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MASTER

**CHEMICAL PROCESSING TECHNOLOGY
QUARTERLY PROGRESS REPORT
April-June 1964**

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**CHEMICAL PROCESSING TECHNOLOGY
QUARTERLY PROGRESS REPORT**

APRIL - JUNE 1964

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2	IDO-14494	2	IDO-14593
3	IDO-14509	3	IDO-14599
4	IDO-14512	4	IDO-14611
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CHEMICAL PROCESSING TECHNOLOGY
QUARTERLY PROGRESS REPORT
APRIL-JUNE, 1964

SUMMARY

The modified ICPP zirconium processing facilities are being prepared for cold start-up testing. The flowsheet is presented for the new process, which utilizes dissolved boron (boric acid) as a nuclear poison to safeguard the operation while processing zirconium based fuels at a greatly expanded rate.

In aluminum fuel processing studies the potential usefulness of dissolved cadmium (nitrate) as a nuclear poison in nitric acid dissolver solutions has been demonstrated where boric acid has limited solubility. In further aqueous process studies, sample ATR fuel plates and Type 6061-T0 aluminum were shown to resist corrosion in the fuel storage basin water.

Electrolytic dissolution of kilogram quantities of actual HTRE-3 fuel elements and APPR fuel plates was successfully demonstrated in the Model 2 pilot plant dissolver. A new dissolver vessel, fabricated of titanium, is functioning perfectly with the vessel itself serving as the cathode; this has eliminated the need for a separate niobium cathode and simplifies the dissolver design.

The platinum anode and niobium basket have shown satisfactorily low corrosion rates over several hundred hours of pilot plant operation. Further pilot plant studies have demonstrated that areas of welding on the dissolving elements have no apparent effect on current utilization, and that boric acid and gelatin in the dissolvent solution appear to inhibit solids deposition, the latter through coagulation of the silica. Laboratory studies have characterized the sludge produced during electrolytic dissolution as consisting of grains dropped from the dissolving surface and silica produced by polymerization following dissolution. There is no significant uranium retention in the sludge. Sprayed ceramic coatings on titanium lost adhesion in the dissolver solution.

The ICPP Waste Calcining Facility (WCF) has operated very smoothly, reducing approximately 323,000 gallons of first cycle aluminum extraction waste to 34,600 gallons of solid calcine in approximately 200 days; only 55 hours of down time have been experienced since starting radioactive operation in December 1963, and the facility has consistently operated at 10 percent or more above design rate. Overall decontamination factors of 6×10^7 for strontium-90 and 2×10^5 for ruthenium-106 have resulted in calculated ground-level localized concentrations of these species under worse-than-average weather conditions, of approximately 0.01 percent and 2.0 percent, respectively, of the "Radioactivity Concentration Guide" (RCG) limits.

The successful calcination of zirconium-aluminum-fluoride wastes from the ICPP hydrofluoric acid process for zirconium-based fuels has been demonstrated in WCF pilot plant equipment. A feed slurry of zirconium-process waste complexed with calcium nitrate was readily handled and calcined at the usual WCF conditions for aluminum-process wastes. Corrosion of equipment components and test specimens was negligible with the fluoride being securely held as CaF_2

in the calcine product. Supporting laboratory studies indicate that the calcine is stable up to at least 800°C.

Additional waste management studies indicate that alumina calcine deposits yield to nitric acid decontamination and that phosphate glasses prepared from calcined alumina were blackened, but otherwise unaffected, by gamma irradiation to 10^{10} R.

Other plant improvement projects reported include: (a) successful removal of strontium and cesium radioisotopes from storage basin water by a clinoptilolite adsorption unit; (b) additional aluminum nitrate-nitric acid solubility data for the freeze-melt aluminum waste separation process; and (c) relationship between analog simulation and a simplified mathematical analysis of air pulser operation.

CHEMICAL PROCESSING TECHNOLOGY
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I. ICPP OPERATIONAL SCHEDULE, PERFORMANCE, AND PROBLEMS (Section Chief: J. W. Garner, Plant Process Assistance)

1. ICPP PROCESSING SCHEDULE (B. R. Wheeler, G. F. Offutt)

Dissolution and first cycle extraction facilities at the Idaho Chemical Processing Plant were operated alternately and on a part-time basis by a small crew while the Waste Calcining Facility was operated at full capacity. Approximately 1200 fuel elements from the Brookhaven Graphite Research Reactor, BGRR, were processed in this manner. The intercycle uranium product was placed in storage for later processing through the second and third extraction cycles.

Limited operation of plant facilities in the case of BGRR elements is desirable to minimize storage requirements and to reduce the high release rate of activity to storage basin water experienced with these bulky elements. An earlier investigation [1] showed that the BGRR elements have been the source of much of the activity in the basin water. An added benefit from part-time processing of BGRR elements is lower out-of-pocket costs for uranium recovery. These lower costs result because a dissolver cannot be operated at capacity with these elements [2], even with a full operating crew, due to unavoidable handling problems; hence, a small crew can be used to better advantage than a full crew.

2. ICPP OPERATIONAL PERFORMANCE (B. R. Wheeler, G. F. Offutt)

Performance of the first cycle extraction system was more satisfactory than during any previous operation. The improved performance was due in part to the raising of an air lift disengaging pot between the extraction and scrub columns prior to the run, thereby improving column hydraulics. Other modifications to the system were reported previously [2].

Low losses of uranium (about 1×10^{-3} g/l in the raffinate stream) were achieved, even with intermittent type of operation. All periods of column operation during this run were less than 16 hours; previously, start-up operation of the columns alone usually exceeded 16 hours. During this run, the columns were successfully shut down and then later restarted while full of process solutions as manpower for operation became available. This was a previously untried procedure at the ICPP.

3. ICPP PROCESS MODIFICATION (B. R. Wheeler, G. F. Offutt)

The new ICPP zirconium headend facilities [3] are being water tested; the flow instruments on the process are being calibrated in preparation for cold shakedown runs. A boron detection instrument for neutron poisoning also remains to be calibrated. The flowsheet is discussed in Section II-1.

II. AQUEOUS PROCESS STUDIES

(Section Chiefs: K. L. Rohde, Chemistry
J. W. Garner, Plant Process Assistance)

1. AQUEOUS ZIRCONIUM FUEL PROCESSING (B. R. Wheeler, Problem Leader; G. F. Offutt)

1.1 Modified ICPP Zirconium Fuel Process

The ICPP zirconium headend facility has been expanded as previously described [3] for processing up to 835 kilograms of zirconium per day. A schematic diagram of the principal components of the dissolution and first cycle extraction system and a chemical flowsheet of process conditions keyed to the equipment are presented in Figures 1 and 2. The flowsheet is based on experimental work [4, 5] reported previously. The mechanics of charging and operating the dissolver on a semi-continuous basis were reported in an earlier quarterly report [3]. Dissolver product overflowing from the dissolver will be mixed with aluminum nitrate solution to complex free fluoride ions and thus prevent corrosion of stainless steel equipment in the extraction system. Aluminum nitrate is also needed in this stream for salting uranium into the organic phase in the extraction column.

The feed evaporator (G-110) will be used only for mixing the complexed dissolver product solution and recycled raffinate from the scrub column. To avoid precipitation of zirconium or aluminum compounds, none of the process streams containing mixtures of fluoride, zirconium, and aluminum will be heated.

Approximately 17 liters per hour of DIBAN will be used in the scrub column to neutralize the acid in the organic stream, IBP, to a satisfactory level. The excess acidity must be removed to obtain a high aqueous-organic uranium distribution coefficient in the stripping column and thereby minimize uranium losses to the organic raffinate. Alternatively, the acid could have been scrubbed from the organic stream with dilute aluminum nitrate solution; this, however, would produce a greater volume of first-cycle waste per gram of uranium recovered.

Ten percent TBP in Amsco diluent will be used as the organic phase during the processing of zirconium fuels through the first extraction cycle. The use of lower TBP concentrations, although considered because ICPP first cycle extraction equipment is not geometrically safe under all conditions with ten percent TBP, is undesirable because a greater volume of waste results. Up to 3000 liters per day more liquid waste would be generated with the use of five percent TBP than with the use of ten percent TBP. The possibilities of a criticality incident when using 10 percent TBP have been analyzed. A critical uranium concentration could be caused by the highly unlikely simultaneous occurrence of the following: (a) processing is underway at a capacity rate with a fuel containing 2.7 percent or greater uranium; (b) the organic-aqueous distribution coefficient for uranium is shifted to an extremely high value by an undetected drastic increase in the aluminum nitrate concentration in the extraction column feed stream; and (c) the flow of the organic stream stops. The occurrence of this highly unlikely hypothetical case will be prevented by hourly checks of the organic flow rate or by the use of a flow alarm.

FLWSHEET FOR ZIRCONIUM HEADEND

STREAM	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
DESCRIPTION	HF	HNO ₃	H ₂ O ₂	DISSOLVENT	FUEL ELEMENT	CHARGE WATER	CHARGE WATER	MAKEUP WATER	DISSOLVER PRODUCT (Continuous)	DISSOLVER PRODUCT (Residual)	COMPLEXER (Initial)	COMPLEXER (Continuous)	COMPLEXER	HF	HNO ₃	Al(NO ₃) ₃	Cl O ₃	COMPLEXED DISSOLVER PRODUCT
FLOW, l/batch	8,253	10		8,272	1,285 (c)	1,425	140	7,240	1,280 (d)	150	2,035	2,185		245	1,940			1,310 (e)
FLOW, l/hr				517 (a)				452 (a)			127 (a)							472 (f)
Zr ⁴⁺ , M								1.07	1.02									0.80
F ⁻ , M	6.56			6.54				6.35	6.04									4.76
Al ³⁺ , M										1.95	1.95	1.95			2.20			0.37
H ⁺ , M	6.56	13		5.52				0.98	0.93	1.46	1.46	1.46		13				1.02
NO ₃ ⁻ , M		13		0.03				0.015	0.014	7.30	7.30	7.30		13	6.60			1.41
Sn, g/l								1.53	1.46									1.14
Cr, g/l										5.20	5.20	5.20						0.99
B, g/l (min.)				3.80		6.7	7.0	3.84	3.65									2.90
U, g/l (irr.)								1.17	1.12									0.88
DENSITY AT 25°C				1.035				1.186	1.177	1.360	1.360	1.360						1.209
U, kg/batch																		
Zr, kg/batch					10 (b)													
Sn, kg/batch					835													
Cr, kg/batch					13													
Xg/batch			179													20.2		

(a) Average rate for a 15-hour dissolution cycle.

(b) Assumes a 40% burnup of uranium.

(c) Includes a 5% jet dilution of 1,225 liters.

(d) Includes a 5% jet dilution of the dissolver contents once each dissolution cycle.

(e) Includes a 5% jet dilution of the contents of E-102 once each dissolution cycle and a 5% jet dilution of the total complexed dissolver-product during transfer to G-106.

(f) Average rate for a 24-hour period.

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Fig. 1 Flowsheet for modified ICPP zirconium headend process.

FLWSHEET FOR FIRST CYCLE EXTRACTION

STREAM	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
DESCRIPTION	DISSOLVER PRODUCT	EVAPORATOR OVERHEAD	1A F	1B R	1A X	1A R	1A P	1B S	1B P	1C P	1C X	1C R	1D R	1D X	1D P	FIRST CYCLE PRODUCT	EVAPORATOR OVERHEAD
FLOW, l/batch	11.31C		12.75D	1.440	12.000	2.750	12.000	1.440	12.000	4.800	4.800	12.000	240	240	4.800	50	4.750
FLOW, l/hr	472	0	530	60	500	530	500	60	500	200	200	500	10	10	200	2.1	198
TBP, %					10.0		10.0		10.0			10.0					
DILUENT				Amsco		Amsco		Amsco				Amsco	Amsco	Amsco			
DENSITY AT 25°C	1.209	1.211	1.230	0.754	1.204	0.802	1.200	0.795	1.002	0.908	0.794	0.757	0.757	1.002	1.275		
Zr ⁺⁺⁺ , M	0.80	0.71			0.71												
F ⁺ , M	4.75	4.22			4.22												
Al ⁺ , M	0.37	0.50	1.5		0.50		1.50										
H ⁺ , M	1.02	0.90			0.75	0.13	-1.13(a)		2.005	0.005				0.005	0.5		
NO ₃ ⁻ , M	1.41	1.75	4.5		1.67	0.14	3.36	0.007	2.022	0.005				0.022	2.0		
Sn, g/l	1.14	1.01			1.01												
Cr, g/l	0.99	0.88			0.88												
B, g/l (mic)	2.90	2.58			2.58												
U, g/l (irr)	0.83	0.78	0.001		7.8x10 ⁻⁴	0.64		0.84	2.10						2.10	200	

(a) The use of Diban in the scrub makes it 1.13M acid deficient.

Fig. 2 Flowsheet for modified ICPP zirconium first cycle extraction process.

The solution leaving the first extraction cycle is concentrated to 200 grams per liter of uranium in an evaporator and then placed in storage tanks. The solution from the storage tanks will eventually be processed through second- and third-cycle extraction systems using a hexone flowsheet typical of those used at the ICPP for other highly enriched fuels.

2. AQUEOUS ALUMINUM FUEL PROCESSING

2.1 Stability of Dissolver Product Solutions Containing Cadmium (D. W. Rhodes, Problem Leader; M. W. Wilding)

The use of a soluble poison for criticality control during the dissolution of ATR fuel at the ICPP would greatly simplify the handling and reprocessing of this fuel by aqueous methods. Boron is currently scheduled for use as a soluble poison for zirconium-type fuels, but the low solubility of boric acid in nitric acid limits its use as a poison for the dissolution of aluminum fuels in ICPP equipment. Cadmium nitrate, which has a higher solubility in nitric acid, appeared to be a better choice for aluminum alloy fuels.

Synthetic dissolver product solutions were prepared containing 0.5, 1.5, or 3.0M nitric acid with 1.5 or 1.8M aluminum nitrate, and 0.05M mercuric nitrate, 10 g/l cadmium (as cadmium nitrate), and 7.5 g/l uranium (as uranyl nitrate). Portions of these solutions were heated at boiling for 72 hours. No solids were observed in any of the solutions, indicating stability of the dissolver product solutions in the temperature range from room temperature to boiling at compositions expected to prevail during processing of the fuel.

2.2 Corrosion of Type 6061 Aluminum Cladding in Storage Basin Water (D. W. Rhodes, Problem Leader; T. L. Hoffman)

Unirradiated sample ATR fuel plates [6] and coupons of Type 6061-T0 aluminum were exposed in the ICPP fuel storage basin for 30 days, examined for evidence of corrosion, and returned to the basin for further exposure. This test was prompted by the earlier evidence [7] that Type 6061 aluminum, particularly in the hardened condition, was subject to pitting corrosion in the storage basin water. The cladding of the ATR fuel will initially have properties equivalent to the T0 state. Fabrication and irradiation may produce hardening, possibly raising the hardness to that equivalent to the T6 or T7 state.

A microscopic examination at 30X, made after the 30-day exposure, showed that each test specimen was covered with a uniform, gray film, typical of aluminum coating. There was no pitting on the sample ATR plates, but a few very small and shallow pits were observed along the sheared edges of the Type 6061-T0 aluminum coupons.

III. ELECTROLYTIC DISSOLUTION SYSTEMS

(Section Chiefs: B. M. Legler, Development Engineering;
K. L. Rohde, Chemistry)

1. PILOT PLANT ELECTROLYTIC DISSOLUTION STUDIES

(L. T. Lakey, Problem Leader; R. G. Denney, W. B. Kerr)

Runs 11, 12, and 13 were completed in the Model 2 pilot plant dissolver, extending the information reported previously [8, 3]. The conditions for these test runs are summarized in Table I. Dissolution data were obtained for an actual HTRE-3 fuel element and for actual APPR fuel plates. In addition, the presence of weld material in a fuel element was examined for its effect on the dissolution rate; boric acid and gelatin were tested as feed additives. A new dissolver vessel fabricated of titanium and designed to serve as a cathode is now in service.

TABLE I
SUMMARY OF CONDITIONS FOR RUNS
11 THROUGH 13 IN THE MODEL 2 ELECTROLYTIC DISSOLVER

Run Number	11	12A ^[a]	12B	12C	12D ^[b]	13A	13B
Duration (hours)	15.16	12.6	23.2	34.5	11.5	23.8	20.5
Dissolver Potential (volts)	15-24	7.8-20.2	14.5-21.6	18.0-21.1	19.0-21.0	19.0	19.0
Dissolver Current (amperes--range)	600	198-500	510-512	430-530	400-475	260-610	290-480
Dissolver Current (amperes--average)	599	343	510	500	436	302	376
Recirculation Rate (l/min)	6	6	6	6	6	6	6
Dissolvent Composition:							
Stainless Steel (g/l)	40.6	52.0	43.7	42.4	40.1	49.7	52.1
Uranium (μ /l)	5.3	0.0	6.3	6.7	6.2	---	---
Boron (g/l)	0.0	0.0	0.0	2.9	3.2	3.1	3.2
HNO_3 (M)	4.6	6.6-2.3	4.0	4.2	3.8	4.4	4.0
Dissolvent Temperature:							
Dissolvent Inlet ($^{\circ}\text{C}$)	37	39	40	41	42	43	44
Dissolver Outlet ($^{\circ}\text{C}$)	63	56	63	62	63	60	62
Dissolver Pressure (psia)	12.0	12.0	12.0	12.0	12.0	12.0	12.0
Acid Feed Concentration (M HNO_3)	7.1	6.1-7.0	7.0	7.1	7.1	7.9	7.9
Acid Feed Rate (l/min)	7.1	---	6.3	6.8	2.9	6.1	5.5
Type of Fuel Element Dissolved	HTRE-3	APPR	APPR	APPR	APPR	APPR	APPR
	(Actual)	(Simulated)	(Actual)	(Actual)	(Actual)	(Simulated) ^[c]	(Simulated) ^[c]

[a] Calibration of conductivity cell.

[b] Beel cleanout portion of run.

[c] Also containing superficial weld material.

1.1 Dissolution of Actual HTRE-3 Elements

In Run 11, an actual HTRE-3 fuel element containing natural uranium and weighing approximately 5.6 kg was dissolved in the pilot-plant electrolytic dissolver [3]. For charging into the dissolver, the element was cut into nine 4-inch-long sections as shown in Figure 3. The average current utilization, obtained during the period when the dissolver was completely filled with dissolving elements, was 0.67 gram of Nichrome-V per ampere-hour. This represents approximately 90 percent of the theoretical utilization of 0.74 gram

Fig. 3 HTRE-3 fuel element section.

a form similar to the welded element sections used in Run 10 [8]. An average current utilization of 0.60 gram of stainless steel (Type 304) per ampere-hour was obtained during the period when the dissolver was full of dissolving elements. This represents approximately 100 percent of the theoretical single cell utilization for this material. In Run 10, a current utilization of 0.53 gram per ampere-hour was observed using simulated APPR elements fabricated of Type 304 stainless steel plates welded together [8]. The reasons for the minor difference in observed current utilization for the simulated and actual elements are not apparent.

No problems were encountered during the cleanout of the dissolver (Run 12D). The final charge, which weighed 1586 grams, was reduced to less than one gram in 11.5 hours at an average current utilization of 0.28 gram per ampere-hour.

1.3 Effect of Welded Metal Structure on Current Utilization

In Run 10, simulated elements, fabricated by welding, dissolved at a lower current utilization than did elements composed of loose plates bound together by wire [8]. At that time, the lower factor was believed due to differences in geometry of the dissolving element. That is, the loose plates would fall apart after the binding wire dissolved and a multiple cell effect would result. It has been suggested that this assumption was not correct, but rather, that changes in metal grain structure during welding were responsible for the lower current utilization of the welded elements. Run 13 was made to isolate the effects of welding from the effects of geometry changes. Simulated APPR elements were made by wiring together loose plates containing welded areas. When these are dissolved, the current utilization measured was higher (0.95 g ss/A-hr) than those measured previously with either wire-bound elements (0.72 g ss/A-hr) or welded elements (0.53 g ss/A-hr). Although the usually high current utilization clouds the comparison, it does indicate strongly that welding does not penalize current utilization through changes in metal grain structure.

per ampere-hour for Nichrome-V [9]. In comparison, in Run 8, a current utilization of 0.71 gram per ampere-hour was measured when dissolving simulated HTRE elements fabricated of loosely bound, Type 304 stainless steel, concentric tubes [8]. This corresponds to approximately 118 percent of the theoretical current utilization for this material [9]. A similar difference in current utilizations was noted previously when comparing dissolution data obtained with loosely bound and welded APPR element sections [3].

1.2 Dissolution of Actual APPR Element Plates

In Run 12, approximately 19.5 kg of APPR element sections containing depleted uranium were dissolved in the pilot dissolver. The sections were fabricated by welding actual APPR fuel plates containing depleted uranium into

1.4 Study of Dissolver Residue and Undissolved Solids in Dissolvent

As in previous runs [3], the undissolved solids content of the circulating dissolvent during Runs 11, 12, and 13 was between 0.2 and 0.5 g/l. Accumulation of solids on the anode surface was noted again in Run 11. In this run, the current was held constant at 600 amperes (equivalent to an anode current density of 1.94 amperes per cm²) by varying the potential as the dissolver resistance changed. The potential had to be increased steadily from a low of 15 volts at the start of the run to 20.8 volts at the end of the run, presumably because of an accumulation of solids on the electrodes.

A similar rise in dissolver potential was noted as Run 12B progressed; in Run 12C, however, after boric acid had been added to the dissolvent the rise in potential stopped, indicating that boric acid may have an inhibiting effect on the solids deposition.

Run 13A was made at a constant potential. The acid feed was nominal 8M nitric acid with approximately 3 g/l boron added as boric acid. After the calibration portion of the run, the current stabilized at about 300 amperes and remained constant. Sludge accumulation in test sections of piping was about half that experienced in Runs 11 and 12.

The system was cleaned prior to Run 13B and gelatin was added to the feed at about 100 ppm. The current stabilized at about 375 amperes throughout this run and the test sections of piping contained between 1/10 and 1/5 the sludge accumulation found after Run 13A. The results observed in Runs 12 and 13 indicate that boron has some effect in inhibiting sludge formation, and this effect is enhanced by the further addition of gelatin.

In Run 12, a sample of dissolver sludge weighing 9.7 grams contained 0.003 gram of uranium. This indicates, on the basis of an estimated two percent of the original weight appearing as undissolved solids, that the uranium loss to the solids would be only 0.006 percent of the original uranium when dissolving APPR elements.

1.5 Effect of Boron Addition on Electrolytic Dissolution

In Runs 12C, and 12D, and 13, boric acid was added to the nitric acid feed to give a boron concentration of approximately 3.0 g/l in the dissolver. The object of adding the boron was to determine if any problems accompanied its possible use as a soluble neutron poison in the electrolytic dissolver. No adverse effects were noted; in fact, the boron may have had a beneficial effect in that it reduced the deposition of solids as discussed in Section 1.4, preceding. A portion of dissolver product containing 50 g/l stainless steel and 3 g/l boron was concentrated to about 100 g/l total metals in a small thermosyphon evaporator; boric acid crystallized out at a boron concentration between 3 and 4 g/l. A more soluble poison may be required if higher concentrations are needed to ensure criticality safety in the dissolver product.

1.6 Simplification of Model 2 Dissolver Design

Between Runs 11 and 12, the stainless steel dissolver vessel was replaced with a titanium vessel. The niobium cathode used in previous runs [3] was not reinstalled and the titanium vessel is now serving as a cathode. No evidence of attack on the titanium had been observed by the end of Run 13.

2. LABORATORY ELECTROLYTIC DISSOLUTION STUDIES

(K. L. Rohde, Problem Leader)

2.1 Distribution and Characterization of Sludge in the Electrolytic Dissolver (R. G. Butzman)

The sludge that is generated during electrolytic dissolution is found in three places in the dissolver system. At the close of a run, there is considerable sludge present in the dissolver vessel; the accumulation here amounts to more than half of the total sludge for the run. The dissolver product solution contains undissolved solids in the order of 0.1 to 0.5 gram per liter. In addition, there is a coating on the inside walls of the equipment which has been deposited by the circulating solution. This coating and the technique for its removal have been described in detail [8].

The granular material from the dissolver and dissolver product was stored in dissolver solution or nitric acid prior to analysis. Sample preparation included washing of the sludge with water to remove nitrates, filtration on a 4.0-5.5-micron opening glass frit, and drying at 115°C prior to analysis. The undissolved solids rinsed from the dissolver vessel, following the dissolution of Type 304 stainless steel, were almost exclusively stainless steel. The combined Fe, Cr, and Ni analyses accounted for greater than 96 percent of the total. There was only about 1.5 percent silica present and very small amounts of Nb, Mn, and Mo. On the other hand, the sludge in the dissolver product solution was only 65 to 85 percent Fe, Cr, and Ni, the balance being primarily silica.

In one sample of sludge from the dissolution of Nichrome (Run 11, Section III-1.1) the analyzed composition, after correction for the stainless steel contamination, exactly corresponded to the composition of 80-20 Nichrome indicating that grain dropping is also experienced with the Nichrome. Microscopic examination (45X) revealed that only a small part of this sludge (from HTRE fuel dissolution) is composed of oxide scale.

The two sludge samples from Runs 11 and 12 were analyzed for uranium. The uranium content of these samples was 0.03 and 0.027 percent, respectively. The estimated uranium losses (to the sludge) for these two runs are 0.001 and 0.002 percent of the total quantity of uranium dissolved during the runs. These low losses are in agreement with earlier laboratory studies [9].

2.2 Reduction of Sludge Coatings on Electrolytic Dissolution Equipment (R. G. Butzman)

When the importance of silica as the adhesive agent in binding the sludge to the walls of vessels and to the electrodes was discovered [8], means were sought for solubilizing the silica. Association of silica and proteins such as gelatin is described in the literature [10], and this phenomenon had already been applied in the flowsheet for aluminum alloy fuels [11].

In laboratory tests, gelatin dosages of 100 to 1000 ppm were added to samples of dissolver product solution and these were treated to simulate dissolver conditions. No adverse effects were experienced. Filtration rate tests indicated that the gelatin had coagulated the silica to a significant degree, and the use of 100 ppm was as effective as the higher concentration. Pilot

plant use of gelatin in Run 13 (Section III-1.4) confirmed its effectiveness in reduction of sludge buildup.

2.3 Corrosion of Components in the Model 2 Electrolytic Dissolver System (C. A. Zimmerman)

The platinum has had an average corrosion rate of 0.06 mil/month over an operating period of 342 hours under varying pilot plant operating conditions.

The niobium basket was completely cleaned in 48 percent HF at room temperature following the completion of Run 13. This basket shows a total metal loss equivalent to 0.2 mil/month after 461 hours of operation.

2.4 Investigation of Ceramic Coatings for Use in the Electrolytic Dissolver (C. A. Zimmerman)

The use of a flame sprayed ceramic as an insulation material in the electrolytic dissolver is of interest because of its ease of application as compared to ceramic sheet material.

Scoping chemical resistance tests of ROKIDE ceramic coatings reported previously [8] showed chromia to be the best of four materials checked. In order to better evaluate this material, samples of alumina and chromia ceramics were obtained on dimpled titanium plates as backing. It was necessary to spray these panels with a base coating of nickel aluminide before coating with the ceramic in order to obtain good bonding. After these specimens were used for impact tests they were checked for chemical resistance in electrolytic dissolver effluent (approximately 4M HNO_3 and 40 to 50 grams/liter of dissolved stainless steel as the nitrates). The chromia gave better results than the alumina, as it had in the scoping tests [8], but neither was suitable for extended use in the dissolver. Failure was by loss of adhesion between the ceramic and the nickel aluminide, presumably caused by penetration of the coating and chemical attack below it. Sprayed ceramic coatings probably can not be used in this application unless a means is available for sealing the ceramic so that it is impervious to the electrolyte.

3. NUCLEAR SAFETY EVALUATION OF ELECTROLYTIC DISSOLVER VESSEL DESIGN (W. G. Morrison)

In order to obtain the most efficient electrolytic dissolver design and stay within the limits of nuclear safety, a rather unusual geometry has evolved for the dissolver vessel. The dissolver concept presently under consideration is in the form of a slab 5-1/4 inches thick, 6 feet long, and 16 inches deep, with the bottom 8 inches of depth tapering to a point. A nuclear safety evaluation of the dissolver design was made for APPR (SM-1) and HTRE-3 fuels.

These two fuels are representative of the proposed processing load for maximum reactivity conditions and were considered on a before-burnup basis with no credit taken for burnable poison content. For simplification in this evaluation, the dissolver was considered as a rectangular slab 5-1/4 inches thick, 16 inches deep, and 6 feet long, rather than as a combined slab and triangular through. A survey of the complete range of compositions possible in

the dissolver showed that for both fuels under consideration, the maximum reactivity occurred at approximately 0.2 metal volume fraction; all subsequent calculations of the dissolver for either fuel were made with the fuel region containing this fraction of metal. The calculated k_{eff} s were 0.86 and 0.80 for APPR and HTRE-3 fuels, respectively. These results are conservatively high because of the geometry simplification assumed. One-dimensional neutron diffusion calculations were made with the MDMM and FOG-3 codes on the IBM-7040. Calculations considered a bare dissolver; it is estimated that water flooding the dissolver would increase the k_{eff} values by about 10 percent. The nuclear safety evaluation of the electrolytic dissolver shows that the dissolver design is safe for processing APPR and HTRE-3 fuels.

IV. NEW WASTE TREATMENT METHODS

(Section Chiefs: K. L. Rohde, Chemistry;
P. Burn, Process Computations)

1. DECONTAMINATION OF ALUMINUM NITRATE BY THE FREEZE-MELT TECHNIQUE

1.1 Solubility of Aluminum Nitrate in Nitric Acid (S. J. Horn)

A proposed method [2] for reducing the inventory of radioactive aluminum nitrate waste involves the use of a multistage freeze-melt system for crystallization of aluminum nitrate from 60 percent nitric acid solution. To assist in determination of solution supersaturation, laboratory experiments were run to determine the phase relationship between aluminum nitrate nonahydrate and nitric acid at various temperatures. These data augment previously reported measurements [8].

Solubilities were determined by saturating a nitric acid solution with aluminum nitrate, at a high temperature, and then allowing the solution to equilibrate at the desired temperature while in contact with solid $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ for a period of one week. Samples of the supernatant solution were then analyzed for aluminum and acid. Samples from the higher temperature saturations were diluted with water in order to prevent crystallization prior to analysis. The solubility data are presented in Figure 4.

Fig. 4 Solubility of aluminum nitrate in nitric acid as a function of temperature.

can remain slightly supersaturated with aluminum nitrate for periods approaching a half hour, even while in contact with suspended crystals of ANN. Further, scrub solutions containing dissolved ANN at concentrations corresponding to saturation at 40°C have been left standing at room temperature for periods of greater than one week without having crystals form, provided no crystalline ANN were present. Subsequent addition of small crystals of ANN result in crystal growth and lowering of the aluminum nitrate concentration to room temperature saturation.

Additional solubility information was obtained in the course of two runs attempted in the laboratory freeze-melt apparatus [2]. Equipment failures terminated these experiments prematurely and they will not be reported; however, the solubility data are of interest. The effluent nitric acid scrub solution from the apparatus was analyzed for aluminum nitrate in order to determine the carry-over of aluminum nitrate into the scrub. Analyses of the scrub solutions showed an aluminum nitrate concentration corresponding to a saturation temperature of 25°C (Figure 4) although temperatures of the effluent scrub solution averaged 13°C and never exceeded 18°C.

Qualitative observations of typical solutions showed that the scrub acid

2. REMOVAL OF FISSION PRODUCTS FROM FUEL STORAGE BASIN EFFLUENT (D. W. Rhodes)

The Isotope Removal System (IRS), a group of clinoptilolite-filled columns [12], has been operated successfully at the ICPP to decontaminate effluent from the fuel storage basin. The need for this unit arose because of fission product leakage from stored fuel elements having apparent minor cladding defects. Although the storage basin effluent that is released to the environs percolates through earth materials that are capable of removing the radioisotopes by ion exchange before the water reaches the regional ground water table, decontamination prior to discharge is prudent.

The average concentrations of the important radioisotopes in the basin water during 1963, prior to start-up of the IRS system, were about 1.6×10^{-3} $\mu\text{C}/\text{ml}$ and 1.2×10^{-3} $\mu\text{C}/\text{ml}$ for cesium-137 and strontium-90, respectively. Upon start-up of the IRS in December, 1963, decontamination factors (DF = concentration of radioisotope in influent/concentration of radioisotope in effluent) of >360 for cesium-137 and approximately 9 for strontium-90 were first obtained. The low DF for strontium-90 was attributed to the large particle size (70 percent >1 mm diameter) of the clinoptilolite. The DF for strontium-90 increased steadily, however, as improvements were made in the particle size distribution and control of flow through the columns. During the month of June, 1964, the DF for strontium had increased to 1100 using clinoptilolite particles in the range of 0.15 to 2.0 mm, with about 60 percent of this material less than 1.0 mm diameter. Flow through the columns was maintained at about 0.2 gal/(ft²)(min).

The successful operation of this unit permits fuel elements with minor cladding defects to be stored in the ICPP fuel storage basin without resorting to expensive and time consuming special canning techniques to prevent the release of fission products from defective fuel.

V. WASTE CALCINATION

(Section Chiefs: J. W. Garner, Plant Process Assistance;
K. L. Rohde, Chemistry;
B. M. Legler, Development Engineering)

1. WCF OPERATION

(G. E. Lohse, Problem Leader; E. D. Cooper, D. E. Black)

Since start-up of the Waste Calcining Facility in December 1963, over 323,000 gallons of waste containing from 20 to 40 curies of radionuclides per gallon have been processed with an overall volume reduction factor near nine fold. Process performance and off-gas decontamination have been excellent. The rate of release of strontium-90 to the atmosphere has averaged less than 0.01 percent of the rate which, during worse-than-average weather conditions, would cause a localized ground level concentration equal to that given in the "Radioactivity Concentration Guide" (RCG) for a 40-hour week; the release rate of ruthenium-106 has averaged less than 2.0 percent of the corresponding RCG value. Overall decontamination factors from the feed to the stack release have been near 6×10^7 for strontium-90 and 2×10^3 for ruthenium-106.

1.1 WCF Performance

Operation of the Waste Calcining Facility (WCF) continued smoothly with no downtime throughout the quarter. Approximately 165,000 gallons of first cycle aluminum nitrate waste were processed during the quarter at an average rate of 75.5 gallons per hour, exclusive of recycle solution. Since starting operation in the WCF, approximately 38,450 gallons (or 62 percent of the available solids storage space) have been used to store the solids resulting from the calcination of 323,000 gallons of radioactive wastes. This solids volume includes unuseable dead space within the filled bins; simple bench scale tests indicate that "coning" of the solids as they pour into the bins will result in a "nonfillable" void space of about 10 percent of the total bin volume. Estimations reflecting this 10 percent void space indicate that only approximately 34,600 gallons of solids storage were actually filled with solid radioactive waste.

The WCF has processed aluminum-waste solutions from two of the underground waste storage tanks. Typical properties of the material contained in these tanks (WM-185 and WM-187) are shown in Table II together with average figures comparing the WCF decontamination performance while processing feed from each of the tanks. Following the introduction of the waste contained in WM-187 [8], the release rate of strontium-90 decreased from a net value of 0.6 to 0.1 millicurie per day. A 30-percent decrease in the strontium concentration in the feed was responsible for part of this decrease. The remainder resulted from installation of new final filter assemblies in the off-gas system. Corresponding decreases in release rates of cesium and cerium isotopes accompanied the strontium decrease. The increase in the release rate of ruthenium, from 180 to 880 millicuries per day, was anticipated from the change in the feed composition. Nonetheless, the ruthenium release was still less than two percent of the rate which, under practically all weather conditions, would cause a localized ground level concentration equal to that permitted by the "Radioactivity Concentration Guide" for a 40-hour week.

TABLE II

COMPARISONS OF WCF WASTE SOLUTION FEED
COMPOSITIONS AND WCF DECONTAMINATION PERFORMANCE

<u>PROPERTIES OF WCF FEED</u>		
<u>Chemical Composition</u> <u>(molarity)</u>	<u>First Tank</u> <u>Processed</u> <u>(WM-185)</u>	<u>Second Tank</u> <u>Processed</u> <u>(WM-187)</u>
Aluminum	1.74	1.54
Acid	0.59	0.89
Sodium	0.04	0.03
Mercury	0.014	0.012
Boron	0.01	0.01
<u>Principal Fission</u> <u>Product Concentrations</u> <u>($\mu\text{c}/\text{ml}$)</u>	<u>First Tank</u> <u>Processed</u> <u>(WM-185)</u>	<u>Second Tank</u> <u>Processed</u> <u>(WM-187)</u>
Cs-137	1760	1020
Sr-90	1460	1010
Ce-144	570	4070
Ru-106	75	320
Cs-134	170	90
Zr-Nb-95	--	95
<u>Heat Generation Rate</u>	<u>First Tank</u> <u>Processed</u> <u>(WM-185)</u>	<u>Second Tank</u> <u>Processed</u> <u>(WM-187)</u>
Btu/(hr)(gal)	0.30	0.69

DECONTAMINATION PERFORMANCE OF WCF

Processing Period	Feb 1964-March 1964 March 1964-May 1964	
Net Feed Rate (gph)	65	75.5
Sr-90 Net Input Rate (mc/day)	8.6×10^6	6.2×10^6
Sr-90 Release Rate (mc/day)	0.6	0.1
Sr-90 Decontamination Factor (raw feed to stack)	1.4×10^7	6.2×10^7
Ru-106 Net Input Rate (mc/day)	4.4×10^5	2.0×10^6
Ru-106 Release Rate (mc/day)	180	880
Ru-106 Decontamination Factor (raw feed to stack)	2.4×10^3	2.3×10^3

1.2 WCF Operating Variables

During the quarter several changes in the operating variables were made. First, the flow of scrubbing solution to the venturi scrubber was decreased from 14.9 to 12.2 gallons per minute. A resulting decrease of about one-third in the ruthenium release rate was observed. Second, the calciner bed temperature was lowered, for a 15-day test period, from 400 to 375°C in an effort to reduce the temperature of the NaK system and to increase the bulk density of the bed material. As predicted by pilot plant data [13, 14], immediate increases in the ruthenium release rate as well as the solids carry-over rate to the scrubbing system were observed. Five days after the temperature change was made, the ruthenium release rate had increased from near 800 to 1900 millicuries per day while the solids carry-over rate increased from about 12 to 16 pounds per hour. Only a slight increase of 2 to 3 percent in the bulk density of the bed material was noted, and the release rate of strontium-90 was not affected. A third change, with the bed temperature still at 375°C, was an adjustment to increase the vacuum in the transport air system. This resulted in a decrease in the inlet transport air flow (from the fluidizing air blowers) and a corresponding increase in the underflow from the calciner cyclone. After the adjustment, the solids carry-over rate to the scrubbing system dropped from 16 to about 14.5 pounds per hour. In the final change, the calciner bed temperature was returned to 400°C. An immediate decrease, to approximately the normal levels previously observed at 400°C, was noted in both the solids carry-over and the ruthenium-106 release rates.

The results of these operational changes indicated that:

- (1) Operation below 400°C is undesirable. The objectionable increase in ruthenium release rate and solids carry-over more than balance the desirable increase in bed density. Further, the increase in carry-over rate of fines (which have a lower density) may actually cause a decrease in the overall product density.
- (2) The calciner cyclone and the venturi scrubber are sensitive to minor changes in operating conditions. Optimum conditions must be determined and closely maintained to achieve the best operation.

1.3 WCF Operating Problems

Leaking valves were discovered at two points in the WCF process. The first leak developed in the recycle system between the scrubbing solution surge tank and the waste hold tanks, necessitating termination of normal recycle. Liquid from the leak flowed through the cell floor drain and then to the hot sump tank. Since the leak rate was steady and approximately equal to the normal recycle rate, solution from the hot sump tank was recycled back to the waste hold tanks. Later, a second leak developed in this system precluding any further transfers between these tanks. Following the second leak, liquid from the leak was sent to the waste evaporator in the main ICPP, concentrated, and returned to the underground waste storage tank from which feed for the WCF is taken. Rerouting the leakage from the WCF through the main plant waste evaporator has not interrupted the satisfactory performance of the WCF.

A metallurgical examination of the NaK expansion tank fitting which failed in February [8] indicated the failures were due to transgranular stress corrosion cracking. Subsequent to the failures, stress analyses of the NaK piping system were made. These calculations indicated that the magnitude of the stresses at the location of the failure exceeded the yield point of the metal. Stresses could occur because no provision was made for expansion of the NaK line in that immediate area. Further analysis indicated that no other similar situations existed throughout the NaK piping system. Continued operation of the NaK system has been without incident.

2. LABORATORY STUDY OF WCF DECONTAMINATION -- REMOVAL OF RESIDUAL ALUMINA

(D. W. Rhodes, Problem Leader; B. E. Paige)

The WCF is a direct maintenance facility; therefore, it will be necessary to remove all of the residual alumina when it becomes necessary to decontaminate the process equipment. In connection with the removal of alumina, studies were made of the dissolution of alumina in various reagents, and the rate of disintegration of small, hard cakes which had formed in the calciner during cold runs.

These experiments indicated that four-molar nitric acid is the best reagent for removing residual calcined alumina from process equipment prior to decontamination. If process equipment is treated for at least one hour with hot four-molar nitric acid, greater than 95 percent of the alumina will dissolve up to a concentration of 25 grams of aluminum per liter. Tenacious cakes and coatings that may have formed will be removed. The nitric acid dissolution can be followed with cold water flushes to slurry and remove the small amount of insoluble material which remains. If time of contact and volume are adequate, additional treatment with the same reagent will be of little value. A second dissolution with any of the other reagents studied will not dissolve a significant amount of alumina.

2.1 Dissolution of Calcined Alumina

Nonradioactive calcined alumina from the pilot plant was contacted in 48 experiments with four reagents (4M HNO₃, 13M HNO₃, 3M NaOH, and 13M NaOH) at two temperatures (30°C and the boiling point), for one hour, five hours, and 20 hours. Experiments were made using either 100 ml or 20 ml of solvent per gram of calcined alumina. The experimental data, reported in Table III as grams of alumina dissolved per liter of solvent, show the effect of the various conditions on the dissolution of the alumina. In every case, one hour at the boiling point dissolved greater than 95 percent of the alumina; however, at the 20-to-1 volume ratio the four-molar nitric acid was the most satisfactory because aluminum nitrate precipitated from the other reagents when the solutions were cooled. At 30°C, four-molar nitric acid dissolved 85 percent of the alumina at the 20-to-1 volume ratio, but 20 hours contact time was required.

In another set of experiments, designed to show the utility of a low-temperature process, dissolution of calcined alumina with four-molar nitric acid for 20 hours at 30°C was followed by a second dissolution step using various reagents and conditions. In the second dissolution, using either three-

TABLE III

COMPARISON OF REAGENTS FOR DISSOLUTION OF CALCINED ALUMINA

<u>4M HNO₃ Reagent</u>				
<u>Temperature</u>	<u>Volume Ratio^[a]</u>	<u>Aluminum Dissolved (g/l)</u>		
		<u>1 Hour</u>	<u>5 Hours</u>	<u>20 Hours</u>
30°C	100/1	0.5	2.4	3.7
	20/1	2.6	11.8	18.2
Boiling	100/1	4.4	4.3	4.4
	20/1	22.3	22.4	21.4
<u>13M HNO₃ Reagent</u>				
<u>Temperature</u>	<u>Volume Ratio^[a]</u>	<u>Aluminum Dissolved (g/l)</u>		
		<u>1 Hour</u>	<u>5 Hours</u>	<u>20 Hours</u>
30°C	100/1	1.0	1.1	2.6
	20/1	1.1	3.5	3.5
Boiling	100/1	4.8	3.9	4.6
	20/1	22.8	23.4	23.5
<u>3M NaOH Reagent</u>				
<u>Temperature</u>	<u>Volume Ratio^[a]</u>	<u>Aluminum Dissolved (g/l)</u>		
		<u>1 Hour</u>	<u>5 Hours</u>	<u>20 Hours</u>
30°C	100/1	3.8	3.8	4.0
	20/1	16.8	13.3	13.5
Boiling	100/1	4.4	4.5	3.1
	20/1	20.8	21.1	15.4

TABLE III (cont.)

COMPARISON OF REAGENTS FOR DISSOLUTION OF CALCINED ALUMINA

13M NaOH Reagent				
Temperature	Volume Ratio ^[a]	Aluminum Dissolved (g/l)		
		1 Hour	5 Hours	20 Hours
30°C	100/1	2.4	3.5	3.6
	20/1	4.8	9.6	17.7
Boiling	100/1	4.2	3.0	--
	20/1	21.1	20.0	8.2

[a] Volume of solvent used per gram of calcined alumina.

molar sodium hydroxide or another batch of four-molar nitric acid, very little additional alumina was dissolved. The undissolved solids contained mostly amorphous alumina with some gamma alumina and small amounts of alpha alumina. The gamma alumina was completely removed by a second dissolution with either four percent sodium fluoride in 20 percent nitric acid at 60°C or 12M nitric acid at 100°C, but the total alumina dissolved was no greater than previous one-step dissolutions using four-molar nitric acid at the boiling point.

Although no reagent or conditions completely dissolved the calcined alumina, the dissolution of most of the alumina will permit the removal of the remaining undissolved solids as a slurry. Solids slurried in any of the reagents studied are acceptable in the process equipment.

2.2 Disintegration of Hard Cakes of Calcined Alumina

During cold operation of the WCF, small, hard cakes of alumina occasionally formed in several areas of the process. Although cake formation has been eliminated during normal operation of the WCF, the comparative rate of disintegration of these cakes was determined with water, four-molar nitric acid, and three-molar sodium hydroxide for further information on the removal of calcined alumina from process equipment.

Since cakes disintegrate in the reagents creating milky suspensions which cannot be readily evaluated, an apparatus (Figure 5) was designed so that the cake sample is visible for comparative evaluation. Using this apparatus, a 240-ml batch of hot or cold reagent was continuously recirculated and sprayed onto a 12-gram piece of the cake until it had completely disintegrated and all of the alumina particles had washed into the reservoir below. The rate of disintegration varied between cakes of different origin. Some cakes were disintegrated rapidly with hot water and were even disintegrated at a reasonable rate in cold water. A cake which had formed in the calciner nozzle area was the toughest and was not affected by hot water. The sample was, however, disintegrated by hot four-molar nitric acid in about 45 minutes. Several comparative runs, using three reagents on three portions of the same sample of

Fig. 5 Apparatus for comparative disintegration of hard cakes of calcine.

cake, showed that four-molar nitric acid disintegrated most of the samples within 10 minutes; this disintegration was about twice as fast as with three molar sodium hydroxide and four times as fast as with hot water.

3. PREPARATION OF GLASS FROM CALCINED ALUMINA

(D. W. Rhodes, Problem Leader;
B. E. Paige)

It has been demonstrated at ICPP that glass can be made directly from nonradioactive alumina calcine produced continuously in the WCF [3]. Studies are continuing to evaluate the characteristics of this glass prior to preparing glass from radioactive calcine from the WCF on a laboratory scale.

3.1 Effect of Irradiation on Alumina-Containing Glasses

This study was conducted primarily to establish the effects of radiation during long-term storage on glass produced from alumina calcine. Four samples were irradiated in an air-filled tube in the MTR Gamma Facility with an initial dose rate of 2×10^7 R per hour. The equilibrium temperature of the samples was about 200°C . The samples received a total dose of 10^{10} R, which is approximately equivalent to the cumulative irradiation of glass prepared from WCF calcine during 100 years of storage.

At 10^7 R total dose, the samples were slightly discolored, varying from yellow to tan, but they were still clear and transparent. At 10^8 R total dose, the samples were somewhat darker in color, and two samples which were highly strained had cracked, apparently from the thermal exposure. At 10^9 R total dose, the samples were dark brown to black, but were still transparent to a light beam.

Figure 6 compares the four samples which were irradiated to 10^{10} R total dose to the same samples with no irradiation. In all cases, the irradiated samples were jet-black and opaque. The irradiation did not affect the physical integrity of the glass. X-ray diffraction analysis showed no difference between irradiated and nonirradiated portions of the same sample indicating the absence of extensive devitrification. Devitrification may, however, result during preparation of the glass due to the chemical action of fission products or during the initial period of storage due to the heat caused by decay of the fission products.

Fig. 6 Effect of irradiation on alumina glass. Samples #1, before irradiation. Samples #2, after irradiation. Sample A was made from alumina calcine containing 2.5 mercury. Sample B contained an excess of alumina calcine and was not homogeneous. Sample C was prepared from alumina calcine which contained 58 percent alpha alumina. Sample D was made from alumina calcine from the WCF by the standard fusion techniques^[3]; irregularities on the bottom surface caused by molding can be seen through this extremely clear specimen.

3.2 Effect of Composition of Calcined Alumina on Glass Composition

In the fluidized bed calcination of aluminum-type wastes at 400°C, the mercury remains with the calcine; however, in converting this calcine to glass at much higher temperatures, the mercury is expected to volatilize from the melt. Although the glass previously reported [3] was prepared from alumina calcine which did not contain mercury, more recent glass specimens have been prepared from calcine containing about 2.5 weight percent mercury. A good quality, clear, blue-green glass was formed, but analysis indicated that more than 99.9 percent of the mercury had volatilized during fusion.

Samples of the alumina-lead-sodium-phosphate glass, prepared either from aluminum nitrate solution or from alumina calcine, were dissolved for analysis by boiling for one hour in 6M nitric acid. Sections of five different glass samples prepared from alumina calcine were analyzed for lead oxide (PbO), aluminum oxide (Al₂O₃), and phosphorus pentoxide (P₂O₅) to determine the homogeneity of the sample. The material balances ranged from 99 to 101

percent and the results indicated a high degree of homogeneity in the molded specimen. The analysis also indicated that glass containing 25 weight percent alumina calcine was only 20 weight percent aluminum oxide, confirming analytical values of about 80 percent aluminum oxide in the alumina calcine used to prepare the glass.

4. CALCINATION OF ZIRCONIUM FLUORIDE WASTE

4.1 Pilot Plant Studies (E. J. Bailey, Problem Leader; J. C. Petrie)

A pilot run was made in the 12-inch-diameter calciner to investigate the feasibility of processing zirconium fluoride wastes with minimum modification of the Waste Calcining Facility and to provide fluidized bed calcined solids for laboratory studies. This run demonstrated that zirconium fluoride type waste can be calcined successfully under conditions compatible with those employed at the WCF and that greater than 99 percent of the potentially volatile fluoride in the waste can be retained in the solids by complexing the fluorides in the feed with a stoichiometric amount of calcium. Evaluation of corrosion data from the equipment and from test coupons indicates that the austenitic stainless steels from which the WCF is constructed perform very well in this service.

Only trace amounts of fluorides were volatilized from the solid product when it was heated to 800°C, indicating that the calcium-zirconium-fluoride compounds that are formed will be stable during storage up to that temperature.

4.11 Description of Pilot Plant Run. The objectives of this run were to determine: (a) the feasibility of processing existing and future aluminum-nitrate zirconium-fluoride wastes at the WCF; (b) the volatility of fluorides during the calcination of the waste; (c) the corrosion rates on materials of construction in the WCF and other materials which could be used in a calciner system; and (d) the properties of the calciner product.

Operating conditions for this run, as summarized in Table IV, simulated as nearly as possible normal operating conditions at the WCF.

Feed for the run simulated the gross constituents in the radioactive wastes which exist and which will be accumulated during future reprocessing of zirconium fuel elements at ICPP. Table V compares the chemical analysis of samples of feed from the test run (Run 07) with actual zirconium process wastes. The zirconium fluoride dissolver effluent is complexed with aluminum nitrate so that the solution can be safely processed and stored in the stainless steel equipment at ICPP.

TABLE IV

OPERATING CONDITIONS FOR
RUN 07 -- CALCINATION OF
ZIRCONIUM FLUORIDE WASTES
IN THE 12-INCH CALCINER

Bed Temperature	400°C
Starting Bed	Alumina produced at the WCF during Run 10
Fluidizing Velocity ^[a]	1.0 ft/sec
Nozzle Air Ratio	250, 500, 625, 700
Feed Rate	10 l/hr
Bed Pressure	Slightly below atmospheric pressure

[a] The fluidizing velocity is defined as the linear velocity which would be attained by the fluidizing air in the empty calciner vessel at the operating temperature and pressure.

TABLE V
COMPOSITION OF ZIRCONIUM FLUORIDE WASTES

Chemical	ZrF ₄ Waste Existing at ICPP	Future ZrF ₄ Wastes	ZrF ₄ Waste Calcined During Run 07 ^[a]
H ⁺ (<u>M</u>)	1.1	0.78	1.03
Zr ⁺⁴ (<u>M</u>)	0.48	0.71	0.43
F ⁻ (<u>M</u>)	3.1	4.22	2.45
Al ⁺³ (<u>M</u>)	0.73	0.50	0.66
NO ₃ ⁻ (<u>M</u>)	2.04	1.63	4.66 ^[b]
B ⁺³ (g/l)	--	2.58	1.82
Sn ⁺² (g/l)	0.53	1.01	0.68
Ca ⁺² (<u>M</u>)	--	--	1.21

[a] Average analytical results of samples of feed taken periodically throughout the run.

[b] Consists of 2.24 moles/l in original waste and 2.42 moles/l from Ca(NO₃)₂.

Laboratory tests had indicated that the addition of calcium to the aluminum nitrate-zirconium fluoride wastes would minimize the volatility of the contained fluoride during calcination [15]. Calcium nitrate was dissolved in the feed for Run 07 to give a calculated stoichiometric ratio of calcium-to-fluoride, and the solution was continuously agitated to prevent settling of the flocculent CaF₂ precipitate. The actual ratio of calcium-to-fluoride, determined from periodic samples of the feed, ranged from 0.93 to 1.07 of the stoichiometric ratio. Fission products and trace amounts of other minor elements were not included in the feed used in Run 07, but little or no effect on the run results should have occurred because of this exclusion.

4.12 Operating Observations. Operating problems encountered during the run were minor. Adjustments to the feed-slurry transfer system were required during the first few hours of operation, but, following this, the run proceeded uninterrupted. Because of a limited feed supply (95 hours at 10 liters/hr), optimum operating conditions were not determined. The run was conducted at only one operating temperature (400°C) and at only a single calcium-to-fluoride ratio.

The mass median particle diameter (MMPD) increased steadily throughout the run, probably as a result of: (a) a low initial nozzle air ratio (NAR), (b) no seed addition during the early part of the run, and (c) the high viscosity

of the complexed feed. When a gradual increase of NAR to 700 failed to lower the MMPD, seed addition to provide nuclei for particle growth was started about 59 hours after the start of the run with the batch addition of 1170 grams of -35 +135 Tyler mesh alumina to the calciner bed. About eight hours later (66-1/2 hours after the start of the run), routine addition of 150 grams of -48 +135 Tyler mesh alumina was initiated every 30 minutes. The MMPD was still increasing at the end of the 95-hour run although the weight percentage of the product passing a +35 Tyler mesh screen had increased from about five to eleven percent, indicating that a decrease in average particle size was imminent.

To determine if the high NAR and seed addition would have controlled the MMPD of the product had calciner feed been available for an extended run, a mathematical model developed by E. S. Grimmett of these laboratories [16] was applied to the conditions of Run 07. To test the correctness of the mathematical model, the computer program was set up to run parallel to the actual operating conditions of the run and to extend the simulated operating conditions beyond the end of the actual run. For example, after 61 hours of actual operation the product MMPD was 0.75 mm; the theoretically predicted value was 0.71 mm. Near the end of the run, 32 hours later, the product MMPD was 0.83 mm and the MMPD predicted by the mathematical model was 0.81 mm. The computer study was extended for 200 hours beyond the starting of routine seed addition. The theoretical MMPD was 0.84 mm at 100 hours and 0.65 mm at 200 hours, thus indicating that the particle growth rate would have been controlled had additional calciner feed been available for an extended run.

4.13 Volatilization of Fluorides. The volatilization of fluorides during the calcination of the waste averaged less than 0.5 percent. Table VI gives the rates of fluoride volatilization based on periodic samples of feed and off-gas. A fluoride volatilization rate of 0.93 percent was reported for similar conditions in static laboratory tests [15].

TABLE VI

VOLATILIZATION OF FLUORIDES DURING
CALCINATION OF ZIRCONIUM FLUORIDE WASTES

<u>Sample Number</u>	<u>Fluoride Rate to Calciner (moles/hr)</u>	<u>Fluoride Rate in Off-Gas (moles/hr)</u>	<u>Percent Volatilized</u>
1	21.09	0.126	0.60
2	23.87	0.233	0.98
3	27.19	0.117	0.43
4	21.79	0.132	0.61
5	21.14	0.102	0.48
6	24.90	0.116	0.47
7	25.60	0.121	0.47
8	29.44	0.110	0.37

During the entire run, approximately 2068 moles of fluoride were fed to the calciner. Analyses of the calcined solids (product, fines, and the final bed) accounted for 2058 moles of fluoride, or 99.52 percent of the input. By difference, the volatilized fluoride, 0.48 percent, compares favorably with that observed in the off-gas samples listed in Table VI.

4.14 Product Properties. The product from the calcination of zirconium fluoride waste has a higher density than the product of calcination of aluminum nitrate waste as seen in Table VII. It is estimated that 90 percent of the alumina starting bed had been replaced when the sample used for the product analysis of Run 7 was taken.

TABLE VII
COMPARISON OF PROPERTIES OF ALUMINUM-
AND ZIRCONIUM-WASTE CALCINATION PRODUCTS

	<u>Run 04</u> <u>(Aluminum Nitrate)</u>		<u>Run 07</u> <u>(Zirconium Fluoride)</u>	
	<u>Product</u>	<u>Fines</u>	<u>Product</u>	<u>Fines</u>
Bulk Density (g/cc)	0.88	0.15-0.20	1.20	0.3-0.38
Absolute Density (g/cc)	2.6	2.0	3.3	3.0
Nitrate Content (wt percent)	2.0	12-15	2.5	10.5
Fluoride Content (wt percent)	--	--	19.0	19.5
Calcium-to-Fluoride Ratio	--	--	1.8-2.2	--

4.2 Corrosion of Calcliner Equipment During Pilot Operation (D. W. Rhodes, Problem Leader; T. L. Hoffman)

Plant and service corrosion test pieces were evaluated after 95 hours service in the pilot plant calciner during calcination of zirconium waste raffinate complexed with calcium nitrate (Run 07 -- Section V-4.1). This scoping study was made on 16 different alloys and two refractories to determine their suitability as construction materials for calciner process equipment.

In general, the austenitic stainless steels performed very well, but additional studies are planned to verify the results of this relatively short-term test.

4.21 Service Test Corrosion Results. Three Inconel-X heater rods that were used in fluid bed heat transfer service corroded at an average rate of 0.4 mil/month. The observed rates in this service varied between 0.2 and 0.8 mil/month; position of the rods in the bed could explain this rate variation.

The Type 304 venturi throat piece in the scrubbing system completely resisted corrosion of the scrubbing solution. The stainless steel Type 347 feed nozzle port lost 0.6 mil/month. A silicon carbide nozzle in the off-gas scrubbing solution lost 2.5 mils/month due to corrosion. These service test losses are considered to be within acceptable limits.

4.22 Test Specimen Corrosion Results. A number of test specimens were mounted in various locations in the pilot plant calcination system during the zirconium fluoride test. Table VIII summarizes the test results, comparing corrosion rates, material, and service. The results compare favorably with the service test results of the pilot plant equipment.

TABLE VIII

CORROSION TEST RESULTS FOR VARIOUS MATERIALS DURING
CALCINATION OF ZIRCONIUM FLUORIDE TYPE WASTE SOLUTIONS

<u>Alloy</u>	<u>Location of Service</u>	<u>Corrosion Rate (mils/month)</u>
SS 304L welded to SS 347	Calcination quench solution	0.04
SS 347 welded to 17-4 PH	Calcination quench solution	0.10
SS 347 welded to 17-7 PH	Calcination quench solution	0.28
SS 310	Vapor above calciner bed	0.05
SS 329	Vapor above calciner bed	0.01
SS 316 (modified)	Vapor above calciner bed	0.03
Timken 16-25-6 (Cr-Ni-Mo)	Vapor above calciner bed	0.04
HR Nichrome	Vapor above calciner bed	0.34
Tophet "A"	Vapor above calciner bed	0.20
Monel	Vapor above calciner bed	0.08
K-Monel	Vapor above calciner bed	0.11
Inconel-X	Vapor above calciner bed	0.41
Cupro-Nickel (70 Cu-30 Ni)	Vapor above calciner bed	34.4
Boron carbide nozzle cap	Fines collection pot	3.2
SS 440 C	Lower part of bed	42.5 ^[a]

[a] The SS 440C specimens came loose from the test rack and were found in the bottom of the calciner. Erosion due to location and movement in the bed could have contributed to the apparent corrosion rate.

4.3 Thermal Stability of Calcined Zirconium Fluoride Waste (D. W. Rhodes, Problem Leader; M. W. Wilding)

Solids from the fluidized bed calcination of zirconium-fluoride-aqueous wastes presumably will be stored in bins similar to those used for the present WCF alumina product, provided volatility of the fluoride or fission products is not excessive.

To study the volatility of fluoride at predicted maximum centerline storage temperatures, samples of product from the recent 12-inch calciner run (Run 07 -- Section V-4.1) were heated at 800°C for 24 hours. A section of stainless steel tubing with connectors at both ends contained the solid. A slow air flow passed

through the solid, thence through two caustic scrubbers connected in series. An analysis of the solid (before and after heating) as well as the scrub solutions indicated that essentially all of the nitrate, but only a trace of fluoride, volatilized at 800°C. Before heating, the solid contained about 19 weight percent fluoride, 2.0 weight percent nitrate, and 0.9 weight percent boron (the boron resulting from its use as a soluble poison during reprocessing). X-ray diffraction showed CaF_2 as the only crystalline species in the original calcine. After heating at 800°C for 24 hours, ZrO_2 (as well as CaF_2) was detected. The amount of amorphous material was reduced in the latter sample.

Apparently the compound or compounds formed of fluoride, zirconium, and calcium are stable, at least up to 800°C, which is above predicted maximum centerline storage temperatures.

VI. PLANT IMPROVEMENTS (Section Chief: P. Burn, Process Computations)

1. AIR PULSER DEVELOPMENT (S. J. Horn)

A simplified mathematical model [3] of the air pulser has been given further study. The simplified model was solved for a sine wave pressure function rather than the more nearly representative square wave function. Pulse amplitudes were calculated using this solution for pulse frequencies between 20 and 80 cycles/min and for air pressure which would yield an in-column pulse amplitude of approximately one inch. In these calculations, frictional effects were ignored completely. These calculated pulse amplitudes agreed with pulse amplitudes obtained from the nonlinear analog simulation [17] within 30 percent. The implications of this general agreement between the highly simplified model [3] and the more sophisticated and experimentally verified analog model [17] are that inertia effects exert the major influence on the operation of the air pulsers on the ICPP pulse columns.

While the analog model has only been verified experimentally for operation with a single liquid phase in the pulser and column [3], unless the presence of two immiscible liquid phases in the column produces large frictional effects, analog simulation should provide a reasonably accurate means of predicting the performance of an air pulser.

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