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FISCAL YEAR 1968

IDAHO NUCLEAR CORPORATION
NATIONAL REACTOR TESTING STATION
IDAHO FALLS, IDAHO

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CHEMICAL TECHNOLOGY BRANCH ANNUAL REPORT FISCAL YEAR 1968

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SUMMARY

The ICPP fuel processing facilities recovered approximately 675 kg of uranium from a variety of aluminum-uranium alloy fuels during 1000 hours of operation of the continuous dissolution system; additional uranium was recovered during custom processing of plastic-coated test reactor elements and broken glass molds used to cast EBR-II fuel pins. Approximately 400 g of neptunium were separated and stored for future purification.

Process support studies have resulted in minor equipment changes to permit co-processing of aluminum and zirconium fuels; dissolution of aluminum fuel in nitric acid gives an aluminum nitrate-containing product which is suitable for complexing the fluoride-containing product obtained from dissolution of zirconium fuel in hydrofluoric acid. Uranium from the blended dissolver solutions will be recovered in a single extraction campaign, resulting in a significant saving in chemical and processing costs, a decrease in the volume of waste solutions, and, ultimately, a reduction in waste calcination and solids storage costs. Effects of blending on process chemistry appear to be minor. Uranium in EBR-II skull oxide was readily dissolved in boiling nitric acid, and distribution coefficients determined in the laboratory appeared to be satisfactory for extraction in either TBP or Hexone; thus, recovery of uranium from this EBR-II pyrometallurgical process scrap appears to be practicable in an ICPP custom process. Silicon in aluminum-uranium alloys has been shown to have a minor effect on the dissolution rate of the alloys. Only the silicon present as the intermetallic, $U(Al,Si)_3$ dissolves; silicon in the alloy in excess of one atom per atom of uranium is not present as an intermetallic and does not dissolve. Surfactancy is caused by the silicon which is dissolved. The quantity and composition of the solid residues are related to the atom ratio of silicon to uranium. Plant test corrosion observations indicate that equipment constructed of several different materials has satisfactory corrosion resistance for continued service in zirconium fuel reprocessing. Studies on the clarification of dissolver product for solvent extraction and measurement of pulse amplitude and liquid level in air-pulsed extraction columns are discussed.

Reprocessing of EBR-II fuel by electrolytic dissolution in nitric acid followed by extraction with TBP has been demonstrated on a laboratory scale. Only 0.1 percent of the total uranium charged was found in solid residues amounting to 2.5 percent of the total fuel; this uranium could be recovered by a mixed nitric-hydrofluoric acid dissolver if desired. Deposition of residues has caused some difficulty in pilot plant operations; satisfactory dissolution rates for stainless steel have been demonstrated in a V-shaped solution contact dissolver. Both laboratory and pilot plant data indicate adequate corrosion resistance of niobium and titanium dissolver components. Preparations for receiving EBR-II fuel at the ICPP fuel storage basin have been completed, and underwater storage tests of fuel pins indicate satisfactory corrosion resistance of the fully clad fuel.

The combustion-dissolution process for graphite fuels, based on burning of the fuel with oxygen in a two-stage fluidized bed, followed by dissolution of the elutriated product oxide in nitric acid, has been shown to operate smoothly at 680 to 730°C, with a fluidizing velocity of 0.9 to 1.1 ft/sec, and an oxygen concentration of 60 to 80 percent. Departure from these conditions can lead to incomplete combustion, sintering of bed material, or burning of the reactor walls. The off-gas cleanup and uranium dissolution systems operate efficiently. Coating of U_3O_8 on the alumina bed has been found to increase in the presence

of uranium carbide, and to decrease in the presence of uranium dioxide or niobium carbide. In laboratory studies, potential combustion modifiers or catalysts were found to be ineffective in accelerating combustion rates. Criticality safety of the process is based on a combination of mass limitation and geometrical control.

Difficulty in recovery of the uranium by fluorination appears inherent in a fluidized bed halide volatility process for Shippingport PWR type fuel.

The Waste Calcining Facility (WCF) was operated with radioactive waste for 6050 hours with 93 percent on-stream time; about 287,000 gallons of aluminum-type and 109,000 gallons of zirconium-type waste solutions were calcined to 3170 and 1670 cubic feet of solids, respectively. The calcination of the radioactive fluoride-bearing zirconium waste was the first such reduction to non-corrosive solids anywhere. Process performance was satisfactory and corrosion of calciner and off-gas decontamination components was negligible. The Type 316 stainless steel heat exchange system containing circulating liquid NaK has undergone significant metallurgical changes during 28,600 hours of operation at 600 to 750°C. Diffusion of alloying elements from hotter to cooler regions, sigma phase formation, and deterioration in some mechanical properties have occurred, but not beyond anticipated changes; the system is still considered serviceable.

Support studies undertaken in preparation for calcination of fluoride-containing zirconium wastes indicate that dolomite, a calcium magnesium carbonate, and calcium nitrate are both effective in retaining fluoride in the calcine. The corrosion-erosion resistance of austenitic stainless steel equipment used in the off-gas scrubbing system was found to be satisfactory in laboratory tests as well as in actual plant performance, and one-year tests indicated that the existing calcine storage bins of Type 304L stainless steel are suitable for long-term storage of calcined zirconium waste. A safety analysis prior to calcination of zirconium wastes indicated that reactions between leaking NaK and calcined solids might be possible but that no undue additional hazards over the previous calcination process would be expected; laboratory tests with NaK and zirconia calcine gave no evidence of the conceivable NaK-oxygen-calcium fluoride reactions at 400 to 800°C in a fluidized bed calciner.

Heating of a fluidized bed calciner by in-bed combustion of a hydrocarbon fuel has progressed favorably in pilot plant operations; use of oxygen rather than air in the fuel atomizing nozzles greatly increases combustion efficiency and reduces the oxygen requirement to nearly theoretical amounts; thermal efficiency of the process is approximately 60 percent compared to 35 percent for indirect methods (eg, furnace heating of circulated NaK); properties of calcined solids are similar to previous solids although nitrate content and total volatiles are lower for calcine produced in the in-bed combustion process. A safety analysis discloses different but no greater hazards than with the present NaK heating system; corrosion studies indicate only a modest metal dusting effect on the Type 347 stainless steel at 500°C. The differing off-gas composition does not appear to affect the adsorption of ruthenium from the off-gas in the silica gel adsorbers.

Supporting studies for other possible Waste Calcining Facility improvements include development of a mathematical model for predicting heat transfer

characteristics of a bayonet tube; this study indicates that no significant improvement could be realized in the existing calciner heat exchanger by decreasing the short-circuiting effect between the core tube and the NaK annulus or by reversing the flow of NaK in the bayonet tube. Control of feed to the calciner by a vortex restrictor rather than by a valve has been demonstrated successfully in a mock-up of the WCF/feed system and will be tested on the calciner in a future WCF run. Laboratory studies indicate that a possible replacement of the off-gas cyclone with stainless steel filters should not lead to problems of ruthenium depositing in the filter pores or corrosion of the filter medium.

Successful performance of a fuel storage basin cleanup system has been demonstrated for approximately two years, during which time no basin water containing radioisotopes has been discharged to the lithosphere; contaminated water is passed through low-cost natural mineral beds to adsorb contaminants and is then recycled to the basin. Survey tests indicate the possibility of recovery of mercury from waste solutions by electrochemical means.

LOFT assistance studies indicate that a number of commercially available, conventional protective coatings and primers are suitable for use in reactor containment buildings although they are difficult to decontaminate of volatile fission products. Observations on fission product behavior in Contamination-Decontamination Experiments have been summarized. Tests of a continuous sampler-monitor for sampling the containment atmosphere during the LOFT experiment show that the sampler will provide reliable data on the noble gas and gaseous iodine concentrations. The LOFT plateout capsule sampler has been shown to be a reliable sampling device although deposition on the sampler will differ from that on the containment wall because of differences in environment. Decontamination of the LOFT Reactor Package was examined in light of the repetitive decontamination required for the LOFT-ECCS program, and alterations to simplify decontamination were recommended.

Other reactor technology support programs reported include: (a) the application of well known decontaminating reagents by foam techniques to increase the efficiency and safety of decontamination operations; (b) advances in uranium aluminide manufacture employing fluidized bed techniques; (c) determination of the volume coefficient of expansion and volume change on melting of uranyl nitrate hexahydrate for use in theoretical studies; and (d) development of an analog computer simulation program for the Advanced Test Reactor.

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I. FUEL REPROCESSING

1. PERFORMANCE OF ICPP FUEL RECOVERY PROCESSES

1.1 Aluminum Fuel Reprocessing by the Continuous Process

(G. E. Lohse; Process Engineering Section)

In FY-1968, the fuel reprocessing facility at ICPP was operated to recover uranium and neptunium from "spent" aluminum-type reactor fuel elements from various reactors. Approximately 675 kilograms of uranium were dissolved in the continuous dissolvers in about 1000 hours of operation. The dissolver solution, along with salvage solution containing about 20 kilograms of uranium, was processed through the extraction systems for recovery of the uranium. Recovery exceeded 99.9 percent. In all, about 218 grams of uranium were lost in 101,400 gallons of waste. About 400 grams of neptunium were recovered and stored for future purification.

Catalyst Consumption During Fuel Dissolution. Prior to startup of this reprocessing campaign, side loops were installed to recirculate dissolver product (hence, mercuric nitrate catalyst) to the dissolvers. Pilot plant tests [1] indicated that an increase in catalyst efficiency (decreased consumption) near 25 percent could be expected from such recirculation. Three tests were conducted at different acid and catalyst rates to examine the effectiveness of the loops. Results of these tests, though not entirely conclusive, indicated beneficial effects (up to 20 percent) when the dissolvers were operated with a dissolvent rate of 110 gal/hr-sq ft; the effects were apparently detrimental, however, when the dissolvent rate was 175 gal/hr-sq ft. Additional tests are necessary for resolving the effects of various parameters on dissolution rates.

Performance of the Organic-Aqueous Product Wash Column. Prior to startup of fuel processing operations, a seven-stage mixer settler for washing TBP from the first cycle aqueous product was replaced with a pulsed plate column. Samples taken during the run indicate that greater than 90 percent of the total organic phosphate and, specifically, greater than 75 percent of the dibutyl phosphate was removed from the aqueous product in the column. Plant operation was improved considerably by replacement of the mixer-settler with the pulsed column; column operation was generally smooth and no process upsets were attributable to its performance.

Strip Column Performance. Samples of the organic raffinate stream from the first-cycle stripping column occasionally contained high uranium and solids. The solids were amorphous to X-ray diffraction, and usually contained over five percent zirconium and silicon and up to five percent phosphate. Fission product ^{95}Zr was the primary gamma emitter present. Filtrates from the samples contained up to 0.2 gram per liter of dibutyl phosphate. The presence of the dibutyl phosphate is believed to be primarily responsible for poor uranium removal in the stripping column. During these periods, the concentration of dibutyl phosphate was considerably higher than normal because aqueous streams from the solvent cleanup system were recycled to the extraction column, re-extracted to the organic phase, then carried along to the stripping column. After recycle of the aqueous solvent-wash stream was stopped, the concentration of uranium in the organic raffinate from the stripping column dropped to acceptable levels.

1.2 Custom Reprocessing at ICPP

1.21 Recovery of Uranium from EBR-II Vycor Glass Molds

(M. E. Jacobson; Chemistry Section)

G. F. Offutt; Process Engineering Section)

During the year about 25.4 kg of 50 percent enriched uranium were recovered from broken Vycor glass mold tubes that are used to cast fuel pins at the EBR-II Fuel Cycle Facility. Uranium was leached from the glass in nitric acid and the leachate was transferred to the ICPP extraction system. This completes a total of four campaigns to date.

The leaching process has been improved considerably since the first two campaigns [2]. Scrap glass now arrives at the ICPP Multicurie Cell in a stainless steel lined three-gallon bucket. This liner is equipped with a simple built-in sparge ring and transfer-filter tube. The bucket is removed from the shielded shipping cask, placed on the Multicurie Cell equipment tray, and a given volume of acid is added to leach the uranium. After leaching, the glass residue is buried in the same bucket. This system of handling eliminates the need for transferring the glass from one container to another and decreases considerably the chances of excessive cell contamination due to dust. No changes have been found necessary in the leaching, transfer, and settling techniques previously reported [2].

Figure 1 shows the equipment system used during the last campaign. This arrangement is quite adequate and no further changes are likely to be made for this continuing leaching program.

Fig. 1 Equipment flowsheet for recovery of uranium from EBR-II glass mold tubes.

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1.22 Dissolution of Plastic-Coated Fuel Elements

(M. E. Jacobson; Chemistry Section)

A total of about 2.4 kg of fully enriched uranium was recovered from aluminum fuel elements and plates which had been coated with Lithcote plastic for a heat transfer experiment. Each aluminum element, containing 195 g of uranium, had about 100 g of plastic on its surface. In order to prevent the degraded but undissolved plastic from reaching the vessels in the ICPP, the dissolution was done in a 55-gallon dissolver temporarily set up in the Multi-curie Cell (Figure 2). A conventional mercury-catalysed nitric acid dissolution

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Fig. 2 Equipment flowsheet for recovery of uranium from plastic coated fuel elements.

reagent was used. The plastic was retained on the dissolver basket and on a filter in the outlet from the dissolver. Each element yielded about 70 cubic inches of expanded, degraded plastic.

2. SUPPORT STUDIES FOR CURRENT ICPP FUEL RECOVERY PROCESSES

2.1 Co-Processing of Aluminum and Zirconium Fuels

Co-processing of aluminum and zirconium fuels is planned for the next ICPP processing campaign. Previously, aluminum and zirconium fuels have been processed separately: aluminum-uranium alloyed fuel has been dissolved in nitric acid and the uranium extracted from the dissolver product in a TBP extraction system^[3]; zirconium-uranium alloyed fuel has been dissolved in hydrofluoric

acid complexed with an aluminum nitrate-nitric acid solution, and the uranium extracted in a TBP extraction system^[4]. With the co-processing system, the dissolver product from the aluminum fuel process will be used as the aluminum nitrate-nitric acid complexing solution for the zirconium fuel process; the combined solutions will then be fed to the TBP extraction system. Significant savings in chemical costs, waste generation and calcination costs, and fuel processing costs will be realized.

2.11 Progress Description and Economics of Co-Processing (G. F. Offutt; Process Engineering Section)

Process Description. A flowsheet for co-processing of aluminum and zirconium alloyed fuels at ICPP is shown in Figure 3. The aluminum fuel dissolver will be operated continuously at an average production rate of 180 liters per hour of dissolver product. At the same time, the zirconium fuel dissolver will be operated semi-continuously at an average production rate of 315 liters per hour of dissolver product (on a 24-hour basis). Aluminum fuel dissolver product will be collected in surge tanks where uranium input measurements will be made prior to adding chromic acid for oxidizing U(IV) to U(VI). Then, zirconium dissolver product will be combined with the aluminum dissolver product as the two solutions flow into the complexing tank. There, three things are accomplished: (a) fluoride ions are tied up (complexed) by aluminum to prevent corrosion of stainless steel equipment by the fluoride; (b) uranium is oxidized to the extractable U(VI) valence state; and (c) nitrate ion is provided to promote solvent extraction of $\text{UO}_2(\text{NO}_3)_2$ from the aqueous phase. The combined dissolver product will flow from the complexing tank to uranium input measurement tanks^[a] and then to the first cycle extraction system, which will use five percent TBP as solvent. The product from first cycle extraction will be further purified in two extraction cycles using Hexone as a solvent. Finally, the product will be converted to solid UO_3 in a fluid bed denitrator and packaged for shipment.

Economics of Co-Processing. Co-processing aluminum and zirconium fuels is economically attractive; the small capital investment for modifications and additions -- approximately \$25,000 -- will be paid off the first year of operation. An immediate savings of \$5,300 per 100 kg of U-235 processed is expected (Table I) with later savings of \$21,000 per 100 kg of U-235 (Table II). Savings will occur in three areas: (a) chemical costs, (b) operating costs, and (c) waste handling costs.

Chemical costs will be reduced because aluminum nitrate and nitric acid for complexing zirconium fuel dissolver product will not be purchased but will be produced by the dissolution of aluminum fuel with nitric acid. Operating costs will be reduced slightly because the processing rate through dissolution and first cycle extraction for co-processing is greater than the average rate when aluminum and zirconium fuels are processed separately. Waste handling costs will be reduced because less waste will be produced. The waste savings will not be realized until later years when the liquid wastes are converted to solids.

^[a] Accountability for uranium in the co-processing scheme will be determined as follows: (a) the aluminum fuel dissolver product will be sampled for uranium content prior to blending with zirconium fuel dissolver product; (b) after the two solutions are blended, the blend will again be sampled for uranium content; the uranium content of zirconium fuel will be calculated by the difference.

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	I BR	I AF	I AX	I AR	I AP	I BS	I BP	I CX	I CR	I CP	I DX	I DR	I DP	FIRST CYCLE PRODUCT
Flow, l/batch	7115	1400	7310 ^(c)																	
Flow, l/hr			422 ^(d)	242 ^(e,f)	500	30	530	450	530	450	60	450	250	450	250	10	250	5.2		
Zr, M			0.90		0.57		0.54		0.54											
F, M	6.60		6.42		4.04		3.81		3.82											
Al, M				1.60	0.56	1.50	0.62		0.62		0.75									
H, M (a)	6.60		2.80	1.50	2.41	1.08	2.33		2.24	0.07		0.001	0.005	0	0.007		0.007	0.40		
NO ₃ , M				6.30	2.30	5.58	2.48		2.40	0.09	2.25	0.017	0.005	0	0.035		0.035	2.11		
Sn, g/l			1.27		0.80		0.76		0.76											
Cr, g/l				3.15	1.15		1.08		1.08											
B, g/l	4.1	5.0	4.1	0.0	2.6		2.5		2.5											
Hg, M				0.007	0.003		0.003		0.003											
U, g/l no .U.			1.41	3.20	2.06	0.60	1.98		2x10 ⁻³	2.33		2.29		1x10 ⁻⁴	2.29		4.12	200		
U, kg/batch no B ²³⁵ U.	10.3 ^(b)																			
Zr, kg/batch	600																			
Sn, kg/batch	9.3																			
TBP, %								5		5		5		5						
Diluent								Amsco		Amsco		Amsco		Amsco						

a: Neglects contribution from H₃BO₃.

b: Based on PWR Core 1, Seed 1 with no burn-up.

c: Includes 195 liters of charge water heel.

d: Actual flow rate after dissolver fills.

e: Includes jet dilution of 5 l/hr.

f: Actual flow rate during dissolution; based on ETR fuel with no burn-up.

Zr Dissolver Cycle Time: 17 1/2 hrs. for dissolution and 6 hrs. down time for recharging; total cycle time = 23 1/2 hrs.

FORM INC-935 (2-68)

Fig. 3 Flowsheet for co-processing of aluminum and zirconium fuels.

2.12 Co-Processing Chemistry
(W. T. Jordan; Chemistry
Section)

As a result of the co-processing of zirconium and aluminum clad fuels, the chemical composition of the complexed zirconium fuel dissolver product will be altered by the addition of silicon and mercury from the aluminum fuel dissolution. Accordingly, a study was made to determine what effect this perturbation might have on the process chemistry.

Aluminum and zirconium dissolver products were simulated by carrying out laboratory-scale dissolutions of the respective uranium alloys. Upon combining the two solutions in flowsheet proportions, after adding chromium trioxide to the aluminum dissolver product to assure complete oxidation of the uranium, the particulate silicon went into solution. After a few minutes standing, a red crystalline solid began to precipitate from the solution. This compound was found to contain mercury and chromium and was identified by X-ray crystallography as mercurous chromate (Hg_2CrO_4).

In the co-processing flowsheet, the recommended concentration of chromium in the dissolver product from dissolution of aluminum (the adjustment reagent) is 0.043M. Mercury can range from 0.002M to 0.05M as required to maintain a satisfactory dissolution rate, 0.007M being the standard operating concentration. At a concentration of 0.002M mercury, there is insufficient mercurous ion for precipitation to occur. At 0.007M mercury, moderate precipitation occurs only after the zirconium solution is added to the chromium-bearing aluminum solution, indicating reduction of mercuric ion in the combining process. At a concentration of 0.04M mercury, sufficient mercurous ion can be present to precipitate the chromate in the aluminum solution.

Since a small amount of solid mercurous chromate and an equivalent loss of oxidizing reagent in the complexed dissolver product might have to be tolerated, it has been recommended that enough additional CrO_3 be added to compensate for that removed from solution, assuming complete precipitation of mercury as mercurous chromate. In this way, adequate chromium for complete oxidation

TABLE I

IMMEDIATE SAVINGS FROM
CO-PROCESSING ALUMINUM AND
ZIRCONIUM FUELS

(100 kg U-235)

<u>Item</u>	<u>Dollars Saved</u>
Chemicals	4,100
Operating Time	1,200 ^[a]
	<u>5,300</u>

[a]

Incremental difference in costs that result from operating the headend facilities fewer days and the Waste Calcining Facility a greater number of days each year.

TABLE II

LATER SAVINGS FROM CO-PROCESSING
ALUMINUM AND ZIRCONIUM FUELS

(100 kg U-235)

<u>Item</u>	<u>Dollars Saved</u>
Reduced Waste Calcining Facility Operation	12,000
Reduced Storage Volume Required for Solid Waste	<u>9,000</u>
	<u>21,000</u>

of uranium to the more soluble and more extractable hexavalent state is ensured. The small quantity of solids precipitated is not expected to be deleterious to extraction column operation.

2.2 Proposed Processing of EBR-II Skull Oxide (M. W. Wilding; Chemistry Section)

The pyrochemical reprocessing of the EBR-II fuel at the EBR-II Fuel Cycle Facility yields an oxidized melt residue unsuitable for recycle in the current pyrochemical process. Like the Vycor glass molds (Section I-1.21), the uranium in this skull oxide occurs in such a concentration and chemical form that recovery by an aqueous process at the ICPP appears to be desirable.

The nominal composition of this material is given in Table III, and the chemical development work necessary for establishing the process is reported in the following paragraphs. Because of uncertainty as to how the material would be charged to the dissolver at ICPP, two separate processing schemes were investigated: the first assumed codissolution of the uranium and the aluminum shipping container; the second assumed that the uranium could be removed from the shipping container before dissolution.

2.21 Codissolution of Skull Oxide and Container -- Uranium Extraction with TBP

Dissolution. It is anticipated that the skull oxide will be shipped to the Idaho Chemical Processing Plant in 6061-T-1 aluminum cans for processing. The anticipated weight ratio of aluminum can to skull oxide is expected to be in the range of 1.3 to 1.6.

TABLE III
APPROXIMATE METAL COMPOSITION
OF EBR-II SKULL OXIDE

<u>Element</u>	<u>Weight Percent</u>
U	75 - 85
Mo	1.3 - 1.9
Ru	0.6 - 1.2
Rh	0.05 - 0.23
Pd	0.03
Zr	0.08 - 2.5
Nb	0.015 - 0.03

Uranium in the skull oxide was approximately 99 percent dissolved in eight hours using a dissolvent containing 1.2M $\text{Al}(\text{NO}_3)_3$, 7.5M HNO_3 , and 0.007M $\text{Hg}(\text{NO}_3)_2$ at 105°C. The composition of the dissolver product resulting from the nitric acid dissolution is shown in Table IV. The aluminum nitrate in the dissolvent represented that to be derived from the dissolution of the shipping container.

The rate of dissolution of uranium in the nitric acid system is shown in Table V.

Approximately 85 to 90 percent of the total skull oxide dissolved. Some solids were in suspension at the end of the dissolution; however, these solids were nearly all dissolved (97 percent) in 4.0M HNO_3 -0.7M HF in five hours at 105°C. The particle size distribution of the solids remaining from the nitric acid dissolution was estimated microscopically with results shown in Table VI.

TABLE IV

COMPOSITION OF DISSOLVER PRODUCT FROM CANNED SKULL OXIDE

Dissolvent: 7.5M HNO_3 , 1.2M $\text{Al}(\text{NO}_3)_3$, 0.007M Hg

Solids Charge: 24 g skull oxide/liter

<u>U(g/l)</u>	<u>H(M)</u>	<u>HNO_3(M)</u>	<u>Al^{+3}(g/l)</u>	<u>% Dissolved</u>
18.06	2.65	6.04	31.7	98.8

TABLE V

RATE OF DISSOLUTION OF URANIUM IN 7.5M HNO_3 ,
1.2M $\text{Al}(\text{NO}_3)_3$, 0.007M Hg at 105°C

<u>Time (hrs)</u>	<u>Uranium Dissolved (g/l)</u>	<u>% Dissolved</u>
0.5	20.4	95.6
1.0	20.7	96.7
2.0	20.8	97.2
3.5	21.0	98.6
24.0	21.4	99.4

TABLE VI

PARTICLE SIZE DISTRIBUTION
OF UNDISSOLVED SOLIDS

<u>Diameter (microns)</u>	<u>Weight Percent</u>
< 10	2
10- 25	40
25- 50	50
50-100	8
> 100	< 1

Extraction and Stripping of Uranium. A dispersion coalescence test was run on the nitric acid-uranium-aluminum dissolver product solution containing undissolved solids. Complete coalescence occurred in 1.5 minutes, a satisfactory coalescence performance; however, there was a slight "hold up" of organic in the aqueous phase beneath the plates. Three extraction stages were run using five percent TBP and an adjusted dissolver product solution that contained 1.6M Al^{+3} , $\approx 1.3\text{M}$ H^{+} , and ≈ 21 g/l uranium; the ratio of organic-to-aqueous was 1:1. Uranium distribution coefficients for the extraction and stripping systems are shown in Table VII.

2.22 Dissolution of Skull Oxide Alone -- Uranium Extraction with Hexone. Since the possibility exists that the skull oxide could be removed physically from the shipping container without the necessity of dissolving the latter, the dissolution of the oxide alone in nitric acid was studied. The resulting dissolver solution had a uranium concentration high enough for extraction with Hexone in a typical ICPP flowsheet.

Dissolution of Uranium in Skull Oxide. Greater than 99 percent of the uranium in the skull oxide was dissolved in two hours using one liter of 11.5M HNO_3 per 465 g of skull oxide. In this system, one mole of uranium is dissolved in 2.5 moles of nitric acid. Increasing the dissolution time to 20 hours did not noticeably increase the amount of uranium dissolved. Table VIII shows the composition of the dissolver product after 20 hours at 90 to 95°C.

Extraction and Stripping of Uranium. The dissolver product was adjusted to the feed composition for a

TABLE VII

URANIUM EXTRACTION (WITH TBP)
AND STRIPPING OF SKULL OXIDE
DISSOLVER PRODUCT

<u>Extraction with 5% TBP</u>		
	<u>Uranium in Organic Phase at Equilibrium</u>	<u>E o/a</u>
	<u>g/l</u>	
Stage 1	9.1	42
Stage 2	0.44	130
Stage 3	0.006	19
<u>Stripping with 0.02M HNO_3</u>		
	<u>Uranium in Aqueous Phase at Equilibrium</u>	<u>E a/o</u>
	<u>g/l</u>	
Stage 1	41	20
Stage 2	1.5	49

TABLE VIII

COMPOSITION OF DISSOLVER PRODUCT FROM SKULL OXIDE ALONE

<u>U (g/l)</u>	<u>H^{+} (M)</u>	<u>Skull Oxide Undissolved (%)</u>	<u>Uranium in Undissolved Solids (%)</u>	<u>Uranium Dissolved (%)</u>
360	7.74	7.2	6	99.5

typical Hexone flowsheet prior to extraction and dispersion-coalescence tests. A standard dispersion-coalescence test was run with the first cycle feed solution, appropriate scrub, and Hexone. Complete coalescence occurred in less than 1.5 minutes, a satisfactory performance. It was observed that extra vigorous agitation caused a stable emulsion to form, making coalescence very slow. The amount of interfacial solid was very minor and was considered to be insignificant in column operation.

Palladium, derived from the fissium and probably present as a colloidal hydroxide, was present in the solids and appeared to be a component of the surfactant. Ferrous sulfamate, always used in the scrub solution in at least one cycle to reduce plutonium, appeared to inhibit surfactancy. Since the potentials for the $\text{Pu}^{+3} = \text{Pu}^{+4} + e$ and $\text{Pd} = \text{Pd}^{+2} + e$ couples are essentially identical, the palladium is apparently reduced to the metal by the ferrous iron and eliminated as a surfactant.

Uranium distribution coefficients for the extraction and stripping were determined with the results shown in Table IX. Both extraction and stripping were satisfactory.

2.23 Conclusions. The laboratory results indicate that the uranium can be dissolved from the skull oxide in boiling nitric acid. The solids that remain after dissolution in nitric acid can be partially dissolved in 0.7M HF - 4.0M HNO_3 . The remaining solid must be removed by flushing the dissolver with water. The distribution coefficients for uranium extraction appear to be satisfactory in either TBP or Hexone, and any fine precipitate that carries over from the dissolver to the extraction process does not seem to impair the efficiency of the extraction-stripping process.

2.3 Effect of Silicon Upon Reprocessing of Aluminum-Uranium-Silicon Alloys (B. E. Paige; Chemistry Section)

Aluminum-uranium fuel elements used extensively in high thermal flux reactors might be manufactured by more economical methods if the quantity of silicon allowed in the fuels could be substantially increased. Silicon in the fuel core alloy suppresses the formation of UAl_4 and stabilizes UAl_3 , thus improving the fabrication characteristics of the alloy. Since silicon has created problems during the reprocessing of this type of fuel, various core and cladding alloys were examined for the effect of silicon content upon dissolution rate, emulsion formation in the liquid-liquid extraction of uranium, and solids production during dissolution. The dissolution study was reported in the Annual

TABLE IX

URANIUM EXTRACTION (WITH HEXONE) AND STRIPPING OF SKULL OXIDE DISSOLVER PRODUCT

<u>Extraction with Hexone</u>		
	<u>Uranium in Organic Phase at Equilibrium</u>	<u>E o/a</u>
	<u>g/l</u>	
Stage 1	25.2	20
Stage 2	3.5	32
Stage 3	0.33	50
<u>Stripping with 0.04M HNO_3</u>		
	<u>Uranium in Aqueous Phase at Equilibrium</u>	<u>E a/o</u>
	<u>g/l</u>	
Stage 1	35.0	27
Stage 2	1.3	440

Report for Fiscal 1967^[2]; the work in the other two areas was completed during the current year. A complete description of the work and the results are presented in a topical report, IN-1194, The Effect of Silicon Upon Fabrication and Reprocessing of Aluminum Alloy Reactor Fuels,^[5] which also includes the metallurgical studies performed by the Metallurgical Development Section of the Reactor Engineering Branch of Idaho Nuclear Corporation. The principal findings are summarized here.

Summary of Reported Results^[5]. This study was confined to aluminum-silicon casting and cladding alloys and to alloys which may be used in fuel-plate cores for the Engineering Test Reactor. The alloys studied contained 0, 22, and 32 weightpercent uranium, a range of silicon contents from 0 to 11 percent, and the remainder aluminum (99.9 percent pure). The dissolution rates in nitric acid were found to be related to the metallurgical compositions of the alloys which, in turn, are related to the silicon contents of the alloys. This effect alone, however, was not sufficient to interfere with the reprocessing of the fuels. The silicon present in the alloy as the intermetallic, $U(Al, Si)_3$, dissolves. On the other hand, the silicon in these alloys in excess of one atom per atom of uranium is not present as the intermetallic and does not dissolve; this creates a bulk of solids which may cause handling difficulty during reprocessing. Surfactancy was found to be due to either polysilicic acid or colloidal silica of less than 35 m μ diameter which formed from the dissolved silica. If sufficient polymerization and agglomeration occur to produce larger particles, surfactancy will not be a problem in dissolver solutions. If surfactancy is produced during the dissolution of aluminum-uranium alloys, the level of silicon in the alloy does not appear to be important, because even a small amount of silicon will produce solutions which require treatment, such as addition of gelatin, to improve coalescence behavior.

2.4 Corrosion Observations for the Zirconium Process Off-Gas System (T. L. Hoffman; Chemistry Section)

As various components of the Chemical Processing Plant become accessible because of modifications or repairs in the plant, corrosion inspections are made. During the past year it was possible to inspect several components of the dissolver off-gas system used with the hydrofluoric acid dissolution process for zirconium fuel.

Valve in Off-Gas Service. A service inspection was made on a Type 304L stainless steel valve from the off-gas condenser for the zirconium fuel dissolver. When open, this valve permits the dissolver vapors to bypass the condenser. The valve was in service for 3,000 hours at about 50°C. Results of this inspection indicate that the stem and plug are resistant to the dissolver vapors. The one-inch, Schedule 40, Monel-400 and Type 304L stainless steel piping associated with this valve were also resistant.

Pipe in Off-Gas Condensate Service. A section of four-inch, Schedule 40, Monel-400 piping that served as the condensate return from the off-gas condenser for the zirconium fuel dissolver was inspected for corrosion damage. Service time for this piping was also 3,000 hours, but the temperature was about 65°C. Although several 5- to 10-mil-deep pits were observed, the Monel-400 piping was judged to be sufficiently resistant to permit continued use in condensate service in the dissolver vapors.

Pipe in Off-Gas Service. A welded spool-piece [six-inch, Schedule 40, Type 347 (Cb, Ta) stainless steel] from the piping near the off-gas blower for the zirconium dissolver was corrosion evaluated. This piping was installed in July 1956 and had been used intermittently at room temperature in mixed nitric-hydrofluoric acid vapor service during the recovery of uranium from zirconium fuels. The plant vessels operated for 5,885 hours, of which 3,315 hours were for fuel dissolution, 2,327 hours for decontamination of the vessels, and 243 hours for heel clean-out.

The spool-piece was sawed in half and the inside surfaces were optically scanned for evidences of corrosive attack. Results from this study show that the general corrosion damage on the spool-piece was nil. Evidences of localized attack in the weld area were sought, but not found.

During the past year, a comprehensive report of the corrosion performance of other portions of the system was issued^[6]; this material was summarized in the previous annual report, IN-1087^[2].

2.5 Corrosion of Type 304L Stainless Steel in Fluoride-Bearing Plant Decontaminating Solutions

(T. L. Hoffman; Chemistry Section)

Decontamination of the Waste Calcining Facility (WCF) following processing of fluoride-containing zirconium waste raffinates generates radioactive solutions containing appreciable concentrations of fluorides. These radioactive solutions are transferred to the Process Equipment Waste (PEW) Evaporator for volume reduction and they are then reprocessed in the WCF.

Experiments were conducted with synthetic fluoride-bearing decontaminating solutions of the type produced during decontamination of the WCF to determine the corrosion rates that may be expected on the tube bundles of the plant evaporators built of Type 304L stainless steel. The corrosion service-test piece was a welded one-inch Schedule 40 pipe used as the heat exchanger surface in a single-tube thermosyphon evaporator. The evaporator was operated at 30 psig steam pressure, and the exposure time on the service piece was 168 hours for each test period. The decontaminating solution contained 1M hydrogen ion, 1M nitrate, and 0.01M aluminum with four levels of fluoride and two levels of zirconium. Results of these tests are listed in Table X.

The maximum observed corrosion rate on the pipe was 4.0 mils per month (mpm), which was accompanied by 10- to 15-mil-deep pits in the pipe welds. This rate was reduced to 1.1 mpm in the same type of solution if the zirconium concentration was increased to 0.026M.

In this decontaminating solution there is a linear relationship between the corrosion rate and the excess fluoride as defined by $(F - [2Al + 4Zr])$; see Figure 4. This expression is based on the stability of the fluoride complexes of aluminum and zirconium. With total fluoride concentrations below 0.025M, sufficient zirconium and/or aluminum should be present to maintain the excess fluoride below 0.07M. Under these conditions, corrosion rates of 1.0 mpm or less are anticipated for the tube bundles of the PEW evaporator.

TABLE X

CORROSION RATES OF TYPE 304L STAINLESS STEEL IN
WCF DECONTAMINATING SOLUTIONS^[a] WITH VARIOUS CONCENTRATIONS
OF FLUORIDE AND ZIRCONIUM

Fluoride (M)	Zirconium (M)	Corrosion Rate (mils per month)	Remarks
0.21	0.026	1.1	---
0.05	0.003	0.3	---
0.10	0.003	1.1	---
0.27	0.003	4.0	Pits in Welds

[a] Base Solution: 1.0M H^+ , 1.0M NO_3^- , 0.01M Al^{+++}

2.6 Clarification of Solvent Extraction Feed

(R. D. Modrow; Process Engineering Section

P. I. Nelson; Development Engineering Section)

Aluminum and complexed zirconium dissolver products are processed through the same first-cycle extraction equipment at the ICPP. In the past, undissolved solids in these dissolver products have caused line blockages and contributed to interface crud formation. In the future, EBR-II fuel, as well as aluminum and zirconium type fuels, will contribute to the solids problem; dissolution of the EBR-II fuel (Section I-3.1) results in two to four weight percent of the fuel remaining as undissolved solids (stainless steel, silicon, and fission particles). In addition, a number of other fuels are being considered for reprocessing at ICPP; the dissolution of many of these fuels (by nature of their composition and burnup) will generate considerable quantities of solids that must be separated from the feed streams before they are introduced to the solvent extraction system.

Fig. 4 Corrosion of Type 304L stainless steel in decontaminating solutions.

Feed Clarification Process and Equipment Description. A common feed clarification system is being installed to remove solids from dissolver solutions before they are fed into the first-cycle extraction system. A solid-bowl centrifuge, similar to those used at Savannah River and Hanford, will be used to remove the solids. The separated solids will be washed free of uranium, slurried, and transferred to waste storage via the process equipment waste system. A block diagram of the headend system is shown in Figure 5.

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Fig. 5 Block diagram of dissolution and feed clarification systems.

A solid-bowl centrifuge was chosen to remove solids from dissolver solutions because it has been proved in highly radioactive service; it is abrasion resistant and requires little maintenance. The bowl is 26 inches in diameter by 16 inches high and is separated into three compartments by horizontal baffles. A maximum of one and one-half cubic feet of solids can be collected in the bowl before feed must be diverted while the solids are processed. The solution remaining in the bowl will be removed by skimmers as the bowl rotates at reduced speed. Perforations in the two bottom baffles permit solution to flow upward through the contained solids to the upper section. Hydraulically operated skimmers dip into the rotating solution in the upper section, and centrifugal velocity forces solutions up through the pipe into an outer bowl housing. From the bowl housing it runs to a sump where it is airlifted to a disengaging pot; the clarified solution then flows to input measurement tanks.

The solids remaining in the bowl are washed several times with high pressure sprays from two headers. One header is for the two upper compartments, and the other is for the lower compartment. These sprays will cut the solids from the bowl wall. The solids will then be slurried by alternately rotating and stopping the bowl, and they will be dewatered by recentrifuging and skimming. After several wash cycles, the solids will be slurried again and jetted via a fixed dip tube in the centrifuge to the process equipment waste system for disposal to waste storage tanks.

Slurry Transfer Studies. Since slurries from the centrifuge have not been handled at ICPP before, it was desirable to mock up the planned slurry transfer line and observe the behavior of a concentrated slurry during its removal from a centrifuge bowl. The mock-up, shown schematically in Figure 6, was fabricated and tested at the Chemical Engineering Laboratory. A stainless steel tank (with no provision for rotation) was used to simulate the centrifuge bowl. A mechanical mixer provided agitation to slurry the solids.

Sand (-100 +150 mesh) was used for most of the testing at concentrations varying from 30 to 70 volume percent. A jet syphon, motivated with steam at

Fig. 6 Mock-up of slurry jet transfer line for feed clarification system.

80 to 100 psig, emptied the simulated bowl at a rate near 15 gpm. A slurry of 80 volume percent alumina fines from calcination studies was also used. Even with this high solids content, the slurry did not show any signs of settling out in the long transfer line. No major problems were encountered in jetting either slurry.

When the sand slurry was not agitated, it settled out rapidly. Thus, a large portion of the sand did not reach the jet suction unless the wall of the vessel was sprayed to direct the solids to the suction. In one test, two cubic feet of sand were jetted (after the sand had settled) by spraying water into the simulated bowl. This jetting took 15 minutes to remove about 90 percent of the sand from the bowl. Therefore, removal of the solids from the bowl is feasible if spraying is continued while the bowl is being rotated.

Twenty runs, each involving the transfer of about 30 gallons of a 50 percent sand slurry, were made. More solids were used in each run than are expected to be handled daily in the plant centrifuge; these twenty runs contained at least 20 percent of the solids that would be jetted during an average year in the plant.

The globe valve and steam jet used in the system were disassembled and inspected. Very small amounts of solids were deposited in the valve body with no indication of a buildup. No visible indication of erosion was found in either the valve or jet. Also, no plugging problems were experienced with the one-inch globe valve.

Results of twenty runs made in the mock-up indicate that erosion, solids buildup, and plugging should not constitute problems in the plant slurry jet transfer line. However, it should be emphasized that the solids used in these tests may not be similar to those which will be encountered in actual plant service.

2.7 Instrumentation Studies -- Air Pulser Amplitude and Liquid Level Measuring System

(L. A. Jobe; Process Engineering Section

P. E. LaMont; Development Engineering Section)

Purpose and Scope of Program. An overall program to develop and improve instrumentation for measurement and control of ICPP processes includes the following:

- (1) Developing instrumentation to measure pulse energy input to air-pulsed extraction columns (pulse energy is a function of pulse amplitude and frequency)
- (2) Measurement of the lowest level of liquid during the air pulsing in order to prevent serious column upsets from pulser air reaching the bottom of the extraction column
- (3) Measurement of liquid levels in storage and feed tanks, evaporators, and cryogenic units.

The first priority was given to the development of instrumentation for the direct measurement of pulse amplitude for which there is no instrument currently available. Simultaneous measurement of the lowest level of liquid in the pulse leg was also desirable. Problems with plugging of dip-tube bubbler level probes and the need to measure rapid level transients from pulsing required development of such instrumentation. Other potential applications of new detectors would include liquid level sensing in cold feed tanks, dissolvers, hot makeup and feed tanks, waste storage tanks, and interface sensing of two liquid phases in extraction columns and separator tanks.

An evaluation of possible methods showed that capacitance and ultrasonic methods appeared most promising; other methods considered were conductance, warm wire resistance, differential pressure, and time domain reflectometry methods. It was decided to proceed with a study of both capacitance and ultrasonic methods until a clear-cut superiority of one over the other was determined. The assistance of the Instrument Development Branch of Phillips Petroleum Co. AED in the design and construction of prototype capacitance and ultrasonic measuring systems was secured.

Pilot plant testing of the measuring systems was carried out at the Chemical Engineering Laboratory. Results to date on the development and testing of the capacitance and of the ultrasonic measuring systems are reported here.

Description of the Test Apparatus. The apparatus used to test the capacitance probe and ultrasonic measuring systems was built to simulate the liquid motion in a two-inch pulse leg of an ICPP plant pulse column. A 20-foot long, vertical, two-inch, Schedule 40 stainless steel pipe was used as the pulse leg, and a long column of two-inch glass pipe was used to visually measure the pulse amplitude and mean level in the pulse leg as shown in Figure 7. A pressure reservoir and can-operated air pulser valves provided an oscillatory force to the liquid. Air pressures ranged up to 15 psig, and frequencies were varied from 30 to 80 cpm (cycles per minute). Pulse amplitudes greater than one foot at frequencies of 60 cpm could not be obtained with a long column of liquid backed up in the glass pipe; therefore, a pressurized liquid reservoir was connected near the bottom of the system in place of the glass pipe for testing the ultrasonic

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Fig. 7 Experimental equipment for testing capacitance and ultrasonic pulse amplitude and level probes.

transducer. This modification reduced the pulsed mass of liquid in the system and resulted in larger amplitudes.

2.71 The Capacitance Probe Measuring System

Description of the System. The capacitance probe tested was a 10-foot long, one-inch OD, thin wall stainless steel tube inserted in and insulated from the two-inch, Schedule 40 pipe, pulse leg. Because the electrical capacitance varied directly with the log ratio of diameters of the inside tube and outside pipe, an inner probe diameter of one-inch was needed to give readily detectable changes in level. A lead connected the probe to a remotely situated capacitance measuring bridge. A block diagram of the capacitance measuring system is given in Figure 8. The bridge was driven by a 20 kc oscillator, and the demodulated output signal was fed to an analog circuit giving an average pulse amplitude

over several pulse cycles. A servomechanism slowly balanced the bridge, and the balance point was used to indicate the mean level. The instrument was statically calibrated to read zero and full scale for empty and full pipes, respectively; the read-out was linear between these two points.

Fig. 8 Block diagram for capacitance-type liquid level measuring system.

Experimental Results

(1) Amplitude and Mean Level Response. Figures 9 and 10 compare instrument output to visually measured amplitudes and mean levels in the pulse leg at various frequencies. The recorded amplitude was generally higher than the visually observed amplitude. Since the actual mean level shifted slightly from cycle to cycle because of small variations in reservoir pressure, the distance of oscillation was greater over several cycles than for a single cycle, and the long time constant on the amplitude circuit "remembered" the extreme positions. The mean level points were slightly scattered and were probably due to observational errors as well as the constantly changing supply pressures.

Frequency response of the probe should not be a problem even though available amplitudes studied were less than those found in the plant at 60 cpm. The liquid level must remain within the region of the probe throughout the entire oscillation in order for the instrument output to correctly represent the amplitude and mean level.

(2) Effect of Liquid Dielectric. Static level calibrations were run using three Amsco solutions containing 0, 5, and 10 percent TBP and one containing 10 percent TBP - 0.1M HNO_3 . The results are shown in Figure 11. The effect of adding polar molecules was to increase the dielectric constant of the fluid, and the probe read higher for a given level of fluid. The error was approximately four percent high for each percent of TBP in the Amsco.

(3) Memory Effect of Insulators and Loss of Insulating Properties. The first insulators used to separate the two concentric plates of the probe were of acrylic plastic. The applied voltage apparently changed the dielectric properties of the insulator, resulting in drifting and changing calibration. The readings depended upon the history of applied voltage and output signals, thus indicating memory effects. Substitution of alumina insulators solved this problem.

Fig. 9 Capacitance probe amplitude measurement.

During abnormal conditions, such as may occur upon power failure, the aqueous phase may reach the capacitance probe in the pulse leg and short out the probe. Tests indicated that the alumina insulators were wet by aqueous solutions and that flushing with organic did not remove the aqueous solution sufficiently to restore the necessary resistance of the insulator. Kynar and Marlex (plastics with high radiation resistance) insulators were not wetted by the aqueous solutions; memory effect tests are to be made on them.

2.72 The Ultrasonic Measuring System

Description of the System. The second most promising measuring system investigated used a commercial ultrasonic transducer, signal generator, and receiver, and a group of laboratory electronic components to give more flexibility and sensitivity in signal receiving and conditioning. Figure 12 is a block diagram of the ultrasonic measuring system used.

Fig. 10 Capacitance probe mean level measurement.

Commercial ultrasonic level sensors are available as either point level or as continuous level sensors. Only the continuous level detector systems could be considered for our applications. Commercial continuous level measuring systems did not provide sufficient resolution for accurate level measurement. In order to meet our requirements (one-inch accuracy in 24 inches at a distance that may vary from five to 25 feet from the transducer), electronic signal generation and signal conditioning equipment was designed with a unique characteristic which allows several echo signals to become lost without disrupting the measuring system. The system was designed to transmit an ultrasonic pulse from the top of the pulser leg through a stainless steel diaphragm barrier, down through air in the pulser leg to the moving liquid surface, and to receive the echo signal. The time of flight of a pulse is a measure of the distance between the liquid surface and the transducer.

Experimental Results. Experimental results are reported in two major areas: irradiation tests of ultrasonic transducers, and the design and testing of the ultrasonic measuring system in an experimental pulse leg assembly at the Chemical Engineering Laboratory.

Fig. 11 Effect of TBP concentration on calibration curves.

(1) Radiation Testing of Transducers. An ultrasonic transducer (sensor) located inside the hot cell where the extraction columns are installed should have an operational life of at least two years. Under continuous operating conditions, the radiation dosage that the transducer should withstand would be approximately 10^8 R at a dose rate of approximately 5×10^3 R/hr.

The radiation resistance of ultrasonic transducers was determined in the Gamma Facility at MTR. The first transducer failed in less than two hours when subjected to a dose rate of 5×10^6 R/hr; its temperature, however, had exceeded the maximum recommended temperature of 140°F by approximately 20°F . Investigation of the transducer parts showed that heat and radiation had apparently caused a failure of the bonding adhesives and potting compounds. A second transducer, kept below 80°F by cooling air, lasted six hours at the same 5×10^6 R/hr before the signal failed. This was again due to the separation of the polyurethane cover from the aluminum disc of the transducer element assembly

Fig. 12 Block diagram of ultrasonic continuous level monitor.

upon gas formation. Various bonding agents were tested under irradiation conditions and the best one was used to rebuild the first transducer after imbedding thermocouples to measure induced temperatures. The polyurethane cover was recemented to the aluminum block of the second transducer and the entire unit was encased in a housing containing a strain gage pressure transducer and gas sampler. It was subjected to gamma radiation dosages from 10^3 to 10^6 R/hr, at which level gas formation was noted. The temperature was limited to 109°F . Approximately 13 ml of gas were collected at about 2 atmospheric pressure and analyzed at 44 percent H_2 , 46 percent N_2 , 4 percent CO , and 5 percent CO_2 . From these tests it was concluded that the transducers could be operated in a field of 10^5 R/hr, especially if the temperature was limited to 80°F .

A third transducer was then irradiated in the Gamma Facility starting with one week's exposure at 10^4 R/hr and followed by seven weeks at 10^5 R/hr. At the end of this time the total dosage was slightly over 10^8 R and the transducer was still operating satisfactorily. Therefore the test was continued at higher temperature levels with one week each at 80, 90, and 100°F , two weeks at 110°F , four weeks at 120°F , and finally two weeks at 125°F . The cumulative dosage was 2.8×10^8 R at that time with the transducer continuing to operate satisfactorily throughout the test. The transducer, upon removal, did appear to have undergone a slight physical distortion. It thus appears that this transducer is capable of functioning under expected radiation levels for over five years, a very acceptable operational period.

(2) Experimental Tests in the Pulser System. A 40 kHz transducer was canned in a stainless steel housing with a 30-mil stainless steel diaphragm for the ultrasonic signal transmission surface. The assembly was installed on top of the pulse leg in the test apparatus. A level calibration was made under static conditions; the instrument output was highly linear. The measuring system achieved a resolution approaching 0.05 percent, more than an order of magnitude better than commercial units.

Problems arising during the application of this method to the measurement of a rapidly changing liquid surface (such as in the pulse leg) have not been

completely resolved. The axis of the transducer and pulse leg had to be perfectly aligned to avoid partial loss of signal strength; and the inside of the pipe wall had to be smooth, with no connecting fittings, to avoid reflections which the transducer would see as an additional surface. This condition eliminated the possibility of simultaneous capacitance and ultrasonic measurements which would have allowed desirable direct comparisons of the two methods.

Under dynamic conditions the level detection system did not perform satisfactorily because of attenuation of the signal (and also noise) as the density of the air in the pulse leg changed during the exhaust cycle. Installation of a symmetrical air manifold and a variable gain amplifier reduced the noise problems somewhat but did not solve the basic problem which was later found to be due to varying density of the air. Placing a restriction on the air outlet line sustained the signal for a longer time. Substitution of a 20 kHz transducer resulted in the major improvement. Unfortunately, this transducer was actually a cluster of seven units considerably larger than the pulse leg; one of these units was centered over the pipe but the driving power to it was only one-seventh of the total. Therefore, a single 20 kHz transducer element is on order to increase the power available.

2.73 Conclusions. At the present time it appears that, if either the Kynar or Marlex insulators do not show any memory effects, the capacitance method for measuring pulse amplitude and mean levels in air-pulser legs should be essentially ready for application in the ICPP processing plant. One limitation of this method is that aqueous solutions that reach the capacitance probe can short out the probe and therefore give erroneous values during that time. The ultrasonic system would not be subject to this limitation, but appreciable work still remains before this method may be usable for the air pulser application.

The ultrasonic measuring system, as already developed, is applicable for liquid level measurements in storage tanks, including high radiation level feed and hold tanks within processing cells and waste storage tanks of the tank farm. Resolution of 0.05 percent can be expected for these applications where the level does not change rapidly. A modest amount of design work would be required to produce a plant instrument based on the necessary components as determined by the experimental ultrasonic measuring system.

3. ELECTROLYTIC DISSOLUTION PROCESS FOR EBR-II FUEL

In the near future, fuel from the EBR-II reactor will cease to be processed in the EBR-II Fuel Cycle Facility by pyrometallurgical processes. Instead, it will be transferred to the ICPP for processing by aqueous electrochemical methods; this will free the EBR-II Fuel Cycle Facility for other investigative work. Planning and preliminary development work for processing this fuel are now underway at the ICPP.

3.1 Dissolution of EBR-II Fuel and Recovery of the Uranium (M. W. Wilding, M. E. Jacobson; Chemistry Section)

The EBR-II fuel assembly is a bundle of 91 elements supported by stainless steel end grids within a hexagonal stainless steel tube. The elements

are 0.18 inch OD by 13.5 inches long; the fuel is 95 percent uranium metal (52 percent enriched) and 5 percent fissium alloy. Each uranium-fissium alloy rod is clad in 9-mil Type 304 stainless steel; 0.7 g of sodium is contained in the annular space between the uranium metal and the stainless steel cladding. The fissium alloy is initially in the form of stable isotopes in the proportions shown in Table XI.

While no simple aqueous reagent could be expected to dissolve this mixture homogeneously, Type 304 stainless steel is readily soluble in nitric acid in an electrolytic dissolver; the uranium and molybdenum from the fuel alloy would also be expected to dissolve chemically or electrochemically in nitric acid. Electrolytic dissolution in nitric acid using a solution-contact dissolver is thus a very promising method for this fuel.

As an alternate approach, the stainless steel cladding can be mechanically stripped from the elements and the uranium-fissium alloy can be dissolved in a solution of boiling 6M nitric acid. Although both processes are chemically feasible, the ICPP plans to reprocess the EBR-II fuel by electrolytic dissolution and extraction with TBP. Experimental information from both types of dissolution on a laboratory scale is presented in the following sections.

3.11 Chemical Dissolution of EBR-II Fuel in Nitric Acid. Greater than 99 percent of the uranium in EBR-II fuel pins can be recovered by dissolving the fuel in boiling 6M HNO_3 , removing the undissolved solids (approximately two percent of the total fuel pin), and then extracting the uranium with Hexone. The effect of time on the dissolution, using boiling 6M nitric acid, is shown in Figure 13. Insufficient acid was added initially in this test so that the acid strength decreased to about 0.1M and the dissolution reaction slowed. When fresh acid (6M HNO_3) was added to the remaining fuel the dissolution continued, leaving approximately two weight percent of the fuel that did not dissolve. An analysis of the undissolved material indicated that approximately four weight percent of the solid (0.08 percent of the total fuel pin) was uranium. Additional laboratory experiments indicated that approximately 50 percent of this solid dissolved in 0.7M HF - 7M HNO_3 (boiling). This HF- HNO_3 treatment presumably could be used as a heel cleanout.

3.12 Electrolytic Dissolution of EBR-II Fuel Elements. The laboratory dissolver used for the electrolytic dissolution of both irradiated and unirradiated EBR-II fuels is shown in Figure 14. The design is similar to that of the pilot plant dissolver discussed in Section I-3.3. The dissolver basket was made of perforated Teflon, 1/16-inch thick. The vessel was likewise made of Teflon: the walls from 1/16-inch sheet and the end plates from 1/2-inch-thick sheet. The cathode was 1/8-inch-thick titanium 55A and the anode was 0.010-inch-thick platinum. The end plates were slotted to allow the anode, cathode, and vessel walls to slide into place, leaving about 1/8-inch clearance between

TABLE XI

COMPOSITION OF FISSIUM
IN EBR-II FUEL

<u>Fissium Element</u>	<u>Weight Percent</u>
Mo	2.5
Ru	2.0
Rh	0.3
Pd	0.2
Zr	0.1
Nb	0.01

the electrodes and the basket or vessel walls. The sheets forming the basket came together at the bottom to form a 22 degree angle. Although the bottom of the basket was closed to hold the fuel, a tab of Teflon came down from the bottom of the basket and extended from the sides about one inch in each direction to eliminate stray currents.

The dissolver was suspended by the electrode leads in a two-liter reaction vessel so that the electrolyte solution was even with the top of the cathode. The spaces between the basket, electrodes, and vessel walls, and the open bottom of the dissolver, allowed the electrolyte to circulate. With the aid of a magnetic stirrer and a small cooling coil, the temperature of the solution was controlled at the desired level.

Each batch of about 12 to 13 grams of fuel was dissolved in one liter of 4M nitric acid. The solution temperature was held at about 50°C while the dissolver was operated with a cathode current density of about 1.1 amp/cm² and an anode current density of about 1.2 amp/cm².

3.13 Solids Produced From EBR-II Fuel Dissolution. The dissolver products obtained from both the electrolytic dissolution and the chemical dissolution in nitric acid contained 2.0 to 2.5 percent of the weight of the fuel as undissolved solids. These insolubles contained ruthenium and other fission elements (except molybdenum), grains of stainless steel (in the case of electrolytic dissolution), and uranium amounting to 0.1 percent of the total uranium charged. In general, all of these uranium-containing solids can be retained on a 1.2-micron filter and, thus, could be recovered by centrifugation. If justified, a large portion of this uranium could be recovered from the solids by treatment with mixed nitric-hydrofluoric acid, a solvent which could not conveniently

Fig. 13 Effect of time on dissolution of uranium from EBR-II fuel.

Fig. 14 Laboratory scale electrolytic dissolver.

be used for the total fuel charge. The undissolved solids content and the uranium distribution resulting from the electrolytic and chemical dissolution of both irradiated and nonirradiated EBR-II fuel are shown in Table XII.

TABLE XII

UNDISSOLVED SOLIDS CONTENT AND URANIUM DISTRIBUTION
RESULTING FROM THE DISSOLUTION OF
EBR-II FUEL ELEMENTS

<u>Type of Dissolution</u>	<u>Burnup (%)</u>	<u>Total Solids (%)</u>	<u>Uranium Distribution</u>		
			<u>In Solution (%)</u>	<u>In Filter Cake [a] (%)</u>	<u>In Solids in Filtered Solution [b] (%)</u>
Chemical	0	2	99.9	0.08	[c]
Electrolytic	0	2	99.9	0.1	<0.01
Electrolytic	0	2.4	[c]	[c]	[c]
Electrolytic	1	2.5	99.9	0.09	<0.03
Electrolytic	1	2.2	99.9	0.08	0.03

[a] After filtration of the dissolver solution through 1.2- μ filter.

[b] As collected from a small aliquot on a 0.45- μ filter.

[c] Not determined.

3.14 Extraction of Uranium with Hexone Using Dissolver Product from Chemical Dissolution. Extraction tests were run on dissolver product solution resulting from the chemical dissolution of an EBR-II fuel segment in nitric acid. Table XIII shows the distribution coefficients obtained by extraction of uranium with Hexone and stripping with nitric acid.

Ferrous sulfamate was used in the first cycle scrub solution (IAS) to inhibit surfactancy. Palladium, derived from the fission, was probably present in the dissolver product solution as a colloidal oxide or hydroxide; without ferrous sulfamate, black solids containing palladium occurred in the interfacial zone. This palladium compound also extracted into the Hexone, carried through into the final product solution, and precipitated as a finely divided black solid. Ferrous sulfamate, usually used in the scrubbing solution to reduce plutonium, appeared to inhibit this transfer, probably by reducing the palladium to the metal. The potentials for the $\text{Pu}^{+3} \rightarrow \text{Pu}^{+4}$ couple and for the $\text{Pd} \rightarrow \text{Pd}^{+2}$ couple are nearly the same.

A proposed Hexone flowsheet for uranium recovery using ferrous sulfamate in the aluminum nitrate scrubbing solution is shown in Table XIV. Analysis of the final uranium product when using ferrous sulfamate in the flowsheet

indicated a concentration of less than 2.0×10^{-4} grams of palladium per liter (the lower detection limit) compared to the original concentration of 1.5×10^{-2} grams per liter. The Pd-U ratio in the first cycle product solution (IBP) is about 3×10^{-6} . Using this flowsheet, palladium in the final uranium product, if any, will not cause the total metal ion concentration of the final product to exceed the allowable shipping limit of 0.75 weight percent, based on the uranium content. Laboratory experiments indicated that the final product, when concentrated to 350 grams per liter uranium, will be free of precipitates.

3.15 Extraction of Uranium with TBP Using Dissolver Product from Electrolytic Dissolution. The dissolver product from electrolytic dissolution was filtered through a 1.2-micron porosity filter to remove the major portion of undissolved solids (primarily fission residue) prior to uranium extraction experiments.

Dispersion-coalescence tests [7] were run using one volume of dissolver product to one volume of 10 percent TBP extractant. The dispersion and coalescence tests for uranium extraction were both acceptable and indicated that no problems should occur in the plant; however, a slight bit of webbing in the organic phase possibly was caused by solids that passed through the 1.2-micron filter.

A 10 percent TBP flowsheet (Table XV) for recovery of uranium from the electrolytic dissolver product solution was used in these tests. Table XVI shows the distribution coefficient for uranium extraction and stripping using this same flowsheet.

Greater than 99.5 percent uranium recovery was obtained in three stages of extraction. As would be expected with 10 percent TBP only 23 percent saturated with uranium, the extraction of acid was fairly high, and this could complicate further treatment in the scrub and strip columns. With the uranium loading experienced in this study, the IAP could hold up to 0.28M acid at saturation. Analysis of the IBR and IBP indicates that 0.18M acid was present in the IAP.

In the scrubbing-contacting process simulating the IB column, a uranium distribution coefficient E o/a of about 1.2 was experienced. This is low compared to the value of eight previously reported in IDO-14556[8]; the difference very likely is due to the great sensitivity of this value to aluminum concentration.

TABLE XIII
URANIUM EXTRACTION AND STRIPPING
RESULTS FOR EBR-II FUEL
DISSOLVED CHEMICALLY

<u>Extraction with Hexone</u>		
<u>Uranium in Organic</u>		<u>E o/a</u>
<u>Phase at Equilibrium</u>		
	<u>g/l</u>	
Stage 1	27.7	17
Stage 2	1.31	13
Stage 3	0.08	18
<u>Stripping with 0.04M HNO₃</u>		
<u>Uranium in Aqueous</u>		<u>E a/o</u>
<u>Phase at Equilibrium</u>		
	<u>g/l</u>	
Stage 1	49	200
	0.7	368

TABLE XIV

FLOWSHEET USING HEXONE FOR THE RECOVERY OF URANIUM FROM EBR-II FUEL

Description	Fuel[b] Charge	Dissolvent	I AF	I AX	I AS	I AP	I AR[a]	I EX	I BP	I BR[a]	First Cycle Product
Flow, l/batch		5C									
Flow, l/hr			8	30	22	30	30	15	15	30	2.79
Extractant				Hexone		Hexone					
Al (NO ₃) ₃ M			1.34		2.0		1.82				
HNO ₃ M		6	2.19				0.22	0.04	0.04		0.2
NH ₄ OH M					0.5		0.0				
U, g/l			122			32.5	0.004		65	0.0002	350
Hg, M		0.005	0.005				0.001				
Al, Kg	0.9										
U, Kg	3.2										
NH ₄ NO ₃ , M							0.37				
Fe(NH ₂ SO ₃) ₂ M					0.05		0.037				

[a] Analysis

[b] Aluminum can containing 50 EBR-II Fuel pins.

TABLE XV

SIMPLIFIED FLOWSHEET USING TBP TO EXTRACT URANIUM FROM
DISSOLVER PRODUCT FROM THE ELECTROLYTIC DISSOLUTION OF EBR-II FUEL

Stream Description	Dissolver Product	Concentrated I BR	I AF	I AX	I AP	I BS	I CX
Flow l/hr	555	31	586	580	580	110	300
U g/l	9.7	20.4	10.3		10.4		
H <u>M</u>	2.8	2.5	2.8		0.2		0.005
NO ₃ <u>M</u>	3.0	9.9	3.4		0.2	1.50	0.005
OH <u>M</u>						0.50	
Al <u>M</u>		1.80	0.09			0.50	
SS g/l	5.0		4.7				
Na g/l	0.13		0.12				
NH ₄ <u>M</u>		1.80	0.09			0.50	
B	trace		trace				
TBP %				10	10		

Uranium stripping was fair; the small distribution coefficient for the the first stage, $E_{a/o} = 8$, probably reflects the transfer of acid. The higher coefficient experienced in the second stage, $E_{a/o} = 40$, suggests that there are no further chemical problems inhibiting transfer of uranium.

In general, there appear to be no unusual chemical problems associated with the extraction of this feed with TBP. The behavior and effects of the nitric acid are important and can be optimized in the plant flowsheet based on existing data. No palladium solids were observed in the final product when TBP was used as the organic extractant; however, no analysis for palladium was made.

3.2 Physical Properties of EBR-II Fuel Processing Solutions (L. C. Lewis; Chemistry Section)

Conductivity, density, and viscosity measurements were carried out on solutions simulating those arising during the electrolytic dissolution of the EBR-II fuel elements. Experimental details and a compilation of the data obtained during this investigation are published in a topical report, IN-1192 [9].

3.3 Operation of an Electrolytic Dissolver Pilot Plant

(R. A. Brown, W. B. Kerr; Development Engineering Section)

Process development for the electrolytic dissolution of EBR-II and other stainless-steel-clad fuels is in the pilot plant stage. A continuous pilot unit^[a], using a 24-inch-long, V-shaped dissolver (Figure 15), has been operated for three 10-day periods, a total time of 700 hours. Stainless steel pipe, simulating fuel elements, was dissolved at an average dissolution rate of 1 g/cm²-hr and current utilization of 0.5 g/amp-hr. The dissolver, using the solution-contact principle for current distribution, showed no signs of corrosion on the platinum-covered niobium anode, the niobium basket, or the titanium dissolver vessel (which serves as the cathode).

Operating conditions were 8M HNO₃ (chosen for low corrosion rates), a dissolver temperature of 140 to 150°F, and 3000 amps. Average metal concentration was maintained at 20 grams per liter ($\pm$ 1 gram per liter) by maintaining a constant acid feed rate. A conductivity cell was used for continuous measurement of metal concentration. Boron, in the form of H₃BO₃, was added as a neutron poison, duplicating proposed plant conditions.

A significant problem in electrodisolution of stainless-steel-clad fuels is the formation of undissolved solids (Section I-3.1). These particles are mainly stainless steel and result from grain-dropping; niobium carbide and silica make up the remainder of the undissolved material. Uranium losses are negligible, but silica-bonded stainless steel sludge reduced heat transfer in the dissolver cooler and caused an increase in dissolver resistance during the first 500-hour operating period. This problem will be dealt with in two ways:

- (1) Operating conditions, such as temperature and current density, will be set for minimum solids generation rates (consistent with other operating constraints)
- (2) Operating procedures and equipment will be modified to cope with unavoidable quantities of solids.

^[a] Described in the previous Annual Report, IN-1087^[2].

TABLE XVI

URANIUM EXTRACTION AND STRIPPING RESULTS FOR EBR-II FUEL DISSOLVED ELECTROLYTICALLY

Extraction with 10% TBP

	Uranium in Organic Phase at Equilibrium	E o/a
	<u>g/l</u>	
Stage 1	7.9	4.6
Stage 2	1.4	5.4
Stage 3	0.2	6.9

Stripping with 0.005 M HNO₃

	Uranium in Aqueous Phase at Equilibrium	E a/o
	<u>g/l</u>	
Stage 1	10.86	8.0
Stage 2	2.8	40

Fig. 15 Electrolytic dissolver.

An Evolutionary Operation Program (EVOP) was used during the first 500 hours of pilot plant operation. This systematic variation of experimental conditions is used to determine optimum operating levels without disturbing normal production. Six EVOP cycles (consisting of five conditions each) were completed; no significant effects were detected for either pipe size or acid concentration. Large variability in the acid feed rate probably masked the effects of the small changes in factor levels.

The pilot unit will be used to develop additional technical and operating data for the following:

- (1) Dissolution rates, current utilization, and undissolved solids formation as a function of operating parameters (temperature, current density, acid concentration, and fuel size) for stainless steel pipe, simulated fuel elements (natural uranium rods sealed in stainless pipe), and EBR-II fuel
- (2) Demonstration of concentration control by current and acid feed rate control; use of the conductivity meter to indicate concentration changes caused by nonuniform dissolution rates for uranium

- (3) Verification of hydrogen evolution rates and dilution, previously shown to be well below the explosive limit (less than 25 percent of the lower explosive limit)
- (4) Technical support for the EBR-II plant dissolver, when installed, and to develop technical information for new fuels.

3.4 Electrode Corrosion

(R. G. Butzman, N. J. Kertamus; Chemistry Section)

Laboratory studies were made with niobium anodes and titanium cathodes, under simulated electrolytic dissolver conditions, to investigate their corrosion resistance for this particular application. The anode for the plant electrolytic dissolver will consist of a niobium plate with a thin sheet of platinum bonded to it. There is only about a 1/4-inch space (which is filled with electrolyte) between the exposed face of the niobium and the cathodic wall of the titanium vessel.

These studies indicated that niobium formed an insulating oxide layer in nitric acid at potentials to 50 volts. For practical considerations, this film allowed only negligible current leakage from the anode to the simulated cathodic container. The corrosion rate of the exposed niobium was appreciably less than 2 mils per month.

It was also shown that titanium could be used satisfactorily as a cathodic material provided that the nitrate level of the dissolver solution was maintained above 7M. Below this level, the corrosion rate was directly proportional to current density and was too high for practical consideration. For example, at 4M nitrate with a current density of 1 amp/cm² (which is reasonable for the process), the corrosion rate exceeded 30 mils per month. Welded areas of test coupons were not preferentially attacked. The corrosion rate was not increased by increasing the temperature of the electrolyte, specifically from 55 to 73°C. Details of this work are reported in a topical report, IN-1191 [10].

3.5 Preparations for EBR-II Fuel Receipt

(G. F. Offutt; Process Engineering Section)

Preparations for receiving EBR-II fuel at the storage basin were completed during the year. Beginning in FY-1969, fuel from EBR-II in the form of complete subassemblies will be shipped to the ICPP fuel storage basin for temporary storage and eventual reprocessing in an electrolytic dissolution system. A fuel subassembly is about 92 inches long, and has a hexagonal cross section -- 2.29 inches across the flats. Within this sheathed subassembly, there is a fuel section composed of 91 fuel elements each about 18 inches long. Upon receipt of the subassemblies at the ICPP basin, the ends will be sawed off leaving only the fuel sections; these will be stored in cadmium poisoned storage racks and processed at a later date in the electrolytic dissolver.

During a test run, the blanket ends were successfully removed from an unirradiated subassembly by cutting with the underwater saw at the storage basin. Examination of the fuel section revealed that the fuel elements will not fall out of the sheath during handling; however, for further assurance, the sheath will be crimped after cutting. The fuel section as cut weighed 8.8 kg; it should contain about 5.62 kg of 50 percent enriched uranium, 0.30 kg of fissionium, 0.06 kg of sodium, and 2.8 kg of Type 304L stainless steel.

Up to four fuel sections will be stored in each position of the existing cadmium poisoned racks in the fuel storage basin. Each rack position consists of 4-3/4-inch ID pipe, 51 inches deep. Two fuel sections will be placed in the bottom of each position and two more on top of the first two. Three fuel sections can fit at one level in each position; however, an end piece from a cut subassembly will be placed beside the two fuel sections at the bottom of each position to prevent a third fuel section from falling into the void space. An endpiece can be easily removed from a rack because it has a special handling fixture attached. Although six subassemblies per rack position are nuclearly safe, there would not be enough room for grasping and removing three fuel sections from the bottom portion of a rack.

A fuel shipping cask for EBR-II fuel was designed and fabricated by Argonne National Laboratory. The cask will be cooled by natural-circulating water and will contain one subassembly. A second cask that will be air cooled also is being designed. During a trial run, the water cooled cask was successfully handled and unloaded, using an unirradiated subassembly, at the ICPP storage basin.

3.6 Corrosion of EBR-II Fuel Elements During Underwater Storage (C. A. Zimmerman, D. W. Rhodes; Chemistry Section)

3.61 Fuel Element Leak Tests of Clad EBR-II Fuel Pins. Prior to processing of EBR-II fuels, it will be necessary to store these fuels for some time, under water, in the ICPP fuel storage basin. The 9-mil, Type 304 stainless steel cladding on these fuel pins will have undergone sensitization in the sodium cooled reactor environment at approximately 516°C. Since stainless steel in the sensitized condition is known to be susceptible to severe intergranular corrosion attack when exposed to mildly corrosive media [11], long-term tests were initiated to determine if the ICPP storage basin water would attack the cladding on the irradiated EBR-II fuel pins.

The results of these tests, after eleven months of exposure in the ICPP storage basin, showed no significant increase in the concentration of radioactive materials during several seven-day test periods in the Fuel Element Leak Test (FELT) apparatus [a]. This is interpreted as indicating that no penetration of the EBR-II fuel element cladding has occurred to date. Previously published results of FELT type determinations, made using an irradiated, aluminum-clad, uranium-aluminum fuel, showed a leak rate of 335 μ Ci/hr when 10 cm² of unclad fuel surface was exposed [12].

The FELT tests were conducted by placing five irradiated EBR-II fuel pins into a stainless steel vessel which was then closed. The vessel was purged with clean water for 24 hours to displace the basin water originally present. A sample of water was then obtained (at the start of the test) and again after seven days exposure to the fuel pins. Comparison of gamma ray spectra of these two water samples for any appreciable increase in the concentration of radioactive materials indicated any penetration of the cladding. The fuel pins were then removed from the stainless steel vessel and returned to storage.

[a] The FELT apparatus is described in Reference 12.

3.62 Leaching of Unclad EBR-II Fuel Pin Segment. As part of the investigation of the storage of EBR-II fuel in the ICPP storage basin, it is desirable to know the behavior of the declad, irradiated, uranium-fissium fuel alloy in basin water. This would be pertinent in the case of extensive cladding corrosion. A laboratory test to determine the rate at which radioactive material leached from an unclad specimen of an irradiated EBR-II fuel pin segment was initiated in 3.1 liters of basin water with a cylindrical fuel pin segment having a surface area of 3.5 cm².

The amount of ¹³⁷Cs in the water increased initially from background (0.86 μ Ci ¹³⁷Cs/liter) to 15.3 μ Ci of ¹³⁷Cs/liter in one-half hour. This rapid increase was probably due to loosely adhering surface material. The initial rapid increase was followed by a slower rise to approximately 47 μ Ci ¹³⁷Cs/liter after 83 days (Figure 16). Chemical analysis of the water at this time indicated no significant change in composition. Additional measurements up to 156 days (3750 hours), however, indicated that the ¹³⁷Cs concentration had increased to 243 μ Ci/liter. No study was made to establish a mechanism for this accelerated leaching rate for ¹³⁷Cs, but other studies on the corrosion of uranium alloys in aqueous solutions [13] indicate accelerated corrosion rates with increasing exposure time. The final concentrations of ⁹⁰Sr and ⁸⁹Sr were 225 and 68 μ Ci/liter, respectively.

Fig. 16 Cesium leached from a declad EBR-II fuel pin segment in water.

An attempt was made to measure other radioisotopes in the water, particularly ⁹⁵Zr, ⁹⁵Nb, and ¹⁴⁴Ce. The concentration of all three decreased with time, with ¹⁴⁴Ce decreasing faster than the other two. After removing the water, the test vessel was filled with a 20 percent nitric acid-3 percent hydrofluoric acid solution. Analysis of this solution showed that the concentration of ¹⁴⁴Ce was about four times higher and the concentrations of ⁹⁵Zr and ⁹⁵Nb were

about three times higher than they had been in the water, indicating that these materials had been adsorbed on the vessel walls and fittings.

Additional tests are being made to confirm these observations. In addition, an irradiated segment of a declad EBR-II fuel pin is being exposed in 6M NaOH to simulate a leak in which water might penetrate the cladding and react with the sodium bonding material between the stainless steel cladding and the uranium-fissium alloy meat.

4. GRAPHITE FUEL REPROCESSING

Development of a fluidized bed combustion-nitric acid dissolution headend process for reprocessing graphite fuels at ICPP is continuing. The process for nuclear rocket fuels consists of the following steps: (a) burning the graphite fuels in a bed of fluidized alumina to remove the graphite; (b) elutriation of the metal oxide combustion products (U_3O_8 and Nb_2O_5) in the off-gas stream from the burner; (c) removal of the elutriated particles from the off-gas by scrubbing with nitric acid, which also dissolves the U_3O_8 ; and (d) separation of the undissolved solids (mainly Nb_2O_5) from the uranyl nitrate solution which is fed to the solvent extraction system for uranium recovery.

Based on the above process, a proposal has been made to install graphite fuels processing facilities at ICPP for high capacity processing of nuclear rocket (Rover) fuels and low capacity demonstrational processing of the Peach Bottom and Ft. St. Vrain High Temperature Gas Cooled (HTGR) fuels.

Pilot plant development studies were made at ICPP during the last year to optimize the two-stage fluidized bed burner design and to examine further the phenomenon of uranium oxide coating on the alumina. A two-inch-diameter fluidized bed miniburner for making short scoping studies has been installed and operated. Also, a moderate laboratory development program was conducted in support of the pilot plant development effort.

4.1 Pilot Plant Studies of the Fluidized Bed Combustion-Nitric Acid Dissolution Process

(A. P. Roeh, D. C. Kilian, L. C. Borduin, O. R. Klemens; Development Engineering Section)

During the year development studies with the graphite fuels pilot plant were continued. Also a graphite fuels miniburner system was installed and operated. The miniburner is used to make scoping studies of graphite fuels burning at a much lower cost than could be made in the larger pilot plant.

4.11 Operability of the Fluidized Bed Pilot Plant

Burner Description. A description of the graphite fuels process pilot plant and an equipment flow diagram was presented in the annual report for Fiscal Year 1967[2]. The key component of this system is the two-stage fluidized bed burner as shown in Figure 17. The burner contains a continuous bed of fluidized alumina passing freely between two zones of different cross-sectional areas designated as the first and second stages. The second stage, positioned above the first stage, has a larger flow area and requires the addition of more

Fig. 17 Two-stage fluidized bed burner.

oxygen to the fluidizing gas rising from the first stage. Fuel is charged into and ignited in the lower stage where most of the graphite is burned. However, small particles of graphite, amounting to approximately one third of the graphite in the fuel, are released from the burning fuel elements and are not consumed in the first stage. These particles are carried into the second stage where they continue burning with fresh oxygen until they are completely consumed or are elutriated from the burner.

Both stages are equipped with the following auxiliary equipment:

- (1) Electrical resistance heaters used for startup of the burner
- (2) A surrounding shroud to provide an annular space for cooling air flow
- (3) Sample lines
- (4) Thermowells for both wall and interior temperature measurements.

In addition, the first stage has fins welded to the outside wall to increase the area for heat transfer to the cooling air and a pipe trace welded to the outside wall for preheating the fluidizing gas.

A centrally positioned charging assembly extends from the top of the burner down through the second stage (Figure 17). Second stage fluidizing gas is preheated in a jacket surrounding the charging tube, and baffles welded to the preheating jacket reduce carryover of alumina from the burner and prevent excessive slugging of the fluidized bed in the second stage.

Experimental Results. Experimental studies of the two-stage fluidized bed burner have been made with the following objectives:

- (1) To evaluate the operability of the system
- (2) To determine the effect on combustion efficiency of:
 - (a) first-stage oxygen concentration
 - (b) second-stage fluidized bed height
 - (c) fluidizing velocity.

Also, a wet off-gas cleanup and uranium dissolution system has been operated, both independently and in conjunction with the burner.

Experimental studies conducted over the past year have demonstrated the simplicity and ease of operation of the combustion-dissolution process. However, the range over which the process variables can be changed while still maintaining ease of controllability of the process is limited. Deviations from the rather narrow range of temperature, fluidizing velocity, and oxygen concentration significantly increase the difficulty of operating the system. The following ranges in operating variables have been established for the graphite fuels pilot plant burner operated at 14.7 psia.

Average Bed Temperature	680 to 730°C
First Stage Fluidizing Velocity	0.9 to 1.1 ft/sec
First Stage Oxygen Concentration	60 to 80 percent

Further restrictions on other operating variables may result from studies that are currently being made to investigate the phenomenon of uranium oxide coating on the alumina fluidized bed particles.

The operating difficulties that have been encountered when operating outside the preceding ranges include:

- (1) Poor combustion efficiency resulting in excessive carbon carryover with the overhead product
- (2) Local sintering of the alumina bed material
- (3) Temperature excursions leading to severe alumina sintering and melting of the burner wall.

Carbon combustion efficiency increases with increasing temperature, increasing oxygen concentration, and increasing fluidized bed height in the second stage. The effects of first stage oxygen concentration and second-stage fluidized bed height on the carbon combustion efficiency are shown in Figures 18 and 19, respectively. Combustion of 95 percent of the carbon in the fuel fed to the burner is considered an acceptable lower limit. This can be achieved with the burner operated within the variable ranges previously listed.

Local sintering of the bed material without detected temperature excursions has occurred when the fluidizing velocity was less than 0.9 ft/sec. Apparently the fluidization quality of the bed is sufficiently poor when the velocity is below 0.9 ft/sec that local disruptions in fluidization resulting in poor heat transfer can occur, thus giving rise to short localized temperature excursions and sintering of small amounts of alumina.

Temperature excursions leading to severe alumina sintering and even melting of a hole in the burner wall can occur when the burner is operated under conditions where a rise in temperature greatly increases the net reaction rate in the burner, thus causing loss of temperature control in the burner. The net reaction rate in the burner is directly dependent on the amount of oxygen available for reaction. Obviously as the oxygen concentration in the fluidizing gas is reduced the reaction rate is also reduced. Also, the amount of oxygen is reduced and (a) the fluidizing velocity is reduced and (b) the operating temperature is increased at a constant fluidizing velocity.

Fig. 18 The effect of oxygen concentration in the first-stage fluidizing gas on the efficiency of graphite combustion.

Operation of the wet off-gas cleanup-uranium dissolution system in conjunction with the burner is very smooth. Effective control of the burner pressure with the steam jet ejector located downstream of the venturi scrubber

has been demonstrated. Condensation of the steam downstream of the ejector provides a very efficient solids removal backup in case of upsets in the venturi scrubber-knockout cyclone system. Efficiencies greater than 99.9 percent for the venturi scrubber-knockout cyclone system and greater than 99.99 percent for the steam injection-condensation system in series with the venturi scrubber-knockout cyclone system have been consistently obtained.

4.12 Study of U_3O_8 Coating on the Alumina Bed in a Miniburner Unit. Throughout the development effort on the Graphite Fuels Processing project, the need for a small scale fluidized bed for making scoping studies had become apparent. Construction of a miniburner (two inches in diameter) has allowed many investigations to be made more rapidly and at lower cost than in the large pilot plant unit.

Fig. 19 The effect of second-stage fluidized bed height on the graphite combustion efficiency.

Equipment Description. The single-stage fluidized bed miniburner (shown in Figure 20) consists of three stainless steel sections.

- (1) The fluidizing-gas heater box located at the bottom of the burner contains six 250-watt tubular elements arranged in a triangular array, perpendicular to the flow of the fluidizing gas.
- (2) The burner section is a two-inch-diameter pipe, 12 inches long, surrounded by a cooling air shroud. A 1/4-inch-thick plate perforated with 3/16-inch holes and located between the heater box and the burner section serves as a fuel support grid.
- (3) The disengaging section is a four-inch-diameter pipe, eight inches long, with a four- to two-inch reducer at the bottom and flanged at the top.

Fuel is charged to the burner section through a 1-1/4-inch-diameter pipe concentric with the filter. Two 1-1/4-inch ball valves, located above the vessel, form an air lock for fuel charging. Solids can be elutriated from the burner by passing the off-gas from the fluidized bed directly to a dry product collection vessel or can be retained in the burner by routing the off-gas through a filter inside the burner. The filter inside the burner is a cylindrical sintered stainless steel filter surrounding the fuel charging tube. The dry product collection vessel is a four-inch-diameter, 14-inch-long stainless steel vessel with a sintered stainless steel disc at the top for disengaging solids from the gas.

Fig. 20 Fluidized bed miniburner.

Product is drained from the collection vessel through a one-inch ball valve located at the bottom of the vessel. Either of the sintered metal filters in the system may be cleaned periodically by applying a pulse of air to the downstream side of the filter.

Instrumentation and Control. The composition and flow rate of the fluidizing gas is controlled by two rotameters. Burner pressure is held constant with a back pressure regulator located downstream of the solids collection vessel. The bed temperature is maintained by adjusting the power input to the electrical heaters and/or throttling the amount of air flowing through the cooling air shroud. Temperatures throughout the system are continually recorded on a multipoint recorder. Two instruments continuously monitor the off-gas. An infrared analyzer records the percentage of carbon dioxide, and a paramagnetic analyzer records the oxygen concentration in the effluent gas. A "Magnahelic" gage indicates the pressure drop across the fluidized bed.

Experimental Operation. Experimental studies in the Graphite Fuels Pilot Plant have, on occasion, resulted in coating of the product, U_3O_8 , on the alumina bed material to as high as 11.4 percent by weight. This phenomenon has been observed in the single-stage graphite burner but was easily corrected by fluidizing the bed for a short time in the absence of combustion. In the two-stage unit, however, fluidization in the absence of combustion has not significantly reduced the amount of coating on the alumina. As a first step toward eliminating this problem, the first series of experiments in the miniburner were directed toward determining what factors, or interaction of factors, cause the coating phenomenon.

A statistically designed set of 16 experiments involving five variables was formulated. The five factors listed in Table XVII were considered important in affecting coating and were varied according to the predetermined pattern over the ranges shown. The following conclusions were reached:

- (1) The amount of U_3O_8 coating on the alumina bed is significantly greater when burning UC_2 bearing fuel than when burning the UO_2 type fuel.
- (2) No significant difference in coating rate is observed when using uncoated alumina or previously coated alumina as bed material. However, when UO_2 type fuel is burned in the presence of the previously coated bed material the amount of U_3O_8 coated on the alumina is reduced significantly.
- (3) The experiments failed to prove any significant effects due to fluidizing velocity or burner pressure.

During a 16-hour experiment in the miniburner at 1300°F, 14.7 psia, and 1.0 ft/sec fluidizing velocity, 4 kg of UC_2 bearing Rover fuel were burned. The burner was then operated for an additional two hours in the absence of fuel. Analysis of the bed material showed a steady rate of coating throughout the 16 hours -- to 19.5 percent U_3O_8 by weight on the final bed. No reduction in the coating was observed over the final two-hour period even though no additional fuel was charged in this period.

One run has been made in the miniburner using niobium carbide coated Rover fuel containing uranium carbide particles. During this run the coating

TABLE XVII

VARIABLES STUDIED IN-BED COATING TESTS

<u>Variable Factors</u>	<u>Level</u>	
	<u>Low</u>	<u>High</u>
Bed Temperature	1200°F	1500°F
Burner Pressure	14.7 psia	25 psia
Fuel Type	UC ₂ bearing	UO ₂ bearing
Alumina	Uncoated	Coated (11.4%U ₃ O ₈)
Fluidizing Velocity	0.9 ft/sec	1.1 ft/sec

rate of U₃O₈ on alumina was very low. Apparently the niobium prevents excessive coating U₃O₈ on the alumina. The niobium oxide elutriated from the fluidized bed as anticipated.

The discovery that the presence of UO₂ or NbC in Rover fuel eliminates the coating problem leads to speculation that the coating phenomenon may be chemical in nature, or may involve a chemical intermediate (between UC₂ and U₃O₈) which initiates coating.

4.2 Survey of Catalysts and Combustion Modifiers for Accelerating Graphite Combustion

(N. J. Kertamus; Chemistry Section)

Although research has been conducted on several alternate methods of reprocessing spent nuclear fuel elements containing graphite as a major constituent [14, 15], the initial step now planned for use at the Idaho Chemical Processing Plant is combustion of the graphite in oxygen in a fluidized bed of alumina. As combustion liberates uranium oxide particles from the graphite matrix, the particles are elutriated from the burner with the fluidizing gas. Downstream from the burner, the uranium oxides are collected and dissolved in nitric acid, and the solution is adjusted for subsequent uranium recovery by solvent extraction.

Results initially obtained from a four-inch-diameter, single-stage pilot plant burner indicated that combustion was only partially complete in the burner and that unburned carbon fines were elutriated from the burner [16]. Modifications considered to eliminate elutriated carbon were operation at a higher temperature, use of a two-stage burner, and acceleration of the rate of burning by catalysis or modification of the combustion reaction. This summary reports results obtained when testing the latter possibility, namely whether graphite combustion can be catalyzed by certain additives. The preceding section (I-4.1) reports the use of a two-stage burner to obtain more complete combustion.

4.21 Experimental Methods and Materials. A Chevenard thermobalance was modified to measure continuously the weight loss of Rover fuel samples in a

controlled environment at constant or programmed temperature (Figure 21). As the sample, quartz combustion tube, and related hardware were brought to the desired temperature, dry nitrogen was used to purge the system. On attaining the desired temperature, the purge gas was changed from nitrogen to oxygen, air, or other oxidizing gas. If desired, water or other liquids could be added through a separate entrance port in the quartz combustion vessel. Rate of addition of gases was controlled and measured through rotameters, while a variable speed pump controlled the rate at which liquids were added.

Fig. 21 Thermobalance modified for combustion studies.

Zero time was defined as the moment when the purge gas composition was changed from nitrogen to the oxidizing gas. Estimated accuracy of the thermobalance and recorder was ± 0.05 g or about two percent of the weight loss in a typical experiment.

The Rover fuel samples used for the study consisted of uranium carbide dispersed in graphite. The elements were broken into sections approximately one quarter of an inch in length and had uncoated coolant channels running lengthwise. Two elements with different histories were used in the experiments. Tests summarized in Figure 22 were made with portions of one element; the remaining tests were made with portions of a second element. There was a small but measurable difference in the combustion rate of the two elements.

4.22 Results and Discussion

Test Conditions. Initially the combustion variables of temperature, oxygen concentration, and gas flow rate were surveyed to establish suitable test conditions. Results from these experiments are plotted in Figure 22.

Fig. 22 Effect of conditions on combustion rate.

Curve D indicates that the same weight loss-time curve or combustion rate was obtained from combustion of Rover elements at temperatures of 700, 800, and 850°C at an air rate of 6.3 cfh. Since, in these experiments, temperature did not influence combustion rate, oxygen availability limited the combustion rate at this low air flow rate.

After increasing the air flow rate to 12.3 cfh, tests were made at temperatures of 700 and 800°C, and the results are shown in Curves A and B (Figure 22). At the higher air flow rate, the combustion rate increased with increasing temperature. The temperature coefficient of combustion gave an apparent activation energy of about 8 kcal/mole for these two tests.

Although the tests at 12.3 cfh in air indicated that oxygen availability did not limit combustion rate as it appeared to do at 6.3 cfh, two additional tests were made to supplement these observations. Air was enriched to 42 percent oxygen and tests were made to determine whether the additional oxygen increased the combustion rate at gas flows of 6.3 and 12.3 cfh.

Results at 6.3 cfh (Curve C, Figure 22) indicated that the combustion rate was increased over that in air alone at the same flow rate, but the rate was slower than the test in air at 12.3 cfh. These observations suggested mass transfer rates over the burning element were significant in determining the rate of combustion, especially at the lower air flow rate. The test with 42 percent oxygen at 12.3 cfh gave results equivalent to those in air alone (Curve B, Figure 22); consequently, mass transfer and oxygen availability were not limiting at the higher gas flow rate.

One test at 600°C at an air rate of 12.3 cfh indicated combustion occurred only after an induction period of 40 minutes. Once combustion was initiated it proceeded at a rapid rate as indicated in Curve E, Figure 22.

In a second series of experiments in air at 12.3 cfh, process conditions were established to estimate the temperature and time required to burn 70 percent of the graphite initially present in the sample. These results are summarized in Figure 23, and suggest that at 700°C, for example, 51 minutes

are required to oxidize 70 percent of the carbon originally present in the sample.

Effect of Nitric Acid Addition. Since nitric acid noticeably reduced the combustion temperature of liquid hydrocarbons (kerosene) in pilot plant studies on in-bed combustion in the waste calcining facility at the ICPP[2], several tests were made to determine whether nitric acid would accelerate the combustion rate of graphite at low temperatures. Tests were made by varying the addition rate of 70 percent nitric acid to air flowing through the combustion apparatus at 12.3 cfh at temperatures of 700 and 800°C; one test was made with nitric acid in nitrogen without the presence of oxygen.

Fig. 23 Conditions for 70% carbon combustion.

Results from these experiments, plotted in Figure 24, indicated that at 700°C nitric acid at 17, 21, and 29 ml/hr did not accelerate the rate of graphite combustion over air alone at an equivalent flow rate. In fact, the combustion rate was actually decreased by the addition of nitric acid. Nitric acid in nitrogen resulted in a very slow reaction; a 14 percent weight loss occurred in 160 minutes.

Fig. 24 Effect of nitric acid on combustion rate.

Effect of Water Vapor. Experiments were conducted with water vapor instead of oxygen as the oxidizing gas. Thermodynamic calculations for the reaction $C + H_2O = H_2 + CO_2$ indicated equilibrium constants (Kp's) of 22 and 37 at temperatures of 900 and 960°C, respectively. In spite of the favorable thermodynamics, tests at 950°C indicated that water vapor alone, or with nitrogen, was not effective as an oxidizing gas. No weight loss occurred.

Several tests were made utilizing four and seven mole percent water vapor in air flowing at 12.3 cfh. Tests with water vapor and air failed to increase the combustion rate over that experienced with air alone.

Effect of Inorganic Salts as Additives. Literature data^[17, 18] indicated the combustion rate of amorphous carbon could be noticeably improved by the addition of sodium carbonate or cupric chloride to the char. (The amorphous carbon was pyrolyzed cellulose whose chars had a high liquid sorption capacity.) The procedure used in the literature studies to add the inorganic salts was impregnation of the char with an aqueous solution of the desired salt, followed by drying and calcination in nitrogen or other inert gas.

Following this approach, one attempt was made to impregnate a Rover fuel sample with a saturated aqueous solution of sodium carbonate. A weighed sample was immersed in a sodium carbonate solution for 24 hours at ambient temperature, then slowly heated to about 100°C where part of the water was evaporated. The sample was then removed from the impregnating solution, dried, and reweighed. The negligible weight change indicated little sodium carbonate sorption occurred, at least when compared to similar experiments performed on activated charcoals; no improvement in combustion rate was obtained. The low liquid sorption capacity prevented the use of impregnation as a means of adding realistic quantities of catalytic salts.

Effect of Phenol as an Oxidant. Literature data^[19] indicated carbon was oxidized by phenol at modest temperature by the reaction $C + C_6H_5OH = CO + C_6H_6$. The literature reference did not indicate what form of carbon was utilized in the reaction; however, it is known that charcoals with high surface areas are more reactive for most reactions than graphite. Tests were made with segments from a Rover fuel element at temperatures of 500 and 700°C. At these temperatures, phenol was brought into contact with the Rover segments in a suitable combustion tube. Results from the survey indicated no reaction occurred between phenol and the Rover segments. Phenol was recovered from the exit side of the tube with no change; no evidence of benzene was noted.

4.23 Conclusions. Test data summarized here suggest that the combustion rate of graphite in Rover fuel elements could not be increased over that observed in air or oxygen-enriched air by the addition of potential combustion accelerators. Nitric acid addition was not effective for increasing the combustion rate, nor was sodium carbonate, a salt known to be an accelerator for the combustion of charcoal. Mass transfer and oxygen availability were important variables that significantly affected the combustion rate of Rover elements.

4.3 Basis for Criticality Safety in the Graphite Fuels Combustion Process (W. G. Morrison; Chemical Technology Staff)

Criticality safety of the graphite fuels reprocessing headend will be based on a combination of mass limitation and geometrical control. Mass limitation applies to the fluidized bed burner and auxiliary equipment. No water or steam is required in these parts of the system so mass limits can be based on dry nonhydrogenous conditions. Conventional geometrical controls will be applied to the scrubber, dissolver, and other parts of the system which use water or steam as a heat transfer medium. Strict administrative controls, operating procedures, and uranium accountability methods must be provided to guarantee compliance with the mass limits to be established.

Briefly, the graphite fuels are burned in a fluidized bed of alumina to convert the uranium to U_3O_8 . Product U_3O_8 , with some unburned carbon and UC_2 , is elutriated from the burner to a collection system and then transferred to dissolution and extraction equipment for recovery of the uranium. Since

appreciable U_3O_8 may be coated onto the alumina particles of the fluidized bed, bed material would have to be removed periodically and would also have to be considered as product.

Figure 25 presents a curve showing the unreflected spherical critical mass of U-235 for the carbon-U(93.5)^[a] mixtures as a function of the carbon-to-U-235 ratio (C/X). This curve was replotted from a calculated curve presented in LAMS-2955[20]. The curve was verified by neutron transport calculations previously shown to be accurate by check calculations on experimental data. This curve is applicable for selecting mass limits on the fuel charging cell, fuel charging tube, and any product collection system prior to the aqueous

Fig. 25 Critical mass for bare spheres of uranium (93.5) and graphite.

scrubber and dissolver. The maximum possible carbon content (C/X values) in those parts of the process will be used in determining the allowable mass for criticality safety control. Physical composition and process conditions for the various fuels to be processed will fix the C/X values for consideration.

In the burner where U_3O_8 has deposited on the alumina particles of the fluidized bed, the critical mass is influenced by both the alumina and the carbon present. Alumina and niobium oxide may be considered as diluents; their effect is to increase the critical mass. Figure 26 presents the results of some calculations to show the unreflected spherical critical mass for burner contents as a function of C/X; the carbon content was varied while the alumina and other metal oxides were held constant. The bed was assumed to be settled with no fluidizing gas. Carbon was assumed to occupy free space in the bed and to reduce

^[a] U(93.5) designates uranium enriched to 93.5 weight percent in U-235.

Fig. 26 Critical mass for bare spheres of burner contents including uranium (93.5), graphite, and alumina.

the void space as the C/X value increased. Since results indicate large critical masses, the mass limitations on the burner must be based on the carbon-U(93.5) system (Figure 25) which would be present in the charging tube. Only the left half of the curve in Figure 25 is applicable because the C/X in the fuel is less than 400. The C/X in the product elutriated from the bed is, of course, lower than the fuel fed to the burner, and it is unlikely that carbon would accumulate in the fluidized bed with its oxidizing conditions. Thus, product critical masses would be large.

Critical masses for U-233 in the carbon-U-233 system are lower than for U-235 and the mass limits for such fuels would have to be set accordingly. This would also be true for other mixed uranium fuels that may be processed in the fluidized bed burner.

5. ZIRCONIUM OXIDE FUEL REPROCESSING

5.1 Halide Volatility Process for Zirconium-Clad Zirconium Dioxide-Uranium Dioxide Fuels

(L. A. Decker; Chemistry Section)

Three distinctly different processes have been considered for fuels like the Zircaloy-clad zirconium dioxide-uranium dioxide fuel of the Shippingport PWR Core 2, Seed 1. Two of these processes (dissolution in fused ammonium bifluoride and a three-step dissolution in aqueous solutions) have been described previously [2,16]. A third process, the subject of this report, involves volatilizing the Zircaloy cladding with anhydrous hydrogen chloride and recovery of the uranium as uranium hexafluoride by fluorination of the residue. All of these processes involve severe chemical conditions. High concentrations of fluoride ion at elevated temperatures are necessary to attack the oxide wafers either in aqueous solution or in fused ammonium bifluoride. Fluorine gas at 550°C attacks the declad wafers slowly to volatilize the uranium in the volatility process.

An investigation of the applicability of the halide volatility process to the PWR fuel was carried out in a cooperative program with Argonne National Laboratory, using Argonne Laboratory facilities. The results of that investigation are summarized here; details are reported in IN-1198 [21]. The two-step flowsheet used (decladding with hydrogen chloride and release of uranium by fluorination) is presented in Figures 27 and 28. This flowsheet was adapted from one developed by Ramaswami et al [22] at Argonne National Laboratory for uranium-zirconium metal alloy fuel. Fuel elements used in the current study were composed of sintered wafers of enriched uranium dioxide and zirconium dioxide (28 percent and 72 percent, respectively) coated with pyrolytic graphite and distributed in Zircaloy-4 fuel plates.

Decladding. The procedure used in the decladding step was the same as that described by Ramaswami [3]: Hydrogen chloride diluted with nitrogen (50 volume percent) was reacted at 350°C with the fuel which had been charged to the reactor and supported in a fluidized bed of alumina (Figure 27). The product from the decladding operation, zirconium tetrachloride, was collected as a dry solid in a condenser made of Pyrex pipe filled with glass wool. The hydrochlorination reaction was monitored by analyzing the off-gas for hydrogen, using a thermal conductivity cell.

Completion of the hydrochlorination reaction left the oxidewafers intact near the bottom of the fluid bed. No uranium was volatilized from the wafers during hydrochlorination. The carbon coating on the wafers was destroyed by reaction with fluorine during the fluorination step or by an intermediate oxidation step with oxygen (95 volume percent) and hydrogen fluoride (five volume percent) at 400°C.

Fluorination. The procedure developed for the uranium alloy fuel [3] required a stepped increase in temperature and fluorine concentration to avoid loss of uranium to the fluid bed material. Using a similar approach with the current fuel, exposure to fluorine concentrations of 10 to 90 percent at temperatures of 250 to 500°C for a total of six hours, but with only one hour at 90 percent and 500°C, recovered only three percent of the uranium. Increasing the severity of the conditions by using 90 percent fluorine for 5-1/2 hours at 550°C, the most severe conditions allowable with the equipment used, increased uranium recovery to

INC-B-12305

Fig. 27 Flowsheet for decladding of Zircaloy-ZrO₂-UO₂ fuel with HCl.

INC-B-12304

Fig. 28 Flowsheet for volatilization of uranium as UF₄.

61 percent. Longer reaction time at 100 percent fluorine would probably increase the recovery of uranium.

The volatilized uranium hexafluoride was recovered by sorption on sodium fluoride in packed beds. Figure 28 represents a method for final cleanup and recovery of the uranium hexafluoride. Two beds operated at 400°C would sorb fission products while permitting UF_6 to pass; two additional beds operated at 100 and 25°C would sorb the UF_6 . Final purification of the uranium hexafluoride would be by desorption from the sodium fluoride at 400°C and collection in a cold trap.

II. WASTE MANAGEMENT

1. OPERATING EXPERIENCE IN THE IDAHO WASTE CALCINING FACILITY

(G. E. Lohse; Process Engineering Section)

Since initial operation of the WCF in 1963, over 1.5 million gallons of liquid wastes have been reduced to solids. In the second campaign which extended from April 1966 through March 1968, about 1.0 million gallons of waste were calcined to nearly 12,300 cubic feet of solids which are stored in stainless steel bins inside a buried concrete vault. During FY-1968, for the first time anywhere, radioactive zirconium fluoride waste was calcined successfully. In general, operation of the facility was satisfactory.

1.1 Operation with Aluminum-Type Waste

Operation of the WCF with aluminum-type waste was continued from the previous fiscal year until November, then was resumed for about three weeks during March 1968. Operating hours in FY-1968, as shown in Table XVIII, totaled 3,628 during which 287,000 gallons were calcined to 3170 cubic feet of solids. The gross feed rate to the calciner averaged 92.6 gph while the net rate of tank farm depletion averaged 79.5 gph. The average net rate to the calciner was 69.8 gph. The difference between the tank farm depletion and the net rate to the calciner is attributable for the most part to evaporation of the influent in the WCF feed evaporator.

Operation with aluminum waste in FY-1968 was complicated somewhat by a leaking scrubbing-solution-recycle valve. The actual rate of depletion of scrubbing solutions from the surge tank was about 24.8 gph. Therefore, the condensation rate in the scrubbing system equaled this average value. The continuous leakage rate through the closed valve to the feed tanks was 10.9 gph. The remaining 13.9 gph was jetted to the ICPP process equipment waste evaporator for evaporation and returned to the liquid waste tank farm. The solids carryover rate from the calciner cyclone to the scrubbing system averaged about 15 lbs/hr and the solids rate from the calciner to permanent storage bins averaged near 60 lbs/hr. The release rate of ^{90}Sr to the environment averaged 0.1 mCi/day and never exceeded 1.5 mCi/day. The release limit established by the AEC is 2600 mCi/day. The release rate of ^{106}Ru averaged 80.6 mCi/day and reached 2136 mCi/day (one day only) during an unscheduled shutdown in October. The established release limit is 52,000 mCi/day.

During that portion of this year's campaign devoted to aluminum processing, three unscheduled shutdowns, totaling 35 hours, were experienced. All of these were due to the failures of components in the NaK pump electrical circuitry.

1.2 Operation with Zirconium-Type Waste

A substantial portion of the high-level waste generated at ICPP results from the recovery of uranium from zirconium-uranium fuels. These fuels are dissolved in hydrofluoric acid and the resulting solutions are adjusted with aluminum nitrate and chromic acid prior to solvent extraction. Aluminum nitrate along with zirconium and boron (added as a neutron poison) complex

TABLE XVIII

WASTE CALCINING FACILITY OPERATING SUMMARY -- FY-1968

	<u>FY-1968</u>
Total Operating Hours	6,415
Operating Time, hrs	
Aluminum waste	3,628
Zirconium waste	2,328
Nonradioactive feed	105
Downtime	354
Net Volume of waste Calcined, gallons	
Aluminum waste	287,000
Zirconium waste	109,000
Net volume rate to blend tanks, gallons/hr	
Aluminum waste	79.5
Zirconium waste	47.0
Gross liquid rate calcined, gallons/hr	
Aluminum waste	92.6
Zirconium waste	88.7
Net volume solids to storage, ft ³	
Aluminum waste	3,170
Zirconium waste	1,670
Ruthenium release to stack, mCi/day	
Aluminum, maximum-average	2,136 - 80.6
Zirconium, maximum-average	135 - 7.3
Strontium release to stack, mCi/day	
Aluminum, maximum-average	1.5 - 0.1
Zirconium, maximum-average	0.04-0.01

the fluoride ion and minimize corrosion of austenitic stainless steel at low temperatures. At elevated temperatures, the complexes are destroyed and corrosion accelerates rapidly. In the fluidized bed calcination of the fluoride-bearing waste solutions, calcium nitrate is added to at least stoichiometric calcium-to-fluoride ratios to form stable calcium fluoride. Decomposition takes place on the surface of inert bed particles with negligible corrosion to the container walls.

In FY-1968, the WCF was operated for about 2328 hours with zirconium fluoride waste. About 109,000 gallons of waste were reduced to 1670 cubic feet of granular, noncorrosive solids. The gross feed rate (Table XVIII) averaged 88.7 gph while the net feed rate averaged 47.0 gph. The calcium nitrate addition rate averaged 16.4 gph, and the scrubbing solution recycle rate averaged 25.2 gph.

A comprehensive material balance for the WCF was obtained during a stable operating period in February. The concentrations of various substances in various streams are shown in Table XIX. During this period the average raw feed

TABLE XIX
CONCENTRATIONS IN WCF STREAMS [a] DURING CALCINATION OF
ZIRCONIUM FLUORIDE WASTES

	<u>Raw Feed</u>	<u>Calcium Nitrate</u>	<u>Recycle</u>	<u>Gross Feed</u>
Aluminum, <u>M</u>	0.66	0	0.39	0.425
Acid, <u>M</u>	1.53	0	3.72	1.79
Fluoride, <u>M</u>	2.32	0	1.17	0.95
Nitrate, <u>M</u>	2.25	7.8	5.62	4.46
Zirconium, <u>M</u>	0.32	0	0.20	0.09
Calcium, <u>M</u>	0	3.9	0.46	0.68
Undissolved Solids, g/l	0.07	0	28.8	47.5
Total Weight kg/hr	230.0	90.6	125.9	451.6

[a] Listed compositions are for aqueous phase and exclude solids.

rate was 51.6 gph, the calcium nitrate addition rate was 16.6 gph, the scrubbing solution recycle rate was 26.0 gph, and the average gross feed rate was 92.4 gph. The undissolved solids in the blended (gross) feed contained 1.0 percent aluminum, 29.2 percent fluoride, 21.9 percent zirconium, and 20.9 percent calcium. The gross solids rate was 107 lb/hr, the net product rate was 76 lb/hr, and the net rate of solids carryover to the scrubbing system was 31 lb/hr.

Based on radiochemical analyses for ^{137}Cs and ^{106}Ru , the off-gas decontamination factors averaged 2.0×10^8 for particulate matter and 3.6×10^5 for volatile ruthenium species. The release rates to the environment for these two radionuclides averaged 0.02 and 1.6 millicuries/day, respectively.

The concentrations in the ICPP stack effluent were less than those recommended in 10CFR20^[a] for general population exposure.

1.3 Operating Problems

Operation of the WCF was interrupted seven times during FY-1968. Most of these interruptions were of short duration and were due to power outages or to electrical shorts on the NaK pump powerstats. Usually operation was restored within a few hours. However, about two weeks after the start of zirconium waste processing, the feed electromagnetic flowmeters, lined with a vitreous enamel (Albyline), failed and forced a shutdown of about 300 hours. These meters had been in use for approximately 19 months in aluminum-nitric acid waste followed by 13 days in the fluoride-bearing zirconium waste. The latter waste was complexed with 0.55 mole of calcium per mole of total fluoride before being passed through the flowmeters. The meters were removed and inspection revealed general removal of the vitreous enamel linings and/or severe pitting to the Inconel tube which supported the lining. New meters lined with Kynar (poly vinylidene fluoride) were installed to replace the corroded Albyline-lined meters. Performance of the new meters was satisfactory in nearly 1900 hours of subsequent operation with the fluoride-bearing waste. Also, during this shutdown, a failed valve was replaced and one quench pump with a broken oil-lubrication line was removed for repairs.

1.4 Long-Term Effect of NaK on Type 316 Stainless Steel in the WCF Heat Exchanger System

(F. L. Hoffman; Chemistry Section)

Type 316 stainless steel was selected as the material of construction for the vessels and piping in the NaK heat transfer system of the Waste Calcining Facility because of its tensile strength and corrosion resistance to oxidizing atmospheres at elevated temperatures. At the time this choice was made there were no data on the effect of long-term exposure of Type 316 stainless steel in NaK (22.8 percent Na - 78.2 percent K) at elevated temperatures. With more than 28,600 hours operating time on the NaK loop of the WCF, this system has now had more service time at elevated temperatures than any other known operational or test loop, and represents a valuable source of information on the performance of Type 316 stainless steel in NaK. Most of the operating time on this loop has been at 600 to 750°C with 51 starts from room temperature. The oxygen level was maintained below 50 ppm during steady operation of the loop.

As part of the overall program of surveillance on the NaK loop, service tests were made on several fittings, on an electromagnetic pump, and on a portion of the piping. The results showed that mass transfer effects, resulting in the removal of carbon from the hot regions of the loop and the deposition of carbon in the colder regions, are encountered with NaK circulated under nonisothermal conditions in contact with Type 316 stainless steel. Analysis showed that about one mil of decarburization had occurred on the NaK side of the piping that was in the hot region and about five mils of carburization had occurred in the NaK electromagnetic pump tube which was in the colder region of the loop. Sigma phase was present in the cross section of the pipe just beyond the decarburized layer. Tensile tests on the exposed material revealed no significant loss in tensile strength; however, elongation decreased approximately 43 percent at room temperature and approximately 63 percent at

^[a] Federal Register, AEC Rules and Regulations, Title 10, Part 20.

1400°F. The exposed pipe cracked badly during an ASTM A 312 flattening test. In Izod "V" notch tests, the impact resistance of exposed pipe was 65 percent less than that of unexposed pipe. ASTM A 262, boiling nitric acid tests, indicated that the piping was sensitized. At least one of the failures experienced in this system could be directly related to excessive external stress. These changes in mechanical properties are qualitatively consistent with the changes anticipated for Type 316 stainless steel in this service.

Type 316 stainless steel should still be considered as a material of construction for similar installations. A detailed discussion of the results of each of the service evaluations is given in IN-1185 [23].

2. STUDIES SUPPORTING THE CALCINATION OF FLUORIDE-CONTAINING ZIRCONIUM WASTES IN THE WCF

2.1 Repression of Fluoride Volatility During Calcination of Zirconium Wastes (M. W. Wilding, D. W. Rhodes; Chemistry Section)

Zirconium-uranium alloy fuels are dissolved in hydrofluoric acid; consequently, the waste solution contains considerable fluoride. If this fluoride was allowed to volatilize during calcination and pass through the off-gas system, it could cause excessive corrosion of the equipment. To retain this fluoride in the calcined product, calcium as calcium nitrate is added to the calciner feed solution to combine with the fluoride, thus greatly reducing corrosion [2]. Experimental work was done recently using dolomite as an alternate source of alkaline earth metal to repress fluoride volatility.

Presumably dolomite, which is a calcium magnesium carbonate ($\text{CaCO}_3 \cdot \text{MgCO}_3$) and a cheaper source of calcium (and magnesium), will react with the fluoride in the same manner as calcium nitrate. To evaluate this possibility, calcium nitrate and dolomite were tested in similar laboratory experiments using synthetic zirconium fluoride waste.

Test Program and Results. The composition of the synthetic zirconium fluoride waste solution used in these experiments is given in Table XX.

Feed solution was sprayed into a two-inch-diameter fluidized bed calciner simulating, in principle, the WCF. This calciner contained zirconium-type calcine from a previous pilot plant calciner run as a starting bed. Three separate experiments were run using a fresh bed of calcine for each experiment. First, calcium as calcium nitrate solution was added to the zirconium fluoride feed to give 0.5 mole of calcium per mole of fluoride, and the resulting slurry was calcined at 400°C. Second, dolomite dissolved in nitric acid was added to the zirconium fluoride feed to give the same mole ratio (0.5)

TABLE XX

COMPOSITION OF SYNTHETIC
ZIRCONIUM FLUORIDE WASTE

1.6M H	5.4M NO_3
0.4M Zr	1.9 g/l B
2.0M F	0.7 g/l Cr
0.6M Al	<0.1 g/l Sn

of calcium plus magnesium to fluoride and the slurry was calcined at 400°C. In the third experiment, the zirconium fluoride was calcined at 400°C without any calcium or magnesium being added. A finely divided precipitate formed when either dolomite or calcium nitrate was added to the feed mixture. X-ray diffraction analysis of both precipitates indicated that calcium fluozirconate ($\text{CaZrF}_6 \cdot 2\text{H}_2\text{O}$) was the major crystalline constituent.

The off-gas from the calciner was scrubbed with 4M sodium hydroxide; after each experiment the scrubbing solution and final bed material were analyzed for fluoride. Table XXI shows the fluoride distribution in each of these experiments.

TABLE XXI

FLUORIDE DISTRIBUTION IN VOLATILITY EXPERIMENTS COMPARING
CALCIUM NITRATE AND DOLOMITE AS FLUORIDE SUPPRESSANTS

Fluoride: Location Studied	Fluoride Distribution in Three Different Calcine Feed Treatments		
	Calcium Nitrate	Dolomite	No Treatment
Original Calcine bed (g)	30.9	30.9	30.9
Added to Calcine in Liquid Feed (g)	31.6	17.8	17.4
In Off-Gas Scrubbing Solution (g)	0.6	1.0	6.6
In Off-Gas Scrubbing Solution (% of fluoride added in feed)	1.9	5.6	37.9

Although the values in Table XXI suggest that the apparent percentage of fluoride in the off-gas was higher in the presence of dolomite than for calcium nitrate, the variation was within experimental error. The effective repression of fluoride by both materials was clearly evident when compared to the system where neither calcium nor magnesium was added (~ 40 percent of the fluoride fed to the calciner volatilized).

These results suggest that dolomite and calcium nitrate are both effective in retaining fluoride in the calcine.

2.2 Corrosion-Erosion Testing With Synthetic Zirconium Scrubbing Solutions (T. K. Thompson; Development Engineering Section T. L. Hoffman; Chemistry Section)

In anticipation of calcining zirconium-complexed fluoride wastes in the Waste Calcining Facility, a program was undertaken to study the corrosion-erosion behavior of major items of equipment subjected to typical scrubbing solutions. It is well known that nitrate ion passivates austenitic stainless steel and that hydrofluoric acid attacks it. Pilot plant studies have shown that fluoride is present in the scrubbing solution in concentrations of approximately 0.1M.

The presence of fluoride, together with particulate ZrO_2 as undissolved solids, caused concern about possible corrosion-erosion problems due to erosion of the passive oxide film at points of high fluid velocity.

To obtain corrosion-erosion data, a simulated scrubbing system was constructed using stainless steel alloys identical to those in the WCF scrubbing system. The flowsheet of the simulated system is shown in Figure 29. The scrubbing test loop was designed to have fluid velocities in test components the same as those in the plant unit, as it was felt that any corrosion and/or erosion would be a direct function of the fluid velocity through a given piece of equipment. Equipment items specifically selected for corrosion are indicated by callouts A through G in Figure 29; their descriptions and materials of construction are listed in

Fig. 29 Corrosion-erosion test loop flowsheet.

Table XXII. The pump used was a Hazelton, double-volute, vertical-centrifugal slurry pump constructed of Type 316 stainless steel. A comparison of operating parameters for both the test loop and the Waste Calcining Facility is shown in Table XXIII.

TABLE XXII
CORROSION-EROSION SPECIMENS

<u>Figure 29</u> <u>Call Out</u>	<u>Specimen Description</u>
A	Silicon Carbide Spray Nozzle
B	Venturi Flowmeter -- Type 304 stainless steel
C	Control Valve, Double Plug, V Port Plug -- Type 316 stainless steel Seats -- Type 347 stainless steel
D	Concentric Reducer Downstream of Scrubber Types 347, 304, and 304L stainless steel
E	Venturi Scrubber -- Type 304L stainless steel
F	Pump Impeller -- Type 316 stainless steel
G	3/4 in. Ell -- Type 347 stainless steel

The synthetic scrubbing solutions were made by mixing finely divided calcine product (from calciner pilot plant runs with nonradioactive zirconium feed-stocks) and different concentrations of nitric acid. The solution was replaced every 100 hours because of losses due to evaporation. The temperature of the scrubbing solution was kept constant throughout each test by heating the sump tank.

Corrosion-erosion rates, calculated on the basis of weight loss, are shown in Table XXIV. Prior to weighing, each specimen was cleaned with 35 weight percent nitric acid, water rinsed, and air dried.

After 1,257 hours of operation using several concentrations of undissolved solids and fluoride ion in the simulated scrubbing solutions, the corrosion-erosion rates of austenitic stainless steel equipment were found to be acceptable. Types 304, 304L, and 347 stainless steels were generally resistant to the scrubbing solution at 60°C. Recent operation of the WCF supports these observations. Approximately 109,000 gallons of the zirconium-complexed fluoride waste have been calcined in the WCF with only limited evidence of corrosion or erosion in the off-gas scrubbing system.

TABLE XXIII

OPERATING PARAMETERS FOR THE WCF AND TEST LOOP

Parameters	WCF[a]	Test Loop
Scrubbing Solution Flow through Ceramic Spray Nozzle	15.8	15.8
Scrubbing Solution Flow to Venturi Scrubber	2.6 orifice	0.4 orifice
Velocity of Scrubbing Solutions in Orifice at Operating Conditions	17.3 ft/sec	18.3 ft/sec
Air Flow to Venturi Scrubber	710	60
Velocity at Throat of Scrubber at Operating Conditions	245 ft/sec	242 ft/sec
[a] WCF data obtained from <u>ICPP Waste Calcining Facility Safety Analysis Report</u> , IDO-14620, Figure V-3, page V-8.		

2.3 Corrosive Effects of Zirconia Calcine in Storage (C. A. Zimmerman; Chemistry Section)

The first measurements have been made after a one-year exposure of metal specimens to nonradioactive calcine from zirconium process raffinate at 200°C. The start of this long-term corrosion test was described earlier [2]. The results indicated less than one milligram weight change had occurred on the welded two-inch-square specimens of aluminum alloy 6061-T6, Types 304, 304L, 316ELC, 347, and 405 stainless steels, and carbon steel. This amounts to corrosion rates of less than 0.0002 mil per year and suggests that the existing storage bins of Type 304 stainless steel are quite suitable for storage of this calcine, and that several other construction materials may be considered for future storage bins for zirconia calcine. The tests are continuing.

2.4 Analysis of Hazard Associated with a NaK Leak During Calcination of Zirconium Fuel Wastes (C. L. Bendixsen; Process Engineering Section)

Prior to calcination of zirconium fuel liquid wastes in the WCF, an analysis was made of the possible hazard associated with a NaK leak in the calcium vessel. Because of the different composition of these wastes as compared with the aluminum nitrate wastes for which the WCF was originally designed, the possible temperature effects of additional exothermic reactions were investigated. [Section II-2.5, (following) reports the results of laboratory studies on possible reactions of NaK with hot zirconium fuel calcine.] The results of these studies indicate that different effects may be expected but that no undue additional hazards are involved.

TABLE XXIV

CORROSION-EROSION RATE OF VARIOUS EQUIPMENT ITEMS IN SEVERAL SYNTHETIC ZIRCONIUM SCRUB SOLUTIONS

		Operating Period I	Operating Period II		Operating Period III
			Part 1	Part 2	
Operating Time:		463 hours	125 hours	115 hours	554 hours
<u>Scrub Solution Composition:</u>					
Total Solids (g/l)		~ 6	~ 30	~ 92	~ 138
Undissolved Solids (g/l)		0.07	0.08	1.80	14.05
H ⁺ (N ^a)		2.5	4.2	3.5	0.9
NO ₃ (M)		2.5	4.1	5.5	3.8
Zr ⁺² (M)		0.005	0.006	0.200	0.195
Al ⁺³ (M)		0.015	0.017	0.500	0.610
F ⁻ (M)		0.13	0.06	1.00	1.30
Temperature:		29°C	55°C	58°C	60°C
<u>Corrosion-Erosion Specimens:</u>		<u>Observed Corrosion-Erosion Rate (mils per month)</u>			
Silicon Carbide Spray Nozzle	A	0.0	Weight Gain		Weight Gain
Venturi Flowmeter	B	0.1	0.5		0.3
Control Valve	C				
Plug		< 0.1	2.4		0.5
Seats		0.5	0.0		3.8
Concentric Reducer	D	0.0	< 0.1		0.3
Venturi Scrubber	E	0.3	0.4		< 0.1
Pump Impeller	F	0.0	0.9		0.4
3/4" ELL	G	0.0	0.3		0.1

Calculated Temperature Transients. A hazards study on the zirconium feed system is complicated by the presence of zirconium fluoride in the feed solution and of solid calcium fluoride in the calciner fluidized bed. The simplified reactions shown in Table XXV were assumed to predominate after evaluation of available experimental evidence and of the free energy of formation for the reactants and products. For a further simplification of the analysis, each reaction was assumed to proceed instantaneously although each reaction may have several intermediate stages. The heats of reaction per gram mole of reacting NaK are also included in the table.

The reaction of NaK with solid CaF_2 and O_2 to yield the products $(\text{NaK})\text{F}$ and CaO is the most important because it produces the greatest amount of heat and because CaF_2 represents 60 weight percent of the fluidized bed in the calciner. Free energy of formation considerations indicate that this reaction is definitely possible at the calciner operating temperature and pressure, but no experimental data are available as to the kinetics of the reaction. As a worst case analysis, the reaction was assumed to take place.

In the absence of excess NaK, $(\text{NaK})\text{OH}_{(1)}$ was selected as the major product in the NaK-water reaction at temperatures above 300°C . Although formation of $(\text{NaK})_2\text{O}$ may be equally possible, the production of $(\text{NaK})\text{OH}_{(1)}$ releases considerably more heat and again represents a worst-case analysis.

The NaK system normally provides all heat necessary for the endothermic calcination reactions and for sustaining a temperature of 400°C for all materials entering or exiting the vessel. The NaK heating system will stop transferring heat into the calciner bed when (a) the NaK pump ceases to circulate NaK, or (b) the high-temperature alarms attached to the NaK tube bundle in the furnace shut off the oil feed (but not the combustion air). Assuming the NaK pump is operating during any postulated NaK leak, the temperature of the NaK in the loop will rise proportionally with the bed temperature as long as the furnace continues to fire. Eventually, the furnace high-temperature alarms will shut off the oil feed to the furnace (this feature was designed to prevent the NaK temperature from reaching the boiling point, 760°C).

In order to simplify this analysis and also establish the worst possible case, stoppage of the NaK pump was selected as the controlling factor instead of a stoppage of the fuel oil to the furnace. If no remedial action is taken, the NaK pump will cease operation when the NaK surge tank empties and allows helium gas to enter the NaK circulation loop. When helium enters the pump, this changes the inductive field on the pump which overloads the electrical breakers and shuts down the electromagnetic pump.

Four possible NaK leak rates were studied for the case of NaK getting into the WCF while calcining zirconium waste solution:

- (1) For a NaK rate of one gallon per minute, it was assumed that the NaK would react with CaF_2 and O_2 . Since this reaction produces the greatest amount of heat per gram mole of NaK (see Table XXV), this represents the worst possible condition at this leak rate.
- (2) A leak rate of 3.3 gallons per minute is the minimum leak rate which could possibly produce a temperature that could melt

TABLE XXV

SIMPLIFIED REACTIONS BETWEEN NaK AND OXIDIZERS IN THE CALCINER VESSEL

	$\Delta H_r^{[a]}$, cal/g-mole NaK ^[b]
90 gph Zirconium Feed:	
$4 \text{ NaK}_{(l)} + 2 \text{ CaF}_{2(s)} + \text{O}_{2(g)} \longrightarrow 4 (\text{NaK})\text{F}_{(s)} + 2 \text{ CaO}_{(s)}$	-65,850
$5 \text{ NaK}_{(l)} + \text{HNO}_{3(l)} + 2\text{H}_2\text{O}_{(l)} \longrightarrow 5 (\text{NaK})\text{OH}_{(l)} + 1/2 \text{ N}_{2(g)}$	-62,860
$20 \text{ NaK}_{(l)} + \text{ZrF}_{4(s)} + 2 \text{ Ca}(\text{NO}_3)_{2(s)} + 8 \text{ CaF}_{2(s)} \longrightarrow$ $20 (\text{NaK})\text{F}_{(s)} + \text{ZrO}_{2(s)} + 10 \text{ CaO}_{(s)} + 2\text{N}_{2(g)}$	-62,600
$30 \text{ NaK}_{(l)} + 2 \text{ Al}(\text{NO}_3)_3(s) + 15 \text{ CaF}_{2(s)} \longrightarrow$ $30 (\text{NaK})\text{F}_{(s)} + \text{Al}_2\text{O}_{3(s)} + 15 \text{ CaO}_{(s)} + 3\text{N}_{2(g)}$	-60,910
$30 \text{ NaK}_{(l)} + 2\text{AlF}_3(s) + 3 \text{ Ca}(\text{NO}_3)_{2(s)} + 12 \text{ H}_2\text{O}_{(l)} \longrightarrow$ $24 (\text{NaK})\text{OH}_{(l)} + 6 (\text{NaK})\text{F}_{(s)} + \text{Al}_2\text{O}_{3(s)} + 3 \text{ CaO}_{(s)} + 3\text{N}_{2(g)}$	-58,080
$6 \text{ NaK}_{(l)} + 2\text{H}_2\text{O}_{(l)} \longrightarrow 2(\text{NaK})\text{OH}_{(l)} + \text{H}_{2(g)}$	-33,550

[a] All heats of reaction are calculated at 1 atm and 298°K.

[b] One mole of NaK as used in these equations has a "pseudo" molecular weight of 33.8, and contains 0.676 mole of potassium and 0.324 mole of sodium.

the calciner vessel before all available NaK had entered the vessel. For this case, all NaK was assumed to react with CaF_2 and O_2 .

- (3) A NaK leak rate of 11.5 gallons per minute represents the stoichiometric amount of NaK which can produce the highest rate of heat release by reacting with all oxidizers entering the calciner. This leak rate could cause the calciner vessel to reach its melting point in the shortest possible time.
- (4) A NaK leak rate of 147 gallons per minute is equal to the maximum conceivable flow of NaK from a single calciner tube if completely sheared at the tube header. For this case the WCF was assumed to be at normal operating conditions with a four psig helium pressure on the NaK system.

Shown in Figure 30 are calculated temperature transients in the calciner for each of the assumed NaK leak rates. As Figure 30 shows, it may be possible

Fig. 30 Time dependency of calciner vessel temperature as determined by the NaK leak rate.

to reach the melting point of the vessel in approximately 1460 seconds (about 24 minutes). However, it is unlikely that any of the rates of temperature rise can be achieved at their respective leak rates for the following reasons:

- (1) Heat losses by radiation and convection to the surrounding walls and piping, which were neglected in this study, account for 5 to 10 percent of heat produced at a vessel temperature of 400°C. This percentage loss will rise as the vessel temperature rises.
- (2) The leak rate will decrease, as will the rate of heat release, as the amount of available NaK in the expansion tank and

loop decreases; this will lower the liquid head which is a portion of the driving force for the NaK leak.

- (3) All the reactions are complex and time dependent to various degrees (see Section II-2.5). Any delay in the rate of specific reaction and type of products formed will lower the maximum achievable temperature computed in this study.
- (4) Although the NaK heating system was assumed to function normally until helium gas gets into the loop to stop the NaK pump, at low leak rates the high temperature alarms for the NaK tubes in the furnace probably will activate first and shut off the oil feed. If so, within a few minutes the circulating NaK will begin to withdraw heat from the calciner and transfer it to the furnace combustion air which will continue to flow. At leak rates under 2.4 gallons per minute, this action would not allow the vessel temperature to rise above 760°C until the NaK pump stops.
- (5) If the bed temperature in the calciner vessel exceeds 760°C, vaporization of the NaK contained in the bulkheads of the NaK heat exchanger will begin. There are two possible paths of least resistance for the resulting NaK gas to flow: (a) the NaK gas could flow through the leak hole and into the calciner vessel -- this would reduce the NaK leak rate, and slow the temperature rise in the calciner; or (b) the NaK gas will flow back through the circulation system to the NaK expansion tank and the NaK furnace tubes. For all possible leak rates, the oil feed to the furnace and the NaK pump will have ceased before vessel temperature reaches 760°C. As the vaporized NaK reaches the furnace where still-flowing combustion air is cooling the tube bundle, condensation will occur and the condensed gas will flow back toward the calciner to replace other NaK still being vaporized. This heat transfer mechanism will again slow the temperature rise in the calciner.

Several NaK leaks have occurred in the NaK system during calcination of aluminum wastes, and subsequent evaluations have shown that, barring any major physical shock to the system, a leak will begin first as a small (usually a pinhole-sized) weep and will be enlarged by the corrosive action of NaK as it reacts with oxygen on the outer surface of the tube. No internal corrosion other than stress corrosion cracking of pipe walls has been observed with the leaks already experienced. Any accurate estimate of the time needed for a pinhole-sized leak to enlarge to a pencil-hole size (about the size needed to permit a one gpm leak rate) is difficult, but the necessary time is probably on the order of several hours.

Small NaK leaks of one gallon per minute or less will be easily detectable by WCF operators. As shown in Figure 30, a leak rate of one gallon per minute without remedial action will result in a 50°C temperature rise in the calciner in less than six minutes; during this time alarms in the furnace room and in the calciner cell will have sounded.

Consequences of Temperature Transients. Although several conditions, such as normal heat losses, possible decreasing leak rate, failure of the NaK

heating loop, and vaporization of NaK in the heating loop, essentially eliminate any possible melting of the calciner vessel, the hazards of such an event are considered. Three postulated problem areas were analyzed: pressurization of either the off-gas scrubbing system, the calciner vessel, or the calciner cell.

The first case assumed pressurizing the off-gas scrubbing system due to the high temperature (approximately 1300°C) off-gas vaporizing significant amounts of the scrubbing solution. However, an analysis of the system, including the quench tower, venturi scrubber, and scrubbing solution cooler, shows that vaporization will not take place. The overall system has the capability under normal operation to cool off-gas at 1300°C and still remain below the boiling point of the scrubbing solution.

In the next case, it was assumed the calciner vessel might be pressurized because of the high temperature of the off-gas; for this situation, however, the maximum possible pressure is less than 25 psia. At this pressure, if the vessel walls do melt or burst, the bed material will readily flow onto the cell floor. Approximately 60 to 75 percent of the vessel contents will be liquid (due to melted NaK and calcium fluorides) with the remainder being dispersed particles or agglomerates. The liquid portion will solidify as it contacts the air and/or cell floor and form as agglomerates, probably of considerable size.

For the last case, it may be conceived that the gas escaping from the vessel wall may slightly pressurize the cell, thereby forcing air through two outlets, the access door and cell vent system. Calculations show the velocity of the escaping gas will slow to less than 0.25 feet per second before entering the two outlets. Such a velocity, by Stokes law, cannot lift a particle greater in size than 50 microns (assuming a particle density of 2.5 g/cc). Accurate prediction of particle size distribution in a liquid-solid bed at temperatures near 1400°C is impossible, but logically, all unmelted particles having a diameter less than 100 microns will have been elutriated from the calciner vessel by the high velocity off-gas before the vessel melted or burst; thus no small particles would be available for the escaping off-gas to transport to the access corridor or to the vent system.

Conclusions. Based on the preceding logic, on our experience with other NaK leaks, and on supporting calculations, the following conclusions are made:

- (1) Any leak into the calciner vessel will begin in a very small hole. Because of the predicted slow propagation of the small hole and since a leak as small as one gpm will cause a noticeable bed temperature rise, it is concluded that WCF operating personnel will have more than sufficient time to detect the leak and take corrective action before any hazard to equipment or personnel may develop.
- (2) If, as a result of an earthquake or other major catastrophe, a major leak did occur and did lead to a melting of the calciner vessel, the end result would not necessarily cause injury to personnel.

2.5 Effect of NaK on a Heated Bed of Zirconia Calcine

(M. W. Wilding; Chemistry Section)

Prior to the calcination of highly radioactive zirconium type wastes in the WCF, experiments were conducted in a laboratory-scale fluidized bed calciner to determine if certain theoretically possible exothermic reactions of NaK with calcium fluoride and oxygen might occur in a bed of heated calcine, eg, in case of a leak of NaK from a heating tube into the calciner. The zirconium-type waste contains 0.65M aluminum, 1.5M acid, 2.25M nitrate, 2.25M fluoride, and 0.3M zirconium. Calcium nitrate is added to the waste prior to calcination to suppress the volatilization of fluoride during calcination. After calcination, the primary constituents of the solid in the bed are 54 weight percent calcium fluoride, 21 weight percent zirconium oxide, and 22 weight percent alumina. One of the highly exothermic reactions which might occur if NaK leaked into the fluidized bed is:

Several other exothermic reactions can be postulated (Section II-2.4, preceding) which, like the reaction above, depend on the formation of calcium oxide and the alkali metal fluorides for driving force. The current experiments included the addition of NaK to an operating bed under various conditions, and heating the bed containing the NaK to 800°C to simulate a temperature excursion in the WCF.

Combustion of NaK in a Heated Calciner Environment. In the first experiment, seven grams of NaK were encased in a gelatin capsule and added to an operating two-inch-diameter, fluidized bed calciner processing zirconium waste. This NaK ignited immediately when it contacted the hot atmosphere (400°C) of the calciner (≈ 3 seconds after addition of the capsule) and burned with an orange-red flame. The temperature of the bed increased about 25°C, but no increase in the temperature of the vapor space above the bed was observed. Grey smoke, possibly oxides of sodium and potassium, was observed in the off-gas.

In a second experiment, approximately seven grams of NaK were added to a fluidized bed of zirconia calcine at 400°C. No liquid waste feed was being added. An increase in temperature of $\approx 200^\circ\text{C}$ was observed in the chamber above the bed when the NaK was added slowly (≈ 6 to 7 seconds) by means of a pipette; by contrast, an increase of only 50°C was noted when the NaK was added rapidly (≈ 1 second) by the same method. These differences in the observed temperature are not believed to be due to differences in the heat of reaction but rather due to slow response of the thermocouple in the second case. It was also observed that when NaK was added to the fluidized bed without liquid feed being added at the same time, the calcine particles produced were of many different colors. X-ray diffraction and visual analysis of these colored calcined particles indicated the following to be present:

- (1) Reddish pink calcine particles identified as CaF_2 , KAlF_4 , and possibly tetragonal ZrO_2 .
- (2) Light brown conglomerates of calcine particles around the fluidized air ports. These were determined to be CaF_2 and one or more unidentified species.
- (3) Dark brown calcine material identified as CaF_2 , and considerable other material that could not be identified.

- (4) Greenish calcine material which contained principally CaF_2 and tetragonal ZrO_2 .
- (5) White calcine material which contained principally CaF_2 and tetragonal ZrO_2 .

Sodium and Potassium Residue from Combustion of NaK. Chemical analysis of the calcine from the second experiment indicated that considerable amounts of sodium and potassium, in the form of reaction products from the NaK, remained in the bed. Oxides of sodium and potassium were not detected in the calcine bed by X-ray diffraction in any of the experiments, possibly because any that may have formed were below the lower concentration limit for detection by X-ray diffraction or possibly because they were amorphous.

Table XXVI shows the increase in sodium and potassium in the calcine after NaK (78 percent K - 22 percent Na) was added to a fluidized bed of zirconia-type calcine, and the resulting bed later heated to 800°C.

TABLE XXVI

SODIUM AND POTASSIUM IN CALCINE RESULTING FROM
THE ADDITION OF NaK

<u>Element</u>	<u>Sodium or Potassium in Calcine Bed</u>			
	<u>Original (Wt%)</u>	<u>Added (Wt%)</u>	<u>Remaining (Wt%)</u>	<u>% of Total Remaining</u>
Sodium	0.35	0.77	0.89	79.5
Potassium	0.01	2.73	1.20	43.8

Nature of Residual Reaction Products of NaK. Obviously, NaK reacted in the heated fluidized bed causing the thermal effects observed; temperature rises of 25 to 200°C were noted as well as flames and smoke. Based on the free energy of formation for Na_2O and K_2O , Na_2O is the more stable of the two; also, the boiling point is 120°C less for potassium than for sodium. Both the free energy and boiling point difference could partially account for the higher percent of sodium retained in the calcine bed. No KF or NaF was identified in the calcine; however, they also may have been amorphous or below the detection limit for X-ray diffraction and thus not observed.

One crystalline product of the reaction detected by X-ray diffraction was KAlF_4 . The fact that this compound was detected indicated that a considerable amount of the potassium must have been present in this compound, leaving a minimum to form KF. The formation of this compound represents an unexpected chemical reaction in that the relatively inert Al_2O_3 that was present in the bed originally must have reacted with the NaK and a fluoride compound to form an entirely new compound. Although values of the heat and free energy of formation apparently are not available for KAlF_4 , they are available for a similar compound, $\text{AlF}_3 \cdot 3\text{KF}$. The likely reaction to form this compound would be

which would give a ΔF of approximately -70 kcal/g mole of potassium.

Conclusions. These experiments demonstrated that NaK would burn if injected into a bench-scale fluidized bed calciner, but without obviously excessive heat excursions due to certain postulated exothermic reactions. This was especially true in a normally operating system receiving liquid feed. The lack of evidence of the end products of these postulated exothermic reactions is encouraging but not conclusive proof that they failed to occur. However, the detection of a new compound (KAlF_4) suggests that at least a reasonable amount of the potassium was associated with an identifiable compound. The very presence of considerable amounts of residual sodium and potassium in the calcine indicates that an analysis of the WCF bed for either metal is probably a valid method for detecting a very slow NaK leak from a heat exchanger tube, should such a leak develop.

3. STUDY OF CALCINATION USING IN-BED COMBUSTION OF FUEL FOR HEATING

3.1 Pilot Plant Studies of the In-Bed Combustion Process (T. K. Thompson; Development Engineering Section)

The in-bed combustion process has been investigated as a possible means of increasing the capacity of the Waste Calcining Facility and of replacing the liquid metal (NaK) indirect heat transfer system which has been responsible for the majority of the unscheduled shutdowns. The process consists of burning a hydrocarbon fuel in a fluidized bed to supply the heat for the endothermic calcination of fuel reprocessing wastes. The fluidizing velocity is controlled at ≈ 1 ft/sec by using a mixture of air and oxygen for the fluidizing gas. Early work [2] dealt with establishing the basic principles and feasibility of the process. Present studies involve the process as applied to zirconium and aluminum wastes over extended periods. A method was devised to reduce the oxygen consumption to economic permissible levels. Two fuels, kerosene and No. 2 fuel oil, were evaluated as well as further elucidation of the effect of nitrate ion concentration in the feedstock on reducing the stable combustion temperature. A comparison was made of the properties of the calcined solids resulting from use of both in-bed combustion and conventional in-bed resistance heaters.

Equipment. A schematic flowsheet of the equipment used for these studies is shown in Figure 31. The unit is basically the 12-inch-diameter calciner used in earlier work, with the in-bed resistance heaters removed and a two-fluid fuel atomizing nozzle and auxiliary fuel supply system added. Details of the fuel and waste nozzle systems are shown in Figure 32. To date, 618 hours of operating time have been accumulated while calcining both aluminum and zirconium wastes using the in-bed combustion process.

Fuel Atomization with Pure Oxygen. The economics of the in-bed combustion process depend primarily upon the amount of pure oxygen required for proper operation. Effects of atomizing the fuel with pure oxygen were studied to determine if combustion efficiency could be increased (and, hence, oxygen consumption reduced) by producing a more intimate mixture of oxygen and fuel droplets. The atomizing device used was a conventional two-fluid atomizing nozzle (Type 1/4J) made by the Spraying Systems Corporation.

Fig. 31 Flowsheet for 12-inch calciner system.

Fig. 32 Details of spray nozzle systems.

The oxygen requirement for complete combustion of the fuel is based on the oxygen present in the fluidizing and atomizing gases; it does not include the oxygen available from decomposition of nitrates in the waste feedstock. By atomizing the fuel with pure oxygen, as compared with air, the gaseous oxygen required for stable operation and complete combustion of the fuel to CO_2 and H_2O was reduced from ≈ 260 percent to 110 percent of theoretical in the experiment exhibited in Figure 33. Using this technique, the lowest gaseous oxygen consumption rate achieved to date has been 97 percent of the theoretical amount, over an operating period of 33 hours.

Fig. 33 Effect of fuel atomizing gas on gaseous oxygen requirement.

Comparison of Kerosene and No. 2 Fuel Oil. Kerosene and No. 2 fuel oil were investigated as fuels for the in-bed combustion process. The theoretical oxygen consumption per Btu of heat generated is equal for both fuels, as is the off-gas composition. Thermal efficiencies of the in-bed combustion process were 61 percent when using kerosene and 58 percent for No. 2 fuel oil, based on one ratio of the heat required to calcine the waste to the total energy input. This can be compared to efficiencies of ≈ 35 percent using indirect methods of heat transfer.

The Role of Nitrate in the In-Bed Combustion Process. Early studies indicated that the operating temperatures were related to the concentration of nitrate ion in the waste feedstock[2]. These tests were continued using nitric acid as feed with both sand and alumina beds. The data indicate that the operating temperature is independent of bed material, but strongly dependent upon nitrate concentration. The results of these studies are shown in Figure 34.

Removal of particulates in the off-gas is partially accomplished by dry cyclone separation and is completed by scrubbing with nitric acid. With indirect heating of the fluidized bed, the nitrate ion is converted to the oxides of nitrogen (NO_2 , NO , N_2O); these oxides are converted to HNO_3 and maintain

acidity of the aqueous scrubbing solution. On the other hand, with the in-bed combustion process the nitrate is converted to nitrogen and oxygen, and no acid is formed. This necessitates the addition of concentrated HNO_3 to the scrubbing solution to prevent high levels of undissolved solids. A typical off-gas analysis for in-bed combustion is shown in Table XXVII.

Properties of Calcined Solids Obtained Using In-Bed Combustion. The properties of the calcined solids produced by the in-bed combustion process are very similar to those produced with conventional indirect heating. The main exceptions are lower total volatiles, lower nitrate content, and the presence of elemental carbon in the solids produced using the in-bed combustion method of heating. A comparison of the physical and chemical properties for both aluminum and zirconium solids is shown in Table XXVIII.

3.2 Safety Analysis for Operation of the Waste Calcining Facility With an In-Bed Combustion Process (C. L. Bendixsen; Process Engineering Section)

Prior to installation and operation of a proposed in-bed combustion system in the Waste Calcining Facility, an analysis has been made of possible radiological hazards associated with failure of such a system. The safety interlock systems proposed for the new process are deemed adequate to prevent exposure of personnel to hazardous conditions.

The in-bed combustion system, which would replace a liquid NaK heating system at the WCF, is expected both to improve the reliability of the overall calcining process and to increase the overall WCF capacity. In the proposed system, a hydrocarbon fuel is fed directly into the hot fluidized bed where it burns and provides heat for the endothermic calcination process. As a result of this change in method of heating, the leak hazards associated with the existing liquid NaK system would be replaced by possible hazards associated with the formation of explosive fuel-air mixtures inside the processing equipment. Since most of the processing equipment would remain unchanged, only differences in the two heating systems were investigated.

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Fig. 34 Effect of nitric acid concentration on in-bed combustion temperature.

TABLE XXVII

OFF-GAS ANALYSIS WITH
IN-BED COMBUSTION

Component	Concentration (Mole %)
N_2	72.4
O_2	21.2
CO_2	5.3
N_2O	< 0.1
NO	< 0.02
NO_2	< 0.01
CH_4	< 0.02
CO	1.0

TABLE XXVIII

PROPERTIES OF CALCINED SOLIDS

Feed	Component	Conventional Indirect Heating	In-Bed Combustion
Zirconium	Al (wt%)	7.1	7.1
	NO ₃ (wt%)	3.0	0.2
	C (wt%)	---	0.07
	Ca (wt%)	28.0	28.0
	F (wt%)	17.0	17.0
	Zr (wt%)	17.0	17.0
	Total Volatiles (wt %)	3.0	0.5
	Absolute Density (g/cc)	3.2	3.3
	Particle Density (g/cc)	2.2	2.1
	Bulk Density (g/cc)	1.3	1.2
	Attrition Index	70.0	60.0
	Intraparticle Porosity	0.4	0.4
Aluminum	Al (wt%)	46.0	46.0
	NO ₃ (wt%)	4.5	2.2
	C (wt%)	0	0.1
	Total Volatiles	8.1	3.1
	Absolute Density (g/cc)	2.6	2.5
	Particle Density (g/cc)	1.4	1.4
	Bulk Density (g/cc)	0.9	1.0
	Attrition Index	70.0	70.0
	Intraparticle Porosity	0.45	0.41

Although all parts of the new heating system were investigated to identify possible safety hazards, only three areas were found to require an intensive analysis:

- (1) The possible accumulation of an explosive fuel-gas mixture during an upset in normal WCF operation
- (2) Explosion hazards during WCF startup
- (3) Fuel-piping leak hazards.

Occurrence of these hazards is considered very improbable because of the inherent stability of the WCF calcination process as established during five years of successful operation and because of the safety equipment that will

be installed with the in-bed combustion system such as temperature alarms and controls and automatic fuel and oxygen shutoff valves. Hazards of operation for the new system will be less than those for the present NaK heating system. This is due mainly to the elimination of NaK leaks outside the calciner cell in personnel operating areas; leak hazards with hydrocarbon fuel piping are considerably lower.

If it is assumed that a combination of circumstances occurs that will involve (a) a serious upset in normal operation, (b) failure of safety devices, and (c) failure of operating personnel to take proper corrective action, a situation can be postulated that could lead to a fuel-air explosion in the WCF. In this worst conceivable case, rupturing of some process vessels along with other possible equipment damage could occur; even then, however, the WCF shielding and ventilation system would prevent significant release of radioactivity to the environment.

3.3 Corrosion in the In-Bed Combustion Process (C. A. Zimmerman; Chemistry Section)

The combustion of hydrocarbons in the bed of the waste calciner has been proposed as a method of providing heat for the calcination process. The gaseous atmosphere in the calciner vessel will contain carbon monoxide and carbon dioxide. A preliminary laboratory investigation of this system extending over 1200 hours has been made using a synthetic in-bed combustion gas. These tests demonstrated that modest corrosion, primarily in the form of metal dusting, occurs on Type 347 stainless steel at 500 and at 600°C. Recent data indicate that the anticipated operating temperature of the calciner will be 400 to 450°C and further tests will be made in this temperature range.

Experimental Procedure. The laboratory corrosion test was conducted in a synthetic combustion gas (Table XXIX) which closely approximates the average off-gas composition (except for water content) as determined by analysis of pilot plant calciner streams. This gas was passed through a water saturator at 65°C, then over the test specimens for a total exposure period of 1200 hours at 500 and 600°C. The gas flow was maintained at ≈ 1 std cu ft per hour. The test specimens were tensile test specimens (Figure 35) machined from Type 347 stainless steel having the certified analysis shown in Table XXX. Test specimens were exposed by hanging from a stainless steel rack in a 1-1/8-inch-ID stainless steel tube supported vertically in a two-section electric furnace. The specimens were exposed in pairs with one specimen machined parallel and one machined perpendicular to the grain of rolling of the steel sheet. Two pairs of specimens were exposed, one pair at 500°C and the second pair at 600°C.

TABLE XXIX
COMPOSITION OF
SYNTHETIC COMBUSTION GAS

Component	Mole Percent
Nitrogen	75
Oxygen	15
Carbon Dioxide	7.5
Carbon Monoxide	2.5

Fig. 35 Sheet tensile specimen.

The ultimate tensile strength and the yield strength of this particular heat of metal before exposure were found to be slightly higher and the percent elongation slightly lower than the ASM Handbook values for annealed Type 347 stainless steel. The measured values, however, did not change appreciably when the specimens were exposed in the previously described atmosphere at 500 and 600°C, and only a slight difference was associated with the direction of the grain of rolling of the specimens. Weight change of the tensile specimens was not significant.

Experimental Results. Metal dusting corrosion was observed in the laboratory experiment, the attack being more severe on the specimens exposed at 600°C (Figure 36) than on those exposed at 500°C (Figure 37). These photomicrographs show more pitting attack and grain growth, as well as a precipitate at the grain boundaries, in the specimen exposed at 600°C. The loss of metal by pitting is readily observed in the photomicrographs of specimens exposed at both temperatures when these are compared with photomicrographs of the unexposed metal (Figure 38). A black deposit found in the bottom of the test vessel was magnetic and was identified as $\alpha\text{-Fe}_2\text{O}_3$ by X-ray diffraction analysis -- no iron carbides were observed.

TABLE XXX

CERTIFIED ANALYSIS OF TYPE
347 STAINLESS STEEL SPECIMENS

Element	Weight Percent
Carbon	0.052
Manganese	1.91
Phosphorus	0.023
Sulfur	0.009
Silicon	0.70
Molybdenum	0.23
Chromium	18.62
Nickel	10.60
Columbium + Tantalum	0.76
Iron	balance

Fig. 36 Specimen exposed at 600°C showing pitting attack, grain growth, and precipitation at the grain boundaries.

Fig. 37 Specimen exposed at 500°C showing pitting attack.

Fig. 38 Unexposed specimen showing absence of pitting, grain growth, and precipitation at the grain boundaries.

In a simulated aqueous scrub system, corrosion specimens of Types 304 and 347 stainless steel were exposed at 65°C and at room temperature in water through which the gas stream flowed, both upstream and downstream from the heated test vessel. These specimens showed no change in weight after 1200 hours of exposure.

Conclusions. Metal dusting corrosion may be associated with the in-bed combustion process if it is used to heat the WCF, although information available to date indicates that the rate of corrosion is not severe at operating temperatures below 500°C. The extent of this corrosive attack possibly can be controlled by obtaining essentially complete combustion to produce as little carbon monoxide as possible and by operating at conditions such that the metal temperature will not exceed 500°C.

3.4 Effect of In-Bed Combustion Gas on Adsorption of Ruthenium on Silica-Gel (D. W. Rhodes, M. W. Wilding; Chemistry Section)

The NaK heating system presently used in the Waste Calcining Facility may be replaced by an in-bed combustion heating system at some future date. Mixing of fuel combustion gases with decomposition products from waste calcination gives a different off-gas composition from that previously encountered. Consequently, experiments were run to determine how effectively ruthenium is adsorbed by silica gel from the off-gas resulting from in-bed firing of kerosene mixed with oxygen in the WCF. A synthetic gas mixture simulating the expected composition of the off-gas stream, and based on observed compositions of an operating pilot plant calciner, was used; the approximate composition of this gas is shown in Table XXXI.

The feed solution, consisting of either 6.6M or 0.1M nitric acid containing 0.03 grams per liter of ruthenium added as RuCl_3 and spiked with ruthenium-106 to give approximately 5×10^5 d/(min) (ml), were calcined in a static bed laboratory calciner. The combustion off-gas was swept through the calciner, where it was contaminated with ruthenium, and on into a silica-gel bed. The superficial gas velocity through the silica-gel column was approximately five feet per minute in each experiment. A solution of sodium hydroxide (4M) in glass scrubbing towers was used to sample the off-gas downstream from the calciner to determine the amount of ruthenium volatilized and downstream from the silica-gel adsorber to determine the amount not adsorbed by the silica-gel column. The results of these experiments are shown in Table XXXII.

TABLE XXXI

APPROXIMATE COMPOSITION OF OFF-GAS FROM CALCINER HEATED BY IN-BED COMBUSTION OF KEROSENE

	<u>Mole Percent</u>
N_2	75
O_2	15
CO_2	7.5
CO	2.5

TABLE XXXII

BEHAVIOR OF RUTHENIUM IN OFF-GAS FROM CALCINATION

<u>Feed Acidity</u>	<u>Ru Volatilized (% of total in feed)</u>	<u>Ru Adsorbed on SiO_2 Column (% of that volatilized)</u>
0.1M HNO_3	8.2	91
6.6M HNO_3	45.0	97

The results of these experiments are similar to results obtained in earlier experiments using air as the fluidizing gas [24]. They indicate that the adsorption of ruthenium on silica-gel during calcination of a nitric acid type waste in the WCF will be about the same for in-bed combustion as for the present system which uses NaK heating.

4. SUPPORTING STUDIES FOR OTHER POSSIBLE WASTE CALCINING FACILITY IMPROVEMENTS

4.1 Mathematical Model for Predicting Heat Transfer Characteristics of a Bayonet Tube

(B. R. Dickey; Development Engineering Section
C. L. Bendixsen; Process Engineering Section)

Large volumes of liquid waste generated in the processing of spent nuclear fuel elements at the ICPP are being converted to granular solids by fluidized

bed calcination in the Waste Calcining Facility. Heat required for this endothermic process is supplied from high temperature NaK circulating through a tube bundle within the bed.

Future processing requirements dictate an increase in the feed rate to the calciner and an accompanying increase in the quantity of heat supplied to the fluidized bed. Increasing either the flow rate or operating temperature of the NaK is not feasible for mechanical and metallurgical reasons.

The existing tube bundle is constructed of bayonet-type tubes having a central core separated from the surrounding annulus by an argon-filled gas gap, ie, a duplex tube with an argon-filled chamber. Higher temperature NaK flows through the core tube and then reverses flow through the annulus as shown in Figure 39. Any significant heat transfer from the core to annulus (short-circuiting) potentially reduces the rate of heat transfer to the bed.

Fig. 39 Bayonet tube details.

A study has been made to (a) evaluate the quantitative effects of short-circuiting on the heat duty of the existing exchanger, (b) determine if a significant increase in duty could be obtained by minimizing conduction and radiation across the gas gap (eg, operating with a partial vacuum and/or using a low emissivity metal for the tube walls), and (c) calculate any increase in exchanger duty as a result of reversing the flow of NaK within a bayonet tube.

Any mathematical model for predicting the rate of heat transfer from the core to the annulus of a duplex tube and from the tube surface to the fluidized bed must have the capability of (a) predicting radiative and conductive heat transfer across a gas gap and (b) predicting conductive and convective heat transfer from the outer tube surface to the fluidized bed. The calculation of the radiative heat transport across the gas gap separating the core tube from the outer annulus requires that the temperature within the core and annulus of the bayonet tube be approximated by a number of perfectly mixed "cells". If radiation is neglected in the mathematical model, an analytical solution to the resulting differential equations can be obtained. Inclusion of radiation across the gas gap requires the solution of a set of finite difference equations to calculate the NaK temperature leaving the annulus. The following assumptions were used in the proposed mathematical models:

- (1) Negligible heat conduction through the NaK in both radial and axial directions

- (2) Negligible resistance between NaK and tube walls
- (3) Negligible heat transfer from the end of the bayonet tube to the fluidized bed
- (4) Constant heat transfer coefficient between the tube surface and the fluidized bed
- (5) Perfectly mixed fluidized bed with respect to temperature
- (6) Negligible convective heat transfer across the gas gap
- (7) Radiation view factors from a given "cell" in the core tube to the opposite cell in the outer annulus are assumed to be unity.

Each model, the resulting equations, and the calculational procedures are discussed in the following paragraphs.

4.11 Mathematical Models

Perfect Insulation Between Core Tube and Annulus. A mathematical model for the heat transfer process within and from a bayonet tube is shown in Figure 40. For the case of perfect insulation between the core tube and the

Fig. 40 Model for heat transfer from core tube to annulus -- radiation neglected.

annulus, the model reduces to that for predicting the rate of heat transfer to the surrounding medium from a hot fluid flowing in a pipe. Physically, this implies that the temperature of the NaK leaving the core tube is identical to the inlet NaK temperature. The differential equation describing the temperature in the annulus, $T_o(X)$, as a function of distance in the annulus is

$$\frac{dT_o(X)}{dX} + \frac{Ua_o}{WC_p} [T_o(X) - T_B] = 0 \quad (1)$$

with the boundary condition $T_o(L) = T_{in}$. The solution to the boundary value problem given by Equation (1) is

$$\theta(X) = [T_{in} - T_B] \text{EXP} [-U_c (L-X)] \quad (2)$$

where

$$\theta(X) = T_o(X) - T_B .$$

For a specified set of conditions, Equation (2) can be used to compute the maximum amount of heat that can be transferred from a single bayonet tube to the fluidized bed. The heat transferred from a duplex tube to the fluidized bed under actual conditions will be less than that calculated by Equation (2), since heat is short-circuited from the core tube to the annulus by conduction and radiation.

Conduction From Core Tube to Annulus. Within the actual duplex tube, heat can be transferred from the core tube to the outer annulus by a combination of conduction through metal walls and radiation and conduction across the gas gap. For the conditions considered herein, the distance across the gas gap is so small that convection can be considered negligible^[25]. Heat is transferred from the core tube, through a metal wall, across the gas gap by conduction, through a metal wall into the annulus, and finally through a metal wall to the perfectly mixed fluidized bed. The differential equations describing the steady state temperature as a function of distance along the core tube and annulus are derived by making a heat balance around a section of the core tube and annulus; the temperatures within the core tube and annulus are given respectively by Equations (3) and (4) below.

$$T_i(X) = T_{in} e^{-U_c X} + U_c T_o \left[\frac{-U_c e^{-U_c X}}{(S_1 + U_c)(S_2 + U_c)} + \frac{S_1 e^{S_1 X}}{(S_1 + U_c)(S_1 - S_2)} + \frac{S_2 e^{S_2 X}}{(S_2 + U_c)(S_2 - S_1)} \right] + [U_c^2 T_o - U_c^2 T_{in} - U_c U_o T_B] \left[\frac{e^{-U_c X}}{(S_1 + U_c)(S_2 + U_c)} + \frac{e^{S_1 X}}{(S_1 + U_c)(S_1 - S_2)} + \frac{e^{S_2 X}}{(S_2 + U_c)(S_2 - S_1)} \right] - U_c^2 U_o T_B \left[\frac{1}{U_c S_1 S_2} + \frac{e^{-U_c X}}{(-U_c)(S_1 + U_c)(S_2 + U_c)} + \frac{e^{S_1 X}}{S_1(S_1 + U_c)(S_1 - S_2)} + \frac{e^{S_2 X}}{S_2(S_2 + U_c)(S_2 - S_1)} \right] \quad (3)$$

$$T_o(X) = \left[U_c (T_o - T_{in}) - U_o T_B \right] \left[\frac{e^{S_1 X} - e^{S_2 X}}{(S_1 - S_2)} \right] + T_o \left[\frac{S_1 e^{S_1 X} - S_2 e^{S_2 X}}{(S_1 - S_2)} \right] - U_o U_c T_B \left[\frac{1}{S_1 S_2} + \frac{e^{S_1 X}}{S_1(S_1 - S_2)} + \frac{e^{S_2 X}}{S_2(S_2 - S_1)} \right] \quad (4)$$

The temperature of the NaK leaving the bayonet tube, $T_O(o)$, is determined by equating the temperatures $T_1(L)$ and $T_O(L)$ calculated using Equations (3) and (4), respectively. A digital computer program, written in FORTRAN, was used to calculate the unknown temperature, $T_O(o)$, for a specified set of conditions.

Conductive and Radiative Transfer Across the Gas Gap. If radiation across the gas gap is superimposed on the conduction, a system of nonlinear differential equations results. The model from which the differential equations are obtained is identical to the model shown in Figure 40 with the exception that radiation is included. The resulting differential equations are solved by a finite difference approximation, a model of which is shown in Figure 41.

Fig. 41 Model for conductive and radiative heat transfer across the gas gap.

The temperatures within the core and annulus are approximated by considering the tube to be divided into a number of perfectly mixed "cells". Radiation and conduction from the core tube are visualized as occurring from a given "cell" in the core tube to its opposite "cell" in the annulus (eg, cell m to cell n). A heat balance around each "cell" results in the following system of equations describing the temperature at points within the core and annulus.

$$T_1 + \frac{U_R \Delta X}{(1 + U_c \Delta X)} T_1 = \frac{T_{in}}{(1 + U_c \Delta X)} + \frac{U_c \Delta X}{(1 + U_c \Delta X)} T_N + \frac{U_R \Delta X}{(1 + U_c \Delta X)} T_N^4 \quad (5)$$

$$T_m + \left(\frac{U_R \Delta X}{1 + U_c \Delta X} \right) T_m^4 = \frac{T_{m-1}}{(1 + U_c \Delta X)} + \frac{U_c \Delta X}{(1 + U_c \Delta X)} T_n + \frac{U_R \Delta X}{(1 + U_c \Delta X)} T_n^4 \quad (6)$$

$$(m = 2, 3, \dots, M)$$

$$(n = M + 1, \dots, N-1)$$

$$T_{M+1} + \left(\frac{U_R \Delta X}{1 + U_R \Delta X + U_c \Delta X} \right) T_{M+1}^4 = \left(\frac{1 + U_c \Delta X}{1 + U_c \Delta X + U_R \Delta X} \right) T_M^4 + \left(\frac{U_R \Delta X}{1 + U_c \Delta X + U_R \Delta X} \right) T_M^4 + \left(\frac{U_c \Delta X}{1 + U_c \Delta X + U_R \Delta X} \right) T_B^4 \quad (7)$$

$$\begin{aligned}
T_n + \left(\frac{U_r \Delta X}{1 + U_r \Delta X + U_c \Delta X} \right) T_n^4 &= \frac{T_{n-1}}{(1 + U_c \Delta X + U_r \Delta X)} \\
+ \frac{U_c \Delta X}{(1 + U_c \Delta X + U_r \Delta X)} T_m + \left(\frac{U_r \Delta X}{1 + U_c \Delta X + U_r \Delta X} \right) T_m^4 &+ \left(\frac{U_o \Delta X}{1 + U_c \Delta X + U_r \Delta X} \right) T_B \\
(n = M + 2, \dots, N-1) \\
(m = 2, 3, \dots, M-1)
\end{aligned} \tag{8}$$

$$\begin{aligned}
T_N + \left(\frac{U_r \Delta X}{1 + U_r \Delta X + U_c \Delta X} \right) T_N^4 &= \frac{T_{N-1}}{(1 + U_c \Delta X + U_r \Delta X)} \\
+ \frac{U_c \Delta X}{1 + U_c \Delta X + U_r \Delta X} T_1 + \left(\frac{U_r \Delta X}{1 + U_c \Delta X + U_r \Delta X} \right) T_1^4 \\
+ \left(\frac{U_o \Delta X}{(1 + U_c \Delta X + U_r \Delta X)} \right) T_B
\end{aligned} \tag{9}$$

The system of Equations (5) through (9) is solved using the following algorithm:

- (1) The steady state temperature of each "cell" is assumed.
- (2) A new temperature is calculated for each cell using the method of "regula falsi" (false position).
- (3) The new "cell" temperatures are used to calculate new values of the functions on the right hand side of Equations (5) through (9).
- (4) A new set of "cell" temperatures is then calculated and the entire process repeated until convergence is obtained.

Effect of Flow Reversal of NaK on Exchanger Duty. The effect on the outlet NaK temperature of reversing the flow of NaK through the bayonet tube requires consideration of the system shown in Figure 42.

A steady state heat balance between the sections X and X + ΔX (see Figure 40) results in the following equations for the temperatures within the core and the annulus. For the core:

$$T_i(X) = T_o e^{U_c X} - U_c T_{in} \left[\frac{S_3^X}{(S_3 - S_4)} + \frac{S_4^X}{(S_4 - S_3)} \right] \tag{10}$$

$$-U_c U_o T_B \left[\frac{1}{s_3 s_4} + \frac{e^{s_3 X}}{s_3 (s_3 - s_4)} + \frac{e^{s_4 X}}{s_4 (s_4 - s_3)} \right] - U_c^2 T_o \left[\frac{e^{U_c X}}{(U_c - s_3)(U_c - s_4)} + \frac{e^{s_3 X}}{(s_3 - U_c)(s_3 - s_4)} + \frac{e^{s_4 X}}{(s_4 - U_c)(s_4 - s_3)} \right]$$

Heat Transferred To Fluidized Bed

Fig. 42 Model for flow reversal of NaK in the bayonet tube.

For the annulus:

$$T_o(X) = T_{in} \left[\frac{(s_3 - U_c) e^{s_3 X}}{(s_3 - s_4)} + \frac{(s_4 - U_c) e^{s_4 X}}{(s_4 - s_3)} \right] + U_o T_B \left[\frac{-U_c}{s_3 s_4} + \frac{(s_3 - U_c) e^{s_3 X}}{s_3 (s_3 - s_4)} + \frac{(s_4 - U_c) e^{s_4 X}}{s_4 (s_4 - s_3)} \right] + U_c T_o \left[\frac{e^{s_3 X}}{(s_3 - s_4)} + \frac{e^{s_4 X}}{(s_4 - s_3)} \right]$$

where

$$s_3 = \frac{-U_o + (U_o^2 + 4U_c U_o)^{1/2}}{2}$$

$$s_4 = \frac{-U_o - (U_o^2 + 4U_c U_o)^{1/2}}{2} \quad (11)$$

The unknown outlet NaK temperature, $T_i(o)$, leaving the core tube is calculated by equating Equations (10) and (11) evaluated at $X = L$.

4.12 Results. Operating conditions and specifications for the NaK heat exchanger are shown in Table XXXIII. Outlet NaK temperatures for several operating conditions are shown in Table XXXIV. The temperatures, T_o , for

TABLE XXXIII

OPERATING CONDITIONS AND SPECIFICATIONS FOR NaK HEAT EXCHANGER

Inlet NaK Temperature	1320°F
Total NaK Feed Rate to Exchanger	42,000 lbs/hr
Type of Tube	Bayonet
Hot NaK Inlet	To Core Tube
Length of a Tube	52 Inches
Overall Heat Transfer Coefficient from Annulus to Fluidized Bed, U	75 Btu/hr-ft ² -°F
Thermal Conductivity of Metal	10 Btu/hr-ft-°F
Number of Tubes in Bundle	42

TABLE XXXIV

TEMPERATURE OF NaK LEAVING ANNULUS FOR INDICATED CONDITIONS

Resistance to Heat Flow	Thermal Conductivity of Insulating Gap (Btu/hr-ft-°F)	Temperature of NaK Leaving Annulus, T _o (°F)
Perfectly Insulated Core	k _g = 0.0	1061.0
Metal Wall with Argon-filled Gas Gap (existing conditions)	k _m = 10.0, k _g = 0.03	1066.7
Solid Metal Wall	k _m = 10.0	1138.9

the conditions shown represent the extremes between which the outlet temperature varies in an actual bayonet tube. Outlet temperatures for the case of a perfectly insulated core tube and a core tube separated from the annulus by a metal wall and gas gap were calculated using Equations (2) and (3), respectively. The outlet temperature calculated using a gas gap with a thermal conductivity of 0.03 Btu/hr-ft-°F corresponds closely to the present operating conditions.

When radiative transfer across the gas gap was included, finite difference Equations (5) through (9) were required to calculate the temperatures in the core and annulus. The numerical procedure was validated by comparing numerical results with a known analytical solution as shown in Table XXXV.

Based on the conditions specified, the effect of heat transfer from the core to the annulus (short-circuiting) on the exchanger duty is given in Table XXXVI.

The effect of emissivity of the metal walls enclosing the gas gap and of the thermal conductivity of the gas on the outlet NaK temperature, T_o, is shown

TABLE XXXV

AGREEMENT BETWEEN ANALYTICAL AND NUMERICAL TEMPERATURES

$$k = 0.03 \text{ Btu/hr-ft-}^{\circ}\text{F}, \epsilon_m = 0.1$$

Location Within Core (ft)	Temperature ($^{\circ}\text{F}$)		Location Within Annulus (ft)	Temperature ($^{\circ}\text{F}$)	
	Analytical	Numerical		Analytical	Numerical
X = 0.0	1320.0	1320.0	X = 4.3	1319.9	1318.9
0.2	1320.0	1319.9	4.2	1311.6	1310.6
0.4	1320.0	1319.8	4.0	1295.3	1294.4
0.6	1320.0	1319.7	3.8	1279.4	1278.6
0.8	1320.0	1319.7	3.6	1263.9	1263.3
1.0	1320.0	1319.6	3.4	1252.0	1250.4
1.2	1320.0	1319.5	3.2	1241.4	1241.1
1.4	1320.0	1319.4	3.0	1227.1	1226.8
1.6	1320.0	1319.4	2.8	1213.0	1212.9
1.8	1320.0	1319.3	2.6	1199.4	1199.4
2.0	1320.0	1319.3	2.4	1188.1	1186.3
2.2	1319.9	1319.2	2.2	1176.5	1173.6
2.4	1319.9	1319.1	2.0	1166.9	1166.3
2.6	1319.9	1319.1	1.8	1152.5	1150.2
2.8	1319.9	1319.0	1.6	1140.5	1139.4
3.0	1319.9	1319.0	1.4	1130.8	1129.2
3.2	1319.9	1319.0	1.2	1120.6	1120.4
3.4	1319.9	1318.9	1.0	1113.9	1113.8
3.6	1319.9	1318.9	0.8	1100.1	1100.6
3.8	1319.9	1318.9	0.6	1092.2	1093.7
4.0	1319.9	1318.9	0.4	1080.1	1082.5
4.2	1319.9	1318.9	0.2	1071.2	1073.6
4.3	1319.9	1318.9	0.0	1062.4	1064.0

in Figure 43. As expected, the radiative transfer superimposed on the conduction resulted in an increase in the outlet NaK temperatures for a given value of the thermal conductivity of the gas.

For the case of a single metal wall separating the core from the annulus, the NaK temperature along the flow path through the core and annulus is shown in Figure 44. Because of the large rate of heat transfer from the core to the

TABLE XXXVI

EFFECT OF SHORT-CIRCUITING ON EXCHANGER HEAT DUTY

Material Separating Core from Annulus	Calculated Exchanger Duty (Millions Btu/hr)	% Efficiency (based on perfectly insulated core tube)
Plain Metal Wall $k_m = 10 \text{ Btu/hr-ft-}^\circ\text{F}$	1.598	69.4
Metal Walls Separated By Gas Gap $k_g = 0.1 \text{ Btu/hr-ft-}^\circ\text{F}$ $\epsilon_m = 0.6$	2.223	96.8
Metal Walls Separated By Gas Gap ^[a] $k_g = 0.03 \text{ Btu/hr-ft-}^\circ\text{F}$ $\epsilon_m = 0.6$	2.250	97.8
Evacuated Gas Gap $\epsilon_m = 0.1$	2.280	99.2
Perfectly Insulated Core Tube	2.300	--

[a] Present operating conditions.

annulus, the temperature of the NaK passes through a minimum downstream from the inlet to the outer annulus.

4.13 Conclusions

- (1) The maximum rate of heat transfer from the NaK tube bundle to the fluidized bed occurs when the core tube is perfectly insulated from the annulus.
- (2) At the current temperature levels in the NaK exchanger, no significant increase in the overall heat transfer rate to the fluidized bed can be realized by increasing the thermal resistance between the core tube and annulus.
- (3) The exchanger duty is independent of the direction of flow of the NaK through the bayonet tube.

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Fig. 43 Dependence of outlet NaK temperature on emissivity of tube walls and thermal conductivity of gas gap.

Fig. 44 Effect of solid metal wall between core and annulus on the temperature distribution.

4.14 Nomenclature

- a_o = area per foot of outer surface of bayonet tube, ft
 a_{mi} = area per foot of inner surface of air gap, ft
 a_{mo} = area per foot of outer surface of air gap, ft
 a_{m1}, a_{mg}, a_{m2} = log mean area of inner tube wall, gas gap, and outer tube wall, respectively, ft
 C_p = specific heat of NaK, Btu/lb-°F
 d_1, d_g, d_2 = thickness of inner tube wall, gas gap, and outer tube wall respectively, ft
 $\bar{F}$ = the quantity $\frac{0.173}{\frac{1}{\epsilon_m} + \left(\frac{a_{mi}}{a_{mo}}\right)\left(\frac{1}{\epsilon_m}\right)^{-1}}, \frac{\text{Btu}}{\text{hr-ft}^2\text{-}^\circ\text{R}^4}$
 k_m, k_g = thermal conductivities of metal and gas respectively, Btu/hr-ft-°F
 L = length of bayonet tube, ft
 $m, M, MP1, n, N$ = designation of constant temperature cells
 S_1, S_2 = constants in the partial fraction expansion of the Laplace Transform Equations (3) and (4)
 S_3, S_4 = constants in the partial fraction expansion of Laplace Transform Equations (10) and (11)
 $T_i(X), T_o(X)$ = temperature at position X in core tube and annulus, respectively, in °F or °R depending on context
 T_{in}, T_o = inlet and outlet temperature of NaK, respectively, °F
 T_B = temperature of a perfectly mixed fluidized bed, °F
 U_c = the quantity $\frac{1}{WC_p \left[\frac{d_1}{k_m a_{mi}} + \frac{d_g}{k_g a_{mg}} + \frac{d_2}{k_m a_{m2}} \right]}, \text{ft}^{-1}$
 U_o = the quantity $\frac{Ua_o}{WC_p} = \text{ft}^{-1}$
 U_R = the quantity, $\frac{\bar{F} a_{mi}}{WC_p}, \frac{^\circ\text{F}}{\text{ft } ^\circ\text{R}^4}$

U = tube surface to fluidized bed heat transfer coefficient, $\frac{\text{Btu}}{\text{hr-ft}^2 \text{-}^\circ\text{F}}$

W = NaK flow rate, lb/hr

X = distance from inlet of core tube, ft

Greek Letters

Δ = an increment

ϵ_m = emissivity of tube walls

θ = the quantity $[T_o(X) - T_B]$

4.2 Valveless Feed Control for the Calciner (P. E. LaMont; Development Engineering Section)

A stainless steel vortex restrictor [2], patterned from a vortex fluid amplifier, was tested in a mock-up of the WCF feed system. The use of a vortex restrictor was suggested after suspended solids in the waste feed to the calciner plugged control valves. Apparent advantages of this fluidic device were that the restrictor contained no moving parts or sharp edges and required no diversion of process streams. In this unusual application, the control fluid was air to avoid dilution of the controlled waste liquid; normally both streams are the same phase. In pilot plant tests, the vortex restrictor successfully controlled the flow of simulated zirconium slurry for long periods, and no solids ever plugged the device.

Description of Vortex Restrictor. A vortex restrictor was fabricated from 2-1/2-inch Type 304 stainless steel shafting. Figure 45 is a schematic representation of the restrictor, and Figure 46 shows the actual device installed in the test loop. The vortex chamber configuration was made similar to a commercial model; this particular chamber was cylindrical with a diameter of one inch and height of 1/2 inch. The ends of the cylinder were slightly concave. The liquid entered the chamber through a 5/16- x 1/2-inch rectangular port; the control air entered tangentially through two 1/16-inch holes drilled on opposite sides of the chamber wall; the two-phase flow left the chamber through a 1/4-inch hole in the bottom along the chamber axis.

Fig. 45 Cut-away view of vortex restrictor.

Tests in the WCF Feed System Mock-Up. Operation of the vortex restrictor was studied in a test loop (Figure 47) capable of recycling simulated zirconium slurry. The run of pipe from the constant head tank to the reservoir incorporated the essential features of the WCF feed system: equivalent gravity head, welded fittings and sloped pipe, electromagnetic flowmeter (or rotameter),

Fig. 46 Vortex restrictor installed in test stand.

Fig. 47 Mock-up of WCF feed system.

and WCF-size spray nozzle. The nozzle was heated by external electrical heaters to simulate calciner operating temperatures, and a vacuum could be drawn on the reservoir to duplicate calciner pressures. The piping configuration connecting the vortex restrictor to the nozzle was compatible with installation in the WCF.

Vortex Restrictor Performance. Figure 48 is a performance curve giving the flow rate of zirconium slurry as a function of the control air setting. The pressure drop across the vortex is also shown. An increase in the control air rate caused an increase in pressure drop; this resulted in a decrease in the rate at which liquid drained from the constant head tank. The air required to adjust the flow to 30 gph, the nominal feed rate to the WCF, was approximately 2 scfm.

Fig. 48 Vortex restrictor performance curve in mock-up of WCF feed system.

For a given control air setting, the net liquid flow rate remained constant for indefinitely long periods. The instantaneous flow rate varied slightly for two reasons: (a) the air supply pressure cycled with compressor operation and (b) slugging between the vortex and nozzle caused slight flow oscillations. Neither of these effects was great enough to upset the flow rate by more than a few percent, but they account for the point scatter in Figure 48. Although the slight vacuum on the nozzle increased the net head on the liquid, the control air required to set a given liquid flow rate was not significantly affected.

An electromagnetic flowmeter was installed in place of the liquid rotameter to act as a flow-sensing element in a feed back control loop with the vortex restrictor as the final control element. A block diagram of the system is shown in Figure 49. The system held the flow of slurry to 30 gph after a snubber was placed between the controller and control-air valve. The system was not studied extensively since the EM flowmeter life in the acid slurry was limited.

Fig. 49 Block diagram of vortex restrictor feedback control system.

Results of Corrosion-Erosion and Plugging Tests. The loop was operated continuously during a number of five-day periods to accumulate a total of 1169 hours. The pipe connecting the vortex restrictor to the nozzle and the nozzle were heated to determine if drying of slurry inside the pipe would cause plugging.

The vortex restrictor did not show any serious signs of erosion or gross corrosion; however, the inside surfaces were etched. The exact rates of erosion and corrosion could not be determined because of the large weight of the restrictor compared to the weight loss. No dried deposits were observed on the inside of the restrictor, pipe, or nozzle. Although the outside surface temperature of the nozzle and pipe was held at 300°C, the heat flux was probably much less than that available in the WCF. The extra mass of control air helped to cool the mixture entering the nozzle; the mixture temperature was 35°C. The temperature of slurry alone was 16 to 25°C higher at the same liquid flow rate and at the same point in the pipe.

Conclusions. Pilot plant testing of the valveless flow control device is complete. The results indicate that the vortex restrictor can:

- (1) Control the flow of slurry feed to the WCF at any desired rate up to the maximum available flow
- (2) Run for long periods of time on an open-loop control system without plugging or upset

- (3) Allow the spray nozzle to run cooler than at present.

A vortex restrictor similar to that used in these tests will be installed in one feed line to the WCF to compare operation with the presently installed bellows-seal valves.

4.3 Ruthenium Behavior on Stainless Steel Filters

(M. W. Wilding, C. A. Zimmerman; Chemistry Section)

The cyclone used to separate solids from the off-gas stream in the WCF may be replaced by stainless steel filters at some future date. Consequently, the behavior of volatile ruthenium as the off-gas passes through the stainless steel filters and the possible corrosion of the filters in the nitric acid vapors are of interest.

Ruthenium Adsorption on Stainless Steel Filters. Experiments were made to determine if volatile ruthenium in simulated WCF off-gas would condense in the pores of stainless steel filters in the temperature range 300 to 350°C. A synthetic feed solution of 6.6M nitric acid containing 0.03 gram per liter of ruthenium spiked with ruthenium-106 was fed into a small laboratory-scale static bed calciner heated to 400°C. The region around the filter was maintained at 300 to 350°C. The off-gas, after passing through the filter, was passed through a silica-gel adsorber maintained at 80 to 90°C to collect the volatile ruthenium, thence into a caustic (4M NaOH) scrubbing solution. Approximately 99.9 percent of the volatile ruthenium passed through the stainless steel filter, leaving one-tenth of one percent retained on the filter. Ninety-nine percent of this retained ruthenium, along with some finely divided corrosion products from the stainless steel calciner vessel, was easily removed from the filter by lightly brushing the surface and washing with cold water. Based on these results, stainless steel filters can be used in an off-gas cleaning system of the WCF without ruthenium being deposited in a "nonremovable" form.

Corrosion of Stainless Steel Filters. Visual observations and filter weight measurements indicated that corrosion of the filter was insignificant over the 104-hour operating period. The weight of the filter actually increased 0.04 percent because of corrosion products that were filtered from the off-gas stream and were not removed in the cold water wash.

4.4 Volatility of Minor Constituents from Calcine

The granular solids produced from highly radioactive aqueous-wastes in the ICPP Waste Calcining Facility are stored underground in large cylindrical bins. The most recently constructed bins were designed for a maximum center-line temperature of 700°C because of the lack of information on the behavior of fission products at higher temperatures. Knowledge of this behavior could permit an increase in the maximum center-line temperature, thus resulting in lower cost storage facilities.

Earlier studies [2,26] have shown that cesium begins to volatilize and migrate within the solids at temperatures between 700 and 800°C. Ruthenium and the nonradioactive mercuric oxide and nitrates, which are present in the WCF solids as minor constituents, begin to migrate at temperatures below 700°C. Another minor constituent, boron, begins to migrate above 1000°C. Current studies have concentrated on the behavior of mercury because it migrates readily and decomposes to metallic mercury, and on cesium-137, a major contributor of heat generated in the bins during storage.

4.41 Migration of Mercury in Calcine (M. W. Wilding; Chemistry Section)

A long-term laboratory experiment was conducted to study the migration of mercury (as mercuric oxide) along a temperature gradient in alumina calcine at temperatures as high as 700°C. In the study, a 7/8-inch-diameter quartz tube four feet long was filled with nonradioactive alumina calcine containing 3.3 weight percent mercury as mercuric oxide. The tube was positioned vertically in a muffle tube furnace with the ends extending outside the furnace. The center of the tube was maintained at 700°C, and a temperature gradient extending from the center in both directions (700 to 60°C) was maintained in the tube for 365 days.

During the first four hours of heating, an orange and a yellow band became visible in the 180 to 200°C temperature zone, the yellow band being a slightly cooler zone than the orange band. After 60 to 90 days of heating, some metallic mercury became visible in the 75 to 150°C temperature zone, and as this metallic mercury appeared, some fading of orange-yellow bands occurred, indicating a conversion to metallic mercury by a decomposition reaction.

The two colored mercuric oxide bands apparently represent condensation products of the mercuric oxide that volatilized in the hotter zone. The yellow oxide is believed to be more chemically active than the red or orange oxide, probably because it is more finely divided[27]. X-ray diffraction analyses indicate that the orange band is mercuric oxide and that some intermediate mercury phase is present in the yellow band.

Chemical analysis of the calcine revealed that mercuric oxide had migrated almost completely from the 450 to 700°C zone and had concentrated in the lower temperature zones, mostly around 180°C. The quantity that migrated was independent of direction (up or down).

Though relative amounts of mercuric oxide and metallic mercury were not determined, the presence of metallic mercury clearly established that mercury will form within the calcine in the WCF solid storage bins when center-line temperatures are above 500°C. In the present solids storage bins, the wall temperature is considerably less than 180°C; thus, the mercury will remain in the calcine. Because of the high surface tension of mercury, it is unlikely that mercury will move by gravity through the packed bed of calcine.

4.42 Migration of Cesium-137 in Calcine (B. R. Dickey, L. T. Lakey; Development Engineering Section M. W. Wilding; Chemistry Section)

To study movement of cesium-137 during storage, volatility experiments were made using radioactive calcine from the WCF. In these experiments, two grams of radioactive calcine were placed in the closed end of an 11/16-inch-diameter by 16-inch-long alumina tube; the remainder of the tube was filled with non-radioactive calcine. Separate tubes, each filled in this manner, were then heated individually in a tube furnace at 900, 1050, and 1200°C. Intermittently, each tube was removed from the furnace, cooled, and scanned axially for the cesium-137 distribution using a gamma-ray spectrometer system. The scanning system consists of a scintillation crystal placed behind a six-inch lead shield containing a 1/16-inch-diameter collimator slit. The signal from the detector was amplified and supplied to a discriminator to isolate that portion due to cesium-137. The

count rate output of the discriminator was measured with a linear-rate-meter and recorded continuously on a single point recorder. By employing a lathe carriage to move the tube slowly past the collimated slit as shown in Figure 50, a continuous plot representing cesium-137 activity along the tube was obtained.

Fig. 50 Alumina tube mounted on lathe carriage for scanning.

Mathematically, the migration of cesium-137 through the calcine was treated as one-dimensional diffusion, as shown in the sketch below.

A mass balance between the planes X and $X+\Delta X$ at time θ yields the following equation describing the concentration of cesium-137 with position and time:

$$\frac{\partial^2 C}{\partial X^2} = \frac{1}{D_e} \frac{\partial C}{\partial \theta} \quad (12)$$

Boundary conditions:

- (1) $\frac{\partial C}{\partial X}(L, \theta) = 0$
- (2) $\frac{\partial C}{\partial X}(0, \theta) = 0$
- (3) $C(X, 0^+) = C_0, 0 < X < a = 0$
 $C(X, 0^+) = 0, X > a$

Application of the finite cosine transform yields the following expression for the concentration of Cs-137 at any point X and time θ :

$$C(X, \theta) = \left(\frac{aC_0}{L} \right) + \frac{2}{L} \sum_{n=1}^{\infty} \frac{C_0 L}{n\pi} \sin \left(\frac{n\pi a}{L} \right) \cos \left(\frac{n\pi X}{L} \right) e^{-\left(\frac{n\pi}{L} \right)^2 D_e \theta} \quad (13)$$

The total amount of Cs-137 that has diffused past the plane $X=a$ (separating "hot" from "cold" calcine) up to the time, θ , is given by

$$Q_{calc} = - \int_0^{\theta} D_e \frac{\partial C}{\partial X}(a, \theta) A d\theta \quad (14)$$

If the linear relationship between the concentration of Cs-137 and voltage is assumed, the following function can be derived:

$$f(D_e) = \frac{A_a V_a}{A_T} - \frac{2LA}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \sin^2 \left(\frac{n\pi a}{L} \right) \left[1 - e^{-\left(\frac{n\pi}{L} \right)^2 D_e \theta} \right] \quad (15)$$

where

A = cross-sectional area of tube

A_a = area under curve (voltage versus distance) in the region
 $0 < X < a$

A_T = area under curve (voltage versus distance) in the region
 $X > 0$

a = length of zone containing radioactive calcine

C = concentration of Cs-137

C_0 = initial concentration of Cs-137 in the region $0 < x < a$

D_e = effective diffusivity

L = total length of constant temperature zone

n = an integer

V_a = volume of radioactive calcine

Q_{calc} = mass of calcine that has diffused past the plane $X=a$

θ = measured time after start of diffusion.

At any time, θ , values of A_a and A_T are measured experimentally. That value of D_e , which results in $f(D_e) = 0$, yields the effective diffusivity at a given temperature.

The activity profiles obtained with the gamma-ray scanning equipment provide a vivid picture of cesium-137 movement at a given temperature. The profiles obtained for various heating periods at 1050°C are shown in Figure 51. The condensation zone corresponds to a temperature range of 750 to 785°C.

Fig. 51 Migration of Cs-137 activity in alumina tube heated to 1050°C.

The effective diffusivities calculated by the method explained previously range from approximately 10^{-6} ft²/hr at 900°C to 10^{-2} ft²/hr at 1200°C. The variation in calculated diffusivities gives some indication that the structure of the alumina is changing during the heating period. Such a change would result from the transition of the alumina from the amorphous form to the alpha form as has been noted previously above 800°C [2].

5. ADDITIONAL WASTE MANAGEMENT STUDIES

5.1 Treatment of Fuel Storage Basin Water (D. W. Rhodes; Chemistry Section)

Decontamination of the fuel storage basin water (raw water) at the ICPP by the use of mineral bed (clinoptilolite) ion exchange columns has been reported previously [28, 29]. Changes that have been made in the system since that time have materially improved the efficiency of the operation and are reported here.

Previously, the contaminated water was passed through the mineral beds and then released to a seepage pit from which it moved through the lithosphere to the ground water. Since September 1966, the decontaminated water has been recycled to the basin as "makeup" water. Consequently, no radioisotopes have been released to the lithosphere from the ICPP storage basin since that time.

Currently, two 55-gallon steel drums containing clinoptilolite are connected in series to form a column. Two columns are used in parallel. Each drum is used in the bottom position [a] for six months, then in the top position for six months after which a lid is sealed on the drum and its contents are buried with other solid wastes. The mineral in the top drum removes essentially all of the cesium-137 as well as part of the strontium-90; as a result, the top drum must be removed after about six months use to avoid creating a radiation hazard.

Using six cubic feet of clinoptilolite per drum requires a total of about 24 cubic feet per year for the entire unit. At a cost of \$9.00 per cubic foot, the total cost per year for clinoptilolite is about \$216.

During one year's operation about 630,000 gallons of water pass through the columns. The radioisotopes contained in these 630,000 gallons are removed from the water and "fixed" on about 180 gallons of clinoptilolite for a volume reduction of about 3500.

In terms of contamination control, the concentration of cesium-137 in the storage basin water has been reduced from a maximum value of about 2×10^{-3} $\mu\text{Ci/ml}$ to about 7×10^{-4} $\mu\text{Ci/ml}$. The concentration of this radioisotope remained approximately constant throughout the past year, indicating that cesium-137 was entering the water at about the same rate as it was being removed. A considerable amount of fuel was being stored in the basin during this period. The concentration of strontium-90 has been reduced from a maximum value of about 1.6×10^{-3} $\mu\text{Ci/ml}$ to about 1×10^{-4} $\mu\text{Ci/ml}$. In addition to being removed by clinoptilolite, strontium-90 is also adsorbed on dust and other particulate matter in the water that eventually settles to the bottom of the basin.

No increase in the concentration of tritium occurred during the year, indicating that the fuel being stored at present is not releasing any significant quantities of tritium. Presumably, most of the tritium in the basin water was

[a] Details of drum arrangement and stream flow are given in Reference 29, IDO-14657.

leached from old aluminum alloy fuels that had been fabricated using a lithium-containing flux which produced tritium when irradiated. Removal of this type of aluminum fuel for processing in early 1965 apparently did remove the source of tritium; since that time, the concentration of tritium decreased at a rate about equal to the rate at which water was being removed from the basin until September 1966 when recycle of the water was started. After 1966, the rate of decrease appeared to approximate the decay rate of tritium.

Apparently the concentrations of radionuclides are near equilibrium concentration values for the condition where the basin is essentially filled with fuel elements. The concentration of tritium appears to be sufficiently low so that no problems exist at present. The concentration of chemicals in the water and the pH of the water appear to be under satisfactory control for corrosion prevention, and the present method of operating the basin is expected to produce negligible changes in any of the characteristics of the basin water.

5.2 Removal of Mercury from First Cycle Raffinate (N. J. Kertamus; Chemistry Section)

Removal of mercury from first cycle aluminum nitrate-nitric acid raffinate would have two advantages. First, as the alumina calcine produced by calcining first cycle raffinate in the WCF is stored, heat generated by radioactive decay causes mercuric oxide to migrate and concentrate as mercuric oxide and metallic mercury in the cooler zones of the stored calcine (see Section II-4.41). The effect of this concentration of metallic mercury on the long-term storage effects such as corrosion is unknown. Second, mercuric nitrate is a major cost item in the reprocessing of aluminum alloy fuels; thus, removal and recycle of mercury could result in a significant dollar savings.

As a possible means of recovering mercury in first cycle raffinate, survey experiments were made to determine whether mercuric ion could be reduced to metallic mercury by an electric potential, using synthetic solutions that simulated first cycle raffinate. The results of the experiments are shown in Table XXXVII.

TABLE XXXVII

ELECTROLYTIC REDUCTION OF MERCURIC ION
IN FIRST CYCLE RAFFINATE
(Aluminum Nitrate 1.6M; Sodium Nitrate 0.09M)

Feed		Product			
Cathode		SS	SS	Hg	Cu
Acid, M	1.06	1.15	1.02	1.03	1.00
Hg, g/l	5.81	4.84	5.76	5.47	3.15
% Mercury Reduced		16.7	0.9	5.9	45.8
% Electrochemical Reduction		100.0	100.0	100.0	98.3

With a soluble cathode such as copper, a simple displacement reaction as well as an electrochemical reduction was possible. For this reason, the product solution was analyzed for copper ion to determine to what extent this alternative mechanism of mercury reduction had been effective.

The data indicated that in synthetic first cycle raffinate solution, stainless steel cathodes were not effective for reducing mercuric ion, although the reduction obtained was totally electrochemical. The most effective cathode was copper in one molar acid solutions. This electrode reduced the concentration of mercuric ion from 5.8 to 3.1 grams per liter, representing a decrease in the concentration of the mercuric ion of 46 percent. Based on the concentration of copper ion in solution, 98 percent of the mercuric ion that was reduced to mercury was reduced by an electrochemical mechanism.

These data indicate that it may be technically feasible to recover mercury from first cycle raffinate by electrochemical means.

III. REACTOR TECHNOLOGY SUPPORT

1. LOFT ASSISTANCE PROGRAM

The Chemical Technology Branch is conducting several development studies under subcontract to Phillips Petroleum Company in support of the Loss-of-Fluid Test (LOFT) at the National Reactor Testing Station. The LOFT project is the field simulation of a loss-of-coolant accident for a pressurized water-cooled reactor. Originally, the program consisted of releasing the coolant deliberately from a 50 MW pressurized water reactor, thus permitting the fuel core to melt and release fission products into the reactor shell and containment building. Subsequently, the LOFT program has been changed to emphasize the testing of core cooling systems and other engineered safeguards.

The specific development studies undertaken by this Branch include: (a) the evaluation of surface coatings and sealants for the interior of the containment shell; (b) the development of procedures for decontamination of the facility; (c) the development of a continuous fission product sampler for the containment atmosphere; (d) the evaluation of plateout and auxiliary samplers; and (e) the design, construction, and operation of a fission product generation and containment unit for conducting the preceding studies, as well as to provide general support for the LOFT program. Progress in each of these areas is reported in the following sections. Additional LOFT support studies in the areas of sampling and sample analysis are being performed by the Analytical Chemistry Branch at the ICPP [30] in close collaboration with the studies being performed by the Chemical Technology Branch.

1.1 Applicability of Conventional Protective Coatings to Reactor Containment Buildings

(B. J. Newby, T. L. Evans; Chemistry Section)

Studies were performed to select commercially available coatings suitable for application on the interior surfaces of pressurized water or boiling water reactor containment buildings with special emphasis on the conditions present during a loss-of-coolant accident. A summary of the principal results, reported here, is taken from a detailed description of the studies as reported in IN-1169 [31]. In these studies, most conditions for testing coatings were selected with respect to an unperturbed nuclear accident in a small power reactor; however, the results would be directly applicable to any nuclear installation where contamination with volatile fission products is possible, including large power reactors protected by emergency core cooling systems.

Commercially available, conventional protective coatings lack one very important characteristic desirable in coatings to be applied to the interior surfaces of reactor containment buildings. These coatings are difficult to decontaminate by conventional techniques when contaminated by volatile fission products. However, a number of these coatings possess, with slight compromise, the other characteristics desirable in coatings to be used in pressurized or boiling water reactor containment buildings:

- (1) They are satisfactorily resistant to decontaminating reagents, pressurized steam, beta-gamma radiation, and abrasion

- (2) When containing glass fabric, they can satisfactorily contract and expand over substrates containing expansion joints without cracking, peeling, or losing adhesion.

For application over steel, commercially available organic primers were tested and found to be:

- (1) Compatible with a variety of finish coats
- (2) Age resistant for over a year, prior to being covered with a finish coat, without adverse effects
- (3) Satisfactorily resistant to pressurized steam, chemical reagents, and radiation when not covered with a finish coat.

In these characteristics, the organic primers tested are as good as, or superior to, the inorganic primers conventionally used by industry for protecting steel.

Coatings on the interior surfaces of reactor containment buildings would provide an iodine sink in case of release of iodine vapor, and would decrease the quantity of iodine available for release from the building to the atmosphere. Some of the coatings tested sorb much more iodine than others at atmospheric pressure and lower temperatures; however, this difference decreases as the pressure and temperature of the contaminating atmosphere become higher. In general, coatings could not be decontaminated from volatile fission product iodine by using high pressure sprays of decontaminating reagents for a reasonable period of time unless the sorption of this fission product was predominantly on particulate matter in the contaminating atmosphere. If containment buildings contained a device that would release particulates simultaneously with fission product release, the coated surfaces inside the building could probably be decontaminated more rapidly and effectively since more iodine would sorb on the particulates. Conventional coatings in containment buildings lacking such a device could be decontaminated by two different methods:

- (1) Removal of part of the contamination by spraying for a short time with high pressure sprays of decontaminating reagents, and obtaining the additional decontamination needed by allowing the relatively short-lived iodine-131 to decay for the appropriate time period
- (2) With careful selection of coatings, the noniodine fission products could be removed by spraying for a short time with high pressure sprays, and the iodine by treatment with high pressure steam for several days.

1.2 Contamination-Decontamination Experiment

(L. T. Lakey, D. E. Black, W. A. Freeby, W. P. Palica; Reactor Safety Studies Section)

The Contamination-Decontamination Experiment (CDE) was installed to augment the Loss-of-Fluid Test Support Studies being conducted at the ICPP for Phillips Petroleum Company. In the CDE, high-level fission product aerosols are produced under conditions simulating those anticipated in the LOFT. The fission product aerosol is generated by melting a small, highly irradiated, short-cooled fuel capsule in the presence of steam, using a radio-frequency induction furnace. The fission products released are transported by

the steam to an 86 ft³ containment vessel in which conditions are controlled to simulate anticipated LOFT conditions. These fission product aerosols are used in studies of contamination and decontamination of various protective coatings and equipment, in testing of various LOFT sampling devices, and for the development of analytical methods for analysis of LOFT samples.

Five tests using irradiated fuel pins have been made in the CDE to date. Contamination of coupons for coating and decontamination studies were emphasized in the first two runs; emphasis was shifted to testing of the LOFT plateout and gas-particulate capsule samplers in the third, fourth, and fifth runs. The fifth test was conducted during August 1967.

Two xenon and two iodine tracer tests were also conducted in the CDE during the current fiscal year. The major objective of these tests was to determine the sampling accuracy of the Continuous Sampler-Monitor (CSM) for these species. Tracer Tests 1 and 2 (xenon) were conducted in February 1968; Tracer Tests 3 and 4 (iodine) were conducted in March and April.

The primary objective of the originally planned LOFT was to characterize a "maximum credible accident" unperturbed by the use of any engineered safeguard systems; however, the unlikelihood of such an accident, and the immediate need for evaluating core cooling safeguard systems, resulted in replacing the original LOFT with a test series to evaluate the performance of emergency core cooling and other safeguard systems. Future work conducted in the CDE will be oriented in this direction.

A report, IN-1172[32], describes the CDE and reviews the information on fission product behavior obtained during the support studies for the original LOFT program. A summary of the information included in this report is given in the following sections.

1.21 Operation and Meltdown. The principal operating conditions for CDE Runs 1 through 5 are presented in Table XXXVIII. Fuel pin meltdown was characterized by an initial rapid release of activity followed by a slower release over the remaining part of the melting period. Examination of the residues from the meltdowns of irradiated fuel pins showed the cladding had formed a friable shell of ZrO₂ where the Zircaloy-clad fuel pin was exposed to the steam atmosphere; however, the uranium core and that part of the cladding shielded from steam were completely melted. A uranium-zirconium alloy, in the form of metallic inclusions, was found in the cladding-UO₂ boundary region. Residue from a typical meltdown is shown in Figure 52.

1.22 Fission Product Behavior. The percentages of the various fission product nuclides released from the fuel pins during meltdown agree relatively well between the five runs. Releases of iodine (15 to 44 percent) in the CDE compare well with releases obtained by Collins and Hillary [33] but were lower than releases reported from a test conducted at ORNL [34] using a steam-air atmosphere. Releases of strontium in the CDE were higher than at ORNL, but releases of tellurium were lower. Releases of Sr-89, Zr-Nb-95, Ru-103, Ba-140, and uranium in the CDE ranged up to 0.7 percent of the fuel pin inventories. The minimum and maximum releases of Mo-99, I-131, Te-132, and Cs-137 were 2.5-8, 15-44, 7-22, and 3-21 percent, respectively. Release of the noble gases, krypton and xenon, determined in Run 4 only, indicated that 86 and 89 percent, respectively, of these gases were released.

TABLE XXXVIII

CDE IRRADIATION AND MELTDOWN CONDITIONS

	<u>Run-1</u>	<u>Run-2</u>	<u>Run-3</u>	<u>Run-4</u>	<u>Run-5</u>
Irradiation Level, nvt	1.55×10^{20}	4.85×10^{19}	1.79×10^{19}	1.27×10^{19}	1.18×10^{19}
Irradiation Time, days	34.4	16.3	30.4	18.5	16.0
Fuel Pin Enrichment, percent	1.5	8	8	8	8
Fuel Pin Fission Heat Generation, kW	2.53	8.65	1.70	1.90	2.02
Total Activity Present at Reactor Shutdown, Curies	10,600	32,250	7,100	7,800	8,200
Total Activity Present at Meltdown, Curies	1,600	6,940	1,700	1,580	1,670
Cooling Time[a], hr	30.8	10.5	7	9.75	9.0
Fuel Burnup, Mwd/tonne	1,200	2,000	740	530	460
Time from Beginning of Heating Until Fuel Pin Initially Melted, min	23	5	4	7	34
Time Fuel Pin Held Molten, min	44	26	20	25	23
Steam Transport Gas Velocity Over Fuel Pin, ft/sec	1.4	1.7	1.8	1.6	1.3
Steam Pressure in Furnace, psig	0	22	22	22	22
Composition of Containment Atmos.	36% Air ^[b] 64% Steam	36% Air 64% Steam	50% Air 50% Steam	50% Air 50% Steam	50% Air 50% Steam

[a] Time from reactor shutdown to start of fuel pin meltdown

[b] 100% steam during meltdown -- air and steam added after meltdown to achieve 36% air and 64% steam at 22 psig

Fig. 52 Photograph of fuel pin following typical meltdown in the CDE.

The fission product accountabilities, particularly of the nonvolatile fission products, showed a general improvement with each succeeding run. Essentially all the activities of the nonvolatile nuclides are now being accounted for; however, the accountabilities of the volatile nuclides (greater than 15 percent release from the fuel) I-131, Te-132, and Cs-137 are lower than desired. Plateout in sampling lines, counting errors due to sample geometry, and nonuniform dispersion of solids in liquid samples are believed to be the major causes of the low accountabilities. Efforts to improve the accountabilities are continuing.

The release data of the principal fission products, other than the noble gases, show iodine, tellurium, cesium, and molybdenum to be the more volatile fission products. Significant fractions of both the volatile and nonvolatile fission products released from the fuel deposited in the CDE transport line. A large percentage (30 to 75 percent) of the fission products transported to the containment vessel are found in the containment condensate with the remaining fractions being found deposited on surfaces within the containment.

1.23 Aerosol Composition and Concentration. During "cold" fuel pin meltdowns in the CDE, the aerosol was found to contain tin, uranium, silicon, and zirconium, with tin (from the Zircaloy cladding) being the major constituent of the aerosol. The air-borne half-time of tin, based on samples taken 5 minutes and 65 minutes after meltdown, was observed to be approximately one hour. Particle size measurements, taken during "cold" runs, showed particles and agglomerates of particles with diameters ranging from 0.001 to 0.7 μ .

Mass spectrometric analyses of the furnace atmosphere during the Run 5 meltdown showed a depletion of oxygen and a buildup of hydrogen -- evidence that a metal-water reaction was occurring.

Hydrocarbon analyses of the containment atmosphere following a fuel pin meltdown, compared to background analyses without a meltdown, indicate that

UO₂ fuel is a possible source of organics which could contribute to the formation of organic iodides.

The nuclides contributing most of the fission product activity in the CDE atmosphere are I-131, Te-I-132, and Mo-Tc-99. Ratios of the activities of the various nuclides in the containment atmosphere at 30 minutes following meltdown to the activities 24 hours following meltdown indicate that all the nuclides for which analyses were made, except iodine and noble gases, were present in the same form, probably particulate. Preliminary results of two iodine tracer tests show that the air-borne half-time of iodine shortly after release in the CDE containment atmosphere is approximately 3-1/2 minutes. The organic iodides constitute from 0.5 to 2 percent of the total radioactive iodine inventory in the fuel, as indicated by differentiation of the iodine forms in the Maypack samplers and by analyses of atmosphere samples by vapor-phase chromatography.

Results of two xenon tracer tests in the CDE containment vessel show that xenon concentration in the atmosphere remains essentially constant during the 5- to 8-hour cooling period following injection of the xenon. Thus, the loss of xenon to the condensate is low; this was substantiated by the low concentrations of xenon in the condensate, which check existing solubility data for xenon.

1.24 Fission Product Deposition. Nuclides of iodine, tellurium, and molybdenum represented the major activities found deposited on the interior of the containment vessel. The uniformity of fission product deposition was influenced heavily by particulates and by condensate flow over the surfaces. Painted surfaces, scanned by gamma-ray spectrometry using a 1/16-inch collimated beam, showed maximum variations of up to five in the noniodine activities. These variations dropped to 2-1/2 when the sample area counted was increased to greater than 5 cm². The iodine deposition is more uniform, showing maximum variations of two whether counted with the 1/16-inch collimated beam or when examining the larger areas. This indicates that only a small fraction of the iodine is associated with particulates. Radiographs of stainless steel and painted surfaces contaminated in the CDE showed that condensate flowing over a surface affects the uniformity of deposition; however, no gross variation in deposition was found from top to bottom of a four-foot-long stainless steel panel over which condensate was flowing.

The level of activity deposited on surfaces in the containment vessel was dependent upon several variables -- surface orientation, material, condensation, and temperature. Surfaces facing up were found to have iodine activity up to two times and particulate activities up to 23 times the comparable activities on surfaces facing down or to the side. Comparisons of washed and unwashed deposition coupons showed that the additional activity (presumably fallout) on the surface facing up was not bound tightly to the surface.

Studies of fission product retention (fission products not easily removed by a water rinse) on six materials contaminated in the CDE showed that the retention of iodine was highest for stainless steel, followed in order of decreasing retention by aluminum, Kynar, Kel-F, Teflon, and glass. Teflon showed the lowest retention of the particulate fission products, tellurium and molybdenum. Activity levels, both iodine and particulate, on painted coupons were greater (up to factors of six) than those on stainless steel coupons contaminated in the same test.

Condensation promotes the deposition of all fission products except noble gases on both painted and stainless steel surfaces. Over the temperature range (150 to 250°F) of the CDE tests, deposition of particulates appears to decrease with increasing temperature on common materials. Temperature appeared to have little effect on iodine deposition on stainless steel surfaces without condensation; on noncondensing painted surfaces, iodine deposition increased markedly at temperatures above the softening point of the paint.

1.25 Decontamination of the CDE. Though decontamination of the CDE is done primarily to permit reuse of the facility, it does provide an opportunity to obtain practical experience on the relative effectiveness of decontamination agents and to test equipment and procedures on a large scale. From experience gained in the five CDE runs, a decontamination method has evolved consisting of (a) spraying the containment vessel and cell interior with an alkaline permanganate solution followed by an oxalic-citrate solution, using the vessel and cell sprays, until radiation levels are low enough for personnel entry; (b) entering the cell and washing equipment and walls using a portable decontamination unit; and (c) completing the cleanup by mopping, brushing, etc. This procedure has proved effective in reducing general radiation levels in the cell from approximately 100 R/hr to less than 1 mR/hr in a week.

1.3 Evaluation of the LOFT Plateout Capsule Sampler

(W. A. Freeby, D. P. Wright; Reactor Safety Studies Section)

Evaluation of the LOFT plateout capsule sampler -- a spherical, remotely removable, fission product deposition sampler developed for the original Loss-of-Fluid Test (LOFT) -- has been terminated, and a report, IN-1204[35], is being prepared. The results of the radiological testing of the capsule sampler are summarized here.

The LOFT plateout capsule samplers were tested in the Contamination-Decontamination Experiment, Runs 2, 3, 4, and 5, where environmental conditions closely simulated those expected in the LOFT experiment. During the LOFT test, these capsules were to be used to obtain data describing the time-dependent deposition of fission products on the containment wall. The objective of radiological testing of the capsules in the CDE facility was to determine if the plateout data obtained from the capsules reproduced the plateout on the vessel wall. Several special plateout samplers were designed and installed for the CDE tests to supplement the data taken from the LOFT capsules.

The results of the plateout studies in the CDE show that the LOFT plateout capsule is a reliable sampling device. Operation, disassembly, decontamination, and analysis do not present any serious problems. However, fission product deposition is dependent upon the sampling environment. Since the sampler will not be at the same temperature, location, and orientation, and will not be subjected to the same condensate flow as the wall, plateout on the sampler will differ from that on the wall. Additional testing with improved simulation of the LOFT conditions is needed to completely evaluate the effect of sampling environment on the LOFT plateout sampler. Specific results of the plateout studies performed in the CDE to date include:

- (1) Both the particulate nature of the deposited activity and the flow of condensate affect the uniformity of deposition. Deposition coupons the size of the LOFT coupons show variations in activity levels (particulate and iodine) up to factors of two. Tho

average variation between coupons from the same capsule is only ± 16 percent, however.

- (2) Deposition on an epoxy paint (Amercoat-66) applied over concrete, carbon steel, and stainless steel surfaces was similar, showing that the base material has no significant effect on deposition.
- (3) Iodine and particulate activities deposited on the LOFT coupons facing up were greater than comparable activities on coupons facing sideways or down by factors up to 2 and 23, respectively.
- (4) Use of Teflon, aluminum, and stainless steel as the material of construction for the sample coupon housing did not affect deposition.
- (5) Cross-contamination during disassembly of the capsule and packaging of the coupons does not appear to be a serious problem.
- (6) Storage of the sampler for periods up to seven days prior to analysis of the activity does not affect the validity of the deposition data.
- (7) Use of a rubber gasket to seal the coupon surfaces after closure of the sampler does not affect the validity of the deposition data.

1.4 Development of a Continuous Sampler-Monitor

(R. E. Schindler, R. L. Nebeker; Reactor Safety Studies Section)

A Continuous Sampler-Monitor is being developed to determine the fission product concentrations in the containment building atmosphere during the Loss-of-Fluid Test. The CSM uses a scrubber located in the containment building to continuously sample the atmosphere and to separate the contained fission products into a liquid and a gas stream. These streams flow through the containment wall to radiation monitors and a sample station located outside the building. The scrubber is located in the containment atmosphere to minimize fission product plateout in long sampling lines. The scrubber washes most of the iodine and particulate fission products out of the containment atmosphere sample into a liquid stream, leaving essentially only xenon, krypton, and organic iodides in the gas stream. After leaving the containment building, the separated streams are monitored individually for the gross levels of iodine and noble gas activity, and are sampled to determine the concentrations of individual isotopes.

Previous testing [2] of the CSM in the laboratory and in the CDE has shown that the scrubber efficiently removes elemental iodine and particulates greater than 0.2μ from the gas stream. Testing of the CSM has been continued in CDE Runs 4 and 5 and in two tracer runs using Xe-133. The results of this testing are discussed in the following paragraphs.

1.41 CDE Tests with Fuel Pin Meltdown. The CSM was tested in CDE Runs 4 and 5 (Section III-1.2) for the purpose of evaluating its performance under simulated LOFT conditions. During the CDE runs, an irradiated fuel pin was melted in a steam atmosphere to release fission products mixed with cladding fumes in a manner simulating the release expected during an unperturbed LOFT meltdown.

The released fission products flowed into a containment vessel containing an air-steam mixture similar to the anticipated LOFT atmosphere, thus providing a test atmosphere simulating that expected from an unperturbed LOFT meltdown.

Equipment and Procedure. The CSM test apparatus used in the CDE Runs 4 and 5 differed by the addition, after Run 4, of two gross gamma monitors, a mass flow recorder, and a condenser on the gas line. A simplified schematic flowsheet of the apparatus used in CDE Run 5 is shown in Figure 53. A two-nozzle scrubber, shown in Figure 54, was used in both tests. The atmosphere sample entered the Teflon scrubber through a sloping hole in the lower part of the wall, then passed upward through two spray cones, and exited through the top.

Fig. 53 CSM flowsheet for CDE Run 5.

The gas flow through the scrubber was controlled at constant atmospheric sampling rates of 200 std ml of air/min in Run 4 and 175 std ml of air/min during Run 5. A constant liquid spray rate of 200 ml/min was maintained in both runs by operating the spray nozzles at the same pressure -- 500 psi. The discharge of scrubbing solution from the scrubber was controlled to maintain a steady liquid level -- by a control valve during CDE Run 4 and by a variable speed pump during CDE Run 5. The concentrations of individual isotopes were determined in both the gas and liquid streams.

CSM operation covered the early part of CDE Run 5 and the middle and end of CDE Run 4. In CDE Run 4, the CSM was not started until two hours after meltdown because of a temporary malfunction of the scrubbing solution discharge

system. After starting, it was operated for five hours, then shut down temporarily to prevent depletion of the CDE containment atmosphere, and finally restarted 24 hours after meltdown for a final set of samples. In CDE Run 5, the CSM operated for the first three hours of the run before stopping when a pump failed. Subsequently modifications corrected both problems. The CSM scrubbing solution was changed from a 0.5M NaOH-0.5M Na₂S₂O₃ mixture in Run 4 to a 0.5M NaOH solution in Run 5.

Results. The most meaningful results obtained from the CSM during CDE Runs 4 and 5 are qualitative observations on the performance of the scrubber and other components. All observations and conclusions are based on limited data and must be considered tentative until additional tests can be conducted.

A comparison of the total quantities of iodine and particulate fission products collected in the CSM gas line during the two CDE runs indicates that large quantities of fission products penetrated the CSM scrubber only during the initial fission product release. In CDE Run 5, in which the CSM sampled the CDE atmosphere during the first three hours of the run, gross quantities of I-131 and Te-132 were found in the gas line and filter system. During CDE Run 4, in which the CSM sampling was started two hours after meltdown, the total quantity of iodine found in the gas filter and line was less than 0.01 percent of the estimated scrubber input. Since the two meltdowns were conducted under similar conditions, the difference in scrubber performance during the two runs can be attributed to the different periods during which the scrubber was operating. The forms of iodine and tellurium which penetrated the CSM scrubber in copious quantity during the first three hours of CDE Run 5 -- probably as fine particulates -- were not present in significant quantities during the period of CDE Run 4 in which the CSM operated.

Fig. 54 CSM scrubber.

The low quantities of iodine penetrating the CSM scrubber during CDE Run 4 indicate that the organic iodide concentrations during CDE Run 4 were very low. Previous scrubbing tests [2] have shown that the CSM scrubber is a relatively inefficient organic iodide scrubber through which most of the methyl iodide in a gas sample penetrates. However, no iodine was detected in a bed of impregnated charcoal placed in the gas filter system to collect all the organic iodides which passed through the scrubber in the gas stream during the entire run. This could happen only if the CDE vessel contained very low concentrations of organic iodides.

Deposition of fission products in the CSM liquid lines does not appear to be a serious problem. The total deposition in the liquid lines was estimated from the analysis of tubing samples taken after the run. During CDE Run 5, it amounted to 2 percent of the Te-132 and less than 0.4 percent of the I-131 that passed through the lines. Deposition in the liquid lines was less in CDE Run 4 than in Run 5.

Conclusions. The following conclusions reached in testing the CSM during CDE Runs 4 and 5 are of a tentative nature because they are based on only a small amount of data:

- (1) Iodine and particulate fission products penetrated the CSM scrubber in gross quantities during the period immediately after meltdown.
- (2) The CSM scrubber effectively scrubbed all the forms of iodine and particulate fission products air-borne two hours or more after meltdown.
- (3) The organic iodide concentrations during CDE Run 4 were very low.
- (4) Fission product deposition in the liquid lines amounted to only a small fraction of the total quantities of fission products flowing through the lines.

1.42 CDE Tests with Tracer-Level Xenon. A primary objective of the CSM is the accurate sampling and monitoring of air-borne noble gases in the LOFT containment building during the LOFT tests. However, samples of the CSM gas stream taken during CDE Runs 4 and 5 contained xenon concentrations which were lower than those found in raw gas samples and were often erratic. Consequently, two tracer-level xenon tests were conducted in the CDE vessel to determine any problems involved in sampling xenon and to determine the sampling accuracy of the CSM for xenon.

Operating Conditions. Operating conditions for the two xenon tracer tests were similar to those used in the high-level CDE runs, except for a shorter test duration and no preheating of the containment vessel. After the CDE vessel was pressurized with steam to 22 psig, a glass ampule containing a known quantity of Xe-133 was broken in an enclosed injection tube, and the xenon was injected into the CDE vessel using argon as a transport gas. Following the xenon injection, the temperature of the containment atmosphere was allowed to decay naturally for 5 to 8 hours.

The concentration of Xe-133 (including stable fission product xenon shipped with the source) injected into the CDE vessel was 0.01 volume parts per

million. This concentration is considerably higher than the xenon concentrations anticipated in the ECCS tests; however, it is only 10 percent of the normal atmospheric xenon concentrations^[36].

Sampling and Analysis. To ensure a valid evaluation of the CSM, three independent sampling systems -- a containment raw gas system, a containment filtered gas system, and the CSM -- were operated simultaneously during each tracer test. Samples from these systems were analyzed using two independent techniques: (a) direct gamma spectrometry counting of the total samples and (b) separation and trapping of the xenon using a vapor phase chromatograph followed by gamma spectrometry counting.

The raw gas and filtered gas sampling systems, which are shown in Figure 55, used the same sample inlet in the CDE vessel. The raw gas sample flowed directly through a short length of tubing to gas sampling cylinders. The filtered gas sample flowed through a heated line (to prevent condensation) and heated filter holder containing glass fiber and silver membrane filters. The sample then passed through a condenser to cool the gas and condense the steam, and finally through the sampling cylinders.

Fig. 55 Raw and filtered gas sampling systems.

The CSM system, as used in the xenon tracer tests and shown in Figure 56, continuously drew a sample stream from the containment atmosphere through the scrubber, which was located in the containment vessel. In the scrubber, the gas sample contacted a 0.1M NaOH spray from a pressure-atomizing nozzle. The gas and scrubbing solution flowed concurrently through a common outlet tube to a heat exchanger and a separator located outside the CDE vessel, then flowed separately through sampling stations, gross gamma monitors, and flow

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Fig. 56 Modified CSM installation.

controllers. The gas and liquid flow rates in 1/4-inch-diameter lines were 210 standard ml of dry air/min and 130 ml of liquid/min, respectively. To simulate the line length of the proposed LOFT installation, 100-foot-long coils were installed in both the gas and liquid lines between the separator and the samplers.

Results. The xenon concentrations measured by the CSM agree very closely with those measured in the raw and filtered gas samples. The atmospheric xenon concentrations were constant throughout both runs; less than 0.005 percent of the xenon injected was found in the condensate. The average xenon concentrations measured by each of the samplers are tabulated in Tables XXXIX and XL. The average CSM total -- the sum of the xenon concentrations in the CSM gas and liquid samples -- differed by less than four percent from the average concentration measured by either of the other samplers when analyzed by the same method.

From 6 to 10 percent of the total xenon in the atmosphere sample taken by the CSM was absorbed by the scrubbing solutions. These values are in good agreement with existing solubility data for xenon [37]. The solubility of krypton -- the other noble gas of interest in LOFT -- in water is about one-half the solubility of xenon [37]. For the same operating conditions used in these tests, the CSM scrubbing solution would absorb from three to five percent of the krypton in an atmosphere sample.

TABLE XXXIX
 CONCENTRATION^[a] OF Xe-133 IN CDE CONTAINMENT
 ATMOSPHERE -- CDE TRACER TEST 1^[b]

	<u>CSM Gas</u>		<u>CSM Liquid</u>	<u>CSM</u>	<u>Filtered Gas</u>		<u>Raw Gas</u>	
	<u>VPC</u>	<u>GRS</u>	<u>GRS</u>	<u>Liq. & Gas</u>	<u>VPC</u>	<u>GRS</u>	<u>VPC</u>	<u>GRS</u>
Average	220	196	12	208	228	211	266	207
No. Samples	3	3	2	2	6	6	2	3
Standard Deviation	3	3	---	---	11	9	---	14
95% Confidence Limits	6	6	---	---	11	9	---	26

[a] Concentration in μCi /standard liter of dry air.

[b] Calculated injection in Run 1 = 260 $\mu\text{Ci/l}$.

VPC -- Separation by vapor phase chromatography followed by analysis by counting.

GRS -- Direct counting of sample cylinder by gamma ray spectrometry.

TABLE XL
 CONCENTRATION^[a] OF Xe-133 IN CDE
 CONTAINMENT ATMOSPHERE -- CDE TRACER TEST 2^[c]

	<u>CSM Gas</u>		<u>CSM Liquid</u>	<u>CSM</u>	<u>Filtered Gas</u>		<u>Raw Gas</u>	
	<u>VPC</u>	<u>GRS</u>	<u>GRS</u>	<u>Liq. & Gas</u>	<u>VPC</u>	<u>GRS</u>	<u>VPC</u>	<u>GRS</u>
Average	62	51	4.1	55	63	53	62	54
No. Samples	8	8	9	8	8	10	3	3
Standard Deviation	5	2.1	0.7	2.2	2.4	2.2	3.5	2.4
95% Confidence Limits	4	1.6	0.5	1.8	2.0	1.6	6.4	4.4

[a] Concentration in μCi /standard liter of dry air.

[b] Calculated injection in Run 1 = 260 $\mu\text{Ci/l}$.

[c] Calculated injection in Run 2 = 79 $\mu\text{Ci/l}$.

VPC -- Separation by vapor phase chromatography followed by analysis by counting.

GRS -- Direct counting of sample cylinder by gamma ray spectrometry.

Conclusions. The following conclusions were reached, based on the results of the two xenon tracer tests:

- (1) Under steady state conditions, the CSM provides representative samples of the xenon in the CDE containment atmosphere.
- (2) The CSM scrubbing solutions absorbed 6 to 10 percent of the xenon from atmosphere samples drawn through it with a gas-to-liquid flow ratio of 1.6.

1.5 Decontamination of the LOFT Reactor Package

(D. E. Black, W. A. Freeby, R. R. Hammer; Reactor Safety Studies Section
B. J. Newby, C. A. Zimmerman; Chemistry Section)

The Loss-of-Fluid Test (LOFT) program being conducted by Phillips Petroleum Company at the NRTS was changed in 1967 from a single test to determine the consequences of a core meltdown to a series of tests (LOFT-ECCS) evaluating the performance of emergency core cooling and other safeguard systems. As a result of the change from a single to multiple tests, Phillips Petroleum Company requested Idaho Nuclear Corporation to review the design of the LOFT reactor package and associated systems to evaluate the decontamination problems introduced by the new multiple use program.

The design of the LOFT decontamination, waste handling, and reactor package systems was essentially complete prior to the change in the test program. The reactor package, which is shown in Figure 57, must be decontaminated and reused several times in the new program. In addition to the reactor shown in Figure 57, the reactor shield tank, the primary coolant and makeup system, the decay heat removal system, the emergency core cooling system, the secondary coolant loop, and special test instrumentation also will be mounted on the dolly.

The two decontamination systems (high pressure and deluge) proposed for the original LOFT test were designed to completely cover only the inside surfaces of the LOFT containment building; decontamination of the reactor package system was to be minimal. Final decontamination of the reactor package was to be accomplished in the NRTS "hot" shops after removal of the reactor package from the LOFT containment building.

The liquid waste and decontaminating solutions from the ECCS tests will be stored temporarily in two carbon steel storage tanks buried underground. For final disposal, the waste will be pumped to a disposal well if activity levels are low enough, or, if necessary, will be transferred by truck or railroad car to other locations for disposal.

1.51 Decontamination Required in LOFT-ECCS Program. The LOFT reactor (50 MW with low enriched UO_2 fuel clad in Zircaloy-4) represents a typical pressurized water reactor. The extent of fission product release from the fuel depends strongly on the damage to the core, and these conditions will vary widely for the ECCS tests proposed. In general, the decontamination following a test will become more difficult as the test series progresses and core damage increases with an accompanying increase in fission product release.

The proposed ECCS tests were grouped into three cases covering very low to minor releases, minor to moderate releases, and the greatest potential release (which might take place if significant core melting occurred before

Fig. 57 Proposed LOFT reactor package.

the core cooling systems were activated). Since essentially no data exist on release and deposition of fission products under the anticipated ECCS test conditions, each of the three cases was related to the originally planned LOFT test, or base case, for which release figures had already been estimated. The comparisons are shown in Table XII.

The gamma radiation fields anticipated in the LOFT containment building for the originally planned LOFT test, or base case, are shown in Figure 58. These curves were estimated for a distance of two feet from the reactor package, using conventional calculational techniques [38,39]. It was assumed that all contamination was distributed evenly over the surface of the containment building and the reactor package. Contributions from the core, beta radiation, and material deposited on the containment building interior were neglected. The contributions of the rare gases were also neglected, since they will not sorb to a significant extent on the surfaces and will be vented to a cleanup system following the test.

TABLE XLI

COMPARISON OF ANTICIPATED ECCS TEST CONDITIONS WITH ORIGINALLY PLANNED LOFT TEST

Case Number	Test Parameter	Total Fission Product Release[a]	Halogen Release[a]	Particulate Release[a]	Containment Contamination Levels[a]	Maximum Cladding Temperature	Percentage of Cladding Failures
1	Normal operation of core cooling system	<0.001 to 0.01	<0.001 to 0.01	<0.001	<0.001 to 0.01	900 to 1000°C	0.1% to 10%
2	Degraded operation of core cooling system	0.001 to 0.1	0.01 to 0.1	0.001 to 0.1	0.001 to 0.1	1300 to 1850°C	25% to 80%
3	Partial core melting before activation of core sprays	0.33	0.33	>1	0.33	2830°C ^[b]	100%
Base Case	Original LOFT test	1	1	1	1	2830°C ^[b]	100%

[a] Values represent fraction of base case which is rated as unity.

[b] Cladding will have completely reacted with steam and UO₂ at much lower temperatures.

Fig. 58 Estimated dose rates for original LOFT test.

The extent of decontamination required for the three release cases is illustrated in Figure 59 in terms of the decontamination factors required to lower the radiation levels to 10 mR/hr. These DF's were determined by dividing the estimated radiation dose surrounding the reactor package at a given time (shown in Figure 58) by 10 mR/hr. Figure 59 indicates that the reactor package system can be decontaminated relatively easily for all but Case 3 (see Table XLI).

1.52 Results of Study

Decontamination Procedures. Decontamination of the reactor package following each ECCS test must reduce the radiation levels without impairing operability of the system. Thus, corrosion must be considered in planning the decontamination operations. Based on experience from the current CDE runs, from previous CDE runs [2], from decontamination experience at the Idaho Chemical Processing Plant, and from data obtained from the literature, three different procedures were chosen which would probably provide the required decontamination. The DF's and corrosion data for most of the generic types of materials proposed for use in the LOFT reactor package are summarized in Table XLII for the three methods. The data presented in Table XLII must be considered as tentative, since little experience is available in situations comparable to the

Fig. 59 Estimated decontamination factors for original and ECCS tests.

ECCS tests. Table XLII shows that all unpainted metals used in the reactor package could be decontaminated with minimal corrosion by spraying with any of the three different decontaminating solutions.

Of the three procedures shown in Table XLII, Procedure B (Turco 4502 [a] followed by Turco 4521 [a] or oxalic acid) is recommended as being the best, considering both the decontamination and corrosion requirements. The corrosion of materials resulting from the recommended decontamination procedure can be reduced by using short contact times and by thoroughly washing all materials with water after each decontaminating treatment. Lower solution temperatures or concentrations would also lower the corrosion, but further development work would be needed to determine if the procedures would still be effective under these conditions.

In general, carefully controlled application of any of the three recommended decontaminating systems would not result in significant corrosion of the reactor package. Valves and other operating components should serve satisfactorily,

[a] Product by Turco Products, Inc., Wilmington, California.

TABLE XLII

DECONTAMINATION TREATMENTS FOR THE REACTOR PACKAGE

Materials	Procedure A: Spray 4 min with 1 lb/gal Turco Alka- line Rust Remover at 30°C followed by 3M HNO ₃ at 60°C for 1/2 min		Procedure B: Spray 5 min with 2 lb/gal Turco 4502 followed by 1/2 lb/gal Turco 4521 or oxalic acid at 80°C for 5 min		Procedure C: Spray 5 min with 2 lb/gal Turco 4502 at 80°C followed by 1/2 lb/gal sodium bisulfite at 80°C for 5 min	
	D. F. [a]	Corrosion (Mils/Treatment)	D. F. [a]	Corrosion (Mils/Treatment)	D. F. [a]	Corrosion (Mils/Treatment)
Carbon Steel, Soft, Cast or Wrought Iron	Fair	0.002	Good	0.004	Fair to Good	0.005
Stainless Steel, Carpenter-20	Fair	0.001	Excellent	0.002	Good	0.002
Aluminum	Excellent	0.008	Excellent	0.012	Good	0.012
Viton A, Carboline- 368, Neoprene, Butyl Rubber, Teflon, Poly- ethylene, Hypalon Rubber	Poor	0.0004 ^[b]	Poor	0.0004 ^[b]	Poor	0.0004 ^[b]
Lead Shot	Good to Excellent	0.008	Fair	0.012	Fair	0.008
Inonel	Excellent	0.002	Good	0.002	Fair to Good	0.002
Stellite	Excellent	0.002	Good	0.003	Fair to Good	0.002
Brass, Bronze, Monel	Excellent	0.006	Good	0.002	Fair to Good	0.002

[a] Excellent D. F. ≥ 500 ; good D. F. = 100 to 500; fair D. F. = 10 to 100; poor D. F. ≤ 10 .

[b] Corrosion essentially nil, but serious degradation may occur.

if the total corrosion occurring during all ECCS tests does not exceed the design tolerances of the fitting surfaces.

Decontamination of the internal surfaces of the LOFT reactor package system also can be accomplished using Procedure B. Because the contamination inside the reactor and primary coolant system is deposited under severe conditions, the decontaminating solutions may require long contact times and high temperatures to achieve satisfactory DF's.

The following chronological procedure is recommended for decontamination of the LOFT reactor package for all three cases:

- (1) Following completion of the test, clean the containment atmosphere using the containment spray and filter systems.
- (2) Decontaminate the interior of the containment building and the exterior of the reactor package using Turco 4502 and oxalic acid. Follow each application of decontaminating reagent with an immediate and thorough rinsing with water.
- (3) Enter the LOFT containment building and survey the reactor package for loose contamination. If loose contamination is present, manually decontaminate to acceptable levels using a steam-detergent (Turco 4324) system. If direct entry into the LOFT containment building at this time is not possible, the loose contamination could be "fixed" on the dolly by applying a coating of Contam-Affix (removable)^[a] as the reactor is removed from the building.
- (4) Transfer the dolly to the TAN Hot Shop for final internal and external decontamination using Turco 4502 and oxalic acid.

Waste Handling Procedures. The waste handling and storage systems designed for the original LOFT tests appear to be satisfactory for the ECCS test series. However, chemicals may have to be added to prevent interaction (eg, formation of precipitates) of the various decontamination reagents with the core cooling and the containment spray solutions. The carbon steel collection and storage tanks are also adequate for temporary waste storage (up to several months) as long as the resulting mixture in the waste tank remains basic during storage.

Suggested Modifications and Routine Replacements. Several modifications of equipment, and routine replacement (following each test) of some components in the reactor package, are recommended for the ECCS tests. These recommendations are based on the assumption that Turco 4502 and oxalic acid, applied as specified in Table XLII, would be used for decontamination. The reactor package should not be painted, since the DF's obtained with paint are unacceptably low.

All piping should be sloped away from the reactor (or toward the reactor if a drain line can be installed in the bottom reactor head), and all low points should be provided with bottom drains and valves. Vent lines should be installed

^[a]Product of Turco Products, Inc., Wilmington, California.

in all high points of the system to allow complete filling and draining of decontaminating solutions. Valves should be provided so that systems which are clean or are only moderately contaminated can be isolated from highly contaminated areas.

It is also recommended that a connection be provided for supplying hot water to the suction side of the decontamination pump for immediate water rinsing of the decontamination system and reactor package after decontamination. A spray system should be installed to provide thorough and complete coverage of the outer surfaces of the reactor package.

Provisions should be made for adding chemicals to the carbon steel waste storage tanks to control pH. The stored wastes should be continually monitored to ensure that they are alkaline, since acid solutions are much more corrosive to carbon steel than alkaline solutions.

Of the materials scheduled for use in the reactor package, all gasket materials, graphitar parts, certain stellite valve parts, and some valves and instrument leads may have to be replaced following each test. Any thermal insulation will have to be replaced if not protected by a sealed outer covering such as aluminum. Other equipment used in the reactor package for which information was available should not be affected appreciably if the decontamination solutions are applied as specified.

2. OTHER REACTOR TECHNOLOGY SUPPORT PROGRAMS

2.1 Decontamination by Reagents-in-Foam

(W. T. Jordan, C. A. Zimmerman; Chemistry Section)

In the past year foam has shown promise as a reactor decontaminant at ETR where a commercial metal cleaning foam has been successfully applied to the top-head portion of the reactor during shutdowns. The advantages to be gained by decontaminating with foam were sufficiently encouraging to warrant a study devoted to development of foams specifically for decontamination. The approach taken was to add conventional decontaminating reagents to the commercial foaming agent used at ETR. If the decontaminating reagent could be carried in foam rather than in a nonviscous liquid medium, it could, because of the adherancy of foam, be held in contact with a structural surface for a greater period of time, thus decreasing the resultant volume of liquid waste and increasing the efficiency of decontamination. Furthermore, since foam may be applied conveniently from a distance, the radiation doses to personnel performing the decontamination could be reduced significantly.

Experimental Observations. The following reagents were selected for testing because of their widespread use in the nuclear industry as decontaminants: alkaline permanganate, oxalic acid, dibasic ammonium citrate, and oxalate-citrate mixtures. Early in the screening it was found that foam could be produced over a wide range of pH. Stable foam was produced, for example, from solutions containing alkaline permanganate, and from solutions containing large amounts of oxalic acid. However, interactions between some reagents and the foaming agent were observed. Permanganate was rapidly reduced to manganate in the presence of the particular foaming agent used; and ammonium citrate has such a large foam inhibitory effect that a large compensating amount of foaming agent had to be added to produce suitable foam.

The decontamination effectiveness of the reagent-enhanced foams was determined by applying each foam to sections of stainless steel tubing removed from the top portion of the ETR vessel where plateout of both activated corrosion products and fission products had occurred. The initial activity of the specimens was 35 to 40 mR/hr at one inch. Results from a number of the tests are collected in Table XLIII.

The best single-step decontaminating foam was that containing oxalic acid. Decontamination factors of up to 9 were obtained when a solution of foaming agent (Fome-Add)[a] containing 40 g/l of oxalic acid was foamed onto the metal specimens. By comparison, the foam used at ETR yielded a maximum decontamination factor of 1.8, ammonium citrate foams gave a maximum decontamination factor of 1.2, and citrate-oxalate foams gave a maximum of 5.0. Alkaline permanganate (Turco 4502)[b] proved to be an effective decontaminant-in-foam despite the aforementioned reduction to manganate. When an alkaline permanganate foam application was followed by oxalic acid foam, decontamination factors up to 20 were obtained. However, comparable decontamination factors resulted from two to three oxalic acid foam applications. Multiple applications of oxalic acid foam were found to be continually effective and have the advantage of requiring only one reagent.

Conclusions. On the strength of the results of this study, oxalic acid-in-foam was recommended for decontamination of the ETR top head. Further, foam decontamination has potential for much broader applications; it would be particularly advantageous for decontamination of structural areas where accessibility is a problem.

2.2 Uranium Aluminide Manufacture Employing Fluidized Bed Techniques (E. S. Grimmet, R. K. Ballard; Chemical Development Section)

By using fluidized bed technology, uranium aluminide has been produced in a four step process from uranyl nitrate and aluminum powder without the costly intermediate production of uranium metal [2].

The conversion is based on four consecutive reactions:

This four-step process is carried out in a fluidized bed reactor.

Previous difficulties were encountered in producing a UO_3 coating on the aluminum powder [Step (1)] of sufficient reactivity to be chlorinated readily via Steps (2) and (3). This problem has been overcome by the addition of small

[a] Proprietary material manufactured by DuBois Chemicals, Division of W. R. Grace Company.

[b] Proprietary material manufactured by Turco Products, Inc., Division of Purex Corporation, Ltd.

TABLE XLIII

RELATIVE EFFECTIVENESS OF REAGENTS IN FOAM

Foam Compositions					Decontamination Factor (Room Temperature)
First Foam Applied to Sample			Second Foam Applied to Sample		
Reagent(s)	g/l	Fome-Add ^[a] ml/l	Reagent(s) g/l	Fome-Add ml/l	
Sprex AC-3 ^[b]	10.9	4.5	none	---	1.8
		13	none	---	1.6
Oxalic Acid	40	14	none	---	9
Ammonium Citrate	20	33.5	none	---	1.2
Ammonium Citrate	15	35	none	---	3
Oxalic Acid	40	14	Oxalic Acid	40	14
Turco 4502 ^[c]	14	4	Oxalic Acid	40	20
Turco 4502	14	4	Ammonium Citrate	20	5
Turco 4502	14	4	Ammonium Citrate	15	5
			Oxalic Acid	25	

[a] A foam additive manufactured by DuBois Chemicals, Division of W. R. Grace Company.

[b] A metal cleaning compound manufactured by DuBois Chemicals, Division of W. R. Grace Company.

[c] Proprietary material manufactured by Turco Products, Division of Purex Corporation, Ltd.

quantities of aluminum nitrate to the uranyl nitrate feed. This apparently alters the crystal structure of the uranium oxide coating during the calcination step, thus producing a reactive form of UO_3 . The small quantities of aluminum nitrate added are converted to aluminum oxide during the first step and then removed from the process as volatile aluminum trichloride during the chlorination step.

Fabrication of a controlled atmosphere glovebox to be used as a containment for this process is currently underway. All future work with enriched as well as natural uranium will be carried out in this facility.

2.3 The Volume Coefficient of Expansion and the Volume Change on Melting for Uranyl Nitrate Hexahydrate (M. R. Fox; Chemistry Section)

The thermal coefficient of volumetric expansion for solid uranyl nitrate hexahydrate (UNH) and the volume change on melting have been determined. These values were needed to calculate the temperature dependence of the atomic density for uranium in this compound. The thermal instability of UNH was recognized, but was found to be insignificant at temperatures up to 60°C for the time periods involved.

Experimental Equipment and Materials. A special pycnometer, shown in Figure 60, was used. Expansion in the pycnometer displaced liquid into the precision-bored glass capillary, where the volume change measurement was made. The body of the pycnometer was constructed of Pyrex; the thermal expansion of the glass components was neglected. The inside diameter of the precision-bored glass capillary tube was 2.79 ± 0.01 mm, corresponding to a volume change of 0.0612 cc/cm. The changes in the level of the liquid in the capillary were determined by the use of a cathetometer. The precision of these readings was ± 0.1 mm, equivalent to a volume change of ± 0.0006 cc.

The pycnometer was standardized with distilled water. During experimental determinations, an organic compound 1, 2, 4-trichlorobenzene (TCB) was used to fill the pycnometer in the space unoccupied by the UNH. It was chosen for its high molecular weight, low solubility of UNH, and for its low viscosity. The thermal coefficient of volumetric expansion for TCB was determined. The expansion of TCB in this pycnometer was large enough to give about a 20 cm change in the level in the capillary

Fig. 60 Pycnometer used for determination of volumetric expansion of UNH.

over the 40°C temperature range studied. Measurements of the density of TCB gave an average value of 1.454 g/cc at 20°C. This agrees well with the value of 1.455 g/cc at 19.8°C found in the literature [40].

Procedure. A known weight of UNH was submerged by a known weight of TCB. The TCB was filled to a level such that when the immersion thermometer was in place, the level of the TCB was above the stopcock (Figure 60). The TCB wetted the UNH sufficiently so that, by swirling, most of the air pockets which might have formed at the surface of the UNH crystals were eliminated. As a result of this procedure, no air bubbles were visible in the pycnometer, even after melting the UNH.

After securing the immersion thermometer and closing the stopcock, the apparatus was weighed and then placed in a controlled-temperature water bath, and the temperature and liquid level in the capillary were followed. The lower end of the thermometer was never more than 0.5 cm above the surface of molten UNH; thus more realistic temperature readings could be made than would have been the case if the thermometer were outside of the pycnometer.

Results. The equation for the thermal expansion of the TCB was found to be

$$V_T = V_0 (1 + 7.88 \times 10^{-4} \Delta T) \quad (16)$$

where V_T = volume of liquid at temperature T when $20^\circ\text{C} < T < 60^\circ\text{C}$, V_0 = volume of liquid at 20°C , and $\Delta T = T - 20^\circ\text{C}$. The equation representing the total volume in the pycnometer was

$$V_T^t = V_T^{\text{UNH}} + V_T^{\text{TCB}} = V_0^{\text{UNH}} (1 + \alpha \Delta T) + V_0^{\text{TCB}} (1 + 7.88 \times 10^{-4} \Delta T). \quad (17)$$

By solving for α in the first term on the right, one may determine the expression for the expansion of UNH. This expression is

$$V_T = V_0 (1 + 5.37 \times 10^{-4} \Delta T) \quad (18)$$

where V_T , V_0 , and ΔT are defined in a manner similar to the terms in the expression for the expansion of the liquid as described for Equation (16).

In passing through the melting point of UNH, a sharp increase in the volume is observed. By knowing the volume of UNH and by assuming that the total volume change observed at the melting point of UNH is due to the expansion of UNH as it liquifies, a volume change of 5.3 percent $\pm$ 0.30 percent was observed.

2.4 An Analog Computer Simulation Program for the Advanced Test Reactor (R. A. Brown; Development Engineering Section)

Operation of the Advanced Test Reactor will be preceded by a major training program. The cornerstone of the training program is a reactor simulator, consisting of an EAI 680 analog computer and special-purpose hardware. The computer program will be developed from a mathematical model of neutron kinetics, and the special purpose equipment will duplicate the behavior of control and safety systems. The training simulator will provide reactor operators with a dynamic replica, including a control console and instrumentation, of the reactor system.

Prior to development of the open-loop simulation and the control console, a closed-loop simulation program for the ATR was prepared [41]. This program, similar to work done by Babcock and Wilcox for Ebasco Services [41], describes the complete ATR system. The objectives of the work were to provide a reference work for subsequent programming, to analyze computer requirements for a wide range of simulation levels, and to provide the means for investigation of system behavior prior to actual operation.

The simulation program was based on a closed-loop mathematical model of the following subsystems:

- (1) Neutron kinetics and reactor power output
- (2) Control rods (manual and automatic reactivity control)
- (3) Primary coolant heat transfer and transport delays
- (4) Secondary coolant heat transfer
- (5) Secondary coolant automatic flow control
- (6) Temperature measurement lags
- (7) Xenon poisoning.

A block diagram of the system is shown in Figure 61.

Fig. 61 Block diagram of ATR system.

The ATR can be simulated on a fully expanded EAI 680. Purchased computer capability is ample for an open-loop simulation. The use of special-purpose hardware for simulation of reactivity control and reactor safety systems, using assumed coolant conditions (open-loop), will allow added sophistication in simulation of neutron kinetics and power distribution. Reactivity changes caused by

xenon poisoning are extremely slow compared to neutron kinetics, making real-time simulation of this phenomena difficult. The xenon poisoning effect could be introduced manually.

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