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IDAHO CHEMICAL PROGRAMS ANNUAL TECHNICAL REPORT
FISCAL YEAR 1971

MASTER

ALLIED CHEMICAL CORPORATION
IDAHO CHEMICAL PROGRAMS - OPERATIONS OFFICE
NATIONAL REACTOR TESTING STATION

Idaho Falls, Idaho - 83401

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DATE PUBLISHED—MAY 1972

PREPARED FOR THE
U.S. ATOMIC ENERGY COMMISSION
IDAHO OPERATIONS OFFICE UNDER CONTRACT AT (10-1)-1375 S-72-1

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Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.95

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**IDAHO CHEMICAL PROGRAMS ANNUAL TECHNICAL REPORT
FISCAL YEAR 1971**

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ABSTRACT

The operating experience in fuel processing, waste calcining, and other waste management activities at the ICPP for FY 1971 is summarized. Processing of zirconium fuels was highly satisfactory, and successful startup and operation of a new fluidized-bed denitration process for conversion of product uranyl nitrate to UO_3 was achieved. The first campaign for fluid-bed calcination of reactor fuel wastes using in-bed combustion of fuel oil to supply heat was completed with 100% on-stream time and at an increased processing rate over the original WCF system. Technical support activities in areas of current and proposed operations at the ICPP are also presented. These include: corrosion studies on processing equipment and fuel storage facilities; modifications to ICPP processes; developments in the electrolytic-dissolution process; developments in the combustion-dissolution process for graphite fuels; plans for future fuel storage; pilot-plant calcination of varied waste solutions; plans for improved environmental protection at the ICPP. Research programs in other areas include: safeguards in uranium accountability; burnup determination for fast breeder reactor fuels; iodine behavior and iodine adsorbents; ion-control membranes for separations processes.

SUMMARY

A highly successful *major fuel reprocessing campaign* was conducted during the year; new data are reported on the *distribution of tritium* in the process. Prior to the campaign, a comprehensive *corrosion evaluation* was made of the critical vessels; when excessive corrosion was discovered on the fixed poison plates in the head of the first intercycle evaporator, a *soluble* poison system using gadolinium nitrate was developed and used successfully. As in the past, *neptunium* and plutonium were isolated in the second cycle for later purification and shipment. About 90 kg of uranium-235 were recovered from problem fuels by *custom dissolution* in the Multicurie Cell to produce feeds compatible with the plant flowsheets. Successful production operation of the *product denitration system* with plant product was achieved this year.

In *plant support studies*, normal paraffin hydrocarbon was evaluated and recommended for use as TBP diluent in uranium extraction flowsheets; salvage solutions were tested for compatibility with the process and properly recycled; ETR scrap was shown to be co-dissolvable with zirconium fuel; a process was developed for decontamination of neptunium and plutonium concentrates now held in storage. *New data* reported include; (a) stability constants and rates of formation of fluoride complexes for use in estimating solution properties for new or modified process flowsheets; (b) resistance of selected plastic materials toward boiling nitric acid and nitric-hydrofluoric acid mixtures of interest in fuel reprocessing. Progress is reported on *studies underway* in the areas of improvement in plant instrumentation and possible changes in application of desiccants and catalysts used in the rare gas plant.

Construction of the production-scale *electrolytic dissolution system* was completed. Settling tanks were installed to remove the bulk of the undissolved stainless steel particles escaping from the dissolver; remaining solids appeared to be handled satisfactorily in full-scale mock-up equipment. Corrosion specimens are being installed on test racks in both the dissolver and the solution surge tank.

Development studies related to the *combustion-dissolution headend process for graphite matrix fuels* have shown that jet grinding successfully reduces the uranium concentration in the fluidized-bed burner and significantly reduces the rate of buildup of niobium in the bed. Formation of nitric-acid-insoluble uranium compounds during the burning process has necessitated the use of hydrofluoric acid for complete uranium recovery: one- and two-step flowsheets utilizing HNO_3 and HF are discussed. Corrosion specimens exposed in the pilot-plant burner indicate satisfactory corrosion resistance of materials of construction.

Other *studies related to future ICPP operations* include: (a) description of proposed storage facilities for Peach Bottom and Fort St. Vrain graphite fuels; (b) outline of a comprehensive safety review document of ICPP; (c) seismic analysis of ICPP structures; and (d) examples of nuclear safety calculations used at ICPP.

The fourth processing campaign in the *Waste Calcining Facility*, and the first using *in-bed combustion of fuel* to supply heat, was completed successfully; on-stream time was 100% for a campaign of 3700 hours on zirconium-fluoride waste. Post-run examination indicated the desirability of changes in materials and design for spray nozzles; feed control valves were still in good condition after 33,000 hours of service but changes in other valves are suggested. Post-service examination of piping from the original WCF NaK system verified the suitability of Type 316 stainless steel for this service.

WCF support studies showed the desirability of using wide-angle internal-mix nozzles or modified external-mix nozzles for fuel oil injection, rather than standard external-mix nozzles, to achieve the most complete combustion. A commercial cleaning agent was able to remove a greasy coating from the silica gel adsorbers in the off-gas system after incomplete combustion in startup operations resulted in fouled beds. Solid calcium nitrate was shown to be a desirable replacement for calcium nitrate solution as a fluoride suppressant during calcination of zirconium wastes. Additional properties of solid calcine products have been characterized, and low corrosion rates for metals exposed to zirconia calcine have been confirmed in four-year tests.

Scoping studies are reported for *planned waste calcination processes*: results of both differential thermal analysis and pilot-plant tests are reported for sodium-containing second-cycle wastes, neutralized Purex waste, and Rocky Flats wastes. While studies are continuing, tests with a newly developed extended-tip nozzle and proper additives (sulfate in particular) appear promising.

In *other waste management projects*, ion-exchange columns containing Amberlite-200 resin are effectively reducing levels of Sr-90 and Cs-137 in waste evaporator condensate. Increasing contamination levels in the fuel storage basin water have led to increased efforts in detection of leaking fuel elements, removal of sludge, decontamination of water, and control of corrosion.

Several *pollution control improvement projects* are under construction or are being planned at the ICPP. An automatic diversion system will divert flow in the service waste drains to a waste storage tank in case of activity detection (eg, from a leaking heat exchange jacket on a process vessel). All dissolver and vessel off-gas systems are being fitted with new deentrainment vessels, superheaters, and high efficiency filters. A backup atmospheric protection system for final filtration of all ventilation and process off-gas streams before release to the stack is being engineered.

Investigations are reported in several additional areas. In a *safeguards program*, a system involving computer control and monitoring of accountability measuring tanks fitted with direct weighing and pneumatic instruments is under way; direct weighing of installed in-line process vessels, by use of load cells under the supporting legs, appears promising. A program of *burnup determination for fast breeder reactor fuels* is outlined, and capsule assemblies of specified isotopes have been prepared for irradiation in the EBR-II. In a study of *absorbents for radioactive iodine species*, silver-exchanged zeolites have shown substantial advantages over charcoal in several important areas, including: nonflammability, high-temperature operability, loading capacity, tenacious retention, and rapid reaction rates. The *behavior of hypoiodous acid* in solution has been studied; appreciable concentrations of HOI do exist in alkaline solutions but the lifetime of the species is dependent on pH. Under a grant from the Office of Saline Water, fabrication of *ion-control membrane* containing a metallic layer with pore diameters of the order of 100 Angstroms is under investigation; applications involve separations processes where the permeability of the membrane would be controlled by an electrically maintained charge density around the pores.

**ALLIED CHEMICAL CORPORATION
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I. FUEL REPROCESSING

1. PERFORMANCE OF ICPP FUEL RECOVERY PROCESSES

1.1 Zirconium Fuel Processing

(C. L. Bendixsen, M. W. Andrews, R. N. Henry, L. C. Lewis)

During FY 1971, overall performance of the continuous system for reprocessing zirconium fuels at the ICPP was generally good with difficulties associated with mechanical breakdowns rather than with technology.

1.11 Process Description. The ICPP processing system for dissolution and recovery of uranium from zirconium fuel consists of four major subsystems: fuel dissolution and centrifuging for product clarification, first-cycle extraction with a TBP-Amsco solvent, second- and third-cycle extraction with a Hexone solvent, and finally, denitration of aqueous uranyl nitrate product. Process flowsheets have been reported previously[1]. The process is conducted in the following manner:

(a) First the dissolver is filled with borated water to cushion the fall of the fuel elements which are charged batchwise. (b) After fuel charging is complete, the charge water is jetted to a storage vessel, and the dissolvent, 6.8 M hydrofluoric acid, is fed to the dissolver at a rate of approximately 530 l/hr. (c) As the fuel elements dissolve, the dissolver product overflows continuously through an overflow loop and is transferred to a complexing tank by a nitrogen gas-lift. (d) Complexing the dissolver product with $\text{Al}(\text{NO}_3)_3\text{-HNO}_3\text{-H}_2\text{CrO}_4$ establishes proper solution conditions for low corrosion, long stability, and good uranium extraction. (e) The complexed solution then is centrifuged to remove insoluble solids and is sent to the first-cycle extraction system, which uses 5% TBP in Amsco-125-90W as a uranium solvent. (f) The first-cycle product is concentrated and stored in critically safe banks to await further processing; when the inter-cycle storage banks are filled, this product is processed through two more extraction stages using Hexone as the extractant for uranium. (g) Aqueous product from the Hexone system is fed to a fluidized bed denitrator for conversion to a granular oxide product prior to packaging and shipment.

1.12 Fuel Dissolution and Centrifuging. Operation of the zirconium fuel dissolver during FY 1971 was troublefree with no unscheduled downtime of the dissolver operations. Two mechanical failures occurred in the centrifuge for dissolver product clarification; both were caused by design deficiencies resulting in excessive vibration of the main shaft near the driving yoke and shaft bearings.

1.13 First-Cycle Extraction. Operation of the first-cycle extraction system was generally good with only one significant period of control difficulties. The period of unsteady column operation occurred because of restrictions in the automatic control system for the first column of the extraction system. The periodic instability in the first column cascaded through the first-cycle extraction system, causing instability in the other three columns. Although uranium losses to waste were not significant during this period, the

rough column operation resulted in first-cycle product being contaminated with aluminum nitrate due to excessive aqueous entrainment (i.e., emulsion formation) in the organic scrub column. Dispersion-coalescence tests conducted on these emulsions indicated that they were unsuitable for second-cycle feed but that they could be blended with incoming feed, up to certain limits, and be recycled through the first-cycle extraction system without compounding the emulsion problems in the extraction column. Dispersion coalescence tests were also conducted on feed streams to the extraction column to rule out the possibility that these streams were the cause of the column upsets.

1.14 *Hexone Extraction System*. As in previous campaigns, recovery of uranium in the Hexone extraction system was relatively troublefree. Uranium recovery efficiency was in excess of 99% with no unscheduled periods of equipment downtime.

1.2 Recovery of Transuranics from Second-Cycle Raffinate (L. C. Lewis, J. E. Johnson)

During FY 1971, neptunium and plutonium were recovered from the second-cycle extraction column raffinate by a TBP extraction in the first-cycle equipment. The concentrated transuranics (in solution with some residual uranium) were placed in intercycle storage for later recovery and shipment. One improvement was made in the flowsheet: Precipitation of the iron from the reductant used as the partitioning reagent was avoided by acidifying the raffinate as soon as possible after it left the second-cycle extraction column.

1.3 Tritium Balance in the First-Cycle Extraction System (R. N. Henry)

During the zirconium processing campaign, several streams in the first-cycle uranium extraction system were sampled and analyzed for tritium. The results from five different sample sets were averaged and a tritium material balance was made using the tritium entering the system in the IFU stream as the base value. As indicated in Figure 1 the fraction of tritium in the IBR, ICR, and ICP streams is very small. The ICR organic stream is recycled to the extraction column as the IAX stream. This organic stream appears to be holding a constant tritium concentration equivalent to about 0.2% of the total entering the system. The three mixer settlers do not remove any significant fraction of tritium from this stream. The IBR stream, with 1.8% of the tritium balance, is recycled to the extraction column as part of the IAF stream. The tritium is leaving the system in the ICP and IAR streams. The ICP stream contains less than 0.1% of the incoming tritium; therefore, by difference, the IAR stream is removing about 99.9% of the tritium from the system.

Additional tritium sampling during the last co-processing campaign indicated that, during dissolution of aluminum fuel in nitric acid, approximately 45% of the tritium was released with the dissolver off-gas and 55% entered the extraction system. During dissolution of zirconium fuel in hydrofluoric acid, approximately 90% of the tritium was released to the off-gas and 10% entered the extraction system.

Fig. 1 Distribution of tritium in the first-cycle extraction system.

1.4 Custom Reprocessing of Special Fuels (M. E. Jacobson)

Custom processing of two additional types of fuel was carried out in the Multicurie Cell during FY 1971. These fuels could not be handled economically in the plant dissolvers because of their special composition.

The first fuel was 92.7 kg of highly enriched, extremely low-burnup fuel containing 86.3 kg of uranium-235, and was discharged from Argonne National Laboratories' Zero Power Reactor-III (ZPR-III). This fuel was a metallic uranium fuel that had been coated with Kel-F; Kel-F is insoluble in plant process streams and would have caused severe problems in the process lines. By custom processing this material, the organic residue could be contained easily in a basket strainer, and a feed stock suitable for use directly in the second cycle was prepared.

The second batch of fuel handled was residue containing approximately 2 kg of uranium-235 salvaged following a 1966 destruct test on a SNAP power generator. There was a total of 37 kg of a mixture of 38% dirt, gravel, and glass, 6% high enriched uranium, and the balance zirconium, either as the hydride or as Zircaloy-II. The fuel was dissolved in 7 M hydrofluoric acid, complexed with aluminum nitrate, and the solids allowed to settle out

before being transferred to the plant for blending with incoming zirconium dissolver feed for first-cycle extraction. The insoluble residue was canned and taken to the burial ground.

1.5 Fluidized-Bed Denitration of ICPP Product

The successful operation of the product denitration system with enriched uranium was achieved this year. This followed a long testing period using both plant and pilot-plant equipment.

1.51 Cold Testing Experience with the Fluidized-Bed Denitrator (G. F. Offutt, W. J. Bjorklund)

Successful cold operation (normal and depleted uranium) of the plant fluidized-bed denitration[1] was completed and supplemental information was gathered using the four-inch diameter pilot-plant unit. The major problem to be solved was that of particle size control. The optimum particle size for smooth operation of the system is near a mass median particle diameter (mmpd) of 0.3 mm. The unit will operate well within a range of 0.15 to 0.40 mm; however, fines can be a problem at the lower sizes. A large particle size is not desirable because of the difficulties in fluidization due to limitations in the off-gas system. Particle growth that had to be corrected by "thermal shocking" or "jet grinding" was the usual case but did not always occur[1]. Various factors were found to influence both particle size and particle size control. They are as follows:

Nozzles. It is believed that slight differences in nozzles may account for the inconsistent results. Proper installation of the nozzle is very important. Fines may be produced by an improperly installed nozzle, ie, one that does not have a good spray pattern, usually caused by air leakage between the air and liquid sides.

Effect of Sulfate. The effect of sulfate of particle growth is still not well defined. Denitration experience at Mallinckrodt Chemical Works indicated that high sulfate caused particle growth[2]. The summary of ICPP experiences with sulfate during cold testing is:

- (1) Particle growth was experienced in numerous runs with sulfate concentration of 2000 to 5000 ppm (based on uranium).
- (2) An eight-day equilibrium run at a mmpd of about 0.2 mm was made in the pilot plant at a sulfate concentration of 700 to 1000 ppm.
- (3) An eight-day run in which particle growth occurred was made in the pilot plant with a sulfate concentration of less than 50 ppm.
- (4) A 23-day run was made in the plant with an equilibrium mmpd of about 0.2 mm. For 15 days the sulfate concentration was about 170 ppm and for the remaining eight days the sulfate concentration was about 800 ppm.

Jet Grinding. Control of the particle size by a 0.043-inch diameter jet grinder supplied with 100 psig air and an impact plate was successfully demonstrated in the pilot plant denitrator (see Figure 2). It was shown, however, that large quantities of fines (-150 Tyler Mesh) can be produced.

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Fig. 2 Demonstration of particle size control (MMPD) by variation in jet grinder pressure.

Temperature. High operating temperature (to 400°C) tends to promote particle growth or create a larger equilibrium particle size. Lower temperature (as low as 300°C) tends to cause the particles to become smaller.

Equipment Changes. Several modifications were made and tested on the plant equipment[1] prior to operation with enriched uranium; a schematic equipment flowsheet is shown on Figure 3. These modifications included:

- (1) Shortening the product collection vessel and modifying the product take-off line to allow cleanout by rodding from the glove box. This proved successful in handling plugging problems.
- (2) Installation of an auger in the bed removal line to help break up chunks which have prevented draining of the bed material. This has worked satisfactorily.
- (3) Use of an acid flooding system for uranium cleanout. Several passes with nitric acid, while heating and sparging the system, were required for complete clean out. The major problem area is leaks in fittings caused by thermal stresses and vibrations during operation.

Fig. 3 Schematic flowsheet of equipment for denitration of ICPP product.

- (4) Installation of a jet grinder for particle size control. Use of this has not been required, to date, in plant production runs.

1.52 Operating Experience with Enriched Uranium (G. F. Offutt, W. J. Bjorklund)

Two production campaigns for the conversion of uranyl nitrate solution to uranium trioxide were completed during the year in the fluidized-bed denitrator system. In the first campaign, approximately 800 kilograms of highly enriched uranium were processed in 14 days of operation. In the second campaign, nearly 500 kilograms of uranium were processed in nine days of operation. The average processing rate for the first campaign was 57 kilograms of uranium per day; for the second campaign the rate was 62 kilograms per day. At times during both runs the denitrator was in standby because feed was not available. The runs were entirely satisfactory and problems were minimal. Table I shows the operating conditions used during the runs.

TABLE I
OPERATING CONDITIONS USED DURING PLANT DENITRATOR RUNS

	Run 1	Run 2
Operating bed temperature	300 - 400°C	380 - 415°C
Fluidizing Air Rate	220 - 350 SCFH	185 - 300 SCFH
Atomizing Air Rate	125 SCFH	80 - 125 SCFH
Feed Rate	4 - 10 l/hr	4 - 10 l/hr
Feed	365 g/l U, 0.1 M HNO ₃	354 g/l U, 0.1 M HNO ₃

During the first campaign, particle size control was found to be dependent on the operating bed temperature. Figure 4 shows the particle growth response to the temperature changes. High temperature (up to 400°C) caused growth and low temperature (as low as 300°C) caused the particles to become smaller. The particle size ranged from a mmpd of 0.15 to 0.42 mm and averaged 0.24 mm in the first run. During the second campaign, the particle size did not respond to temperature and remained at a near equilibrium state of 0.2 mm.

Sampling schemes used during the runs showed the product to be homogeneous after being mixed in a twin shell blender. The only significant problem encountered during operation was frequent restrictions in the product overflow line. This was kept clear by using a rodding device from inside the glove box.

Fig. 4 Effect of temperature on particle size (MMPD) and size distribution (wt%) during fluidized-bed denitration of uranyl nitrate.

2. SUPPORT STUDIES FOR CURRENT ICPP

FUEL RECOVERY PROCESSES

2.1 Corrosion Evaluation of Zirconium Process Vessels (T. L. Hoffman)

To ensure operability of processing equipment throughout the zirconium fuel reprocessing campaign, selected equipment was inspected for corrosion prior to start of the campaign. Corrosion was evaluated by observation of plant test coupons and, in some cases, actual items of process equipment. With the exception of the boron-stainless steel plates in the head of the plant product evaporator, the principal process equipment was determined to be suitable for the planned campaign. In the case of the product evaporator, the measured corrosion on test coupons was severe enough to raise doubt as to the continued effectiveness of the boron-stainless steel grid as a secondary safeguard for nuclear criticality; alternate provisions for criticality control were instituted (Section 2.2, following). Inspection also indicated that a 100-mil corrosion allowance remained for the walls of the zirconium fuel dissolver. A Monel-400 cooling coil that had been in service for 13,000 hours was badly corroded; however, processing operations were altered and the coil was removed from service and not replaced. Several Monel-400 and Type 304L stainless steel remote control valves were replaced with new valves after 12,000 hours service.

2.2 Gadolinium as a Soluble Nuclear Poison (W. G. Morrison, L. C. Lewis)

Use of gadolinium as a soluble nuclear poison for secondary criticality safety control in the first-cycle product evaporator (H-130) was evaluated. The H-130 evaporator concentrates a dilute aqueous uranyl nitrate solution from the first-cycle solvent extraction system to about 300 g uranium per liter. The thermosyphon evaporator body and heat exchanger portions are constructed of geometrically safe six-inch-diameter or smaller pipe; however, the vapor disengaging head is constructed of nongeometrically safe 30-inch-diameter by four-foot-long pipe. A fixed poison insert of boron-stainless steel plates was provided in the initial installation for criticality safety control in the vapor disengaging head in event concentrated uranyl nitrate solution inadvertently entered the head. A recent routine inspection of corrosion coupons taken from the evaporator head showed that the fixed poison insert could have suffered severe corrosion since the previous inspection (Section 2.1).

Because of the uncertain condition of the fixed poison insert and the tight processing schedule, a soluble poison was considered the best means to ensure criticality safety control. Gadolinium was selected as the poison rather than cadmium or boron because of process costs and compatibility with the process chemistry.

The criticality safety calculations were performed for a three-dimensional mock-up of the dissolver with the KENO-II Monte Carlo criticality program[3] using the 16 group Hansen and Roach cross section sets[4]. Gadolinium cross sections (from LASL) were verified by comparison of KENO-II program results with clean critical solution experiments containing soluble gadolinium[5]. The calculational results for the criticality experiments agreed within 0.5% of the experimental results. The calculations for the evaporator, shown in Figure 5, show that 2 g gadolinium per liter of first-cycle product is sufficient to provide effective criticality safety control.

Laboratory studies demonstrated that gadolinium would not extract during the stripping operation and that traces of fluoride present would not precipitate the gadolinium as the fluoride. Further studies showed that two Hexone extractions would reduce the gadolinium to a level below the product specification for neutron absorbers. These studies were borne out by actual plant experience.

Fig. 5 Effect of gadolinium concentration on k_{eff} in the first-cycle uranium product evaporator.

2.3 Co-Dissolution of ETR and Zirconium Fuel Elements (M. W. Andrews)

A short-term laboratory study was made to determine the feasibility of adding ETR aluminum fuel elements to the zirconium fuel dissolver for co-dissolution. As a result of favorable dissolution rates observed, two cans containing pieces of ETR fuel elements were successfully co-dissolved.

The laboratory work was necessitated by the discovery that two aluminum fuel storage cans, each containing pieces of aluminum alloy ETR fuel elements, were leaking appreciable amounts of radioactivity into the ICPP fuel storage basin. If feasible, co-dissolution of these cans and element pieces with the zirconium fuels then being processed at ICPP would eliminate the need for storage and the subsequent increased basin water contamination. Coupons similar in composition and construction to the cores of those fuel pieces (31% depleted uranium and 2.8% silicon, UAl_x alloy metallurgy with a powder-formed boron foil made from aluminum and B₄C compacted and rolled into a 0.001-inch-thick sheet) were dissolved in several solutions at 70°C. In 7 M aqueous HF, the dissolution rate was found to be 21 mg cm⁻² min⁻¹. In a synthetic dissolver product containing 1.0 M Zr and 6.6 M F, the coupons dissolved at 29 mg cm⁻² min⁻¹. The conditions in the plant dissolver generally vary between these limits. In an earlier experimental study[6], zircaloy-II was found to dissolve at 15 mg cm⁻² min⁻¹, or at about one-half the UAl_x alloy dissolution rate. A fine, black, powdery residue was left around the interior of the Teflon beaker used in the dissolutions and was attributed to undissolved powder from the Al-B₄C foil. Because of the small amount of foil present in the canned elements, no solids problem was anticipated in the solvent extraction system.

2.4 Normal Paraffin Hydrocarbon as a Tributyl Phosphate Diluent (J. E. Johnson)

An investigation was made into the advisability of changing the TBP diluent in the first-cycle solvent at ICPP from Amsco kerosene to normal paraffin hydrocarbon (NPH), a mixture of C₁₀-C₁₄ straight-chain alkanes. This change has been made at both the Savannah River Plant and the Hanford Purex Plant, resulting in higher Purex cycle decontamination factors and better solvent cleanup properties. The improved solvent characteristics were attributed to the greater chemical stability of n-paraffins relative to highly branched alkanes. A calculated estimate of the radiation exposure of the first-cycle solvent at ICPP indicates that chemical degradation by nitric acid is probably more important than radiation damage.

A sample of NPH was obtained from South Hampton Chemical Company and tested for comparison with Amsco. It easily met all specifications currently in force for Amsco, while recent shipments of Amsco have greatly exceeded the chromyl chloride reactivity limit. Since NPH costs only about 10% more than Amsco and shows prospects for retaining good solvent quality for longer running times, the change from Amsco to NPH as TBP diluent at ICPP was recommended.

2.5 Recovery of Neptunium-Plutonium Concentrates (J. E. Johnson)

The assignment to recover and decontaminate neptunium from the Np-Pu-U mixture currently in storage at ICPP was changed to recovery of Np and Pu together, minimizing the disposal of Pu in plant waste system. Thus, the possibility exists for partitioning the uranium from neptunium and plutonium in an acid-deficient Hexone extraction with

ferrous sulfamate, followed by re-extraction of the raffinate in an acid-Hexone system with chromic acid oxidation. If the Np-Pu product is sufficiently decontaminated, it could be concentrated and shipped off-site.

Laboratory work performed on samples of the Np-Pu-U mixture revealed that Np and Pu can be quantitatively extracted in an acid-Hexone system provided that the feed material is subjected to sufficiently vigorous oxidizing conditions. Decontamination of the Np-Pu product was sufficient for off-site shipment in containers formerly used for uranium product solution. Therefore the process indicated above was recommended.

2.6 The Stability Constants and Rates of Formation and Fluoride Complexes (R. R. Hammer)

In the processing of nuclear fuels, hydrofluoric acid-nitric acid solutions containing a number of metal ions are commonly obtained. The stability of the solutions to precipitation, the corrosion of process equipment, the extraction coefficients of uranium in TBP and Hexone, and other solution properties are a function of the concentrations of the many chemical species in solution. These properties of solutions have been correlated with the concentrations of the chemical species present in solutions, and the solution properties have been estimated from these correlations for use in preparation of flowsheets for proposed processes.

The concentrations of the various chemical species in solution may be calculated from the stability constants for the formation of the numerous complexes in solution. However, for a number of metal complexes, the stability constants have not been determined previously, have not been determined at the high ionic strengths (μ) of process solutions, or have not been determined in the multicomponent media similar to the process solutions.

Using a fluoride specific ion electrode, the stability constants for a number of fluoride complexes were determined at 25°C ($\pm 0.02^\circ\text{C}$) in HNO_3 or NaNO_3 solution and are given in Table II. The details of the experimental procedure and calculation methods will be described in a topical report to be issued on completion of the study.

The rates of formation of the fluoride complexes of Al^{+3} and Zr^{+4} were studied at 25°C. The data for the rate of formation of AlF^{+2} from Al^{+3} and HF are in good agreement with published data [7]. The reactions (1), (2), and (3)

were too fast to measure with the equipment used; equilibrium for these reactions was established within one minute. Since reaction (3) is very rapid, the formation of ZrF^{+3} , ZrF_2^{+2} , and ZrF_3^+ must also be very rapid.

Further kinetic data are being generated to indicate the rates of formation of other complexes. This information is useful for ensuring that residence times are sufficient to produce adequate complexing before the solution leaves a tank for more corrosion-vulnerable parts of the facility.

TABLE II

STABILITY CONSTANTS FOR FLUORIDE COMPLEXES AT 25°C^[a]

	Equilibrium Constants for	
	($\mu = 0.96 \text{ M}$) ^[b]	($\mu = 2.88 \text{ M}$) ^[b]
I. $\text{Al}^{+3} - \text{HF-HNO}_3$ System		
$\text{Al}^{+3} + \text{HF} = \text{AlF}^{+2} + \text{H}^+$	$\beta_1 = 1570$	$\beta_1 = 1510$
$\text{Al}^{+3} + 2\text{HF} = \text{AlF}_2^+ + 2\text{H}^+$	$\beta_2 = 2.15 \times 10^5$	$\beta_2 = 2.40 \times 10^5$
$\text{Al}^{+3} + 3\text{HF} = \text{AlF}_3 + 3\text{H}^+$	$\beta_3 = 1.4 \times 10^6$	$\beta_3 = 3.04 \times 10^6$
$\text{Al}^{+3} + 4\text{HF} = \text{AlF}_4^- + 4\text{H}^+$	$\beta_4 = 1.4 \times 10^6$	$\beta_4 = 5.0 \times 10^6$
II. $\text{Zr}^{+4} - \text{HF-HNO}_3$ System		
$\text{Zr}^{+4} + \text{HF} = \text{ZrF}^{+3} + \text{H}^+$	$\beta_1 = 6.1 \times 10^5$ ^[c]	$\beta_1 = 6.9 \times 10^5$ ^[c]
$\text{Zr}^{+4} + 2\text{HF} = \text{ZrF}_2^{+2} + 2\text{H}^+$	$\beta_2 = 1.35 \times 10^{10}$	$\beta_2 = 1.55 \times 10^{10}$ ^[c]
$\text{Zr}^{+4} + 3\text{HF} = \text{ZrF}_3^+ + 3\text{H}^+$	$\beta_3 = 2.13 \times 10^{13}$	$\beta_3 = 1.97 \times 10^{13}$
$\text{Zr}^{+4} + 4\text{HF} = \text{ZrF}_4 + 4\text{H}^+$	$\beta_4 = 3.13 \times 10^{15}$	$\beta_4 = 5.0 \times 10^{15}$
$\text{Zr}^{+4} + 5\text{HF} = \text{ZrF}_5^- + 5\text{H}^+$	$\beta_5 = 1.5 \times 10^{17}$	$\beta_5 = 1.7 \times 10^{17}$
$\text{Zr}^{+4} + 6\text{HF} = \text{ZrF}_6^{2-} + 6\text{H}^+$	$\beta_6 \approx 1.6 \times 10^{18}$	$\beta_6 \approx 1.8 \times 10^{18}$
III. $\text{Gd}^{+3} - \text{HF-HNO}_3$ System		
$\text{Gd}^{+3} + \text{HF} = \text{GdF}^{+2} + \text{H}^+$	$\beta_1 = 6$	$\beta_1 = 5$
$\text{GdF}_3(\text{s}) + 3\text{H}^+ = \text{Gd}^{+3} + 3\text{HF}$	$K_{\text{sp}} = 1.1 \times 10^{-7}$	$K_{\text{sp}} = 4.5 \times 10^{-7}$
IV. $\text{H}_3\text{BO}_3 - \text{HF-HNO}_3$ System		
$\text{H}_3\text{BO}_3 + \text{HF} = \text{H}_4\text{BO}_3\text{F}$	$\beta_1 = 16$ ^[d]	$\beta_1 = 24$ ^[d]
$\text{H}_3\text{BO}_3 + 2\text{HF} = \text{H}_3\text{BO}_2\text{F}_2 + \text{H}_2\text{O}$	$\beta_2 = 130$ ^[d]	$\beta_2 = 100$ ^[d]
$\text{H}_3\text{BO}_3 + 3\text{HF} = \text{H}_2\text{BOF}_2 + 2\text{H}_2\text{O}$	$\beta_3 = 5.08 \times 10^5$ ^[d]	$\beta_3 = 6.0 \times 10^5$ ^[d]
$\text{H}_3\text{BO}_3 + 4\text{HF} = \text{HBF}_4 + 3\text{H}_2\text{O}$	$\beta_4 = 4.14 \times 10^7$ ^[d]	$\beta_4 = 5.40 \times 10^7$ ^[d]
V. $\text{Nb}^{+5} - \text{HF-HNO}_3$ System		
$\text{Nb}(\text{OH})_n^{(5-n)+} + \text{HF}$ $= \text{NbOH}_{(n-1)}\text{F}^{(5-n)+} + \text{H}_2\text{O}$	$\beta_1 = 130$	$\beta_1 = 130$
$\text{Nb}(\text{OH})_n^{(5-n)+} + 2\text{HF}$ $= \text{Nb}(\text{OH})_{(n-2)}\text{F}_2^{(5-n)+} + 2\text{H}_2\text{O}$	$\beta_2 = 1.55 \times 10^4$	$\beta_2 = 1.55 \times 10^4$
$\text{Nb}(\text{OH})_n^{(5-n)+} + 3\text{HF}$ $= \text{Nb}(\text{OH})_{(n-3)}\text{F}_3^{(5-n)+} + 3\text{H}_2\text{O}$	$\beta_3 = 2 \times 10^5$	$\beta_3 = 2 \times 10^5$
$\text{Nb}(\text{OH})_n^{(5-n)+} + 4\text{HF}$ $= \text{Nb}(\text{OH})_{(n-4)}\text{F}_4^{(5-n)+} + 4\text{H}_2\text{O}$	$\beta_4 = 4.54 \times 10^8$	$\beta_4 = 4.54 \times 10^8$
VI. HF-NaNO_3 System		
$\text{H}^+ + \text{F}^- = \text{HF}$	K	μ ^[e]
	1341	1.33×10^{-3}
	1239	1.16×10^{-2}
	914	1.06×10^{-1}
	839	1.06
	889	2.13
	1325	3.19
	2720	5.30

[a] The stability constants given in this table were estimated by graph-techniques. The data will be further refined and published in a topical report.

[b] Only nitric acid contributed significantly to the ionic strength.

[c] Estimated from published values.

[d] Not corrected for ionization of the acid.

[e] Only NaNO_3 contributed significantly to the ionic strength.

2.7 Resistance of Plastics to Mineral Acid (B. J. Newby)

Reclaiming enriched uranium from some of the more recently developed reactor fuels by aqueous techniques requires dissolution in solutions that are much too corrosive for many metallic materials of construction conventionally used in ICPP vessels. Thus, nonmetallic materials (plastics) are frequently considered for various applications in ICPP process vessels and instrumentation, eg, for baskets, insulating liners for electromagnetic meters, insulating spacers, electric cable insulation, unbreakable transparent covers, and corrosion resistant liners for vessels. To maintain current information for these applications, the literature is frequently surveyed and new materials which appear promising for a particular projected application are evaluated experimentally.

During the past year, a number of plastic materials that showed promise for the above uses were tested for their resistance to mineral acids. Materials having good acid resistance will be tested for their resistance to gamma radiation. The literature suggests that the materials tested had all or most of the following characteristics: good resistance to chemicals and high temperature; could be readily shaped or molded; were good electric insulators; had high impact, tensile, and flexural yield strength; were hard; and had low water absorption.

All selected materials were tested for resistance to boiling 8 M nitric acid, and to boiling 8 M hydrofluoric acid - 2 M nitric for 24 hours; some were also tested in boiling 10 M nitric acid - 5 M hydrofluoric acid for 24 hours. The results of the tests are summarized in Table III. Of the plastics tested, only the aromatic polyester, Ekonol, and the ETFE fluoropolymer, Tefzel 200, gave satisfactory resistance to the acids of interest.

2.8 Evaluation of Silica Gel Desiccant and Rhodium Catalyst Removed from the Rare Gas Plant (R. R. Hammer)

During the latter stages of operation of the Rare Gas Plant (RGP) during FY 1970, flow of krypton-rich process gas through the cold traps in the cryogenic unit was restricted and stopped several times. Analysis of gas samples taken downstream from the catalytic converters, which used rhodium-coated catalyst to decompose nitrous oxide, indicated high N₂O concentrations (up to 1% as compared to a nominal 0.1%). In addition, relatively high dew points (as high as +5°F) measured in process gas downstream of a desiccant bed containing silica gel also indicated that excess water vapor may have contributed to the plugging of the cold traps. Samples of the desiccant and of the rhodium catalyst were obtained and laboratory tests were made to determine the reasons for their inefficient operation.

It was recommended that the silica gel desiccant be replaced by an acid resistant molecular sieve which would give both a low dew point of the effluent gas and trouble free operation.

The original rhodium catalyst used to decompose N₂O in the RGP gas system consisted of dark grey, 1/8-inch, cylindrical pellets containing 0.5% rhodium metal on an alumina base. The color of the used catalyst removed from the converters had changed to a mixture of grey and nearly white pellets. The chemical form of the rhodium on the white pellets could not be determined directly; hydrogenation at 820°C liberated water vapor and produced dark grey pellets identical to the original catalyst, indicating that the white rhodium compound is an oxide, or possibly a nitrate.

TABLE III

RESISTANCE OF PLASTICS TO MINERAL ACIDS

Material	Vendor	Generic Types	Chemical Resistance in Boiling Acid		
			8 M HNO ₃	8 M HF - 2 M HNO ₃	10 M HNO ₃ - 5 M HF
Ryton PPS-40% GF	Phillips Petroleum Co.	Glass Fiber Reinforced Polyphenylene Sulfide	[b][g][h] [k][j][i]	[b][f][g][h] [i]	[p]
Kemid 3010	Chemplast Inc.	Glass Fiber Reinforced Polyimide	[b][d][n]	[b][d][g][h]	[p]
Ucardel P-4174	Union Carbide Corporation	A Polysulfonestyrene Acrylonitrile Copolymer	[d][e]	[b][c][m]	[p]
Amoco AI-11	Amoco Chemicals Corporation	Poly(amide-imides)	[b][d][k]	[b][h]	[o]
Lexan 500	General Electric	Polycarbonate	[b][h]	[b]	[b][e][g][h]
Arylon T-1801	Uniroyal Chemical	Polyaryl Ether	[b][g][h] [k][l][m]	[c]	[e][f][g][h] [k]
Ekonol	The Carborundum Co.	Aromatic Polyester	[a]	[a]	[a]
Tefzel 200	E. I. DuPont de Nemours and Company	ETFE Fluoropolymer	[a]	[a]	[a]

[a]	Unaffected.
[b]	Discoloration.
[c]	Blistered.
[d]	Partial dissolution or disintegration.
[e]	Lost shape.
[f]	Pits and voids on surface.
[g]	Brittle.
[h]	Surface easily broken, flaked, or powdered-off.
[i]	Extreme alligatoring.
[j]	Cracking.
[k]	Surface roughened.
[l]	Coupon swollen in size.
[m]	Surface wrinkled.
[n]	Fibers became loose from plastic.
[o]	Complete disintegration.
[p]	Test sequence discontinued.

Laboratory tests were made with the regenerated catalyst in an attempt to determine the operating conditions which caused oxidation of the catalyst in the RGP. Samples of the regenerated catalyst were heated in air and in NO_2 atmospheres at temperatures as high as 800°C for up to 20 hours without visibly changing the catalyst. Rapid oxidation of the catalyst, however, occurred in air at 930°C . The oxidized catalyst resembled the used catalyst from the catalytic converters after 40 minutes at 930°C . At 875°C , 60 hours exposure of the original catalyst to an air atmosphere was required to produce a similar amount of oxidation. Since the measured temperatures in the catalytic converters did not exceed 650°C during operation in 1970, hotter spots of higher catalyst surface temperatures must have existed to cause the oxidation of the catalyst. It was recommended that the minimum operating temperatures of the catalytic converter be reduced to 350°C during the next campaign; efficient decomposition of N_2O by the rhodium catalyst can be obtained for catalyst temperatures as low as 325°C .

Tests also were made to determine conditions necessary for regeneration of the catalyst. Regeneration of the catalyst was obtained at 630°C in three days in a 3% hydrogen - 97% nitrogen gas mixture, but at 550°C such regeneration would require greater than one week. The catalyst was regenerated quickly and completely in this gas mixture at about 800°C . Additional studies are being made to find methods of regenerating the catalyst while in the RGP catalytic converters, which cannot be heated externally to the higher temperatures. In-place regeneration of the catalyst is distinctly advantageous to periodic removal and laboratory regeneration.

2.9 Plant Support Instrumentation Projects (L. A. Jobe)

Plant support instrumentation projects were under active investigation in six different areas during this fiscal year.

2.91 Pulse Amplitude and Mean Level Indicator. Final design and procurement of all materials were completed for a capacitance-type measuring system for the air-pulser pulse leg of the 1A extraction column. The final design incorporated minor modifications to allow alternative measurements by capacitance and time domain reflectometry (TDR) techniques. Insufficient maintenance availability, due to high radiation levels where the probe was to have been located, prevented its installation during the last major maintenance period. The need for such a system for simplifying diagnosis of pulser equipment malfunction, as well as its normal function of measuring the operating pulse amplitude and the mean liquid level in the pulse leg, was evident during the processing campaign just completed.

2.92 Water-Purged Venturi Flowmeter. A water-purged venturi meter was installed in the 1A column feed line in 1965 to replace an electromagnetic flowmeter which had been used for feed flow measurements prior to zirconium processing with hydrofluoric acid. This venturi flowmeter system was water purged to prevent diffusion of radioactivity back into the operating corridor, where the flow transmitter was located. This feed system has required periodic flushing of the purge lines and the venturi meter to remove what have appeared to be deposits and plugs within the venturi. With the installation of the centrifuge on the head end of the process, it was anticipated that problems with suspended solids in the flowmeter would disappear. Such has not been the case and flowmeter operation was more erratic, if anything, during the FY 1970 processing campaign. As a result of this, a mock-up of the hydraulic system representing the 1A column feed system was erected in the chemical engineering laboratory. A plastic venturi of identical design was used. At the latter stages of the tests, an electromagnetic flowmeter was inserted for comparison. Both water and air purge tests were carried out over a period of several weeks; no appreciable drifting or irregularity of flow was noted.

Conclusions of this study are that the difficulties with the venturi flowmeter will not be overcome by operational adjustments. Flowmeter designs not susceptible to plugging, of rugged construction, and inherently reliable, are needed to give first-cycle input flow measurement at a confidence level desired for plant operation.

2.93 Acidity Measurement by Electrodeless Conductivity Meter. Electrodeless conductivity meters offer a possibility for in-cell measurement of composition of radioactive solutions. Since specific conductance varies with type of ion and its concentration, on-line measurement of free acidity in streams (eg, dissolver product) should be possible. Synthetic 6N mixtures of aluminum nitrate (using stock ANN solution) and nitric acid, ranging from 6N Al-ON nitric acid to ON Al-6N nitric acid, produced a very usable curve of conductivity versus acidity (or alternatively, Al concentration) between 0.07 and 0.7 mho/cm, respectively. Three electrodeless conductivity meters (two of the same make but of different age) were tested. Automatic temperature compensation is very desirable, but the coefficient varies with composition. Adjustable temperature coefficient compensation available on two of the meters was above the required range for these solutions.

2.94 Level Probes for Electrolytic Plant. New level sensing probes (fixed level, shorting type) were designed and constructed for the surge tank and sump when inspection revealed that the original probes were made of glass and would be subject to damage by vibration or shock and also subject to corrosion because construction was of dissimilar metals. The new probes were fabricated from thermocuring, resilient PVC plastic and were sealed to the specially machined tee connection by a drive pin. The design of the tee allows adjustment of the probe level within a 1/2-inch range, to be fixed during cold testing. The probes are designed to be replaceable, if necessary.

2.95 In-Bed Combustion Control. Dynamic tests of instruments and the entire system for in-bed combustion control disclosed inherent instabilities of several components. Necessary modifications were made to stabilize these components and, thereby, the system.

2.96 Waste-Solids Level Measuring System. The system finally selected for continuous solids-level measurements for the third generation solids storage bins was a time domain reflectometry (TDR) technique. Several other methods had been considered for continuous measurement of solids levels, including capacitance, compressive shorting of electrical resistance (Metritape), infrasonic, and two ultrasonic methods. Radiation, temperature, composition effect, or sensitivity limitations had removed all of these except one ultrasonic method. Although the capacitance method is in common use for solids-level measurement in bins and was originally planned for installation in one of the bins, experimental measurements of cold calcine showed a six-fold variation of capacitance as a function of composition over the six different samples of calcine, and a variation of 10^5 as a function of temperature, with peak capacitance values occurring at approximately 100°C.

No commercial manufacturer of ultrasonic or TDR equipment had any experience under conditions similar to our requirements. Tests with a TDR unit in a one-tenth-scale bin in the Chemical Engineering Laboratory demonstrated that a three-inch change in solids level was discernible with simple equipment. This is equivalent to approximately 1/2% resolution in the large storage bins, which is better than required.

3. ELECTROLYTIC DISSOLUTION PROCESS

3.1 Progress on ICPP Electrolytic Dissolution Process (G. F. Offutt)

The electrolytic dissolution system was constructed essentially as described in the FY 1969 Annual Report[8]. Construction was completed in February 1970. The remainder of the fiscal year was spent doing equipment checkout and modifications. The modifications were minor, with one exception, and involved process improvements to make operation, and especially decontamination, more efficient. The one major modification was the addition of settling tanks to the system (Section 3.2). These tanks (Figure 6) will collect about three fourths of the undissolved stainless steel particles to minimize solids handling problems downstream of the dissolution system. The tanks are remotely removable and are sized to contain all the undissolved solids generated during one campaign. Upon completion of a campaign the tanks will be removed from the system, the content sampled for uranium in a hot cell, and disposed of.

Cold testing will be completed during the next fiscal year with hot operation tentatively scheduled for June 1972.

3.2 Handling of Solids from the Electrolytic Dissolution System (L. C. Lewis, G. F. Offutt)

Study of the solids handling problems associated with electrolytic dissolution system was continued during the year. These studies consisted of two phases: (a) Study of the ability of the existing centrifuge system, including piping to and from it, to handle the solids; (b) Testing of settling tanks for collecting the solids prior to their leaving the electrolytic dissolution system. As a result of these studies the piping from the electrolytic dissolution system to the centrifuge was changed and two settling tanks (eight-inch diameter by 50 inches long) were installed in series in the product take-off line from the dissolution system (Figure 6).

3.21 Centrifuge System Testing. A manifold of one-inch-diameter pipe that was part of the piping system leading from the electrolytic dissolution system to the centrifuge was mocked up in full scale, of glass, in the laboratory. A low-solids-content water slurry of stainless steel particles was fed to this manifold for six hours. Valved-off sections of piping from the manifold that led to other processes became plugged. As a result of this test, the manifold in the plant was bypassed and direct piping was routed to the centrifuge.

A potential trouble area in the solids-disposal piping leading from the ICPP centrifuge to intermediate waste collection tanks was also mocked up in full scale. This included a diversion box and six-inch-diameter piping around the box. A water slurry of stainless steel particles, with and without silica gel, was tested. Conclusions from these tests were: (a) Significant quantities of solids would deposit in the piping at low flow rates, in the presence or absence of silicic acid. (b) Flow rates above 12 gpm would prevent significant depositions from forming in either case. (c) Deposits (dams) in the piping could be removed by water flow rates of 12 gpm if they did not contain silicic acid, but could not be removed by even higher rates if they did contain silicic acid. As a result of these tests, administrative controls will be used to maintain adequate flows of water during centrifuge cleanout to prevent solids buildup in the piping downstream of the centrifuge.

Fig. 6 Schematic flowsheet of electrolytic dissolution system.

3.22 *Settling Tank Testing.* Pilot plant tests were done with a five-inch diameter by four-foot-long Plexiglass tank mounted in either a horizontal or vertical position, using a slurry of stainless steel particles in water. Tests with the tank in a horizontal position were done with and without baffles. Tests with the tank mounted in a vertical position (top entrance) were done with cyclone tube entrances at the top of the tank or extended to 12 inches below the top, and with a straight tube entrance extended to 12 inches from the top. None of the designs proved to be significantly different in efficiency of solids removal; all removed about three-fourths (by weight) of the particles. The design chosen for the plant unit was two vertical tanks, in series, with cyclone tube entrances at the top. These tanks are eight inches in diameter and 50 inches tall. They will contain all the solids generated during a run. After the run, they will be removed from the cell remotely, sampled, and disposed of. Flow rates through the tanks will be up to 50 liters per hour.

3.3 Results of Solids Testing with a Full Scale Mock-Up of the Plant Centrifuge Airlift (R. N. Henry)

A series of pilot-plant tests was conducted with a full scale mock-up of the airlift which removes solution from the case of the plant centrifuge to determine its performance if solids from the electrolytic process were inadvertently flushed from the centrifuge. The mock-up equipment used during the tests is depicted schematically in Figure 7. The overall performance of the airlift was very good, with only two of the eight severe tests conducted resulting in plugging of the airlift. These two tests were conducted with stainless steel fines mixed with sodium meta silicate and nitric acid which were allowed to settle and harden in the bottom of the airlift. Once the solids hardened, the airlift was unable to clear the solids plug. However, back-flushing of air through both legs of the airlift cleared the solids plug.

Fig. 7 Schematic flowsheet of airlift equipment.

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Evaluation of the results of the tests led to the following conclusions:

- (1) The sudden addition of cup-fulls of granular solids to the feed leg of the airlift will not restrict the flow or permanently plug the line.
- (2) The airlift is capable of lifting solids as large as 1/2-inch diameter up to the collection pot.
- (3) The longer the solids are permitted to settle, the more difficult they are to remove from the airlift system.

3.4 Flammability of Hydrogen-Oxygen-Nitrogen Oxide Mixtures (J. E. Johnson, L. C. Lewis)

A literature survey was made concerning the effects of nitrogen oxides on hydrogen-oxygen flammability and explosion limits. Mixtures of these gases are expected in the off-gases from the electrolytic dissolver. Results of the survey are presented in detail in ICP-1002[9]. It was concluded that, although small concentrations of nitrogen oxides do sensitize stoichiometric H_2-O_2 mixtures toward thermal ignition, they do not increase the flammability of hydrogen near its composition limits for combustion.

3.5 Corrosion Surveillance in the Electrolytic Dissolver Head-End System (C. A. Zimmerman)

Corrosion specimens of the various materials of construction used in the electrolytic dissolver head-end system, as well as candidate materials for future use in such systems, will be exposed in the plant equipment during cold testing and hot operation. Two test racks will be utilized: one stainless steel test rack will be in the surge tank; the second, fabricated from niobium, will be placed in the blanked off section of the electrolytic dissolver basket.

A materials survey of the equipment in the present electrolytic dissolver head-end system has been completed. Metals used in contact with processing solutions are Types 304-L, 316, 347, and 17-4 PH stainless steel, titanium, niobium, and 90 - 10 platinum - iridium alloy. Plastic materials in contact with the processing solution are polyvinyl chloride, polyvinylidene chloride, and Kynar.

4. GRAPHITE FUELS PROCESSING (A. P. Roeh, L. C. Borduin, R. E. Foster)

Development of a combustion-dissolution head-end process for reprocessing graphite fuels at ICPP is continuing. The process consists of the following general steps: (a) oxidation of the graphite matrix and metallic carbides in an inert bed of fluidized alumina, (b) elutriation of the metal oxide combustion products from the alumina bed, (c) removal of the elutriated particles from the off-gas, (d) dissolution of the uranium and niobium compounds using nitric and hydrofluoric acids, (e) complexing of fluoride solutions with aluminum, (f) separation of any undissolved solids from the uranium bearing solutions, (g) solvent extraction recovery of the uranium, and (h) denitration of the uranyl nitrate product. Figure 8 is a block diagram showing the principal steps in two possible modes of operation.

Fig. 8 Block flowsheet of combustion-dissolution process for graphite fuels.

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During the past year, pilot-plant burner runs have been made to: (a) further establish the operational reliability of the burner, (b) determine the effectiveness of jet grinders in decreasing the uranium and niobium concentrations in the bed, and (c) explore means to minimize the formation of nitric acid insoluble uranium. Laboratory studies have been made to: (a) establish the chemical feasibility of the dissolution processes, (b) establish dissolution rates and the times required for complete uranium dissolution at various concentrations of HNO_3 and HF , (c) evaluate corrosion rates for candidate dissolver construction materials, and (d) establish stability regimes for the various HF dissolvent effluents after complexing with aluminum nitrate.

4.1 Pilot-Plant Studies of Fluidized-Bed Combustion-Dissolution Process (L. C. Borduin)

Details of the fluidized-bed burner development for graphite matrix fuels are reported in IN-1423[10]. Additional studies are summarized in the following sections.

4.11 Uranium Retention in the Burner. The separation of uranium from the fluidized bed is based on elutriation of essentially all the U_3O_8 particles from the burner. Early development studies indicated the feasibility of this separation technique because of the consistently small size of the U_3O_8 particles (90% less than $45\ \mu$) formed during oxidation of the uranium dicarbide microspheres. Subsequent pilot-plant studies revealed that significant amounts of uranium are retained in the burner as a coating on alumina particles, as niobium-uranium oxide compounds, or as nonelutriable-size U_3O_8 particles.

Statistically designed experiments, discussed in the annual report for FY 1970[1], showed that a "steady state" uranium concentration could not be realized by manipulating the fluidizing velocity and oxygen concentration. This led to the investigation of jet grinding as a method of controlling the uranium concentration in the pilot-plant burner.

4.12 Effect of Jet Grinder on Uranium Retention. Based on the promising results from scoping studies of jet grinders operating in an alumina bed coated with U_3O_8 , four jet grinders were installed in the pilot-plant burner. The effect of jet grinders on the uranium concentration in the fluidized bed is shown in Figure 9. The upper curve, representing operation without jet grinders, shows uranium content in the burner for 13 consecutive runs with the same bed material. The variations in accumulation rate apparent in this plot are due primarily to changes in fluidizing velocity. A mean fluidizing velocity of 1.33 ft/sec was in effect during the first 230 hours and last 15 hours of run time while a velocity of 1.05 ft/sec was in effect during the interim period. The lower curve shows the results of 10 consecutive days of operation with four jet grinders. The starting bed for this series of runs contained ~10 kilograms of uranium; the uranium content steadily decreased to the final level of 4 kilograms. Therefore, jet grinders are obviously an effective means of controlling the uranium content of the burner.

Further studies are planned to determine the effect of jet grinder position within the burner on uranium elutriation efficiency. The discovery of a higher uranium concentration in the upper reaches of the fluidized bed suggests placement of a grinder at this upper level to gain greater efficiency in grinder operation.

4.13 Niobium Retention in the Burner. Niobium carbide, present as a coating on some surfaces of graphite fuels, undergoes in-situ oxidation to Nb_2O_5 in the combustion process. Much of the Nb_2O_5 breaks into elutriable-size particles; however, a significant percentage resists attrition and is retained as flakes in the burner. Minimizing the niobium oxide content in the burner is desirable because: (a) decreased fluidization quality is anticipated with high niobium concentrations (~30%) and (b) the oxide is a suspected factor in the form of nitric acid-insoluble niobium-uranium compounds. Although early studies indicated that the flakes would be broken up by the turbulent action of the bed, later runs have shown the niobium to accumulate gradually in the bed.

4.14 Effect of Jet Grinder on Niobium. Although a steady state niobium concentration in the bed was not achieved with four grinders in the pilot-plant burner, the rate of niobium accumulation (0.4 kg/day) is less than half the rate without jet grinders. If this rate remained constant, the bed would have a useful life of at least 40 to 60 days of continuous operation. However, there is some evidence the accumulation rate is decreasing which might result in an acceptable steady state concentration in the bed.

4.15 Effect of Jet Grinder on Formation of Nitric-Acid Insoluble Uranium Compounds. Laboratory studies (reported in IN-1457[1]) showed that Nb_3UO_{10} , a nitric-acid-insoluble compound and a known constituent of the overhead product, can be formed by heating a mixture of Nb_2O_5 and U_3O_8 powders above $1500^{\circ}C$. Nb_3UO_{10} could not be formed by heating mixtures of UC_2 and Nb_2O_5 or U_3O_8 and NbC . The postulated mechanism for the formation of HNO_3 -insoluble uranium was, therefore, based on the presence of the oxides in high temperature regions associated with oxidation sites. As anticipated, the reduction in uranium oxide content of the fluid bed by the jet grinders resulted in a reduction in HNO_3 -insoluble uranium. The observed HNO_3 -insoluble uranium production peak corresponds to a peak in the combined uranium and niobium concentration in the bed.

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Fig. 9 Effect of jet grinders on the uranium content of a fluidized alumina bed.

Although the jet grinders caused a reduction in HNO_3 -insoluble uranium, a loss of 5 to 10% uranium could still be anticipated if only a nitric acid dissolution were used.

4.16 Combustion Efficiency. The use of jet grinders in the fluidized-bed combustion process has consistently resulted in lower combustion efficiencies (a reduction of 3 to 4%). This effect is largely attributed to the increased fluidizing velocity and subsequent reduction of particulate residence time in the bed caused by the volume of gas introduced via the jet grinders, and also to the location of the grinders within the burner. More than 20% of the total gas fed to the burner enters through the grinders. Their location near the bottom of the second stage results in high velocities in the region where combustion of particulate graphite occurs. Apparently, there is a net reduction in retention time causing the lower combustion efficiencies. The use of oxygen rather than air caused a slight (1 to 2%) increase in combustion efficiency; however, a further reduction in carryover of unburned carbon is desired. Studies are planned to determine if a slight increase in nominal bed temperature (50 to 100°F) will restore the combustion efficiency to the desired level of 95% or greater.

4.2 Processing of Burner Product (B. E. Paige, R. E. Foster)

Details of the development of a process for dissolving burner product are reported in IN-1484^[11]; results of additional studies are reported in the following sections.

4.21 Laboratory Studies. Previously proposed flowsheets for the recovery of uranium from burner product proposed only leaching with nitric acid to dissolve the uranium oxide elutriated in burner product; however, some product contains HNO_3 -insoluble uranium, identified as $\text{Nb}_3\text{UO}_{10}$, which requires hydrofluoric acid for dissolution. Acceptable dissolution rates of $\text{Nb}_3\text{UO}_{10}$ and Nb_2O_5 have been achieved in several mixtures of HF-HNO_3 . The dissolution rate increased with increasing HF concentration, but high fluoride-to-niobium mole ratios resulted in unstable solutions when complexed with aluminum. Above 8 M HF the uranium solubility in the dissolver product ranges from 20 to 44 g/l. A low concentration of HNO_3 (~0.1 M) in the HF dissolvent will prevent the formation of UF_4 and assure the precipitation of only UO_2F_2 if the uranium solubility limit is exceeded.

The fluoride in dissolver solutions must be complexed with aluminum and other complexing ions to prevent corrosion of stainless steel equipment used for feed adjustment, extraction, and waste handling at ICPP. Stability studies were made for the Nb-Al-F system. Within a limited range of compositions, the solutions are stable, and fluoride can be adequately complexed to prevent corrosion in stainless steel; addition of uranium or other fluoride complexers to these stable solutions causes formation of precipitates. These data showed that a dilute uranium extraction flowsheet must be used with the fluoride solutions because both corrosion and stability problems would occur when the uranium is extracted from a solution greater than 0.25 M uranium (minimum uranium concentration for second extraction cycle feed).

4.22 Process Flowsheets. Two potential process flowsheets for dissolution of the burner product and preparation of suitable feed for the solvent extraction process have been under study. A two-step-dissolution, split-extraction flowsheet is attractive because of the relatively low volume of waste solution generated; use of this "split-extraction" flowsheet, however, may be hampered by limited solution storage capacity and a requirement for more operating labor. An alternative approach is a two-step-dissolution, combined-solution extraction flowsheet which requires fewer operations but results in a larger volume of waste because of required dilution. Additional studies are planned in an effort to modify the latter

flowsheet into a true single-dissolution process with more desirable solution-volume relationships.

The "split-extraction" process for recovering greater than 99% of the uranium in the graphite burner product includes a nitric acid leach to remove the bulk of the uranium, separation of the undissolved solids from the uranyl nitrate solution, and the dissolution of niobium pentoxide and nitric-acid-insoluble uranium ($\text{Nb}_3\text{UO}_{10}$) in 14 M hydrofluoric acid. This sequential dissolution provides a second-cycle concentrated uranyl nitrate extraction feed and a first-cycle fluoride-complexed extraction feed. The proposed flowsheet for this process using a hypothetical burner product as shown in Figure 10 is chemically feasible.

The bases for the proposed flowsheet are: (a) a fluoride-to-niobium ratio of 7.3 to produce a stable solution and (b) a concentration of 0.4 M aluminum and a fluoride-to-aluminum ratio of 1.6 (for the fluoride not complexed by niobium) for the complexed dissolver solutions to assure stability and minimum corrosion of Type 347 stainless steel. A single dissolver can be used if it is made of Incoloy-825. Relative advantages of this flowsheet are: (a) separation of a portion of the dissolver solution as concentrated feed directly to second-cycle extraction, (b) significant reduction of the amount of undissolved solids by essentially complete dissolution of niobium, and (c) a very large reduction in waste volume by minimizing the volume of fluoride solution; fluoride solutions cannot be concentrated because of formation of unstable solutions.

An alternative process, which has been proven chemically feasible, combines the nitric acid and hydrofluoric acid extraction feeds and dilutes with nitric acid to less than 4 g/l uranium to produce a single extraction feed for first-cycle extraction. A proposed flowsheet for this alternative process using a hypothetical burner product is shown in Figure 11. The high hydrogen ion concentration in the final diluted combined extraction feed makes it necessary to increase the "free fluoride" concentration in the feed. A fluoride-to-niobium ratio of 8.0 was selected to produce good stability characteristics; a fluoride-to-aluminum ratio of 2.4 was selected to assure minimum corrosion of SS-347, yet maintain stability. Corrosion scoping studies on SS-347 using the diluted combined extraction feed, with and without uranium, indicated a corrosion rate of 0.1 to 0.2 mpm.

Studies on a modification of the latter flowsheet, possibly enabling dissolution in a mixed reagent and having more favorable solution-volume relationships, are underway.

4.3 Corrosion Tests in the Pilot-Plant Graphite Burner (C. A. Zimmerman)

Test specimens of Hastelloy X, Hastelloy C, Inconel 621, Inconel 625, Nichrome, Carpenter alloy 20 Cb-3, and Type 347 stainless steel have been exposed at the top of the perforated lower section of the pilot-plant graphite burner. These specimens are exposed in the fluidized bed in an area where the temperature is expected to be about 850 to 900°C.

Visual inspection of these coupons after 600 hours exposure and decontamination using hot alkaline permanganate and hot nitric acid indicated that none of the materials had experienced severe corrosion. The Hastelloy X and Nichrome specimens, and the Type 304-L stainless steel inner-bed basket, had all suffered corrosion due to abrasion where the jet grinders were inserted into the fluidized bed.

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Fig. 10 Proposed flowsheet for sequential dissolution-separated extraction of graphite burner product.

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Fig. 11 Proposed flowsheet for sequential dissolution-combined extraction of graphite burner product.

5. OTHER STUDIES RELATED TO FUTURE ICPP OPERATIONS

5.1 Storage of Peach Bottom I Core I Fuel (J. D. Hammond)

The Peach Bottom fuel storage facility is being constructed as described in FY 1969 annual report^[1]. The 47, water-tight, underground storage silos have been completed on schedule. A safety analysis, confirming the safety of the facility for storing the Peach Bottom I Core 1 fuel has been issued as IN-1465^[12].

The first shipment of Peach Bottom fuel will be taken to the TAN Hot Shop and the basket of spent fuel will be removed from the transport cask. After a basket of simulated fuel is inserted, the cask will be transported to the storage facility at ICPP for demonstration of detailed procedures for storing and retrieving the fuel. At the completion of these handling tests, the cask will be returned to the TAN Hot Shop; the spent fuel will be reloaded into the cask and transported to ICPP for storage. All subsequent fuel shipments will be transported directly from Peach Bottom, Pennsylvania to ICPP.

5.2 Storage of Fort St. Vrain and Peach Bottom I Core 2 Fuel (G. E. Bingham)

Presently, there are no commercial reprocessors for High-Temperature-Gas-Cooled Reactor (HTGR) fuels. Consequently, the AEC's Division of Production has requested that provisions be made for storing one full core of Fort St. Vrain fuel and the entire Peach Bottom I Core 2 fuel at the Idaho Chemical Processing Plant (ICPP).

In general, the design requirements for this proposed fuel storage facility are as follows:

- (1) Receive and handle fuel from the Fort St. Vrain and Peach Bottom reactors
- (2) Store one core of Fort St. Vrain and Peach Bottom fuel, 1482 and 804 elements, respectively
- (3) Provide adequate cooling and shielding for the stored fuel
- (4) Perform all operations with the fuel remotely.

Fuel Description -- Fuel from both the Fort St. Vrain and Peach Bottom reactors will be stored in the facility. A Fort St. Vrain fuel element is in the form of a hexagonal graphite block, about 14 inches across the flats, 31 inches long, and weighing 300 lb. A Peach Bottom fuel element is a 3.5-inch OD graphite cylinder, 12 feet long, and weighs 90 lb. Both types of fuel will be stored in closed canisters. The canisters will be 18-inch OD by 8 feet long, will have a tight fitting lid, and will be constructed of carbon steel. Each canister will provide storage for either three Fort St. Vrain or 12 Peach Bottom elements^[a].

[a] The Peach Bottom elements will be cut prior to storage, with only the center 90 inches of each element being stored.

Facility Description -- Based upon these requirements, a facility has been designed and is shown in Figures 12 and 13. The entire facility will be constructed of concrete with the external walls backed with an earth berm for shielding purposes. The facility will contain several functional areas as described in the following paragraphs.

The *Cask receiving area* will be constructed as an extension of the west end of the existing CPP-603 cask receiving area. In this area, the cask will be (a) removed from the transport vehicle, (b) positioned on a fuel transfer dolly, and (c) checked for fission gas. If no fission gas leakage is detected, the cask will be vented and the cask closure bolts removed. A portion of the cask receiving area will include a transfer pit containing a cask transfer dolly. The dolly will be used to transfer the cask from the receiving area to the fuel handling cave.

All operations with the graphite fuel (other than storage) will be performed in the *fuel handling cave*. To perform the necessary operations, the cave will be equipped with a remote manipulator, a saw, and a vacuum cleaner system.

All fuel handling operations will be performed remotely from the facility *control room*. All instrumentation and recorders will also be located in the control room. For ease of operation, the control room will be provided with shielding windows for viewing the fuel handling cave and the fuel storage area.

The *fuel storage area* will contain racks which provide both spacing and support for the 18-inch ID by 8-foot long fuel storage canisters. The storage racks will space the canisters 24 inches center-to-center and three inches off the floor for criticality and cooling purposes.

A *crane maintenance area* will be provided on one end of the facility, opposite the fuel storage area. This area will permit contact maintenance of the five-ton-facility crane and other remote equipment (saw and manipulator) in a relatively low radiation area.

The facility will be provided with a *cooling air system* to remove heat from the stored fuel: approximately 1×10^6 Btu/hr for a full facility. The cooling system blowers will draw outside air through roughing filters, past the stored fuel, through prefilters and HEPA filters, and then discharge it to the atmosphere through a 50-foot stack. The system will contain two fans, one operating and one standby, both of which will be supplied with normal and emergency power.

5.3 ICPP Safety Review Document

(D. E. Black, W. R. Carpenter, W. G. Morrison, R. L. Nebeker, W. P. Palica,
W. L. Slagle, R. R. Smith)

As part of the AEC's "Fire, Safety, and Operating Continuity" effort, a comprehensive safety review of ICPP systems and facilities currently is under way to determine if hazards exist (a) to individuals working at the plant, (b) to other persons at the NRTS, or (c) to populations beyond the perimeter of the NRTS as a result of the operations conducted at the ICPP. All major existing ICPP facilities and processes will be examined during the review except those for which safety analysis reports (SAR) have been prepared recently.

Fig. 12 Cross section plan of proposed HTGR fuel storage facility.

Fig. 13 Artists conception of proposed HTGR fuel storage facility.

Although other safety reviews have been conducted previously at the ICPP, these generally have covered individual processes or units using older modeling and calculational techniques. The results of this current safety review will be documented in the "ICPP Safety Review Document" (SRD) which will be similar in content to safety analysis reports prepared normally for major AEC projects prior to construction. In this case, the SRD will cover a facility which has operated safely and without adverse environmental impact on the populace for over 20 years.

The SRD, scheduled for completion in March 1973, will provide a detailed technical description of ICPP facilities and processes which will be updated periodically as required. The technical descriptions also will be useful as training material to acquaint personnel with the ICPP area and the sophisticated processes. Guidelines, bases, supporting information, references, and calculational methods for analyzing the consequences of abnormal events (eg, earthquakes, explosions, fires, tornadoes, etc) will be assembled in the SRD for use in future ICPP safety evaluations. On-site and off-site effects of postulated accidents will be evaluated, and changes in procedures and/or equipment will be recommended where they would clearly result in improved operation or environmental safety. An additional benefit of the SRD will be the identification of items that will result in reduced costs at the ICPP.

Potential effects associated with long-term operation also will be evaluated during the safety review. The management control package (such as Policy and Procedure Manuals, Standard Operating Procedures, Detailed Operating Procedures, independent reviews, etc) used to assure safety at ICPP will be described. The use of these controls and the methods of interfacing to assure the safe operation of the plant will be discussed.

The design basis accident (DBA) concept will be used to evaluate upper-limits accident consequences associated with operation of the ICPP. For purposes of the SRD, a DBA is a hypothetical accident which is technically feasible and which results in the greatest acceptable potential release of radioactive material to the environment or produces the highest acceptable radiological dose for a given operation. Only those DBA's which require no more than two concurrent or consequent events will be considered; three or more would render the postulated event incredible. The use of the DBA will prevent the necessity of evaluating the quantitative consequences of every conceivable individual accident; the consequences of only the upper-limit accidents will be evaluated in detail. If the consequences of the worst accident are within AEC guidelines, then all other accidents with lesser consequences are also acceptable (though undesirable).

Examples of potential hazards to be treated in the SRD are:

- (1) Effects of natural phenomena (earthquakes, volcanoes, tornadoes, floods)
- (2) Criticalities (magnitude and factors affecting associated fission product releases)
- (3) Radiation exposures and shielding
- (4) Fission product behavior (attenuation between source and point of release as well as transportation through air and soil)
- (5) Explosions and fires
- (6) Accident interaction and propagation.

Two project milestones were fulfilled during FY 1971. These were (a) developing in detail the contents and format of the report and (b) transmittal of a trial section to AEC-ID demonstrating the general method of approach and systemization employed to evaluate postulated accident consequences.

5.4 Seismic Analysis of ICPP (W. L. Slagle)[a]

Because of the potential disruptive effects of earthquakes, seismic analysis of selected ICPP systems and facilities was a high-priority item for the ICPP Safety Review. An earthquake conceivably could initiate an accident, or simultaneously trigger two or more events previously considered unrelated which, for example, might result in a criticality.

Some geological studies of the NRTS were made previously, and geological faults near Arco and Howe were identified by Bonilla and Chase in 1967; these faults were excavated by Malde in 1968 and 1969. Based on these studies, the elapsed time since the most recent tectonic movement on these faults was estimated to be less than 30,000 years ago, and possibly as recently as 4000 years ago. Consequently, these faults are considered active according to the definition accepted by the AEC for reactor siting purposes. During June 1971, a seismic risk evaluation of the NRTS was made by Woodward-Lundgren and Associates[13]. This study concluded that a bedrock acceleration of 0.33 g[b] could occur at the ICPP from a maximum credible earthquake of Richter magnitude 7-3/4 on the Arco fault. This acceleration is equivalent to a ground surface acceleration of about 0.5 g for structures not founded on bedrock, because a soil amplification factor of about 1.5 is applicable at ICPP.

Prior to May 1970, major structures at the ICPP were designed to meet Zone 2 (moderate damage) earthquake standards of the Uniform Building Code (UBC). In 1969, the UBC seismic risk map was revised to include the NRTS in seismic risk Zone 3 (major damage zone) instead of the previously assigned Zone 2. On May 21, 1970, AEC Headquarters directed that the new seismic risk map and applicable criteria be applied to the design of future AEC structures; thus, for the ICPP safety review, it was necessary to determine the effects of a Zone 3 earthquake on Zone 2 facilities.

The Idaho Nuclear Corporation-developed STRAP-D[14] computer code and modeling techniques were employed to analyze the seismic response of sensitive buildings and systems at ICPP. The maximum stresses in these structures during earthquake loading were calculated. This loading consisted of subjecting the *base* (or foundation) of the facilities to the ground acceleration records of four of the strongest earthquakes measured in the U. S. (the 1940 El Centro, 1949 Olympia, 1966 Parkfield, and 1952 Taft earthquakes). For the facilities analyzed, the 1940 El Centro earthquake caused the highest stresses of the four earthquakes. A range of scale factors was applied to the 1940 El Centro earthquake record to relate stress to peak ground acceleration, and the facilities were subjected to the resulting ground acceleration histories. From this relation, the peak ground acceleration which each facility could withstand without failure was obtained. The main process building (CPP-601), Z cell, large liquid waste storage tanks, and vaults housing the liquid waste storage tanks were found to be capable of safely withstanding earthquakes with peak

[a] Dr. J. A. Dearien and L. J. Siefken of the Nuclear Safety Program Division, Idaho Nuclear Corporation, performed the analysis.

[b] g equals the gravitational acceleration.

bedrock accelerations in excess of 0.5 g. These structures are founded on bedrock. The Spent Fuel Storage Facility basin can safely withstand earthquakes with ground accelerations less than 0.29 g (~0.2 g bedrock). Earthquakes with bedrock accelerations greater than 0.15 g may be expected to cause a structural failure of the ICPP main exhaust stack. (The Spent Fuel Storage Facility and main exhaust stack are not founded on bedrock.) Several of the process-related tanks in CPP-601 were found to be incapable of withstanding earthquakes with peak ground accelerations greater than 0.33 g.

Methods of increasing the earthquake resistance of the ICPP structures not capable of withstanding earthquakes with a peak bedrock acceleration of 0.33 g are currently under investigation. Methods which have been suggested are: (a) attach anchors to the top center points of the walls in the Spent Fuel Storage Facility; (b) add extensive external bracing to the main exhaust stack; (c) add cross-bracing to the supports of the process-related tanks in CPP-601. These modifications will increase the earthquake resistivity of the ICPP systems to acceptable levels.

5.5 Nuclear Safety of a Dry Fuel Storage Cabinet (W. R. Carpenter)

To provide safe storage of fuels used for research projects, criticality safety calculations were performed for a dry, cadmium-poisoned fuel storage rack using the KENO II Monte Carlo criticality code with 16-group Hansen and Roach Cross Sections. The criticality safety of the rack was evaluated for storing:

- (1) intact fuel elements
- (2) stacks of fuel plates
- (3) fuel alloy pieces or powder in tubes or bottles.

Each of the 66 rack storage locations (11 shelves with 6 storage locations per shelf) was assumed to contain a single plate-type fuel element (3-1/2 inches by 3-1/2 inches by 36 inches long) with 500 g of 93% enriched uranium per linear foot (a total of 1500 g U/element). Because the rack was to be installed in a laboratory which contained an overhead fire protection sprinkler system, the calculations were performed assuming the storage cabinet was immersed in a uniform water spray whose water density varied from zero g/cc (no water) to one g/cc (complete immersion in water). The calculation showed that k_{eff} increased continuously with increased water density from $k_{eff} = 0.20$ (dry) to 0.70 (flooded with water). Based on these results, the storage rack is critically safe for up to 500 g of uranium per linear foot of storage location for the three forms of fuel mentioned previously.

When installed, the actual dry fuel storage rack varied from the dimensions originally specified in that: (a) the cadmium-polyethylene-cadmium flux traps between shelves were 35-1/4 rather than 36 inches long, exposing 3/4 inch of the fuel elements to each other in the horizontal direction, and (b) the horizontal center-to-center spacing of the fuel elements was reduced from 6 to 5-5/8 inches. A reevaluation of the cabinet in the flooded (most reactive) condition showed the calculated k_{eff} increased from 0.70 to 0.73 because of these variances. Thus, the rack is safe as installed.

5.6 Revision of KENO Computer Program (W. R. Carpenter)

The addition of the KENO-II[3] Program to the NRTS IBM 360/75 computer library has increased both the capability and accuracy of the criticality evaluations performed for ICPP. KENO-II is a Monte Carlo criticality program which can be used to analyze multi-group, multi-regional, three-dimensional problems. It incorporates both specific and generalized geometry options to describe any system which can be represented by quadric surface equations. Major improvements of KENO-II over the previous version of KENO, include: (a) mixed box orientation in the solution matrix, (b) dimensional search, (c) increased internal storage, (d) improved program checks and diagnostics, and (e) direct access to a 16-group Hansen and Roach nuclear cross section library disk.

Most significant improvement in the new version was the incorporation of a "mixed box" orientation option. Both KENO-II and the earlier KENO versions would handle a three-dimensional description of a basic cell (box) which can be placed into a three-dimensional solution matrix. The new program allows the description of more than one box which can be positioned arbitrarily in the solution matrix. The dimension search option allows a one-step calculation of critical (or subcritical) size rather than requiring three or four separate steps. Increased internal program storage allows calculation of more complex systems than possible previously. The improved checks, diagnostics, and direct access to the cross section disk provide greater user convenience and a substantial decrease in time requirements for both the user and the computer.

Two additional IBM 360/75 computer codes for use with KENO-II have been added to the ICPP calculational package. These are: (a) PICTURE[15] which is a specialized code for printing a picture of any desired plane of a system described by the generalized geometry package of KENO-II, and (b) TRIANGLE[16], which computes the necessary parameters and punches all of the generalized geometry KENO-II input cards necessary to describe a touching triangular array of two-region cylinders.

II. WASTE MANAGEMENT

1. OPERATING EXPERIENCE IN THE IDAHO WASTE CALCINING FACILITY

(G. E. Lohse, J. A. Wielang, M. P. Hales)

At the Idaho Chemical Processing Plant, radioactive aqueous wastes resulting from the reprocessing of spent nuclear fuel elements are converted to granular solids in the Waste Calcining Facility (WCF). The WCF uses a fluidized-bed calciner and a sophisticated off-gas system for producing a dry granular solid and for preventing environmental pollution. Since 1963, in four separate campaigns of varying lengths (Table IV), over 1.4 million gallons of aluminum nitrate waste and 0.6 million gallons of zirconium-fluoride waste have been converted to about 30,000 cubic feet of solids. These granular solids are stored in underground stainless steel bins contained in buried concrete vaults. The fourth WCF processing campaign was completed in FY 1971.

TABLE IV

HISTORICAL PRODUCTION SUMMARY OF WCF

<u>Campaign</u>	<u>Period</u>	<u>Waste Processed Gals</u>	<u>Solids Produced Ft³[a]</u>
H-1	12-8-63 to 10-15-64	511,000	7,500
H-2	4-1-66 to 3-24-67	989,000	12,800
H-3	8-14-68 to 6-4-69	329,000	5,150
H-4	8-3-70 to 1-3-71	<u>224,690</u>	<u>4,150</u>
	Totals	2,053,690	29,600

[a] Includes nonradioactive solids from "cold" run operation.

1.1 Brief Description of the WCF with Heat Supplied by In-Bed Combustion

In the WCF, corrosive aqueous radioactive waste is calcined to noncorrosive solids in a four-foot-diameter fluidized bed. Solutions are injected through pneumatic atomizing nozzles into the heated bed of granular solids which are fluidized with preheated air. The sprayed feed deposits layerwise on bed particles and decomposes to solids and gaseous products. Part of the solid bed particles are removed continuously and transported pneumatically to stainless steel bins contained within buried concrete vaults; the off-gases are decontaminated in a series of devices including wet scrubbers, silica-gel adsorbers, and high-efficiency filters before discharge to the environment.

Heat required for calcination is now supplied by an in-bed combustion system in which fuel oil and oxygen are injected directly into the hot (360°C) fluidized bed.

Combustion of the fuel within the fluidized bed releases the heat precisely where it is needed -- in direct contact with the moving bed particles. The absence of direct flame contact with metal walls of the vessel in an in-bed combustion system and the resulting low vessel wall temperature minimizes problems of thermal stress and corrosion.

1.2 The Fourth WCF Processing Campaign

The fourth WCF processing campaign was begun in August 1970 after an approximate two-month period required for "cold" checkout and improvement of the new in-bed combustion system[1]. During the two-month period, standard external atomizing nozzles for fuel atomization were demonstrated to be inadequate because of incomplete fuel combustion and were replaced with wide-angle internal-mix fuel nozzles which provide satisfactory combustion (Section 2.1).

The production summary for the campaign is shown in Table V. About 217,600 gallons of zirconium-fluoride waste and 7,100 gallons of aluminum nitrate waste were converted to about 3370 cubic feet of solids in 3,713 hours of operation. The on-stream time was 100%. The gross feed rate to the calciner averaged 107.8 gph, while the net feed, including jet dilution from transfer to the WCF, averaged 67.0 gph. The gross feed rate included 19.6 gph of calcium nitrate added for complexing the fluoride and 21.2 gph of recycled scrubbing solution. The latter solution included about 5.8 gph of 13 M HNO_3 which was required to dissolve solids scrubbed from the calciner off-gas.

Off-gas decontamination for particulate solids was greater than 10^7 (about the same as previous campaigns), while that for ruthenium was near 10^6 (about 10-times previous values). The performances of the various off-gas system components are presented in Table VI.

The considerable removal of ruthenium by the filters indicates that a large amount of this isotope was in the particulate form; in previous runs, the ruthenium downstream of the scrubbing system was mostly volatile and was removed by the adsorbers, with negligible removal by the filters. The probable reason for ruthenium being in particulate rather than volatile form is that the calciner was operated at 500°C instead of 400°C ; volatility of ruthenium is reported to be lower at 500°C [17]. The release rates for cesium and ruthenium were less than 0.1 mCi/day and the concentrations in the ICPP stack were well below AECM-0524 values for uncontrolled area release.

During the campaign the silica-gel adsorbers were bypassed for one week in order to determine the contribution of the silica-gel to ruthenium and cesium removal and to release rate and species of nitrogen oxides. This test indicated that the ruthenium DF decreased by a factor of five, whereas the cesium DF remained about the same. Thus, part of the ruthenium apparently was volatile and was normally removed by the silica-gel; the cesium remained in particulate form and was removed by the filters. The nitrogen oxides essentially were unchanged and their concentration in the ICPP stack was about 225 parts per million parts of air.

1.3 Inspection after Completion of Campaign

Following decontamination, the fuel and feed nozzles and numerous valves were removed for inspection; other components were inspected in place. Observations were as follows:

1.31 Fuel Nozzles. The caps of the fuel nozzles were damaged severely, whereas the internal "liquid nozzles" were undamaged. The caps, which were fabricated from Armco

TABLE V

WCF PRODUCTION SUMMARY, RUN H-4

<u>I. Liquid Waste Origin</u>		<u>Volume, Gals</u>	<u>Type</u>
A. WM-183		7,070	Al
B. WM-187		210,645	Zr
C. WM-189		<u>6,975</u>	Zr
Total		224,690	
 <u>II. Time Distribution</u>			
A. Date WCF "Hot" Processing Began -- August 3, 1970			
B. Date WCF "Hot" Processing Terminated -- January 5, 1971			
C. Total Hours Processing Time -- 3,713			
D. Total Hours Off-Stream Time -- 0			
E. On-Stream Efficiency -- 100%			
 <u>III. Chemical Usage</u>			
	<u>Total</u>	<u>Usage Per Gal</u>	<u>Raw Waste</u>
A. Gaseous Oxygen	20,000,000 ft ³	89.0 ft ³ /gal	
B. Calcium Nitrate	440,000 lbs	1.96 lbs/gal	
C. Kerosene	80,000 gals	0.36 gal/gal	
D. Nitric Acid (13M)	21,400 gals	0.095 gal/gal	
 <u>IV. Feed Data</u>			
		<u>Total Gal</u>	<u>GPH</u>
A. Liquid Waste to WCF (WM-183, WM-187, WM-189)		224,690	60.5
B. Volume Waste Measured in Blend Tanks		248,760	67.0
C. Jet Dilution (B-A)		24,070	6.5
D. Calcium Nitrate Solution to Blend Tanks		72,763	19.6
E. Recycle to Blend Tanks		78,844 ^[a]	21.2
F. Gross Liquid Calcined (B+D+E)		400,376	107.8
 <u>V. Solids Storage</u>			
A. Volume solids produced (est.) -- 4,150 ft ³ (includes 780 ft ³ from cold startup)			
B. Total volume solids in WC-136 (est.) -- 22,100 ft ³			
C. Total volume solids in WC-115 and WC-136 (est.) -- 29,600 ft ³			
D. Volume reduction factor (H-4 Run) hot operations -- 8.9			

[a] Includes 21,400 gallons 13 M HNO₃

TABLE VI
PERFORMANCE OF WCF OFF-GAS COMPONENTS

<u>Radionuclide</u>	<u>Decontamination Factor</u>			
	<u>Scrubbing System</u>	<u>Adsorbers</u>	<u>Filters</u>	<u>Overall</u>
Cesium-137	2760	8	630	1.4×10^7
Ruthenium-106	80	12	850	8×10^5

17-4PH steel hardened to H-900 condition, had been in service for 3,713 hours. Metallurgical examination showed that the cylindrical portions of the caps were free of metallic deterioration, but that the spherical faces of the caps were carburized, with accompanying intergranular oxidation and detachment of grains (metal dusting). The examination suggests that the temperature on the faces reached at least the carburizing range (750 to 1000°C) and possibly reached the melting temperature (2500°C). (A similar deterioration of a pilot-plant nozzle showed dendritic structure in the face; this is prominent in "castings" but is not found in forgings.)

These observations strongly suggest that the use of stainless steel alloys in this type of atomizing cap is unsatisfactory. A different nozzle design and/or perhaps the use of refractory metal, such as tungsten, will be investigated for this service.

1.32 Feed Nozzles. The feed nozzle caps (Type 17-4PH steel) and the tips of the "liquid" nozzle bodies sustained moderate abrasive damage, similar to the damage observed after the second and third processing campaigns. In contrast, the caps (Type 440-C steel) after the first campaign showed little abrasive damage, but some corrosion by the decontamination solution was evident. This information suggests that harder materials and possibly other cap designs be tested in order to develop more durable atomizing equipment for the feed system.

1.33 Feed Valves. The three feed control valves were removed -- one was completely disassembled -- for inspection. The plugs and seats of all valves were in excellent condition and the valve bellows of the disassembled valve showed essentially no corrosion. The materials of construction of the seats and plugs for these valves were Type 347 stainless steel and Armco 17-4PH (H-1075), respectively; the bellows was a welded leaf design, fabricated from 0.016-inch Type 347 steel sheet. Two of these valves have been in processing service for over 33,500 hours without failure.

1.34 Adsorber Valves and Piping. During operation many problems were encountered in washing the silica-gel adsorbers because of deteriorated plugs and seats on the adsorber isolation valves. Following shutdown and decontamination, all valves in critical locations in the adsorber service were removed and inspected and are being rebuilt. The Stellite facings on the plugs and seats of block valves on lines from the adsorber bottoms were completely corroded away. Valves in gaseous service from lines at the tops of the adsorbers were slightly corroded. The plugs and seats are to be resurfaced with Type ER-308L welding rod, then machined to tolerances. New bellows for these bellows-sealed valves are to be installed.

1.35 Scrubbing System. A visual inspection of the spray nozzles at the top of the quench tower and a TV scan of bottom welds indicate very minor, if any, corrosion during

the fourth processing campaign. Inspection of a block valve in the scrubbing solution line to the quench tower showed negligible corrosion to this valve.

1.4 Performance of Types 316, 304L, and 318 Stainless Steel Piping Used in the Former WCF NaK Heat-Exchange System (T. L. Hoffman)

Service test examinations were conducted on several fittings and on portions of the WCF piping that had been exposed for varying time periods in circulating hot nonisothermal NaK in the former WCF heating system. Results of the examination[18] are reported here, even though the heating system for the WCF has been changed, since the prolonged service in handling liquid metals at elevated temperature is unique.

1.41 *Type 316 Stainless Steel.* Service test examinations were conducted on three pieces of three-inch, Schedule 40, Type 316 stainless steel piping -- all of which had been in service conducting hot NaK from the heater to the calciner in the ICPP Waste Calcining Facility (WCF). One piece of pipe was in service during the first 16,300 hours of operation with 1,120 hours below 600°C and 15,180 hours above 600°C and with 37 starts from room temperature. This pipe was replaced by another which was in service during the last 16,300 hours of operation with 300 hours below 600°C, 16,000 hours above 600°C, and with 15 starts from room temperature. The third piece of pipe was in use during the entire period of NaK loop service, ie, for approximately 32,600 hours as enumerated above.

The principal effect shown on the Type 316 piping was carbon depletion at the NaK-pipe wall interface. The presence of sigma phase formation, as evidenced by metallographic examination and accompanying embrittlement, was indicative of a fundamental change in the microstructure of the alloy due to exposure at elevated temperatures. General corrosion damage was nil on all specimens.

The results suggest that sigma phase transformation in Type 316 stainless steel (when in NaK service at 700°C) increases with increasing service time; at the same time, the observed hardness values appeared to be quite constant through the 32,600 hours total exposure time. The impact strength of the alloy appears to decline to a minimum level within something less than 16,000 hours service and remains at that level for an indefinite time period. Although the general corrosion loss of Type 316 piping was nil, almost complete carbon depletion occurred at the NaK-piping interface.

The observed tensile and yield strengths of the specimens exposed for the two different time periods compared favorably with the published values of unexposed Type 316 stainless steel at 500°C: 73,000 and 46,000, respectively. When tested at 500°C in air, the elongation was 11% on pipe sections that were exposed to NaK during both periods, 75% lower than the average published percentage (43%) for the unexposed alloy. Izod impact tests showed that specimens of the pipe which had been in high temperature NaK service absorbed 66% less kinetic energy in breaking than similarly tested specimens from unexposed piping. A flattening test, "ASTM A 376 Seamless Austenitic Steel Pipe for High Temperature Central Station Service", showed that exposed pipe remained ductile. However, a pipe section that was exposed in NaK service at 700°C for 16,300 hours broke when flattening continued until the opposite walls of the pipe met.

Post-test microhardness surveys of the Type 316 pipe sections from the NaK loop had measured averaged diamond pyramid hardness (DPH) values of 158 and measured averaged Rockwell superficial 15-T scale (1/16-inch ball) values of 89 which correspond to Rockwell B - scale of 86.

1.42 *Type 304L Stainless Steel.* An examination was conducted on a 3 x 3 x 3 inch, Schedule 80, Type 304L stainless steel tee fitting which permitted the liquid metal to circulate through the loop and flow into the NaK expansion tank. The tee fitting was in service during the last 15,567 hours of the NaK loop operation of which 261 hours were below 600°C and 15,307 hours were above 600°C with 13 starts from room temperature.

Evaluation of this Type 304L stainless steel specimen showed carbon depletion at the NaK-metal interface; there were significant amounts of carbide precipitation at the grain boundaries and only trace quantities of sigma phase formation in the cross section of the tee. These observations are suggestive of only minor changes in micro-structure of the alloy due to exposure at 700°C over 15,600 hours of service.

The post-service examination indicated that the general corrosion damage on the tee was nil. The concentration of sigma phase was estimated at less than 1% while carbide phases were present in concentrations of about 2%. The band of decarburization found on the NaK side of the wall of the tee appeared to be about 1 mil thick.

The results of mechanical tests, at 760°C in air, for tensile and yield strengths as well as elongation percentage of specimens from the pipe tee (23,000 psi, 17,000 psi, and 43%, respectively) compared favorably with published values of the unexposed alloy. Izod impact tests showed that specimens were ductile and not brittle. Sections of the Type 304L stainless steel tee had averaged diamond pyramid hardness (DPH) values of 195 which corresponds to Rockwell B-scale of 90.

1.43 *Type 318 Stainless Steel.* The 0.5-inch thick, lower, semi-elliptical, Type 318 stainless steel head on the NaK expansion tank was examined after 32,600 hours of NaK loop operation of which 1,410 hours were below 600°C and 31,190 hours were above 600°C with 52 starts from room temperature.

The most significant observed effect from the evaluation of the Type 318 stainless steel was almost complete absence of carbon depletion at the NaK-metal interface. Sigma phase formation, which was identified in cross sections of the columbium-molybdenum austenitic stainless steel alloy, and accompanying embrittlement are indicative of fundamental change in the microstructure of the alloy due to exposure at elevated temperatures. General corrosion damage was undetectable on the steel after 32,600 hours of service.

Mechanical tests at 500°C in air showed that the tensile and yield strengths of the Type 318 stainless steel specimens (99,000 psi and 70,000 psi, respectively) were about 30% higher than published values for the unexposed alloy. The observed elongation percentage of the exposed sections was 5%, 88% lower than the average published percentages for unexposed alloy. The Izod impact test with a subsized specimen gave a relatively low result of 1.2 foot-pounds, indicating brittleness.

1.44 *Conclusions.* The results of this work suggest that Types 304L, 316, and 318 stainless steel alloys are suitable for materials of construction for nonisothermal loops containing NaK at 600 to 700°C. Because there appears to be a relationship between the failure of pipe fittings and applied stress on the components, applied stress should be minimized in the design of any future loops.

The presence of sigma phase in Type 316 or 318 stainless steel, which increases in concentration with increasing exposure time at temperatures above 600°C, does not appear

to affect greatly the servicability of the steel as long as the sigma particles are small and dispersed. Owing to significantly greater yield and ultimate tensile strengths after 32,600 hours of exposure, Types 316 and 318 stainless steels are favored for construction materials for NaK loop service. It should be noted, however, that embrittlement, which is usually associated with sigma phase formation, may cause failures in areas of high external stress. When sigma phase inhibition is desirable, the use of fully austenitic low-carbon stainless steels is suggested; Type 304L is useful because it was shown to have retained its impact strength and the lowest sigma phase concentration after 15,600 hours in NaK service. To inhibit decarburization with associated corrosion losses in NaK service, Type 318 (Mo,Cb) stainless steel is suggested because the alloy resists precipitation of carbides in the grain boundaries.

2. SUPPORT STUDIES FOR CURRENT WCF OPERATIONS

2.1 Pilot-Plant Studies on In-Bed Combustion Nozzles

(T. K. Thompson, L. L. Taylor, W. B. Kerr)

A series of runs was completed in a pilot-plant calciner to characterize and solve the problems of incomplete fuel combustion encountered during the WCF startup operation. In a comparison of combustion efficiencies of kerosene with API No. 2 fuel oil, atomized with oxygen through standard external-mix nozzles, there was no significant different in operation between the two fuels; with the external-mix nozzles, the amounts of particulate carbon and unburned hydrocarbons were approximately those encountered in the WCF. These results emphasized and confirmed the inadequacy of the standard external-mix atomizing nozzles.

A spray nozzle test setup in which water was atomized with air showed that the standard external-mix nozzles produced a "wet" spray; in contrast, internal-mix atomizing nozzles and a modified external-mix nozzle produced a "dry" spray. A "dry" spray is indicative of a very fine droplet size which is mandatory for good combustion efficiency. Subsequent pilot-plant calciner runs confirmed the visual results from the spray nozzle tests: combustion efficiencies increased from about 80% with the external-mix nozzle to about 98% with either a wide-angle internal-mix nozzle (Spray Systems Company designation) or a modified external-mix nozzle. Combustion efficiency was better at 500°C than at 450°C, and was better at an oxygen/fuel volume ratio of 1800 than at 1400. Also, the wide-angle internal-mix nozzle distributed the expended kinetic energy over a greater volume of bed and should have produced less attrition. The modified external-mix nozzle appeared to be prone to abrasive attack.

Based on the above observations, it was recommended that wide-angle internal-mix nozzles be installed in the WCF and that calcination be carried out at 500°C using kerosene as fuel.

2.2 Cleaning of WCF, Silica Gel, Off-Gas Adsorbers

(B. J. Newby)

Measurable quantities of hydrocarbons and carbon accumulated in the silica gel adsorbers of the WCF under adverse operating conditions during initial startup of the WCF using the in-bed combustion heating system. Laboratory tests were initiated to evaluate

methods of cleaning the silica gel. For this work, several samples of silica gel were exposed to the actual WCF off-gas upstream of the adsorber; some samples were black with carbon. When filter paper was used ahead of the sampler to trap the carbon, the white silica gel slowly turned yellow and then orange from adsorbed hydrocarbons.

Passing preheated air through the silica gel samples at 100, 160, and 316°C had little effect on cleaning the contaminated samples. Washing with water or 1 M nitric acid at 60°C removed part of the carbon and hydrocarbons, but left a greasy coating on the silica gel particles. Sodium hydroxide (1 M) removed the contaminants readily but dissolved the silica gel, particularly if warmed. Passing steam (at roughly atmospheric pressure) for about five hours through silica gel at 106°C removed all of the carbon and practically all of the hydrocarbons while decrepitating the silica gel only slightly. A commercial decontamination agent, Turco 4324, removed all the carbon and much of the hydrocarbons without visibly damaging the silica gel. A solution containing 0.2 vol% Turco 4324 was used to clean the WCF silica gel adsorbers.

2.3 Use of Solid Calcium Nitrate in the Calcination of Zirconium Fluoride Waste (B. J. Newby)

Calcium nitrate, as a saturated solution, is added to first-cycle zirconium fuel processing waste to suppress fluoride volatility during calcination of the waste in the WCF. A volume reduction of 17.5% would result from adding calcium nitrate in a dry form rather than as the saturated solution presently used, thus increasing the processing rate of the WCF. Laboratory experiments showed that calcium nitrate added as a solid to simulated first-cycle zirconium fluoride waste could be dissolved satisfactorily at 24°C by sparging with air. A finely divided precipitate, formed when solid calcium nitrate was dissolved in the waste solution, was determined to be $\text{CaZrF}_6 \cdot 2\text{H}_2\text{O}$ or $2.5\text{H}_2\text{O}$, a compound which also forms in "plant" waste when calcium nitrate is added as an aqueous solution. The density of the resulting slurry is 1.297 g/ml. Based on these results, solid calcium nitrate can be substituted for a saturated solution of calcium nitrate in the WCF feed tanks.

2.4 Gold-Nickel Alloy Seal Bellows for WCF Valves (T. L. Hoffman)

Seventy-five-percent gold, twenty-five-percent nickel alloy has been shown to have excellent corrosion resistance to the mixed hydrofluoric-nitric acid solutions of the WCF scrub solutions[1]. However, before this alloy could be used to form seal bellows for valves in WCF service, tensile, yield, and elongation properties of the alloy at elevated temperatures were determined because the alloy was insufficiently ductile for forming at room temperature. Room temperature tensile tests showed that it had about 2% elongation (the measure of ductility) with ultimate and yield strengths of 175,000 and 87,500 psi, respectively. Welds prepared by electron beam had an ultimate strength of 107,000 psi.

High temperature tensile tests at 400 and 600°C showed that the ductility of the alloy increased with increasing temperatures. At 510°C the elongation of the gold - nickel alloy was about 13%. Using precision dies at that high temperature, flat discs of the alloy were formed into convolution segments which were then circumferentially welded together by electron beam techniques to fabricate a test bellows assembly. Intentions are to flex this bellows to failure; providing its performance is satisfactory, a full size bellows will be installed in the WCF.

3. PROPERTIES OF SOLID CALCINE PRODUCT

3.1 Solubility of Gamma Alumina (B. J. Newby)

Significant quantities of crystalline gamma alumina have been produced in pilot-plant experiments using an in-bed combustion heating system to calcine aluminum nitrate-nitric acid waste solutions. The solubility of this material is of interest since it is important that fines caught in the WCF off-gas train be dissolved in the scrubbing solution to facilitate recycle to the calciner.

Calcine containing gamma alumina was digested at boiling temperature in 2 M nitric acid (approximate composition of WCF scrubbing solution) for three days to determine if the gamma alumina would dissolve. X-ray diffraction analysis of the residue revealed that gamma alumina is resistant to dissolution in this scrubbing solution. Therefore, the formation of gamma alumina in the WCF should be minimized.

3.2 Characteristics of Zirconia Calcine (M. W. Wilding)

Zirconia calcine resulting from calcination of aqueous radioactive waste containing primarily fluoride, nitrate, zirconium, calcium, and aluminum was studied to determine chemical and physical changes that occur during heating in the range of 800 to 1350°C, and the effect of such heating on the leachability of the chemical and radiochemical constituents. The calcine remained granular and free flowing on heating up to 700°C; at 800°C or above, a sintered mass was produced. Both fluoride and cesium volatilized above 800°C, with the amount volatilized increasing significantly above 1000°C. The principal crystalline species in the calcine, after heating, were zirconia (tetragonal and monoclinic) and calcium fluoride. The most pronounced effect on the leachability of the product was significant reduction in the leachability of strontium. Details of this study are reported in IN-1486[19].

3.3 Corrosive Effects of Zirconia Calcine in Storage (C. A. Zimmerman)

No significant corrosion of metal coupons has been observed after four years storage in nonradioactive zirconia calcine at elevated temperatures. Welded two-inch square corrosion test specimens of carbon steel, aluminum alloy 6061-T6, and Types 304, 304L, 316 ELC, 347, and 405 stainless steel continue in most cases to show weight gains after four years of exposure -- two years at 200°C and two years at 300°C. The weight gain is presumably due to the formation of an oxide film which is thin and tightly adhering. The results to date indicate that the existing Type 304 stainless steel tanks are suitable for storage of this calcine. The details of this test and the test conditions have been described previously[20].

3.4 Installation of Test Coupons Into the Third Calcine Storage Bins (T. L. Hoffman)

Design criteria for the third set of calcine storage bins currently being erected provide for a special-purpose bin for storing granular solids with high heat generation rates. The special-purpose bin and six other Type 304 stainless steel bins are designed for 500 years of useful life. Accordingly, long-term integrity is reflected in the specifications for construction of these bins.

As a measure of the useful life of the special-purpose bin, WC 140-1, a continuing corrosion surveillance program is required. Welded cylinders and plates are hung on five separate Type 304 stainless steel cables in the bin (Figure 14). Welded coupons from mill certified Types 405, 304, and 304L stainless steels, and AISI-SAE Type 1025 carbon-steel have been used. It is proposed to withdraw a cable at the end of the 5th, 10th, 20th, 40th, and 80th year of service for detailed corrosion evaluation of these coupons. Thus, a measure of the remaining useful life of the bin will be provided as well as insight into the performance of alternate materials of construction.

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Fig. 14 Corrosion coupon arrangement for third calcine storage bins.

4. SUPPORTING STUDIES FOR PLANNED WASTE CALCINATION PROCESSES

4.1 Decomposition of Sodium Nitrate as Related to the Calcination of High Sodium and Potassium Nitrate Containing Wastes (B. J. Newby)

Sodium and potassium nitrates pose special problems in fluidized-bed calcination; the large temperature range in which the nitrates exist in the molten undecomposed state makes the fluidized bed prone to agglomeration. Laboratory studies, using differential thermal analysis (DTA) -- X-ray diffraction techniques, are being made to obtain basic data on the calcination chemistry of wastes containing high concentrations of sodium and/or potassium nitrates and to examine possible additives which might lower the decomposition temperature of the two nitrates or convert them to a form more suitable for calcining. Three different types of wastes have been examined: (a) ICPP second-cycle waste which contains

sodium nitrate arising from the use of sodium carbonate to remove residual uranium from the organic stream in the extraction process; (b) Savannah River Plant waste containing sodium nitrate created by neutralizing the acid waste with sodium hydroxide before storage in carbon steel tanks; and (c) Rocky Flats waste blends which may contain potassium nitrate or potassium and sodium nitrates if the blends contain one or more of their Caustic, Americium Chloride, and/or Molten Salt Chloride wastes.

4.11 The Differential Thermal Analysis Technique. In the differential thermal analysis (DTA) as used in this report, the measured variable is the temperature difference between the sample and a contiguous reference (high-fired Al_2O_3) as they are being heated. The abscissas of the DTA curves (Figures 15, 16, and 17) represent the temperature to which the sample is being heated (T) and the ordinates the temperature differences between the sample and reference material (ΔT). A trough in a DTA curve represents an endothermic reaction; a hill in the curve corresponds to an exothermic reaction.

ANC A 589

Fig. 15 Thermogram of sodium nitrate.

ANC A 590

Fig. 16 Thermogram of sodium nitrate (10 g) mixed with sugar (3.1 g) in aqueous solution and dried at 105°C.

Fig. 17 Thermogram of sodium nitrate (1.25 g) mixed with high-fired α -alumina (0.985 g).

Wastes of interest were dried at 105°C or less, following which a DTA curve was made on the dried material; an air sparge stream of 0.7 SCFH was used to dissipate decomposition gases during the DTA. Following this, several grams of the material were heated in a muffle furnace to each of the various temperatures at which DTA curves indicated changes in the material. Separate samples of the material heated to each of the temperatures of interest were examined by X-ray diffraction; the available literature and X-ray information were used to help interpret the curves. Explanations for many of the phenomena indicated by the DTA curves could not be verified by the literature or by X-ray and are the investigator's own interpretations.

4.12 Sodium Nitrate Thermograms. The Chemistry during pyrolysis of pure sodium nitrate and mixtures of sodium nitrate with compounds of interest must be understood if the decomposition chemistry during calcination of wastes containing these chemicals is to be understood. Thus, DTA curves were made of sodium nitrate and of sodium nitrate mixed with compounds that might lower the decomposition temperature. The thermogram of sodium nitrate (Figure 15), indicates that sodium nitrate melts at 305°C and may not be completely decomposed until heated to about 833°C; between 305 and 833°C, the molten sodium nitrate can cause the calcination bed to agglomerate. No residue has ever been found in a DTA sample cup after having heated sodium nitrate to 1000°C; X-ray diffraction has identified only sodium nitrite as a decomposition product during the pyrolysis of sodium nitrate, and only sodium nitrate during the pyrolysis of sodium nitrite. Thus, what happens during the decomposition of sodium nitrate, except for the reversible reaction $2 \text{NaNO}_3 \rightleftharpoons 2 \text{NaNO}_2 + \text{O}_2$, is not clear; the sodium nitrate and nitrite may evaporate before being converted to Na_2O , or the latter, once formed, might sublime.

Sodium nitrate is decomposed by reducing reagents but such reagents, with the exception of poor reducing reagents such as sugar, would not remain in the oxidizing atmosphere of the calciner long enough to be effective. The thermogram for sodium nitrate mixed with sugar (Figure 16) shows sodium nitrate decomposing between 420 and 773°C which indicates that sugar does lower the decomposition temperature range of sodium nitrate. The decomposition temperature range is lowered even more by mixing sodium nitrate with certain oxides such as Al_2O_3 , SiO_2 , V_2O_5 , TiO_2 , Fe_2O_3 , and MgO . Osipovs and Ievins[21], and Sugiyama and Takahashi[22] suggest that sodium nitrate is decomposed by forming a compound with some of the oxides and that other oxides may act as a catalyst during the decomposition. The thermogram of a mixture of sodium nitrate with one of these oxides (Al_2O_3) shows sodium nitrate decomposing over a temperature range of 396 to 694°C (Figure 17).

4.2 Calcination of ICPP Second-Cycle Wastes

Scoping studies are under way on the in-bed combustion calcination of second-cycle wastes that contain relatively large amounts of sodium nitrate. These wastes mainly arise from the use of sodium carbonate to remove residual uranium from the organic stream in the extraction process. The presence of sodium nitrate in the calcine product causes the fluidized bed to agglomerate at ~25% (wt) nitrate content in the product. The most promising method to decompose the sodium nitrate in the feed is by chemically reacting the nitrate using feed additives, eg, aluminum ion, sulfate ion, and fluoride ion. A typical composition of second-cycle waste is shown in Table VII.

TABLE VII
TYPICAL COMPOSITION OF SECOND-CYCLE WASTE

<u>Component</u>	<u>Molarity</u>
H ⁺	0.10
Al ⁺³	0.87
Na ⁺	2.31
Hg ⁺²	0.001
Fe ⁺²	0.02
NH ₄ ⁺	0.04
SO ₄ ⁻²	0.06
PO ₄ ⁻³	0.03
F ⁻	0.01
NO ₃ ⁻	5.08

4.21 Thermogram Studies of Second-Cycle Waste (B. J. Newby)

The DTA curve for this waste shows that the $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ present melts and decomposes to the oxide below 165°C; the NaNO_3 melts at 305°C and reacts with aluminum oxide to form the aluminate between 640 and 875°C. The second-cycle waste has been blended with ICPP first-cycle zirconium waste in pilot-plant experiments (Section 4.22) to convert the sodium nitrate to a form more suitable for calcining. The thermogram of this blend shows that the sodium nitrate is converted to Na_3AlF_6 between 446 and 767°C.

4.22 Pilot-Plant Calcination of Second-Cycle Wastes (T. K. Thompson, L. L. Taylor)

Aluminum ion can conveniently be obtained by blending ICPP first-cycle aluminum waste with the second-cycle waste; the desired calcine product is NaAlO_2 . In short-term scoping studies, a blend with a Na/Al mole ratio of ~1 has been successfully calcined; however, NaNO_3 has been identified in product formed at 550°C.

Sulfuric acid is an inexpensive source of sulfate ion and produces a $\text{Na}_3\text{Al}(\text{SO}_4)_3$ product with a Na/SO_4 mole ratio of ~ 1 in the blended feed. Acid costs will be $\sim 3¢/\text{gal}$ of second-cycle waste.

Existing ICPP first cycle zirconium fluoride waste is the source of fluoride ion for blending with second-cycle waste. With a F/Na mole ratio of ~ 1.8 , the calcine products are ZrO_2 and Na_3AlF_6 (cryolite). The majority of experimental work has pertained to this flowsheet because of the economic incentive associated with eliminating the $\text{Ca}(\text{NO}_3)_2$ that is currently added to the zirconium waste to complex the fluoride ion during calcination. The cryolite flowsheet has been run in both four-inch and twelve-inch diameter pilot-plant calciners for continuous operating periods of up to five days. Operation was generally successful with the exception of excessive corrosion in the secondary cyclones. A schematic of the pilot-plant calciner is shown in Figure 18.

Fig. 18 Schematic drawing of typical pilot-plant for waste calcination.

The observed corrosion was localized in the secondary cyclones of both the four- and twelve-inch pilot-plant calciners. A corrosion evaluation of the solution remaining in the scrub tank, after the five-day run in the twelve-inch calciner, projected a corrosion rate of 1.4 mils/mo at 100°C . A suggested corrosion mechanism postulates that the Na_3AlF_6 in the fines preferentially dissolves before the ZrO_2 and Al_2O_3 , resulting in an excess of uncomplexed fluoride downstream of the venturi scrubber. The ZrO_2 and Al_2O_3 dissolve later, resulting in a final scrubbing solution that is relatively incorrosive. This hypothesis remains to be tested.

4.3 Calcination of Neutralized Purex Waste

A modest program was begun for developing a fluidized-bed calcination process for solidifying neutralized Purex waste. This waste is a basic, high-sodium waste typical of the NaOH neutralized acidic wastes stored at Savannah River in carbon steel tanks. The

composition of this waste, shown in Table VIII, is mainly NaNO_3 with $\text{Fe}(\text{OH})_3$ and MnO_2 precipitates. Various sodium compounds that are possible candidates for a suitable calcined product are shown in Table IX. A desirable calcine product has a high melting point and volume reduction factor and a low relative feed volume. High solubilities are beneficial if a wet off-gas cleanup system is used but may be detrimental for long-term storage of the calcined product. The main problem in calcining this waste is the high sodium nitrate content; sodium nitrate exists in the molten undecomposed state from ~ 307 to $\sim 750^\circ\text{C}$ and tends to cause the bed to agglomerate.

TABLE VIII

COMPOSITION OF NEUTRALIZED PUREX WASTE

<u>Constituent</u>	<u>Molarity</u>
NaNO_3	4.0
NaOH	0.3
$\text{Fe}(\text{OH})_3$	0.2
Na_2SO_4	0.2
NaAlO_2	0.6
Na_2CO_3	0.3
MnO_2	0.2
NaF	0.02
$\text{Hg}(\text{NO}_3)_2$	0.001
Na_3PO_4	0.01
NaCl	0.01
NaI	0.001
$\text{Mg}(\text{OH})_2$	0.01
$\text{Ca}(\text{OH})_2$	0.003

TABLE IX
CANDIDATE SODIUM CALCINE PRODUCTS

Compound	Molecular Weight	Absolute Density (g/cc)	Melting Point (°C)	Solubility ^[a] Hot Water (g/100cc)	Theoretical ^[b] Volume Reduction Factor	Relative Feed ^[c] Volume	Additives Required
NaAlO ₂	81.97	2.6 ^[d]	1800	vs	16.9	3.24	Al(NO ₃) ₃ -2.24% of 2.2M
Na ₃ AlF ₆	209.94	2.90	1000	sl s	12.7	1.97	Al(NO ₃) ₃ -0.747% of 2.2M HF 0.224% of 70%
NaF	41.99	2.558	988	~5	9.5	1.12	HF-0.12% of 70%
Na ₂ SiO ₃	122.06	2.40	1088	s, d	6.2	1.056	SiO ₂ - 0.056%
Na ₄ SiO ₄	184.02	2.4 ^[d]	1018	s	7.6	1.028	SiO ₂ - 0.028%
Na ₂ SO ₄	142.04	2.698	884	42	6.9	1.16	H ₂ SO ₄ -0.16% of 97%
NaNO ₃	84.99	2.261	307	180	4.5	1.00	None
Na ₂ O	61.98	2.27	1275 ^[a] (sub)	d	9.6	1.00	None

[a] Abbreviations used:

s - Soluble
v - very
sl - slightly
d - decomposes
sub - sublimes

[b] Theoretical volume reduction factors are based on absolute densities and are defined as the ratio of the volume of neutralized Purex waste plus any additive, if required, to the volume of solids produced.

[c] The basis for the relative feed volume is one of neutralized Purex waste; the relative feed volume equals one, if no additives are required. The amount of additive is based on converting the sodium in the NaNO₃, Na₂CO₃, Na₃PO₄, and NaOH seed constituents to the desired product, assuming that the Na₂SO₄, NaAlO₂, NaF, NaCl, and NaI would remain unchanged during calcination because their melting points are greater than the calcination temperature.

[d] Estimated.

4.31 Thermogram Studies of Savannah River Waste (Neutralized Purex) (B. J. Newby)

The thermogram of Savannah River waste is essentially that of the pyrolysis of sodium nitrate. The maximum temperature in the decomposition temperature range (497 to 768°C) is lower than that of pure sodium nitrate indicating that the decomposition is probably influenced by the presence of MnO₂, Fe₂O₃, and other oxides present in smaller amounts.

Thermograms were made of Savannah River waste mixed with additives that might lower the decomposition temperature of the sodium nitrate even further, either by acting as a catalyst or by forming a stable compound with the sodium nitrate. The additives were: 80 to 120 mesh silica, sand, high-fired α -alumina, 2.1 M aluminum nitrate solution, ammonium sulfate, and sulfuric acid. The thermograms for the waste mixed with sand and with 80 to 120 mesh silica were similar; most of the sodium nitrate is converted to Na₂SiO₃, possibly mixed with Na₂Si₃O₇, between 441 and 750°C. In the presence of α -alumina, much of the sodium nitrate decomposed between 451 and 721°C; a sodium aluminate is formed at higher temperatures. By adding aluminum nitrate, most of the sodium nitrate in the waste is converted to a sodium aluminate between 446 and 665°C; however, more than 2 volumes of 2.1 M aluminum nitrate must be added to 1 volume of waste to react with all of the sodium nitrate. When ammonium sulfate is used, some of the sodium nitrate in the waste is converted to a sodium aluminum sulfate between 236 and 335°C; the rest of the sodium nitrate is converted to sodium sulfate between 477 and 660°C. When sulfuric acid is added, the sodium nitrate is converted to a sodium bisulfate; a sodium aluminum sulfate is formed and the bisulfate is changed to the sulfate via the pyrosulfate as the waste mixture is subjected to higher temperatures.

Additives that could be mixed with Savannah River waste as a homogeneous solution would be preferred over those which must be added as a solid or slurry because the Savannah River waste is already a thick slurry and must be diluted before it can be sprayed into a calciner. Thus, aluminum nitrate, ammonium sulfate, or sulfuric acid would be

preferred over various oxides. The sulfuric acid might be preferred over the other two reagents because it takes only a small volume of concentrated sulfuric acid to react with all the sodium nitrate in a given volume of waste and the small volume of acid makes the waste much more mobile, probably by putting some of the slurry into solution. Results of preliminary calcination tests with sulfuric acid are discussed in the following section (4.32).

4.32 Pilot-Plant Calcination of Purex Waste-Sulfuric Acid Combinations (T. K. Thompson)

Scoping studies have been conducted with straight neutralized Purex waste and with the H_2SO_4 additive in four-inch-diameter fluidized bed calciners shown in Figure 20 in Section 4.42 of this report. Bed temperatures of 775°C were necessary to calcine successfully the straight waste without bed agglomeration or nozzle caking with a standard external-mix waste feed nozzle. However this high temperature may create problems with cesium isotope volatility. Considerable difficulties with nozzle caking were experienced in runs at lower temperatures, including a drying run at $\sim 275^\circ\text{C}$. Nozzle caking was also observed with the H_2SO_4 additive at bed temperatures of 500°C with standard external-mix atomizing nozzles.

Tests with a standard external-mix nozzle indicated that the face of the nozzle was wetted by the liquid atomized. The bed particles would then adhere to the wet face of the nozzle forming a "cake". This "cake" would grow outward from the face of the nozzle and would either stop the atomized waste feed flow or break off from the nozzle face and a new "cake" would start forming. In the latter case, these "cakes" were approximately one to two inches in diameter and would settle to the bottom of the fluidized bed and create channeling, hence poor fluidization and mixing, in the four-inch-diameter calciner vessel.

Various waste nozzle configurations were investigated to prevent the hot bed particles from contacting the wet nozzle face and/or eliminate the wet nozzle face. The final design is shown in Figure 19. Several scoping runs with this nozzle have been made using the neutralized Purex- H_2SO_4 feed and have demonstrated the complete elimination of nozzle caking at a calcination temperature of 500°C .

Fig. 19 Modified extended-tip waste feed nozzle.

4.4 Calcination of Rocky Flats Waste

4.41 Thermogram Studies of Rocky Flats Wastes (B. J. Newby)

Studies were initiated to determine the feasibility of calcining Rocky Flats wastes. DTA and X-ray diffraction studies were used to obtain thermograms for: (a) ion column effluent waste, (b) a blend of ion column effluent and caustic wastes, and (c) a blend of ion column effluent, caustic, americium chloride, and molten salt chloride wastes. Typical compositions of these wastes streams are listed in Table X.

TABLE X
COMPOSITIONS OF ROCKY FLATS WASTES

Waste Relative Volume	I (Ion Column Effluent) 1.000	II (Caustic) 1.000	III (Americium Chloride) 0.0185	IV (No. 1 Molten Salt) 0.0397	V (No. 2 Molten Salt) 0.2008
Components (Molarity)					
H ⁺	7.101	---	---	---	3.000
Na ⁺	0.018	---	---	3.260	---
Ca ⁺⁺	0.098	---	---	---	---
Mg ⁺⁺	0.123	---	---	0.080	---
K ⁺	0.017	4.660	1.280	1.920	---
Al ⁺³	0.072	---	---	---	---
Fe ⁺³	0.023	---	---	---	---
Pb ⁺⁴	0.022	---	---	---	---
NO ₃ ⁻	7.550	---	---	0.160	1.00
F ⁻	0.340	1.370	---	---	---
Cl ⁻	0.017	1.290	0.280	4.680	---
OH ⁻	---	2.000	1.000	0.500	---
C ₂ O ₄ ⁼	---	---	---	---	1.000

Preliminary results indicated that the nitrates of the ion column effluent waste are converted to oxides or fluorides below 560°C and should calcine without difficulty. The thermograms of the two blends are essentially that of the pyrolysis of potassium nitrate (potassium nitrate melts at 330°C and decomposes between 452 and approximately 1000°C) indicating difficulty in calcining.

4.42 Pilot-Plant Calcination of Rocky Flats Wastes (T. K. Thompson, J. A. Wielang)

Scoping studies have been completed on the fluidized-bed calcining of various wastes from the Rocky Flats operations. The types and compositions of the various wastes investigated are shown in Table X. Tests were conducted in four-inch-diameter pilot-plant units that used either in-bed combustion of kerosene or electrical heaters on the outside wall of the vessel to provide process heat. A schematic of the pilot-plant equipment is shown in Figure 20.

Fig. 20 Schematic drawing of four-inch pilot-plant calciner system.

Ten runs were made with various waste blends mixed in proportion to the relative volume of each waste shown in Table X, and the results are summarized in Table XI. The run that used the acidic blend of wastes (Run 2) was successful; Runs 3 through 9, made with a standard external-mix nozzle, were terminated because of severe nozzle caking which interfered with fluidization. The blend of acidic and basic wastes (Run 1) resulted in severe corrosion to the 300 series stainless steel feed nozzle due to the high chloride concentration in an acidic medium.

After development of an "external-tip" waste feed nozzle (Figure 19, Section 4.32), a blend of basic waste was successfully calcined in Run 10 without any cake formation.

TABLE XI

SUMMARY OF SCOPING STUDIES -- ROCKY FLATS WASTES

Run	Heating Method	Waste Feedstock	Waste Feedrate	Bed Temperature	Fluidizing Velocity	Remarks
1	Electrical Resistance Heaters	Blend of I, II, III, IV, V	0.5 to 1.2 1/hr	460°C	1.8 ft/sec	Excessive corrosion of 300 series stainless steel due to high Cl concentration in an acid medium
2	Electrical Resistance Heaters	Blend of I and V	0.5 to 1.75 1/hr	460°C	1.18 ft/sec	Successful run, no nozzle caking
3	Electrical Resistance Heaters	Neutralized Blend of I, II, III, IV, V[a]	~1.6 1/hr	220°C	1.14 ft/sec	"Caking" on waste feed nozzle
4	Electrical Resistance Heaters	Neutralized Blend of I, II, III, IV, V	~0.55 1/hr	220°C	1.14 ft/sec	"Caking" on waste feed nozzle
5	Electrical Resistance Heaters	Neutralized Blend of I, II, III, IV, V	~1.3 1/hr	550°C	1.18 ft/sec	"Caking" on waste feed nozzle
6	Electrical Resistance Heaters	Blend of II, III, IV	~1.0 1/hr	310°C	1.18 ft/sec	"Caking" on waste feed nozzle
7	Electrical Resistance Heaters	Blend of II, III, IV	~0.5 1/hr	290°C	1.15 ft/sec	"Caking" on waste feed nozzle
8	In-Bed Combustion	Blend of II, III, IV	~0.4 1/hr	550°C	1.08 ft/sec	"Caking" on waste feed nozzle
9	In-Bed Combustion	Blend of II, III, IV	~0.8 1/hr	600°C	1.08 ft/sec	"Caking" on waste feed nozzle
10	Electrical Resistance Heaters	Blend of II, III, IV	~1 1/hr	500°C	1.1 ft/sec	No "caking" with the modified-external tip nozzle.

[a] This was a blend of all wastes (I, II, III, IV, and V) which was neutralized with solid NaOH to a pH of ~9. Dicalite filteraid was added in the amount of 33 wt% of the precipitated solids. About 51% of the liquid was decanted after allowing the precipitate to settle. The precipitate was then suspended in the remaining liquid with agitation. The resulting mixture was the feedback for Runs 3, 4, and 5.

5. OTHER WASTE MANAGEMENT STUDIES

5.1 Decontamination of Evaporator Condensate by Ion Exchange
(D. W. Rhodes, M. W. Wilding)

All of the potentially radioactive waste generated at the ICPP, except the known high-level waste which is processed separately, is routed to an evaporator waste collection tank. This amounts to about 1,200,000 gallons of liquid waste annually and includes waste from laboratory sinks and safety shower drains, cooling water from a uranium product denitrator, process sampler drains, cell floor drains, equipment decontamination, and some wastes from the test reactor areas at the NRTS. From the waste collection tank, the liquid waste is transferred to a thermosyphon-type evaporator; two 5000-gallon condensate hold tanks receive the condensate from this evaporator for sampling and analysis before discharge, or recycling if advisable.

Recently, two ion exchange columns containing Amberlite-200 cation exchange resin have been installed to further decontaminate the condensate before it is released to an injection well. The primary purpose of the new ion exchange system is to reduce the long-lived radio-nuclides, Sr-90 and Cs-137, to as low a level as practicable, with particular emphasis on the removal of Sr-90.

5.11 *Test Results.* During the last processing campaign, a test program was undertaken to evaluate decontamination achieved and the effective life of a resin bed before regeneration was necessary. The results, shown in Figures 21 and 22, indicate good removal of Cs-137 for about 3000 bed volumes. Beyond this point, breakthrough of Cs-137 was evident, with 100% breakthrough occurring at about 5000 bed volumes. Strontium breakthrough began at about 4000 bed volumes, but was still only about 1% at 6000 bed volumes (~270,000 gal). Removal of Ce-144 was essentially complete throughout the test. The effectiveness of the removal is indicated by the C values in Figures 21 and 22. The lower value represents the AEC, Appendix 0524, limit for drinking water in an uncontrolled area, and the upper value represents a similar limit for a controlled area.

Very little Ru-106 or ZrNb-95 were removed by the ion exchange resin. However, because of the relatively short half-lives (<1 year) and low biological toxicity of Ru-106 and ZrNb-95, and their moderate-to-low concentration in evaporator condensate, no additional attempt was made to remove these radionuclides.

5.12 *Conclusions.* The breakthrough data indicate that the need for regeneration will be determined by Cs-137. This is a convenient phenomenon: because Cs-137 is a gamma emitter (while Sr-90 is a beta emitter), Cs-137 can be used readily to determine breakthrough by appropriate instrumentation. In addition, the permissible level for Cs-137 in drinking water is about 70 times greater than Sr-90; thus, a higher breakthrough value for Cs-137 is permissible and, if regeneration is determined by Cs-137 leakage, removal of Sr-90 will be adequate when a cycle is terminated.

5.2 Operating Experience with the ICPP Fuel Storage Basin

Fuels received for reprocessing at ICPP are accumulated in the storage basin until a sufficient amount of compatible fuel has been received to justify a reprocessing campaign. The elements are stored under water either in multi-element poisoned racks or in suspended buckets arranged in a geometrically controlled safe array. Radionuclides accumulate in the basin from elements with ruptured cladding or from scrap^[a]; fission product cesium is removed on mineral exchange beds; other radionuclides may remain soluble or precipitate as part of the sludge on the basin floor. Because the activity of the basin water has been at an all-time high during the last year, a strenuous effort has been made to identify, and contain or remove, any leaking elements or cans. Further, plans are being developed for accelerated cleanup of accumulated sediment and dissolved radionuclide contaminants.

5.21 Chemistry and Decontamination of Fuel Storage Basin Water (D. W. Rhodes, M. W. Wilding)

The fuel storage basin at the ICPP continued to operate with water recycle. The water was filtered to remove particulates, and calcium hypochlorite (10 to 20 lb/year) was added to inhibit the growth of microorganisms. Sufficient sodium nitrate was added to maintain the nitrate level at about 200 mg/l for protection of the aluminum alloy fuel elements against corrosion.

The storage of cans containing scraps and pieces of irradiated fuel elements has resulted in significant contamination of the water by cesium-137 and strontium-90. To

[a] All scrap is canned but some are not of leak-tight design.

ANC-B-594

Fig. 21 Breakthrough curve for Cs-137 in evaporator condensate.

ANC-B-593

Fig. 22 Breakthrough curve for Sr-90 in evaporator condensate.

control this contamination, an Isotope Removal System (IRS), consisting of eight 55-gallon drums of clinoptilolite, had previously processed a bypass stream of basin water at the rate of about 1 gpm. To accelerate the removal of fission products, the IRS was modified to handle about 10 gpm. The resulting high radiation readings on the 55-gallon drums containing the clinoptilolite made replacement of the drums difficult. For this reason, the IRS was further modified so that the clinoptilolite could be regenerated by washing with 2.5 M $(\text{NH}_4)_2\text{SO}_4$; three such regenerations have been accomplished. The highly contaminated regenerant is returned to the ICPP for evaporation, storage, and subsequent calcination.

Near term plans to further decontaminate the water include an additional, interim, ion-exchange unit using a synthetic ion exchange resin in addition to the natural mineral clinoptilolite. The synthetic ion exchanger, which will be used to remove cesium-137, will be shielded by immersing it in the basin water. Long-range plans include a "cleanup" system in a separate building, using an ion exchange system to remove fission products from the water and a vacuum system to remove particulate matter from the floor of the basin.

5.22 Surveillance of Radioactive Materials in the ICPP Fuel Storage Basin (C. A. Zimmerman)

Examination of Individual Elements in the FELT Apparatus -- As part of this effort a periodic fuel element leak test (FELT)[23] of EBR-II fuel pins clad with Type 304L stainless steel has been continued. Tests of three fuel pins after 42 months storage in the ICPP basin continue to indicate no penetration of the fuel pin cladding. Observations of these three fuel pins which are representative of several hundred EBR-II elements in the basin will be continued.

Fuel element leak tests of other localized sources of basin water contamination have been continued. These tests have disclosed one can of EBR-II scrap which was contributing significant contamination to the basin water. This can has been isolated and will be individually processed on a custom basis in the Multicurie Cell late in FY-72.

To prevent further introduction of radionuclides from freshly discharged fuel elements, spot checks were made in a FELT unit of suspect elements from the ATR in which cladding abnormalities such as pimples, pits, and blisters were observed. Tests of ATR fuel elements without defects were made to establish a basis for comparison with fuel elements showing cladding abnormalities. Tests to date do not indicate any appreciable leakage of radioactive material from the abnormal ATR fuel plates.

Large-Scale Screening for Leaking Fuel Elements -- In order to identify areas containing leaking elements, fuel rack elimination tests were undertaken. A steel cap that fits over the top of a storage rack to reduce convection mixing with the bulk of the basin water was used for initial rack elimination tests. Racks containing scrap from the fuel cycle facility at EBR-II and a rack containing Tory-II fuel elements were tested. In addition, the cap was set on the basin floor at various locations, including where a spill occurred early in 1969. None of the areas checked showed increases that could be considered significant above the basin background level. This cap is being superseded by a cap that will totally enclose a rack to isolate it from the rest of the basin. Intermittent sampling will provide leak rates on the total element load in a rack. Specific location of leaking elements can then be done on an individual basis in the fuel element leak test apparatus.

5.23 Preparations for Sludge Removal (R. N. Henry)

During the years the basin has been in operation, dust from the air, from casks, and from fuel assemblies, debris from sawing the nonfissile parts of fuel elements, and corrosion products from fuel elements and basin equipment have been deposited in the water and settled to the floor of the basin. This material, when disturbed, causes a reduction in visibility as well as being a source of radionuclides contaminating the basin.

Samples of the sediment that has collected on the floor of the fuel storage basin were taken at various points to provide information for design criteria on a sediment removal system. Particle size distribution and radiation level of the sediment were of particular interest. The sampling results indicate that the radiation field created by general sediment, during a cleaning operation with a swimming pool type vacuum cleaner, will be tolerable; average fields of 30 mR/hr at a distance of one foot from the vacuum cleaner hose may be expected. However, radiation fields from solids near the fuel element cutting facility in the south basin are expected to produce fields of about 2 R/hr at one foot from the hose.

Particle size distributions such as that shown in Figure 23 were determined by Stokes Law settling velocity experiments. The distribution shown in Figure 23 represents about 45% of the solids in the basin; the other 55% are larger than 50μ in diameter. As can be seen in Figure 23, about 15% of the solids in this distribution are less than 15μ in diameter; this material is sufficient to create visibility problems in the basin should the solids be returned to the basin water by an inadequate filtering system. Design work is currently under way for a CPP-603 basin sludge removal system.

Fig. 23 Particle size distribution in fuel storage basin solids.

5.24 Effects of Dissolved Boron in the ICPP Fuel Storage Basin (C. A. Zimmerman)

The use of a soluble compound of boron in the ICPP storage basin as a nuclear poison would permit the safe storage of an increased number of fuel elements with little change in procedures or added expense. An experiment was initiated to determine the effect of boron in the ICPP basin water and to investigate the corrosion of various metals and alloys currently known to be in contact with basin water.

Corrosion rates of the various materials tested -- carbon steel, aluminum alloys 1100, 6061, and 2219, Zircaloy II, cadmium, and Type 304 stainless steel -- were found to be in an acceptable range. However, boron cannot be recommended for use as a soluble nuclear poison in the ICPP storage basin because a white crystalline material, identified by X-ray diffraction as ulexite ($\text{NaCaB}_5\text{O}_9 \cdot \text{H}_2\text{O}$), formed in sufficient quantities to interfere with water clarity and to limit the concentration of soluble boron to a relatively low value.

5.25 Corrosion of Cadmium Foil from Poisoned Fuel Storage Racks (T. L. Hoffman)

Some racks used for fuel storage in the ICPP basin consist of an array of cylindrical tubes, the tube walls being constructed of cadmium foil sandwiched and sealed within aluminum cladding. Decad segments of such a tube were exposed to ICPP basin water to determine the cadmium corrosion rate if the aluminum cladding should fail. After six months exposure, the top and bottom edges of the 20-mil thick cadmium foil were perforated in several places. The results show a minimum penetration rate of 3.3 mils per month (m/m) and an overall rate of 0.1 m/m. A similar cadmium foil segment exposed for 13 months in the basin water was badly pitted and severely corroded. These observations indicate that, if the cadmium in a poisoned fuel storage tube is exposed in basin water, localized attack on the cadmium can be expected which might alter the fuel-poison geometry.

5.3 ICPP Pollution Control Projects (H. V. Chamberlain)

Title II design has been completed for two improvements at the ICPP that will reduce the possibility of radioactivity release to the environment. These improvements are to be installed on the plant service waste system and on the off-gas systems.

5.31 *Service Waste System Diversion.* Accidental release of radioactivity to the ground through the service waste system could occur from a failure of heat transfer surfaces in process vessels, allowing activity to leak into process cooling water or steam condensate. To prevent this from occurring, diversion capability is to be provided on the fuel processing and the waste calcining systems in the plant. Each diversion system will consist of (a) in-line, sodium iodide crystal, gamma-monitoring instruments on the service waste stream to initiate signals for operating diversion valves, (b) valves for diverting the radioactively contaminated service waste stream to a diversion sump located adjacent to an existing monitoring station, and (c) pumps in the diversion sump to transfer the contaminated water to a large waste storage tank for interim storage and subsequent reprocessing. Contaminated liquid diverted to the waste tank will be evaporated in an existing process waste evaporator with the overheads being processed through an existing ion exchange column before being returned to ground. The evaporator concentrates will be sent to interim storage in a second-cycle waste storage tank before being calcined.

5.32 *Off-Gas System Cleanup.* Modifications to the off-gas systems also are being made to minimize the release of particulate radioactivity to the atmosphere from the existing dissolver and vessel off-gas systems. Equipment for reducing the radioactivity released to the stack will be installed on the two dissolver off-gas systems from the aluminum and the zirconium fuel dissolution processes and on the vessel off-gas system. Each of the three cleanup systems will consist of a deentrainment vessel to remove water droplets entering with the off-gas, a heater to superheat the gas above its dew point, and a high efficiency filter to remove the remaining particulate activity in the gas stream.

Construction of these systems is to be completed in FY-72.

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

The present off-gas cleanup systems at ICPP provide adequate decontamination of process off-gases during normal operation; however, these systems do not provide atmospheric protection in the form of continuous filtration of cell ventilation air or polishing of process off-gas. New filter installations are being designed for the existing dissolver and vessel off-gas systems (DOG and VOG) as part of another project (Section 5.32) to reduce further the quantity of particulate activity released during normal operation; however, these modifications do not provide for redundant filtration in the event of a breach in the primary process off-gas filtration system nor will they provide filtration of cell ventilation air at ICPP. A maloperation or process accident such as an in-cell fire or explosion could grossly contaminate the cell air which is presently exhausted directly to the ICPP off-gas stack and thence to the atmosphere. A proposed Atmospheric Protection System will correct these inadequacies.

The proposed system consists of a deep fiber glass bed prefilter in series with HEPA final filters for the ventilation air and a separate, smaller, acid-resistant system for the NO_x -containing process off-gases. The prefilter will consist of five layers of fiber glass filter material of various densities and separated by stainless steel screens. The gas flow will be from bottom to top and from lower density to higher density fiber glass. A spray system will be installed within the bed to backwash the prefilter which should extend its lifetime.

Final filtration will be provided by 13 banks each containing 12 HEPA filters. The HEPA filter banks will be arranged in parallel and adequate valving provided so that replacement can be accomplished while the system is operating. Replacement will be accomplished by contact maintenance using bagging procedures. Buildings and structures will be designed in accordance with all applicable AEC criteria, Zone 3 seismic loading in particular.

The system will be capable of handling approximately 150,000 cfm of ventilation air and process off-gases. The process off-gas consists of two types of gas streams: one contains NO_x and the other is rich in H_2 . Off-gas streams containing NO_x (about 3000 cfm) must be processed in an acid resistant system because of the high probability of forming nitric acid. Hydrogen-containing gas streams must be maintained either above or below the explosive concentrations of H_2 .

The filter efficiency for the system will be at least 99.97% for 0.3 micron DOP particles. The system will have a 20-year life, be fire resistant, and will have the necessary physical integrity to sustain an explosion resulting in a filter pressure differential of 2 psi. Instrumentation will be provided to monitor continuously pressure drops and radiation levels. Suitable air sampling equipment will also be provided, along with additional blower capacity to handle the increased pressure drop.

Alternatives considered to a deep-bed prefilter and HEPA final filter were (a) commercial prefilters and HEPA final filters and (b) a sand bed filter. Although the commercial prefilter system has a lower capital cost and pressure drop than the proposed system, it was rejected because of higher operating costs and poor resistance to fire and overpressure. The sand filter has excellent resistance to over-pressure and fire, and low operating cost, but was less desirable because of high capital costs and possible disposal problems with the filter media.

5.5 Treatment of Tan Waste (M. W. Wilding, W. B. Kerr)

Liquid waste accumulated at TAN from various programs during the past 15 years is currently stored in two 50,000-gallon carbon steel tanks. Future wastes will be transported to the ICPP for processing, but the high-salt, alkaline waste currently in the tanks contains approximately 2500 ppm chloride which prevents storing and processing this waste in the stainless steel equipment at the ICPP. Consequently, a method for removing and solidifying this waste was investigated.

The relatively small volume (80,000 gallons) of waste limits the amount of money that can be reasonably allotted for equipment for a "one time" treatment: consequently, a simple method is needed. Laboratory studies indicated that the waste could be solidified by two different, relatively simple processes: (a) it could be concentrated about 10-fold, then transferred to drums and mixed with vermiculite and cement to produce a hard solid; or (b) it could be concentrated about 15-fold to produce a hard solid cake without additives. Currently, the waste is undergoing a 10-fold concentration in a 3500-gal tank evaporator; solidification of this concentrate will be made during the next year using one of the methods described above.

5.6 Long-Range Waste Management Study (G. W. Hogg)

A detailed study of NRTS waste management and pollution control practices has been completed. The purpose of the study was to develop a firm basis for a long-range, site-wide waste management and pollution control program to help assure compliance with present and future waste management regulations and directives. Information was assembled from all areas at the NRTS; representatives assigned to each facility area collected operating, analytical, and engineering data. A task force was assigned the responsibility of coordinating the study, analyzing the data, and writing a report.

Detailed descriptions of the first-order waste generators and waste handling practices at the NRTS were written; from these descriptions, the wastes were summarized by type. A literature survey of waste practices at other sites, waste handling technology, and regulations applicable to the NRTS was completed. The study provided a general overview of the NRTS waste management practices and problems: specifically noticeable were (a) the large NRTS chemical consumption, (b) the availability of much general, poorly coordinated waste management data, (c) the need for additional specific waste generation data to allow analysis of waste problems at the generator source, and (d) the need for improved auditing and documenting practices. Recommendations for improving long-range waste management and pollution control at the NRTS were outlined.

III. OTHER CHEMICAL PROGRAM ACTIVITIES

1. SAFEGUARDS PROGRAM -- PLANT INPUT MEASUREMENTS

(F. O. Cartan, G. L. Booman)

During FY 1971, this program was directed toward improved accuracy in measurement of plant input accountability tank content, either as volume or weight. There are three interrelated parts of this program: (a) an evaluation of direct weighing of the tank content; (b) an upgrading of the accuracy of the present pneumatic level system by a direct instrumental measurement of the level and density probe pressures; and (c) a computer controlled system for operation of either the pneumatic or direct weighing systems providing printout of volumes, weights, specific gravities, and monitoring of the essential mixing, sampling, and transfer steps. The combined system should eliminate human error, speed the measurements, and produce a significant improvement in the accuracy of plant input accountability measurements. The proposed system has direct application to accountability-safeguards measurements in commercial nuclear fuels reprocessing plants. Figure 24 is a block diagram of the proposed system.

1.1 Direct Weighing System

To meet in-cell requirements for a direct measurement of plant input tank content, a suitable weighing system must operate reliably in radiation fields of 1000 R/hr or greater, without in-cell maintenance, for periods of from one to two years. A hydraulic weighing system was chosen as most likely to have the necessary long-term stability, accuracy, and reliability.

No commercial weighing system met the requirements. A vendor, Brookline Instruments, made an experimental 10,000-lb capacity, radiation-resistant weighing system for trial operation. This system used mercury for the hydraulic fluid and seal-welded stainless steel diaphragms in the load sensors which were mounted under the legs of the vessel. All exposed surfaces and connecting tubing within the radiation area are stainless steel. Only the load sensors are in a radiation area; other portions of the system, the force totalizer, and the readout are located in cold areas. The system has a design accuracy of 0.02%. The system was installed on vessel G-155, one of the ICPP input accountability tanks, in December 1970. A preliminary calibration was made by weighing water into the tank and by placing lead weights on the tank. While there was some nonlinearity at low loadings, the resolution of the instrument was approximately one pound. A complete calibration was impossible because of plant schedules, and a final calibration will be made at the conclusion of the present plant run.

The system was continuously operative for six months. There were two minor failures in the readout electronics during this period but no other problems. Temperature differences between the tank and its connecting piping introduced substantial forces into the system and biased the indicated tank weight. To reduce these forces, a number of piping clamps were removed. To correct for the remaining forces, thermocouples were installed on important pipes. These thermocouples provided the temperature inputs needed for on-line computer correction of the thermal piping forces. A multipoint recorder was used for temporary measurement of these temperatures.

ANC-A-583

Fig. 24 proposed plant input measuring system.

During the plant run, the differences between the weighing system output and weights calculated from the normal plant measurements averaged less than 0.5%. The apparent precision, assuming no error in the plant volume and density measurements and using only a rough correction for pipe temperatures, was 0.4%. Hence, the performance is at least equivalent to the present system and probably better. When sufficient experience has been obtained with the system so that individual pipe temperature corrections can be made, the precision is expected to improve significantly.

1.2 Pneumatic System

A pneumatic system is used currently for measurement of liquid levels and specific gravities. Its use for input measurements is limited by the accuracy (approximately 0.5%) of plant instruments. This system will be upgraded for input measurements by a high accuracy (0.02%) pressure transducer connected to the primary pneumatic signals. The measured pressures will be converted by the computer to the corresponding specific gravities, volumes, and weights, and then printed.

After investigating several possible pressure transducers, a Non-Linear System X-5 pressure transducer was purchased. This instrument has a range of 0 to 100 inches of water and a 10-volt output. The instrument was found to be noisy on delivery but NLS modified it to meet specifications by reducing its frequency response. An accurate measurement requires 10 seconds. The maximum error found was 0.01 inch of water over the full 0 to 10 inch range, an accuracy of 0.01%.

Since the transducer is expensive, a solenoid valve pressure-signal multiplexer was built so that the transducer could be switched to any of three tanks. An air-purged protective box was built. The box, connecting cables, and the operations area junction box were installed in the plant, but testing of the system will have to await another processing campaign.

1.3 Computer-Monitors

The objective of this part of the program was the demonstration of a single system using pressure switches as sensors to monitor the plant input accountability tanks and to validate the solution transfers. A small minicomputer manufactured by the Data General Corporation, the Nova 1200, was purchased. Matching computer interfaces were designed and built for the Brookline weighing system, the thermocouple signal multiplexer, the digital voltmeter, the monitoring pressure switches, and the pneumatic signal multiplexer. These interfaces include a provision for manual operation when the computer is unavailable. Demonstration of this system will also have to await the next processing campaign.

2. BURNUP DETERMINATION FOR FAST BREEDER REACTOR FUELS

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

Compared to thermal light water reactors (LWR), the design, development, and operation of fast breeder reactors (FBR) require nuclear data for a much broader energy range and for a greater variety of nuclear reactions. At the present time, the lack of these data is one of the most serious problems associated with the FBR program.

Of importance to the successful design and operation of the FBR's is an economic fuel cycle. This requires accurate nuclear data for fuel design and operation to establish shielding requirements and to plan for long-range fissile material requirements. At the present time, large uncertainties associated with the nuclear data are resulting in increased program and design costs, including: (a) extra margin being provided in core design; (b) more restrictive limits on fuel performance objectives; (c) over-designed shielding requirements for reactor vessels, shipping containers, and fuel fabrication and reprocessing plants; and (d) unknown future fuel requirements.

Two important criteria for the evaluation of the fuel cycle economics are an accurate measure of the number of fissions (ie, "burnup") which occurred in the fuel and the availability of accurate chemical methods for the analysis of fuel components.

2.1 Program Objectives

The objective of this project is the development of methods for the accurate determination of nuclear fuel burnup in fast breeder reactor fuels; the emphasis is on future fast breeder power reactor fuels having long residence time and high burnup. The principal measurement technique under study is chemical analysis of stable and long-lived fission product nuclides. Based on a recently completed program to develop burnup methods applicable to fuels irradiated in light water power reactors[24,25], isotope dilution mass spectrometry has been selected as the most reliable technique for the determination of stable and long-lived fission products. The degree of reliability of a burnup determination based on a stable fission product analysis depends on three factors: the accuracy of the values used for the fission yields, the accuracy of the relationship between the number of fissions and the number of fission product atoms present at the end of the irradiation, and the reliability of the analysis methods.

Specific goals of this project are: (a) the accurate measurement of the fast fission yields of selected fission product nuclides for many fissioning isotopes and the determination of the capture-to-fission ratio for several of these heavy element nuclides in neutron spectra which approximate that expected in large fast breeder reactors, (b) the measurement of fission product burnout as a function of fuel burnup, (c) the selection of specific fission product nuclides as useful fission monitors for various fuels, (d) the development of the relationships for computing burnup, (e) the development of chemical separations and mass spectrometric analysis methods for the determination of the selected fission product nuclides, and (f) proof testing of the most promising methods. Details of the program objectives and plans have been reported in IN-1456[26].

2.2 Experimental Program

Because of the uncertainty of the neutron spectra in future large FBR's, two assemblies were fabricated for irradiation in the EBR-II reactor; absolute-fission-yield and capture-to-fission-ratio measurements will be made. The first assembly contained gram quantities of individual samples in duplicate of the highly enriched isotopes of ^{233}U , ^{235}U , ^{238}U , ^{239}Pu , ^{240}Pu , ^{241}Pu , ^{242}Pu , ^{241}Am , ^{243}Am , and ^{237}Np , and was irradiated in a mean neutron energy spectrum of ~ 250 keV for 3150 MWd. This assembly was discharged from the reactor at the end of FY-71.

The second assembly contained gram quantities of individual samples in duplicate of ^{233}U , ^{235}U , ^{239}Pu , ^{240}Pu , and ^{241}Pu surrounded by a BeO shield to "soften" the normal EBR-II neutron spectrum to give an anticipated mean neutron energy of ~ 100 keV. This assembly will be irradiated early in FY-72; the expected burnup will be ~ 3000 MWd. These two irradiations will bracket the neutron energies expected in the future FBR's and give fission yield data as a function of neutron energy.

The fissionable and fertile materials to be irradiated were individually mixed with high purity nickel powder (99.99+%) and weld-sealed in nickel capsules which were machined from high purity (99.99%) nickel rod. The individual nickel capsules were stacked inside of a stainless steel cylinder and sealed. This cylinder was then placed inside of a standard stainless steel cylinder supplied by the EBR-II project. All void volumes in the nickel capsules and the stainless steel cylinders were filled with helium. The quantities of the various heavy elements to be irradiated were determined from calculations using estimated cross section data and flux data to give $\sim 1 \times 10^{19}$ fissions with the reactor operating at 62.5 MW for 50 days. The expected integral neutron flux is 5.4×10^{21} n/cm².

The BeO-shielded subassembly is of the type normally used for the depleted uranium blanket in EBR-II. This subassembly holds a total of 19 pins. Eighteen of these pins contained BeO and the 19th capsule, located in the center of the assembly, contained the fission yield experiments. The capsules for this experiment were prepared in the manner outlined above.

The materials irradiated in each of the assemblies are listed in Table XII. Because ^{238}U , ^{242}Pu , ^{237}Np , ^{241}Am , and ^{243}Am have a high neutron energy threshold for fission, little fissioning would occur in the "softer" spectra; hence, they are not included in the BeO shielded irradiations.

Following the irradiation and at least a three-month cooling period, the samples will be dissolved, the fission gases quantitatively collected and analyzed, and the dissolver solution analyzed for the desired fission products. The principal measurement technique will be isotope-dilution mass spectrometry. The sample dissolution and analysis will start mid FY-72.

Essentially all of the mass spectrometric isotope dilution spikes required for the individual fission products were prepared and standardized. Chemical separation methods compatible with the sample matrix were developed and evaluated for Cs, Rb, Sr, Ba, Zr, Mo, and the rare earths.

TABLE XII
MATERIALS IRRADIATED IN EBR-II

<u>Isotope</u>	<u>Enrichment, %</u>
$^{233}\text{U}_3\text{O}_8$	99.54
$^{233}\text{U}_3\text{O}_8$	99.99 ^[a]
$^{235}\text{U}_3\text{O}_8$	98.2
$^{235}\text{U}_3\text{O}_8$	99.999 ^[a]
$^{238}\text{U}_3\text{O}_8$	99.95
$^{239}\text{PuO}_2$	99.10
$^{239}\text{PuO}_2$	99.97 ^[a]
$^{240}\text{PuO}_2$	98.30
$^{240}\text{PuO}_2$	99.86 ^[a]
$^{241}\text{PuO}_2$	94.64
$^{241}\text{PuO}_2$	>99.99 ^[a]
$^{242}\text{PuO}_2$	99.09
$^{242}\text{PuO}_2$	99.80 ^[a]
$^{241}\text{AmO}_2$	96.0
$^{243}\text{AmO}_2$	99.8
$^{237}\text{NpO}_2$	----
[a] For capture-to-fission ratio measurements.	

3. IODINE ADSORBENTS PROGRAM

(D. T. Pence, F. A. Duce, W. J. Maeck)

The objective of this program is to develop an inorganic material for the removal of different airborne iodine species from a variety of atmospheres which might be encountered in the nuclear industry. Currently, charcoal is the material used for this purpose; however, it has the disadvantages of iodine desorption at relatively low temperature, flammability, low iodine adsorption capacity, unsatisfactory performance with steam atmospheres, and can form explosive mixtures with nitric acid vapors. An alternate approach is the use of inorganic adsorbents in which a stable iodine compound is produced and which do not have the operational limitations of charcoal.

Experimental results[27,28,29,] show that fully silver-exchanged Type-X zeolite efficiently adsorbs and strongly retains both inorganic and organic iodine species. Compared with charcoal adsorbents, this material has the advantages of nonflammability, high temperature operability, more tenacious retention of iodine, a higher loading capacity, and rapid reaction rates with various iodine species.

The planned program schedule includes three phases: (a) a detailed study of the elemental and methyl iodide adsorption efficiency of fully silver-exchanged X-type silver zeolite; (b) similar studies on other types of silver zeolite, other metal-exchanged zeolites, and partially-exchanged silver zeolite; and (c) detailed adsorption studies of the most promising materials selected during phase (b).

3.1 Experimental Results

Studies of the adsorption efficiencies of fully-exchanged silver zeolite, Type-X, for elemental iodine and methyl iodide as a function of actual face velocity, relative humidity, and temperature have been completed. These results, reported in detail elsewhere[28,29], showed fully-exchanged silver zeolite to be the most efficient adsorbent reported. The following are general conclusions of the tests conducted to date: (a) methyl iodide adsorption efficiencies greater than that of impregnated charcoals have been obtained using silver zeolite, even at twice the actual face velocity of that used in the charcoal tests; (b) the adsorption efficiency of silver zeolite in highly humid atmospheres is very sensitive to the degree of silver exchange; (c) the mechanism of the adsorption process is a chemical reaction with the formation of silver iodide in the zeolite structure; (d) the adsorption efficiency is greater at higher temperatures because of the increased reaction rate; and (e) the reaction product is insoluble in water and is thermally stable to about 900°C.

In addition, some special purpose tests were conducted which were designed to evaluate the methyl iodide adsorption efficiency of fully-exchanged silver zeolite, Type-X, under adverse conditions. These conditions included: (a) prolonged exposure to steam, (b) exposure to high radiation fields, (c) dynamic and static exposures to laboratory air, and (d) exposure to a variety of gases.

When silver zeolite was exposed to flowing steam for five to six hours prior to the introduction of methyl iodide, the adsorption efficiency of the fully exchanged silver zeolite decreased as much as 35%; however, similar tests with MSA 85851 charcoal showed a 65% decrease in methyl iodine absorption. The methyl iodide which was absorbed by the silver zeolite was not purged from the bed with additional exposure to steam; this is in contrast to the tendency for methyl iodide to purge from charcoal adsorbents under flowing steam conditions.

The effect of radiation on the methyl iodide adsorption efficiency of silver zeolites was determined by exposing three different silver zeolites to 10^8 R of gamma radiation (10^6 R/hr) prior to the adsorption tests. The results of these adsorption tests on fully exchanged Type-X, AW 500, and Zeolon showed no significant differences from those not exposed to radiation. In addition, no induced radioactivity was detected, and there was no apparent change in the physical properties of the irradiated samples.

Several samples of fully exchanged silver zeolite, Type-X, were examined for aging and weathering effects. In one case, a sample was exposed to a laboratory atmosphere under static conditions for a period of six months. In another case, the adsorbent material was placed in a holder and laboratory air was drawn through the adsorbent at a rate of about 250 ft/min face velocity for a period of six months. The samples were then tested to determine their methyl iodide adsorption efficiencies. There was no significant change in the adsorption efficiency of the material subjected to the static test. In the dynamic test in which 10^8 adsorbent-bed-volume changes of air were drawn through adsorbent, the adsorption efficiency decreased by about one-half of one percent, to 99.5%.

The results of the tests to determine the effects of various gases on the methyl iodide adsorption efficiency of fully exchanged silver zeolite, Type-X, are shown in Table XIII. Of the various gases tested, only the sulfur-containing compounds had serious deleterious effects on the silver zeolite adsorption efficiency for methyl iodide.

The elemental iodine and methyl iodide adsorption efficiencies of several other silver zeolites and other metal cation-exchanged zeolites were examined. In general, the elemental iodine adsorption efficiencies of all the silver zeolites are greater than 99% even in high humidity atmospheres. Some of the other metal-exchanged zeolites (such as Cu, Hg^{+2} , Pb) adsorbed greater than 90% of the airborne elemental iodine in dry atmospheres; however, as the relative humidity was increased, the adsorption efficiency decreased rapidly. The silver zeolites showed good methyl iodide adsorption efficiencies which decreased with increasing relative humidity at a rate depending on the silver content[29]. The other metal-substituted zeolites tested were determined to be ineffective for methyl iodide adsorption except in dry atmospheres.

TABLE XIII

THE EFFECT OF VARIOUS GASES ON THE ADSORPTION
OF METHYL IODIDE ON SILVER ZEOLITE^[a]

Conditions: AgX; 12 - 14 mesh, 30.0g
Relative Humidity - ~90 percent
Temperature - 90°C
Actual Face Velocity - 46 fpm
Methyl Iodide Conc. - ~1 µg/m³
Duration - 1 hr pre-equilibration with pollutants,
1 hr loading with pollutants,
1/4 hr purge without pollutants.

<u>Pollutant</u>	<u>Concentration (Volume Percent)</u>	<u>Adsorption Efficiency (Percent)</u>
O ₂	10	99.94
CO ₂	10	99.95
H ₂	1.9	99.97
C ₃ H ₅	10	99.89
NO ₂	10	99.79
H ₂ S	0.06	42.20
SO ₂	1.9	31.48
Kerosene ^[b]	0.05	99.91
Hexone	2.2	99.99

[a] Approximately 10⁴ adsorption bed volume changes during each test.

[b] Test conducted at 60°C.

4. IODINE BEHAVIOR STUDIES

(D. T. Pence, J. H. Keller, T. L. Thomas)

Hypoiodous acid, HOI, has been shown^[30] to be easily volatilized from aqueous iodine solutions under certain conditions. Because of the significance of this reaction to the reactor containment spray program, an investigation was initiated to study the iodine chemistry in dilute solution more closely.

The chemical iodine hydrolysis and subsequent reactions were studied at 25°C, at several iodine concentrations (10^{-4} to 10^{-5} M) and at pH values of 6 to 10. Two instrumental techniques were developed to follow the reactions: a spectrophotometric method to follow the I_2 and I_3^- concentrations, and an iodide specific-ion electrode to monitor I^- concentration. The HOI concentrations were calculated from the measurement data and the following equilibria:

These equilibria are known to be established within a fraction of a second and can be used to account for the observed I^- and I_3^- concentrations measured immediately after the I_2 injection. The overall consumption of HOI is described by the following disproportionation reaction:

The pH dependency of the rate at which the HOI is consumed was verified experimentally. For example, at a pH of 8 the concentration of HOI at zero time was reduced by a factor of 10 in 100 minutes, and by a factor of 100 in 24 hours; by comparison, only 4 and 50 minutes, respectively, were required to effect the same reduction at a pH of 9.

The results of these studies indicate that appreciable concentrations of HOI do exist in alkaline iodine solutions, at least in the range 10^{-4} to 10^{-5} M iodine, but the lifetime of the species decreases rapidly with increasing pH. A detailed report of the study is in preparation.

5. ELECTROCHEMICAL STUDIES FOR THE OFFICE OF SALINE WATER --

ION-CONTROL MEMBRANES

(J. R. Delmastro, G. L. Booman)

5.1 Introduction

Electrochemical studies of fundamental interfacial processes which are important to desalination technology were begun in 1968 under a grant from the Office of Saline Water. Preliminary investigations of interfacial phenomena led to the concept of porous metallic membranes for separation processes, where the charge density around pores could be regulated by an external electrical circuit, thus controlling the permeability of the repulsion-attraction field in the diffuse double layer next to the electrode would seem feasible in both reverse osmosis and electrodialysis separations.

Primary emphasis during FY 1971 has been on investigating various techniques suitable for fabricating metal membranes with pore diameters of the order of 100 Angstroms. These metal membranes are to be evaluated for electrodialysis and reverse osmosis applications as well as for model studies of interfacial charge effects on membrane salt rejection efficiency. Experimental evaluation of these microporous metallic membranes will allow the determination of how well-defined, Angstrom-size pores with known surface structure and surface charge can control the attraction-repulsion properties of components of saline and brackish waters. Application of recently developed techniques for thin film

technology -- notably radio frequency sputtering and micro-pore formation by preferential etching in the region of defect tracks caused by bombardment with fission fragments -- shows great promise for fabrication of porous metallic membranes.

5.2 Preliminary Studies

Initial metal plating studies of thin glass films were performed by thermal decomposition of the commercial organo-metallic proprietary solution, Hanovia Liquid Bright Gold. By employing this technique, very thin metallic gold films were produced on five-micron glass substrates. The resulting gold films appeared to be homogeneous and had adequate conductivity. Fission fragment tracks were produced in the thin glass substrates by thermal fission of U-235. These fission fragment tracks were selectively etched in dilute hydrofluoric acid with ultrasonic stirring until holes in the glass could be detected by optical microscopy. Electron microscopy was used to examine the pores produced in the thin glass substrates and to determine the nature of the deposited thin gold films. The pores produced in the thin glass substrates are quite circular and of fairly uniform size. It appears that what are initially conical pits become parallel-walled spores rapidly after breakthrough. However, the thin metallic gold films produced by firing liquid films of Hanovia Bright Gold to 600°C are very porous. These gold films were examined directly when the glass substrate was sufficiently thin to permit the electron microscope beam to penetrate. They were also examined after carbon replication of the surface films. Both of these methods indicate that the metallic films are not continuous. Instead, they are composed of dense opaque clumps of gold particles which often form a lacy interconnected network over the surface. The open sections of the film are often much larger than 1000 Angstroms, giving too high a porosity to be used for membrane studies with imposed potential control.

5.3 Present Plan for Fabrication of Porous Membrane

A survey of the literature and suppliers of thin film equipment indicated that more continuous films can be produced by vacuum evaporation or sputtering techniques. R. F. sputtering was selected over vacuum evaporation as the best technique for our thin film fabrication problem because of its versatility, ease of film-thickness control, suppression of nucleation effects, ease of cleaning substrates by sputter etching, and sputter etch capability for forming appropriate membrane supports. One can sputter deposit films of complicated materials such as stainless steel and maintain control of composition. Deposition rates are not much different for most metals or alloys, and even insulator materials can be deposited readily. The thickness of sputtered films is very reproducible under the same operating conditions. ICPP recently acquired a Randex r.f. sputtering module and an Ion Equipment Corporation table-top vacuum system. The sputtering module has been installed on this ion-pumped vacuum system.

The present plan for fabrication of the porous metallic membranes is outlined in Table XIV. It will employ r.f. sputter deposition of alternating layers of metals and dielectric materials to create a sandwich structure supported by a porous substrate layer. Micropores will be formed by preferential etching in the region of defect tracks caused by fission-fragment bombardment. The proposed sequence of fabrication steps is outlined below.

Step A: Deposit sequentially 100- to 500-Angstrom layers (referred to as layers #2-5 in Table XIV of metal and insulating material on a 50- to 100-micron thick glass or metal substrate (layer #1) to form a thin sandwich. This procedure forms a metal membrane layer (#4) covered on both sides with thin layers of dielectric material (layers #3 and #5).

TABLE XIV

METAL MEMBRANE STRUCTURE AND STEPS IN FABRICATION BY THIN-FILM TECHNIQUES

Layer # and Composition	Layer Thickness	Function of Layer	Hole Diameter	Deposition Order	Etch Order	Method of Forming Holes in Layer
5. Dielectric	100-500Å	Insulating	100-200Å	4	4	Bombarded simultaneously with layer #3. Fission fragment tracks etched with HF.
4. Metal	100-500Å	Metal Membrane (Controlled Charge)	100-200Å	3	5	Holes chemically etched through pattern in dielectric layers
3. Dielectric	100-500Å	Insulating	100-200Å	2	4	Bombarded simultaneously with layer #5. Fission fragment tracks etched with HF.
2. Metal	100-500Å	Substrate Etch Stop	100μ	1	3	Chemically etched through pattern in glass or metal substrate layer.
1. Glass or Metal	50-100μ	Substrate and Support	100μ	0	2	Chemically etched with HF through pattern in masking layer.
0. Masking Material	1-2μ	Substrate Etch Pattern Mask	100μ	5	1	Hole pattern generated by sputter etching through metal mask.

Step B: Chemically etch 100-micron diameter holes in the supporting substrate (layer #1) by using a masking layer of sputtered molybdenum or other suitable material (layer #0) with the thin metal layer (#2) functioning as a stopping layer for the etching step.

Step C: Remove the masking layer and chemically etch through the stopping layer (#2) by using the 100-micron holes in the substrate as a pattern.

Step D: Irradiate the resulting sandwich structure with fission fragments to produce damage tracks in layers 3 and 5, and chemically etch 100- to 200-Angstrom or smaller diameter holes in the thin layers of dielectric (layers #3 and #5).

Step E: Chemically etch holes through the metal membrane layer (#4) using the small holes in the surrounding dielectric layers as a mask.

Work has been directed toward the completion of Step B, ie, the development of methods for etching 100-micron diameter holes in the substrate layer (#1). This layer of backing material is required to provide strength and ease of handling for the thin sandwich structure which includes the metal membrane layer. Holes in the substrate layer must be chemically etched through a mask to produce large open areas (~100 μ diameter holes) through the 50 to 100 microns of substrate material to the adjacent thin sandwich. Our studies of substrate materials have employed commercially available cover glasses which are 50 to 100 microns thick and 5/8 inch in diameter. Experiments involving chemical etching of these glasses, masked with photoresistive material, were unsuccessful. Poor adhesion of the photoresist to the glass and dissolution of the resist in HF etchant solutions proved troublesome. Consultation with product application specialists at Eastman-Kodak indicated that the problems which we encountered are typical in application of positive photoresists as a mask on glasses with strong etchants. The molybdenum masking technique mentioned previously does not require use of photoresist. It was developed by Brown et al[31] at General Electric for etching high resolution patterns in silicon nitride with concentrated HF. This technique should also be applicable to etching glass substrates. The pattern of 100-micron holes in the molybdenum masking layer can be generated directly by sputter etching the molybdenum through a sputter-etch mask. Suitable metallic sputter etch masks have been obtained from Buckbee Mears Co.

5.4 Experimental Studies

Preliminary experiments have been performed using the Randex r.f. sputtering module. These experiments included various advanced thin film techniques which are being applied in the membrane fabrication sequence. Thin layers of copper, platinum, and glass were sputtered onto 5/8-inch diameter glass substrates. A four-inch platinum target was fabricated by bonding thin platinum sheet to a copper target holder. The sputter etch capability of the Randex sputtering module was used to generate a pattern of 100-micron diameter holes in the thin layers of copper and platinum by sputter etching through a suitable sputter etch mask. Initially sputtering experiments were performed without rigorously cleaning the glass substrates. Adhesion of the deposited metal films was extremely poor. The sputter-deposited platinum layers were lifted off the glass substrates within several minutes after immersion in 20% HF etching solutions. Glass microscope slides and the above-mentioned circular substrates were subjected to a rigorous chemical cleaning procedure. Step layers of sputtered platinum and glass on these substrates were employed in the determination of the low-power sputter deposition rates (in Angstroms per minute). The thickness of these deposited layers of platinum and glass were measured by the Tolansky technique. These measurements were performed for us by Mr. Al Lang of Randex Corporation employing a Varian "A-Scope" interferometer. Adhesion of these deposited layers was markedly better than those deposited on uncleaned substrates. However, the sputter-deposited platinum layer was still lifted off the glass substrates within minutes by 20% HF solutions. Subsequent investigations and conversations with participants at the Varian Vacuum and Thin Film Technology Seminar indicated that adhesion of platinum or gold films deposited directly onto glass substrates is extremely poor. A thin (less than 500 Angstrom) intermediate layer of an oxide-forming metal such as chromium, molybdenum, tungsten or titanium is recommended before deposition of platinum or gold on glass substrates. Adhesion of these films is excellent if the substrates have been properly cleaned. We have purchased sputtering targets of molybdenum and chromium for possible application as intermediate metallic layers. We are designing a system which will permit cleaning and handling of the glass substrates in a dust-free environment. Air filtration modules giving a "Class 100" dust-free environment will be installed to protect the substrate cleaning and sputtering deposition operations. Contamination of the substrate surfaces must be minimized to ensure strongly adherent, pinhole-free deposited thin films

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. Work performed during FY 1971 was under management of Idaho Nuclear Corporation under Contract No. AT (10-1)-1230 with the U. S. Atomic Energy Commission, Idaho Operations Office. On July 1, 1971, this organization was transferred to Allied Chemical Corporation which assumed responsibility for continued operation of the Idaho Chemical Processing Plant facilities. Plant Operations, Technical Support, and Research and Development continued uninterrupted under the same branch and section organization.

ALLIED CHEMICAL CORPORATION
IDAHO CHEMICAL PROGRAMS - OPERATIONS OFFICE

SEPTEMBER 15 1971

APPROVED *F. H. Anderson*

V. REFERENCES

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"Development of a Continuous Sampler-Monitor for the LOFT Containment Atmosphere", R. E. Schindler, R. R. Hammer, D. E. Black, L. T. Lakey

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3. OTHER PUBLICATIONS

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