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CHEMICAL AND PROCESS DEVELOPMENT BRANCH ANNUAL REPORT
FISCAL YEAR 1965

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J. R. Bower, Editor

**PHILLIPS
PETROLEUM
COMPANY**

ATOMIC ENERGY DIVISION

**NATIONAL REACTOR TESTING STATION
US ATOMIC ENERGY COMMISSION**

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CHEMICAL AND PROCESS DEVELOPMENT BRANCH ANNUAL REPORT
FISCAL YEAR 1965

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SUMMARY

The ICPP processed aluminum-, zirconium-, and stainless steel-based fuels during the latter half of this period, while the first half was largely occupied with calcination of existing waste solutions in the Waste Calcining Facility (WCF). Operation of the aluminum fuel recovery process, both on a continuous basis and on an intermittent day-to-day basis as manpower permitted during full-time operation of the WCF, was highly successful. During intermittent operation, startup and shutdown of the extraction columns each day, with operation only on the day shift, did not penalize either uranium recovery or decontamination efficiency. The new ICPP semicontinuous zirconium fuel process was operated for the first time during this year; following a period of startup adjustments, the process was operating smoothly at the close of the reporting period. Stainless steel fuels were processed by the sulfuric acid process in the existing SIR process equipment. Recovery was successful although operating difficulties were encountered with inadequate equipment; modifications are not planned since further operation of this process is not now anticipated.

In process-associated development work, silicon-rich, aluminum alloy fuels were found to impose serious restrictions on the usual mercury-catalyzed, nitric acid dissolution process because of low dissolution rates and formation of insoluble residues. Portions of ATR fuel elements fabricated with Type 4043 aluminum alloy weld metal (5 percent silicon) required up to 30 times the usual dissolution time and gave an insoluble residue of approximately 2 percent of the fuel weight. Zirconium process studies resulted in several new findings: (a) the usual species of uranium tetrafluoride solids associated with the ICPP process ($\text{UF}_4 \cdot 3/4 \text{H}_2\text{O}$) may be dissolved at moderate temperature (55°C) by agitation with dilute (0.03M) chromic acid; (b) uranium tetrafluoride solubility in water is not affected by the presence of boric acid, but is enhanced by the presence of oxygen (air) in the normal nitrogen atmosphere in the dissolver; (c) adjusted dissolver product is stable at moderate acid concentrations and high fluoride-to-aluminum ratios (within limits shown on a stability plot incorporating aluminum, fluoride, zirconium, boric acid, and total acid concentrations); and (d) specified mixtures of zirconium and aluminum process raffinates will be stable if blended in the waste storage tanks. Dibasic aluminum nitrate, DIBAN, was shown to be effective in scrubbing excess acid from zirconium process extraction product and was shown to be stable under proposed conditions for use and storage. The flowsheet used for preparing plant-scale quantities of DIBAN is discussed. Other current process support studies discussed include extraction column operating problems, air-pulser development, means for solids flow control in a pulsed solids-liquid contractor, and effects of weld imperfections on corrosion of plant waste storage vessels.

Reprocessing of EBR-I Core 2 and Core 3 fuels has been studied on a laboratory scale, and plant flowsheets based on dissolution in mixed nitric-hydrofluoric acids have been proposed. This process, with somewhat different HF-to- HNO_3 ratios, is effective for both the zirconium-clad fuel and the stainless steel-uranium fusion mixture. Recovery of neptunium from ICPP fuel reprocessing solutions has been partially demonstrated; over 90 percent of the available neptunium was separated from second-cycle raffinates and stored as a concentrate during a recent aluminum fuel processing campaign. Uranium recovery from graphite fuel, to the extent of 99 percent or better, was demonstrated on a laboratory scale using a combustion-leach process; uranium leachability was impaired if the combustion temperature exceeded

800°C, but irradiation or thermal history of the fuel had no apparent effects. Alternate processes showing promise are a grind-leach process and a mixed nitric acid-sulfuric acid oxidation, both of which gave quantitative recoveries of uranium in exploratory experiments. Electrolytic dissolution accomplishments in the ICPP pilot plant are summarized although additional development at this site has been suspended. Equipment and process development were carried to a point permitting design of a plant-scale process.

The ICPP Waste Calcining Facility (WCF) had a highly successful first year of operation. Approximately 512,000 gallons of radioactive liquid waste were converted to 7500 cubic feet of solids weighing 412,500 pounds in a 312-day campaign; on-stream time was 99.3 percent during this campaign. Excellent performance was obtained in the WCF off-gas system; calculations indicate that at the point of maximum integrated radiation concentration at ground level (1600 meters from the stack), the total dose over the entire period of operation would have been about 0.1 rad. In no instance was Sr-90 found in any of the vegetation samples, fallout samples, or high-volume air samples. No corrosion problems of major importance were observed on any of the WCF equipment items although some replacements are being made where better or longer lived materials have come to light. New calcined-solids storage bins have been designed and are under construction. Until their completion, WCF operation has been suspended since the original storage bins were filled during the recent campaign. Advanced calcining studies in both the laboratory and pilot plant indicate the possibility of calcining essentially all of the varied fuel processing wastes at the ICPP in the WCF. Appropriate blending of wastes or addition of chemicals can be employed to inhibit unfavorable reactions which might otherwise accompany calcination of certain individual raffinates, eg, zirconium-fluoride, stainless steel sulfate, ammonium nitrate-containing, or sodium nitrate-containing wastes. The heat generation rate of calcined waste, determined calorimetrically, was in excellent agreement with the value derived from the analytical composition and decay characteristics of individual isotopes. Thermal stability studies of calcined waste indicated that some migration of cesium and ruthenium might be expected at 800°C but that strontium and cerium were stable up to 1200°C. Conversion of calcined waste to glass in laboratory studies gave a water-resistant product; the leaching rate of fission products (at 25°C) was found to be approximately equal to the dissolution rate of the glass and was not affected by devitrification of the glass brought about by heating. Other calcination support studies performed include: a mathematical analysis of particle growth and size distribution in the fluidized bed; a recommendation for a glass supporting medium in the off-gas filters; a design for a valve to control flow of solids; and an investigation of heat transmission through soil for possible application to buried waste materials.

ICPP fuel storage basin water has been satisfactorily decontaminated from strontium-90 and cesium-137, escaping from damaged fuel elements, by use of ion-exchange beds filled with clinoptilolite, a naturally occurring mineral. A device to detect and measure fission product leakage from damaged fuel elements is described. The probability of serious galvanic corrosion between storage racks and various fuel cladding materials in the storage basin environment is considered slight on the basis of an experimental study of electrochemical corrosion. Use of calcium hypochlorite rather than gaseous chlorine to control growth of microorganisms in the storage basin has been shown to cost less and to reduce the potential corrosion problem.

LOFT assistance studies have been directed at studying coating materials for the interior of the reactor containment building and decontamination techniques which will permit early reentry after release of fission products associated with reactor core meltdown. High-pressure sprays have not been effective in removing iodine from organic coatings which are penetrated deeply by the contaminant; high-pressure steam has been effective in some cases. A simulated reactor containment shell for Contamination-Decontamination Experiments (CDE), in which coatings and decontamination techniques can be tested in the presence of fission products released from fuel meltdown, is being constructed in a shielded cell of the ICPP Hot Pilot Plant. This will permit more meaningful tests. Design of a continuous sampler-monitor for the containment building atmosphere is discussed in principle.

In other reactor support studies, surface contamination (principally Co-60 in a hafnium dioxide layer) was removed from hafnium control rods by immersion in a molten sodium hydroxide bath; little or no attack of the metal base was evident. Irradiated aluminum-clad elements were cleaned of surface contamination by immersion in a hot solution of 0.5M phosphoric acid - 0.001M chromium trioxide, followed by immersion in hot 3.0M nitric acid. Decontamination factors of >200 were obtained, but the aluminum surface was left in a readily corroded state. Results of the decontamination of test reactor loops were also evaluated.

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I. FUEL REPROCESSING

1. PERFORMANCE OF ICPP FUEL RECOVERY PROCESSES

1.1 Aluminum Fuel Processing (B. R. Wheeler, G. F. Offutt; PLANT PROCESS ASSISTANCE SECTION)

1.11 Process Performance. High-enriched, uranium-aluminum alloy fuels containing 505 kg of uranium were processed at the ICPP during the year in Run 21. Table I shows the fuels processed and the quantity of uranium in each. A 99.90 percent recovery was achieved in the first extraction cycle; a 99.95 percent recovery was achieved in the combined second and third extraction cycles.

This processing campaign was unique for the ICPP in that 66 of the 505 kg of uranium were recovered on a part-time basis covering a span of four months. Manpower not needed for operation of the Waste Calcining Facility was used to process fuels, usually on the day shift only. Highly burned up fuels, such as those from Chalk River which are very slow in dissolving, and small batches of fuel which required separate accountability were dissolved and processed through the first extraction cycle during this period. No adverse effects were noticed from starting up and shutting down the system once each day. Uranium recovery in the first extraction cycle averaged 99.88 percent during the part-time processing period.

Overall decontamination of the recovered uranium was excellent; the product easily met the required specifications. Table II shows decontamination factors (DF's) for uranium based on three sets of samples taken from each extraction cycle. The average DF's for uranium in first and second extraction cycles are similar to those reported for the previous aluminum processing campaign, Run 20 [1]; however, the average DF's for the third extraction cycle were much higher than those reported for the previous run. Consequently,

TABLE I
FUELS PROCESSED
DURING ICPP RUN 21

Fuel Type	Number of Elements Dissolved	Total Uranium Charged (kg)
BGRR	1221	13.28
NRX	279	6.82
McMasters	9	1.48
NRU	68	3.52
NRL	36	4.82
SWE	216	25.17
IRL	28	3.96
FNR	28	3.50
GTR	24	3.31
MTR	290	40.90
OWR	20	[a]
LPTR	21	3.80
LITR	225	35.50
UF	1	[b]
ETR	859	304.10
CP-5	18	[c]
STR	2	[c]
Spert	243	26.10
NASA	193	28.70[d]
Total	3781	504.96

[a] Included with MTR.

[b] Included with LITR.

[c] Included with ETR.

[d] From accountability estimates, others from samples of dissolver product.

TABLE II
LOG DECONTAMINATION FACTORS
FOR URANIUM PRODUCT DURING RUN 21

<u>First Extraction Cycle</u>			
<u>Date of Sample</u>	<u>Gross Beta</u>	<u>Gross Gamma</u>	<u>Zr - Nb</u>
November 7	2.7	1.7	1.8
November 12 to 13	2.9	2.1	2.0
November 23 to 24	<u>2.3</u>	<u>1.7</u>	<u>0.8</u>
Average	2.7	1.9	1.7
<u>Second Extraction Cycle</u>			
<u>Date of Sample</u>	<u>Gross Beta</u>	<u>Gross Gamma</u>	<u>Zr - Nb</u>
November 30	3.2	3.5	3.3
December 4	1.8	2.7	2.5
December 8	<u>1.6</u>	<u>2.4</u>	<u>1.9</u>
Average	2.7	3.1	2.9
<u>Third Extraction Cycle</u>			
<u>Date of Sample</u>	<u>Gross Beta</u>	<u>Gross Gamma</u>	<u>Zr - Nb</u>
November 30	1.0	1.1	2.8
December 4	2.7	1.8	2.6
December 8	<u>2.2</u>	<u>2.1</u>	<u>3.5</u>
Average	<u>2.4</u>	<u>1.9</u>	<u>3.1</u>
Overall Average	7.8	6.9	7.7

overall average DF's for the three extraction cycles were about a factor of ten higher than those reported for Run 20. The reason for the unusually high DF's observed in the third extraction cycle during this run as compared to those observed for Run 20 is not known. Also, the cause of variation of the decontamination factors during the run is unknown.

The flowsheets used on this run were similar to the ones used for previous runs [2]. Figure 1 shows the flowsheet for the first extraction cycle, and Figure 2 shows the flowsheet for the second and third extraction cycles.

Modifications made to the extraction system prior to the processing campaign significantly improved the operation of the system. One such modification was the elevation of the airlift disengaging pot on the organic stream between the extraction and scrub columns into a shielded portion of the process makeup area. This change improved the hydraulics of the scrub column and allowed the extraction system to "line out" in a much shorter time than during previous

(a) Based on 500 kg of aluminum per day from 30 percent burnup MTR elements

(b) Volume for irradiated fuel

CPP-S-3585

Fig. 1 Flowsheet for dissolution and first-cycle extraction of high-enriched aluminum alloy fuels.

campaigns. Another major modification involved lowering the jacklegs on the aqueous outlet streams of the second and third extraction cycle columns. This change improved the hydraulics of these columns which significantly improved interface level control. Also, the vent lines to the samplers on the columns in the second and third extraction cycles were enlarged to minimize column upsets when samples were taken.

1.12 Processing Problems During First Extraction Cycle. From the beginning of the continuous operation portion of the run, the seven-stage mixer-settler (used to scrub the TBP from the strip column product stream with Amsco) did not function properly. Aqueous flow through the mixer-settler was erratic, which made it difficult to control the density of the product stream out of the product evaporator. Shutting off the first stage mixer motor temporarily solved this problem. Then, about midway through the run, the Amsco raffinate stream from the mixer-settler stopped even though the Amsco scrub stream was still being introduced. The remainder of the run was completed with the mixer-settler out of service. After the run it was found that Versene, which had been used prior to the run as a decontaminating solution, had plugged the raffinate line. The poor performance of the mixer-settler did not seriously affect the throughput or efficiency of the extraction system, however.

A combination of pulser trouble and suspected solids in the dissolver product (from Spert fuel) caused the first-cycle extraction column not to function properly during the last part of the run. The system was operated for about two days at half rate because the extraction column would flood at higher rates. During this time, several batches of raffinate containing significant quantities of uranium were produced and had to be recycled. One cause of these problems was a worn pushrod on the air-pulser poppet valve; this resulted in inadequate opening of the valve and thus reduced the pulse amplitude. Also, solids are believed to have contributed to the trouble by accumulating on the sieve plates in the column because, after the pulser trouble had been corrected, the column still flooded at flowsheet rates. As a result, the first-cycle extraction system was operated at 3/4 flowsheet rate during the last four days of the run. About two weeks later, when the system was started up again to recover neptunium from some raffinate, the extraction column performed properly at full flowsheet rates. It is believed that solids were gradually washed from the extraction column during the last part of the fuel processing campaign.

1.13 Processing Problems During Second and Third Extraction Cycles. Second-cycle product, containing about 20 kg of uranium, was inadvertently transferred to a hot salvage cell because of a leaking RVC valve on a transfer pump between the second and third extraction cycles. All of the uranium was recovered; 18 kg were recovered by recycling the product to the second extraction cycle system; the remaining amount was recovered later along with neptunium from the second cycle raffinate. This problem was temporarily solved by shutting down the extraction system and capping the line from the transfer pump to the hot salvage cell.

Rate control of the feed flow to the second cycle extraction column was poor, as it has been in the past. The feed was metered to the columns by one of two Lapp pumps with remote heads. In the future it is planned to use the pumps in conjunction with a Clarkson feeder; this is expected to improve feed flow-rate control.

1.2 Zirconium Fuel Processing (B. R. Wheeler, G. F. Offutt; PLANT PROCESS ASSISTANCE -- W. G. Morrison; STAFF)

1.21 Process Description. The zirconium fuel processing campaign begun during the year and currently in progress at ICPP is proving the feasibility of using a high-capacity aqueous process for the zirconium alloyed fuels. Now, up to 800 kg of zirconium per day (equivalent to about 9 to 10 kg of uranium per day as PWR seed fuel elements) can be dissolved and processed through the first extraction cycle as compared to only about 90 kg of zirconium per day in the old batch process [3]. This high-capacity process is made possible by employing a soluble neutron poison for primary criticality control in an otherwise non-geometrically-safe dissolver, an approach being pioneered during the current campaign [4]. The safety aspects of using boron as a neutron poison to prevent nuclear excursions have been thoroughly investigated [5] and are summarized in Section I-1.23.

Zirconium alloyed fuels are dissolved semicontinuously in hydrofluoric acid solutions in a modified batch dissolver constructed of Monel (Figure 3). A dissolution and first-cycle extraction flowsheet typical of those used in the startup phase of the campaign and based on extensive experimental work [6,7] is shown in Figure 4. Some process improvements may be expected as the campaign progresses thus resulting in some changes being made in this flowsheet. These flowsheet changes will be covered in detail in future reports. During processing, zirconium fuel elements are charged, batchwise, to the Monel dissolver after it is filled with water (containing 5.0 g/l minimum of natural boron as a nuclear poison) to cushion the force of falling elements. Up to 600 kg of zirconium are charged per batch; the fuel charge is held in a controlled position by a 13-inch-diameter slotted basket inside the 42-inch-diameter dissolver. After fuel charging is complete, the cushioning solution is jetted to a storage vessel, and flow of dissolvent (6.6 - 7.3M HF containing ≈ 4 g/l boron added as boric acid) is started to the dissolver [a]. The dissolvent is fed continuously to the dissolver for about 12 hours while the dissolver temperature is controlled at approximately 60°C.

Fig. 3 Schematic representation of dissolver for zirconium fuels.

[a] The boron content of the dissolvent is continuously monitored by a neutron attenuation instrument to guarantee the presence of the neutron poison in the dissolver. This instrument consists of a neutron source and two neutron detectors, all enclosed in Monel sleeves, suspended in the acid feed tank. The instrument output controls a solenoid valve in the acid feed line to the dissolver and will not permit acid flow unless the boron concentration is higher than the minimum desired concentration of 3.8 g/l.

STREAM	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17 and 18	19	20	
DESCRIPTION	FUEL CHARGE	DISSOLVENT	CHARGE WATER	DISSOLVER PRODUCT	COMPLEXING SOLUTION	COMPLEXED DISSOLVER PRODUCT	IBR	IAF	IAx	IAr	IAP	IBS	IBP	ICx	ICr	ICP	IDx	IDR	IDP	FIRST CYCLE PRODUCT
Flow, l/hr	532 (a)		548 (a)	141 (a)	472 (b)	65	537	500	537	500	65	500	225	500	225	10	200	19		
TBP, %								10.0		10.0		10.0		10.0						
Diluent								Amsco		Amsco		Amsco		Amsco		Amsco				
Zr ⁺⁺⁺⁺ , M			1.0		0.75		0.66		0.66											
F ⁻ , M	6.54		6.34		4.75		4.18		4.18											
Al ⁺⁺⁺ , M				2.0	0.38	1.5	0.52		0.52		1.50									
H ⁺ , M	6.78 (e)		2.49 (e)		1.87 (e)		1.60 (e)		1.46 (e)	0.15	-1.13 (d)		0.005		0.005		0.005	0.5		
NO ₃ ⁻ , M	0.03		0.02	6.0	1.17	4.5	1.57		1.42	0.16	3.36	0.01	0.005		0.02		0.02	2.0		
Sn, g/l			1.42		1.07		0.94		0.94											
Cr, g/l				4.9	0.95		0.83		0.83											
B, g/l	4.1	7.0	4.1		3.1		2.72		2.72											
U, g/l			119 (c)		0.82	0.001	0.72		8 x 10 ⁻⁴	0.77		0.77			1.72		1.72	200		
Density at 25°C	1.03		1.118		1.20	1.23	1.21	0.79	1.20	0.80	1.19	0.79	1.00	0.79	1.00	0.76	1.00	1.27		
U, kg/batch	72 (c)																			
Zr, kg/batch	600																			
Sn, kg/batch	93																			

(a) Average rate for a 12-hour dissolution cycle

(b) Average rate for continuous extraction (24-hour day) includes some jet dilution

(c) Assumes a 40% burnup of uranium (Critical safety assured in absence of burnup, i.e. for up to 16.7 kg fully enriched uranium)

(d) The use of DiBAN in the scrub makes it 1.13M acid deficient

(e) Total acid

CPP S-3583

Fig. 4 Flowsheet for dissolution and first-cycle extraction of zirconium alloy fuels.

Dissolver product overflows continuously from the dissolver and is transferred by a nitrogen-gas lift to a feed adjustment tank (made of Carpenter 20 Cb stainless steel) for continuous complexing. Complexing, or adjustment, establishes proper conditions for low corrosion, long stability, and good uranium extraction. Complexed dissolver product overflows continuously from the complexer vessel to tanks in the first-cycle extraction system. The first extraction cycle for the zirconium alloyed fuels is similar to that used in the continuous processing of aluminum fuels except that five to ten percent TBP is used as the extractant (rather than 3-1/4 percent TBP) because of the difference in dissolver product composition. To assure solution stability, the feed and waste streams in the first extraction cycle are never heated or evaporated. The second and third solvent extraction cycles used for the zirconium process are identical to those used for aluminum alloyed fuels, as shown in Figure 2, Section I-1.1.

1.22 Process Performance. The process has proved to be very satisfactory. An average processing rate of 764 kg of zirconium per day was maintained over one three-week period; rates vary with the actual fuel being processed. Uranium losses have been relatively low -- between 0.2 and 0.9 percent of the uranium input. Decontamination has been good; average gross beta and gamma decontamination factors of 1×10^3 and 8×10^3 , respectively, have been obtained in the first-cycle of solvent extraction. This highly satisfactory operating experience assures the continuing desirability of using this high-capacity aqueous process for the zirconium alloyed fuels.

Although several problems have occurred thus far in the campaign, most of these problems were of a startup nature and were not entirely unexpected since thorough pilot plant proving of this process was bypassed to save both time and money. The problems encountered include corrosion failures of an idle evaporator with titanium tubes in the solvent extraction system and of a flowmeter having a vitreous enamel liner; the emulsification of process solutions due to excessive acid-deficient conditions in the scrub column of the solvent extraction system; and miscellaneous minor instrumentation problems.

1.23 Nuclear Safety Evaluation of the Zirconium Dissolver Vessel Design. The ICPP began using soluble neutron poison as primary nuclear safety control in chemical processing operations early in 1965. This soluble poison innovation enabled use of large non-geometrically-safe equipment for routine dissolution of enriched uranium-zirconium alloy fuel and permitted about a ten-fold increase in zirconium fuel processing capacity. Soluble poison as a natural boron compound is added continuously to the dissolver system in the aqueous dissolvent stream.

Extensive neutron diffusion calculations were performed to indicate the safety of the poisoned dissolver under all possible normal and abnormal operating conditions. Initial calculations showed that a metal-volume fraction of 0.6 was the most reactive condition for PWR fuel to be processed. For this condition, together with the most severe abnormal operating condition conceivable, a natural boron concentration of 3.8 g/l was calculated to give a k_{eff} of 0.9; under normal operating conditions, the maximum k_{eff} expected is less than 0.8 with this boron concentration which was selected for plant use. A detailed report of the nuclear safety design calculations is presented in IDO-14647 [8].

A closed-loop, borated-water cooling system was installed for heat removal and to ensure no dilution of boron in event of a leak into the dissolver system.

No other water lines were connected to the dissolution equipment. Dual boron detectors were installed in the dissolvent tank for continuous monitoring of the boron concentration. If either instrument indicates less than the required boron concentration, a solenoid valve in the dissolvent line closes to prevent flow to the dissolver.

In situ neutron multiplication measurements were made as part of the pre-startup tests. These tests were made with unirradiated PWR fuel subassemblies. Fuel arrays containing up to 9.9 kg U-235 were flooded with borated water containing 3.8 g/l. Maximum multiplication measured was less than two. Multiplication measuring equipment was left in place to monitor initial dissolutions. Both unirradiated and irradiated fuel dissolutions were monitored. Count rates measured were essentially constant during the course of the individual dissolutions and approximately equal to the background counts. Also, there was no gradual increase in count rates which would be indicative of a heel buildup during actual plant dissolution operations over a significant period of time. In confirmation of this, a complete cleanout of the dissolver after this trial period produced a heel of less than one percent of the total uranium throughput.

1.3 Stainless Steel Fuel Processing (B. R. Wheeler, R. W. Legan; PLANT PROCESS ASSISTANCE SECTION)

The ICPP inventory of stainless steel fuel elements from the Vallecitos Boiling Water Reactor (VBWR) was processed in the existing SIR process equipment in E and F Cells so that uranium accountability data could be obtained during the 1965 calendar year. A summary of the run is presented in the following sections. Full details of the operation, including the capabilities of the plant, operating difficulties, modification to the process flowsheet, and a brief description of the process equipment, are reported in a topical report, IDO-14658 [9].

1.31 Process Description. A schematic diagram of the principal components of the dissolution and first-cycle extraction system and a typical chemical flowsheet of process conditions are shown in Figure 5.

The VBWR fuel elements were dissolved by a two-step batch dissolution process. In the first step, the stainless steel was dissolved in 37 liters of 6M sulfuric acid or about 300 percent of the stoichiometric amount of acid required. Steel wool was charged to the dissolver with the fuel elements to initiate the reaction, and a digestion time of 2.5 hours was required. A uranium dioxide slurry left after the first dissolution step was dissolved by addition of 15 liters of 6M nitric acid to the sulfuric acid solution; the mixture was maintained at the boiling point for an additional hour. The dissolver contents were then transferred to a coarse feed adjustment tank which contained concentrated nitric acid. Adjustment with nitric acid was necessary for salting the uranium into the organic phase during the subsequent extraction step. The dissolver was then water rinsed, before being recharged with fuel elements, to remove nitrate ions which passivate stainless steel to sulfuric acid even in the presence of steel wool. During rinsing, the dissolver was washed to a nitrate ion concentration below 0.01M before the next sulfuric acid dissolution step was started. A complete dissolution cycle required slightly over five hours.

The adjusted dissolver product from the dissolution steps was processed through a solvent extraction system using 10 percent TBP in Amsco to isolate

Fig. 5 Flowsheet for dissolution and first-cycle extraction of stainless steel alloy fuels.

the uranium. Concentrated product from the first cycle was stored for future processing through two hexone extraction cycles.

1.32 Process Performance. Fuel elements containing a total of 37.0 kg of uranium (32.8 kg of U-235) and approximately 514 kg of stainless steel were processed during the run. In addition, eight kilograms of uranium in a uranyl sulfate solution were processed through the solvent extraction system. Overall uranium recovery from the first extraction cycle was 99.69 percent. Total uranium losses to the extraction, scrub, and strip column raffinate streams were 93.2, 2.1, and 44.5 grams, respectively. Average rates achieved during the run were as follows: a dissolution rate of 1.05 kg of uranium daily, a solvent extraction rate of 0.97 kg of uranium daily, and a waste generation rate of 267 gallons per kg of uranium processed. Approximately 89 percent of the waste from the run was generated as raffinate from the extraction column. The remainder was generated as raffinates from the scrub column and a solvent wash mixer-settler.

The high uranium losses during the run were largely caused by two related factors, viz, erratic flow rates of streams to the extraction column and a high concentration of siliceous solids in the dissolver product. Although there were alternate means for transferring the aqueous dissolver product stream to the extraction column (ie, an airlift or a feed metering pump), satisfactory flow control was impossible with either. The best control was achieved with the airlift; however, solids periodically plugged the airlift which necessitated using the pump.

While attempting to maintain the flowsheet rate of 32 l/hr, the aqueous feed rate to the extraction column ranged from 0 to 80 l/hr with a standard deviation on a day-to-day basis varying from 4.5 to 13.3 l/hr. Flow control for the organic stream was significantly better. The rate ranged from 25 to 42 l/hr with a standard deviation varying between 1.8 and 4.0 l/hr. As a consequence of these widely varying flow rates, the volume ratio of the aqueous and organic streams also varied; the standard deviation of this ratio varied from 0.16 to 0.44. When the average volume ratio of the aqueous-to-organic streams increased from 1 to 1.4, a four-fold increase in uranium losses to the raffinate stream was observed. During one period of exceptionally erratic flow rates, the uranium concentration in the raffinate stream was over an order of magnitude higher than during periods of steady flow.

As the run progressed, an accumulation of siliceous solids in the feed tanks became increasingly troublesome. The solids increased the feed flow control problems and periodically plugged the feed lines. Water used to flush the plugged lines adversely affected the process by diluting the feed and lowering the salting strength in the extraction column. In addition, 32 hours of processing time were lost while the plugged lines were flushed.

The siliceous solids content varied in different portions of the run. The feed containing the highest concentration of siliceous solids contained less than 24 percent of the uranium recovered during the run; however, greater than 53 percent of the uranium losses experienced during the run were incurred during this period.

At flowsheet rates, the wash column consistently flooded; therefore, the volume ratio of the organic and aqueous phases in this unit was reduced from

1/10 to 1/48. A test mock-up of the column showed that the 1/4-inch packing was the cause of the problem and that the problem could be eliminated by replacing the packing with 3/8-inch Raschig rings or by pulsing the existing column. Neither approach could be employed for this run.

1.33 Conclusions. There is now no intent to employ again the small-scale equipment used on this run for processing other stainless steel alloyed fuels. An electrolytic dissolver is currently being installed at the Savannah River Plant for processing this type of fuel. However, should an incentive ever develop to process additional stainless steel fuel at ICPP using the sulfuric acid process, consideration would be given to modifying the product wash column and the feed control system for the extraction column. Also, consideration would be given to the removal of solids from the dissolver product by proven mechanical methods or by development of some chemical dissolution technique.

In future operations, the processing rate of similar stainless steel fuel could be increased to 1.5 kg/day while the volume of generated waste can be reduced by a factor of 2.8 by making the following flowsheet changes:

(1) By using less sulfuric acid for dissolving the stainless steel; it is believed 200 percent of the stoichiometric requirements would suffice.

(2) By using more concentrated acids; it is believed 7M sulfuric acid and 13M nitric acid concentrations would be suitable for this process.

2. LABORATORY AND PILOT PLANT SUPPORT STUDIES FOR CURRENT ICPP FUEL RECOVERY PROCESSES

2.1 Silicon in Aluminum Alloy Fuels -- Problems Related to Processing of ATR Fuel (K. L. Rohde, R. G. Butzman; CHEMISTRY SECTION)

Over the years at the ICPP, silicon in aluminum alloy fuels has been directly and indirectly responsible for a number of processing problems. Appreciable experimental work has been done with specific fuel types in order to anticipate and resolve processing difficulties associated with silicon. Fuel element components with an overall silicon content ranging from 0.3 to 1.3 percent have been tested in the laboratory [10, 11]. (Test reactor elements containing up to 1 percent silicon--and, on occasion, some exceeding that amount--have been successfully processed in the plant.) The chief areas of concern are reduced rates of fuel dissolution and the presence of undissolved solids in the dissolver product. The latter can contribute to surfactancy in the extraction columns, can cause clogging at various places in the lines, and also can increase slightly the uranium loss.

2.11 Historical Background. Varying conditions within the process streams result in differences in behavior of the siliceous substances; ie, the amount of silicon present in the fuel does not always dictate the degree of trouble that will occur downstream from the dissolver. Laboratory studies by B. E. Paige et al [12] (plus plant application) have demonstrated that, in some cases, siliceous solids in the dissolver product from aluminum fuel can be tolerated. The addition of 100

ppm gelatin successfully inhibited surfactancy in pulsed solvent extraction columns using TBP [13].

Investigation of aluminum alloy dissolution rates in mercury-catalyzed nitric acid by R. D. Fletcher et al revealed that silicon is among the three elements found to have the greatest passivating effect [14]. The best means of combating the silicon effect in this case is increased catalyst concentration. Dissolution rates for several aluminum alloys were measured in 0.005 and 0.05M mercury [14]. The increase in dissolution rate in going to the higher mercury concentration, expressed as instantaneous dissolution rate at 15 g Al/l, ranged from a factor of 6 (for pure aluminum) to greater than a factor of 100.

The most recent study involving silicon-bearing fuel was performed with some unirradiated, trial ATR fuel specimens which were unusually rich in silicon. These particular elements were fabricated by welding the fuel plates at their edges with Type 4043 aluminum alloy weld metal to form sideplates, instead of the previous practice of swaging the fuel plate edges into grooved sideplates of low silicon aluminum alloy. Type 4043 aluminum contains five percent silicon which results in an overall silicon content of 1.35 percent for a 19-plate fuel element. The method of fabrication that employs the welding technique represents a significant cost savings over the grooved sideplate fuel assembly. The objective of the current investigation was to determine the process implications of using these fuel elements in the ATR.

2.12 Experimental Findings with ATR Fuel. An ATR fuel specimen, composed of fuel plates and Type 4043 aluminum alloy sideplates, was dissolved in mercury-catalyzed nitric acid. Dissolution was very slow, requiring about 30 hours at boiling to complete. The calculated overall silicon content for this test piece was 1.7 percent, somewhat above the average content of an entire fuel element. The resulting dissolver product mixture contained undissolved solids amounting to 1.96 percent of the initial fuel element weight. Emission spectrographic analysis showed these granular solids to be an estimated 30 to 60 percent silicon, about 10 percent aluminum, and to contain small amounts of copper and iron. An X-ray diffraction analysis revealed the major crystalline components to be silicon and aluminum. Silica could not be detected; however, SiO₂ and its hydrates are almost invariably amorphous under these conditions.

In order to form a basis of comparison for the dissolution rate of Type 4043 aluminum alloy to other aluminum alloys, a "standard" test was performed. A coupon of Type 4043 aluminum (prepared from an ATR element sideplate) was dissolved in 6.6M HNO₃-0.05M Hg(NO₃)₂ at 90 + 1°C. The alloy was quite resistant under these conditions, requiring about 25 hours to dissolve. Table III compares dissolution rates of Type 4043 aluminum, high-purity aluminum, and aluminum alloy X-8001 [11], all under the same conditions. The difficulty of dissolving the Type 4043 alloy is apparent.

For the purpose of comparison with the difficultly dissolvable ATR side plates, a dissolution test was made on the ATR fuel plates only in 6.3M HNO₃ - 0.012M Hg(NO₃)₂ with continuous boiling. The fuel plates completely dissolved in 45 to 50 minutes; dissolution was an estimated 95 percent plus complete in 30 minutes. The undissolved granular solids resulting amounted to 0.90 weight percent of the fuel plates and had a composition of about 50 percent silicon, 30 percent aluminum, < 0.5 percent uranium, with small amounts of boron, magnesium, iron, copper, manganese, and nickel.

TABLE III
DISSOLUTION OF ALUMINUM ALLOYS
IN NITRIC ACID DISSOLVENT AT 90°C

Material	Batch Dissolution Time to 30 g Al/l (minutes)	Instantaneous Dissolution Rate at 15 g Al/l (mg/cm ² -min)
High-purity Al	10	290
Al alloy X-8001	14.5	160
Type 4043 Al alloy	570	2

In summary, the ATR fuel experimentation showed that

- (1) The Type 4043 aluminum alloy sideplates dissolved only about one-thirtieth as rapidly as the fuel plates
- (2) The solids produced were largely a silicon-rich alloy of silicon and aluminum which was essentially insoluble in nitric acid, even when the nitric acid was made 0.7M in hydrofluoric acid
- (3) The solids were not sufficiently surface active to indicate difficulties in a pulse column
- (4) There was no significant holdup of uranium on the solids
- (5) The principal process difficulties with this fuel would be associated with the low dissolution rate and the bulk of the solids to be handled through the solvent extraction system.

As a result of these tests, other sideplate materials suitable for weld build-up are being sought.

2.2 Zirconium Process -- Uranium Solubility (K. L. Rohde, R. G. Butzman; CHEMISTRY SECTION)

2.21 Solubility of Uranium Tetrafluoride in Chromic Acid. The species of uranium tetrafluoride which has been produced by inadvertent reprecipitation following the batch dissolution of uranium-zirconium fuel has been identified by X-ray analysis to be mostly $UF_4 \cdot 3/4 H_2O$ with small amounts of an unidentified material [15]. A small amount of the uranium tetrafluoride may also come out of solution routinely and coat on the inside surface of the dissolver vessel. This must be removed periodically by dissolution with chromic acid (CrO_3 dissolved in water). The zirconium fuel process flowsheet initially called for a heel cleanout with 0.1M CrO_3 solution at 95°C. However, the heating arrangement for the dissolver vessel is such that it is not convenient to achieve this temperature within the dissolver. Therefore, the dissolution rate of $UF_4 \cdot 3/4 H_2O$ in 0.1M CrO_3 has been investigated to determine what conditions are required for an effective heel cleanout in the dissolver.

Uranium tetrafluoride was prepared in the laboratory by dissolving pure uranium wire in 10M HF solution at near boiling temperatures; precipitation is spontaneous under these conditions. Examination by X-ray diffraction of the resulting precipitate indicated the major crystalline component (ie, >80 percent) to be $\text{UF}_4 \cdot 3/4 \text{H}_2\text{O}$. In a series of experimental runs to redissolve the precipitate, quantities of uranium tetrafluoride and volumes of chromic acid solution were selected so as to give a final uranium concentration of 5.0 g/l. Weighed portions of uranium tetrafluoride were introduced into the dissolving solution as a granular solid.

The first dissolution test, using 0.1M CrO_3 and a temperature of 55°C, had 7.1 times the stoichiometric amount of CrO_3 required by Equation (1).

Two subsequent tests were made at 5 and 2 times the stoichiometric amount. All of these tests employed intermittent stirring, ie, a few seconds of stirring every 4 or 5 minutes. During these tests, it became apparent that the dissolution rate was probably more a function of agitation than of CrO_3 concentration. Therefore, a fourth and final test was a repeat of Test 3, with the exception that it was stirred continuously. The results are summarized in Table IV.

TABLE IV
DISSOLUTION OF URANIUM TETRAFLUORIDE
IN CHROMIC ACID AT 55°C

Test Number	CrO_3 Concentration (M)	Excess of CrO_3 over Stoichiometry (percent)	Type of Stirring	Time Required for Complete Dissolution (minutes)
1	0.100	610	Intermittent	23
2	0.070	400	Intermittent	43
3	0.028	100	Intermittent	90
4	0.028	100	Continuous	40

These data indicate that a 100 percent excess of chromic acid is ample for uranium removal under conditions where agitation is possible and a temperature of at least 55°C can be achieved. Experience in the plant will be required to define the most practical conditions for individual pieces of equipment where agitation or temperature control are problems.

2.22 Solubility of Uranium Tetrafluoride in Dissolver Charging Water. It has been suspected that uranium tetrafluoride (traces left behind from preceding batch dissolutions) dissolving in the charging water may be indirectly responsible for variations in the uranium material balance during zirconium fuel processing. Analyses of the charging water have shown it to contain varying amounts of dissolved uranium at different times. Experimental work was designed to

determine if the boric acid concentration in the water or the composition of the atmosphere over the charging water influence uranium solubility. (While the charging water is in the dissolver, it is under a nitrogen atmosphere; but while it is on standby in a holding tank, it is under an air atmosphere.)

Demineralized water from the plant was used to prepare "charging water" in the laboratory. Three test solutions with boron concentrations of 0, 4.0, and 7.0 g/l were prepared with boric acid. Laboratory-produced uranium tetrafluoride (analyzed as >80 percent $\text{UF}_4 \cdot 3/4 \text{H}_2\text{O}$) was used as the solute. The samples were equilibrated for 120 hours at 30°C. Results are shown in Table V.

TABLE V
SOLUBILITY OF URANIUM TETRAFLUORIDE IN WATER
CONTAINING BORIC ACID AND IN CONTACT WITH AIR OR NITROGEN

Calculated Boron Concentration (g/l)	Type of Atmosphere	Dissolved Uranium (g/l)
0.0	Air	1.84 ± 0.22
4.0	Air	1.74 ± 0.20
7.0	Air	1.82 ± 0.22
0.0	N ₂	0.140 ± 0.02
4.0	N ₂	0.133 ± 0.02
7.0	N ₂	0.120 ± 0.02

These data indicate that (a) the boron concentration has essentially no effect on the solubility of uranium tetrafluoride but that (b) the exclusion of oxygen from the system would greatly reduce the solubility of uranium tetrafluoride in the dissolver charging water.

2.3 Zirconium Process -- Stability of the Adjusted Dissolver Product (K. L. Rohde, M. W. Wilding; CHEMISTRY SECTION)

In order to determine the most desirable composition for the adjusted dissolver product stream in certain zirconium process flowsheets and to determine specifically the effect of added nitric acid on the stability of these streams, the stability of pertinent solutions containing fluoboric acids was determined at 23°C as a function of total acid concentration. Table VI shows the solution compositions tested and whether each was stable at the end of a 4- or 30-day incubation period. The data for 4.44M fluoride and 0.73M zirconium are correlated on Figure 6 which indicates that instability can generally be associated with the concentration ratio $[\text{F}-4(\text{B}+\text{Zr})]/\text{Al}$. Where precipitation did occur, the solid was largely $\text{ZrF}_4 \cdot 3 \text{H}_2\text{O}$. While the data given are perfectly applicable at the stated zirconium and fluoride concentrations, they should not be extrapolated to other concentrations.

TABLE VI

SOLUTION COMPOSITIONS TESTED FOR
ZIRCONIUM DISSOLVER PRODUCT STABILITY

Experiment Number	Al(M)	F(M)	Zr(M)	B(M)	H ⁺ (M) (Total)	Period of Stability (days)
1	1.4	4.44	0.73	0.235	1.50	> 4
2	1.0	4.44	0.73	0.235	1.50	> 4
3	0.58	4.44	0.73	0.235	1.50	> 4
4	0.48	4.44	0.73	0.235	1.50	> 30
5	0.38	4.44	0.73	0.235	1.50	> 30
6	0.34	4.44	0.73	0.235	1.50	> 30
7	1.4	4.44	0.73	0.235	1.70	0
8	1.0	4.44	0.73	0.235	1.70	0
9	0.58	4.44	0.73	0.235	1.70	0
10	0.48	4.44	0.73	0.235	1.70	> 4
11	0.38	4.44	0.73	0.235	1.70	> 30
12	0.34	4.44	0.73	0.235	1.70	> 30
13	1.4	4.44	0.73	0.235	1.95	0
14	1.0	4.44	0.73	0.235	1.95	0
15	0.58	4.44	0.73	0.235	1.95	0
16	0.48	4.44	0.73	0.235	1.95	0
17	0.38	4.44	0.73	0.235	1.95	0
18	0.34	4.44	0.73	0.235	1.95	0
19	1.17	3.25	0.53	0.171	1.32	> 30
20	0.83	3.25	0.53	0.171	1.32	> 30
21	0.48	3.25	0.53	0.171	1.32	> 30
22	0.40	3.25	0.53	0.171	1.32	> 30
23	0.32	3.25	0.53	0.171	1.32	> 30
24	0.28	3.25	0.53	0.171	1.32	> 30
25	1.4	4.44	0.73	0.235	1.43	> 4
26	1.0	4.44	0.73	0.235	1.43	> 4
27	0.58	4.44	0.73	0.235	1.43	> 4
28	0.48	4.44	0.73	0.235	1.43	> 30
29	0.38	4.44	0.73	0.235	1.43	> 30
30	0.34	4.44	0.73	0.235	1.43	> 30

Fig. 6 Stability of adjusted dissolver product and raffinate compositions at 23°C (point numbers refer to experimental compositions listed in Table VI).

The zirconium raffinate consisted of 0.51M zirconium, 0.50M aluminum, and 4.2M fluoride; the aluminum raffinate was 1.7M aluminum and 1.0M acid.

A study of the data from earlier studies of blending [19,20,21] revealed that the zirconium raffinate could be added to the heel of aluminum raffinate under certain conditions without danger of precipitation. These conditions are: (a) temperature maintained below 35°C and (b) addition of 90,000 gallons or more of zirconium raffinate to the 10,000 gallons of aluminum raffinate within approximately one month.

Figure 7 shows the stability of aluminum-zirconium fluoride raffinate blends after a period of one month at 35°C as a function of aluminum and zirconium concentration. The temperature limitation is extremely important since rapid precipitation had been experienced at 55°C [19]. The data indicate that for about one month, all mixtures resulting from blending of current zirconium and aluminum raffinates are stable at 35°C and, therefore, localized precipitation due to lack of mixing should not be experienced. Observations for 54 weeks indicated that the chosen blend of 90 percent or greater zirconium raffinate would be stable for a prolonged period.

The observation that as the process solution approached saturation with respect to $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$, the addition of nitric acid decreased the stability is in complete agreement with earlier data on the system [16, 17]. It was observed that the addition of nitric acid did increase stability when the fluoride-to-zirconium/aluminum mole ratio was too low and $\text{ZR}(\text{OH})\text{F}_3 \cdot \text{H}_2\text{O}$ was the precipitating species, or when the mole ratio was too high and aluminum fluoride was the precipitation species [16]. These new data will also clarify the suggestion made elsewhere [18] that stable solutions are generally obtained across a wide range of zirconium and fluoride concentrations by the addition of nitric acid.

2.4 Stability of Blended Zirconium and Aluminum Raffinates (K. L. Rohde, B. J. Newby; CHEMISTRY SECTION)

Stability results obtained from blending zirconium and aluminum raffinates were studied to indicate if zirconium raffinate could be routed to tanks formerly used for aluminum raffinate without danger of precipitation. This storage involved a blending problem since a substantial heel (10,000 gallons) of aluminum raffinate remains in a 300,000 gallon tank after it is emptied as far as practicable by jet transfer.

Fig. 7 Stability of blends of aluminum and zirconium process raffinates at 35°C.

2.5 Testing and Production of DIBAN for Use in ICPP Extraction Columns

A semi-continuous dissolution process for the recovery of uranium from spent zirconium-uranium alloy fuels has recently been installed at ICPP [22]. The extractant used in one flowsheet tested during the shakedown operations (Figure 4, Section I-1.2) was ten percent TBP in Amsco diluent. Use of this high TBP concentration in the extractant -- concentrations as low as five percent can be used -- permits extraction with reduced salting strength and thereby can reduce the volume and improve the stability of the aqueous waste produced. Unfortunately, use of the higher TBP concentration results in greater extraction of nitric acid, which could cause increased uranium losses in the strip column raffinate.

Flowsheet conditions proposed to prevent the potential increase in uranium losses include: (a) use of dibasic aluminum nitrate (DIBAN) in the scrub column to neutralize the nitric acid co-extracted with the uranium and (b) use of a more dilute acid stream for stripping.

2.51 Pilot Plant Studies on Effectiveness of DIBAN and Reduced Acid Concentration in Strip Solution. (J. C. Petrie, R. K. Ballard; DEVELOPMENT ENGINEERING SECTION).

Extraction studies were made in the pilot plant to determine the effectiveness of the proposed flowsheet (Figure 4). Operating conditions in the pilot plant simulated the important plant column operating conditions such as pulse amplitude and frequency, total volume velocity, and aqueous-to-organic flow ratio.

The scrub column test verified the following reaction between DIBAN and nitric acid.

For every mole of DIBAN fed to the column, two moles of nitric acid were consumed. Column operation was smooth, and no excessive "crud" formation occurred at the column interface.

The strip column operation was tested using dilute acid (0.005M HNO_3) to strip the uranium from the organic stream. An HETS value of 5.0 feet was obtained in the test which indicated that the uranium stripping efficiency would be adequate in the plant.

In summary, DIBAN effectively neutralized the excess acid in the organic stream of the scrub column, and a dilute acid strip effectively transferred the uranium from the organic stream in the strip column. The pilot plant testing of the scrub and strip column operation for the zirconium fuel processing thus indicated that the plant columns should operate as planned.

2.52 Stability of Basic Aluminum Nitrate Solutions (K. L. Rohde, M. W. Wilding; CHEMISTRY SECTION).

The stability of highly acid deficient aluminum nitrate solutions was studied briefly to determine the suitability of such solutions for actual plant use as scrub solutions.

A study of the stability of 0.7M aluminum nitrate solutions as a function of acid deficiency over the range 0.2 to 1.6N^b showed that, at room temperature, 0.74M aluminum nitrate formed a permanent aluminum hydroxide precipitate at pH 3.6 with an acid deficiency of 1.6N^b. Samples having lower pH and acid deficiency remained stable at least 72 hours. These data confirm and add additional information to the data of Newby [23] and Slansky [24], all of which are shown in Figure 8. Newby showed the relationship of acid deficiency and pH at 2.2M aluminum concentrations; Slansky showed this same relationship with aluminum concentrations from 0.5M Al to 2.0M Al.

Fig. 8 Relationship of acid deficiency to pH of DIBAN solutions with varying aluminum content.

Two types of precipitation are possible in acid-deficient scrub solutions which must be considered in plant application. At acid pH values greater than 3.6 with 0.74M aluminum, a permanent precipitate of aluminum hydroxide will be formed. At lower pH values, aluminum hydroxide may be precipitated locally as base is added to the aluminum nitrate solutions, but this will dissolve with agitation or temporary warming.

From this study and the previous work [23, 24], it appears that a 0.7M aluminum nitrate solution will be stable at room temperature at 0.1N acid deficiency and $\text{pH} \approx 3.45$. Other suitable conditions may be extrapolated from the data.

2.53 Surfactancy Associated With Zirconium in Acid-Deficient Solutions
(K. L. Rohde, L. A. Decker; CHEMISTRY SECTION).

During a cold shakedown run on the zirconium process flowsheet, the plant IB (scrub) column flooded and carried solids over into the IC (strip) column. It was concluded that hydrous zirconium oxide had formed an emulsion-stabilizing surfactant with other substances present under the acid-deficient conditions. Spectrographic analysis of the solids column showed major amounts of aluminum (presumably derived from the slight precipitate in the DIBAN solution used as scrub), zirconium (from that zirconium extracted in the IA column), and phosphorous (from DBP). Stable emulsions were not formed when the pH of the scrub solution was below 2.0, as compared to 2.5 which had been used in the plant initially; corresponding adjustment was made in the plant flowsheet.

2.54 DIBAN Production for Process Use (J. C. Petrie, R.K. Ballard; DEVELOPMENT ENGINEERING SECTION).

DIBAN in a 4M solution, purchased from a commercial supplier degraded rapidly during storage due to the precipitation of aluminum oxide (Al_2O_3). This made the material unacceptable for plant use.

Earlier pilot plant tests had shown [25] that DIBAN could be produced by dissolving aluminum metal in a low-acid, aluminum nitrate solution in the presence of a mercury catalyst. Based on the earlier tests, the ICPP Pilot Plant recirculation dissolver was operated to produce about 20,000 liters of 2.2M DIBAN. The flowsheet for this operation is shown in Figure 9. Some mercury-bearing solids were formed, but their concentration was reduced from 5.0 to 0.5 g/l in the product by providing a settling time of eight hours for the dissolver effluent.

Fig. 9 Flowsheet for DIBAN production in the pilot plant recirculation dissolver.

Samples of the DIBAN produced in the pilot plant have been stored at room temperature to determine the storage life of the solution. The solution has shown no signs of degradation after six months of observation.

2.6 Washing of TBP-Amsco Extraction Solvent (K. L. Rohde, R. G. Butzman; CHEMISTRY SECTION).

An evaluation of the TBP-Amsco solvent recovery system has been initiated. The sodium carbonate technique, which is currently in use at the ICPP, has remained essentially unaltered since its inception several years ago. Specifically, two undesirable effects which may be associated with the washed solvent have been experienced during reprocessing of aluminum fuel. These are (a) very poor decontamination for zirconium-niobium in the extraction and scrub columns and (b) surfactancy in the extraction column. The former leads to excessive contamination of downstream equipment and the latter to restricted production rates. It has been considered that more recently developed wash schemes might be superior to the present ones. The primary goal of the evaluation program is to determine by laboratory and plant tests the relative effectiveness

of the sodium carbonate method and others, thereby providing justification for keeping the present technique or replacing it with a better one. In addition, more quantitative criteria for solvent quality and means of measuring them are needed.

Experimental Program: A search of the literature revealed that washing methods employing some type of sodium carbonate solution treatment are the best known for TBP-Amsco recovery.

Following the literature survey, three variations of the existing ICPP solvent washing method were chosen for comparative testing in the laboratory. These involved the reagents listed in Table VII; all used at flow ratio A/O = 1/10. The three sequential steps listed for each test refer to the three mixer-settlers in series which constitute the solvent washing equipment.

The laboratory tests, will be carried out when representative samples of degraded solvent from the plant streams become available.

2.7 Air Pulser Development (S. J. Horn; DEVELOPMENT ENGINEERING SECTION)

Concurrent with the installation of air pulsers on extraction columns at the ICPP, a mathematical model has been under development describing the characteristics of air pulsers. Such a model is a valuable aid to pulser operation and serves as a guide when designing air pulsers for other columns. The mathematical model developed is a nonlinear, second-order differential equation which expresses the summation of static and dynamic forces acting on the liquid in the pulse column and pulse leg. The static forces are the liquid heads in the pulser system, and the dynamic forces are the inertial and frictional resistances to flow.

Initial development work at the ICPP covered the analog simulation and testing on a 10-inch diameter column [26, 27]. This work has now been extended to three additional extraction columns having diameters of 1.31, 2.07, and 3.07 inches. When testing the air pulsers on these plant columns, provisions were made to obtain experimental data by temporarily substituting rigid plastic tubing for the stainless steel pulse legs. This permitted the analog simulation to be checked with experimental data.

A comparison of pulse amplitudes obtained by analog simulation with those measured in the column pulse legs showed that the computed values deviated considerably from the measured pulse amplitudes and the deviations became greater as the column diameter decreased. With the 1.31-inch-diameter column, a deviation of 30 percent was noted. A study of the original mathematical model [27] and the solutions obtained from the analog computer disclosed that the friction term contained the source of error; specifically, the part of the friction term which expresses the pressure drop due to flow through the sieve plates in the pulse column appeared to be the source of error.

TABLE VII

POSSIBLE VARIATIONS IN TBP-AMSCO WASHING SYSTEM

Test Number	Reagents
1 (present method)	(1) 0.04M HNO_3 (2) 0.5M Na_2CO_3 (3) 0.04M HNO_3
2	Test 1 plus centrifugation
3	(1) 0.5M Na_2CO_3 (2) 2.0M NaOH (3) 0.04M HNO_3
4	(1) 0.3M Na_2CO_3 (2) 0.3M Na_2CO_3 + 0.1M KMnO_4 (3) 0.04M HNO_3

In the original mathematical model [27], the pressure drop due to flow through the sieve plates was expressed by a modified orifice formula, using a constant orifice coefficient of 0.68. While it was recognized at the time that this value was only approximate, pulse amplitudes obtained from the analog computer solutions closely checked the amplitudes measured on the 10-inch column; and, consequently, a more sophisticated mathematical model was considered to be an unnecessary refinement. With the 10-inch-diameter pulse column, however, inertial resistance is much more important than frictional resistance; consequently, errors in expressing frictional resistance had less effect on the final analog computer solution.

Studies of flow through sieve plates [28] have indicated that the orifice coefficient in this application can be greater than 0.9 at moderate velocities. Subsequently, the mathematical model was modified to include the dependence of the orifice coefficient on the velocity through the plate. A relation of the form

$$C_o = K(N_{ReP})^{1/8}$$

where

C_o = orifice coefficient

N_{ReP} = Reynolds's number for a sieve plate based upon the hole diameter

K = proportionality constant

was used in the analog computer program. This refinement in the program brought the difference between the computed and measured pulse amplitudes to within 10 percent except for the 1.31-inch-ID pulse column.

Studies are now underway to clarify the frictional resistance to flow through sieve plates using a laboratory pulse column of dimensions similar to that of the smaller pulse column.

2.8 Solids Flow Control For a Pulsed Solids-Liquid Contactor (E. S. Grimmet; DEVELOPMENT ENGINEERING SECTION).

In a study made locally several years ago [29], the operating characteristics of a pulsed solids-liquid contactor were described. This device has many possible applications in the nuclear processing field; for example, continuous ion-exchange operations, continuous leaching of solids, purification by crystallization, etc. However, little attention was then given to the problems of continuously feeding and metering solids into the column and of removing them from the column.

In a recently completed study at the ICPP, a solids transport and control system has been developed for the pulsed solids-liquid contactor. In principle, solids are fed to the contactor by a constant-flow-rate slurry feeder and are withdrawn from the unit by a constant-inventory slurry feeder; both devices employ fluidized beds for the introduction of solids and slurry gas lifts for movement of solids from one point in the system to another. A complete discussion of the system is published in IDO-14648 [30]; a summary of the results follows.

The feed flow system developed during this study (Figure 10)^[30] receives solids from a slurry gas lift or a solids makeup system and feeds them to the top of the solids-liquid contactor. The system utilizes a bed of solids, fluidized with water or other appropriate process fluid, which is maintained at a constant density by regulating the flow of the fluidizing liquid. The constant density bed is withdrawn at a constant volumetric rate and is introduced into the top of the contactor. Using this system, it is possible to feed Dowex-50 ion-exchange resin into the contactor at controlled rates over a wide range of resin flow rates.

Fig. 10 Feed flow system for a solids-liquid slurry.

The bottom flow system removes solids from the bottom of the contactor and transports them by a gas lift to the top of the same contactor, to the top of a second contactor, or to the next piece of equipment in a process. The bottom flow system developed in this study also uses a fluidized bed. This bed received solids from the downcomer of the bottom plate of the contactor and discharges them into a slurry gas lift line. The solids inventory in the bed is controlled by a system which measures this inventory and regulates the solids outflow so that the inventory remains constant. This system was also tested with Dowex-50 resin over a wide range of solid feed rates and contactor pulse frequencies and amplitudes. Under all test conditions, the system functioned smoothly and met the established performance criteria [30].

A study was also made of the performance of a 1/4-inch-pipe air lift and of 4.1-mm- and 7-mm-ID glass tubing slurry air lifts. Slurries were transported successfully in these small diameter lifts, but the performance data could not be correlated with those from published work based on larger diameter lifts.

2.9 Effect of Weld Imperfections on Corrosion in Waste Tanks (D. W. Rhodes, T. L. Hoffman; CHEMISTRY SECTION).

A corrosion evaluation is being conducted on specimens containing common weld imperfections to determine the significance of these in limiting the life of storage tanks containing raffinates from radiochemical processing. In any large field-welded structure, the two most common imperfections, burnthrough and tungsten inclusion, are difficult to avoid totally. The purpose of the present work is to show to what extent, and by what means, these imperfections are sites for the initiation of corrosive attack in order to determine whether the specifications for welding should be made more exacting.

Samples were trepanned from the bottom of two raffinate storage vessels during their erection recently at the ICPP. The vessel bottoms were assembled by butt-welding Type 304L stainless steel plates, using the tungsten-inert gas process with American Welding Society, Classification ER 308, bare electrodes. Trepanning was conducted so as to include a 10-inch-long weld deposit between two semicircular wrought plates, 0.325 inch thick.

These samples included imperfections associated with the welding practices that were used to erect the vessels. Some contained areas where excessive heating or "burnthrough" existed. Burnthrough could cause permanent damage by unfavorably altering the chemical and mechanical properties of the weld deposit or its adjacent wrought alloy. (For example, intergranular oxidation occurs during incipient melting of the alloys under an inadequate concentration of inert gas.) Another defect observed in the samples was tungsten inclusion in the weld deposit. This condition arises from choking or sticking the tungsten electrode tip into the molten deposit during the initial welding steps.

Two additional trepanned samples used for the experimental work were representative of welding which meets the minimum local requirements for the erection of large vessels in the field. In addition to these samples, specially prepared "imperfect" and "acceptable" welded coupons were fabricated in the shop using the tungsten-inert gas welding process. These were corrosion-evaluated together with coupons from the trepanned storage vessel samples.

The welds were first tested according to the provisions contained in ASTM A262, "Recommended Practice for Boiling Nitric Acid Test for Corrosion-Resisting Steels" (Huey tests). Weld-tabs from the storage vessels, as well as

from the shop, lost less than 1 mil per month average after five 48-hour boiling periods. Detailed data are given in Table VIII. On three shop welds

TABLE VIII

RESULTS OF HUEY TESTS WITH COUPONS OF TYPE 304L
STAINLESS STEEL CONTAINING COMMON WELD IMPERFECTIONS

Condition of Coupon	Coupons from Raffinate Tanks (mils/month penetration)						Average
	1st Period	2nd Period	3rd Period	4th Period	5th Period	6th Period	
Tungsten Inclusion	1.2	0.7	0.6	0.6	0.5	---	0.7
Burnthrough	0.6	0.5	0.5	0.6	0.5	---	0.5
Acceptable	0.4	0.4	0.4	0.4	---	---	0.4

Condition of Coupon	Coupons Welded in Shop (mils/month penetration)						Average
	1st Period	2nd Period	3rd Period	4th Period	5th Period	6th Period	
Tungsten Inclusion	1.3	0.9[a]	0.7	0.6[b]	0.6[c]	0.6	0.8
Burnthrough	0.6	0.5	0.5	0.5	0.6	0.8	0.5
Acceptable	0.6	0.5	0.5	0.5	0.6	0.7	0.5

[a] White deposit identified as W₂O₃ by microprobe examination.

[b] W-308L intermetallic solid solution identified.

[c] Pits and cracks were observed at W-included sites. Crack length = 3 to 4 times the diameter of the W-inclusion.

involving tungsten inclusion, several white spots between 40 and 80 mils in diameter were visible after the second and succeeding 48-hour boiling periods. Without sectioning the welds, these spots were identified by microprobe techniques as tungsten, or tungsten-308 L intermetallic alloys. At the end of the fifth boiling period, pits up to 20 mils deep were observed. Cracks up to 200 mils long radiated from these pits. Similar effects were sought for but were not found on any of the weld-tabs from the storage vessels.

Other weld-tabs from the storage vessels and from the shop were immersed at 35°C in synthetic first-cycle raffinate representative of the reprocessing of zirconium fuel. In these bench-tests, a sufficient quantity of raffinate was used to cover the weld-tabs and provide a volume of at least 125 ml/in.² of tab surface. The observed general corrosion rates after 572 days were less than 0.015 mils/month (Table IX). No pits or cracks were observed on weld-tabs that were known to contain tungsten inclusions or excessive burnthrough. Presumably, acceptable weld deposit metal covered all the known imperfections of the tabs. Therefore, this test failed to reveal any defective weld structure which would affect the tank life.

In summary, exposed tungsten inclusions corroded rapidly in nitric acid, causing pits and subsequent accelerated corrosion in the immediate area. No effect of covered inclusions was noted during the test reported; but presumably, as these become exposed by the uniform penetration of the surface, accelerated local corrosion would also be experienced. In the course of these tests, there was no evidence of any effect due to "burnthrough".

TABLE IX
CORROSION RATES OF TYPE 304L STAINLESS STEEL
IN ZIRCONIUM FLUORIDE PROCESS RAFFINATE AT 35°C

<u>Condition of Coupon</u>	<u>Coupons from Raffinate Tanks (mils/month penetration)</u>		
	<u>120 Days</u>	<u>240 Days</u>	<u>572 Days</u>
Tungsten Inclusion	---	---	0.011
Burnthrough	0.005	0.003	---
Acceptable	---	---	0.004
<u>Condition of Coupon</u>	<u>Coupons Welded in Shop (mils/month penetration)</u>		
	<u>120 Days</u>	<u>240 Days</u>	<u>572 Days</u>
Tungsten Inclusion	0.017	0.009	0.009
Burnthrough	---	---	0.006
Acceptable	0.008	0.005	0.006

3. SUPPORT STUDIES FOR SCHEDULED ICPP PROCESSING OPERATIONS

3.1 Reprocessing of EBR-I Core 2 Fuel (K. L. Rohde, M. E. Jacobson; CHEMISTRY SECTION)

The Experimental Breeder Reactor-I (EBR-I) has had several cores of varying composition during its period of operation. Cores 1, 2, and 3 each contained about 50 to 60 kg of fully enriched uranium. Core 1 was processed at ICPP during 1954 [31]. During the past year, development work was completed to ensure the chemical feasibility of recovery of Cores 2 and 3 at ICPP. Since each core presented unique problems, they are discussed separately; Core 2 in this Section (3.1) and Core 3 in the following Section (3.2).

Large portions of Core 2, which was a 98-percent-uranium, 2-percent-zirconium alloy clad in stainless steel, were melted in the reactor during a transient; the core was subsequently disassembled and examined, and the pieces of fuel rod and melt were packaged in small steel cans [32]. Because of the unusual nature of the material, the reprocessing has been delayed for several years.

3.11 Proposed Chemical Flowsheet. Table X gives the calculated compositions of both the melted and unmelted fuel rods. In terms of chemical material balance for reprocessing, the differences are not particularly significant; but the intimate mixing of zirconium, uranium, and stainless steel components in the melt suggested that mixed nitric-hydrofluoric acids should be used for the dissolvent in an expendable plastic or metal vessel. On these bases, the chemical material balance flowsheet of Table XI was written, and the dissolution was tested

TABLE X
TYPICAL COMPOSITION OF EBR-I CORE 2 FUEL

Melted Fuel[a]			Unmelted Fuel Rods[b]		
		(g/kg of uranium)			(g/kg of uranium)
Fuel Alloy	{ Uranium Zirconium	1000 20	Fuel Alloy	{ Uranium Zirconium	1000 20
Stainless Steel	{ Iron	95	Stainless Steel	{ Iron	74
	{ Chromium	27		{ Chromium	21
	{ Nickel	14		{ Nickel	11
NaK	{ Na K	3	NaK	{ Na K	1
		9			5
O (as oxide)		52			
Total		1220	Total		1132

[a] Based on analysis of melt samples[32].

[b] Based on geometry of original fuel[32], burnup[32], and the amount of fuel to be processed.

TABLE XI
CHEMICAL MATERIAL BALANCE FLOWSHEET FOR INTEGRAL
DISSOLUTION AND INITIAL EXTRACTION OF EBR-I CORE 2 FUEL PINS

Fuel Charge: 1020 g uranium-zirconium alloy 106 g stainless steel cladding 6 g NaK							
	Dissolution Reagent	Dissolver Product	Neutralization Reagent	Adjustment Reagent	Adjusted Feed	Scrub	Extractant (hexone)
Volume, l	5.0	5.0	2.0	1.5	8.5	23.0	31.5
H ⁺ , M	12.6	6.0	---	---	0.24	---	---
U, g/l	---	200.0	---	---	118.0	---	---
Zr, g/l	---	4.0	---	---	2.4	---	---
Fe-Cr-Ni, g/l	---	21.0	---	---	12.5	---	---
NaK, g/l	---	1.2	---	---	0.7	---	---
Al, M	---	---	---	2.0	0.35	2.0	---
NH ₄ ⁺ , M	---	---	14.0	---	3.3	0.43	---
NO ₃ ⁻ , M	12.0	8.4	---	6.0	6.0	6.0	---
F ⁻ , M	0.6	0.6	---	---	0.35	---	---
OH ⁻ , M	---	---	14.0	---	---	0.43	---

on aliquots of the fuel. The solvent extraction portion of the flowsheet is conventional and did not require preliminary testing.

3.12 Safety Aspects of Handling the Fuel. Prior to any chemical manipulations of the fuel, detailed consideration was given to several unusual safety problems.

(1) NaK Release. This fuel had last been handled in an atmosphere of nitrogen containing 1 to 1.5 percent oxygen and a relative humidity of about two percent. Since the NaK would have to react with oxygen or water during some phase of the reprocessing, it was determined that small batches of fuel containing about five grams of NaK would be exposed to the normal air atmosphere of the shielded cell in which the cans were opened and allowed to react spontaneously. Provisions were made for control of any fire which might occur, and the shielding and ventilation system of the hot cell protected operating personnel. For the dissolution tests, a vessel was provided having a head space equivalent to 400 percent of the dissolvent volume. Incremental addition of the reagent was also planned to avoid violent reactions. These steps were based on the belief that the NaK in the unmelted fuel rods was present as a thin film inside the cladding and the NaK in the melts was present in small unassociated pockets. The reactivity of either of these could be controlled by the dissolution rate of the major constituents which, in turn, was controlled by the rate of addition of the reagent.

(2) Sensitivity of Uranium-Zirconium Alloy in Nitric Acid. The potential hazard of explosion of the epsilon phase of uranium-zirconium was avoided by providing sufficient fluoride to ensure an excess of four moles of fluoride per mole of zirconium in the dissolver product solution.

3.13 Results of the Development Studies.

(1) Reactions of NaK. Slight fuming and some isolated brief flames were noted as the cans were opened and the fuel pieces and melt were exposed to the moist air of the hot cell. There was no indication of sustained, exothermic reaction, and it is judged that there will be very small probability of fire. The fuel and melt pieces became sticky very rapidly as moisture from the air reacted with the sodium-potassium oxides on the surface.

(2) Dissolution. Dissolution of various small samples of melt and fuel, following the flowsheet of Table XI, proceeded rapidly. It was not necessary to supply heat to initiate or sustain the reaction; the fuel reacted essentially instantaneously as reagent was added. In view of this high reactivity, it may be desirable to reduce the concentrations of acids in the dissolver reagent of Table XI for larger scale dissolutions. There were no residues from dissolution, except for thermocouple wires which were incorporated in the melt pieces.

3.14 Large Scale Processing. Preliminary plans have been made for the equipment and operating procedures for the processing of a full core. A "custom" approach involving small batches and close surveillance of the operation will be used because of the safety problems discussed earlier and the criticality problems associated with handling compact masses of fully enriched uranium. Dissolution will be conducted in the ICPP Multicurie Cell which is equipped for remote-handling, direct-viewing operations in a shielded environment.

3.2 Reprocessing of EBR-I Core 3 Fuel (D. W. Rhodes, M. W. Wilding; CHEMISTRY SECTION)

Two dissolution procedures for EBR-I, Core 3 fuel (fully enriched, 98-percent-uranium, 2-percent-zirconium fuel meat clad in Zircaloy-2) have been devised which will completely dissolve the fuel pins, prevent precipitation of zirconium fluoride salts, avoid excessive dissolver corrosion, and prevent the formation of the epsilon phase of the alloy. Both procedures use nitric-hydrofluoric acids. In the first, all of the required reagent is charged to the dissolver initially, but the dissolver temperature is limited to about 50°C to limit corrosion until the cladding has dissolved and the fluoride is partially complexed; then the temperature is raised to the boiling point to accelerate the dissolution of the uranium alloy. In the second, the dissolution is initiated in nitric acid-dilute hydrofluoric acid, and the required additional reagent is added incrementally as the dissolution proceeds. Either approach requires careful control of dissolution conditions. The first is preferred for plant use because of the greater operating simplicity.

3.21 Fuel Description. The fuel rods are in the form of cylinders, 0.364 inch diameter by approximately 20 inches long, and contain 98-percent uranium, 2-percent zirconium clad with 0.020-inch Zircaloy-2. Each rod consists of three sections. The two end sections contain natural uranium, and the 8.5-inch-long center section contains approximately 240 g of uranium-235. The end sections of natural uranium have already been removed from the fuel rods, leaving only the fully enriched section for reprocessing.

3.22 Dissolution.

(1) Batch Dissolution with Temperature Control. A batch-type dissolution that appears to satisfy the plant requirements would be to treat the fuel rods with an initial charge of nitric-hydrofluoric acid dissolvent at 50°C to dissolve the Zircaloy cladding. This would take approximately one-half hour then the temperature should be slowly raised to the boiling point to obtain maximum dissolution rate on the uranium alloy. It is expected to take two to three hours for the dissolution of one batch. Table XII shows a simplified flowsheet for this type dissolution based on available laboratory information [33].

(2) Batch Dissolution with Incremental Reagent Addition. A Niflex-type batch dissolution process was studied by making an initial addition of hydrofluoric-nitric acid dissolvent to the fuel in the dissolver, heating to 80°C, then continuously adding the remaining portion of the hydrofluoric-nitric acid over a two-hour period. Table XIII shows a simplified flowsheet for this type of batch dissolution, and Figure 11 shows the fluoride-to-zirconium mole ratio during the dissolution period. The F/Zr mole ratio is maintained above 3.4 to avoid formation of the unstable epsilon phase [34,35].

3.23 Corrosion. A plant dissolver of Carpenter-20 alloy is available and has been considered for the dissolution of the EBR-I Core 3 fuel. Literature data for the corrosion of this alloy in mixed nitric acid-hydrofluoric acid systems have been extrapolated for the proposed flowsheet. The anticipated 5 to 20 mils per month general corrosion rate for the Carpenter-20 alloy vessel, while high, will be tolerable for the short run proposed.

TABLE XII

EBR-I CORE 3 DISSOLUTION USING TEMPERATURE CONTROL

	<u>Fuel</u>	<u>Dissolvent</u>	<u>Dissolver Product</u>
Volume for batch, liters	----	3.2	3.1
U, g/batch	526 (2 pins)	----	526.0
Zr, g/batch	58	----	58.0
U, g/l	----	----	169.6
Zr, <u>M</u>	----	----	0.21
F, <u>M</u>	----	0.86	0.89
H ⁺ , <u>M</u>	----	6.86	2.64
NO ₃ , <u>M</u>	----	6.00	4.11

TABLE XIII

EBR-I CORE 3 DISSOLUTION USING INCREMENTAL ACID ADDITION

	<u>Fuel</u>	<u>Dissolvent</u>	<u>Dissolver Product</u>
Volume for batch, liters	----	2.45	2.53
Temperature	----	80°C	----
U, g/batch	526 (2 pins)	----	526.0
Zr, g/batch	58	----	58.0
U, g/l	----	----	227.4
Zr, <u>M</u>	----	----	0.27
F, <u>M</u>	----	1.38	1.45
H ⁺ , <u>M</u>	----	10.85	5.59
NO ₃ , <u>M</u>	----	9.50	7.20
Dissolution Rate	7 to 10 mg/cm ² -min

Fig. 11 Fluoride-to-zirconium mole ratio during dissolution of EBR-I, Core 3, fuel.

3.3 Neptunium Recovery at ICPP (B. R. Wheeler, W.P. Palica; PLANT PROCESS ASSISTANCE SECTION) (K. L. Rohde, L. A. Decker; CHEMISTRY SECTION)

Transuranic neptunium-237 can be reclaimed at the ICPP to help fill a continuing AEC need [a] for this material by employing proven recovery techniques similar to ones being used or developed at Hanford [36,43,44,45], Savannah River [37,38,40,41,42], and Oak Ridge [39]. At least 400 to 600 grams of neptunium will be available for recovery each year from normal fuel reprocessing. In addition, stored high-activity waste

solutions at the ICPP contain about two kilograms of neptunium equally distributed between the first- and second-cycle waste solutions. Programmatic direction to recover and purify neptunium-237 from normal fuel processing operations, but not from wastes, has been given by the AEC; however, recovery from both sources was investigated and is reported herein.

Neptunium can be extracted from aqueous process solutions only if it is in the IV or VI valence states. Ordinarily, unless a reductant or oxidizer is added to aqueous solutions containing neptunium, a significant portion of the neptunium will be in the inextractable V valence state. This accounts for neptunium being in both first- and second-cycle wastes at ICPP. During past fuel processing campaigns, the extractable species of neptunium was picked up by the TBP organic phase along with uranium in the first cycle of processing while the inextractable species went out with the first-cycle raffinate. In the second cycle of processing, the neptunium was partitioned into the raffinate phase because an acid-deficient Hexone system, as employed at ICPP, does not extract any significant amount of neptunium regardless of the valence.

3.31 Proposed Processing Scheme. Neptunium can be reclaimed from existing ICPP process streams and liquid wastes by solvent extraction, for the most part, in existing equipment. In general, the process consists of separating neptunium, uranium, and plutonium from fission products, partitioning the neptunium from the plutonium and uranium, and purifying the neptunium using an ion-exchange column prior to packaging.

[a] Neptunium-237 is needed for research and for the production of plutonium-238 which has become an important heat source in space power units [36]. Neptunium is formed from radioactive capture of neutrons by uranium as shown by the following reactions:

Most of the neptunium available for recovery at ICPP originates by the first reaction because the principal fuels processed are those which are highly enriched.

(1) Neptunium Recovery During Fuel Processing. Neptunium-237 can be recovered routinely at ICPP during future fuel processing campaigns. By shifting the valence to the VI state with chromic acid, the neptunium is extracted by 3-1/4-percent TBP in Amsco along with the plutonium and uranium. Neptunium and plutonium accompany the uranium through the scrubbing and stripping columns and become part of the feed-stock for the second fuel processing cycle. Neptunium and plutonium do not extract into the acid-deficient Hexone system of the second fuel processing cycle and are retained in the raffinate. The raffinate then becomes the feed for the fission product decontamination cycle of neptunium recovery. A simplified flow diagram for neptunium recovery from reactor fuels is shown in Figure 12.

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Fig. 12 Proposed flow diagram for recovery of neptunium from reactor fuels.

The first neptunium recovery cycle is required for fission product decontamination. It consists of feed preparation, extraction, scrubbing, stripping, and product concentration. The raw feed must be treated before processing by addition of chromic acid to shift the valences of neptunium to the VI state and plutonium to the IV state. The feed may also be concentrated in the headend evaporator. Based on development studies and a plant-scale test, it is estimated that at least 90 percent of the neptunium and plutonium will be extracted by ten percent TBP in the extraction column; most of the fission products remain in the aqueous raffinate. The organic stream is scrubbed with an acid-deficient aluminum nitrate solution to furnish salting strength and to neutralize any residual acid. The neptunium and plutonium are then back-extracted into an aqueous stream. The product from the fission product decontamination cycle is concentrated and stored until a sufficient amount of neptunium has accumulated for further processing.

A plutonium partition cycle is needed to separate plutonium from the neptunium. This cycle is similar to the fission product decontamination cycle except that smaller flow rates and a lower concentration of TBP (six percent) are involved. Because of the lower flow rates involved, smaller size columns and

vessels will be used. The product from the fission product decontamination cycle is first concentrated in an evaporator. Ferrous sulfamate is then added to shift the valence to neptunium (IV) and plutonium (III); the latter is nonextractable in TBP. The neptunium is extracted by six percent TBP in Amsco, scrubbed with aluminum nitrate, stripped by an aqueous stream, concentrated, and then sent to storage. The bulk of the fission products entering this cycle, except for some small quantities of zirconium-95 and niobium-95, remain in the extraction column raffinate with the plutonium. Residual amounts of these two fission products are separated from neptunium in an ion-exchange system, a proven method of purification.

Plutonium could be recovered from the plutonium partition cycle raffinate if desired. Actual disposition of the plutonium will depend on the quantity of the material; depending on economics, it could be discharged to waste or recovered and packaged in the same facilities that will be used for the neptunium [40].

The ion-exchange system for final decontamination of the neptunium product, shown on Figure 13, is based on development work performed at Savannah River Laboratory [37,38,40,41,42] and Hanford [36,43,44,45]. This system has been designed but will not be installed until sufficient concentrated neptunium solution has been collected to warrant the installation. The neptunium solution will be pumped from storage to a jacketed tank where concentrated (6M) nitric acid, hydrazine, and ferrous sulfamate are added and mixed. This feed solution flows by gravity through a bed of either DOWEX 1-X4 or DOWEX 21K ion exchange resin. Most of the contaminants pass through without adsorption, but the neptunium, some plutonium, and some fission products remain on the resin. A wash containing HNO_3 (6M), hydrazine, and ferrous sulfamate effectively removes the residual plutonium; a hot (70°C) wash containing HNO_3 (8M) and either sodium or potassium fluoride is used to remove the fission products zirconium and niobium. These washes are followed by the elution of neptunium with dilute (0.35M) nitric acid. The final neptunium product is routed to a storage tank in a new packaging facility.

Because neptunium is an alpha emitter, special precautions must be taken to prevent the spread of contamination during the packaging operation; this packaging is done inside a shielded glove box, similar to one shown in Figure 13. The glove box is vented to the off-gas system and has a drain to the existing waste system. Thus, there will be no airborne contamination problem, and spilled neptunium will be flushed from the packaging area. Neptunium is drained from the previously mentioned product storage tank into a four-liter loadout tank for measuring and sampling. The measured quantity of neptunium product is then drained into a one-gallon polyethylene shipping container. This container is placed into a plastic bag, the bag sealed, and the container (with several others) is placed into a lightly shielded cask for shipment.

(2) Neptunium from Stored Wastes. Although presently not economically attractive, neptunium in stored waste solution at ICPP could be recovered. The neptunium concentrations in the stored waste solutions, along with other pertinent information, are shown in Table XIV. The presence of more recoverable uranium in second-cycle wastes than in first-cycle wastes provides a greater economic incentive for processing of second-cycle wastes. The higher neptunium concentration of the solution in Tank WM-102 is the successful result of shifting the valence of neptunium, extracting it in the first fuel processing cycle, and

Fig. 13 Proposed layout for Np-Pu purification and packaging facility at the ICPP.

partitioning it in the second cycle during a previous fuel processing campaign. This second-cycle waste has been stored separately from other wastes.

Figure 14 shows a simplified flow diagram of neptunium recovery from stored liquid wastes. These liquid wastes would be intermittently jetted through an existing line into a newly installed surge tank. From the surge tank, the wastes would be continuously jetted through a new line to the fission product decontamination cycle. Neptunium recovery from this point would be identical to that described in the previous section except that a higher concentration of TBP (15 percent) would be used in the fission product decontamination cycle. Since first cycle wastes contain little or no uranium, the uranium partition cycle could be bypassed for these wastes.

TABLE XIV
ANALYSES OF WASTE SOLUTIONS IN STORAGE AT ICPP

	First-Cycle Wastes			Second-Cycle Wastes			
	WM-180	WM-182	WM-183	WM-102	WM-181	WM-184	WM-186
Np:Concentration, g/l	1.9×10^{-4}	6.66×10^{-4}	9.86×10^{-4}	3.90×10^{-3}	4.49×10^{-4}	7.23×10^{-4}	4.14×10^{-4}
Np: Total, g	186	666	434	55	202	759	108
U-235:Concentration, g/l	---	---	---	3.4×10^{-3}	1.3×10^{-2}	1.7×10^{-2}	1.3×10^{-2}
U-235:Total, g	---	---	---	48	5,850	17,850	3,380
Al ⁺ ³ , M	1.65	1.72	1.50	1.76	0.55	0.89	1.44
H ⁺ , M	0.13 ^[a]	1.26	0.82	0.08	0.96	0.28	0.83
Na ⁺ , M	0.22	0.10	0.05	0.09	2.04	2.39	0.09
Volume, liters	977,000	1,000,000	440,000	14,000	450,000	1,050,000	260,000

[a] Acid deficient.

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Fig. 14 Proposed flow diagram for recovery of neptunium from stored wastes.

3.32 Development Work.

(1) Neptunium Recovery from Aluminum Fuel Raffinates. The neptunium fission product decontamination cycle was demonstrated at the ICPP during December 1964 on a full-operating plant scale when neptunium in the second fuel-processing cycle raffinate was recovered and decontaminated from fission products. Neptunium and uranium were extracted from spent fuel in the first fuel processing cycle; neptunium was then separated from the uranium and retained in the second fuel processing cycle raffinate. The valence of neptunium in this raffinate was shifted to the VI state using chromic acid as an oxidant. The raffinate was then processed through existing extraction equipment using ten percent TBP. About 28 grams of neptunium (better than 90 percent of that available) were recovered, concentrated, and stored. (Analytical

determinations indicated that less than three percent of the neptunium was lost to waste.) The plutonium partition cycle and purification of neptunium by ion exchange have yet to be attempted at the ICPP.

Attempts to extract neptunium as Np (IV) after reduction with ferrous sulfamate have been unsuccessful because of low acidity and insufficient residence time in process for complete reduction.

(2) Neptunium Recovery from Zirconium Alloy Fuel Raffinates. Laboratory data from simulated solutions show that neptunium can be extracted from fluoride solutions resulting from processing of zirconium alloy fuels. The simulated solution contained 0.78 g/l chromium (VI) which was added at a concentration of 4.2×10^{-3} g/l to oxidize the Np (V) spike. Contacting a portion of the solution with 10 percent TBP in three stages gave distribution coefficients of 7.6, 5.8, and 1.5, respectively. About 99 percent of the neptunium would be extracted during the first cycle of a neptunium extraction process if three stages could be obtained.

(3) Neptunium Recovery from Solutions Held in Waste Storage Tanks. The second-cycle raffinates containing most of the neptunium from the processed fuel are sent to tanks which also receive the waste solutions from decontamination procedures. The decontamination waste solutions add several ions which might complex neptunium and interfere with recovery, ie, fluoride, citrate, tartrate, and oxalate. The effect of these ions on the extractability of the neptunium was determined in the laboratory by actual extraction experiments.

Much of the volume of the waste solutions was high in sodium nitrate (2M) and low in acid (0.3M). After concentrating by evaporation and/or adjusting the acid content of four different waste solutions, the extraction coefficients were determined with 30 percent TBP in hydrocarbon diluent by contacting in three stages and analyzing the resulting solutions. The distribution coefficients were determined for each solution in the oxidized (Np VI) state, one solution in the supposedly reduced (Np IV) state, and one solution which had no pretreatment (see Table XV). With adequate salting strength and neptunium in the oxidized state, adequate recovery could probably be obtained with TBP concentrations as low as 10 percent in light of the excellent results obtained with 30 percent TBP.

TABLE XV
DISTRIBUTION COEFFICIENTS FOR NEPTUNIUM BETWEEN
WASTE SOLUTIONS AND 30 PERCENT TRIBUTYL PHOSPHATE (TBP)

Solution from Tank Number [a]	Np Concentration (g/l)	$E^{o/a}$ (oxidized)	$E^{o/a}$ (reduced)	$E^{o/a}$ (no pretreatment)
WM-102	5.5×10^{-3}	110	---	---
WM-181	6.4×10^{-4}	80	---	---
WM-184	1.0×10^{-3}	163	1.5	---
WM-186	4.5×10^{-3}	114	---	0.5

[a] See Table XIV for tank analyses.

Tests were run on samples from second-cycle waste tanks to determine if emulsions would form with the organic extractant. The two phases separated clearly and rapidly in each case; therefore, no emulsification troubles would be expected during plant operation with second-cycle wastes. However, no further work is planned on recovering neptunium from stored waste solutions at the ICPP.

4. GRAPHITE FUEL PROCESSING

(D. W. Rhodes, L. A. Decker; CHEMISTRY SECTION)

The Rover series of nuclear rocket test reactors will produce enough graphite-uranium dicarbide fuel to justify installation of a process to recover the uranium from them. A process involving burning the graphite followed by chemical dissolution of the resulting uranium oxide was chosen as the most likely process based on development work at Oak Ridge National Laboratory[46] and Brookhaven National Laboratory [47]. To operate such a process at the Idaho Chemical Processing Plant, information was needed on the effect of thermal history of the fuel on recoverability of the uranium and the effect of temperature of combustion on the quantitative leachability of the uranium from the ash.

The composition of the fuel element for the Rover reactors is such that severe chemical conditions must be used as a first step in liberating the uranium for recovery. The fuel elements are composed of uranium dicarbide dispersed in graphite which has been extruded into the shape of hexagonal rods. The coolant channels, which are drilled lengthwise, are coated with niobium carbide. The uranium dicarbide particles are coated with an impervious layer of graphite to retain fission products.

4.1 Combustion-Leach Process

Several specimens of Rover fuel were burned and leached to determine the effect of thermal history of the fuel, temperature of combustion, and acid concentration during leaching on the recoverability of uranium from the graphite fuel. The rate of combustion was followed by determining the amount and rate of carbon dioxide produced. Table XVI compares the effect of temperature on rate of combustion by showing the time required to oxidize sixty percent of the carbon in the specimen. A temperature of 800°C in air gave a satisfactory combustion rate. The temperature of combustion had a definite effect on the leachability of uranium as shown in Table XVII. With the exception of Fuel A, temperatures over 800°C apparently produced a solid solution of oxides which reduced the amount of uranium leached by hot 8M nitric acid. No difference was observed in the leachability of irradiated and unirradiated specimens, nor did acid concentration (8 to 16M) or thermal history of the fuel affect the leachability of the uranium.

The laboratory studies thus demonstrated that the uranium can be recovered from test fuel elements from the Rover reactors by burning in air and leaching the residue with nitric acid. A recovery of greater than 99 percent of the uranium was obtained in every case in which the temperature was maintained at 800°C or lower during combustion. Based on previous studies, fluidized bed burning is believed to provide the necessary low temperature during combustion. A flowsheet for the burn-leach process is shown in Figure 15.

TABLE XVI

TIME FOR SIXTY PERCENT COMBUSTION OF CARBON
INITIALLY PRESENT IN ROVER FUEL SPECIMENS

Number of Samples	Combustion Atmosphere	Temperature of Combustion (°C)	Average Time for 60 Percent Completion (minutes)
4	Air	800	21
3	Air	1000	17
1	Air	1200	13
3	10 percent oxygen, 90 percent nitrogen	800	33

TABLE XVII

URANIUM RECOVERY IN COMBUSTION-LEACH PROCESS

Fuel Element	Temperature of Combustion (°C)	Percent U Leached with 8M HNO ₃ (boiling)
A	800	99.0
	1000	99.2
B	800	99.4
	1000	98.2
	1200	82.5
C	800	99.0
	1200	88.0
KIWI-B4D	800	99.8

Fig. 15 Proposed burn-leach flowsheet.

At present, this appears to be the most suitable process for use at ICPP for reprocessing Rover fuels. It has the advantage of removing the bulk of the diluent material (graphite) during the burning operation, but it will require careful handling because of the high temperatures.

4.2 Alternate Processes

In the development work at the ICPP, certain alternate processes were briefly

investigated to see if a process superior to the burn-leach process was available. The following three alternate processes were investigated for possible use at the ICPP: (a) grind-leach, (b) mixed nitric-sulfuric acid oxidation, and (c) electrolytic decomposition.

4.21 Grind-Leach. An obvious alternate process would be to leach the uranium from the fuel elements after grinding, to produce a solution of uranium in nitric acid. The uranium carbide in the fuel is soluble in nitric acid; however, the coatings on the particles prevent contact between the nitric acid and the uranium carbide unless the coating is first ruptured by grinding. The particles are of such a size that the fuel elements must be ground to less than 200 mesh to ensure that all of the particles are broken.

A recovery of 99.3 to 99.5 percent was obtained in each of several tests in which the fuel was ground to less than 200 mesh (U. S. standard) and leached with 15.7M nitric acid. Samples from two elements of different thermal histories indicated no difference in the behavior of the uranium. A sample from the KIWI-B4D test reactor fuel which was treated similarly gave a recovery of 100 ± 2 percent (uncertainty in analysis). The recoverability of the uranium by extracting with 20 percent TBP was demonstrated. A feed with 8.91 g/l uranium and 14.8M nitric acid gave extraction coefficients of 7.4, 18.1, and 21.5 for the first three stages, respectively.

Although these laboratory data were very encouraging, the grind-leach process is not being seriously considered for large-scale application because of formidable engineering problems involving grinding, liquid-solids separation, and waste solids handling and storage.

4.22 Mixed Nitric-Sulfuric Acid Oxidation. In a second alternate process, large, intact pieces of graphite fuel can be disintegrated within a few seconds by treatment at 120°C with a solution that is, by weight, 78 percent sulfuric acid, 14 percent nitric acid, and 8 percent water. The solution penetrates the coatings on the uranium carbide particles within a few hours and dissolves the particles. Contacting three fuel specimens with varied thermal histories with the solution for 10 hours gave 99, 99.97, and 100 percent recovery of uranium. An irradiated sample from KIWI-B4D treated similarly showed a recovery of only 94 percent. The low recovery in that single case may have been due to insufficient washing of the residue.

This process represents an interesting alternative to the combustion-leach process and will be studied further. Corrosion in the dissolver may be a difficult problem to handle.

4.23 Electrolytic Disintegration. The third alternate process, electrolytic disintegration, was found to be unsuccessful in recovering the uranium quantitatively although it is capable of reducing large pieces of fuel to fine particles.

5. ELECTROLYTIC DISSOLUTION STUDIES

(L. T. Lakey, W. B. Kerr, A. P. Roeh; DEVELOPMENT ENGINEERING SECTION)

Recovery of uranium from stainless steel-containing fuel elements has been investigated by a number of techniques including sulfuric acid processes

(SIR and Sulfex), aqua regia (Darex process), fused-salt volatility, and electrolytic dissolution in nitric acid. Among these, the electrolytic process appears to offer significant advantages (eg, fewer corrosion problems, a nitrate dissolver product which requires no complexing before processing through existing extraction systems, less liquid waste than that made in the SIR and Darex processes, and no solid waste such as produced in the fused salt process).

The electrodisolution of stainless steel reactor fuels in nitric acid was first tested by Pitzer [48] in 1951. By 1958, the need of reprocessing capacity for stainless steel and Nichrome fuels appeared to be growing rapidly and development work on an electrolytic process was started at both the Savannah River Laboratory [49] and the Idaho Chemical Processing Plant (ICPP). At the ICPP, the development effort was directed primarily at the dissolution of fully enriched fuels, the most prominent of which are the stainless steel cermet from the Army Package Power Reactor (APPR) program and the Nichrome cermet from the High Temperature Reactor Experiment (HTRE) in the Aircraft Nuclear Propulsion program.

Prior to the initiation of the pilot plant program at the ICPP, a considerable amount of basic literature studies and laboratory testing had already been accomplished [50, 51, 52, 53, 54]. Through these, the controlling electrochemical reactions and the effects of electrolyte composition and temperature were generally known. Also, data had been compiled on the conductance and physical properties of electrolytes [55], and numerous materials had been investigated for their application in an electrolytic dissolver [50, 56]. It was also known that the dissipation of electrical energy (I^2R loss) in the solution was the largest source of heat in the dissolution process [57] and that an accumulation of undissolved solids could be anticipated [50]. One major problem, that of maintaining an even current flow to the fuel from the anodic electrode upon which the fuel normally rested, had been solved by providing a small solution gap between the fuel element and electrodes [58]. This configuration is commonly referred to as the "solution-contact" dissolver.

In spite of the large amount of information available from the early work, certain process problems remained which required further development work on at least a pilot plant scale. These included the effects of fuel and electrode geometry upon the current which could be passed through the dissolver, the rate of formation and composition of the dissolver off-gas, methods of controlling the composition of the dissolver product, and methods of coping with the undissolved solids in the dissolver and extraction systems. In addition, it was desirable to verify the information which had been developed in the laboratory work regarding the effects of electrolyte composition and temperature, applied voltage, and other factors.

After considering fuel element configurations (see Table XVIII), charging problems, and criticality limitations, a horizontal, wedge-shaped-trough configuration employing the solution-contact principle was selected as the most promising for development on a pilot plant scale. A pilot model of such an electrolytic dissolver system was installed at the ICPP in 1963.

Equipment and process development on a pilot plant scale were carried to the point permitting design of a plant-scale process. The pilot plant studies and a conceptual design of the proposed plant installation are described extensively in IDO-14643. A brief summary is presented in the following sections.

TABLE XVIII

PHYSICAL CHARACTERISTICS OF POTENTIAL HIGH-ENRICHED
STAINLESS STEEL FUELS FOR AN ELECTROLYTIC DISSOLUTION PROCESS

Fuel	Shape	Outside Dimensions
PM-1	Tube	0.506 inch OD by 33-1/2 inches long
PM-2A	Box of Plates	2.863 inches by 2.863 inches by 27 inches long
PM-3A	Tube	0.506 inch OD by 33-1/2 inches long
SM-1 (APPR)	Box of Plates	2.863 inches by 2.863 inches by 27 inches long
SM-1A	Box of Plates	2.863 inches by 2.863 inches by 27 inches long
Borax V Superheater	Box of Plates	3.633 inches by 3.875 inches by 36 inches long ^[a]
NSP Superheater	Tube	0.706 inch OD by 77-1/2 inches long
OMRE	Box of Plates	2.8 inches by 2.9 inches by 40 inches long ^[a]
Spert III	Box of Plates	2.95 inches long by 2.95 inches by 38 inches long
VBWR	Box of Plates	2.98 inches by 2.98 inches by 45 inches long ^[a]
HTRE	Concentric Tubes	3.52 inches OD by 30 inches long

[a] After cutting off inert ends.

Since the assignment within the past year of highly enriched stainless steel and Nichrome fuels to the Savannah River Plant by the AEC, further work on both the pilot plant studies and design of a plant installation has been suspended.

Dissolver Design and Operation

The electrolytic dissolver evolved from ICPP studies is a long, V-shaped, horizontal trough approximately 5 inches wide at the top and 16 inches deep which operates at a potential of 15 to 25 volts dc. A platinum sheet anode operates at a current density of 1 to 2 amp/cm² and is insulated from the titanium vessel which serves as a cathode. Fuel elements, oriented horizontally, are charged into a perforated niobium or plastic basket which is electrically insulated from both the anode and the cathodic vessel. The electrolyte, a solution of nitric acid and metal nitrates, is recirculated from the dissolver through an external cooler to remove the electrically generated heat. Fresh acid is continuously added, and product solution is continuously withdrawn. Electrical current flowing through the electrolyte between the electrodes is intercepted by the fuel element which becomes anodic with respect to the cathode and dissolves. The pilot plant dissolver consisted of a four-inch-long portion of such a dissolver and was full scale in all respects except its length.

Capacity of Dissolver: During eighteen test runs in the pilot plant system which were made under a variety of processing conditions with both actual and simulated elements, an average processing rate of approximately 1.05 g/hr/cm² of anode area was attained. This rate corresponds to an average current utilization of 0.66 g/amp-hr and an average anode current density of 1.59 amp/cm². In-line conductivity and density instruments were found to be useful

for monitoring the product composition and operating conditions. No corrosion problems were encountered with the titanium vessel, niobium basket, or platinum anode.

Effect of Fuel Characteristics: Because of masking by the effects of variations in electrolyte composition, fuel geometry, and sludge film resistances, the effect of variations in fuel charge composition was not evident. Fuel size, however, appears to affect current utilization, with smaller elements yielding higher current utilization values than larger elements.

Effect of Dissolver Loading: In the case of a dissolver only partially filled, such as would occur when processing elements shorter than the dissolver, current utilization will drop because of current bypassing the metal element through the solution. An insulating plate placed in the unused portion of the dissolver has been found to be an effective means of maintaining a high current utilization with short elements. Variations in the level of the fuel loaded into the dissolver have little effect on current utilization or anode current density until the level drops below the half-full mark.

Effect of Dissolvent Composition: Changes in composition of the dissolvent affect the current because of the associated changes in solution conductivity. At a given dissolved metal concentration, the conductivity (and, hence, the current) passes through a maximum and then decreases again as the acidity of the dissolvent is increased. This maximum current will occur at an acid concentration that varies from approximately 6.5M for pure acid solutions to 3M at a metal concentration of 90 g/l. In the pilot plant system, the depletion of acid with dissolution averaged approximately 0.067M for each g/l increase in metal concentration. No definite effect upon current utilization was observed as a result of variations in solution conductivity.

Effect of Dissolvent Temperature: The dissolver current is affected by two competing mechanisms as the temperature of the recirculating dissolvent is increased. At a constant voltage, an increase in dissolvent temperature produces an increase in solution conductivity which in turn allows a higher current through the dissolver. At some higher temperature, dependent on the applied voltage, the conductivity of the solution continues to increase, but a rapid increase in anode film resistance counteracts the increased conductivity and causes a decrease in dissolver current. In the pilot plant dissolver, maximum current densities were obtained at average dissolvent temperatures of about 49°C.

Effect of Dissolvent Potential: The dissolver and fuel load present a constant resistance at applied voltages from 7 to 25 volts, the range limitation of the experimental power supply. Therefore, the dissolver current is directly proportional to the applied voltage over this range. The resistance differs for each fuel type, but in each case, the resistance was constant for each fuel tested. No detrimental effects were noted at any of the voltages used; it is suggested, therefore, that still higher voltages constitute a means of raising the dissolver capacity substantially.

Effect of Undissolved Solids: Particles of metal were released during the process as undissolved solids which, without special treatment, combined with siliceous components from the fuel to produce an adherent sludge coating on surfaces of the dissolver and external tanks and piping. The sludge coating decreased the dissolver current and, in one case, plugged the circulation loop.

However, the addition of gelatin at a concentration of 100 to 200 ppm to the acid feed prevented the formation of this sludge and allowed the particles to circulate with the dissolvent. The undissolved solids contained insignificant quantities of uranium and did not interfere with the extraction of uranium when processed through a pulsed-plate extraction column.

Off-Gas Production and Composition: Off-gas released during the dissolution process varied from 3.6×10^{-3} scfm/amp-hr when dissolving stainless steel to 14×10^{-3} scfm/amp-hr when dissolving Nichrome. The off-gas is made up primarily of oxygen, nitrogen, and oxides of nitrogen. Hydrogen concentrations of the undiluted off-gas were below six volume percent; with air dilution, hydrogen concentration can be controlled below hazardous levels.

II. WASTE MANAGEMENT

1. THE IDAHO WASTE CALCINING FACILITY (WCF)

1.1 Processing of High-Level Radioactive Aqueous Waste in the WCF (G. E. Lohse, E. D. Cooper, D. E. Black; PLANT PROCESS ASSISTANCE SECTION)

The initial operation of the Waste Calcination Facility (WCF) with high-level radioactive aqueous wastes was completed in October 1964. This facility, the world's first production unit, converts aqueous wastes, resulting from the recovery of uranium from aluminum-uranium reactor fuels, to granular solids in a fluidized bed calciner. During this campaign, which lasted for 312 days, about 512,000 gallons of liquid waste were converted to 7500 cubic feet of solids weighing 412,000 pounds. Less than 60 hours of downtime occurred throughout the entire campaign. Process performance was excellent, and decontamination of the calciner off-gas stream was very satisfactory.

1.11 Process and Equipment Description. The heart of the facility is a four-foot-diameter fluidized bed calciner shown schematically in Figure 16. Radioactive waste solutions are injected through three pneumatic atomizing nozzles into the heated (400°C) bed of granular solids which is fluidized with

Fig. 16 WCF calciner vessel and auxiliary equipment.

air. The feed flows at a nominal total rate of 92 gallons per hour. This feed rate includes batch recycle of off-gas scrubbing solution at an equivalent rate of 23.5 gallons per hour.

Thermal decomposition of the nitrate salt solutions to metallic oxides (primarily alumina), water vapor, and nitrogen oxides is the principal reaction occurring during calcination. Solid products build up in layers on the bed particles while gaseous products and some particulate matter are swept from the vessel with the fluidizing gases. The average bed particle size is controlled at the desired value by controlled attrition of bed particles achieved by varying, as necessary, the volumetric ratio of atomizing air to liquid feed. The bed level is maintained six to eight inches above the feed spray zone at all times (by adjusting the rate of product removal) so that the spray contacts bed particles in a fluidized state.

Heat for the decomposition is supplied to the fluidized bed by an internal heating bundle through which sodium-potassium eutectic alloy (NaK) at temperatures up to 760°C is circulated. The NaK is pumped by an electromagnetic pump and is heated by an oil-fired furnace. Preheated fluidizing air is introduced through 14 orifices equally spaced in an air distributor plate which supports the bed. Each orifice is surmounted by a cap which helps to distribute the air more uniformly in the bed and to minimize backflow of solids if the fluidizing air flow stops. Operation at a superficial fluidizing velocity between 0.75 and 1.0 ft/sec has been satisfactory over the usual mean-bed-size range of 0.4 to 0.7 mm. This size range was chosen as the best compromise between the diametrically opposed considerations of high heat transfer rates and low rates of elutriation of fine solids from the bed.

Solid product is transported from the calciner to the storage bins from two sources by means of a pneumatic transport system. About 60 percent of the product is removed from the bottom of the calciner through the takeoff line connecting the calciner and the product transfer system. Dilution air, added to the takeoff line near the junction with the calciner, regulates the rate of product withdrawal; the product rate varies inversely with the dilution air flow rate. About 40 percent of the product is elutriated from the calciner with the off-gas and is separated from this gas in the calciner cyclone. These solids are transferred by air jet into the solids transport line where they combine with the solids removed from the bottom of the calciner. The product is transported to a second cyclone above the storage bins where it is separated from the transport air. The solids fall by gravity into the bins, and the transport air is returned to the overhead space of the calciner to be decontaminated with the process off-gas. Since no other motive force is normally applied, the driving force for the transfer system is limited by the pressure drop between the product takeoff point and the top of the calciner where the transport gas reenters.

The off-gas from the calciner cyclone is decontaminated as it passes through a series of devices, which include (in sequence) a spray quench tower, a venturi-scrubber and associated cyclone-type entrainment separators, silica gel adsorbers, and high-efficiency filters, before it is discharged to the atmosphere. Essentially all of the particulate matter leaving the calciner cyclone is removed in the wet scrubbing system. Solids collected (and largely dissolved) in the scrubbing solution are recycled intermittently to the calciner feed tank. The rate of condensation in this system is established (through control of the scrubbing solution temperature) to maintain the concentration of the dissolved

solids in the solution at a level safely below saturation, and the rate of recycle is set equal to the condensation rate. The solution is recirculated through the scrubbing system and recycled to the feed tank by a vertical centrifugal pump. After leaving the wet scrubbing system, the off-gas passes through silica gel adsorbers and high-efficiency filters. Three adsorbers are operated in parallel; each contains 6000 pounds of silica gel. Each of the three final filter units, installed in parallel, contains a prefilter and a high-efficiency, AEC-type filter.

1.12 Summary of Processing Campaign. In the following sections, the feed and product of the WCF are described, and cleanup of the off-gas is discussed. Full details of the campaign are reported in IDO-14662 [59].

(1) Waste Processed. All 512,000 gallons of waste processed during this campaign were aluminum nitrate-nitric acid solutions derived from the processing of aluminum-uranium alloy fuel elements; they were obtained from three storage tanks whose contents had slightly varying chemical compositions as follows: Al, 1.5 to 1.7M; H^+ , 0.5 to 0.9M; Hg, 0.011 to 0.014M; Na, 0.04 to 0.06M.

The waste contained the full range of aged (3 to 7 years) fission products. At the time of processing, the activity of the waste varied between 15 and 35 curies per gallon; about 1.4×10^7 curies of various radionuclides were fed to the calciner. The principal nuclides were Cs-137, Sr-90, Pm-147, Ce-144, Ru-106, and Cs-134.

(2) Solids Product. The bed product of the WCF is granular; that produced during this campaign had an average particle size (mass median particle diameter) of approximately 0.56 mm. The product was principally aluminum oxide (amorphous form), but it contained approximately 4.0 percent nitrates (calculated as N_2O_5), 2.9 percent mercury (calculated as HgO), and 0.6 percent fission product oxides by weight. The product transferred to the storage bins during this campaign had an average heat generation rate (due to radioactive decay) of 0.52 Btu/hr-lb as of October 1964.

(3) Off-Gas Cleanup. One of the major requirements of radioactive waste solidification processes is decontamination of the off-gas from the calcination vessel. These off-gases contain both particulate solids and volatile species which are radioactive. The most accurate determination of the concentration of these species is obtained by radiochemical counting of off-gas samples. Two techniques used in this campaign were (a) filtration and adsorption and (b) direct counting of large bottles of off-gas. In the first method, metered side streams of off-gas were passed continuously through 0.45-micron "millipore" filters and then through a series of adsorbers filled with known weights of polyethylene chips; polyethylene is an extremely selective adsorbent for volatile ruthenium compounds which constitute the only radioactive species volatilized significantly during fluidized bed calcination. The filters were analyzed for Sr-90 and for gamma emitters, such as cesium, cerium, and ruthenium. The polyethylene chips were leached with caustic or acid to remove particulate matter and were counted directly for ruthenium. (Ruthenium was not removed from the chips by leaching.) Direct counting of 22-liter, off-gas samples gave close agreement with the filtration and adsorption method.

Excellent performance was obtained in the WCF off-gas cleaning system. The release rate for Sr-90 was consistently less than 0.2 percent of that which,

during worse-than-average weather conditions, would cause localized ground level concentrations equal to those given in the Radioactivity Concentration Guide (RCG) for a 40-hour week. The release rate of Ru-106 was consistently less than five percent of its corresponding RCG value. By sampling at various points in the off-gas train, decontamination factors for the principal radio-nuclides in successive off-gas components were obtained. These factors are summarized in Table XIX.

TABLE XIX
DECONTAMINATION FACTORS FOR WCF
OFF-GAS COMPONENTS FROM FEED TO STACK

Nuclide	Calcliner and Cyclone	Scrubbing System	Silica Gel Adsorbers	Filters	Composite
Cs-137	6.0	690	9	280	1.0×10^7
Sr-90	6.5	600	12	160	7.5×10^6
Ru-106	2.5	11	410	[a]	2.8×10^3

[a] Analyses indicated that the Ru-106 concentration in the off-gas stream was higher downstream of the filters than upstream of the filters. This difference is believed to be the result of two factors: (a) sampling inaccuracies and (b) volatilized ruthenium in the vessel off-gas stream which joins the calciner off-gas stream between these two sample points.

In addition to the water vapor and the volatile species of ruthenium, approximately five percent of the mercury and practically all of the nitrogen oxides in the feed appear as gaseous components in the off-gas leaving the calciner cyclone. The wet scrubbing system removes approximately 80 percent of the mercury vapor and 30 percent of the nitrogen oxides from the off-gas. The silica gel adsorbers and final filters together remove essentially all of the remaining mercury, but nitrogen oxides are not removed by either the adsorbers or filters and are discharged to the atmosphere.

1.13 Environmental Effects from Operation of the WCF. The point of discharge of the WCF off-gas was the ICPP stack. This is a reinforced concrete structure, 73 meters high, with an effective inside diameter of 3 meters. Stack gas consists of ventilation air from the plant and off-gas from the plant processes. Since the ICPP was not processing fuel during this period of WCF operation, the only source of significant radioactivity was from the Waste Calcining Facility. The stack flow was $57 \text{ m}^3/\text{sec}$, one one-hundredth of which was WCF off-gas.

Monitoring was conducted during and after operation of the WCF. This involved high-volume air samples, fallout plates, and vegetation and soil samples. Detectable, but nonhazardous, amounts of Ru-106 were found on vegetation as far as 16,000 meters from the stack, with a maximum of $2.2 \times 10^{-3} \text{ } \mu\text{Ci/gram}$ at 1600 meters [60]. Comparison of these activities with concentrations of Ru-106 in air indicates the deposition velocity was about 0.5 cm/sec.

There was no significant hazard from operation of the WCF. Calculations indicate that at the point of maximum integrated concentration (1600 meters), the total dose over the entire period of operation would have been about 0.1 rad. In no instance was Sr-90 found in any of the vegetation samples, fallout samples, or high-volume air samples.

1.14 Post Run Observations and Modifications. The WCF was satisfactorily decontaminated to desired levels after the first radioactive run so that the desired inspection could be made and routine maintenance performed. Inspection showed little, if any, wear to calciner and off-gas components. During the run, a few valves developed troublesome leaks, and inspection of valves throughout the plant showed that the 4-mil-thick bellows (Type 304L stainless steel) on most of the leaking valves had been penetrated by corrosion. These bellows will be replaced with 7-mil-thick, corrosion-tested material.

The pumps and blowers operated satisfactorily during the run, but post-run inspections disclosed that one of the vertical-shaft, scrubbing-solution pumps requires rebuilding. Though no abrasion of the pump parts was found, the impellers of both pumps had loosened and one had dropped from the shaft. A new shaft and bearings will be installed in the damaged pump prior to startup. The retaining nuts will be modified to prevent loosening of the impellers.

Several changes are being made in the plant in preparation for the next run. These include:

- (1) The transport air return from solids storage is being rerouted to eliminate pockets and to reduce the length of run and, hence, the pressure drop in the system.

- (2) An off-gas sample cabinet is being installed which will incorporate the design features which have been found to be most satisfactory during prior tests. Three stations will be built into the one temperature-controlled cabinet. A single steam jet will provide the motivation for all three samplers.

- (3) The decontamination lines to the process vessels and piping are being isolated so that process liquids and gases cannot back up into nonradioactive areas and nonradioactive solutions cannot leak into normally dry lines during operation.

- (4) A valve leak drain system is being installed in the off-gas cell to detect valve bellows failure and then to return any valve leakage to the off-gas scrubbing system rather than having it flow to the floor drain as has been the case in the past.

1.2 Design Features of Additional Solids Storage Facilities for the WCF. (G. E. Lohse, E. D. Cooper, D. E. Black; PLANT PROCESS ASSISTANCE SECTION)

Approximately 96 percent of the usable volume in the original WCF solids storage facility was filled during the initial radioactive operation of the WCF. Thus, a new solids storage facility is required before operation of the WCF can be resumed. To date, design of the new facility is complete; the concrete vault base and walls have been poured; and most of the excavation is back-filled. The construction is scheduled for completion in February 1966.

Modification of the original design criteria has reduced the estimated cost of the new facility considerably. The savings were effected in large part by elimination of shrouds on the storage bins, reduction in the size of the vault, deletion of a vault cooling-air-filter system, use of the existing bin vent system, and simplification of the future solids retrieval system. These items are discussed briefly in the following paragraphs.

The new storage facility will contain seven bins with a combined net storage capacity of approximately 30,000 cubic feet. This additional storage capacity will meet the currently estimated requirements of the ICPP until approximately 1972. Each bin will be constructed of Type 304 stainless steel and will have a diameter of 12 feet and a height of 42 feet. Diameter of the bins was chosen so that the maximum temperature of the stored solids (which will occur at the bin center line) will be 700°C for solids having a heat generation rate of 0.3 Btu/hr-lb. Elliptical heads will be used for the top and bottom of each bin. Solids from the WCF calciner will be transported pneumatically to a cyclone above the bins where they will be separated from the air stream and will fall by gravity through bin fill lines into the bins. Simplified sketches of the new storage bin arrangement are given in Figures 17 and 18.

Pneumatic valves for positive shutoff and flow control of solids will be installed in two of the bin fill lines so that solids generated from special types of waste can be segregated. Valve details are discussed in Section II-2.7. Off-gas from solids stored in the new bins will be routed to the bin vent system serving the present solids storage facility; there the vapors will be condensed, and any particulate matter present will be filtered from the gas before it is discharged to the atmosphere.

Solids stored in the bins may be retrieved at a future date through six-inch lines running from the top of each bin through the vault ceiling. All but two of the lines extending above the vault ceiling will be covered with concrete covers similar to those used in the existing ICPP waste tank farm. The remaining two lines (which also will be shielded) will provide direct access to two of the bins for sampling and for placement and retrieval of corrosion coupons. Final connection of removal lines will be made at the time solids retrieval is desired.

The bins will be placed in a cylindrical, concrete vault. The vault will have an inside diameter of 46 feet and a height of 69 feet; the vault wall thickness will be 24 inches. To provide an additional margin of safety in the event of earthquakes, the vault will rest on bedrock. Emergence of direct radiation beams will be prevented by offsets in piping and instrument lines and by offsetting or extra shielding at structural joints. An equipment vault (housing the solids storage cyclone and isolation valves in the transport air system) and an instrument room will be located above the bin vault.

Heat resulting from the radioactive decay of fission products stored within the bins will normally be removed by conduction through the solids to the bin walls and by natural convection of air flowing past the bins. Air will enter the cooling air system through an inlet "roughing filter" and will flow through ductwork to the bottom of the vault. From the bottom of the vault, it will rise over the faces of the bins, cooling the bins, and leave the vault through the cooling air outlet duct. The heated air will be released to the atmosphere through a 50-foot stack. Unlike the present solids storage facility, shrouds will not be used to direct the flow of the cooling air around the bins. Pilot plant tests indicate

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Fig. 17 Elevation view -- new WCF storage bins.

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Fig. 18 Plan view -- new WCF storage bins.

corrosion of the metal. Cooling air flow will also reduce vault wall temperatures and potential high-temperature deterioration of the concrete.

Instrumentation in the new facility will be similar to that of the current facility [61]. However, the new facility will have fewer in-bed thermocouples and will have additional thermocouples located such that radiative, convective, and conductive heat fluxes may be determined in the bins, the vault, and the surrounding soil. The additional temperature points will allow a complete evaluation of the heat transfer mechanisms associated with this system.

1.3 Corrosion Evaluation of WCF Process Equipment (D. W. Rhodes, T. L. Hoffman; CHEMISTRY SECTION)

Following the successful ten-month run and subsequent decontamination of the WCF, a corrosion evaluation was made of various functional pieces of equipment, either in place or after the item had been removed from the WCF. The results of this corrosion evaluation are summarized below.

1.31 Radiant Coil for the Liquid Metal Heater. The radiant coil in the liquid metal (NaK) heating system is made of Type 316 stainless steel and had been operated at about 1400°F for approximately 8500 hours since the last inspection. Micrometer measurements on 8 of 32 vertical header tubes in the coil indicated a loss of 3 to 5 mils during the run. All vertical tubes were coated with a porous, nonuniform scale. Pits underneath the scale were less than 5 mils deep. Corrosion damage was considered to be very minor.

1.32 Calciner Baffle Plate. A baffle plate made from Type 347 stainless steel was obtained from an area above the fluidized bed within the calciner vessel. This plate had been in service for 10,000 hours at air temperatures between 325 and 410°C. No intergranular attack had occurred. Microhardness surveys gave values equivalent to Rockwell B-77 and B-91, which are normal

values for this alloy. A corrosion film on the baffle plate was too thin to measure accurately but was estimated to be less than 10^{-3} mils. Corrosion on this plate was considered to be negligible.

1.33 Stainless Steel Nuts and Bolts. Several Type 304 stainless steel nuts that were exposed to 30 percent nitric acid in the off-gas scrubbing system failed by losing their threads while the Type 304 stainless steel bolts associated with the nuts were not attacked. A metallographic examination indicated that localized attack had occurred at the grain boundaries of the nuts. Chemical analysis indicated that the carbon concentration in the nuts and bolts was 0.151 and 0.050 percent, respectively. With the higher carbon concentration in the nuts, carbide precipitation may have occurred during fabrication, and the carbide precipitate subsequently dissolved in the nitric acid. A low-carbon analysis or a stabilized steel such as Type 304L or Type 348 will be used in the future.

1.34 Valves. Ten bellows-seal valves that had malfunctioned during WCF service up to 12,500 hours were examined. These valves had developed leaks around the valve seat, the plug, or the bellows convolutions. The bellows were made from 4-mil-thick, Type 304L stainless steel. The corrosion rate of Type 304L stainless steel is about 0.6 to 0.8 mil per month in 5M nitric acid at 50°C. Accordingly, 4-mil-thick stock would be expected to fail in about 5 to 7 months service. Type 304L stainless steel bellows stock of 7 mils thickness is now available commercially and will be used to replace the 4-mil stock as required.

A throttling valve, with a 17-7 PH plug and 17-4 PH seat that had been hardened by heat treatment at 900°F to Rockwell C-45 and at 1100°F to Rockwell C-35, respectively, was completely resistant to the scrubbing solution (5M HNO₃, 1M Al⁺₃, 0.02 percent solids) after 8500 hours service. These results indicate that the 17-7 PH plug and 17-4 PH seat combination is resistant to both erosion and corrosion in the scrubbing solution and should be used where throttling valves are required in the WCF.

1.35 Summary. No corrosion problems of major importance were observed on any of the WCF equipment items. The minor corrosion problems can be essentially eliminated by use of proper materials of construction for the intended use.

1.4 Corrosion of Type 316 Stainless Steel in NaK Service -- A Literature Survey (C. A. Zimmerman; CHEMISTRY SECTION)

Calcination in the WCF is accomplished in a fluidized bed which is heated by circulating NaK in a Type 316 stainless steel tube bundle in the bed. Although the use of liquid metals for heat transfer service is quite common and corrosion failures were not anticipated, a review of the pertinent literature data on the performance of Type 316 stainless steel in this service was desirable. The results of this literature search have been published in IDO-14651 [62], and are summarized here.

Information from the literature indicates that the impurities in the circulating fluid and the temperature of operation are the major factors controlling corrosion in circulating sodium or NaK heat transfer systems. The impurities which have been found to exert the greatest influence are carbon, oxygen, and nitrogen. Oxygen, if it is the only contaminant, seems to be acceptable as long as the concentration remains below about 100 ppm. Oxygen concentrations above 50 ppm appear to increase carburization and decarburization

reactions in commercial sodium which contains about 50 to 60 ppm of dissolved carbon. When nitrogen is the cover gas, nitriding of steels has been reported to occur at the liquid metal-cover gas interface. Corrosion of nitrided steel is apparently promoted by the presence of oxygen. Nitrogen buildup in cover gas systems has been observed where no source of the nitrogen was readily determinable.

Sensitization, sigma-phase formation and mass transfer are directly influenced by elevated temperature (above 550°C). Changes in metal structure (sensitization and sigma-phase formation) have not been shown to result in failure in sodium or NaK systems although the sensitized structure is known to be very susceptible to intergranular corrosion in the presence of aqueous media. Mass transfer can be minimized by proper design of the system, selection of construction materials, and use of a low temperature differential in the system as well as control of impurities in the circulating fluid.

2. LABORATORY AND PILOT PLANT STUDIES IN SUPPORT OF THE WASTE CALCINING FACILITY

2.1 Calcination of ICPP Wastes as Blends or With Additives (D. W. Rhodes, M. W. Wilding; CHEMISTRY SECTION) (E. J. Bailey, J. C. Petrie; DEVELOP- MENT ENGINEERING SECTION)

In addition to the aluminum nitrate-nitric acid waste that has been calcined successfully in the WCF, wastes containing zirconium fluoride, ammonium nitrate, sodium nitrate, and sulfuric acid are being considered for calcination in the near future. All of these latter wastes will require modified or new techniques before calcination in the WCF can be accomplished.

In fluidized-bed calcination, decomposition of the waste takes place on hot particles in the bed rather than at the surface of the calcination vessel; corrosion of the vessel is generally negligible. However, anions such as fluoride and sulfate can volatilize and produce corrosive environments in the off-gas cleanup system. Wastes containing high concentrations of sodium ion tend to produce glass-forming solids which coat the vessel walls and heat exchanger surfaces or agglomerate into unmanageable masses and reduce the heat transfer properties of the bed. Calcination of wastes containing mercury and high ammonium ion concentration can produce a potentially explosive mercuri-amidonitrate compound which may build up as undissolved solid in the off-gas scrubbing solution.

To calcine these wastes, it was obvious that (a) additional treatment would be required to inhibit the volatility of corrosive fluoride and sulfate, (b) either additives or specifically controlled calciner conditions would be necessary to assure complete decomposition of ammonium nitrate, and (c) additives would be required to decompose sodium nitrate and prevent agglomeration in the bed when sodium content was high. While addition of new chemical reagents would probably achieve these objectives, it also became apparent that the variety of waste solutions available could provide a source of certain desirable additives. Thus, a program of blending existing ICPP wastes prior to calcination was considered in order to make use of neutralizing, complexing, and stabilizing effects potentially available in existing wastes without adding to the waste volume by use of new additives.

Another aspect considered in the blending of wastes was the specific heat generation rate of the solids produced by the calcination. The calcined-solids storage bins were designed to contain solids (at a center line temperature of 700°C) with a heat generation rate of 0.3 Btu/hr-lb. Material having a higher heat generation value obviously could not be introduced into the bins without incurring risk of bin damage, and it would be uneconomical to introduce wastes with extremely low heat-generation rates into these heat-controlling, size-limited bins. Blending of high-level with low-level waste to obtain the design value is the obvious compromise. In all probability, any of these wastes can be blended with aluminum nitrate-nitric acid waste, the principal waste at the ICPP, to achieve this objective. Thus, it appears that many of the chemical objectives can be realized simultaneously with heat-generation control by blending of the wastes. A systematic approach, shown on Figure 19, for attaining the chemical

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Fig. 19 Proposed combinations of ICPP waste for calcination in the WCF.

objectives has evolved, and laboratory and pilot plant efforts have been directed along these lines. Blending of aluminum nitrate-nitric acid wastes for heat generation control is not shown on Figure 19; it is anticipated that this waste can be blended with any of the others, and this will be tested in the pilot plant operations, as appropriate, as the program develops.

Promising laboratory results indicate that by blending ICPP wastes in appropriate combinations, it will be possible to calcine many of them in the WCF with addition of a minimum of extraneous chemicals. Pilot plant results have added support to the favorable prospects of calcining zirconium fluoride- and sodium nitrate-containing wastes, either by blending and/or use of additives; additional pilot plant work is proceeding to confirm the other favorable laboratory findings.

2.11 ICPP Waste Solution Sources and Compositions. The specific waste solutions currently generated or in storage at the ICPP, that are scheduled for calcination in the WCF, are as follows:

(1) Aluminum Nitrate-Nitric Acid. This waste is the "normal" ICPP waste produced by the processing of enriched uranium-aluminum alloy fuels using a nitric acid-mercuric nitrate dissolvent. The largest volume of waste at the ICPP is of this type; about 500,000 gallons of this waste have already been calcined successfully in the WCF.

(2) Ammonium Nitrate-Aluminum Nitrate. This waste resulted from earlier processing of enriched uranium-aluminum alloy fuels by a Redox-type process. The ammonium nitrate results from ammonium hydroxide being added to neutralize the nitric acid dissolvent.

(3) Zirconium Fluoride-Aluminum Nitrate. This waste results from the processing of enriched uranium-zirconium alloy fuel in a hydrofluoric acid dissolvent followed by the addition of aluminum nitrate to complex the fluoride.

(4) Stainless Steel Sulfate. This waste results from the processing of enriched uranium-stainless steel alloy fuel using sulfuric acid as the dissolvent for the stainless steel followed by nitric acid addition to dissolve the uranium.

(5) Second- and Third-Cycle Waste Containing Sodium. Most of this waste is aqueous raffinate from hexone extraction cycles used to provide additional decontamination of the uranium following the first-cycle TBP extraction step; processing of aluminum-, zirconium-, and stainless steel-type fuels all contribute to this waste. In addition, solutions used for the decontamination of process equipment are mixed with this waste.

The approximate chemical compositions of the five types of waste are shown in Table XX.

TABLE XX

APPROXIMATE COMPOSITION OF WASTES IN STORAGE AT THE ICPP

Chemical	Nitric Acid - Aluminum Nitrate	Ammonium Nitrate - Aluminum Nitrate	Zirconium Fluoride - Aluminum Nitrate	Stainless Steel Sulfate	Second and Third Cycle
H ⁺ , <u>M</u>	1.0	-0.13[a]	1.0	3.2	0.9
Al ⁺³ , <u>M</u>	1.7	1.7	0.7	---	0.7
Hg ⁺⁺ , <u>M</u>	0.018	0.027	---	---	0.001
Na ⁺ , <u>M</u>	0.065	0.0087	---	---	2.5
Zr ⁺⁴ , <u>M</u>	---	---	0.4	---	---
NH ₄ ⁺ , <u>M</u>	---	1.37	---	---	0.06
Stainless Steel, <u>M</u>	---	---	---	0.1	---
BO ₃ ⁻³ , <u>M</u>	---	---	0.17	---	---
NO ₃ ⁻ , <u>M</u>	5.8	7.1	2.2	2.5	5.5
F ⁻ , <u>M</u>	---	---	2.5	---	---
SO ₄ ⁼ , <u>M</u>	---	---	---	0.6	0.08
Remarks on Calcination Problems	Chemical Process Developed	Mercury and Ammonia May Volatilize	Fluoride May Volatilize	Sulfate May Volatilize	High Sodium May Cause Agglomeration

[a] Acid-deficient.

2.12 Calcination of Zirconium Fluoride Raffinate With Added Calcium. Earlier laboratory work [63] has shown that the addition of 0.5 mole of calcium per mole of fluoride to the zirconium process waste prior to calcination causes essentially all of the fluoride to remain in the solid product during calcination at 400°C. This has been confirmed by pilot plant tests using synthetic wastes. A complete discussion of the tests is published in IDO-14653 [64]; a brief summary of the results is given here.

Simulated zirconium fluoride waste was complexed with 0.5 mole of calcium nitrate per mole of fluoride. The resulting slurry was readily pumped through the calciner feed nozzles. Calciner operating conditions closely approximated those of the WCF during the recently concluded, radioactive aluminum nitrate waste calcination campaign (Section II-1). Results of the exploratory test demonstrated that (a) zirconium fluoride waste could be calcined in a fluidized bed; (b) calcium, added to the feed, formed calcium fluoride and caused the fluoride to be retained in the calcined solids; and (c) corrosion of process equipment and sample coupons located throughout the pilot plant system was generally less than 2.0 mils per month. Based on the chemical analysis of samples of the off-gas from the calciner, less than one percent of the fluoride in the calciner feed was volatilized.

The properties of the product from calcination of zirconium waste are compared in Table XXI with those of the product from calcination of aluminum

TABLE XXI
COMPARISON OF PROPERTIES OF VARIOUS CALCINED WASTES

	<u>Product from Calcination of Aluminum Nitrate Wastes</u>		<u>Product from Calcination of Zirconium Fluoride Wastes</u>	
	<u>Product</u>	<u>Fines</u>	<u>Product</u>	<u>Fines</u>
Bulk Density, g/ml	0.88	0.15 to 0.2	1.2	0.30 to 0.38
Absolute Density, g/ml	2.6	2.0	3.3	3.0
Nitrate Content, weight percent	2.0	12 to 15	2.5	10.5
Fluoride Content, weight percent	---	---	19.0	19.5
Ca/F Mole Ratio	---	---	0.45 to 0.55	---

waste. Both materials were calcined in the 12-inch-diameter calciner under similar operating conditions. An alumina starting bed was used during the zirconium fluoride waste calcination test. Theoretically, about 90 percent of the original alumina bed had been "washed-out" when the final product samples were obtained for analysis.

The yellow, granular product from calcination of zirconium fluoride wastes contained, by weight, about 25 percent zirconium oxide, 30 percent aluminum oxide, and 40 percent calcium fluoride, the remainder being trace compounds and nitrates. Calcium fluoride was the only crystalline structure detected by X-ray analysis of samples of the calciner product and fines.

Thermal stability under simulated solids storage bin conditions was tested by placing a small amount of the pilot plant product in a section of stainless steel tubing which was then heated to 800°C for 24 hours. A small air purge was passed through the solids to remove volatilized products. Nearly all of the nitrate, but only a trace of the fluorides, volatilized at 800°C.

Because of the promising results of the pilot plant calcination study, additional laboratory experiments were made recently to determine if a lesser amount of calcium would be effective in controlling fluoride. The calcium was added to the feed solution as calcium nitrate just prior to calcination.

The results of experimental runs with several calcium-to-fluoride mole ratios are shown in Table XXII. The data for the first two ratios represent single runs; the data for the last ratio are averages of two runs.

TABLE XXII
DISTRIBUTION OF FLUORIDE FOR THE BATCH
CALCINATION OF ZIRCONIUM FLUORIDE RAFFINATE AT 400°C

<u>Ca/F</u> (mole ratio)	<u>Fluoride in Calcine</u> (weight percent)	<u>Fluoride in Scrub^[a]</u> (weight percent)	<u>Total</u> <u>Fluoride Recovered</u> (percent)
0/1.0	87.3 ± 10 percent	7.1	94.4 ± 10 percent ^[b]
0.2/1.0	89.9 ± 10 percent	1.9	91.8 ± 10 percent
0.05/1.0	90.4 ± 10 percent	1.7	92.1 ± 10 percent

[a] Scrubbers were used in series, and the negligible fluoride content of the final scrubber indicated little or no loss as unaccounted for off-gas.

[b] Analytical uncertainty can account for apparent lack of 100 percent material balance.

Fluoride evolution during these tests (second and third) with lower ratios of calcium to fluoride are comparable to that observed during the pilot plant fluidized bed study. However, the adequacy of these lower ratios remains to be demonstrated in pilot plant scale tests which are being planned. The laboratory static bed calciner [63] does not necessarily provide an environment comparable to the pilot plant fluidized bed calciner with respect to either mass or energy transfer.

2.13 Calcination of Zirconium Fluoride Raffinate Blended With Second- and Third-Cycle Waste. An alternate approach to inhibition of fluoride volatility is to blend the zirconium fluoride raffinate with second- and third-cycle waste which contains appreciable quantities of sodium (2.4M). The sodium should react with the potentially volatile fluoride, replacing the calcium discussed in the preceding section (Section II-2.12), and result in retention of the fluoride in the calcined solid, if thermally stable at the calcination temperature (400°C). This blending approach, through dilution and complexing of sodium, should also ease the calcination of second- and third-cycle waste which, by itself, agglomerates seriously during fluidized bed calcination because of the relatively high concentration of sodium nitrate (Section II-2.14).

In exploratory tests [63], an equal volume mixture of the two waste solutions was calcined in the laboratory static bed calciner. Approximately one percent of the fluoride was volatilized or carried out of the calciner as fine dust as indicated by a chemical analysis of the scrubbing solution. The solid product contained crystalline NaNO_3 , Na_3AlF_6 , and ZrO_2 . The solid was readily friable with no indication of agglomeration in the bed at 400°C .

In a subsequent test in the pilot plant, glass-like cakes were formed during the calcination of the blended wastes in a 32-hour run. However, successful calcination of the blended wastes was achieved by addition of sugar at a rate of 4 grams of sucrose per gram of sodium in the waste and calcining at 500°C . The effect of sugar on the process is discussed in the following section (Section II-2.14).

2.14 Calcination of High-Sodium-Content Waste from Second- and Third-Cycle Raffinates. The second-cycle solvent extraction waste, which contains primarily about 2.4M sodium nitrate and 0.7M aluminum nitrate, is being considered for future calcination in the WCF. The principal problem to be overcome with this waste is that sodium nitrate tends to form agglomerates rather than granular solids during calcination [65]. Also, calcination experience at ICPP has shown that the undesirable alpha form of alumina may be produced when the sodium nitrate concentration exceeds 0.25M in the calciner feed [66]. Alpha alumina, which is quite friable, causes excessive elutriation of solids from the calciner vessel and, being insoluble in nitric acid, causes an increase in the amount of undissolved solids in the off-gas scrubbing solution. The noncrystalline amorphous form of alumina is preferred as calciner product, and its formation is promoted by the presence of boric acid in the calciner feed [66].

The use of additives to control the calcination process -- in addition to the blending with zirconium fluoride wastes discussed in Section 2.13, immediately preceding -- has been investigated in recent ICPP studies and is the subject of this section.

(1) Pilot Plant Tests. A series of scoping tests on the fluidized bed calcination of simulated second-cycle waste was conducted in the twelve-inch-diameter pilot plant calciner. The objectives of these tests were (a) to determine if chemical additives for the feed would prevent agglomerate formation in the fluidized bed and (b) to determine if the aluminum nitrate in the simulated waste would form the undesirable alpha alumina during calcination.

Operating conditions for the pilot plant tests approximated those selected for calcination of radioactive aluminum nitrate wastes [61] at the WCF. A liquid feed rate of 8 to 10 l/hr was used with a nozzle air-to-liquid ratio of 500 and a fluidizing air velocity of 1 to 1.5 ft/sec. Because of the generality of the objectives, the tests were conducted as a series of short operating periods, each starting with a new bed of prescreened sand ($-28 + 100$ Tyler mesh), to eliminate the complicating effect of the past history of the starting bed. The short operating periods satisfied the objectives because agglomerate formation, or bed caking, was indicated in one to two hours by diverging temperatures in the bed; and past experience indicated that the alpha alumina content of freshly generated fines closely approximated the equilibrium alpha alumina content of the fluidized bed [64].

Calciner feed was chosen to simulate the existing second-cycle waste now stored at ICPP. The compositions of the existing wastes and the pilot plant calciner feed are compared in Table XXIII. Additives tested for possible improvement of the calcination process, are listed in Table XXIV.

(2) Results. The results of these tests, summarized in Table XXIV indicate that the second-cycle waste can be calcined in a fluidized bed if sugar is added in a proportion of four grams of sucrose per gram of sodium and the bed temperature is maintained at 500°C. The calciner was operated for about 12 hours at 500°C with feed containing four grams of sugar/gram of sodium. No agglomerate formation was evident during operation under these conditions, or in the bed at the time it was removed. Under other conditions, however, agglomerate formation was evident; eg, after two hours operation with a bed temperature of 450°C and after three hours operation when the bed temperature was 500°C and the sugar was added at only 2 grams/gram of sodium.

A decided heat benefit was gained during calcination by adding sugar to the feed. For example, less external heat was required to operate at 500°C with feed containing sugar at 4 grams/gram of sodium than was required to operate at 400°C with no sugar, all other calciner operating conditions being comparable. Argonne National Laboratory reported a reduction of about 33 percent in the external heat requirements when sugar was used in the processing of Purex-type wastes [67].

Boric acid, phosphoric acid, and oxalic acid were all ineffective as additives to the feed in preventing caking in the calciner. Boric acid was added because of its influence on alpha alumina formation. However, based on analysis of the calciner cyclone fines, alpha alumina was not present in the calcined products from the successful tests; therefore, the addition of boric acid may not be necessary, as it is with first-cycle aluminum waste, to prevent the formation of troublesome alpha alumina during the calcination of second-cycle waste. Phosphoric acid was added to test the effect of its known tendency to form

TABLE XXIII

COMPOSITION OF EXISTING HIGH-SODIUM CONTENT
SECOND-CYCLE WASTE AND PILOT PLANT CALCINER FEED

Constituent	Second-Cycle Waste at ICPP		Pilot Plant Calciner Feed (molarity)
	Tank WM-181 (molarity)	Tank WM-184 (molarity)	
H ⁺	0.96	0.28	0.9
Na ⁺	2.05	2.40	2.4
Al ⁺³	0.55	0.89	0.7
Hg ⁺²	0.0013	0.0007	0.0010
NO ₃ ⁻	5.14	5.82	5.5
PO ₄ ⁻³	0.03	0.03	0.03
SO ₄ ⁻²	0.096	0.007	0.08
NH ₄ ⁺	0.063	0.019	0.06

TABLE XXIV

SUMMARY OF FLUIDIZED CALCINATION TESTS OF SECOND-CYCLE WASTE

Feed Additives	Bed Operating Temperature	Results
A. None	400°C	Bed caked after 6 hours
	400°C	Bed caked after 1 hour
	300°C	Bed caked after 1 hour
B. Boric Acid (0.1M B in feed solution)	400°C	Bed caked after 1 hour
	500°C[a]	Bed caked after 2 hours
C. Sugar (2g/g of sodium)	400°C	Bed caked after 1-1/2 hours
	500°C	Bed caked after 3 hours
D. Sugar (4 g/g of sodium)	500°C	No caking -- operated about 12 hours and run voluntarily terminated
	400°C	Bed caked after 2 hours
	450°C	Bed caked after 3 hours
E. Phosphoric Acid (1.5M in feed solution)	400°C	Failed -- heaters burned out
F. Oxalic Acid (1.2M in feed solution)	400°C	Bed caked after 1 hour

[a] Feed rate reduced in order to maintain the bed temperature at 500°C.

glass-like materials with sodium compounds when calcined. It did, indeed, form glassy coatings on heat transfer surfaces which interfered with operation before any bed caking became evident. Addition of oxalic acid, known to be the final degradation product in the denitration of acidic waste with sugar, appeared to have no effect on the progress of bed caking.

2.15 Calcination of Ammonium Nitrate-Containing Raffinate and Blends with Aluminum Nitrate-Nitric Acid Raffinate. Another waste solution scheduled for future calcination in the WCF is an acid-deficient, ammonium nitrate-containing waste from which ammonia and mercury may volatilize. Complete decomposition of ammonium nitrate during calcination and retention of mercury in the solid product are desirable to ensure that ammonium nitrate is not redeposited as a solid in the off-gas system and does not react with mercury in the scrubbing solution to form insoluble mercuri-amidonitrate-type compounds which are potentially explosive.

A laboratory study was directed toward retaining the mercury in the calcined product and completely decomposing the ammonium ion during calcination at 400°C. The results of calcining ammonium nitrate, ammonium nitrate with nitric acid, and blends of ammonium nitrate-aluminum nitrate synthetic waste with aluminum nitrate-nitric acid waste are shown in Table XXV. These results are

TABLE XXV

DECOMPOSITION OF AMMONIA AND VOLATILITY
OF MERCURY DURING BATCH CALCINATION AT 400°C

Feed Solution	Ammonia Decomposed (weight percent of total)	Mercury Volatilized (weight percent of total mercury)
1. Ammonium nitrate, 1.4M	74.2	No mercury in feed
2. Ammonium nitrate, 1.4M; Nitric acid, 5.6M	86.7	No mercury in feed
3. Ammonium nitrate, 1.4M; Aluminum nitrate, 1.65M; Nitric acid, 0.8M	> 99.2	No mercury in feed
4. Ammonium nitrate - aluminum nitrate synthetic waste	> 97.5	15
5. Aluminum nitrate - nitric acid synthetic waste	No ammonium nitrate in feed solution	4[a]
6. Blend: nine volumes of (4), one volume of (5)	> 97.9	9
7. Blend: one volume of (4), one volume of (5)	> 94.7	7

[a] This value was at the lower detection limit for mercury by the method used.

based on analytical determinations for ammonia and mercury in the scrubbing solution, the equipment washes, and the solid residue. Pilot plant operations to confirm the adaptability of the findings to fluidized bed calcination remain to be explored.

The data in Table XXV (Experiments 1 and 2) suggest that the calcination of ammonium nitrate alone, or the ammonium nitrate-nitric acid mixture, resulted in only partial oxidation of the ammonium ion. The reactions occurring were probably as follows:

Reaction (3) is easily reversible and probably accounts for the formation of solid ammonium nitrate that was observed in the off-gas line in calcining these materials.

When aluminum nitrate was present in the waste (Experiments 3 and 4), the slower decomposition rate of this compound and the probable decomposition reaction,

combined to produce a strongly oxidizing atmosphere resulting in essentially complete oxidation of the ammonium ion. Blending the ammonium nitrate-aluminum nitrate synthetic waste with aluminum nitrate-nitric acid synthetic waste (Experiments 6 and 7) also resulted in essentially complete decomposition

of the ammonium ion. The addition of this latter waste is effective because it dilutes the concentration of the ammonium ion and also maintains the concentration of aluminum nitrate at about the same level, thus producing an atmosphere conducive to the decomposition of the ammonium ion.

The addition of aluminum nitrate-nitric acid synthetic waste also reduced the amount of mercury volatilized from the ammonium nitrate-aluminum nitrate waste during calcination (Experiments 5, 6, and 7). The strongly oxidizing atmosphere from the blends is probably conducive to the formation of mercuric oxide rather than metallic mercury. In one run, with the ammonium nitrate-aluminum nitrate waste alone, metallic mercury was collected in the off-gas line. With no acid waste present, apparently conditions can prevail during calcination which result in the formation of metallic mercury.

These laboratory data obtained with the static bed calciner suggest that if the ammonium nitrate-aluminum nitrate waste has a residence time of a few hours in a calciner at 400°C, essentially complete decomposition of the ammonium ion will occur. If, however, fines are formed in converting the liquid waste to a solid, they may be transported almost immediately to the scrubbing system, and the undecomposed ammonium nitrate will be collected in the nitric acid scrubbing solution. This, however, would be recycled through the calciner and, thus, should cause no difficulty.

Operation at lower temperatures does not appear to be desirable since calcination of ammonium nitrate at 250°C indicated considerably less decomposition of the ammonium ion than was obtained at 400°C. As a consequence, solid which is dried in the cooler spray zone of the WCF and remains in the fluidized bed for only a short time could contain a considerable amount of ammonium nitrate.

2.16 Calcination of Stainless Steel Sulfate Waste and Blends with Aluminum Nitrate-Nitric Acid Waste. Stainless steel waste currently stored at the ICPP contains about 0.6M sulfate (Table XX), all of which is potentially volatile. Inasmuch as aluminum sulfate is thermally stable at the calcination temperature used in the WCF (400°C), one approach to inhibit sulfate volatility is to blend the sulfate-containing waste with an aluminum-containing waste so that the sulfate will be retained in the solid product as aluminum sulfate. The results of laboratory experiments in which synthetic waste solutions were blended to give various aluminum-to-sulfate ratios and were then calcined at 400°C in a static bed calciner are shown in Table XXVI.

From the data in Table XXVI, it appears that to prevent volatility of sulfate, sufficient aluminum must be added to react chemically with the sulfate, forming aluminum sulfate which is retained in the solid product. X-ray diffraction analysis indicated that crystalline aluminum sulfate was present in the solid product. This product was friable, and the feed solution appeared to be suitable for fluidized bed calcination.

2.17 Conclusions on Calcination of Blended Wastes. The wastes currently in storage at the ICPP appear to be suitable for fluidized bed calcination if properly blended with each other as summarized in Figure 19. Some of these conclusions are based only on results of calcination in a laboratory-scale static calciner operated at a constant temperature of 400°C. In a fluidized bed calciner, the heat exchanger surfaces are at a somewhat higher temperature and may cause

TABLE XXVI

VOLATILITY OF SULFATE DURING CALCINATION OF
STAINLESS STEEL RAFFINATE BLENDED WITH ALUMINUM RAFFINATE

Aluminum-to-Sulfate Ratios		Sulfate Volatilized (at 400°C)
Chemical Equivalent	Molar	Percent
0	0	65
0.25/1.0	0.17/1.0	41
0.50/1.0	0.33/1.0	33
1.10/1.0	0.73/1.0	< 0.8

additional reactions to take place. Additional pilot plant tests will be required to evaluate the effectiveness of the latter proposed blending schemes.

2.2 Heat Generation Rate of Calcine (D. W. Rhodes, M. E. Jacobson; CHEMISTRY SECTION)

The heat generated by radioactive decay during long-term storage of highly radioactive solid wastes must be considered in the design of properly sized storage facilities to avoid undesirably high temperatures. An accurate value for the heat generation rate is required to determine the permissible bin thickness for given center line temperature and heat transfer conditions. To measure accurately the heat generation rate of highly radioactive calcine from the WCF, an adiabatic calorimeter was constructed of lead. The rate of temperature rise of the lead, which absorbed greater than 99 percent of the beta-gamma radiation, was then measured under adiabatic conditions.

2.21 Experimental Equipment. The equipment consisted of a hollow lead sphere inside a stainless steel vacuum vessel which was immersed in a large water bath. The water bath was enclosed in an insulated box, and the entire assembly was housed inside a plywood shelter. A cutaway view of the equipment is shown in Figure 20. Complete experimental details are reported in IDO-14665 [68].

The water bath temperature was maintained at essentially the same temperature (within $\pm 0.0003^\circ\text{C}$) as the lead sphere by electrical heaters. The amount of heat being supplied by the heaters was controlled automatically. Thermistors on the lead sphere and vacuum vessel transmitted the need for heat through a control system consisting of a differential voltmeter, a 10,000-ohm potentiometer, a recorder, and a thermonitor.

2.22 Experimental Findings. Test runs were made with an electrical resistance heater inside the lead sphere as a source of heat. The measured heat generation rates are plotted against the rate of temperature increase for three different runs in Figure 21. Analysis of the data indicated excellent agreement with theory [68], substantiating the reliability of the calorimeter.

The lead sphere was then filled with highly radioactive calcined alumina from the WCF, and the rate of temperature increase of the lead sphere as a

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Fig. 20 Cutaway view of calorimeter and accessory equipment.

function of time was measured under adiabatic conditions. A run of 46.5 hours indicated a heat generation rate of 0.343 ± 0.004 Btu/hr-lb. The time temperature curve for this run is shown in Figure 22. This experimental heat generation rate agrees well with the value obtained by using the concentration and radioactive decay characteristics of each radioisotope to calculate the heat generation rate, ie, 0.337 Btu/hr-lb.

The adiabatic system used for heat generation measurements functioned smoothly and accurately. The measurements obtained are believed to be within two percent of the true value and are entirely adequate for designing storage bins for the calcine. In future work, heat generation measurements will be made of calcined alumina prepared from fresher wastes, of calcined zirconium fluoride wastes, and of calcined stainless steel wastes.

2.3 Stability of Calcine at High Temperatures (D. W. Rhodes, M. W. Wilding; CHEMISTRY SECTION)

The desirability of using center line temperatures greater than 400°C in the storage bins for WCF calcine (Section II-1.2) necessitated an investigation of the volatility and migration of the fission products and other minor constituents in the calcine. Table XXVII shows the results of an analysis for radioactive and nonradioactive monor constituents in WCF calcine as produced by calcination at 400°C.

Fig. 21 Rate of temperature increase as a function of heat generation rate.

Fig. 22 Temperature increase of lead calorimeter using calcine from the WCF.

TABLE XXVII

MINOR CONSTITUENTS IN CALCINE
FROM ICPP WASTE TANK NUMBER WM-187

Radioactive	Nonradioactive	December 1964 Concentration
Ce-144		5.49×10^{10} d/min-g
Cs-137		2.31×10^{10} d/min-g
Cs-134		1.40×10^9 d/min-g
Ru-106		3.03×10^9 d/min-g
Sr-90		1.79×10^{10} d/min-g
	B	0.1 percent
	Hg	2.2 percent
	N (reported as N_2O_5)	4.0 percent

2.31 Experimental Techniques. Nonradioactive calcine was first heated in a combustion tube-type furnace, and temperatures were determined at various positions in the furnace to establish a temperature profile for subsequent experiments. Two types of experiments were then conducted: the first was designed to measure the loss of minor constituents (volatility) from a small sample at a given temperature; the second attempted to show the extent of migration of these minor constituents through calcine along a temperature profile.

In the volatility experiments, two grams of WCF calcine product were placed in a small alumina tube, 3/8 inch ID by six inches high. A thermocouple was placed in the center of the sample, and the tube was then placed so that the sample was in the hottest position in the furnace. A slight vacuum was pulled on the system to create a mild flow of air past the tube containing the sample, thence out through two caustic scrubbers (4.0M NaOH) connected in series. Individual samples were heated to 600, 700, 800, 900, 1000, 1100, and 1200°C for 24 hours. The solid calcine was analyzed before and after heating. The equipment was washed with hot 4.0M nitric acid, and these washes as well as the scrubbing solutions were analyzed to obtain a material balance.

In the migration experiment, two grams of WCF calcine were placed in an alumina tube, 3/8 inch OD by 1-1/2 inches high. A thermocouple was placed in the calcine, and the tube containing the calcine and thermocouple was placed in the bottom of a second alumina tube, 7/8 inch ID by 18 inches high (Figure 23). Sixteen inches of nonradioactive calcine were added to cover the radioactive sample. The tubes were left open to the atmosphere during heating. The radioactive calcine, which was located in the hottest zone of the furnace, was heated at 800°C for fourteen days. Figure 23 shows the temperature profile in the experimental equipment. After heating, samples of the originally nonradioactive calcine were removed from the tube, pneumatically, at one-inch intervals and transferred to sample bottles for analysis.

Fig. 23 Arrangement of migration tube experiment.

2.32 Results and Conclusions. The experimental results are shown in Figures 24 and 25. Figure 24 shows the percent volatility of those constituents which had significant volatility from 600 to 1200°C, and Figure 25 shows the distribution of the minor constituents that migrated into the nonradioactive calcine column and were detected at various levels along the temperature profile. The results of the two experiments were in agreement. No strontium-90 or cerium-144 volatilized from the WCF calcine at the temperature studied. Cesium-137 appeared to be slightly volatile at 800°C and became increasingly more volatile as the temperature increased. However, cesium that volatilized from the 800°C zone was all condensed before the temperature fell to 600°C. Ruthenium appeared to be only slightly volatile (<1 percent) at the temperatures studied and appeared to condense in the 650 to 400°C zone (Figure 25). No

Fig. 24 Volatility of minor constituents from WCF calcine.

Fig. 25 Distribution of constituents volatilized at 800°C and condensed in an alumina-filled column with a decreasing temperature profile (system maintained at temperature equilibrium for 14 days).

ruthenium data were plotted in Figure 24 because the values were consistently less than one percent except at 900 to 1100°C at which temperature a value near two percent was obtained. Nitrate volatilized above 400°C and condensed in a colder zone. Mercury was volatilized above 600°C and condensed in the 400 to 125°C zone. Boron volatilized above about 1000°C.

X-ray diffraction analysis of the heated calcine indicated gamma alumina to be a major constituent at 700, 800, and 900°C. At 1000°C, there was a minor amount of alpha alumina present; and at 1100 and 1200°C, approximately 15 percent beta alumina and over 50 percent alpha alumina were present. In a long-term experiment in which the calcine was heated at 800°C for 12 months, greater than 50 percent of the alumina was converted to alpha alumina.

The preceding results indicate that some migration of cesium and ruthenium will occur at 800°C, which could modify somewhat the heat generation characteristics of stored calcine. Significant migration of mercury and nitrate will occur; some of these constituents may reach the walls of the container, and the corrosion significance of this during long-term storage is being studied. In addition, alumina stored at 800°C, and possibly as low as 600°C, will convert to the alpha crystalline form over a long period of time.

2.4 Leachability of Calcine and of Glass Prepared from WCF Calcine (D. W. Rhodes, B. E. Paige; CHEMISTRY SECTION)

The fixation of radioactive process wastes in an insoluble medium such as glass has been considered extensively, here and abroad, as a method for long-term storage of highly radioactive wastes. The operation of the ICPP Waste Calcining Facility (WCF) demonstrated that fluidized-bed calcination can produce

a solid waste which is safer and more economical for permanent storage than liquid waste. This material is believed to be a safe form for permanent storage at the NRTS. However, the conversion of the calcine to an alumina-phosphate glass has been shown to be feasible[69] and can be accomplished at locations where the need for still safer storage compensates for the higher costs.

The current study reports the effects of irradiation and heating on the physical characteristics of alumina-phosphate glass during storage and the results of leaching of the glass with aqueous solutions. The leachability of the fission products from WCF calcine itself (at 25°C) was also determined for comparison purposes.

2.41 Experimental Techniques. Alumina-phosphate glass was prepared remotely from full-level radioactive calcine from the WCF. The glass was prepared from 25 weight percent alumina calcine, 40.5 percent P_2O_5 and 18.6 percent Na_2O added as $NaH_2PO_4 \cdot H_2O$, and 15.9 percent PbO . Each gram of the calcine used for these studies contained 10.5 millicuries of cesium-137, 7.6 millicuries of strontium-90, 26.0 millicuries of cerium-144, and 1.4 millicuries of ruthenium-106. The sodium monobasic phosphate, lead oxide, and the calcine were mixed as solids and fused in a porcelain crucible. The mixture was heated two hours at 400°C to dehydrate and convert the phosphate to sodium metaphosphate and then heated to 570 to 650°C over a two-hour period to avoid excessive foaming. The glass was formed by heating the mixture for 16 hours at 900°C. The test specimens were molded in graphite crucibles of known dimensions and cooled slowly to anneal. Polariscopic examination showed that the specimens were not stressed. Chemical analysis of samples which were prepared from each fusion during the molding showed that the molded specimens had a uniform chemical composition, by weight, of 19.5 percent Al_2O_3 , 41.8 percent P_2O_5 , and 16.7 percent PbO . The balance was Na_2O except that silicon dioxide, which varied from 0.2 to 2 percent, was also present, probably as a result of using a porcelain crucible for the fusion.

Two of the glass specimens were heated at 450°C for 30 days to simulate short-term storage. Figure 26 (A) shows the dark translucent specimens as they were molded. Figure 26 (B) shows that the specimens became gray and opaque

Fig. 26 Vitreous and devitrified alumina-phosphate glass prepared from full-level WCF calcine. (A) Vitreous, (B) Devitrified.

during the heat treatment, indicating that devitrification had occurred. In addition, X-ray diffraction analysis showed a high degree of crystallinity in the heat-treated sample while the sample which was not heat treated was completely vitreous. Earlier work [70] showed that irradiating the glass to 10^{10} R total dose did not affect the physical integrity of alumina-phosphate glass and that the glass remained vitreous.

A leaching apparatus was designed to circulate the liquid with minimum attrition of solids. Figure 27 is a schematic diagram of the glass apparatus used for leaching the WCF calcine. The use of an air lift for circulation of the liquid made multiple experiments in a 33-by 34-inch cell (Figure 28) inexpensive to

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Fig. 27 Continuous leaching apparatus.

Fig. 28 Remote cell for four sets of leaching apparatus.

install and simple to operate. In the case of solid glass specimens, the funnel was omitted, and the glass was placed directly in the bottom reservoir. Also, in this case, the Tygon return line was extended, and a cover glass was used to reduce evaporation. In all experiments, 500 ml of liquid was circulated at approximately 100 ml per minute. The extractant was completely removed at each sampling and replaced with fresh liquid. Samples were analyzed for cesium-137 by gamma spectrometry, for strontium-90 by radiochemical separations, and for cerium-144 and ruthenium-106 by radiochemical separations where concentrations were high enough. Aluminum was determined by spectrographic analysis after concentrating the solutions.

2.42 Experimental Results.

(1) Leaching of Calcine. To furnish a basis for comparison with other forms of solid waste, the leaching rate of fission products from WCF calcine was measured using distilled water at $25 \pm 1^\circ\text{C}$. Twenty-gram samples of full-level

calcine were leached as described in Section II-2.41. Cesium leached at a higher rate than strontium during the first 48 hours, but strontium leached more rapidly thereafter. Figure 29 shows that 80 percent of the cesium and 40 percent of the strontium were leached during the first 7 weeks of the leaching test and that most of the leaching occurred during the first two or three days. Only 1.1 percent of the cesium and 1.5 percent of the strontium were leached in an additional 7 weeks of testing. The material balance for these leachings was 86 percent for cesium and 121 percent for strontium. Thus, if WCF calcine is contacted with water, even for a short period, a large fraction of both cesium and strontium will be leached from it.

Fig. 29 Leachability of cesium and strontium for WCF calcine (20 g of calcine leached with 500 ml of water at 25°C).

Less than 0.01 percent of the cerium was leached per hour from the calcine, and 96 percent was found in the calcine after the seven weeks of leaching. Only 50 percent of the ruthenium was found in the residual calcine, but less than 0.01 percent was found in the leaching liquid.

During the first hour of leaching of WCF calcine with 0.5M HNO₃ at 25°C, 20 percent of the cesium was leached while only 2 percent of the alumina was dissolved. Following this initial period, both alumina and fission products dissolved at about the same rate. The lesser amount of alumina reported dissolved in earlier work [71] was probably due to the high alpha alumina content of the calcine studied previously and the low ratio of acid to calcine. In view of the complete disintegration of the calcine in the current study, conversion of the alumina to the alpha form is a necessary prerequisite to removal or recovery of fission products from WCF calcine with dilute nitric acid.

(2) Leaching of Glass. Leaching rates of alumina-phosphate glass at $25 \pm 1^\circ\text{C}$ in distilled water were determined using two vitreous specimens and two heat-treated specimens prepared from full-level radioactive calcine. These specimens weighed about 40 grams and had a surface area of about 35 cm². The high level of activity made it feasible to use a single molded piece, permitting the surface area and other experimental conditions to be defined to a far greater degree than is feasible with the crushed-glass techniques required for low levels of activity.

(a) Relative Leaching of Al, Cs, and Sr. The leaching rate from glass was determined for several different fission products and for aluminum to show whether the leaching is entirely due to the solubility of the glass or is due to preferential leaching of certain materials. Figure 30 shows that the leaching rates obtained from strontium compare favorably to the curve prepared from the leaching rate of aluminum. The cesium values are also very similar although they may be slightly higher for this short period of leaching. These data show that the leaching at 25°C is primarily due to the solubility of the glass.

(b) Effect of Devitrification.

It has been generally agreed that glass would devitrify during storage as a result of the fission product heat; therefore, a prime objective of this work was to determine the effect of heat treatment on the leaching rate of alumina-phosphate glass. With the surface area and other experimental conditions carefully defined, the effect of devitrification on leaching was determined using glass specimens that were identical except that one was vitreous and one was devitrified. The leaching curve, presented in Figure 31, includes points for both vitreous glass and devitrified glass. These points represent average leaching rates for cesium, strontium, and aluminum. The glass which was devitrified by heating one month at 450°C had the same leaching rate as the vitreous glass. These studies indicate that devitrification caused by heating during storage will not increase the rate of leaching, provided a vitreous glass is formed initially by selecting the correct composition and fusing until the glass is homogeneous.

Fig. 32 Relative leachability of cesium and strontium from calcine and from glass using distilled water at 25°C.

Fig. 30 Relative leachability of aluminum, cesium, and strontium from alumina-phosphate glass (glass leached with water at 25°C).

Fig. 31 Effect of devitrification on leachability of alumina-phosphate glass (glass leached with water at 25°C).

(c) Relative Leachability of Calcine and Glass. Since the surface area of the calcine is not known, a comparison of the leaching rate of calcine to that of glass was made on the basis of total fission products leached per day. Figure 32 shows the leaching rates of calcine-containing glass and the leaching rates of the WCF calcine. The relative stability of alumina-phosphate glass in distilled water at $25 \pm 1^\circ\text{C}$ is demonstrated by the fact that only ≈ 0.005 percent of the cesium and strontium leached from the glass in 7 weeks while 80 percent of the cesium and 40 percent of the strontium leached from alumina calcine in the same period. Glass stored in larger volume would probably have a lower surface-area-to-weight ratio than the test specimens, and the radioactivity leached per day would be even less than the values reported.

2.5 Particle Growth and Size Distribution in Fluidized Bed Processes -- A Mathematical Model with Computer Solutions (E. S. Grimmer, B. R. Dickey; DEVELOPMENT ENGINEERING SECTION)

Fluidized bed processes deal with particles in intimate contact with an upward flowing stream of fluid, usually a gas. Depending upon the process, these particles may grow or disintegrate, enter or leave the system, take up or reject heat, transfer heat from one part of the system to another, provide surface area for catalytically induced reactions, or react with the flowing stream of fluid. In most processes, many of these phenomena occur together in a complex but interrelated way.

The current study deals with those factors which affect change in the particle population and size distribution in a fluidized bed system. Complete details of the study are reported in IDO-14634 [72]; a summary of the results is reported here.

The formulation of a mathematical model of a fluidized bed process is based on the assumption that fluidization is so complete that the bed is at all times perfectly mixed. This assumption implies that at any instant, simultaneous bed samples taken at random locations in the bed will contain identical distributions of particle sizes.

Within this perfectly mixed bed of particles, several rate processes take place which may change the particle size distribution and number of particles in the bed. Consider a group of particles whose diameters lie within a particle-size interval, ΔL . At any time, the number (or weight) of particles in this interval depends upon the particle growth rate into and out of the interval, the particle attrition rate into and out of the interval, the elutriation rate out of the interval, the product rate out of the interval, the feed deposition rate into the interval, and the seed rate into the interval.

By suitable mathematical manipulation, these processes can be combined to form a general partial differential equation describing the system in terms of a number of independent process operating variables. The equation follows:

$$\begin{aligned} \frac{\partial^2 W(L,t)}{\partial L \partial t} = & S(t) \frac{\partial W_s(L,t)}{\partial L} \\ & \text{seed addition} \\ & + \frac{G(L)}{\rho L} F(t) \frac{\partial W(L,t)}{\partial L} \\ & \text{feed deposition} \\ & + AB(L) \frac{\partial^2 W(L,t)}{\partial L^2} + \frac{\partial AB(L)}{\partial L} \cdot \frac{\partial W(L,t)}{\partial L} \\ & \text{attrition} \\ & - g_i(L) \frac{\partial^2 W(L,t)}{\partial L^2} + \frac{\partial g_i(L)}{\partial L} \cdot \frac{\partial W(L,t)}{\partial L} \\ & \text{particle growth} \end{aligned}$$

$$- \frac{P(t)}{W} \cdot \frac{\partial W(L,t)}{\partial L} - \frac{(A)EK(L)}{W} \cdot \frac{\partial W(L,t)}{\partial L}$$

product removal elutriation

where

(A) = cross-sectional area of fluidized bed

AB(L) = attrition rate function

C_g(L) = feed deposition rate function

EK(L) = elutriation function

g_i(L) = particle growth rate function

L = particle diameter

F(t) = solid feed rate function

P(t) = product rate

S(t) = seed rate function

W = bed weight

W_s = cumulative weight fraction of seed material

ρ = density of deposited material

This equation is much too complex to solve analytically for most practical applications. However, a modification of the Runge-Kutta method for solving differential equations can be used for this purpose when programmed for an IBM 7040 computer. The equation was solved by this program for several fluidized bed calcination runs, and the results were compared with the actual calciner runs. Three of these runs are described in detail in IDO-14634[72].

Simulated calciner runs were compared with actual calciner runs made in 3-inch-diameter, 12-inch-diameter, and two-foot-square calciners. From fair to excellent simulation of the actual particle size distribution of the beds for all three runs was obtained. A comparison of some of the features and operating conditions for the three calciners is shown in Table XXVIII.

TABLE XXVIII

A COMPARISON OF SOME OF THE FEATURES
OF THREE CALCINERS USED FOR TEST RUNS

Feature	Calciner Size		
	24 Inches	12 Inches	3 Inches
Cross-sectional area of bed, ft ²	4.0	0.777	0.051
Nominal bed weight, kg	300.0	45.0	1.0
Nominal product rates, kg/hr	4.6	0.57	0.12
Product rate/bed weight	0.015	0.013	0.124
Bed cross-section/bed weight	0.013	0.017	0.051
Product rate/bed cross section	1.14	0.73	2.42

An examination of Table XXVIII shows that there are striking differences between the sizes and operating conditions for the three calciners. The closest similarity between them is the ratio of the product rate to the bed cross-sectional area, and here there is a three-fold difference. In view of these different characteristics and the generally good simulation of the actual calciner runs, it can be concluded that the mathematical model is generally applicable to a wide range of fluidized bed calciner sizes and operating conditions.

2.6 WCF Off-Gas Filter Support Medium (D. W. Rhodes, C. A. Zimmerman; CHEMISTRY SECTION)

As a part of a continuing program to reduce operational costs in the WCF, an asbestos-type and a glass-type filter support were tested as a part of the off-gas cleaning system. After a period of actual use in the WCF, a crystalline deposit was found in the filter system; this was analyzed and found to contain magnesium nitrate. Since formation of crystalline deposits can lead to plugging of the filter system with subsequent disruption of plant operations, the asbestos-type and glass-type filter support media were tested as possible sources of magnesium and, in addition, were treated to determine their relative chemical resistance to 4M nitric acid and vapors of this acid mixed with air.

Emission spectrographic analysis showed that the asbestos-type material contained approximately 20 percent by weight of magnesium and, thus, could be the source of magnesium. Chemical resistance tests in boiling 4M nitric acid and in air plus vapor from boiling 4M nitric acid at 65 to 70°C and at 94 to 96°C demonstrated that the asbestos-type filter support suffered a weight loss over three times greater than the glass-type support under the same conditions. Thus, the glass-type filter support is better suited for use in this service.

2.7 Solids Flow Control Valve (J. C. Petrie, E. D. Cooper; DEVELOPMENT ENGINEERING SECTION)

A solids flow control valve with no internal moving parts has been developed and tested for use in the new solids storage facility for calcined material from the WCF. The valve will be used to control the flow of calcined solids to two of the seven storage bins in the new facility. The purpose of the valve is to provide a means of segregating chemically different calcined solids should processing beyond calcination become desirable. Except when one of these pneumatic valves is "opened", the waste solids will fall into the lowest of the entrance pipes to the other five bins until all five are filled sequentially.

Figure 33 demonstrates the principle of operation for the solids flow control valve. A complete discussion of the valve and its testing is reported in IDO-14666 [73]. Granular solids under gravity flow in a round pipe are stopped at an offsetting horizontal section by the angle of repose of the solid material. A small flow of air injected at the vertical-to-horizontal transition disrupts the angle of repose thereby permitting the solids to flow through the valve into the desired channel. The rate at which air is injected controls the solids flow rate through the valve. A similar valve operating on the same principle was developed at Hanford [74].

Details of the valve to be installed at the new solids storage facility at the WCF are shown in Figure 34. A full-scale model of this valve was tested to determine operating curves, optimum locations for the air inlet, and possible

Fig. 33 Operating principle of the solids flow control valve.

Fig. 34 Solids flow control valve.

areas of erosion [73]. The results of the testing have shown that the valve will control the flow of solids over the desired range (50 to 1800 lb/hr) with minimal erosion.

3. HEAT DISSIPATION FROM BURIED WASTE

(D. E. Black, B. R. Dickey; DEVELOPMENT ENGINEERING SECTION)

Currently, burial of high-level radioactive solid materials, such as the product of the Waste Calcining Facility (WCF), requires rather expensive storage facilities. Much of the cost of such a facility can be attributed to the necessity for cooling. Burial of waste solids at shallow depths within a containment structure having a simplified (or possibly no) cooling system would reduce waste management costs appreciably. Before those economies can be realized, however, a careful evaluation of heat transfer from such a system must be undertaken.

To this end, a program has been initiated to study the factors affecting the transmission of heat through soil. The initial phase of the program includes: (a) evaluation of the soil physical properties which affect the heat transfer (ie, thermal conductivity, specific heat, moisture content, and density); (b) development of a mathematical model describing heat transmission in the buried heat-source/soil system; (c) preparation of a computer program for solving the equations derived from the model; and (d) determination of the accuracy of the model by experimentally simulating the heat-source/soil system with a buried electrical heating element. After verification, the model and computer program will be used to optimize the design of future storage facilities for high-level wastes. The final phase of the program will consist of comparison of the results of the computer program with those obtained from the actual burial of a radioactive source.

3.1 Experimental Program

An electrical simulation of the buried-source soil system was initiated in April 1965. The experimental setup consists of a 1500-watt electrical heater buried 10 feet below the surface of the soil. Nine thermowells (each containing three thermocouples located six, ten, and fourteen feet below the surface of the soil) are buried at various radial distances from the central heater location. Core holes, cased with plastic pipe, are located on a triangular pitch around the heater. Moisture contents at various depths in the soil have been determined by lowering a neutron moisture detector into the core holes and taking readings at various depths.

Since early April, temperature and moisture data for the soil have been recorded for a constant power level (to the heater) of 950 watts. Time-temperature plots indicate that the readings have not yet reached equilibrium values; observations will continue at this power level until the temperatures reach equilibrium. Equilibrium values of the temperature and moisture content of the soil will also be obtained at other power levels.

A mathematical model describing the heat transfer through the soil surrounding the buried heater has been developed. Solution of the two-dimensional, time-dependent, partial-differential equation derived from this model has been simplified by using a finite Fourier sine transformation. Application of this technique reduces the two-dimensional, time-dependent equation to a one-dimensional, time-dependent problem. A computer code (for an IBM 7040) has been written which solves the transformed partial differential equation by use of finite difference equations. Inversion of the transformed temperature to actual temperatures is then required for those points in the system of interest. Preliminary comparison of the computer curves with experimental data indicates good agreement between the two.

In order to determine optimum locations for eventual test burial of high-level radioactive solid materials, in situ determinations of the thermal conductivities will be conducted using a commercially available, "thermal conductivity probe". The probe, consisting of a cylindrical rod of high conductivity material, is inserted into the soil location to be tested, and a constant power is applied to a heating element located within the probe. Temperatures obtained from sensors located at the center line of the probe are plotted versus the natural log of the elapsed time. This curve asymptotically approaches a constant value of $(Q/4\pi k)$. Since Q (the power per unit length of the probe) is known, the thermal conductivity can be determined from the slope of the asymptotic line [75]. The probe will be used to determine the thermal conductivities of soils at several different locations within the boundaries of the NRTS, at temperatures ranging from 100 to 1000°F.

3.2 Future Applications

Results of this study will also supply supporting data for future study of the feasibility of burial of "troublesome" spent nuclear fuel elements which are limited in quantity and present difficult reprocessing problems.

4. FUEL STORAGE BASIN STUDIES

4.1 Measurement of Fission Product Leakage from Fuel Elements Stored in Water (D. W. Rhodes; CHEMISTRY SECTION)

During the interim period between the discharge of fuel elements from a reactor and the recovery of uranium from the fuel, it is common practice in the atomic energy industry to store the fuel elements under water. Underwater storage is an economical and efficient means of providing both shielding and cooling of the irradiated fuel during the storage interval which may be as long as several years.

Due to the wide variety and large number of fuel elements that are stored in the ICPP fuel storage basin, occasionally the cladding of one or more elements has been penetrated inadvertently by corrosion or by mechanical handling, thus allowing fission products to leach from the irradiated fuel. The presence of fission products, particularly long-lived ones, in the water is undesirable because (a) the exterior of the transfer casks, which often are shipped off-site, may become contaminated during the underwater loading and unloading operations and (b) water that is discharged from the basin as a part of the corrosion control program must be decontaminated before it can be released to the environs.

4.11 ICPP Detection Program. To detect fuel with defective cladding, a Fuel Element Leak Tester (FELT) was designed and tested at the ICPP. The detection of fission product leakage from faulty fuel elements was accomplished by placing the suspect fuel elements in a closed stainless steel cylinder containing uncontaminated water (Figure 35). Details of construction and operation are reported in IDO-14654 [76].

In summary, the measured rate of increase in the fission product content of the water indicated the rate at which fission products were being leached from the fuel elements. The leakage rate was measured for various uranium-aluminum alloy fuel elements clad with aluminum and was found to be constant for at least 300 hours. Fuel elements cut to deliberately expose 10 cm^2 of the irradiated uranium-aluminum alloy had a measured leakage rate of $335 \mu\text{Ci/hr}$. The measured background rate for the stainless steel cylinder and apparently undamaged fuel was $0.5 \mu\text{Ci/hr}$. The measured leakage rate of fuel considered to have minor cladding defects fell between these two values. Figure 36 shows curves [76] depicting the leaching rate of the apparently undamaged fuel (I), the defective fuel (II), and the cut fuel with a known area exposed (III).

CPP-S-3375

Fig. 35 Fuel element leak tester (FELT).

4.12 Conclusions. This method of leak testing permits the early identification of fuel elements with damaged cladding so that contamination of storage basin water can be minimized. The operation of the unit was both convenient and efficient. Very little time was required for the actual testing, and no shielding facilities other than the water normally present in the storage basin was required. The equipment can be used to test nearly any type of solid fuel for defects; fuels of unusual dimensions or shapes can be accommodated by using a cylinder of the proper size for the fuel of interest.

4.2 Decontamination of Storage Basin Water (D. W. Rhodes, M. W. Wilding; CHEMISTRY SECTION)

The storage of a large number and a wide variety of irradiated fuel elements under water at the ICPP produces water slightly contaminated with cesium-137 and strontium-90. Each month, approximately 100,000 gallons of this water is removed from the basin for corrosion control purposes, decontaminated, and released to the environs. Both cesium-137 and strontium-90 are removed by passing this effluent through an ion-exchange bed using the naturally occurring mineral clinoptilolite as the ion exchanger. No other fission product exceeds its drinking water tolerance in the basin water so these are the only two contaminants of concern.

The mineral clinoptilolite is a naturally occurring zeolitic mineral that has been studied extensively at Chalk River [77] and at Hanford [78] for possible use as an ion exchanger to remove cesium and, to a lesser extent, strontium from radioactive waste solutions. The availability of the mineral in large natural beds in southern Idaho suggested that it might be used to remove these isotopes from ICPP storage basin water.

4.21 Results of ICPP Program. The actual operation for about one year of a unit handling approximately 100,000 gallons per month of effluent is discussed in IDO-14657 [79]. Approximately 24 cubic feet of mineral were required to obtain an effluent with an average concentration of strontium-90 near drinking water tolerance and a concentration of cesium-137 well below drinking water tolerance. The results of approximately one year of operating experience are shown in Figures 37 and 38 [79].

Initially, the clinoptilolite used in the columns was oversized (1 to 6 mm diameter) because of inadequate crushing and sieving procedures; consequently, the removal of strontium was inadequate up to about April 1964 (Figure 37). Removal of cesium-137, on the other hand, to well below drinking water tolerance was achieved for every month after startup of the decontamination system as shown in Figure 38. After the proper size material (0.25 to 2.0 mm) was obtained for the columns (April 1964), the strontium concentration in the effluent averaged

Fig. 36 Fission product leakage from aluminum-clad fuel elements stored in water.

Fig. 37 Concentration of strontium-90 in basin water and effluent.

about 2.5×10^{-6} microcuries per milliliter for the rest of the operating period as shown in Figure 37. Using an average influent concentration for strontium-90 of about 5×10^{-4} microcuries per milliliter, the average decontamination factor was about 200. The total volume of effluent discharged during this period was about 1,300,000 gallons, all of which percolated through a considerable depth of earth materials providing additional decontamination before the effluent reached the ground water table.

Although the use of clinoptilolite columns to remove strontium-90 and cesium-137 from the storage basin effluent has been successful, this is considered to be an interim approach. Close surveillance of the fuel stored in the basin and general "basin cleanup" procedures are expected to reduce the concentration of these two radioisotopes below drinking water tolerances within about five years, making decontamination of the effluent unnecessary.

4.3 Storage Basin Water Chemistry (D. W. Rhodes; CHEMISTRY SECTION)

Control of growth of microorganisms in the fuel storage basin at the ICPP has, in the past, been obtained by adding chlorine to the water. For several years, approximately three pounds of chlorine per day were added as gaseous chlorine to approximately 1,500,000 gallons of water.

Fig. 38 Concentration of cesium-137 in basin water and effluent.

Following conversion to the use of calcium hypochlorite, added as a slightly acidified solution, several months experience shows that chemical consumption has been reduced to about three pounds of chlorine per month (added once per month as calcium hypochlorite) with continued maintenance of water clarity. This reduced chlorine addition has resulted in reduced chemical costs and in a lower concentration of potentially corrosive chloride ion in the basin water.

4.4 Electrochemical Corrosion of Fuel Cladding in Storage Basin Water (D. W. Rhodes, T. L. Hoffman; CHEMISTRY SECTION)

The attractive structural and corrosion resisting properties of austenitic stainless steel, Zircaloy, and Nichrome alloys have resulted in their being used to an increasing extent as cladding for nuclear fuel assemblies. In many instances, these alloys may be stored under water in contact with existing fuel storage racks or other nuclear fuel assemblies where dissimilar metals are present. Since the galvanic relationships among metals are influenced by the nature of the environment, studies of the galvanic component of the corrosion

of coupled dissimilar metals were made in storage basin water to obtain information pertaining to the corrosion of these metals in contact with each other during underwater storage.

To evaluate the possible tendency toward galvanic corrosion, the potentials of Type 1100 aluminum, SAE 1020 carbon steel, and zinc (storage rack components) and several cladding materials were measured relative to a standard calomel electrode. The descending galvanic series in storage basin water was as follows: zinc, SAE 1020 carbon steel, Type 1100 aluminum, reactor-grade Nichrome, Type 304 stainless steel, Type 348 stainless steel, Zircaloy-2, and Zircaloy-4.

In addition, the limiting current density was measured when the various metal coupons and aluminum in basin water were coupled externally. This current was taken as the galvanic component of the corrosion of the metals in the couple [a]. Where aluminum was anodic in the couple, the calculated corrosion rate due to the galvanic component of corrosion was always less than 0.001 MPM. With carbon steel and zinc anodic, the calculated corrosion rates due to the galvanic component were 0.001 and 0.002 MPM, respectively. These corrosion rates are not directly extrapolatable to actual corrosion rates to be experienced in the basin since galvanic corrosion is grossly influenced by the relative areas of the effective electrode surfaces; therefore, each real situation must be evaluated on its own merits. Further, the galvanic corrosion measured here as a current between dissimilar metals is only one component of the total corrosion to be expected on the metals.

These experiments do indicate, however, that there is very little probability for disastrous galvanic corrosion between Type 1100 aluminum and the various cladding metals listed earlier. Examination of a storage rack compartment made of Type 1100 aluminum in which a galvanized capsule, representing a fuel storage cylinder, had been stored for eight months revealed no corrosion of the aluminum.

[a] Here, the galvanic component of corrosion is defined as that portion of the total corrosion contributed by the current flow between the dissimilar metals of the couple.

III. REACTOR TECHNOLOGY SUPPORT

1. LOFT ASSISTANCE PROGRAM

A Safety Test Engineering Program (STEP) has been established by the Atomic Energy Commission for the purpose of conducting engineering-scale tests which will demonstrate the behavior of nuclear systems under accident conditions and provide information regarding the consequences of nuclear accidents. This effort is part of the nuclear safety program of the Division of Reactor Development and Technology. Phillips Petroleum Company has been assigned a major responsibility in this program. One phase of the program being conducted at the NRTS is the Loss-of-Fluid Test (LOFT). This program [80] embodies the testing of a complete nuclear system typical of pressurized water power reactors under conditions which simulate as closely as possible those which might be present in an actual loss-of-coolant accident.

In this test, a sequence of complex interrelated events will begin with the simulated rupture of the coolant piping. After release of the coolant, the core will overheat and result in melting of the fuel and cladding (Zircaloy-4) and release of gross fission products. A fraction of the fission products will ultimately escape into the containment building where some will deposit on the walls and equipment. It is anticipated that all of the rare gases, a significant fraction of the iodine, cesium, and tellurium, and less than one percent of the other fission products will leave the reactor vessel and at least partially plateout on the interior surfaces of the LOFT containment building. During and after the core meltdown, samples will be taken both in the reactor and in the containment building to provide quantitative information on fission product behavior. Following the termination of the experiment, which is expected to last about five days, the internal pressure in the containment building will be reduced to atmospheric with internal pressure-reduction sprays, and the airborne fission products will be largely removed by the halogen and particulate removal system. This will be followed by remote decontamination using high-pressure sprays to remove fission products from the containment building walls and equipment.

The Chemical and Process Development Branch was assigned responsibility for the following studies in support of the LOFT program:

- (1) Selection of a suitable coating and sealant for the containment building interior
- (2) Development of optimum decontamination procedures and methods for removing mixed fission products from the reactor and the containment building interior
- (3) Development and testing of a continuous fission product sampler-monitor for the containment atmosphere
- (4) Design, construction, and operation of a fission product generation and containment test installation for use in the above assignments.

Other assignments are related to those given above and include a study of deluge solutions, proof tests of LOFT samplers, disposal of liquid wastes, reprocessing of the LOFT fuel, and planning and consulting services.

A number of specific studies in each category have been proposed. Progress on the program is reported in the following four sections.

1.1 LOFT Coating Selection Studies [a] (K. L. Rohde, B. J. Newby; CHEMISTRY SECTION)

Studies are being made to select a coating material for the interior of the LOFT containment building which will both duplicate the fission product plateout to be expected in a typical reactor containment building and be readily decontaminated by the remotely operated decontamination spray system in LOFT. The coating should also be resistant to possible decontaminating reagents that might be used in the containment building, be resistant to pressurized steam up to 40 psig and 138°C for as long as three days, and be resistant to a radiation dose as great as 1×10^9 R in a steam atmosphere.

Because of its high probability of release from the hot reactor vessel, iodine will represent the major contaminant for a short time after the LOFT test. If entrance to the building is to be made after a short cooling time, it is anticipated that very high decontamination factors must be obtained for iodine. Therefore, the contamination-decontamination behavior of iodine has warranted the earliest and most extensive study. It is anticipated that the concentration of radionuclides of moderate and long life on the walls of the building will be great enough to require effective decontamination from many of these also. Therefore, additional effort has been devoted to studies of the behavior of fission products other than iodine when these are deposited on surfaces from a gas stream. The resistance of coatings to pressurized steam, radiation, and chemical reagents was also studied.

1.11 Behavior of Molecular Iodine Toward Coating Materials. The contamination-decontamination behavior of molecular iodine was studied on coupons of stainless steel, carbon steel, Teflon, polyethylene, and coupons covered with 19 different protective coatings. Some of the coatings were recommended by the LOFT architect-engineer; others were selected as a result of consultations with paint manufacturing companies and consultants; and others were selected on the basis of a literature search. The coatings included epoxies, urethanes, phenolics, vinyls, and polyesters. Coupons were contaminated with molecular iodine generated by adding hydrogen peroxide to a basic sulfite solution containing sodium iodide tracer and carrier, and by heating the solution at 400°C. The iodine was released with some water vapor in a stream of nitrogen

[a] The experimental work reported in this document was carried out for the specialized purpose of obtaining fission product contamination-decontamination information on materials in the specific application and environment listed in the report. Any conclusions as to the relative merits of these commercial coatings apply only to the use of the materials in the specific application and environment mentioned. The fact that some of the materials were less desirable than others for the specific application does not imply that they are generally inferior.

and deposited on coupons at a temperature of 40°C. The coupons were decontaminated by spraying them for one minute at 20 psig (0.9 gal/min) with 3M nitric acid, 1M sodium hydroxide-0.5M sodium thiosulfate, or a solution of 1 lb/gal of Turco Alkaline Rust Remover at 80°C. Under identical contamination conditions, sorption of iodine was 1.5 µg/sq inch on stainless steel, 0.6 µg/sq inch on Teflon, 64 µg/sq inch on carbon steel, and varied between 6 and 200 µg/sq inch on organic coatings. A decontamination factor of about 130 was obtained for stainless steel, 400 for carbon steel, 30 for Teflon, and 2 for polyethylene; the decontamination factors obtained from 17 of the coatings varied between 1.2 and 6.3; a decontamination factor of 12 was obtained from the other two coatings. Increasing the number of coats in a coating system resulted in no decrease in iodine sorption and no increase in iodine removal. No particular generic type of coating was obviously superior in terms of iodine decontamination; the variation in detail of formulation within the generic types is apparently more significant than the variation between generic types. Iodine penetrated quite deeply into protective coatings; penetration of greater than eight mils was observed in several cases.

1.12 Behavior of Molecular Iodine Toward Decontamination with Pressurized Steam. Pressurized steam over a long period of time removed iodine from organic protective coatings contaminated at 40°C much more effectively than did spraying the coatings with hot high-pressure sprays of decontamination solutions for a short time. The same autoclaving conditions removed different amounts of iodine from different coatings. Coupons covered with 17 of the coatings mentioned in the previous section were contaminated with molecular iodine as previously described and autoclaved for 3 days at 110 to 138°C and 13 to 40 psig steam pressure. The iodine decontamination factor from one coating was only 5.2, but the decontamination factors obtained from the other 16 coatings varied between 10 and 1100. Iodine removal was strongly dependent on the pressure and temperature of the steam. Table XXIX shows the variation of iodine removal between autoclaving temperatures of 110 and 138°C for representative samples of the coatings.

Recent tests indicate that steam autoclaving is probably not effective in removing iodine which is deposited in the presence of high-pressure steam. Investigation of this aspect is continuing.

1.13 Behavior of Radioactive Iodine and Other Radionuclides Toward Protective Coatings. Painted carbon steel and unpainted carbon steel and stainless steel coupons were contaminated at the Oak Ridge National Laboratory in the Containment Mock-Up Facility in a moist atmosphere by fission products released from melted "simulated irradiated" uranium dioxide. The coupons were decontaminated by spraying with 3M nitric acid at 80 or 85°C (for 1 or 10 minute periods, at a pressure of 20 or 80 psig, and a flow rate of 0.9 or 1 gal/min) followed by spraying with a solution of 1 lb/gal of Turco Alkaline Rust Remover under the same conditions; water rinses were used after each decontamination step. Cesium-137 and iodine-131 were found on the coupons. Table XXX shows the behavior of these fission products toward various covering materials. The iodine behavior toward the covering materials agreed with previous experience; iodine could be removed only poorly from organic protective coating surfaces but was readily removed from steel surfaces. Cesium behavior was similar to that of iodine with the exception that it was removed from protective coatings better than iodine by a factor of at least 10. Increasing the length of spraying

TABLE XXIX

VARIATION IN IODINE REMOVAL WITH STEAM
TEMPERATURE AND PRESSURE FOR REPRESENTATIVE COATINGS
(Painted coupons were contaminated at 40°C
with iodine, counted, then autoclaved for three
days at the temperature-pressure shown, and again counted.)

Coating ^[a]	Generic Type	Original Iodine Contamination ($\mu\text{g}/\text{in.}^2$)	138°C - 40 psig (iodine DF)	110°C - 13 psig (iodine DF)
1 Coat Amercoat-66 Prime, 1 Coat Amercoat-66 Surfacer, 2 Coats Amercoat-66 Seal/Gloss with 25 Weight Percent 2-Nitropropane	Epoxy	105	830.0	11.0
1 Coat Phenoline-300 Orange 3 Coats Carboline-B-15	Urethane	6	5.2	2.8
Amercoat-33HB	Vinyl	7	24.0	9.0
Phenoline-300	Phenolic	26	27.0	14.0
Phenoline-305	Phenolic	30	57.0	9.0
Devran-500	Epoxy	15	260.0	60.0

[a] Unless designated otherwise, each coating system consists of one coat of primer and one coat of finish.

time and the pressure at which the decontamination solution was applied did not always increase iodine and cesium removal.

Coupons contaminated as described in the previous paragraph were also autoclaved with steam for three days at 40 psig and 138°C, and the results are shown in Table XXXI. The autoclaving removes iodine effectively from organic protective coatings, but does not remove cesium as effectively as spraying with 3M nitric acid followed by Turco Alkaline Rust Remover as discussed above. The autoclaving conditions remove iodine and cesium effectively from uncoated stainless steel, but not from uncoated carbon steel. The removal of these fission products from carbon steel is probably poor due to the tendency of the steel to rust when contacted with steam.

Coupons painted with a variety of coatings (epoxies, phenolics, vinyls, a polyester, and a chlorinated rubber) were also contaminated at the Nuclear Safety Pilot Plant at ORNL with activity generated from molten irradiated uranium dioxide clad in stainless steel. These specimens were decontaminated by stirring in 3M nitric acid followed by stirring in 1 lb/gal Turco Alkaline Rust Remover, both at 80°C. The decontamination factors for iodine ranged between 1.3 and 7.2, those for tellurium between 1.9 and 11, and for neptunium between 1.2 and 4.6.

1.14 Chemical Resistance Tests. Chemical resistance tests were made on steel coupons painted with a variety of organic protective coatings. The coated coupons were immersed at 60°C for 30 days in solutions that might be used as decontaminating reagents in the LOFT Containment Building. The physical condition of the coatings was noted after 1, 5, and 30 days of immersion. A summary of the results is shown in Table XXXII. Phenoline-300 and Amercoat-HB66 were resistant to more decontamination solutions than any of the other coatings tested.

TABLE XXX

DECONTAMINATION OF CESIUM AND IODINE FROM VARIOUS MATERIALS
(Coupons were contaminated from melted "simulated irradiated"
uranium dioxide and decontaminated by spraying with 3M HNO₃
followed by spraying with 1 lb/gal Turco Alkaline Rust Remover.)

Material	Cs-137 Decontamination Factor	I-131 Decontamination Factor
Carbon steel painted with Phenoline-300 ^[a]	10	1.4
Carbon steel painted with Phenoline-300 ^[b]	110	1.9
Carbon steel painted with 4-coat Amercoat-66 system with nitropropane ^[b]	55	1.9
Carbon steel painted with Amercoat-33 HB ^[a]	45	1.7
Carbon steel painted with Amercoat-33 HB ^[b]	14	1.4
Carbon steel painted with Amercoat-HB 66 ^[a]	13	1.9
Uncoated stainless steel ^[a]	$\geq 10^4$	$\geq 10^3$
Uncoated stainless steel ^[b]	$\geq 10^3$	$\geq 10^2$
Uncoated carbon steel ^[a]	$\geq 10^4$	$\geq 10^5$
Uncoated carbon steel ^[b]	$\geq 10^3$	$\geq 10^3$

[a] Decontaminated by spraying with 3M HNO₃ at 80°C for one minute at a pressure of 20 psig and a flow rate of 0.9 gal/min, rinsing with water, spraying with 1 lb/gal of Turco Alkaline Rust Remover at 80°C for one minute at a pressure of 20 psig and a flow rate of 0.9 gal/min, and rinsing with water.

[b] Decontaminated by spraying with 3M HNO₃ at 85°C for 10 minutes at a pressure of 80 psig and a flow rate of 1 gal/min, rinsing with water, spraying with 1 lb/gal of Turco Alkaline Rust Remover at 85°C for 10 minutes at a pressure of 80 psig and a flow rate of 1 gal/min, and rinsing with water.

TABLE XXXI

REMOVAL OF IODINE AND CESIUM FROM COATING
MATERIALS BY PRESSURIZED STEAM AT 138°C AND 40 psig
(Coupons were contaminated from melted "simulated-irradiated"
uranium dioxide; autoclaving time was three days.)

Materials	Cesium-137 Decontamination Factor	I-131 Decontamination Factor
Carbon steel painted with 4-coat Amercoat-66 system with nitropropane	2.9	$\geq 10^3$
Carbon steel painted with Devran-600	12.0	131.0
Uncoated carbon steel	5.0	3.8
Uncoated stainless steel	$\geq 10^3$	$\geq 10^2$

1.15 Steam Atmosphere Resistance Tests. Steel coupons coated with various protective organic coatings were autoclaved at 138°C and 40 psig for 3 days. Included in these coatings were epoxies, urethanes, phenolics, a vinyl, and a polyester. One of these coatings (the polyester) resisted these conditions completely; the surfaces of urethane, one epoxy, and all the phenolics tested cracked and/or peeled; the other coatings blistered without the surface being broken.

1.16 Radiation Resistance Tests. Coated steel coupons were exposed in a steam atmosphere at a beta-gamma dose rate of approximately 2.0×10^6 R/hr until a total dose of 10^9 R was received. Coatings tested were Phenoline-300 and -305, Amercoat-33HB and -HB66, Devran-500, and Carboline-1323. The coupons were examined after a dose of 10^7 R had been received as well as at the end of the exposure period. A radiation dose of 10^7 R did not affect any of

TABLE XXXII

RESISTANCE OF COATINGS TO CONTINUAL SUBMERGENCE
IN PROSPECTIVE DECONTAMINATION REAGENTS AT 60°C
(Coating Painted on Carbon Steel Coupons)

Coatings	Deionized Water	3M Nitric Acid	0.8M Nitric Acid - 0.001M Mercuric Nitrate - 0.001M Mercurous Nitrate	0.4M Oxalic Acid - 0.16M Ammonium Citrate - 0.34M H ₂ O ₂ Adjusted pH to 4 with Ammonium Hydroxide	0.2M Potassium Permanganate - 0.25M Sodium Carbonate - 0.25M Sodium Bicarbonate - 3.5 g/l EDTA	1M Potassium Iodide
Phenoline-305	S	0	I	X	S	S
Amercoat-33HB	S	0	X	X	S	X
Devran-500	S	0	0	X	S	S
Phenoline-300	S	0	I	S	S	S
Amercoat-HB66	S	0	I	S	S	S
Carboline-1323	S	X	X	S	S	S
Carboline-1321, -1324, -1341		0				
Carboline-1327		0				

Coatings	Turco 4306D (8 oz/gal)	Turco 4518 (8 oz/gal)	Turco Power Steam (1 lb/gal)	Turco Alkaline Rust Remover (1 lb/gal)	Turco 4502 (1 lb/gal)	5 wt% Versene	1 wt% Alconox - 1 wt% Versene	1 wt% Mulsor 224	2 wt% Victamul 116C	Supreme (1 lb/gal)
Phenoline-305	S	S	S	S	S	S	S	X	S	S
Amercoat-33HB	S	S	S	S	0	X	I	I	X	S
Devran-500	0	S	S	S	S	S	S	I	I	S
Phenoline-300	S	S	S	S	S	S	S	S	S	S
Amercoat-HB66	X	S	S	S	X	S	S	X	X	S
Carboline-1323	S	S	I	I	0	S	S	X	S	S
Carboline-1321, -1324, -1341					I					
Carboline-1327					0					

"S" = Coating is unaffected or slightly affected by 30 days submergence, it is recommended for considerable contact service with the reagent, but not for tank lining service. OK for decontamination service.

"X" = Coating does not survive the 30-day submergence, but lasts 5 days or longer, it is recommended for service where contact with reagent will aggregate no more than 10 percent of the time OK for decontamination service

"I" = Coating withstands more than 1 day, but less than 5, the coating should be in contact with the solution involved only rarely and then for relatively short periods. Probably not suitable for decontamination service.

"0" = Coating failed in less than one day, it is not recommended for service in contact with that chemical

the coatings significantly. After a dose of 10^9 R, Amercoat-HB66, Carboline-1323, and Phenoline-300 showed only discoloration; Phenoline-305 and Devran-500 blistered very badly and were discolored; and Amercoat-33HB was discolored and peeled.

1.17 Conclusions. Both plateout and decontamination characteristics of a radionuclide on a given surface are important in arriving at the contamination level that will remain on a surface after it has been decontaminated. The plateout of iodine on stainless steel and Teflon is less than on carbon steel and protective coatings; the plateout varies widely for protective coatings.

High-pressure sprays of hot decontaminating solutions do not remove iodine readily from organic protective coatings; present data indicate that one should not expect to obtain an iodine decontamination factor of greater than 10 with such a system. The removal of iodine from steel surfaces with pressure sprays gives decontamination factors of 10^3 or greater. Pressurized steam removes iodine effectively from many protective coatings, depending on conditions prevailing at the time of contamination.

Present data indicate that one should not expect to obtain a cesium decontamination factor from protective coatings of greater than 100 with hot pressurized sprays of decontaminating solutions; these sprays will remove cesium from steel surfaces by a factor of 10^3 or greater. Pressurized steam does not remove cesium readily from carbon steel, but is effective in removing this fission product from stainless steel. Removal of tellurium and neptunium from coatings appears to be poor.

1.18 Future Programs. Laboratory-scale studies of the physical and chemical properties of protective coatings and the behavior of fission products on protective coatings will be continued to define the limits of utility of these materials and the limitations placed on the execution of the LOFT experiments due to the presence of these coatings in the containment building. An additional laboratory study will yield data on the depth and rate of penetration of fission products into the coating under conditions representative of those prevailing during the LOFT experiment so that the severity of the contamination problem can be evaluated. Kinetic data, obtained in similar experiments, for the removal of fission products by steaming or spraying with decontaminating reagents will be used to determine the optimum time cycle for application of the chemical reagents.

If required, promising alternates, such as a dual system with the outer layer having plateout properties representative of conventional coatings but being completely strippable by the decontaminating reagents, may be studied for their special value to LOFT.

1.2 LOFT Decontamination System Studies (R. D. Modrow)

As part of the development effort on decontamination procedures, tests were conducted with commercially available nozzles to determine spray characteristics and decontamination factors available using tracer level of radioiodine as the contaminant.

1.21 Evaluation of Decontamination with Sprays. The initial work on decontamination with sprays has been done with painted and stainless steel

coupons contaminated with radioiodine. The data, which are presented in Table XXXIII, were obtained in a semiscale test where the nozzle-to-coupon distance was about five feet. The data for coupons contaminated with molecular iodine released from NaI solution using a steam-nitrogen transport gas indicate that (a) the duration of contact time between the solution and the surface is important although the increase in decontamination factor (DF) is not in proportion to the increase in time and (b) the temperature of the decontaminating agent plays an even more important role. Water, even at 85°C, is an ineffective decontaminating agent; Turco Alkaline Rust Remover is ineffective at 20°C, but reasonably effective at 85°C. It appears that DF's of 10 to 20 are possible for radioiodine but that order of magnitude higher DF's are not possible, even with extended time, when using Turco Alkaline Rust Remover at 85°C. Additional tests are planned to gain a better understanding of the effect of spray impact, which has not been explicitly determined yet, as well as the effects of using a series of decontaminating solutions, of varying the coverage, and of recycling the solutions.

Although the duration of contact time between the coupons and the reagent did influence the DF in these tests, the effect was not apparent in the coating

TABLE XXXIII

DECONTAMINATION OF COUPONS IN AN ENGINEERING-SCALE SPRAY BOOTH
(Removal of Radioactive I₂) [a]

Coverage ^[b] (gal/ft ²)	Solution Temperature (°C)	15 Degree Spray ^[c]			45 Degree Spray		
		Contact Time (sec) ^[d]	D F Water	D F TARR ^[e]	Contact Time (sec)	D F Water	D F TARR ^[e]
0.1	20	3.5	1.0	1.1	27	1.0	1.1
0.1	20	3.5	1.0	1.1	27	---	---
0.1	85	3.5	1.0	5.1	27	1.0	8.6
0.1	85	3.5	---	7.2	27	1.1	7.8
0.1	85	3.5	---	5.7	27	---	---
1.0	20	35.0	1.0	1.2	275	1.0	1.3
1.0	20	35.0	1.0	1.2	275	---	---
1.0	85	35.0	1.3	15.0	275	1.6	23.0
1.0	85	35.0	---	---	275	1.0	22.0
10.0	85	347.0	---	---	2750	---	29.0

[a] Carbon steel coupons painted with Amercoat-HB 66 undercoat and finish were used; horizontal distance from nozzle to coupons was five feet; Spraying System Co. nozzles 1/8 inch GG 1514 and 3/8 inch GG 9.5 were used; the coupons were contaminated with molecular iodine released from NaI solution using a steam-N₂ transport gas.

[b] Coverage is the volume of solution contacting a unit surface area in the course of the test; for the 15 degree spray, the spray rate was 1.71 gal/ft²-min; and for the 45 degree spray, the spray rate was 0.22 gal/ft²-min.

[c] Sprays with a small included spray angle yield a relatively higher impact(lb-force/in.²) at a surface than sprays with a large included spray angle for a given pressure.

[d] Contact time is the total period that solution is being sprayed on the coupons.

[e] Turco Alkaline Rust Remover (1 lb/gal of water).

studies described in Section III-1.13. These latter studies were done with coupons contaminated at ORNL by melting "simulated-irradiated" uranium dioxide and then decontaminated at ICPP with 3M HNO₃ followed by Turco Alkaline Rust Remover. It should be noted that several variables of possible importance were different in these two studies. They are (a) the spray apparatus, (b) the technique of introducing the iodine, (c) the time elapsed between contamination and decontamination, and (c) the age of the paint. Of these four, the age of the paint may be the most important and may account for the low DF's obtained in the coating studies presented in Section III-1.13.

Preliminary work on the decontamination of newly painted surfaces (painted with Amercoat-HB66 primer and finish one week prior to contamination) indicates that the average DF is only 1.5 in contrast to a DF of 10 or 15 for coupons aged for about six months. The study on the effect of aging the paint will be continued during fiscal year 1966.

1.22 Evaluation of Sprays. In order to specify spray nozzles for use in LOFT and in the semiscale spray tests, a study has been started to evaluate various types of nozzles. The initial evaluation of sprays was done with a limited number of nozzles that emit a full cone of spray droplets in a circular pattern. Included spray angles of 0 (straight stream), 15, and 45 degrees were tested at up to 125 psig with water; and it was found that only the straight stream and 15-degree sprays had a range of at least 20 feet. These full-cone nozzles would most likely be applicable to a fixed-header decontamination system. Where a rotating header system might be used, as has been suggested for the LOFT building, a flat spray pattern might be most suitable. A number of nozzles yielding a flat spray pattern as well as some nozzles yielding a 30-degree, full-cone spray, will be tested for applicability to LOFT.

The nozzles studied to date, along with information on their capacities at various operating pressures, are listed in Table XXXIV. The evaluation has included a study of the nozzle capacity, the spray coverage, and the spray quality. The coverage was measured by using a clear plastic backstop as the vertical surface; the quality was measured by collecting the spray fallout prior to contact with, and backsplash from, this vertical surface, ie, a measure of the portion of the spray which wets the wall.

TABLE XXXIV
NOZZLE CAPACITIES

Nozzle, Type, and Number ^[a]	Included ^[b] Spray Angle (degrees)	Nozzle Capacity (gpm)					
		50 psig		100 psig		125 psig	
		Rated	Actual	Rated	Actual	Rated	Actual
Straight Stream, 1/4 inch U0006	≈ 0	0.67	0.43	0.95	0.62	1.1	0.75
Full Jet, 3/8 inch GG 1550	≈ 15	5.6	5.6	7.1	8.0	8.7	8.8
Full Jet, 3/8 inch GG 9.5	≈ 45	2.0	2.1	2.8	2.8	3.1	3.1

[a] The nozzle description refers to spray nozzles manufactured by Spraying Systems Co., Bellwood, Illinois.

[b] These nozzles emit a full-cone spray with an included spray angle as indicated.

In general, the quality of the spray from the straight stream and 15-degree, full-cone nozzle increased with an increase in water pressure. The quality of the spray was estimated by collecting in a movable tray the spray that did not hit or was splashed from the vertical surface which was located 20 feet from the spray nozzle. The data showed that for the straight stream spray, 55 percent of the water was collected at 50 psig and only about 20 percent was collected at 125 psig, indicating that 45 percent and 80 percent, respectively, wetted the wall at the two pressures. Likewise, for the 15-degree-angle spray, about 70 percent of the spray wetted the wall at 30-psig spray pressure; and 80 percent of the spray wetted the wall at 125 psig. In both cases, the bulk of the fallout and backsplash was collected within about 18 inches of the vertical surface.

1.23 Future Program. Semiscale tests on the use of sprays, solutions, and techniques for removing fission products from protective coatings will be continued. Most of the study will be with small coupons, highly contaminated with fission products in the Contamination-Decontamination Experiment (CDE) (Section III-1.3 which follows). However, large painted panels, also contaminated in the CDE, may be used to determine if the data obtained with the small coupons are applicable to large surface areas.

1.3 Contamination-Decontamination Experiment (L. T. Lakey, R. D. Modrow, R. E. Schindler; DEVELOPMENT ENGINEERING SECTION)

A Contamination-Decontamination Experiment (CDE) is being installed to produce mixtures of fission products under conditions simulating those expected during the LOFT program. These mixtures will be used in the LOFT support programs for studies of coatings and their decontamination, for developing analytical methods for LOFT samples, and for testing various LOFT sampling devices. In the CDE, the fission product mixture will be generated by melting a small, irradiated fuel capsule in the presence of steam using a radio-frequency-induction furnace. The fission products will be transported by the steam to a simulated reactor vessel and, thence, to a simulated containment vessel. Contaminated coupons and samplers in the vessels will then be removed for use in the various programs. A schematic diagram of the CDE is shown in Figure 39.

The CDE will be located in Cell 2 of the ICPP Hot Pilot Plant. This cell is equipped with a three-ton crane, three manipulators, two windows, and a cask-transfer dolly. Facilities are also provided for sampling radioactive liquids and disposing of them. With a few piping additions, this cell can be connected to a plant off-gas system containing charcoal beds and filters designed for controlling radioiodine releases to the atmosphere.

The CDE is expected to be operational during the latter part of 1965, and the planned program will extend through 1968.

Fig. 39 Schematic diagram of the Contamination-Decontamination Experiment (CDE).

1.4 Continuous Sampler-Monitor for the Containment Building Atmosphere (S. J. Horn, R. E. Schindler; DEVELOPMENT ENGINEERING SECTION)

As the LOFT experiment proceeds, the composition of the atmosphere within the containment building will change due to the evaporation of reactor coolant and the eventual melting of the reactor core and the concomitant release of fission products. In order to evaluate adequately the release and dispersion of fission products throughout the containment building, it is necessary to analyze the atmosphere for changes in composition. During the course of the LOFT experiment, iodine, rare-gas daughters, and particles will deposit upon exposed surfaces by adsorption, settling, or condensation of steam. The rate and the extent to which these phenomena occur must be followed by analysis of the atmosphere.

The continuous sampler-monitor, shown schematically in Figure 40, is a system (on which development was initiated in FY 1965) for continuously collecting a sample of the containment building atmosphere. The heart of the system is a jet-spray scrubber which collects the sample and separates the fission product iodine from the rare gases. Only the scrubber is located within the containment building; filter, monitors, and analytical apparatus will be located outside the containment building. Fission product analyses will be made using gamma-ray spectrum stripping techniques[81]. By separating the two major fission product groups, ie, rare gases and iodine, accurate analyses are possible.

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Fig. 40 Schematic flowsheet of the Continuous Sampler-Monitor.

The atmospheric sample obtained by the continuous sampler is separated into two streams. The liquid stream will contain the iodine, condensed steam, and the majority of the particles. The gas stream will contain air, rare gases, and nonscrubbable iodine and particles.

The principal problems under investigation are (a) the evaluation of the efficiency of the scrubber in separating various forms of iodine from a gas stream and in removing particles under simulated LOFT conditions and (b) the design and development of continuous systems for preparing the gas and liquid streams for analysis.

2. DECONTAMINATION OF CERTAIN REACTOR COMPONENTS

2.1 Decontamination of Hafnium Metal Control Rods (K. L. Rohde, R. R. Hammer; CHEMISTRY SECTION)

Hafnium metal is presently being used as a control rod material in the Shippingport Pressurized Water Reactor [82]. A large number of rods have had to be replaced because of radioactive contamination in the course of refueling or modifying such reactors even though the hafnium metal control rods potentially have much longer lifetimes. Since hafnium in metal form sells for about \$110/lb, it may be economically feasible to recover the metal for reuse.

From an examination of a segment of a used control rod and from consideration of the chemical and radiochemical effects of exposure in such a nuclear reactor, it appears that it would be most economical to decontaminate the hafnium metal by allowing a sufficient cooling time for the decay of the short-lived activities, by pickling the surface of the rod to remove the surface film and occluded long-lived activity, by purifying the hafnium by conventional metallurgical techniques (if nonradioactive contaminants are excessive), and by refabricating the control rods.

2.11 Probable Contaminants. The radioactive components in the hafnium control rod should consist of the activation products as produced in the following reactions:

The Ta-181 is produced from the decay of Hf-181. The Ta-182 activity was calculated from the Ta-181 concentration which was estimated from the depletion data given in "The Metallurgy of Hafnium" [83]. Table XXXV gives the calculated activities of Ta-182, Hf-175, and Hf-181 and the amount of tantalum in the hafnium control rod. A period of about eight years would be required for the activity of Ta-182 to reach a sufficiently low level; however, it would require less than five years for the isotope Hf-181 and less than seven years for Hf-175 to reach the same level.

Radioactive activation products originating from the cooling system contaminate the surface of the hafnium control rods. From a decontamination of a loop in a pressurized water reactor, the following radioisotopes were identified [84]:

Co-60 and/or Fe-59, Mn-54, Zr-95 and/or Nb-95[a], Cr-51, Ce-144[a].

Co-60 was found in the largest quantity in the decontaminating solutions with Cr-51 and Mn-54 in smaller quantities. Since Co-60 has such a long half-life (5.3 years), it would take many years for the Co-60 to decay to an insignificant level.

TABLE XXXV

ESTIMATED ACTIVITIES OR CONCENTRATIONS FOR VARIOUS
IMPURITIES CONTAINED IN 25-g COUPON AFTER 5 YEARS
IRRADIATION AT 3×10^{13} n/cm²-sec

	Cooling Time				
	0	2 Years	4 Years	5 Years	8 Years
Ta	0.1%	0.1%	0.1%	0.1%	0.1%
Ta-182	10^{10} dis/sec	10^8 dis/sec	10^6 dis/sec	10^5 dis/sec	250 dis/sec
Hf-181	10^{12} dis/sec	10^8 dis/sec	500 dis/sec	2 dis/sec	0 dis/sec
Hf-175	10^{13} dis/sec	10^{10} dis/sec	10^7 dis/sec	10^5 dis/sec	3 dis/sec

[a] Fission products released from a ruptured fuel rod.

2.12 Experimental Findings. Exploratory experiments were undertaken in order to determine the procedures necessary for purification and decontamination of the hafnium metal.

A section of hafnium control rod which had been stored for about 9.3 years was obtained. The main radioactive component was found to be Co-60. The other components were in such small quantities that it was not possible to definitely identify them from a γ -ray spectrum obtained from a small coupon.

An analysis of the control rod gave a tantalum concentration of less than 0.07 percent. Since the history of this particular control rod in the reactor is uncertain, it is not known whether this amount of tantalum is a representative concentration for discarded control rods. With such a small concentration of tantalum, purification from nonradioactive components would not seem necessary.

A section of the hafnium control rod was cut into coupons, 1/2- by 1- by 5/32-inch, weighing approximately 25 grams each. These coupons were treated to remove the surface contamination. The most successful treatment tried to date involves the use of molten sodium hydroxide. This reagent slowly dissolves the hafnium dioxide layer with little or no attack of the metal. The results given in Table XXXVI are presented in order of increasing decontamination factor obtained by various experimental conditions involving molten sodium hydroxide treatment.

The activities of the samples just removed from the sodium hydroxide bath were considerably higher than those indicated for the final activities due to the sodium hydroxide film retained by the specimens. Since the sodium hydroxide contains the Co-60 removed from the coupons, it was necessary to immerse the samples in dilute hydrochloric acid to remove the residual sodium hydroxide.

TABLE XXXVI

RESULTS OF DECONTAMINATION OF HAFNIUM IN MOLTEN SODIUM HYDROXIDE

<u>Sample Number</u>	<u>Initial Co-60 Activity (dis/sec)</u>	<u>Final Co-60 Activity (dis/sec)</u>	<u>Treatment Conditions</u>
1	650	55.0	2 min, 450°C, + 30 min, 350°C + 30 min, 550°C
2	780	45.0	10 min, 570°C
3	620	19.0	30 min, 550°C
4	730	13.0	10 min, 450°C + 80 min, 350°C
5	1720	7.6	60 min, 570°C
6	4580	7.9	60 min, 570°C

The data given in Table XXXVI indicate that the rate of decontamination is increased by increasing the bath temperature. Samples Nos. 5 and 6 were treated in exactly the same manner; and even though the initial activities of the two samples were different, the final levels of activities were the same within experimental error. It is likely that longer periods of treatment or treatment in another uncontaminated molten sodium hydroxide bath would further reduce the Co-60 activity of these samples. However, while molten caustic seems to be an effective reagent for decontamination of hafnium, further work is required to find optimum conditions for the process.

Other less successful decontamination procedures were investigated. Approximately 2/3 of the activity was removed rapidly with concentrated nitric or hydrochloric acids. The remaining activity was only very slowly removed by the nitric and hydrochloric acid solutions. The activity was almost completely removed by removing the oxide layer with emery cloth. It is apparent that the Co-60 was mainly associated with the hafnium dioxide layer, probably as a solid solution.

A five percent solution of hydrofluoric acid completely removed the oxide layer; however, it also removed 15 to 20 percent of the hafnium metal. Hydrofluoric-nitric acid solutions behaved in a similar manner. Hot concentrated sulfuric acid removed the oxide layer, deposited a thin gray layer of material over the surface, and removed approximately 15 percent of the hafnium metal.

2.2 Decontamination of Reactor Loops (C. A. Zimmerman, K. L. Rohde)

Samples of alkaline permanganate and ammonium citrate decontaminating solutions were obtained from two ETR reactor loop decontaminations in order to determine the source of contamination and evaluate the decontamination procedures used. Gamma-scan analysis of these decontamination solutions has shown that the radioactive materials removed from the loops were principally activated corrosion products formed during loop operation, with cobalt-60 being the principal nuclide removed. The average decontamination factor for these two loop decontaminations was 7.6, a factor adequate for the conditions prevailing.

2.3 Decontamination of Irradiated Aluminum-Clad Fuel Elements (C. A. Zimmerman, M. E. Jacobson, K. L. Rohde)

Six irradiated aluminum-clad fuel elements were decontaminated to prevent the possibility of contaminated surface deposits accidentally coming off in subsequent use.

These fuel elements were chemically decontaminated remotely by immersion in a hot solution of 0.5M phosphoric acid-0.001M chromium trioxide until the light-colored film was removed, followed by immersion in a hot 3.0M nitric acid solution for 3 to 5 minutes. Decontamination factors greater than 200 were obtained using this procedure. Irradiated aluminum-clad fuel elements, cleaned and decontaminated by this procedure, are left with the aluminum in a highly active, readily corroded state.

IV. REFERENCES

1. J. R. Bower (ed.), Chemical Processing Technology Quarterly Progress Report, July-September 1963, IDO-14625 (February 1964).
2. J. R. Bower (ed.), Idaho Chemical Processing Plant Technical Progress Report, October-December, 1959, IDO-14512 (June 1960).
3. J. R. Bower (ed.), Chemical Processing Technology Quarterly Progress Report, October-December, 1963, IDO-14635 (March 1965)
4. J. R. Bower (ed.), Zirconium Processing Capability of the Idaho Chemical Processing Plant, IDO-14645 (October 1964).
5. W. G. Morrison, Criticality Aspects of the Revised Zirconium Dissolution System, IDO-14647, (unpublished)
6. B. J. Newby, An Improved Aqueous Process for Zirconium Alloy Nuclear Reactor Fuels. Part II. Continuous Dissolution with 5 M Hydrofluoric Acid, IDO-14619 (September 1963).
7. K. L. Rohde et al, An Improved Aqueous Process for Zirconium Alloy Nuclear Reactor Fuels. Part I. Preliminary Laboratory Studies, IDO-14594 (October 1962).
8. W. G. Morrison, Criticality Aspects of the Revised Zirconium Dissolution System, IDO-14647 (unpublished)
9. R. W. Legan et al, ICPP Processing of VBWR Stainless Steel Fuel, IDO-14658, (unpublished).
10. J. R. Bower (ed.), Chemical Processing Technology Quarterly Progress Report, October-December 1961, IDO-14583 (March 1962).
11. J. R. Bower (ed.), Chemical Processing Technology Quarterly Progress Report, January-March 1962, IDO-14589 (June 1962).
12. H. V. Chamberlain, B. E. Paige, and G. A. Raab, Treatment for Improved Processing of Reactor Fuels, IDO-14496 (February 1960). (Confidential)
13. B. E. Paige, K. L. Rohde, and B. J. Newby, Emulsion Control in Liquid-Suspension Extraction, U. S. Patent 3,154,376 (October 1964).
14. R. D. Fletcher, M. E. Jacobson, and H. R. Beard, Effect of Alloying Constituents on Aluminum Dissolution Rates, IDO-14606 (April 1963).
15. K. L. Rohde et al, An Improved Aqueous Process for Zirconium Alloy Nuclear Reactor Fuels. Part I. Preliminary Laboratory Studies, IDO-14594 (October 1962).
16. O. W. Parrett, Modifications for the STR Fuel Recovery Process, IDO-14522 (December 1960).

17. A. G. Chapman and C. M. Slansky, The Solubility of Zirconium Tetrafluoride in Nitric Acid from 0 to 80°C, IDO-14442 (April 1958).
18. H. E. Henry, Recovery of Uranium From Zirconium-Uranium Alloy, DP-826 (May 1963).
19. J. R. Bower (ed.), Chemical Processing Technology Quarterly Progress Report, July-September 1961, IDO-14574 (December 1961).
20. J. R. Bower (ed.), Chemical Processing Technology Quarterly Progress Report, October-December 1961, IDO-14583 (March 1962).
21. J. R. Bower (ed.), Chemical Processing Technology Quarterly Progress Report, October-December 1962, IDO-14611 (June 1963).
22. J. R. Bower, Zirconium Processing Capability of the Idaho Chemical Processing Plant, IDO-14645 (October 1964).
23. J. R. Bower (ed.), Chemical Processing Technology Quarterly Progress Report, July-September 1961, IDO-14574 (December 1961).
24. L. L. Burger, I. M. Rehn, and C. M. Slansky, Properties of the System: Uranyl Nitrate-Aluminum Nitrate-Nitric Acid (or Sodium Hydroxide)-Sodium Dichromate-Sodium Nitrate-Water, Part V. pH Values, HW-14559.
25. J. R. Bower (ed.), Chemical Processing Technology Quarterly Progress Report, October-December 1963, IDO-14635 (March 1964).
26. J. R. Bower (ed.), Chemical Processing Technology Quarterly Progress Report, October-December 1960, IDO-14553 (May 1961).
27. M. E. Weech, R. S. P'Pool, and D. K. MacQueen, Interim Report on the Development of an Air Pulser for Pulse Column Application, IDO-14559 (September 1961).
28. M. E. Whatley et al, Chemical Technology Division, Unit Operations Section Monthly Progress Report, August 1963, ORNL-TM-776 (June 1964) pp 6-23.
29. C. E. Stevenson, Idaho Chemical Processing Plant Technical Progress Report, April-June 1959, IDO-14494 (March 1960).
30. E. S. Grimmett and N. deNevers, Solids Flow Control for a Pulsed Solids-Liquid Contractor, IDO-14648 (March 1965).
31. A. E. Erhard, Processing of the Core Fuel Used Initially in the Experimental Breeder Reactor (EBR-1), IDO-14331 (December 1955).
32. J. H. Kittel, M. Novick, and R. F. Buchanan, The EBR-1 Meltdown -- Physical and Metallurgical Changes in the Core, ANL-5731 (November 1957).
33. E. M. VanderWall, E. M. Whitener, and D. L. Bauer, Dissolution of Zirconium and Zircaloy-2 in Nitric-Hydrofluoric Acid Mixtures at Reflux Temperatures, IDO-14497 (September 1959).

34. T. A. Gens, Explosive Reactions During Reprocessing of Reactor Fuels Containing Uranium and Zirconium or Niobium, CF-58-11-31 (November 1958).
35. R. P. Larsen et al, A Study of the Explosive Properties of Uranium -- Zirconium Alloys, ANL-5135 (July 1954).
36. R. E. Isaacson and B. F. Judson, Neptunium Recovery and Purification at Hanford, HW-SA-3283 (December 1963).
37. G. A. Burney, Anion Exchange of Neptunium in Nitrate Solutions, DP-531 (December 1960).
38. G. A. Burney, Separation of Neptunium and Plutonium by Anion Exchange, DP-689 (April 1962).
39. J. R. Flanary et al, Recovery of Np-237 by the Neptex Solvent-Extraction Process, ORNL-2235 (April 1957).
40. R. N. Tetzlaff, Chemical Processing Pu-238, DP-729 (October 1962).
41. Plutonium Ion Exchange Processes. Proceedings of the US-UK Technical Exchange Meeting, Oak Ridge National Laboratory, April 25-27, 1960, TID-7607.
42. W. E. Prout and L. P. Fernandez, Recovery of Neptunium From Purex Waste by an Agitated Bed of Anion Exchange Resin, DP-453 (February 1960).
43. J. P. Duckworth and L. R. Michels, New Neptunium Recovery Facility at the Hanford Purex Plant, HW-SA-2928 (March 1963).
44. J. P. Duckworth and J. R. LaRiviere, New Neptunium Purification Facility at the Hanford Purex Plant, HW-SA-3282 (December 1963).
45. J. L. Ryan, Concentration and Final Purification of Neptunium by Anion Exchange, HW-59193 (Rev.) (September 1959).
46. L. M. Ferris, A Burn-Leach Process for Recovery of Uranium From Rover Fuel: Terminal Report of Laboratory Development, ORNL-3763 (March 1965). (C)
47. L. P. Hatch et al, Progress of Individual Activities, January-March, 1964, Volatility Process Development, BNL Log C 11425 (April 1964) (confidential)
48. E. C. Pitzer, Electrolytic Dissolution of Stainless Steel Clad Fuel Assemblies, KAPL-653 (December 1951). (Secret)
49. V. P. Caracciolo and A. A. Kishbaugh, Electrolytic Dissolver for Power Fuels, DP-896 (October 1964).
50. C. M. Slansky, K. L. Rohde and H. T. Hahn, Review of Research and Development at the Idaho Chemical Processing Plant on the Electrolytic Dissolution of Nuclear Fuel, IDO-14535 (January 1961).

51. M. R. Bomar, Series Electrolytic Dissolver for Nuclear Fuels. I. Scoping Studies, IDO-14563 (November 1961).
52. J. R. Aylward and E. M. Whitener, Electrolytic Dissolution of Nuclear Fuels. Part II. Nichrome in Nitrate Solutions, IDO-14575 (December 1961).
53. J. R. Aylward and E. M. Whitener, Electrolytic Dissolution of Nuclear Fuels. Part III. Stainless Steel (304) in Nitrate Solutions, IDO-14584 (June 1962).
54. H. T. Hahn, J. R. Aylward, and M. R. Bomar, Evaluation of the Metal-to-Metal Contact Basket-Type Electrolytic Dissolver, IDO-14604 (May 1963).
55. D. P. Pearson, Physical Properties of Nitrate Solutions of Iron-and-Nickel-Base Alloy Nuclear Fuels, IDO-14602 (January 1963).
56. L. A. Decker, The Effect of Radiation and Nitric Acid-Nitrate Salt Solution on Some Non-Metallic Materials, IDO-14598 (December 1962).
57. J. R. Bower (ed.), Chemical Processing Technology Quarterly Progress Report, April-June 1960, IDO-14534 (November 1960).
58. J. R. Bower (ed.), Chemical Processing Technology Quarterly Progress Report, April-June 1961, IDO-14567 (November 1961).
59. G. E. Lohse, D. E. Black, et al, Operation of the WCF with Highly Radioactive Aqueous Wastes: Report of the First Processing Campaign, IDO-14662 (unpublished).
60. D. F. Bunch et al, Environmental Effects From Operation of the WCF, A paper presented at the 1965 annual meeting of the Health Physics Society, Los Angeles, California, June 14-17, 1965.
61. L. T. Lakey and J. R. Bower (eds.), ICPP Waste Calcining Facility Safety Analysis Report, IDO-14620 (December 1963).
62. C. A. Zimmerman, Corrosion of Type 316 Stainless Steel in NaK Service--A Literature Survey, IDO-14651 (February 1965).
63. R. L. Hickok and J. S. Madachy, Interim Report on the Calcination of Zirconium Fluoride Waste Solutions, IDO-14537 (March 1961).
64. J. C. Petrie et al, Fluidized Bed Calcination of Simulated Zirconium Fluoride Waste in Exploratory Pilot Plant Tests, IDO-14653 (July 1965).
65. J. M. Morgan, Jr., D. K. Jamison, and J. D. Stevenson, (comps. and eds.), Report of the Second Working Meeting on Fixation of Radioactivity in Stable, Solid Media, (Held) at Idaho Falls, Idaho, September 27-29, 1960, TID-7613 (February 1961).
66. B. P. Brown et al, Development of a Fluidized Bed Calcination Process for Aluminum Nitrate Wastes in a Two-Foot-Square Pilot Plant Calciner. Part III. Intermediate Process Studies -- Runs 11 through 22, IDO-14618 (February 1964).

67. J. W. Loeding et al, The Fluid-Bed Calculation of Radioactive Waste, ANL-6322 (May 1961).
68. D. W. Rhodes and M. E. Jacobson, Measurement of Heat Generation Rate of Highly Radioactive Calcined Alumina, IDO-14665 (October 1965).
69. J. R. Bower (ed.), Chemical Processing Technology Quarterly Progress Report, October-December 1963, IDO-14635 (March 1964).
70. J. R. Bower (ed.), Chemical Processing Technology Quarterly Progress Report, April-June 1964, IDO-14646 (January 1965).
71. M. E. McLain and D. W. Rhodes, Leaching of Fission Products from Calcined Process Wastes, IDO-14440 (April 1958).
72. E. S. Grimmer, Particle Growth and Size Distribution in Fluidized Bed Processes -- A Mathematical Model with Computer Solutions, IDO-14634 (to be published).
73. E. D. Cooper and J. C. Petrie, Directional Flow Control Device for Granular Solids, IDO-14666 (1965) (to be published).
74. J. M. Gerhart, Development of a Valve for the Control of Streams Composed of Powdered or Granular Solids, HW-53440 (November 1957).
75. H. S. Carslaw and J. C. Jaeger, Conduction of Heat in Solids, 2nd ed. Oxford: Oxford Clarendon Press, 1959.
76. D. W. Rhodes, Measurement of Fission-Product Leakage From Fuel Elements Stored in Water, IDO-14654 (March 1965).
77. W. G. Mathers and L. C. Watson, A Waste Disposal Experiment Using Mineral Exchange on Clinoptilolite, CRCE-1080 (January 1962).
78. L. L. Ames, Jr., Zeolitic Extraction of Cesium From Aqueous Solutions, HW-62607 (September 1959).
79. D. W. Rhodes and M. W. Wilding, Decontamination of Radioactive Effluent With Clinoptilolite, IDO-14657 (July 1965).
80. T. R. Wilson, O. M. Hauge, and G. B. Matheney, Feasibility and Conceptual Design for the STEP Loss of Coolant Facility, IDO-16833 (Rev. 1) (April 1963).
81. R. G. Helmer et al, A Linear Least-Squares Fitting Program for the Analysis of Gamma-Ray Spectra Including a Gain-Shift Routine, IDO-17015 (September 1964).
82. Naval Reactors Branch Division of Reactor Development, United States Atomic Energy Commission, The Shippingport Pressurized Water Reactor, Massachusetts: Addison-Wesley Publishing Company, Inc., 1958.

83. D. E. Thomas and E. T. Hayes (eds.), The Metallurgy of Hafnium, Washington, D.C.: U. S. Government Printing Office, 1960.
84. C. A. Zimmerman, ICPP, unpublished results.

V. REPORTS AND PUBLICATIONS
ISSUED DURING FISCAL YEAR 1965

1. IDO REPORTS

1. L. T. Lakey, G. E. Lohse, and W. P. Palica, Development of Fluidized Bed Calcination of Aluminum Nitrate Wastes in the Waste Calcining Facility, IDO-14608 (May 1965).
2. H. T. Hahn et al., Removal of Tributyl Phosphate and Its Degradation Products From Acidified Uranyl Nitrate Solutions, IDO-14630 (August 1964).
3. B. M. Legler and B. P. Brown, Pneumatic Atomizing Nozzles in Fluidized-Bed Calcining. Part II. Process Tests, IDO-14631 (July 1964).
4. J. C. Petrie and D. E. Black, Dry Collection and Disposition of Solids From Fluidized-Bed Off-Gas, IDO-14633 (July 1964).
5. L. A. Decker and M. E. Jacobson, Reprocessing of Coated OMRE Fuel, IDO-14641 (July 1964).
6. J. R. Bower, Zirconium Processing Capability of the Idaho Chemical Processing Plant, IDO-14645 (October 1964).
7. E. S. Grimmer and N. deNevers, Solids Flow Control for a Pulsed Solids-Liquid Contractor, IDO-14648 (March 1965).
8. C. A. Zimmerman, Corrosion of Type 316 Stainless Steel in NaK Service -- A Literature Survey, IDO-14651 (February 1965).
9. L. A. Jobe, Instrumentation and Control Practices in U.S.A. Reprocessing Plants, IDO-14652 (April 1965).
10. D. W. Rhodes, Measurement of Fission-Product Leakage From Fuel Elements Stored in Water, IDO-14654 (March 1965).

2. OTHER PUBLICATIONS

1. J. A. Buckham, L. T. Lakey, and J. A. McBride, "Development of Fluidized Bed Waste Calcination Process", Chem. Eng. Progr., Symp. Ser., 60 No. 53 (1964) pp 20-31.
2. E. S. Grimmer, "Selection and Performance of NaK Heating Systems for a Fluidized Bed Process." Paper presented at 7th National Heat Transfer Conference, AIChE, Cleveland, Ohio, August, 1964.
3. E. D. Cooper, D. E. Black, and C. B. Amberson, "A Performance Comparison of Pilot and Plant Scale Fluidized Bed Calciners." Paper presented at 55th National Meeting, AIChE, Houston, Texas, February 7-11, 1965.

3. PAPERS PRESENTED
AT TECHNICAL SOCIETY MEETINGS

1. E. S. Grimmett, "Analog Verification of the Sources of Fines in a Fluid-Bed Calciner." Paper presented at 55th National Meeting, AIChE, Houston, Texas, February 7-11, 1965.
2. T. L. Hoffman, "Corrosion Resistance of Stainless Steel Tanks Containing Highly Acidic Radioactive Waste." Paper presented at Annual Meeting of the National Association of Corrosion Engineers, St. Louis, Missouri, March 15-19, 1965.
3. D. W. Rhodes, "Measurement of Fission Product Leakage from Fuel Elements Stored in Water." Paper presented at 149th Annual Meeting ACS, Detroit, Mich., April 4-9, 1965.
4. B. J. Newby and K. L. Rohde, "Fission-Product Sorption by Protective Coatings." Paper presented at International Symposium on Fission Product Release and Transport Under Accident Conditions, Oak Ridge, Tennessee, April 5-7, 1965.