION RATIOS FOR THE EXTRACTION OF AMERICIUM
FROM VARIOUS ACID STRENGTH Zr-Al DISSOLVER SOLUTIONS
WITH 30% DBBP IN KEROSENE

Acidity (<u>M</u> H ⁺) ^[a]	E_a^o ^[b]
1.41	0.91
1.17	1.17
1.05	1.41
0.94	1.85
0.74	3.37
0.60	3.40

[a] Standard deviation of each measurement is ± 0.08 M H⁺.[b] All values have an estimated accuracy of $\pm 10\%$.

TABLE XLIII

DISTRIBUTION COEFFICIENTS AND METAL CONCENTRATIONS FOR
SUCCESSIVE EXTRACTIONS

Isotope	Extraction					Final Concentration in Aqueous Phase
	1	2	3	4	5	
$^{239}\text{Pu } E_a^{\circ}$	2.39	2.69	2.72	2.97	3.11	
ng/ml	120	35	9.6	2.6	0.65	0.16
$^{241}\text{Am } E_a^{\circ}$	3.34	3.58	3.26	3.26	3.53	
ng/ml	120	28	6	1.4	0.33	0.07

TABLE XLIV

EXTRACTION OF Am FROM Zr 1st-CYCLE RAFFINATE USING 30% DBBP IN KEROSENE

(1st-Cycle Raffinate Adjusted from 2.1 to 0.6 $\underline{M}$ H^+

with NH_4OH Before Extraction)

	$^{241}\text{Am}(\text{ng/ml})$	E_a°
Before Extraction	42.5 ^[a]	---
After 1st Extraction	4.35 ^[a]	8.8 ^[a]
After 2nd Extraction	0.60 ^[b]	6.2 ^[b]

[a] Estimated accuracy is $\pm 5\%$.

[b] Estimated accuracy is $\pm 10\%$.

DHDECMP: Di-hexyl-N, N-diethyl-carbamyl-methylene-phosphonate, DHDECMP (which is a bidentate extractant), has recently been shown to be an effective extractant for Am from acidic nuclear wastes^[44]. The possible use of DHDECMP for actinide removal from ICPP waste is being investigated.

DHDECMP^[a] diluted to 30% with kerosene resulted in two organic phases when contacted with both 0.6 M H⁺ and 1.44 M H⁺ synthetic dissolver solution. However, both 30% DHDECMP in CCl₄ and 30% DHDECMP in heptane gave one organic phase. Distribution coefficients, E_a^O , of 3 and 14, respectively, for Am from unneutralized Zr-Al dissolver solution (1.44 M H⁺), were obtained with these reagents. Back extraction with water proved to be ineffective due to impurities in the DHDECMP that have an affinity for Am in low acid media. A purification procedure suggested in the literature^[36] for DHDECMP analogues was unsuccessful in removing the contaminant. A purification procedure suggested by W.W. Schulz of ARHCO^[45] has been followed, which yields a product with favorable forward- and back-extraction characteristics for americium. This procedure involves the hydrolysis of 30% DHDECMP in CCl₄ with 6 N HCl for 48 hours at 60°C, followed by scrubbing sequentially with water, 1 N NaOH, and water. The resulting organic is heated slowly to 140°C to remove CCl₄, diluted to 30% with heptane, and equilibrated with an equal volume of 1.5 N HNO₃.

Several batches of 30% DHDECMP in heptane have been prepared as described above; and the distribution coefficient, E_a^O , for the extraction of Americium-241 from a synthetic Zr-Al dissolver solution measured. Values of E_a^O varied from 7.4 to 11.0. Back extraction with water proved satisfactory in all cases, with less than 1% of the Americium-241 originally present in each organic remaining after two equal-volume water extractions.

Variations in the extraction of Am from Zr-Al dissolver solution with different batches of purified DHDECMP are not presently understood. Samples of DHDECMP as received and after purification have been sent to an organic specialties laboratory (Huffman Laboratories, Inc., Wheat Ridge, Colorado) for analysis.

Results of extraction and stripping studies obtained to date on one purified batch of 30% DHDECMP in heptane are shown in Tables XLV and XLVI. Tracer techniques described previously have been used where possible to obtain distribution data. The synthetic coprocessing dissolver solution used in this study was 1.57 M H⁺ and contained 0.1 mg La/ml. This La concentration approximates the rare earth concentrations in ICPP coprocessing wastes. In all cases, the extractions were carried out for 15 minutes using an automatic mixer.

Mercury is strongly extracted from either an oxidizing or reducing sample matrix by 30% DHDECMP in heptane. A search for an aqueous back extractant has been unsuccessful. After the acid level in the organic is reduced by water scrubbing, mercury can be removed by electrolytic replacement on copper gauze. The distribution of Ru is little affected by the addition of oxidants or reductants.

[a] DHDECMP obtained from Wateree Chemical Co., Inc., Lugoff, South Carolina.

TABLE XLV

EXTRACTION AND STRIPPING DISTRIBUTION RATIOS

Conditions:			
1. Zr-Al Dissolver Solution Made 0.01 <u>M</u> in CrO_3 Before Extraction.			
2. 30% DHDECMP in Heptane Used as Extractant.			
Element	E_a^0 (Extraction)	E_a^0 (1st H_2O Strip) [a]	E_a^0 (2nd H_2O Strip) [a]
Pu	11.1	0.45	0.87
Am	10.9	0.34	0.038
Ce	6.8	0.97	0.071
Zr	0.018	---	---
Cr	0.59	3.9	2.1
Ru	0.58	3.3	4.5
Hg	21	>100	>100
Fe	0.016	---	---
H+	0.40	---	---

[a] All values have an estimated accuracy of $\pm 10\%$.

TABLE XLVI

EXTRACTION RATIOS

Conditions:			
1. Zr-Al Dissolver Solution Adjusted to 0.06 <u>M</u> Ferrous Sulfamate before Extraction.			
2. 30% DHDECMP in Heptane Used as Extractant.			
Element	E_a^0 (Extraction) [a]	E_a^0 (1st H_2O Strip) [a]	E_a^0 (2nd H_2O Strip) [a]
Cr	<0.005	---	---
Ru	0.45	---	---
Hg	5.9	---	---
Pu	10.1	0.28	0.19

[a] All values have an estimated accuracy of $\pm 10\%$.

Distribution coefficients for Am from Zr-Al coprocessing 1st-cycle raffinates (from a recent ICPP fuel reprocessing campaign) with DHDECMP have been determined. Extraction data obtained are given in Table XLVII. Equal volumes of organic to aqueous phases were used for all extractions. No interfacial scum was observed.

TABLE XLVII

EXTRACTION OF Am FROM Zr-Al COPROCESSING 1st-CYCLE

RAFFINATE WITH 30% DHDECMP IN HEPTANE

(Zr-Al 1st-Cycle Raffinate 1.6 M in Acid)		
	$^{241}\text{Am}(\text{ng/ml})$	E_a^0
Before Extraction	25.6 ^[a]	---
After 1st Extraction	2.35 ^[a]	9.9 ^[a]
After 2nd Extraction	0.27 ^[b]	7.7 ^[b]

[a] Estimated accuracy $\pm$ 5%.

[b] Estimated accuracy $\pm$ 10%.

8.44 Analytical Methods Development. A major requirement of this program is the availability of reliable analytical methods for the measurement of low levels of specific alpha emitters in samples having a high salt concentration and high levels of beta-gamma activity.

For the determination of Americium-241, a procedure with three different measurement options has been developed. The first option employs isotopic dilution mass spectrometry in which a known amount of Americium-243 is used as a spike. The second is isotope dilution gamma-ray spectrometry using a Ge(Li) detector in which Americium-243 again is used as a spike, and the 60 keV gamma-ray of Americium-241 and 75 keV gamma-ray of Americium-243 are measured. The high degree of radiochemical purity of the americium fraction achieved by the separation procedure allows for a third measurement option, which is the measurement of the 60 keV gamma-ray using NaI(Tl) gamma-ray spectrometry. However, at present, this last option will not give quantitative results because the recovery of Am through the procedure is not complete. The poor resolution of NaI(Tl) precludes the use of Americium-243 spike technique. Thus, it will be necessary to improve the separation technique to achieve quantitative recovery. At present, yields in the range of 75% are easily obtained. The sensitivity of the three measurement options is <0.1 nanogram for mass spectrometry and approximately 0.5 nanogram for gamma-ray spectrometry.

Because the +3 actinides are not individually separated in the developed procedure, high resolution alpha spectrometry can be used to determine ^{242}Cm and ^{244}Cm relative to ^{241}Am .

The developed separation procedure is based on a combination of solvent extraction and ion exchange. Briefly, the method consists of diluting (20-fold) the ICPP Zr-Al dissolver solution sample with 1 M lactic acid, pH 2.3, extracting with 0.3 M HDEHP in heptane, and scrubbing the organic phase with 0.01 N HNO_3 . If isotope dilution is to be used, Americium-243 spike should be added prior to extraction, allowing at least one hour for exchange.

The americium is stripped from the organic phase with 10 N HNO_3 containing NaBrO_3 , which oxidizes the Ce to +4 and prevents the stripping of this highly radioactive nuclide. Separation from U, Pu, Np, and the fission products also is obtained. The aqueous phase is evaporated to near dryness, diluted with water, and the Am is coprecipitated with $\text{Fe}(\text{OH})_3$ using NaOH. The precipitate is washed with H_2O , centrifuged, dissolved in concentrated HCl, and passed through an anion column. The Am passes through the column while Fe and other strongly chloride complexed ions are retained on the column. The effluent is evaporated to dryness and then dissolved in 0.01 N HNO_3 .

If mass spectrometry is the measurement option, the sample is further purified by passing the solution through a cation column, washing the column with several column volumes of 2 N HCl, eluting the Am with 6 N HCl, and evaporating to dryness. Although the +3 rare earths are not separated from the Am, no serious difficulties are experienced in the mass spectrometric determination of the Am.

For gamma-ray analysis, the 0.01 N HNO_3 solution is loaded on a stationary-phase HDEHP column. The column consists of sized diatomaceous earth that has been treated with silicon vapors, dried, and then treated with an amount of HDEHP equal to 10% of the weight of dried material. After loading of the sample, the column is washed with 4 column volumes of 0.01 N HNO_3 ; and the Am is eluted, free of the rare earths, with 0.02 M $(\text{NH}_4)_5\text{DTPA}$ in 1 M lactic acid, pH 2.8. (This is an application of the "TALSPEAK" process.) The bulk of the Am is eluted with about 6 column volumes. This effluent can be directly counted on either Ge(Li) or NaI(Tl) gamma-ray spectrometry systems. For alpha counting, this effluent is acidified to approximately 0.1 N H^+ and purified on a cation column as described above for mass spectrometry. This final effluent is dried and fumed with HClO_4 to remove any remaining organics or NH_4 salts before electroplating onto an alpha counting plate.

8.45 Discussion. Both DBBP and DHDECMP appear to be potentially useful for removal of actinides from ICPP wastes. Partial neutralization of wastes, necessary for DBBP extraction, poses a problem in solution stability that must receive further study. Analogues of DBBP and DHDECMP have been obtained from Wateree Chemical Co., Inc.; and these will be evaluated for actinide extraction. Preliminary laboratory studies with di-butyl-N, N-diethyl-carbamyl-methylene phosphonate, DBDECMP, are favorable, especially regarding reagent purification because impurities that interfere with Am back extraction are readily removed by caustic scrubbing.

8.5 INEL Radioactive Solid-Waste Repackaging Facility Studies (WMT Funded)
(W.B. Kerr, R.A. Brown, R.J. Thompson, S. Winston, R.L. Nebeker)

Studies in support of the proposed Radioactive Solid-Waste Repackaging Facility at the INEL were continued in FY 1974. Previous studies are reported in the FY 1973 annual report, ICP-1047^[2].

About 2,300,000 ft³ of solid waste interred at the INEL Burial Ground is alpha-contaminated waste from the AEC's Rocky Flats operation. Because of the concern over long-term isolation of such waste from the biosphere, the AEC plans to move this waste to a permanent repository. The Idaho Chemical Programs Office of Allied Chemical Corporation was requested to perform a series of studies to evaluate the problems associated with a large-scale exhuming and treatment operation.

Previous studies^[2] indicated that the retrieval and repackaging operation could cost over 100 million dollars during a ten-year period. Because of the high estimated cost and the lack of demonstrated methods and control procedures, the AEC has directed that a demonstration-scale facility be built. Safe operation will be demonstrated on a small scale before the full-scale effort is initiated. This demonstration program is expected to involve the retrieval and treatment of approximately 30,000 ft³ of waste each year for three years. Funds for this program have been allocated to Allied Chemical Corporation, with the retrieval and transportation portions of the program being directed by Aerojet Nuclear Company.

Conceptual Design: The Radioactive Solid-Waste Repackaging Facility is a new plant to be located on an undeveloped site of approximately 25 acres adjacent to the northwest corner of the existing INEL Burial Ground. The Ralph M. Parsons Company contracted to provide a conceptual design and cost estimate for the burial ground support facilities and the radioactive solid-waste treatment building.

The conceptual design includes five buildings and the yard and site work necessary to integrate them into an operable facility. Four of the buildings serve supporting functions for the solid-waste treatment building, as follows:

- (1) The vehicle survey building is a 2,000 ft², single-story building, containing 1,750 ft² of survey area and 250 ft² of support area. An access pit is provided to permit surveying the underside of the various vehicles.
- (2) The 2,828 ft², single-story vehicle service building includes space for servicing all on-site and Burial Ground vehicles. A service pit is provided to allow access to the underside of all vehicles, and pumps for dispensing gasoline and diesel fuel are provided exterior to the building.

- (3) The 7,600 ft², single-story administration building, serves as the control center for the total Burial Ground facility; security, computer and data logging, medical, cafeteria, and administrative functions are included. The computer and its peripheral equipment will be used for data acquisition, logging, data display, alarming, and the computation and printout for the assay equipment in the treatment building; it will also be used for the Burial Ground data collection and inventory control.
- (4) A 9,500 ft², single-story support building houses clothing change rooms, heating and ventilation areas, a boiler area for plant steam supply, laundry facilities, a low-level alpha analytical laboratory, a health physics office and equipment room, and the main plant switchgear.

The treatment building is a three-story, concrete, steel-frame structure. The basement and first floor areas are primarily dedicated to treatment operations and the second floor to utilities and ventilation systems. The building is designed to meet the general requirements for a plutonium processing facility as described in AECM 6301. The gross floor area is 79,727 ft². The building height is approximately 74 feet, with 7 feet below grade. It is designed to receive, store, transport, sort, size-reduce, repackaging, assay, and ship INEL transuranic waste exhumed from existing burial sites. Necessary security, fire protection and suppression, ventilation, and radiation protection and monitoring systems are provided.

Operation of the facility is visualized as follows. The exhumed, packaged transuranic waste materials are segregated into drums and boxes and are campaigned on this basis. The exhumed waste containers are monitored, and boxes and wrapped or contaminated drums are routed into the treatment room. Noncontaminated (cold) drums are diverted into a cold-drum handling room where they are opened and identified under an exhaust hood. Drums containing cold treatable waste (waste could be highly contaminated but wrapped in plastic) are dumped into a special air-locked bin connected to the treatment room. Drums, which contain nontreatable waste or are highly contaminated inside, are rerouted back to the air lock and into the treatment room.

Boxes and drums entering the treatment room are opened and identified. Drums of nontreatable waste are resealed, placed either in larger drums or boxes meeting 20-year containment criteria, and sealed for pad storage. Drums containing treatable waste are dumped onto a transport conveyor for inspection and dispensing to a sorting conveyor. This conveyor is all metal for receiving wastes that are being dumped to an atmospheric condition for the first time. Should a hazardous condition (spontaneous fire, chemical, etc.) exist, it can be contained on this all-metal conveyor system. The operators working the sorting conveyor, through gloves outside the treatment room, can control dispensing of material for sorting and handling.

Major pieces of equipment contained in boxes or drums are size-reduced, dry-cleaned by grit blasting, and compacted, if desirable. Wood, including exhumed boxes and massive pieces of plastics (shielding) are cut into pieces suitable for packing into the standard box. Sheet plastics, paper, and other shreddable combustibles are shredded and compacted into a

drum. The treated materials are lowered into their respective containers, sealed, monitored, and moved to decontamination and/or assay.

Estimated Costs: The estimated cost (3/1/74) for the treatment and other supporting buildings is \$15.2 million, including 20% contingency and 10% engineering, design, and inspection. Escalation because of inflation will significantly increase the total project cost.

The annual operating costs for treating 30,000 ft³/yr of retrieved waste and storing it on ITSA pads are estimated to be \$3.7 million. This includes container costs, ITSA storage, direct and indirect labor, and expendable equipment. Capital and annual costs are summarized in Table XLVIII.

TABLE XLVIII

COST SUMMARY FOR INEL TRANSURANIC WASTE REPACKAGING

DEMONSTRATION FACILITY^[a]

Capital (3/1/74)		\$15,200,000
Annual Costs (FY-75)		
Container Costs	\$75,000	
Storage on ITSA	\$25,000	
Direct & Indirect Labor	\$3,375,000	
Expendable Equipment and Supplies	<u>\$100,000</u>	
	\$3,575,000	
Contingency	<u>\$25,000</u>	<u>\$3,600,000</u>
Program costs (less retrieval costs) for three year demonstration, treating approximately 90,000 ft ³ of waste at FY-75 costs.		<u>\$26,000,000</u>

[a] No attempt has been made to update these figures for escalation because of the uncertainty of existing economic conditions.

Schedule: The projected schedule for design, review, and construction allows 39 months from the time funds are available until the project is complete.

Alternatives Study: A preliminary study^[2] indicated that it was not economically justifiable to retrieve and repackage the waste immediately, followed by further retrieval and reprocessing, prior to shipment to ultimate storage. The study showed that it was more

economical to cover the present burial sites with an impermeable cover until the location, container, and waste-content criteria for final storage had been established and then handle the waste one time only. An extension of the preliminary study has been initiated. This study will examine economics, environmental effects, and personnel safety for the many alternates to the current plan for retrieval and repackaging.

Program Plan: A detailed plan document for Allied Chemical Corporation's portion of the INEL Radioactive Solid-Waste Repackaging Program had been prepared by mid-FY 1974. However, an AEC-ID major program directive (March 1974) advised Allied Chemical of a one-year delay in funding for this program. About the same time, the conceptual design and cost estimate were also received; and these two items rendered a major portion of the original program plan out of date. The program plan is being revised and will be issued early in FY 1975.

III. ADDITIONAL IDAHO CHEMICAL PROGRAMS ACTIVITIES

1. DISPOSAL OF SODIUM-POTASSIUM ALLOY FROM EBR-I (WMT FUNDED)

(L.C. Lewis, R.R. Hammer, M.E. Jacobson, A.P. Hoskins)

The decommissioning of the EBR-I reactor requires the disposal of 5,000 gallons of liquid metal coolant (NaK-78). Basically, the process for NaK disposal consists of reacting the alkali metal with water in a concentrated caustic medium. This caustic product will be placed in drums for long-term storage or reuse. Some will be contaminated with fission products.

The development program for this operation required the determination of the necessary engineering and safety parameters, development of special tools and techniques, and resulted in the successful operation of a small-scale pilot-plant test. Fabrication of the actual facility is scheduled for early FY-75 with operation to take place during the second quarter of FY-75. This schedule will result in the EBR-I facility being fully decontaminated and decommissioned for turn-over to the National Park Service by mid-1975.

2. TRA WATER CHEMISTRY AND WASTE MANAGEMENT SUPPORT (RRD FUNDED)

(W.F. Holcomb, R.L. Nebeker and R.R. Kimmitt)

Allied Chemical Corporation continues to provide chemistry and waste management support at the Test Reactor Area (TRA) to Aerojet Nuclear Company. Chemistry support included both routine and special analyses for maintaining the reactor primary and secondary coolant systems within chemistry specifications. Samples were obtained at specified frequencies, and the sample data were interpreted for both routine and nonroutine problems. The TRA plant water chemistry manual was updated, as required, to reflect changes in water treatment methods as the secondary system was converted to a nonchromate corrosion inhibitor system. Test coupons were monitored to determine corrosion rates during and after the changeover. A study of methods for controlling biological growth in the TRA water systems was completed; this resulted in a recommendation for the use of ozone as a means of killing the growth in the existing system. Studies of water utilization and chemistry surveillance at TRA were completed; a plan for converting the existing demineralization system into a four-column operation using weak and strong, acid and base resins was proposed as a result of this study. Cost reductions would result from this type of operation.

The TRA Water Chemistry and Waste Management Coordinator also acted as Technical Program Task Manager for the Water Recycle and Waste Management Program at TRA. The TRA waste management program plan was updated, and the TRA portion of the INEL Environmental Statement on Waste Management was prepared. System design descriptions were prepared for those TRA waste management projects for which funding was available, and support information for ICPP projects was submitted.

The frequency and accuracy of liquid and gaseous effluent sampling was increased, and the issuance of computer printouts showing daily effluent releases was initiated. The development of real-time monitoring instrumentation for radioactive effluents continued. Waste containing $\text{CrO}_4^{=}$ was effectively treated by reducing the chromate with SO_3 so the waste could be discharged to the environment. Current interrupters and test stations were installed on the existing cathodic protection system to allow more efficient testing of the system, and testing of the existing anodes was initiated.

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

(W.A. Emel, A.L. Erickson, M.C. Kussy, R.L. Tromp, W.J. Maeck)

The preferred method for measuring burnup on fast breeder reactor (FBR) fuels is the fission product-residual heavy atom method. This method is applicable regardless of the levels of burnup, is independent of the fuel composition, and does not require specific knowledge of the fuel composition prior to irradiation.

In this method, the irradiation fuel specimen is dissolved; and the selected fission product and the heavy atoms are determined. The computational relationship is:

$$\text{Burnup} = a/oF = 100 \frac{\frac{A}{Y}}{H + \frac{A}{Y}}$$

where

a/oF = atom percent fission

A = atoms of the selected fission product monitor

Y = effective fractional fission yield value of A

H = residual heavy atoms.

The successful application of this method requires accurate measurement of the fission product and heavy nuclide atom concentrations and an accurate value for the fission yield of the measured fission product. Currently, the fission product and each heavy nuclide concentration can be determined with an uncertainty of 0.25%. The largest uncertainty in this method is the value of the fission yields of the various fissioning nuclides for neutron spectra characteristic of FBRs. Presently available fast fission yield values are limited to ^{235}U and ^{239}Pu , which were measured in neutron spectra much harder than those expected for FBRs. The uncertainty of applying these fission yield data to the determination of burnup in FBR cores is estimated to be 3 to 5%. There are no reliable fast fission yield data for other important fissile nuclides such as ^{238}U , ^{241}Pu , and ^{233}U .

The primary goals for the ICPP program are the accurate measurement of the absolute fast fission yields for many heavy element nuclides for neutron spectra characteristic of FBRs, and the development and proof-testing of methods for the determination of burnup for FBR fuels. Secondary goals are the measurement of (a) the capture-to-fission ratio for several of the heavy element nuclides and (b) selected fission product cross sections.

The irradiation program for this study, and other background material, are discussed in Idaho Chemical Programs Annual Technical Report, ICP-1022^[19]. Preliminary ^{235}U fast fission yield data, a description of neutron environment associated with the irradiation, and a discussion of data evaluation techniques are given in Idaho Chemical Programs Annual Technical Report, ICP-1047^[2].

Accomplishments during this reporting period were (a) completion of fission product measurements on a sample of ^{235}U irradiated by ANL-Chicago in EBR-II for fast fission yield measurements, (b) the first comprehensive measurement of ^{233}U fast fission yields, (c) the measurement of ^{238}U fast fission yields, (d) the initial development of a system for the correlation of fission yields with neutron energy, and (e) invited participation at an IAEA meeting on requirements of fission product nuclear data.

3.1 ^{235}U Fast Fission Yields

The chemical separation, mass spectrometric analyses, data reduction, and final calculations were completed for a ^{235}U fission yield capsule, prepared and irradiated by ANL-Chicago in EBR-II. Analyses were conducted for the isotopes of rubidium, strontium, zirconium, molybdenum, cesium, barium, lanthanum, cerium, neodymium, samarium, and uranium. The estimated time to complete this additional work was nine man-months. Also analyzed at the request of ANL was a dissolver solution of EBR-I, Mark-III ^{235}U fuel for the isotopes of cerium, neodymium, and samarium.

All data and discussions of the data were forwarded to R.P. Larsen, ANL-Chicago. These data have been incorporated into the discussion in Section III-3.4 pertaining to variations in ^{235}U fission yields with neutron energy.

3.2 ^{233}U Fast Fission Yields

Two capsules of highly enriched ^{233}U , irradiated in the unshielded assembly in EBR-II (mean neutron energy ~ 400 keV), were dissolved and analyzed for over 40 stable and long-lived isotopes. The measurement technique was isotope-dilution mass spectrometry.

Because of the low burnup, about 1%, the summation technique was used to establish the number of fissions. By definition, the sum of the total atoms in either mass peak is the number of fissions. For these two capsules, $\sim 85\%$ of each mass peak was measured; and the balance of the fission product atoms were established by interpolation or estimation. The measured, interpolated, and estimated fission product atoms for each of the two capsules

are given in Table XLIX. Also listed is the total number of atoms in each mass peak and the number of fissions used to calculate the individual fission yields.

The absolute yields were calculated by dividing the measured number of atoms of each individual nuclide by the measured number of fissions. The calculated yields for the light mass peak are given in Table L and for the heavy mass peak, in Table LI. In general, excellent agreement was obtained. The uncertainties associated with the reported values are estimated to be $\pm 2\%$ relative. A detailed error analysis is in progress.

Of particular interest is the change in the ^{233}U yields as a function of neutron energy. Unlike ^{235}U (see Section III-3.4), very little if any systematic changes in the ^{233}U yields were observed, at least over a neutron distribution ranging from thermal to Row 8 of EBR-II. Thus, for burnup measurements, little or no correction will be required for the change in the neutron spectrum.

This is the most comprehensive set of ^{233}U fast fission yields reported to date.

3.3 ^{238}U Fast Fission Yields

The analyses were complete for three sets of capsules irradiated in the unshielded assembly in Row 8 of EBR-II. Isotope-dilution mass spectrometry was the measurement technique for over 40 stable and long-lived isotopes. Because ^{238}U has a low fission cross section and the resultant number of fission product atoms formed was low, each "set" of capsules consisted of the combined dissolution of two individual capsules, which were irradiated in adjacent positions in the irradiation assembly.

The summation technique was used to establish the number of fissions; however, it was necessary to commingle the data from the three samples because two of the capsules were observed to have lost gas; and for two, the zirconium natural contamination was so great that no reliable data could be obtained. Because of the low number of fissions which occurred, the natural contamination level from the background levels in the target materials and the chemical reagents used in the separation were sufficient to increase the uncertainty in the measurements. The commingled number of fissions was obtained by first normalizing the measured atoms of each nuclide to the sum of measured atoms of the Nd isotopes ($\Sigma \text{Nd-143} + 145 + 146 + 148 + 150$) for each set of capsules, then averaging this value over the three sets of data and calculating a normalized number of fissions by summing the mean values. A listing of the individual normalized values, their mean, the normalized number of fissions, and the calculated fission yields are given in Table LII for the light mass peak and Table LIII for the heavy mass peak. The normalized number of fissions for the two mass peaks derived by this approach agree to $\sim 1\%$. For calculating the individual fission yields, the normalized number of fissions for the heavy peak was used because the data were more complete and believed to be more reliable.

Although a rigorous error analysis on these data has not been completed, it is estimated that the majority of the heavy peak yields will have an uncertainty of $\sim 5\%$

TABLE XLIX

SUMMARY OF MEASURED, INTERPOLATED, AND ESTIMATED NUMBER
OF ATOMS IN EACH ^{233}U CAPSULE

Capsule Number	2		31	
Mass Peak	Light	Heavy	Light	Heavy
Σ measured atoms	8.173E18	8.393E18	9.106E18	9.379E18
Σ interpolated atoms	1.345E18	0.621E18	1.484E18	0.702E18
Σ estimated atoms	0.188E18	0.683	0.216E18	0.713E18
Number of fissions	9.706E18	9.702E18	10.806E18	10.794E18
$\Sigma (L+H)/2$	9.704E18		10.800E18	

TABLE L

^{233}U FAST FISSION YIELDS --- LIGHT PEAK

Mass No.	Capsule		Mean
	2	31	
75-80	0.60 ^[a]	0.58 ^[a]	0.58 ^[a]
81	0.37 ^[a]	0.37 ^[a]	0.37 ^[a]
82	0.57 ^[a]	0.60 ^[a]	0.58 ^[a]
83	0.998	1.00	1.00
84	1.63	1.64	1.64
85	2.11	2.13	2.12
86	2.77	2.79	2.78
87	3.83	3.85	3.84
88	5.12	5.12	5.12
89	5.78 ^[b]	5.80 ^[b]	5.79 ^[b]
90	6.43	6.47	6.45
91	6.38	6.49	6.44
92	6.48	6.59	6.54
93	6.85	6.98	6.92
94	6.68	6.81	6.74
95	6.30	6.28	6.29

TABLE L (contd.)

Mass No.	Capsule		Mean
	2	31	
96	5.64	5.75	5.70
97	5.46	5.41	5.44
98	5.15	5.12	5.14
99	4.78 ^[b]	4.74 ^[b]	4.76 ^[b]
100	4.41	4.35	4.38
101	3.84	3.64	3.74
102	2.92	2.76	2.83
103	2.10 ^[b]	1.98 ^[b]	2.04 ^[b]
104	1.27	1.20	1.24
105	0.796 ^[b]	0.768 ^[b]	0.782 ^[b]
106	0.324	0.331	0.328
107	0.14 ^[a]	0.16 ^[a]	0.15 ^[a]
108	0.072 ^[a]	0.084 ^[a]	0.078 ^[a]
109-115	0.18 ^[a]	0.18 ^[a]	0.21 ^[a]
Σ Yields			100.01

[a] Estimated yields from adjusted thermal fission yield data and from mass peak reflection plots.

[b] Value obtained by interpolation from mass peak reflection plots.

TABLE LI

²³³U FAST FISSION YIELDS -- HEAVY PEAK

Mass No.	Capsule		Mean
	2	31	
116-124	0.23 ^[a]	0.23 ^[a]	0.23 ^[a]
125	0.143 ^[c]	0.138 ^[c]	0.140 ^[c]
126	0.30 ^[a]	0.29 ^[a]	0.30 ^[a]
127	0.66 ^[a]	0.60 ^[a]	0.63 ^[a]
128	1.13 ^[a]	1.16 ^[a]	1.14 ^[a]
129	1.86 ^[a]	1.71 ^[a]	1.78 ^[a]
130	2.58 ^[a]	2.59 ^[a]	2.58 ^[a]
131	3.73	3.74	3.74

TABLE LI (contd.)

Mass No.	Capsule		Mean
	2	31	
132	5.04	5.05	5.04
133	5.98	6.03	6.00
134	6.29	6.32	6.30
135	6.33	6.41	6.37
136	6.87	6.90	6.88
137	6.72	6.77	6.74
138	6.61	6.43	6.52
139	6.33	6.41	6.37
140	6.25	6.26	6.26
141	6.31 ^[b]	6.31 ^[b]	6.31 ^[b]
142	6.37	6.35	6.36
143	5.53	5.55	5.54
144	4.40	4.42	4.41
145	3.20	3.21	3.20
146	2.39	2.39	2.39
147	1.67	1.68	1.68
148	1.20	1.20	1.20
149	0.701	0.713	0.707
150	0.466	0.464	0.465
151	0.306	0.312	0.309
152	0.191	0.193	0.192
153	0.11 ^[b]	0.11 ^[b]	0.11 ^[b]
154	0.033	0.034	0.034
155-160	0.05	0.05	0.05
Σ Yields			99.98

[a] Estimated yields from adjusted thermal fission yield data and from mass peak reflection plots.

[b] Values obtained by interpolation from mass peak reflection plots.

[c] Radiochemical measurement ¹²⁵Sb.

TABLE LII

^{238}U FAST FISSION YIELDS BY NORMALIZATION PROCEDURE --
LIGHT MASS PEAK

Capsules		Normalized Values			Fission Yield
Mass No.		40-41	28-34	42-47	
75-80					0.0787 ^[a]
81					0.127 ^[a]
82					0.255 ^[a]
83	[c]		0.02652	0.02652	0.395
84			0.05482	0.05482	0.816
85			0.05187	0.05187	0.772
86			0.08596	0.08596	1.28
87	0.1066			0.1075	1.59
88	0.1414			0.1371	2.04
89				0.1806 ^[b]	2.69 ^[b]
90	0.2214			0.2269	3.34
91				0.2924	4.35
92				0.3257	4.85
93				0.3462	5.16
94				0.3309	4.93
95	0.3203	0.3382	0.3265	0.3283	4.88
96			0.3979	0.3979	5.93
97	0.3578	0.3694	0.3626	0.3632	5.41
98	0.3814	0.3955	0.3841	0.3870	5.76
99				0.4137 ^[b]	6.16 ^[b]
100	0.4356	0.4470	0.4386	0.4404	6.56
101	0.4330			0.4330	6.44
102	0.4518			0.4518	6.72
103				0.4030 ^[b]	6.00 ^[b]
104	0.3542			0.3542	5.27
105				0.2634 ^[b]	3.92
106	0.1727			0.1727	2.57

TABLE LII (contd.)

<u>Capsules</u>	<u>Normalized Values</u>				
<u>Mass No.</u>	<u>40-41</u>	<u>28-34</u>	<u>42-47</u>	<u>Mean</u>	<u>Fission Yield</u>
107					1.27 ^[a]
108					0.62 ^[a]
109-117					0.75 ^[a]
(1) Σ normalized measured atoms				5.3111	
(2) Σ normalized interpolated atoms				0.8577	
(3) Σ estimated yields, %				3.101	
(4) Total normalized fissions [(1+2)/ 0.96899]				6.7821	
Σ calculated fission yields based on fissions from heavy peak					100.93

[a] Estimated yields.

[b] Value based on interpolation.

[c] Blank indicates no reliable measurement.

TABLE LIII

²³⁸U FAST FISSION YIELDS BY NORMALIZATION PROCEDURE ---
HEAVY MASS PEAK

<u>Capsules</u>	<u>Normalized Values</u>				
<u>Mass No.</u>	<u>40-41</u>	<u>28-34</u>	<u>42-47</u>	<u>Mean</u>	<u>Fission Yield</u>
118-124					0.273 ^[a]
125					0.056 ^[a]
126					0.072 ^[a]
127					0.13
128					0.51 ^[a]
129					1.11 ^[a]
130					1.79 ^[a]
131	[c]	0.2158		0.2158	3.21
132		0.3466		0.3466	5.16
133	0.4410	0.4540	0.4405	0.4452	6.63
134		0.5339		0.5339	7.95

TABLE LIII (contd.)

Capsules		Normalized Values			Fission Yield
Mass No.	40-41	28-34	42-47	Mean	
135	0.4570	0.4638	0.4592	0.4600	6.85
136		0.4742		0.4742	7.06
137	0.3953	0.4021	0.3967	0.3980	5.93
138	0.3811	0.3926	0.3702	0.3813	5.68
139	0.3971	0.4122	0.3753	0.3949	5.88
140	0.4147	0.4050	0.3896	0.4031	6.00
141				0.37 ^[b]	5.51 ^[b]
142	0.3131	0.3139	0.3087	0.3119	4.65
143	0.3012	0.3062	0.3021	0.3032	4.52
144	0.2970	0.2978	0.2966	0.2978	4.44
145	0.2494	0.2507	0.2499	0.2500	3.72
146	0.2266	0.2251	0.2263	0.2260	3.37
147	0.1674	0.1673	0.1678	0.1675	2.49
148	0.1388	0.1370	0.1384	0.1381	2.06
149	0.1070	0.1044	0.1061	0.1058	1.58
150	0.0839	0.0810	0.0833	0.0827	1.23
151	0.0532	0.0512	0.0539	0.0528	0.786
152	0.0344	0.0349	0.0345	0.0346	0.515
153				0.0244 ^[b]	0.363 ^[b]
154	0.0137	0.0147	0.0140	0.0141	0.210
155-160					0.27 ^[a]
(1) Σ normalized measured atoms				6.0375	
(2) Σ normalized interpolated atoms				0.3944	
(3) Σ estimated yields, %				4.211	
(4) Total normalized fissions [(1+2)/0.95789]				6.7147	
Σ calculated fission yields based on fissions from heavy peak					100.01
[a] Estimated yields.					
[b] Value based on interpolation.					
[c] Blank indicates no reliable measurement.					

relative. This meets the error limitations for ^{238}U yield data as required for the determination of burnup on FBR mixed oxide fuel because the number of fissions originating from ^{238}U will be less than 10%.

3.4 Variation of ^{235}U Fission Yields with Neutron Energy

As previously stated, the most important parameter in the measurement of burnup is an accurate knowledge of the fission yield of the monitor nuclide. For thermal reactor fuels, the standard method is the isotope-dilution mass spectrometric determination of ^{148}Nd and the residual heavy elements. This same method is being applied to fast reactor fuels with, however, a larger uncertainty in the ^{148}Nd fission yield value. In general, the fast reactor fission yields reported in the literature have wide variations and are not associated with a given neutron spectrum. Thus, any effect of neutron energy on fission yields is not accounted for. Studies in our laboratory show that this effect is significant, even for different positions in the same reactor.

Because of their importance as burnup monitors for fast reactor fuels, the fast reactor fission yields of the neodymium isotopes have been measured more than any other element. These data and a set of thermal values for comparison purposes are given in Table LIV. Some literature values were omitted because they were relative yields with no assigned uncertainties. In the last row, the range (in units of relative percent) of the available fast-reactor yields for each neodymium isotope; and the sum of the isotopes is given. These ranges are 6 to 8% for masses 143 through 148, increasing to 16% for ^{150}Nd . This demonstrates that a major source of error in a burnup measurement of fast-reactor irradiated ^{235}U fuel is the uncertainty of the fission yield value for the burnup monitor. To now, no one has systematically evaluated these data with respect to the possibility of neutron energy dependency. In fact, the opposite has occurred, especially by the compilers of fast-reactor fission yield data where the tendency has been to average the literature values, sometimes using weighting factors dependent on the reported accuracy of the data.

In the process of evaluating our new ^{235}U fast fission yield data and comparing it to other data, the noted differences were considered to be too large to be attributed to measurement error; and Walker's^[19] method of evaluating relative isotopic data was undertaken. During this evaluation, relative neodymium isotopic data became available for ^{235}U irradiated in the axial blanket of EBR-II and Row 4 of EBR-II. A comparison of the relative isotopic data for these samples and the literature values given in Table LIV are given in the top half of Table LV. The systematic changes are apparent when the data are ordered by neutron spectrum hardness. To amplify these changes, isotopic ratios were calculated and are given in the bottom half of Table LV. For the ratio of ^{150}Nd to ^{143}Nd , the change between thermal values and the very hard EBR-I spectrum is ~20%.

To improve the usefulness of this type of correlation, a quantitative assessment of the spectrum hardness; that is, a neutron energy index, was needed. Several types of index were considered, including mean neutron energy, median neutron energy, mean and median neutron energy for fission of a given heavy isotope, fraction of neutrons in a given energy

TABLE LIV
NEODYMIUM THERMAL AND FAST REACTOR FISSION YIELDS FOR ^{235}U

<u>Measurer</u>	<u>Reactor</u>	<u>Fission Yield (%)</u>					<u>Σ FY</u>	<u>Reported Error (%)</u>
		<u>^{143}Nd</u>	<u>^{145}Nd</u>	<u>^{146}Nd</u>	<u>^{148}Nd</u>	<u>^{150}Nd</u>		
Lisman ^[46]	Thermal	5.90	3.86	2.95	1.68	0.638	15.03	1
Maeck ^[47]	EBR-I	5.70	3.79	2.94	1.73	0.739	14.90	2.5
Sinclair ^[48]	DFR	5.98	3.93	3.06	1.75	0.73	15.45	3
Larsen ^[49]	EBR-II	5.59	3.70	2.83	1.65	0.685	14.46	1.5
Robin ^[50]	RAPSODIE	5.73	3.81	2.96	1.70	0.714	14.91	2
Robin ^[51]	OSIRIS	5.65	3.75	2.89	1.72	0.72	14.73	2
Maeck ^[2]	EBR-II	5.77	3.80	2.92	1.67	0.668	14.83	1.5
Range in Values (%)		7	6	8	6	16	7	

TABLE LV

ISOTOPIC COMPOSITION AND RATIOS OF NEODYMIUM ISOTOPES FOR ^{235}U
IRRADIATED IN DIFFERENT REACTOR SPECTRA

<u>Sample Data</u>	<u>Thermal</u>	<u>EBR-II Blanket</u>	<u>EBR-II Row-8</u>	<u>DFR Sinclair</u>	<u>EBR-II Larsen</u>	<u>RAPSODIE Robin</u>	<u>EBR-II Row-4</u>	<u>OSIRIS Robin</u>	<u>EBR-I Core</u>
<u>Isotopes</u>									
^{143}Nd	0.3926	0.3898	0.3891	0.3870	0.3867	0.3843	0.3840	0.3836	0.3826
^{145}Nd	0.2568	0.2589	0.2563	0.2544	0.2560	0.2554	0.2545	0.2546	0.2544
^{146}Nd	0.1963	0.1975	0.1969	0.1981	0.1958	0.1984	0.1985	0.1962	0.1973
^{148}Nd	0.1118	0.1110	0.1126	0.1133	0.1141	0.1140	0.1149	0.1167	0.1161
^{150}Nd	0.0425	0.0429	0.0450	0.0472	0.0474	0.0479	0.0481	0.0489	0.0496
<u>Isotopic Ratios</u>									
150/143	0.1083	0.1101	0.1157	0.1220	0.1226	0.1246	0.1253	0.1275	0.1296
150/145	0.1655	0.1657	0.1756	0.1855	0.1852	0.1875	0.1890	0.1920	0.1950
148/143	0.2847	0.2848	0.2894	0.2928	0.2950	0.2966	0.2992	0.3042	0.3034

range, and the ratio of cross-sections values for two selected fissioning isotopes. Unfortunately, little spectral information was available for much of the literature-reported yield data. Of the possible indices considered, the effective fission cross section for ^{238}U relative to ^{235}U (σ_{f8}/σ_{f5}) was selected because more yield data could be associated with this index than any of the others, especially EBR-II data because the reactor has been mapped with these monitors. For some of the other data, measurement data existed or was obtained from the authors. Because ^{238}U has a threshold for fission near 1 MeV and the ^{235}U fission cross section is nearly constant from 0.01 to 10 MeV, the ratio of σ_{f8}/σ_{f5} is an indicator of the fraction of the flux with an energy greater than 1 MeV.

The isotopic ratio of ^{150}Nd to ^{143}Nd for those data, which could be associated with the spectral index (σ_{f8}/σ_{f5}), are shown in Figure 39. That the neodymium isotopic

Fig. 39 Change in neodymium isotopic ratio with neutron energy.

composition of fissioned ^{235}U is correlated with neutron energy is clearly demonstrated. Of particular interest is the change in the neodymium ratio within the EBR-II reactor.

Having established that the $^{150}\text{Nd}/^{143}\text{Nd}$ isotopic ratio can be correlated with neutron energy, it is proposed that this ratio be considered as a spectral index for correlating fission yields with neutron energy. It has the advantages of sensitivity, is automatically obtained in a neodymium measurement for burnup (hence, other reactor or nuclear physics data are not required), and can be measured with a high degree of accuracy.

Using the $^{150}\text{Nd}/^{143}\text{Nd}$ ratio as a spectral index, the literature yield data given in Table LIV have again been examined. Figure 40 is a plot of the reported yields as a function of the $^{150}\text{Nd}/^{143}\text{Nd}$ ratio. This technique of ordering the literature-reported yield values by neutron energy shows that the majority of the range in the reported data (Table LIV) is associated with a change in the yields with neutron energy. All of the sets of neodymium fission yield values, with one exception, now fall within $\pm 2.5\%$ of the best straight-line fit of the data. The exception is the DFR data, which is believed biased because of an error in the value of the number of fissions used to calculate the absolute yields. These data now allow the selection of the most appropriate fission yield value for a given neutron energy, thus minimizing the error associated with the fission yield monitor in the measurement of burnup of ^{235}U in a fast reactor.

This initial study appears most promising, and more advanced studies are in progress. It is anticipated that other fission yields can be correlated by a similar technique.

3.5 IAEA Panel Meeting

An invited review paper "Fission Product Nuclear Data Requirements for the Determination of Nuclear Fuel Burnup: A Review", ICP-1040, provided the basis for an oral presentation, subsequent discussion, and contribution to the International Atomic Energy Agency Panel Meeting on Fission Product Nuclear Data, held November 26-30, 1973, at Bologna, Italy. The abstract of the paper follows:

This paper reviews and expresses specific needs for improved fission product nuclear data for the determination of nuclear fuel burnup. The various techniques for measuring burnup, both destructive and nondestructive, are discussed with regard to applicability and to fission product nuclear data requirements. The highest priority fission product nuclear data requirements are for the fast-reactor fission yields as a function of neutron energy and for decay scheme data for radionuclides used as burnup monitors. New data showing the variation of fission yields with neutron energy and the need to associate all fast fission yields with a well defined spectral index are given.

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Fig. 40 Change in neodymium fission yields with neutron energy.

IV. IDAHO CHEMICAL PROGRAMS ORGANIZATIONAL CHART

This report was prepared and issued within the framework of personnel and responsibilities reflected by the accompanying organization chart.

IDAHO CHEMICAL PROGRAMS - OPERATIONS OFFICE

PAGE 1

APPROVED: *F. H. Anderson*
DATE: January 15, 1975
* On Loan to HTGR Program Office

IDAHO CHEMICAL PROGRAMS - OPERATIONS OFFICE

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