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CHEMICAL TECHNOLOGY BRANCH ANNUAL REPORT
FISCAL YEAR 1967

J. R. Bower, Editor

IDAHO NUCLEAR CORPORATION
NATIONAL REACTOR TESTING STATION
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CHEMICAL TECHNOLOGY BRANCH ANNUAL REPORT FISCAL YEAR 1967

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SUMMARY

The principal ICPP fuel dissolution processes were maintained in standby during this period while the Waste Calcining Facility was in full-time operation. As schedules permitted, however, small lots of fuels which required separate accountability or which were expected to be unusually difficult to dissolve were processed through batch dissolution equipment. In addition, the fuel from Core 2 of Experimental Breeder Reactor I (EBR-I), which had undergone partial melt-down in the reactor, was successfully recovered in small-scale equipment operated under direct visual control in a heavily shielded cell. Similarly, uranium was readily recovered from broken Vycor glass molds used for casting EBR-II fuel pins.

Process support studies indicated that silicon in aluminum-uranium-silicon alloys had no adverse effect on dissolution of the alloys; on the other hand, copper in aluminum, as in alloy 2219, seriously reduced the dissolution rate in mercury-catalyzed nitric acid. Corrosion observations during zirconium fuel processing indicated generally favorable experience under properly controlled conditions but very rapid corrosion with improperly chosen materials or conditions of operation. Criticality review of the ICPP partially reflected 7 1/2-inch-diameter continuous dissolvers showed them to be safe for any possible loading and configuration of disintegrated fuel (or meat) from the new ETR fuel elements (505 g U-235, 93 percent enriched).

A combustion-dissolution process for graphite fuels, based on a two-stage fluidized bed burner for combustion of the graphite and a continuous elutriation process for removal of metal oxide products from the operating fluidized bed, has performed satisfactorily in initial tests of a newly installed pilot plant. Uranium buildup on the bed can be controlled, separation of the oxide products without carryover of bed material appears to be satisfactory, and up to 97.5 percent of the graphite from Rover fuel elements has been burned off. Several common alloys have proved satisfactory as materials of construction for the burner. Uranium is readily dissolved from the elutriated burner ash by nitric acid treatment.

An electrolytic dissolver pilot unit for studying dissolution characteristics of EBR-II fuel (enriched uranium alloy core, bonded with sodium, and clad in stainless steel) has been designed and is being installed. A two-step dissolution process for Zircaloy-4-clad ZrO_2 - UO_2 fuels, a possible alternate to a three-step aqueous process or a halide volatility process, produces a solution suitable for solvent extraction by dissolving the cladding in 10 M HF, dissolving the oxide core in fused ammonium bifluoride, and combining all in a solution complexed with aluminum nitrate.

The Waste Calcining Facility operated throughout the period, converting approximately 595,000 gallons of first cycle aqueous waste to 6600 cubic feet of solids in 15 months of the second operating campaign. (Since initial operation in 1963, about 1,100,000 gallons of highly radioactive wastes have been reduced to solids.) Though some unscheduled shutdowns have occurred, general operation of the facility continues to be excellent. Metallurgical changes in portions of the Type 316 stainless steel NaK heat exchange system, as a result of over 19,000 hours service at or above 600°C, have contributed to the principal temporary shutdowns of the system.

Pilot plant calcination of zirconium-hydrofluoric acid wastes, complexed with calcium nitrate, was successfully demonstrated in a 212-hour run at 400°C and a Ca/F mole ratio of 0.55. A process for heating the fluidized bed calciner by in-bed combustion of a hydrocarbon fuel has been demonstrated by burning kerosene in the bed of a 12-inch-diameter pilot plant calciner to calcine nitrate-containing wastes at 438°C; a significant increase in energy input, and a corresponding increase in calcining capacity, appears to be possible as compared with the existing heating system. Additional pilot plant studies indicate (a) that dolomite is superior to sand as a calciner startup bed (if nonradioactive calcined alumina is not available); (b) that a vortex restrictor, using air as the controlling medium, may be a useful substitute for a valve for feed control to the calciner; and (c) that the WCF scrubbing system should satisfactorily withstand the corrosion-erosion characteristics of acidic zirconia-containing solutions present while calcining zirconium fuel wastes. An improved computational algorithm has been developed for the mathematical model describing the transient particle size distribution within the fluidized bed calciner.

Heat transfer studies, during calcination in a fluidized bed pilot unit, have demonstrated that heat transfer rates from multiple horizontal tubes to fluidized beds can be predicted by a dimensionless correlation of easily defined terms. Further, the heat transfer rates can be increased many-fold by use of finned surfaces in place of bare tubes. Heat transfer within storage facilities has been studied from the standpoints of: (a) heat dissipation from buried radioactive sources; (b) heat transfer across vertical cylindrical air gaps; and (c) effects of fission product migration on temperatures within a mass of calcine stored under conditions permitting the centerline temperatures to approach the fusion temperature of alumina (2000°C).

Additional waste management studies reported include (a) the volatility of minor constituents from calcined waste stored at up to 800°C; (b) the corrosive effects of zirconia calcine in storage; (c) the removal and recovery of mercury from WCF feed; and (d) a computer program for blending ICPP wastes to give maximum permissible heat generation rates in the existing calcine storage bins.

Continuing LOFT assistance studies have indicated a number of reactor containment shell coatings that are resistant to LOFT experimental conditions; embedding woven glass fabric in the coatings makes them resistant to cracking when applied over expansion joints in concrete. Four possible methods for decontaminating coating systems are described. Penetration of iodine into coatings, probably the most troublesome aspect of fission product contamination, has been described on a mathematical basis, permitting the scaleup of plateout data on protective coatings from laboratory experiments to pilot plant scale vessels. The Contamination-Decontamination Experiment (CDE), an experimental unit for releasing fission products from melted irradiated fuel specimens into a confined, controlled-atmosphere test chamber, has performed efficiently in four separate high-activity runs to provide the environment for testing protective coatings, sampling systems, fission product behavior, and decontamination techniques. Tests of a continuous sampler-monitor for sampling the containment atmosphere during the LOFT experiments, indicate its effectiveness for removing inorganic iodine vapors and particulates larger than 0.1 micron; smaller particulates and organic iodides are trapped much less effectively. Tests in conjunction with CDE Run 3 provided revealing information regarding the nature and action of particulates and iodine during and after a fuel pin meltdown. Fission product

plateout sample capsules have operated successfully in the two latest CDE tests and the results are discussed to show the effects of coupon orientation, structural shielding, temperature and condensation, and sampler location on the particulate contamination collected. Examination of residues from fuel pin meltdown in the CDE disclosed formation of a physically stable shell of ZrO_2 where the Zircaloy clad fuel pin was exposed to the steam atmosphere, although the uranium core and cladding area shielded from steam were completely melted. A report has been issued giving values for physical properties of UO_2 , ZrO_2 , and Zircaloy-4 in temperature ranges most usable for the analysis of a loss-of-coolant accident.

Other reactor technology support programs include development of a method for producing uranium aluminide (UAl_3) in a fluidized bed reactor using uranyl nitrate and aluminum as starting materials; no metallic uranium is handled anywhere in the process and the product leaves the process in its desired size and shape. Removal of boehmite from aluminum fuel element surfaces, leaving a passive surface, has been accomplished by treatment in boiling 1.0 M phosphoric acid — 0.4 M chromium trioxide solution, followed by film removal in 3M nitric acid.

Pilot Plant laboratories, designed to accommodate modular units, are being put into operation at the ICPP. The modular concept permits broad flexibility, rapid installation and interchange of equipment, minimum interference of construction with experimental activity, and generally high efficiency in use of space, material, and manpower.

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I. FUEL REPROCESSING

1. PERFORMANCE OF ICPP FUEL RECOVERY PROCESSES

1.1 Aluminum Fuel Reprocessing

(R. E. Commander; Production Engineering)

1.11 Summary of Operations. The main ICPP fuel dissolution processes were not in operation during this period due to limited fuel inventories in storage and the scheduling of the Waste Calcining Facility for full time operation. Advantage was taken of this situation to decontaminate the main processing plant and make desirable modifications (Section I-1.4). However, several small lots of uranium-aluminum alloy fuels which required separate accountability or which were expected to present unusual difficulty in dissolution were processed through the batch dissolution equipment as manpower permitted. Following batch dissolution, the fuels were blended as appropriate and the uranium was recovered and decontaminated by three cycles of Hexone extraction.

1.12 Fuel Dissolution. The batch process equipment in D Cell was used for the part time dissolution and feed adjustment of several aluminum alloy fuels (JRR-2, NRU, and NRX), during the period from March 16, 1967 to May 24, 1967. The amount of uranium processed in each type of fuel is shown in Table I.

TABLE I

ALUMINUM ALLOYED FUELS PROCESSED DURING FISCAL YEAR 1967

<u>Fuel Type</u>	<u>Number of Elements Dissolved</u>	<u>Total U Charged (kg)</u>	<u>U-235 Charged (kg)</u>
JRR-2	24	21.53	4.25
NRX	60 ^[a]	4.12	3.32
NRU	52	3.10	2.43

[a] This number included forty-five (45) 27-inch elements and fifteen (15) 8-inch elements.

The fuels processed were dissolved with a solution of nitric acid, water, and mercuric nitrate catalyst. For all fuels the acid concentration of the dissolving solution was 5.5M; the catalyst concentration was set at 0.01M for the JRR-2 fuel and at 0.05M for the Chalk River fuels.

The dissolver product was transferred to the coarse feed adjustment tank where it was sampled for uranium input and adjusted to $0.26 \pm 0.10M$ acid deficient (allowing for the calculated final volume after boildown) by the addition of NH_4OH . The feed solution was then boiled down in the fine feed tank to obtain the proper specific gravity and acid deficiency for processing in the Hexone extraction system.

The dissolution of the JRR-2 fuel was quite similar to that of MTR-type fuel, and no major problems were encountered. Confirming previous experience, the Chalk River fuels (NRX and NRU) dissolved more slowly and revisions in the dissolution procedure were made during the processing to correct some of the problems. For both the NRX and NRU fuels, the volume of dissolving solution required for each batch was greater than the volume of the dissolver. Because of this, the dissolution of each batch was done in two parts, with the dissolvent being added in two separate increments. It was found that dissolution of the first part of each batch proceeded quite readily (10 hours exposure), but the dissolution of the second portion was very slow (up to 50 hours). Experience indicated the desirability of reducing the amount of dissolvent used in the second portion of the dissolution by 30 percent (for NRX fuel) to 50 percent (for NRU fuel) to avoid high acid conditions in the final dissolver product.

While dissolving the first increment of the last three batches of NRU fuel, the catalyst concentration was increased and a longer digestion period (14 hours) was used. In each case, a highly acid deficient solution was obtained. These solutions were held and blended with the highly acidic solutions obtained in the second portion of each dissolution. The resulting blends were close to flow sheet specifications and required little additional adjustment. On the last two batches, however, samples of the final blends contained a solid precipitate, the main constituent of which was mercury. In the final batch, the precipitate was redissolved by reacidification and digestion of the solution. The normal feed adjustment was then carried out without further complication.

After processing of the JRR-2 fuel was completed, a heel cleanout of the dissolver indicated that nearly complete dissolution had been achieved. For the NRX fuel, however, it was necessary to make three more extensive heel cleanouts to ensure that all the fuel had been dissolved. For the NRU fuel, a considerably longer digestion period for the last batch was used, thereby making it necessary for only one heel cleanout to be made.

1.13 Hexone Extraction of Uranium. The Hexone extraction equipment was started up and operated on three separate occasions following processing of the JRR-2, NRX, and NRU fuels through the D cell dissolution equipment. Because of the limited volume of storage for dissolver product when the continuous head-end process was not being used, the product from dissolution of each fuel type had to be processed through the solvent extraction equipment before dissolving operations could be resumed.

The Clarkson feeder (Section I-1.4) which was recently installed to correct feed control difficulties from N Cell storage to the P Cell extraction column was used for the second time, and no problems were encountered. Good control of the feed rate was maintained at all times at an average of 18 to 20 liters per hour. This value approximates the maximum capacity of the feeder as it was installed, but if the necessity arises the rate may be easily increased by interchanging the feed cups with larger ones.

Because of the dilute uranium solutions produced in D Cell, a dilute flow sheet with a nominal uranium concentration in the feed of 10 grams/liter was used for each of the extraction runs. Dissolution of NRX and NRU fuel resulted in solutions containing only 1 to 2 grams/liter uranium, but these solutions were blended to about 10 grams/liter of uranium by mixing with more concentrated uranium solution of Vycor glass leachate (Section I-1.3) which had been previously stored in N Cell.

Decontamination in the three Hexone extraction cycles was good and the product easily met all specifications. Equipment performance for the Hexone extraction process was generally good.

1.2 Recovery of Uranium from EBR-I Core 2 Melt

(M. E. Jacobson, Chemistry Section; G. F. Offutt, Process Engineering Section)

Core 2 of Experimental Breeder Reactor I was partially melted in-reactor, and in this condition it represented a unique problem for the recovery of the approximately \$500,000 worth of enriched uranium. The melt contained uranium, zirconium, and stainless steel from the fuel, and sodium and potassium from the reactor coolant. Because of the safety problems associated with this material, and the unusual and heterogeneous composition, the fuel was dissolved in 1-kg batches in a shielded cell under direct visual surveillance. The pieces of melt and relics of cladding and fuel rod dissolved readily in 12M nitric acid-0.6M hydrofluoric acid solution with the reaction controlled by the rate of addition of the reagent. A geometrically safe dissolver fabricated from Carpenter-20 stainless steel was used. The uranium was decontaminated by conventional solvent extraction techniques. The operation proceeded without difficulty with six batches of fuel being dissolved per day. The successful recovery of this uranium at an out-of-pocket cost of \$0.38/gram suggests that other nonspecification fuels of unusual composition can also be processed economically at ICPP. The development work preliminary to this recovery was reported in the preceding Annual Report [1] and the details of the campaign are reported in IN-1088 [2].

1.3 Recovery of Uranium from EBR-II Vycor Glass Molds

(R. D. Modrow, G. F. Offutt; Process Engineering Section; M. E. Jacobson; Chemistry Section)

About 30.6 kg of 50 percent enriched uranium were recovered from broken Vycor glass molds that are used to cast fuel pins at the EBR-II Fuel Cycle Facility. Uranium was leached from the glass scrap with nitric acid in the ICPP Multicurie Cell and extracted from the leachate in the ICPP extraction system. Two runs--one in July 1966 and one in January 1967 lasting about three weeks each--were made during FY 1967. They will continue at approximately six-month intervals as long as fuel is processed routinely in the EBR-II Fuel Cycle Facility.

1.31 Process Description. The glass arrived at the ICPP Multicurie Cell, a shielded remote-handling cell, in three-gallon cans contained in a lead cask. After transferring a can inside the Multicurie Cell, the glass was poured into an 11-inch-OD plastic vessel which served as a dissolver. Then, a fixed volume of 6M HNO_3 was added to leach the uranium from the glass. After overnight sparging of the glass-acid mixture, the resulting leachate was decanted, and the glass was rinsed three times with water. During the first run the leachate and rinses from each bucket of scrap were immediately transferred to a critically safe collection vessel in the ICPP uranium recovery cell (J-Cell) and combined for an overall uranium input measurement; during the second run the leachate and rinses were transferred to a six-inch-ID vessel where thorium oxide (ThO_2) solids were allowed to settle out before transferring the decanted leachate to J-Cell. (Thorium oxide is used to lubricate the glass molds at EBR-II before the uranium is cast in them, and a large quantity -- up to 15 weight percent of the glass -- was present as ThO_2 with the glass scrap.)

Nuclear safety was ensured in the Multicurie Cell by allowing a maximum of only eight liters of solution in the dissolver vessel at one time. The six-inch-ID settling vessel was dimensionally safe; it was placed more than three feet from the dissolver so that there was negligible interaction between the two.

Following the leach and rinse operations, the glass was returned to the transfer can and sent to the burial grounds. The ThO_2 solids separated from the leachate were also transferred to cans (which contained vermiculite to soak up liquid) and buried.

After making input measurements in J Cell, the solution was transferred to N Cell for interim storage until it can be processed through the hexone solvent extraction system with dissolver product from future processing of aluminum fuels.

1.32 Processing Experience. Seventeen cans of glass were leached during the first run, and eleven were leached during the second run. Separation of the ThO_2 solids by settling in the six-inch-ID vessel was very successful during the latter run. This separation was made because solvent extraction experiments on the leachate from the first run indicated that the solids contributed to the formation of emulsions. Analysis of the 800 ml of solids that were collected indicated that they contained only 0.35 percent uranium by weight.

Material balances made at the EBR-II Fuel Cycle Facility indicated that the first glass shipment contained 23.8 kg of uranium and the second shipment contained 11.9 kg. About 18.7 kg of uranium were recovered from the first and 11.9 kg were recovered from the second for recoveries of 78 percent and essentially 100 percent, respectively.

Scrap containing irradiated fuel that was out of the reactor only 50 days was processed; however, most of it was at least 120 days cooled. During the first run some buckets containing up to 18,000 curies of radioactivity were handled; however, troublesome floor contamination outside of the Multicurie Cell was experienced with these full, high-activity-level cans. Experience showed that when the cans were less than 2/3 full of glass, and contained less than 12,000 curies of radioactivity, processing was relatively easy.

In the future the processing scheme will be improved by having the scrap shipped in cans with liquid-tight stainless steel liners. Leaching will then be done in the cans, and the troublesome transfer of glass to and from the dissolver will be avoided. The cell will become less contaminated and a savings in clean-up time is expected at the end of each run.

1.4 ICPP Modifications

(R.D. Modrow, J. C. Petrie; Process Engineering Section)

Advantage has been taken of the standby status of the ICPP during WCF operation to modify equipment for improved operation. Equipment deficiencies noted during zirconium fuel processing have been corrected. Natural recirculation loops on the aluminum fuel dissolvers have been added to improve uniformity of the dissolver product and to decrease mercuric nitrate consumption. A Clarkson feeder, installed to transfer uranium product from intercycle storage to the second extraction cycle at a uniform flow rate, has been proved in limited plant operation. The aluminum fuel charging cave is being modified to accommodate ATR fuel and provide interim storage for more fuel elements. A solid

bowl centrifuge is being installed to clarify column feed and thereby eliminate plugging of process lines and lessen interface crud formation. Design work is nearly complete on a product wash column in the first cycle extraction process and for replacing the two-inch-diameter columns in the second extraction cycle with five-inch-diameter columns.

1.41 Aluminum Fuel Headend. Two major modifications to the aluminum fuel processing headend are being made. The first, the addition of a recirculating loop on each of the two dissolvers for aluminum fuel, is expected to reduce the consumption of mercuric nitrate catalyst by a factor of three for the same dissolution rate [3]. In addition, the product composition is expected to be more uniform. Second, the chute to the charging cave over the dissolvers is being changed to accept the longer ATR fuel elements, and the shielding on the charging cave is being increased to allow interim storage of more fuel elements.

1.42 Zirconium Fuel Headend. Several alterations in the zirconium headend should result in increased dissolution rate, decreased operating problems, and the ability to recover rare gases from zirconium fuels. First, operation of the dissolver at both a higher liquid level and a higher temperature will be made possible by raising the off-gas outlet line and increasing its size. A ten percent decrease in the volume of liquid waste is expected to result from a potential 0.1 mole per liter increase in the zirconium concentration made possible by the changed operating conditions. Second, an alternate acid feed line at the top of the dissolver charging chute is being added to break fuel element bridges that occur occasionally in the charging chute. Dissolver acid will normally be added near the bottom of the dissolver; however, if bridging occurs, acid will be added at the top of the chute to dissolve some of the bridged fuel, allowing it to fall to the bottom of the dissolver. Third, because of mechanical and electrical difficulties, an off-gas blower is being replaced with a steam jet. A new line being installed in conjunction with the new jet will enable routing of the dissolver off-gas through the Rare Gas Plant as an alternate to a direct vent to the stack. In the past, the dilute hydrogen-air mixture from the dissolver was not routed to the Rare Gas Plant; however, after installation of inter-connecting piping, the hydrogen-rich off-gas steam from zirconium fuel dissolution can be processed for rare gas recovery. An integrator on the dissolver off-gas hydrogen analyzer will enable calculation of the approximate amount of undissolved fuel in the dissolver, thus providing better process control. A fourth change will provide separate borated process water systems for the dissolver and condenser cooling jackets which were originally connected in series. Originally, it was impossible to heat the dissolver and cool the condenser at the same time. Now, a new heat exchanger will allow a higher operating temperature in the zirconium fuel dissolver than in the condenser.

1.43 Column Feed Clarification. Aluminum dissolver product and complexed zirconium dissolver product are both processed through the same first-cycle extraction equipment. In the past, undissolved solids have contributed to line plugging and interface crud formation with these dissolver products. To minimize these difficulties, a common feed clarification system will be installed to remove solids from dissolver solutions before they are fed into the first-cycle extraction system. A solid bowl centrifuge was selected because it has been proved in highly radioactive service, is abrasion resistant, and requires little maintenance. When removal of solids from the centrifuge is necessary, the dissolver product will bypass the centrifuge, and the cake in the centrifuge bowl will be washed with the use of high-pressure sprays. Finally, the washed

solids will be slurried and transferred to waste storage via the Process Equipment Waste system.

1.44 First-Cycle Process Piping. Piping changes on the headend evaporator will permit, during zirconium fuel processing, an aluminum nitrate scrub stream and an organic wash stream to be concentrated independent of any zirconium-bearing stream. This mode of operation -- previously not possible because of the instability of the zirconium-bearing solutions when heated^[4] -- will reduce the volume of waste produced by an estimated ten percent during future zirconium processing campaigns; a modest increase in the processing rate for zirconium dissolver product may also be realized. The headend evaporator will continue to be used to concentrate combined aluminum dissolver product and recycle streams before uranium recovery in the extraction columns.

1.45 Increased Capacity of Hexone Cycles. Design work has been completed on a project to replace the two-inch-diameter columns in the second cycle of the Hexone solvent extraction system with five-inch-diameter columns. With the larger columns, a major plant capacity limitation will be removed.

1.46 First Cycle Product Wash. A new perforated-plate, pulsed column will be installed in the first-cycle extraction process to replace an existing seven stage mixer-settler which removes residual organics from the product prior to its entry into the intercycle evaporator. Performance, throughput, and recurring mechanical problems prompted the planned replacement of the mixer-settler.

1.47 Clarkson Feeder. In the past, product from intercycle storage has been transferred to the second extraction cycle by a Lapp reciprocating-type pump. Irregular feed rates from this pump have contributed to system instability. A Clarkson feeder, which has small cups on a motor driven rotating wheel, has replaced the reciprocating pump as a metering device, and it has been shown to deliver a more uniform flow to the IIA column. Uranium solutions have been transferred via the Clarkson feeder with excellent results; no mechanical problems have occurred and the uniform feed rate to the IIA column has improved its operating stability.

2. SUPPORT STUDIES FOR CURRENT ICPP FUEL RECOVERY PROCESSES

2.1 Dissolution of Aluminum-Uranium-Silicon Alloys

(Bernice E. Paige; Chemistry Section)

Fabricators of reactor fuel have requested that substantial quantities of silicon be allowed in the fuel core alloy because it suppresses formation of UAl_4 , stabilizes UAl_3 , and thus improves the fabrication characteristics of the alloy. A joint study is being made by the Metallurgical Development Section of the Reactor Engineering Branch and the Chemistry Section of the Chemical Technology Branch to determine the advantages and disadvantages of the use of silicon in test reactor fuel elements. This investigation is to cover all phases of the fuel cycle and includes metallurgical studies and laboratory tests of the effect upon chemical reprocessing. The present study indicates no adverse effects of the silicon on dissolution rates of the alloys. Future reports will cover the effects of the silicon upon extraction and solids handling in the chemical reprocessing of reactor fuels.

In the present work only two and three component alloys were used in order to obtain an accurate impression of the origin of the effects noted. In earlier dissolution studies [5, 6], the aluminum-silicon alloys contained other metal constituents, and the uranium-aluminum alloys were usually clad in aluminum alloy. Fourteen castings of various alloys of aluminum, uranium, and silicon (simulating fuel meat and cladding) were prepared by the Metallurgical Development Section, rolled to 0.10-inch-thick sheets, and cut into coupons. The alloys studied contained 0, 22, and 31 percent uranium, a range of silicon contents from 0 to 11 percent, and the remainder aluminum (99.9 percent pure). In the uranium alloys, the uranium contents were selected to be representative of the fuel plate core composition in 400- and 500-gram ETR fuel elements. The particular levels of silicon used were selected on the basis of the solubility of silicon in aluminum and the proposed levels in fuel meat and cladding.

Dissolution tests were initiated in 6.6M nitric acid-0.007M mercuric nitrate at the boiling point (103-104°C) using 4.8 moles of acid per mole of aluminum and a uniform surface area to volume ratio. All dissolutions were continued until no metal remained. The data for the amounts dissolved were obtained by analysis of the solutions. The instantaneous dissolution rates for the alloys are reported (Table II) as milligrams of aluminum dissolved per square centimeter of surface per minute ($\text{mg}/\text{cm}^2\text{-min}$) at the level of 30 grams per liter of aluminum in the dissolver solution. Since the early portions of the dissolution obeyed a parabolic rate law, the instantaneous dissolution rates were determined from the slope of a graphical presentation of the square of the aluminum concentration versus the dissolution time.

The dissolution rates measured for these alloys are satisfactory for processing schedules at the ICPP and are comparable to rates measured previously for pure aluminum. The acidity of the dissolver solutions varied from about 1.5 to 3.2M at 30 grams of aluminum per liter, but no correlation was evident between the acidity and the instantaneous dissolution rates. The dissolution rates for aluminum are depressed by the presence of uranium in the alloy, especially when it does not contain silicon. This effect is far in excess of the dilution of the alloy by the uranium on either a volume or atomic basis. The presence of silicon in aluminum-uranium alloy at any concentration from 0.6 to 5 percent enhances the dissolution of the aluminum. Possibly, there is

TABLE II
INSTANTANEOUS DISSOLUTION RATES
FOR ALUMINUM-URANIUM-SILICON ALLOYS^[a]
(mg/cm²-min)

Silicon Concentration	Uranium Concentration		
	0%	22%	31%
0.0%	26	9	4
	26	9	4
0.6%	23	--	8
	22	--	8
1.5%	26	--	10
	23	--	8
3.0%	--	26	12
	--	25	11
	--	--	11
	--	--	13
	--	--	12
5.0%	27	16	10
	28	13	11
11.0%	9	--	--
	7	--	--

[a] Determined at 103°C at a level of 30 g/l aluminum in solution.

a maximum instantaneous dissolution rate for aluminum-uranium alloys with 3 percent silicon present, but the total time required for the dissolution was about the same as for the other silicon-containing alloys indicating that only the initial rate was higher. The five values presented in Table II for 31 percent uranium-3 percent silicon are for alloys which were rolled different numbers of times to achieve the same thickness reduction; no difference in rates was observed. The dissolution rates for the aluminum alloys which contained no uranium decreased when the silicon content exceeded 5 percent. In earlier studies [5] with aluminum alloys containing small amounts of other metals, this effect occurred at a lower silicon content.

No difference was found in the dissolution rates for rolled and cast aluminum coupons. The dissolution rate of 26 mg/cm²-min for pure aluminum reported in Table II was for coupons rolled to 0.1-inch thickness. A cast ingot of the pure aluminum, machined to the same size coupons and dissolved at identical conditions, had a dissolution rate of 30 mg/cm²-min. This is comparable, considering the difference in temperature and catalyst, to 17 mg/cm²-min obtained for cast coupons at 90°C and 0.005M mercuric nitrate showing that the new data can be

compared directly with earlier data for various commercial aluminum alloys [5].

Figure 1 shows typical dissolution curves for 31 and 22 percent uranium alloys. It shows that during the early stages of the dissolution with the 31 percent alloy, and for the complete dissolution with the 22 percent alloy, there was preferential dissolution of aluminum compared to uranium. In the alloys containing 22 percent uranium this effect was greater than in the alloys containing 31 percent uranium. For each alloy the difference between the fraction of uranium and aluminum dissolved was fairly constant during the dissolution of

Fig. 1 Comparison of aluminum and uranium dissolution in aluminum-uranium-silicon alloys.

the first half of the coupon. For some dissolution operations, homogeneous dissolution of uranium and aluminum is assumed in the criticality calculations. This evidence of slight preferential dissolution of aluminum over uranium should be taken into consideration in the criticality evaluation of these operations.

2.2 Dissolution of Aluminum Alloy 2219 (R. G. Butzman, Chemistry Section)

Aluminum alloy type 2219-T62 is currently under consideration as a possible cladding material for future test reactor fuel assemblies. Type 2219 is an aluminum-copper alloy developed especially for elevated temperature applications; it has higher strength in the temperature range, 260 to 316°C, than any other wrought aluminum alloy presently available.

Dissolution rate measurements for 2219 aluminum were performed on coupons and small unirradiated test reactor fuel plates in 6.0M HNO₃ catalyzed with mercuric nitrate at the boiling point. The mole ratio of nitric acid to aluminum was 4.8/1. Table III lists the rate data obtained.

TABLE III

DISSOLUTION RATES FOR TYPE 2219 ALUMINUM IN 6.0 M HNO₃ AT BOILING

Sample	Metallurgical State	Hg Catalyst Concentration M	Instantaneous Dissolution Rate at 30 g/l Dissolved Aluminum mg/cm ² -min
Coupon	T62	0.2	0.9
Coupon	T62	0.05	0.7
Coupon	T62	0.005	1.4
Test reactor fuel plate	T62	0.005	0.5
Test reactor fuel plate	Hot rolled	0.005	0.3

Coupons of this alloy in the T62 state and fuel plates clad with this alloy dissolved at a rate of about one mg/cm²-min, which is about 1/25 the rate of high purity aluminum. These preliminary experiments with 2219-T62 aluminum suggest that dissolution in mercury-catalyzed nitric acid is too slow for normal plant production rates.

An extensive study of dissolution rates for a variety of aluminum alloys in mercury-catalyzed nitric acid was made by Fletcher and others in 1962 [5]. Their work showed that copper and nickel ions in solution produced an anti-catalytic effect. Attempts by Fletcher's group to overcome the passivating effects of copper by "contact activation" and increased mercury catalyst concentration were unsuccessful. Alternate methods that may be suitable for dissolving this

alloy, but were not investigated at this time, include electrolytic dissolution or dissolution in sodium hydroxide [7].

2.3 Corrosion Observations During Zirconium Fuel Reprocessing

(D. W. Rhodes, T. L. Hoffman, C. A. Zimmerman; Chemistry Section)

2.31 Dissolvent Make-Up and Storage Equipment. The dissolvent make-up and storage tank, constructed of carbon steel lined with "Goodyear - Plioweld", was examined after one and one-half years service. This vessel was exposed to aqueous 7 M hydrofluoric acid solution containing 4 g/l of boron (added as boric acid) and a trace of nitric acid (0.03M) during part of this service. The examination revealed that the coating was slightly discolored in the bottom section of the vessel but was still soft and pliable. The cooling coil, boron detectors, and stirring equipment, all fabricated from Monel, showed less than 2.0 mils per month corrosion. A loose black deposit, calculated as representing approximately 2-1/2 percent of the lining on the lower 1/3 of this vessel, was found on the bottom of the tank. Analysis of this deposit indicated that it contained copper sulfide and elemental sulfur. The copper presumably came from the Monel fittings in the tank and the sulfur from the tank lining. Both the tank and the fittings are still in serviceable condition.

2.32 Headend Dissolver. Corrosion of the headend dissolver, constructed of Monel-400, was evaluated during processing operations. A 3/4-inch-diameter Monel pipe, extending from the top to the bottom of the vessel, was installed temporarily in the headend dissolver to monitor corrosion during processing. Inspection of this pipe indicated a uniform corrosion rate of 7.5 mils per month for the operating dissolver.

2.33 Product Evaporator. The product evaporator is constructed of Type 304L stainless steel with Type 304 stainless steel plates containing boron suspended in the disengaging head space for criticality control in the event of a malfunction. Stainless steel corrosion coupons (Type 304L and Type 304 containing 1.5 percent boron) suspended in the disengaging section of this vessel were examined after 20 months of exposure. Based on the results of this examination, the stainless steel plates containing boron lost an estimated 1.0 mil of metal from each exposed surface. The Type 304L stainless steel of the vessel body lost 0.02 mil of metal.

Laboratory corrosion tests of stainless steel containing boron, carried out in the vapors above solutions undergoing evaporation (Table IV), indicate that nitric acid processing solutions containing 0.1M fluoride, and no aluminum for complexing, lead to excessive corrosion, while solutions containing no fluoride or 0.1M fluoride along with excess aluminum for complexing (3 moles aluminum per mole fluoride) result in low corrosion rates.

2.34 Titanium Equipment. Failure of a titanium elbow in a thermosyphon evaporator during a recent zirconium processing campaign was apparently due to attack by the processing solutions containing complexed fluoride. This attack was accelerated in a stressed area along the inside radius of a mitred and welded elbow at the bottom of the thermosyphon section. This evaporator was not being used, but had not been removed from the processing system since it was presumed that the completely complexed stream in a stagnant condition would not be excessively corrosive. After the failure, the idle vessel was removed from the processing system for the remainder of the campaign.

TABLE IV

VAPOR PHASE CORROSION OF TYPE 304L STAINLESS STEEL CONTAINING 1.5% BORON

Solution Number		1	2	3
Solution Composition				
U	<u>M</u>	0.84	0.84	0.84
NO ₃	<u>M</u>	3.78	3.78	4.68
H	<u>M</u>	2.1	2.2	2.2
F	<u>M</u>	---	0.1	0.1
Al	<u>M</u>	---	---	0.3
Corrosion Rates (mpm) and Test Exposure				
24 hours @ 85°C		---	6.8 ^[a]	0.2 ^[a]
23 hours @ b.p.		0.16	8.6 ^[a]	0.11
90 hours @ b.p.		0.30	8.6	0.32

[a] Results of a single determination -- other results represent the average of two determinations.

Laboratory corrosion tests (Table V) indicate that titanium experiences severe corrosion and is not acceptable for service in normally complexed zirconium fluoride processing solutions. Further tests are being undertaken to determine whether fluoride at any concentration may be allowable for zirconium processing streams in contact with titanium.

2.35 Vitreous Enamel Flowmeter Lining. An electromagnetic flowmeter with a vitreous enamel lining which was used during aluminum fuel processing failed in zirconium fuel processing service. Specimens of the blue vitreous enamel material (Albyline), used for lining the electromagnetic flowmeter, were tested in a number of processing and decontaminating solutions. As a result of these tests it was concluded that the vitreous enamel was resistant to aluminum nitrate solutions, but was unsuitable for extended use in processing solutions containing fluoride, even in the presence of excess aluminum nitrate as a complexing agent.

Corrosion tests were run with solutions containing fluoride complexed with calcium [(Ca)/(F)=0.5]. This greatly reduced corrosion rates compared to those experienced without calcium. The average corrosion rate of 2.8 mils per month was sufficiently low to permit limited use of this lining material in processing of calcium-complexed streams containing fluoride, eg, feed to the Waste Calcining Facility. The enamel appears sufficiently resistant to alkaline decontaminating agents to withstand the short exposures used for decontamination.

TABLE V
CORROSION OF TITANIUM IN SYNTHETIC ZIRCONIUM PROCESSING SOLUTIONS
AT 35°C [a]

<u>Solution Number</u>		<u>Complexed Dissolver Product First Cycle Raffinate</u>			
		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
<u>Solution Composition</u>					
F	<u>M</u>	5.32	4.43	3.74	3.81
Zr	<u>M</u>	0.76	0.65	0.63	0.53
Al	<u>M</u>	0.41	0.37	0.56	0.45
B	<u>M</u>	0.28	0.30	0.25	0.25
H	<u>M</u>	1.84	2.02	1.33	1.75
U	g/l	1.13	1.0	---	---
<u>Corrosion Rates (mpm)</u> <u>on Welded Specimens</u>					
20 Hour Exposure		56	590	225	750
87 Hour Exposure		14 ^[b]	---	---	---
110 Hour Exposure		---	---	43 ^[b]	---

[a] Rates are averages of two or more determinations.

[b] Decrease in corrosion rates in extended tests may reflect depletion of the reactive components in the solution.

2.4 Nuclear Safety in the ICPP Dissolvers (W. G. Morrison; Chemical Technology Staff)

Increased uranium loading of the Engineering Test Reactor (ETR) fuel elements prompted a reappraisal of the nuclear safety aspects of the ICPP continuous dissolver. The aluminum-alloyed ETR fuel elements were increased to 505 g U-235 maximum from 405 g U-235, the previous high loading. Meat composition of the 505 g uranium-aluminum alloyed fuel elements is 28 wt% uranium, 93 percent U-235. The nuclear evaluation of the ICPP dissolver (7.5-inch inside diameter, partially reflected) showed that the highest k_{eff} calculated was about 0.87 for ETR fuel meat at a metal volume fraction (MVF) of 0.15 in the dissolver. Figure 2 presents a curve showing k_{eff} versus MVF for the 505 g U-235 fuel elements. A similar reactivity curve with a maximum k_{eff} of 0.84 at 0.15 MVF was obtained for the 405 g U-235 ETR fuel elements (23.8 wt% uranium). As usual, this evaluation was based on unirradiated fuel with no burnup and no credit for any burnable poison content in the fuel. Also, nuclear safety evaluations of dissolvers for the aluminum process at ICPP are based on fuel element meat composition only, because it would be possible to dissolve aluminum cladding and nonfueled side plates leaving a mass of fuel meat. Metallic fuel is present in the dissolver in varying and unknown configurations throughout the dissolution operation. The entire range of MVF was considered in order to cover any fuel configuration possible. The normal operating k_{eff} is

Fig. 2 K_{eff} curve for ICPP continuous dissolver containing ETR fuel element meat [28 percent U (93 percent ^{235}U)] and water.

appreciably less than the calculated maximum based on the metal volume fraction of 0.60 to 0.65 expected in the dissolver under normal conditions [8].

The nuclear evaluation was performed using the FOG one-dimensional code (NAA-SR-6104) [a] on the IBM-7040. Four-group nuclear constants for the diffusion calculations were generated using the GAM-1 (GA-1850) [b] and TEMPEST-II (AMTD-111) [c] codes for the fast neutron groups and thermal group, respectively.

[a] NAA-SR-1604, H. P. Flatt, "The FOG One-Dimensional Neutron Diffusion Equation Codes", Atomics International (1961).

[b] GA-1850, G. D. Joanou and J. S. Dudek, "GAM-1: A Consistent P-1 Multi-group Code for the Calculation of Fast Neutron Spectra and Multigroup Constants," General Atomics (1961).

[c] AMTD-111, R. H. Shuddle and J. Dyer, "TEMPEST-II: A Neutron Thermalization Code", Atomics International (1961).

3. GRAPHITE FUELS REPROCESSING

Development of a fluidized bed combustion-nitric acid dissolution process for reprocessing graphite (eg, nuclear rocket) fuels at ICPP is underway. The combustion-dissolution process, shown in simple schematic form, in Figure 3, consists of the following steps: (a) burning of the graphite fuels in a bed of fluidized alumina; (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 solution, which is fed to the solvent extraction system for uranium recovery. Undissolved solids will be monitored for uranium content, and those which contain a significant amount of uranium will be isolated and stored for future processing. This process was selected because of (a) its compatibility with existing solvent extraction facilities at ICPP, (b) its simplicity relative to other graphite fuels processes, and (c) the ease of usage also as a demonstration facility for reprocessing the High Temperature Gas Cooled (HTGR) power reactor fuels.

Fig. 3 Combustion-dissolution process for graphite fuels.

A four-inch-diameter fluidized bed graphite fuels burner and dry ash collection system was installed and tested during FY 1966. A description of this pilot plant and the results of the initial tests are reported in IDO-14680[1], the Annual Report for FY 1966. Results from these initial tests revealed that the

metal oxide combustion products could be separated from the inert alumina bed by elutriation in the off-gas stream. However, during these tests only 65 percent of the graphite in the fuel was burned, and a significant amount of uranium oxide remained in the burner.

Pilot plant development studies at ICPP during the past year have continued to examine the dry physical separation of the metal oxide combustion products from the inert alumina particles in the fluidized bed and to maximize the graphite combustion in the fluidized bed. A moderate laboratory development program was conducted in support of the pilot plant development effort.

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

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

During the fiscal year, additional tests were made in the four-inch-diameter fluidized bed burner, and a graphite fuels pilot plant was fabricated and installed in the High-Bay Chemical Engineering Laboratory. Operational testing of the equipment and initial experimental tests of the burner have been completed in the new pilot plant.

3.11 Fluidized Bed Burner Operation. As previously reported[1], two major problems associated with the in-bed separation of product ash from the inert alumina were (a) the excessive amount of unburned graphite carried overhead and (b) coating of uranium oxide on the alumina bed. These problems have been solved during the past year. In early studies, thirty-five percent of the total graphite in the fuel charged to a single-stage burner was carried overhead with the product ash. Since the burner was operated with an excess of fuel present most of the oxygen was consumed in the lower portion of the burner, leaving an insufficient amount to react with particles released from the burning fuel and rising through the upper portion of the burner. Subsequent tests with a two-stage fluidized bed burner showed that at least 97.5 percent of the graphite in Rover fuel can be burned compared to 65 percent for a single-stage burner. The fluidized bed is continuous between the first and second stages. The second stage is mounted above and contiguous to the first stage and has a larger diameter than the first stage. The fluidizing velocities in the two stages are made approximately equal by the addition of oxygen to the second stage. Sufficient oxygen is present in the second stage to burn any small graphite particles carried up from the first stage.

Originally, it was concluded from short tests in the single-stage burner that about 4 wt% of the uranium oxide particles in the fluidized bed were too large to elutriate from the burner. Further examination revealed that the retained uranium was not in the form of large uranium oxide particles but as small particles coated on the alumina. These particles thus appeared in the uranium analysis of the larger size fractions in the fluidized bed samples. In longer runs, the steady state concentration of uranium oxide coating on the alumina particles in the single-stage burner was shown to level out at 2 to 4 wt%. Most of this uranium oxide coating on the alumina can be removed and elutriated from the single-stage burner by fluidizing the bed for about two hours without charging additional fuel elements. Tests to determine the steady state concentration of the uranium oxide coating on the alumina bed in a two-stage burner are planned.

Experimental data showing typical uranium behavior in the fluidized bed burner are shown in Figure 4. The lower portion of this figure shows the uranium buildup in the bed during a 51-hour run. Within 15 hours, a steady state level had apparently been reached: at mid-run, an equipment malfunction allowed the temperature to rise and disturb the equilibrium, but within 10 hours after correction was made the uranium level had returned to 4 wt% and remained in the 2 to 4 wt% range for the rest of the run.

Fig. 4 Uranium buildup in the fluidized bed during combustion of uranium-graphite fuels.

The upper curve in Figure 4 represents an unusual run, but illustrates the ease of eliminating excess uranium oxide from the fluidized bed. This run was made with a different type of alumina, a larger alumina particle size, a higher fluidizing velocity, and a higher temperature than with all other runs. During this run, the uranium oxide coated very heavily on the alumina. The coating increased at a fairly steady rate of about 1.5 wt% per hour over a period of 20 hours. One or a combination of the above four factors is believed to have caused the heavy coating because this is the only run in which it occurred. This uranium oxide coating was subsequently reduced from 32 wt% to 1.4wt%, and the uranium oxide was elutriated from the burner by continuing the fluidization for two hours without charging fuel to the burner. Thus, a heavy coating of uranium oxide on the alumina, if it should occur in the future, can be easily removed and elutriated from the burner. At the end of each campaign, the uranium remaining in the bed in a nonelutriatable form can be leached with acid before the bed is discarded. Thus, uranium losses from the burning operation are expected to be negligible.

3.12 Graphite Fuels Process Pilot Plant. Based on the encouraging results from the four-inch-diameter burner, a graphite fuels pilot plant was fabricated and installed in the High-Bay Chemical Engineering Laboratory. This pilot plant consists of a two-stage fluidized bed burner with a combination wet off-gas cleanup and uranium dissolution system and a dry overhead product collection system. The pilot plant is also designed for charging full length Rover fuel elements to the first stage of the burner, thus eliminating the fuel element size reduction facilities that would otherwise be necessary for a Rover fuels process.

(1) Equipment Description The graphite fuels pilot plant is constructed in two modules, (a) burner and dry product collection module and (b) wet off-gas cleanup and uranium dissolution module, with each module having the capability of being operated independently or in conjunction with the other. A simplified flow diagram of the pilot plant is shown in Figure 5.

Fig. 5 Graphite fuels pilot plant equipment flow diagram.

The original four-inch-diameter burner [1] is used for the first stage of the two-stage burner; the second or upper stage is constructed from type 316 stainless steel pipe (Schedule 40, six-inch-diameter, and 10 feet long) mounted on top of the first stage with a flanged reducer. Thus, the two-stage burner consists of a continuous fluidized bed, the cross-sectional flow area of the second stage being twice that of the first stage. In a similar manner to the first stage, the second stage is equipped with external electrical heaters for startup and a sheet metal jacket for cooling air. Both sections are insulated with high temperature magnesia insulation.

Rover fuel elements are charged to the burner through a charging tube extending through the center of the second stage to the top of the first stage. The first stage is fluidized by gas entering the bottom of the burner and the second stage is fluidized by the gas from the first stage plus additional gas that enters the bottom of the second stage through a jacket surrounding the charging tube. Perforated horizontal plates are located in the second stage to reduce the formation of large gas bubbles, smooth the fluidizing action, and increase the residence time of small particles.

Solids elutriated from the burner and carried in the off-gas stream can be collected by a dry collecting system using sintered stainless steel filters or by a wet scrubbing system using nitric acid. The wet off-gas cleanup and uranium dissolution module consists of a venturi scrubber, cyclone, York Mesh demister, uranium dissolution tank, steam-jet exhauster, off-gas condenser, and an absolute filter. A fines feeder for metering fine granular solids into a stream of air is connected to this module to allow the wet off-gas cleanup system to be operated independently of the burner.

The off-gas stream carrying elutriated solids from the burner (or from the auxiliary fines feeding system) is contacted with nitric acid in the venturi scrubber where the solids impinge on the liquid droplets generated in the venturi. Liquid droplets are removed from the gas stream by the cyclone and the York Mesh demister, both of which drain to the dissolution vessel. Because of the large pressure drop through the scrubber, a steam jet exhauster is required to raise the absolute pressure of the off-gas for exhaustion to the building off-gas system. The water vapor is then condensed from the off-gas, and the gas heated above its dew point and filtered by an absolute filter before entering the building off-gas header. Off-gas condensate can be routed to the dissolution tank if it contains a significant amount of uranium, or it can be routed to the cold-waste drain.

Two glove boxes are used in conjunction with the pilot plant unit in order to prevent spread of alpha contamination in the laboratory. Fuel is charged to the burner through a double valve airlock system from a glove box on top of the burner module. Remote actuators for the charging valves are located in the glove box. A full flow sample filter that can be valved into the off-gas system at various points to determine the efficiency of the wet off-gas cleanup system is also located in the fuel charging glove box. A second glove box near the bottom of the module contains the fluidized bed sample outlets and the dry product outlet. Samples can be obtained from five locations in the fluidized bed by manipulating sample valves controlled by actuators located in the glove box.

(2) Experimental Results. Detailed experimental studies in the complete pilot unit have not yet been undertaken. However, preliminary studies with the two-stage burner have shown that (a) the fluidized bed can be operated and controlled without difficulty (even with different fluidizing velocities in the two stages), (b) at least 97.5 percent of the graphite charged can be burned in the bed, (c) charging whole Rover fuel elements to the first stage of a two-stage burner is feasible, (d) uranium oxide particles can be elutriated by the off-gas, and (e) continuous operation is possible without frequent bed leaching.

Typical operating conditions for the pilot plant burner are as follows:

Temperature	700 - 800°C
Fluidizing Gas Feed	
First Stage	30 - 100% O ₂
Second Stage	100% O ₂
Fluidizing Velocity	1.0 ft/sec
Fluidized Bed Height	
First Stage	5 ft.
Second Stage	7 ft.
Inert Bed Material	-40 +70 mesh Norton RR Alundum

3.2 Corrosion Observations in the Graphite Burner (T. L. Hoffman; Chemistry Section)

Following initial tests with unirradiated graphite fuel in the fluidized bed burner, the unit was disassembled and examined for evidence of corrosion. After 73 hours at 600 to 950°C, plant test components in the graphite burner suffered a maximum corrosion rate of 0.5 mils per month (Table VI). The alloys studied were Types 330, 310, 304, Carpenter-20 (Cb) stainless steel, and Nichrome (1% Mn, 19% Fe, 15% Cr, Bal. Ni). All of these alloys appeared to resist corrosion equally well in the burner environment, which is given in Table VII.

TABLE VI
CORROSION OF VARIOUS ALLOYS AFTER
73 HOURS IN THE GRAPHITE FUEL BURNER
Temperature: 600-950°C

Type Alloy	Plant Test Piece	Corrosion Rate (Mils per Month)
Type 330 SS	Fluidizing Baffle w/o Blade	0.16
Type 330 SS	Blades for Fluidizing Baffle	0.28
Type 310 SS	Fluidizing Baffle w/Blades	0.40
Type 310 SS	Fuel Support Grid	0.19
Type 304 SS	Baffle Support Rod	0.05
Type Carpenter-20 (Cb)	Baffle Support Rod	0.05
Nichrome	Baffle Support Rod	0.05

3.3 Leaching of Uranium from Burner Ash (L. A. Decker; Chemistry Section)

The product from the graphite fuels burner will consist mostly of finely divided (-100 mesh) uranium oxide, U₃O₈. Dissolution of the uranium oxide in nitric acid is to be accomplished in a downflow contactor such that the residence time is sufficient to assure complete recovery of all soluble uranium. A series

TABLE VII
COMPOSITION OF THE ATMOSPHERE IN THE GRAPHITE FUEL BURNER
(Percent)

<u>Atmosphere</u>	<u>O₂</u>	<u>N₂</u>	<u>CO</u>	<u>CO₂</u>
Inlet	46	54	---	---
Outlet	2	54	1-5	39-43

of experiments with product from the prepilot plant burner showed that all of the uranium would be dissolved in 15 minutes with 4M nitric acid at 95°C. Eight molar nitric acid dissolved all of the uranium in five minutes at 100°C, and 15.7M acid accomplished this in six minutes at 80°C.

4. SUPPORT STUDIES FOR OTHER SCHEDULED ICPP PROCESSING OPERATIONS

4.1 Electrolytic Dissolution Studies

(L. T. Lakey, B. R. Dickey, W. B. Kerr; Development Engineering Section)

The electrolytic dissolution of stainless steel reactor fuels in nitric acid was first tested by Pitzer^[9] in 1951. By 1958, the need for reprocessing capacity for stainless steel and Nichrome fuels appeared to be growing rapidly, and development work on an electrolytic process was started at both the Savannah River Laboratory^[10] and the Idaho Chemical Processing Plant (ICPP). Studies at ICPP were directed primarily at the dissolution of fully enriched fuels, the most prominent of which were the stainless steel cermet from the Army Package Power Reactor (APPR) program and the Nichrome cermet from the High Temperature Reactor Experiment (HTRE) in the Aircraft Nuclear Propulsion program. When it became clear in 1965 that only limited quantities of these fuels would require reprocessing, they were assigned to the Savannah River Plant and development work at ICPP was suspended. At that time an electrolytic dissolver, employing the solution-contact principle, had been developed at ICPP to a point where a plant-scale process could be designed^[11]. Results from this development program included (a) demonstration of acceptable dissolution rates for actual fuels, (b) determination of the effects of operating variables upon the dissolution rates, and (c) development of methods for controlling the concentration of metals in the dissolver product solution. Fabrication and testing of a dissolver considered suitable for plant installation, however, were not included in the development program.

Recently, the reprocessing of EBR-II fuel was assigned to ICPP. Evaluation of methods for processing the EBR-II and other stainless steel type fuels proposed for future processing has resulted in the decision to install an electrolytic dissolution headend at ICPP. The EBR-II fuel contains a moderately enriched uranium alloy core comprising more than 60 percent of the total element weight, and utilizes a sodium bond between the core and stainless steel cladding, as compared to the greater than 90 percent stainless steel in the cermet fuels

studied earlier. These differences have made it necessary to reactivate the electrolytic dissolution development program at ICPP.

4.11 The ICPP Pilot Plant Electrolytic Dissolver. A 24-inch-long pilot plant dissolver of the open-top trough design developed during the earlier work, and having 3000-ampere capacity at 20 volts, is being fabricated and assembled into a system for further test work. This dissolver is identical, except for length, to that proposed for plant installation. Pilot plant studies will include (a) proof-testing of the dissolver design for materials suitability, operation, and adequate capacity; (b) evaluation of special hazards such as splashing and evolution of hydrogen resulting from the reaction between the sodium bonding and the nitric acid; (3) evaluation of an electrodeless conductivity measurement system for controlling the concentration of the dissolver product solution; (d) determination of the process significance of small amounts of insoluble alloying agents in the fuel; and (e) determination of the nitric acid consumption at the low metal concentrations proposed for this fuel.

A pictorial drawing of the pilot plant dissolver is shown in Figure 6. The removable niobium basket will be perforated and slotted on both anode and cathode sides and will be separated from both the anode and cathodic dissolver body by alumina insulating discs. The anode will consist of a 1/4-inch-thick-niobium plate clad with 0.03 inch of 90 percent platinum-10 percent iridium alloy on the surface facing the basket and will be separated from the cathodic dissolver body by alumina insulating discs. Additional insulation will not be required between the back of the anode and the dissolver body because current flow across this small solution gap will be prevented by the valve characteristics of the niobium. The current which flows from the platinum alloy of the front surface of the anode will also be directed through the basket, due to the valve characteristics of niobium, by bending the niobium anode around the end of the basket, thus making the current path through the basket the shortest path between anode and cathode.

The dissolvent, approximately 3 M nitric acid containing about 10 grams per liter of dissolved metal, enters the bottom of the dissolver and passes upward through the basket to the level of the overflow weir near the top of the cathodic side of the dissolver. Solution overflowing from the dissolver will be pumped through an external cooler and returned to the dissolver. The metal content of the dissolvent will be controlled by the addition of 4 M nitric acid and simultaneous withdrawal of product solution. A simplified flow sheet of the system is shown in Figure 7.

Fig. 6 Electrolytic dissolver.

Fig. 7 Flow sheet of electrolytic dissolution system.

4.2 Ammonium Bifluoride Process for Zirconium Clad Zirconium Dioxide-Uranium Dioxide Fuels

(L. A. Decker, T. L. Evans; Chemistry Section)

Three distinctly different processes are being considered for fuels like the Zircaloy-clad zirconium dioxide-uranium dioxide fuel of the Shippingport PWR Core 2 seed 1. One of these processes, described in this report, involves dissolution of the mixed oxide fuel core in fused ammonium bifluoride. A second process using a three-step aqueous dissolution flow sheet has been described previously and a third, a halide volatility process, is currently under study at Argonne National Laboratory in a cooperative program with Idaho Nuclear Corporation. Upon completion of the Argonne studies, the three processes will be evaluated to select one for further development and installation at the ICPP.

Results of recent ICPP studies on the fused salt alternate are presented here. The fuel elements are composed of sintered wafers of enriched uranium dioxide (28 percent) and zirconium dioxide (72 percent), coated with pyrolytic graphite, and distributed in Zircaloy-4 fuel plates. These sintered oxide wafers are resistant to dissolution by the common fuel reprocessing solvents. Long exposure to high concentrations of fluoride ion at elevated temperatures eventually dissolves the wafers.

Anhydrous, fused ammonium bifluoride provides a system that is high in fluoride concentration (42 M) at a higher temperature than is possible with aqueous systems. The mixed zirconium dioxide-uranium dioxide in the wafers will dissolve in fused ammonium bifluoride at temperatures greater than 190°C. A two-step aqueous-fused salt dissolution method is outlined in the flow sheet represented by Figure 8.

4.21 Decladding. The Zircaloy-4 cladding dissolves rapidly and completely in 10 M hydrofluoric acid if the fluoride to zirconium mole ratio is 5 or higher.^[13] If the decladding solution is sufficiently low in uranium concentration, it could be sent directly to waste storage; otherwise, it would be combined with the product from the fused salt dissolution of the zirconium dioxide-uranium dioxide meat.

The Zircaloy-4 cladding is soluble in the fused salt but this would not be a desirable decladding method because the zirconium forms a thick slurry of ammonium fluozirconate, $(\text{NH}_4)_3\text{ZrF}_7$, at a slurry loading higher than two moles per liter, thus requiring a great excess of ammonium bifluoride just to dilute the slurry. The ammonium fluozirconate is soluble in aqueous systems along with the ammonium bifluoride, but the resulting solution is too high in fluoride ion concentration to allow practical solvent extraction of the uranium in the equipment at ICPP. Fortunately, the two-step dissolution method allows the use of the fused salt to dissolve the highly resistant oxides but avoids the problem of thick slurry and high fluoride concentration in the solvent extraction feed solution.

4.22 Dissolution. The dissolution of the zirconium dioxide-uranium dioxide wafers in fused ammonium bifluoride proceeds at 190°C at a rate high enough to process about five batches per day in one piece of equipment. Dissolution would be carried out in the same vessel as the decladding step after removing the aqueous hydrofluoric acid solution and raising the temperature of the vessel to the dissolution temperature.

The anhydrous dissolver product containing the uranium has a uranium

INC-B-11065

Fig. 8 Flow sheet for two-step aqueous-fused salt dissolution of advanced PWR fuel.

solubility of about 37 g/1000 g of solution (at 190°C) as shown in Figure 9. Most of the zirconium from the zirconium dioxide will be present as the insoluble ammonium fluozirconate since the solubility of that compound in the anhydrous solution is about 0.10 mole/1000 g at 190°C as shown in Figure 10. The flow sheet calculations assumed a solubility of 0.05 mole/1000 g to allow for cooling to 150°C upon transferring to the adjustment vessel.

The corrosion data shown in Table VIII indicate that several materials could be used to contain the fused salt at a temperature of about 190°C.

4.23 Adjustment. The anhydrous dissolver product containing the uranium can be dissolved and the fluoride complexed with a solution of aluminum nitrate. Chromic acid will rapidly dissolve the resulting uranium tetrafluoride by oxidizing the uranium to U(VI). The proper acidity for rapid oxidation of uranium is obtained by adjusting with nitric acid. The complexed solution is then suitable for feed to the solvent extraction columns where the uranium is extracted with tributyl phosphate.

4.24 Conclusion. This two-step aqueous-fused salt process is proposed as a possible alternate to the three-step all aqueous process [12] but appears to have no advantage over the latter at present. Final selection of a process will await an evaluation study after a halide volatility process has also been studied.

Fig. 9 Solubility of uranium in anhydrous NH_4HF_2 versus temperature.

Fig. 10 Solubility of zirconium in anhydrous NH_4HF_2 versus temperature.

TABLE VIII

CORROSION RATES FOR VARIOUS METALS IN FUSED AMMONIUM BIFLUORIDE

Metal	Corrosion Rate (mils/mo)	
	<u>140°C</u>	<u>190°C^[14]</u>
Carpenter-20	1	
Monel		6.4
Hasteloy C		3.2
310 SS		5.7

4.3 Chemical Destruction of Dowex Resin (M. W. Wilding; Chemistry Section)

Dowex 1-X4 resin used to recover Np-237 or other radioisotopes from process streams can be completely dissolved in hot (70 to 90°C) 0.2M KMnO_4 -2.0M HNO_3 solution for disposal when the useful life of the resin has been expended. The solution containing the dissolved Dowex resin can then be concentrated to half its original volume without the formation of precipitates. The resin would be dissolved so that it could be safely and easily pumped into waste storage tanks, thus eliminating many of the problems which could be encountered in disposal of the radioactive resin by other means.

Dowex 1-X4 resin was treated in laboratory experiments with various concentrations of potassium permanganate, chromic acid, and nitric acid as shown in Table IX. Dissolution at 70°C in 0.2M KMnO_4 -2.0M HNO_3 was quite effective and only mildly corrosive (less than 2.0 mils per month) to austenitic stainless steels. One liter of this solution dissolved 40 grams of resin in eight hours. A low nitric acid concentration was purposely chosen to avoid the instability that has occurred at about 10M nitric acid^[15].

The solution containing the dissolved resin was concentrated to about one half the original volume. The concentrated solution was stable, but solids began to form as the evaporation continued.

TABLE IX

TEST CONDITIONS AND RESULTS DURING TRIAL
DISSOLUTION OF DOWEX 1-X₄ RESIN

<u>Temp.</u> <u>(°C)</u>	<u>Time</u> <u>(Hours)</u>	<u>CrO₃</u> <u>(M)</u>	<u>KMnO₄</u> <u>(M)</u>	<u>HNO₃</u> <u>(M)</u>	<u>Observations</u>
20	24	16			Physically degraded but not dissolved
70	24	16			Physically degraded but not dissolved
90	24	8		2.0	Physically degraded but not dissolved
20	24		1.5		No apparent degradation
90	24		1.5		No apparent degradation
20	24		0.2	2.0	No apparent degradation
90	6		0.2	2.0	Completely dissolved
90	8		0.2	1.0	Dissolved except for a trace of resin
70	8		0.2	2.0	Completely dissolved

II. WASTE MANAGEMENT

1. THE IDAHO WASTE CALCINING FACILITY

1.1 Operating Experience in the Current WCF Processing Campaign (G. E. Lohse; Process Engineering Section) (T. L. Hoffman; Chemistry Section)

The second processing campaign in the Waste Calcining Facility (WCF) was started in mid-March 1966, with nonradioactive simulated waste; and after equilibrium conditions were attained, radioactive waste was started to the calciner on April 1. In the succeeding 15 months, about 595,000 gallons of waste from three tanks have been converted to about 6,600 cubic feet of solids which are stored in permanent storage bins. Since initial operation of the WCF in late 1963, about 1.1 million gallons of highly radioactive waste have been reduced to solids. In general, operation of the facility continues to be excellent.

1.11 Operating Summary. During the second processing campaign, the average "on-stream" feed rate, as shown in Table X, has been about 91 gallons per hour (14 percent above design), while the net rate has averaged about 65 gallons per hour. The on-stream time has been about 79 percent. During the last quarter of this period, the average net feed rate has been increased to nearly 78 gallons per hour by evaporation of the feed just prior to calcination. The release rate of ruthenium to the environment has averaged about 380

TABLE X

WASTE CALCINING FACILITY OPERATING SUMMARY -- RUN H-2

	Run to Date, <u>June 30, 1967</u>
Total operating time, hrs	10,950
Operating time (with hot feed), hrs.	8,610
Net volume of waste calcined, gals.	595,000
Net volume liquid to blend tanks, gallons/hr	65.4
Gross liquid calcined, gallons/hr	91.3
Net volume solids to storage, ft ³	
From hot operation	6,590
Ruthenium release rate to stack, mCi/day	
Maximum-Minimum	3160-0.3
Average	380
Strontium-90 release rate to stack, mCi/day	
Maximum-Minimum	52-0.006
Average	0.20

millicuries per day and has ranged from 0.3 to 3160 mCi. The former value resulted during calcination of 15-year old waste, while the latter occurred during a temporary shutdown period with the ruthenium adsorbers on-stream. The established release limit for ruthenium is 52,000 mCi/day. The release rate of strontium-90 has averaged about 0.2 mCi/day and has ranged from 0.006 to 52 mCi. The strontium release exceeded one mCi/day on only 11 days during this campaign, and for 10 of these the higher releases resulted from excessive penetration through a defective off-gas filter. Normal release values were achieved merely by replacing the filter. The established release limit for strontium-90 is 2,600 mCi/day.

Flexibility of the WCF for processing various types of waste was demonstrated as two separate types of wastes were fed to the calciner at alternate 18-hour intervals for a five-month period. One waste contained a high concentration of ammonium nitrate, while the second contained a sodium concentration about double that contained in other ICPP first-cycle wastes. This processing procedure was used to minimize the ammonium concentrations in the feed and off-gas scrubbing solutions. No process upsets resulted and pseudo-equilibrium conditions in the calciner and scrubbing systems were obtained. At present, the wastes from these two tanks have been combined in one vessel and the mixture is being fed to the calciner.

Overall operation of the WCF has been satisfactory except for five unscheduled shutdowns due to leaks; there were additional minor problems not involving shutdowns, with the feed control system, the ruthenium adsorbers, and the final filters. Four of the shutdowns were caused by leaks in the NaK heating system and are discussed in Sections II-1.2 and -1.3. The other leak, in the solids transport system, and problems encountered with feed control, adsorbers, and final filters are discussed below. All problems except for NaK or solids leaks encountered during WCF processing were solved without calciner shutdown.

1.12 Solids Transport Abrasion. Two leaks in the solids transport system have occurred since the beginning of the second WCF campaign. In neither case was any air-borne activity released from the process cells or filter system. The first leak was discovered after the calciner was shut down in September 1966 because of a NaK leak in the tube bundle of the calciner NaK heat exchanger. The solids leak was located in one of the two product takeoff lines, and an estimated 12 cubic feet of solids were discovered on the calciner cell floor. Removal was accomplished by a combination of pushing with a long-handled scraper and water flushing the solids to a floor drain, and also by dissolving part of them with nitric acid. The leak was attributed to the abrasive action of the alumina product on certain sections of the pipe.

The second leak also occurred in the same product line, but was located closer to the calciner in a fitting at the junction of the solids removal control air and product takeoff lines. About two cubic feet of solids were discovered on the floor in a routine daily inspection, and were removed in a similar manner to that described above. Misalignment in the fitting presumably caused severe abrasive action. The second product takeoff line was removed and inspected, but abrasive action on this line, which was constructed properly, was minimal. Selected sections of the piping (Types 304L and 347 stainless steel) were replaced with heavier wall piping or with Type 17-4PH stainless steel, heat treated to Rc 40 hardness.

1.13 Feed Control. Considerable feed control problems associated with plugging of feed lines, valves, and nozzles were experienced during the initial months of the campaign[1]. One nozzle plugged completely on May 15, 1966, and remained plugged until the unscheduled shutdown in September. The plugging was attributed to silica gel which collected in the feed evaporator and then collected at the electrodes of the flowmeter as the liquid was fed to the calciner. The feed rates to the other two nozzles were increased, and the overall feed rate continued to be over 10 percent above design.

A second nozzle plugged on June 14, 1966, and remained plugged for seven days. Surprisingly, the calciner operated well with the one remaining nozzle, and a feed rate of 71 gallons per hour was maintained. The versatility of the WCF to continue to operate at satisfactory rates with only one nozzle was adequately demonstrated. At no time was the calciner operation shut down, or slowed appreciably, due to feed line plugging.

1.14 Adsorber Operation. Four large beds of silica gel containing 6300 pounds each are installed in parallel to adsorb ruthenium from the WCF off-gas. The adsorbers continued to keep ruthenium release rates at an average of 380 mCi/day, well below the maximum allowable limit. Fluctuations in the ruthenium release were frequently observed, and these were caused by alternate processing of different wastes or by unscheduled shutdowns during which feed to the calciner was shut off. At one time an abrupt increase in the ruthenium release rate was attributed to breakthrough of ruthenium from one of the adsorbers. This adsorber was taken off stream, and the ruthenium release rate decreased immediately. After regeneration of the silica gel, the adsorber was placed back on stream and the ruthenium release remained low.

1.15 Final Filter Operation in Presence of Ammonium Nitrate. Early in July 1966, while processing aluminum nitrate waste containing a high concentration of ammonium ion, the pressure drop across the final filters increased about 4 inches, to 10.5 inches of water, during a four-day period of operation. The off-gas filters were replaced, and ammonium-free waste was started into the WCF because it was believed that the rapid rise in pressure drop was related to the ammonium waste. However, a rapid pressure drop rise occurred with the new filters until the temperature of the off-gas entering the filters was decreased from 85 to 80°C. After the temperature change, a dramatic four-inch decrease in pressure drop across the filters was observed. An analysis of the operation indicates that trace quantities of ammonium nitrate (first from the waste during calcination and later -- while ammonium-free waste was being calcined -- from residual material in the calciner, scrubbing system, and/or silica gel absorbers in the off-gas train) may deposit on the filters and form crystals to partially plug the filter gas passages. The connection between temperature and pressure drop could be due to a temperature effect on the size of ammonium nitrate crystals. At 84.5°C, a marked change occurs in dimensions of ammonium nitrate crystals.

1.16 Packless Valve Failures. Considerable corrosion occurred on the discs and welds of the Type 348 stainless steel bellows of valves that were removed from the feed system for repair. An inspection of the bellows of one of these packless valves revealed that transgranular stress corrosion cracking, intergranular attack, pitting, and cyclic fatigue had occurred. Both mechanical and corrosive conditions contributed to the metallic disintegration.

The operating experience to date indicates an approximate service life of nine months in nitric acid feed solutions. This is similar to earlier experience with this type valve[16]. Although thicker discs and welds will increase the service life with respect to corrosion, a light gauge material is required to obtain the mechanical characteristics required for the successful operation of bellows-seal valves.

1.2 NaK Heating Problems in the Current WCF Campaign (G. E. Lohse; Process Engineering Section)

The heat required for the decomposition of the calciner feed is supplied through an indirect heat transfer system which uses an eutectic liquid metal (NaK) to transfer heat from an oil-fired radiant heater to the fluidized bed. Details of this system are presented elsewhere[17]. The material of construction of this system is primarily Type 316 stainless steel, which was selected over other austenitic steels because of its greater initial strength at elevated temperatures.

Performance of this NaK heat transfer system generally has been satisfactory. However, most of the unscheduled calciner shutdowns to date have occurred because of failure of liquid metal system components and piping. Operation of the system was first begun in 1961; up to June 1967, there had been 44 startups from room temperature, about 1300 hours of operation below 600°C, and over 20,000 hours of operation above 600°C. Over 75 percent of the operating time has been accumulated during operation of the WCF with radioactive feed. During the first processing campaign (about 7600 operating hours), two NaK leaks which occurred from the same fitting (a riser from the NaK header to an expansion tank) located in a nonradioactive portion of the facility were responsible for 51 of 57 hours of downtime. Details of these failures are described in IDO-14662[18].

In the second (current) WCF processing campaign, four additional failures in the NaK system have caused shutdown for repair or replacement of components. The first of these occurred after 3542 hours of operation (16,200 accumulative hours) from the same area, ie, the riser to the expansion tank, as the leaks in the first campaign. This time the riser was changed from 1-1/2- to 3-inch pipe and a flexible connection was installed in the helium line at the top of the expansion tank to reduce stress levels. Operation was resumed and continued for 800 hours until a failure of the field coils on the NaK pump forced a second shutdown. During a testing period to confirm the NaK pump failure, a NaK leak from the heat exchanger inner-tube area to the helium monitoring chamber[17] was also discovered. This, along with maintenance on other WCF components exclusive of the NaK system, required a shutdown of about two months. Satisfactory repair of the NaK pump was achieved merely by replacing the field coils, but restoration of the heat exchanger to its original integrity was not attempted after it was determined that operation without the helium monitor was practical and did not introduce any undue hazard.

The fluidized bed heat exchanger, as originally designed[17], consisted of 42 bayonet tubes each having a helium filled annulus between the NaK-containing tubes and the outer heavy walled jacket tube. Changes in pressure in the helium chamber were intended to indicate any leakage in tube walls. Except for failure of both a NaK tube and a helium jacket tube, it is not possible for NaK to leak into the fluidized bed.

Previously, calculations reported in the WCF Safety Analysis [17] indicated that NaK leak rates up to one gallon per minute would not even noticeably increase the temperature of the fluidized bed. On the other hand, NaK leak rates of 14.8 gallons per minute or greater would cause a rapid increase in the bed temperature, and this effect would constitute a means of discovery of large NaK leaks. However, complete severance of a tube would be necessary for large leaks.

A comprehensive review of the system at the time of the second failure indicated that the consequences of a NaK leak into the calciner were unchanged, and only the detection capabilities for small NaK leaks were affected. To compensate for loss of the helium monitor for detecting small leaks, a continuous level recorder with appropriate alarms was incorporated in the NaK expansion tank to alert operating personnel of changes in the volume of NaK in the circulating loop. Additionally, analysis of bed and scrubbing solution samples for potassium (present in the feed only in very low concentrations) permits detection of NaK leaks as low as 100 cc/hr. Thus, small NaK leaks can be detected before they become serious. Further review indicated that the tensile strength of the Type 316 stainless steel samples removed from the system was very near that of new metal, and, because the outer helium jacketing tubes have twice the wall thickness of the inner NaK return tubes, the tubes were considered strong enough to contain NaK at all operating temperatures. Therefore, the decision was reached to continue operation of the facility without repair of the heat exchanger. The helium monitoring chamber was isolated from the helium blanketing supply and a new drain was installed from the chamber to an existing NaK drain line.

Following this shutdown, the system was operated satisfactorily for 3050 hours before a NaK leak occurred from one of the drain lines for the main NaK piping. Another brief shutdown was required to replace a damaged fitting in the immediate vicinity of the leak. After about 1000 hours, the fourth failure was detected from the NaK pump tube. The pump was removed from the system, rebuilt with available spare parts, and reinstalled. Currently the NaK system is functioning smoothly and no serious problems are anticipated. Results of metallurgical examination of components removed from the NaK piping are presented in Section II-1.3, following.

1.3 Effect of NaK on Stainless Steel Piping in the WCF Heat Exchange System (T. L. Hoffman; Chemistry Section)

Stainless steel, Type 316, was selected as the material of construction for the vessels and lines in the NaK heat transfer system of the Waste Calcining Facility because of its tensile strength at elevated temperatures and its resistance to NaK and nitrate vapors at elevated temperatures. At the time this choice had to be made there were no data on the net effect of long-term exposure of Type 316 stainless steel to NaK at 600 to 750°C. Today, with greater than 20,000 hours operating time on the NaK loop of the WCF, this system has had more time at elevated temperatures than any other known operational or test loop and, therefore, represents a valuable source for information on the response of this material to NaK at elevated temperatures. In general, the material has performed very well although a specific limitation has now been defined by experience. This is a susceptibility to failure by brittle fracture under applied stress. This dictates careful arrangement of vessels in the loop and requires thorough design analysis of the supporting structures.

The liquid metal in this system is the sodium-potassium eutectic alloy, 22.8 wt% Na-78.2 wt% K. Most of the operating time on the loop has been in the temperature range 600 to 700°C with 44 starts from room temperature. During steady operation the oxygen content of the NaK has been maintained below 50 ppm.

1.31 Evaluation of Piping From the Hotter Portion of the Loop. A service test examination was conducted on a portion of line that was installed upstream from the NaK heater in the ICPP Waste Calcining Facility. This three-inch Schedule 40 pipe was in NaK service for 1,118 hours below 600°C and 15,174 hours above 600°C, and had undergone 37 starts from room temperature without failure.

The test piece was cut from the loop so as to include a custom-made wrought tee fitting having 0.55-inch-thick walls that were welded into the piping. The overall length of the specimen, which included the pipe and tee, was 33 inches.

A metallographic examination of the piping and weld joints in the assembly indicated carbide precipitation at the grain boundaries and concentrations of up to 11 percent sigma phase (hard intermetallic compound of the general formula FeCr), as shown in Figures 11 and 12. A band of decarburized material 1 to 2 mils thick was found on the NaK side of the pipe wall (Figure 13). An 0.2- to 0.3-mil-thick porous oxidation film was observed on the outer surface of the pipe wall (Figure 14). This film was only partially soluble in boiling nitric acid and was magnetic.

The averages of duplicate analyses for carbon and nickel were 0.03 and 12.6 percent, respectively, on 5-mil-deep turnings from the inside of the pipe, and 0.09 and 13.2 percent, respectively, on similar turnings from the outside surface of the Type 316 pipe. General corrosion damage on the specimen after this 16,292-hour service was nil.

From X-ray diffraction studies, the presence of sigma phase was confirmed as a constituent in the NaK exposed piping. Carbide phases that were present in the NaK-exposed piping were not extracted or identified. The results of ASTM A262 tests, "Boiling Nitric Acid Test for Corrosion-Resisting Steels", on piping that had been exposed for 16,292 hours are recorded in Table XI. The corrosion rates increased with time on piping that had had 5 mils removed from the inside and outside surfaces, so that, at the end of the third period, the rate was 2.7 mils per month. On the other hand, piping that was tested before the inside and outside surfaces were removed suffered more than 10 mpm corrosion. After the tests, intergranular attack was observed on the piping.

The mechanical properties of the three-inch test pipe at 20°C and at 760°C in air are recorded in Table XII. The observed tensile and yield strengths compare favorably with published values for unexposed Type 316 stainless steel. However, the observed average elongation percentages of the exposed pipe were 46 percent and 63 percent lower than the average of the published values at 20 and 760°C, respectively. Izod impact test results show that pipe specimens which had been in NaK service absorbed 65 percent less kinetic energy in breaking than similarly tested specimens from unexposed pipe.

66-9-1126

10% OXALIC ACID ETCH

750X

Fig. 11 Sigma particle in X-Section of 3-inch Schedule 40 Type 316 SS pipe after 15,000 hours at 760°C.*

66-9-1127

10% OXALIC ACID ETCH

750X

Fig. 12 Cross section of 3-inch Schedule 40 Type 316 SS pipe after 15,000 hours at 760°C.*

66-9-1128B

10% OXALIC ACID ETCH

750X

Fig. 13 Decarburized zone of inside edge of 3-inch Schedule 40 Type 316 SS pipe after 15,000 hours at 760°C.*

66-9-1128

10% OXALIC ACID ETCH

750X

Fig. 14 Outside, or air side, of 3-inch Schedule 40 Type 316 SS pipe after 15,000 hours at 760°C.*

* PHOTO REDUCED ONE THIRD IN SIZE.

TABLE XI

CORROSION OF WROUGHT TYPE 316 STAINLESS STEEL PIPE IN BOILING
65 PERCENT NITRIC ACID AFTER 16,292 HOURS SERVICE IN
NaK at 760°C

Specimen	Penetration mpm (8 Hr Test Periods)				Intergranular Attack
	1	2	3	Average	
Before Removal of Inside and Outside Surfaces	14.0	10.2	10.6	11.6	Severe
After Removal of Inside and Outside Surfaces	1.1	1.5	2.7	1.8	Mild

TABLE XII

MECHANICAL PROPERTIES OF TYPE 316 STAINLESS STEEL BEFORE AND
AFTER EXPOSURE TO HIGH TEMPERATURE NaK

	Tensile Strength (Ksi)[a]	Yield Strength (Ksi)[a]			Elongation in 2 inches (%)	Flattening Test ASTM A312	Subsize Izod Impact (Ft-lb.)
		0.2% Offset	0.1% Offset	0.02% Offset			
Published Values (no NaK service)							
at 20°C	70-110	28-55 ^[b]	25-42 ^[c]	21-42 ^[c]	40-70 ^[b]	Satisfactory	NA ^[d]
at 760°C	30-45	19-30 ^[b]			20-60 ^[b]		
Measured Values (after 16,292 Hours in NaK Service)							
at 20°C	96	51	47	28	30	Failed	3.6
at 760°C	36	15			14-16		
Unexposed Tests							
at 20°C						Satisfactory	10.2

[a] Kilo pounds per square inch.
 [b] ASM Handbook, Vol. 1, 8th Ed., page 504.
 [c] The Elevated Temperature Properties of Stainless Steels, ASTM Data Service Publication DS 5-51, December 1965.
 [d] There are no published values since this is not a standard test.

The exposed pipe broke completely into two halves during an ASTM A 312 flattening test, when flattening was continued until the opposite walls of the pipe met. On an unexposed pipe section, flattening was continued until opposite walls of the pipe met without producing cracks that could be observed at 15X in the section.

The hardness survey showed that the wrought pipe had diamond pyramid hardness numbers (DPH) that ranged from 150 to 180, which correspond to 79

R_b and 87 R_b , respectively. Welds had a hardness of 130 DPH which correspond to 71 R_b . These values are within the published range of values for unexposed Type 316 stainless steel.

1.32 Evaluation of Expansion Tank Connector Failures. Two service failures have occurred at the welds joining the pipe tee connectors and the nozzles of the NaK expansion tanks. Type 316 stainless steel was the material of construction of the weld deposits, nozzles, and connectors. Service time for one joint was approximately 3240 hours at 600 to 760°C, and about 360 hours below 600°C. There were four startups from room temperature. The other joint experienced 39 startups from room temperature with 15,800 hours of operation between 600 and 760°C and 1150 hours below 600°C.

During the post-failure examinations of these joints, cracks were observed in welds; in addition, the piping which was exposed for 17,000 hours (15,800 at 600 to 760°C) cracked (Figure 15). Cracks in the weld were propagated both transgranularly and intergranularly (Figure 16). Notches which are sites for local stress raisers were found in each of these weld structures.

Neither sigma phase nor carbide precipitation was found on either the wrought piping or the cast weld deposit of the joint that was exposed for 3600 hours. Electron microscope fractographs of this weld are typified by the classic striations or crack front arrest lines shown in Figure 17. This fatigue failure appeared to be caused by multi-cycle, low stress forces.

On the weld that was in service for 17,000 hours, sigma phase and carbide precipitation were observed at the grain boundaries. Eight crack front arrest lines were observed on a fractured surface at 30 diameters. Because of the number and width of these fatigue striations, the cyclic stress undoubtedly resulted from the thermal stresses that were imposed on the system during the 39 startups. The topography of the fractured welds surface is shown in Figure 18.

1.33 Evaluation of a NaK Drain Line Fitting Failure. A service failure occurred at a weld joining a forged concentric reducer to the drain pipe for the main NaK loop. Type 316 stainless steel was the material of construction on this forging, weld deposit, and pipe. Service time on this forging was 19,200 hours at 600 to 760°C and 1300 hours below 600°C. There were 43 startups from room temperature.

The postfailure examination showed that both the weld and reducer were cracked, accompanied by perforations in the weld area and the wall of the forged reducer. Cracks in the reducer were difficult to classify; these propagated both transgranularly and intergranularly.

A band of decarburization was observed on the NaK side of the reducer. Sigma phase and carbide precipitation at the grain boundaries were found in cross sections of the weld deposit and reducer. Electron microscope fractographs of the fracture in the weld are typified by elongated shaped dimples. These data suggest that shearing forces were imposed upon the weld, causing a ductile fracture. Fractographs of the fracture in the forged reducer suggest ductile tearing as in the weld fracture, but this observation is confused by a fracture profile which is a cleavage-type brittle fatigue fracture.

MTR(REML) 66-11-1512

45-SECOND VILELLA'S ETCH

500X

Fig. 15 Crack on inside of pipe tee connector after 15,800 hours at 600 to 760°C.*

MTR(REML) 66-9-1125

10% OXALIC ETCH

50X

Fig. 16 NaK expansion tank weld failure after 3,240 hours at 600 to 760°C.*

MTR(REML) 639-2

CARBON REPLICA

14,500X

Fig. 17 Surface topography of nozzle-connector weld failure after 3,240 hours at 600 to 760°C, showing crack front arrest lines.*

MTR(REML) 644-5

CARBON REPLICA

14,400X

Fig. 18 Surface topography of weld failure after 15,800 hours at 600 to 760°C, showing uniformly distributed faceted particles. Striations are absent.*

* PHOTO REDUCED ONE THIRD IN SIZE.

1.34 Conclusions. Most, if not all, of the failures in the Type 316 alloy in the WCF have been associated with brittle fractures in forged fittings or transition pieces where extra working had been done on the material. Apparently, the residual stress from this working plus the applied stress placed on the structure in thermal cycling has led to the failures. Information accumulated at this site since 1959 indicates that Type 304L stainless steel, in room temperature tests, has twice the impact resistance of Type 316 stainless steel after 10,000 hours exposure to NaK at 650°C. However, because the tensile strength is lower and no practical experience with Type 304L steel at WCF operating conditions has been obtained, extensive experimental evaluation would be required before a NaK loop of Type 304L steel could be designed with confidence. Thus, although there have been an undesirable number of failures in the Type 316 steel in the NaK loop, a material of construction superior to Type 316 steel has not yet been proved. An alternate method of heating the WCF calciner, or less demanding operating conditions for the NaK loop, is highly desirable to ensure uninterrupted operation.

2. ADVANCED WASTE CALCINATION STUDIES

2.1 Pilot Plant Calcination of Zirconium-Hydrofluoric Acid Wastes (S. J. Horn, T. K. Thompson; Development Engineering Section)

A 212-hour run was made in the 12-inch-diameter pilot plant calciner to study the calcination of simulated zirconium-hydrofluoric acid waste, complexed with calcium nitrate. Steady state operation was achieved, and results indicate that this type of waste can be successfully calcined at 400°C if a Ca/F mole ratio of at least 0.55 is maintained in the waste feed.

The 12-inch-diameter pilot plant calciner differs from the Waste Calcining Facility in that the primary cyclone for separation of fines from the off-gas is followed by a venturi scrubber and a condenser while the Waste Calcining Facility has a quench spray tower followed by a venturi scrubber and no condenser. Also, the Waste Calcining Facility off-gas requires additional cleanup in the form of silica gel beds to remove RuO_4 and absolute filters to remove the last traces of fines; the pilot unit does not handle radioactive material and thus does not require this final cleanup equipment.

The feedstock for the run was a zirconium-hydrofluoric acid solution simulating the waste obtained from processing of zirconium-based fuels, blended with accumulated off-gas scrubbing solution in a feed-to-scrub volumetric ratio of three to one. A calcium nitrate solution was added to complex the fluoride ion in a Ca/F mole ratio of 0.55. The resulting feedstock was a slurry containing a finely divided, calcium fluozirconate precipitate. Average feed compositions are shown in Table XIII.

Operating conditions for this experiment are shown in Table XIV. A 70-hour period of steady state operation was achieved for all operating parameters with the exception of scrubbing system compositions and the mass median particle diameter, which tended to oscillate throughout the run. However, the particle size could be changed by adjusting the relative flow rates of air and waste to the atomizing nozzle. A material balance over the 70 hours of steady state operation was within two percent of the theoretical calculations. The

TABLE XIII

AVERAGE FEED COMPOSITION OF
SIMULATED ZIRCONIUM WASTE

<u>In Solution:</u>	
H ⁺ (N _a)	1.40
Zr (M)	0.073
Al (M)	0.314
NO _w (M)	3.80
Ca (g/l)	29.60
F ⁻ (g/l)	14.05
Cr (g/l)	0.396
B (g/l)	1.08
Sn (g/l)	less than 0.015
<u>In Solids:</u>	
Zr (wt%)	31.2
Ca (wt%)	14.1
F (wt%)	31.25
Al (wt%)	approximately 1.0
<u>Solids Plus Solution:</u>	
Total Solids (g/l)	126.9
Undissolved Solids (g/l)	53.8
<u>Overall Molar Composition:</u>	
Al (M)	0.334
Zr (M)	0.252
Ca (M)	0.930
F (M)	1.614
Ca/F Mole Ratio	0.585

steady state values of various experimental parameters are shown in Table XV. The average chemical compositions of the calcined solids and of the scrubbing solution are shown in Tables XVI and XVII, respectively. Analysis of the off-gas for fluoride showed 10 micrograms of fluoride per liter of gas at an off-gas rate of 44 scfm.

The results of this work indicate that zirconium wastes can be successfully calcined at 400°C with a 1.0 ft/sec fluidizing velocity with the resulting product having a satisfactory attrition resistance.

TABLE XIV

OPERATING CONDITIONS FOR PILOT PLANT CALCINATION OF ZIRCONIUM WASTE

Starting Bed Material	Alumina calcine
Starting Bed Weight	139.7 lbs
Calculated Incipient Fluidization Velocity	0.39 ft/sec
Bed Temperature	400°C
Nozzle Air Ratio	650 and 700
Fluidizing Velocity	1.0 ft/sec
Average Feed Rate	16.1 l/hr
Run Duration	212 hours

TABLE XV

STEADY STATE VALUES OF EXPERIMENTAL PARAMETERS

Fluidized Bed Density	1.1 g/cc
Bed Height	31.2 inches
90% Bed Replacement Time	110 Hours
Bed Weight	204 lbs.
Calcined Solids Rates	
Product	4.3 lb/hr
Fines	0.33 lb/hr
Solids to Scrub System	0.12 lb/hr
Properties of the Fines	
Absolute Density	3.15 g/cc
Bulk Density	0.38 g/cc
Properties of the Product	
Mass Median Particle Diameter	0.62 mm (approximate)
Bulk Density	1.4 g/cc
Absolute Density	3.35 g/cc
Particle Density	2.2 g/cc
Attrition Index	78
Intra-Particle Porosity	0.35

TABLE XVI

CHEMICAL COMPOSITION OF CALCINED SOLIDS

<u>Component</u>	<u>Product</u>	<u>Fines</u>
NO ₃ (wt%)	2.5	8.0
Zr (wt%)	17.1	19.2
F (wt%)	13.0	19.6
Ca (wt%)	28.2	30.5
Al (wt%)	7.1	6.0
Total Volatiles at 700°C (wt%)		9.5

TABLE XVII

CHEMICAL COMPOSITION OF SCRUBBING SOLUTION

H^+ (<u>Na</u>)	≈ 4.2
NO_3^- (<u>M</u>)	≈ 4.6
Zr^{+4} (g/l)	≈ 1.3
Al^{+3} (g/l)	≈ 0.5
F^- (<u>M</u>)	≈ 0.17
Ca^{+2} (<u>M</u>)	≈ 0.06
Undissolved Solids (g/l)	None by Visual Inspection
Total Solids (g/l)	≈ 8.5

2.2 Fluidized Bed Calcination Using In-Bed Combustion of Fuel

(T. K. Thompson, S. J. Horn; Development Engineering Section)

An in-bed combustion process is being investigated as an alternate means of supplying heat directly to a fluidized bed calcination process without involving the use of a liquid metal (NaK) heat transfer medium. The process consists of spraying kerosene or kerosene vapor directly into a preheated fluidized bed through a two-fluid atomizing nozzle, while simultaneously calcining nitric acid or a nitrate-containing waste in the bed. Combustion occurs spontaneously and can be controlled by regulating the concentration of oxygen in the fluidizing gas. Above-bed burning is indicated by a vapor space temperature greater than the bed temperature; whereas in-bed burning is indicated by a bed temperature equal to or greater than the vapor space temperature. The presence of the decomposition products from the calcination of nitrate-containing waste solution is essential for operation at temperatures less than 675°C. Startup of the process has been achieved at temperatures as low as 400°C by preheating the bed. Theoretical calculations indicate that a significant increase in energy input to the 12-inch-diameter calciner is possible as compared with the original heating system.

2.21 Combustion Tests in a Four-Inch-Diameter Fluidized Bed. Preliminary tests to determine minimum combustion temperatures were conducted in a four-inch-diameter open-top vessel shown in Figure 19. This unit simulated the calciner vessel only, since no off-gas system existed. A two-fluid atomizing nozzle in the two-inch-diameter section was used to atomize the fuel with an adjustable mixture of air and pure oxygen. The fluidizing gas mixture could be adjusted to provide any desired proportion of air and oxygen. Preheating of the bed was accomplished by using external electrical resistance heaters.

Results obtained in the four-inch unit indicated that a minimum bed temperature of 650°C was required for spontaneous ignition and smooth in-bed burning of either kerosene or diesel fuel. Varying the proportions of air and oxygen, bed material or depth, and fuel material had no apparent effect on this

minimum temperature. These tests were carried out using both alumina and zirconia calcine fluidized beds.

2.22 Calcination with In-Bed Combustion. A 12-inch-diameter calciner, equipped with an off-gas scrubbing system, was used in studies to determine if calcination of simulated wastes and combustion of kerosene could be accomplished simultaneously. A flow sheet of this unit is shown in Figure 20.

Preliminary tests in the 12-inch unit substantiated the data obtained in the four-inch unit, indicating that unit size played a negligible overall role in the in-bed combustion process. When a thermal load, consisting of water feed at seven liters per hour, was imposed on the process, above-bed burning occurred at temperatures around 675°C. These tests were conducted with the top flange removed from the calciner vessel.

Fig. 19 Four-inch-diameter calciner.

Fig. 20 Simplified flow sheet of in-bed combustion calciner system.

When nitrate-containing wastes were substituted for the thermal load, the combustion conditions changed dramatically. Results indicate that the aluminum nitrate type wastes can be calcined at temperatures as low as 440°C while maintaining in-bed burning of the kerosene. Similarly, zirconium-type wastes can be calcined at 460°C. Indications of process stability were apparent with both types of waste. In addition, this test was repeated using only nitric acid as feed. With 2M HNO_3 , the minimum temperature at which spontaneous ignition and stable in-bed combustion could be maintained was 455°C; and with 13M HNO_3 , the minimum temperature was 400°C. The operating conditions for each case were identical, with the exception of the lower bed temperature achieved with the 13M nitric acid.

Tests were made to determine the minimum bed temperatures required for in-bed ignition of kerosene while acidic aluminum nitrate waste was being sprayed into the fluidized bed composed of alumina particles. The procedure was to preheat the bed to a temperature of 50°C above the desired test temperature. The heaters were then shut off and the aluminum nitrate feed started. When the bed reached the desired temperature, kerosene injection was started. Results to date indicate that spontaneous ignition can be achieved in alumina beds at bed temperatures of 400°C and greater. These tests were duplicated using a dolomite startup bed material. Results to date indicate that ignition followed by in-bed burning occurs at bed temperatures of 460°C and higher.

Tests were conducted to determine the minimum amount of pure oxygen required in the 12-inch diameter calciner. Experimental results indicated that 3 to 4 scfm of oxygen were required in addition to the 1.0 scfm of pure oxygen and 18.7 scfm of total air that were expected. Analyses of the off-gas showed no evidence of incomplete combustion nor did samples of the scrub or solid product. The discrepancy between the theoretical and actual oxygen requirements indicates that excess oxygen over the stoichiometric quantities may be necessary to achieve stable in-bed combustion.

2.3 Startup Beds For the WCF

(S. J. Horn, T. K. Thompson; Development Engineering Section)

The need for a heat stable, abrasion resistant, acid soluble startup bed material compatible with the calcination process in the Waste Calcining Facility (WCF) has been apparent since the March 1966 startup of the WCF. Prior to 1966, nonradioactive calcined alumina from startup test operations was available for use as a startup bed. After the supply of this material was exhausted, a substitute bed material was needed. During the 1966 startup, alumina mixed with sand was used as the starting bed. Part of this sand was elutriated from the bed and carried into the feed system, via blended scrub solution, where it contributed significantly to feed control problems because of its insolubility in nitric acid and consequent tendency to plug valves and orifices. A literature search for alternate starting bed materials resulted in three materials being selected for testing: Magnorite X (MgO), aragonite (CaCO_3), and dolomite [$\text{CaMg}(\text{CO}_3)_2$]. The selection was based primarily on thermal stability at calcination temperature, solubility in nitric acid, and availability of materials.

Preliminary tests, such as screen analysis, attrition resistance, and solubility in WCF scrub solution were undertaken to characterize the materials. Dolomite was subjected to calcination conditions at a temperature of 400°C in the two-inch-diameter calciner to determine if its high carbonate content would react with the acidic waste at calciner operating conditions and result

in destruction of the bed particles. This test was successful in all respects: no decomposition of the dolomite was evident, and the alumina calcine coating adhered to the particles. Subsequent testing of all three materials was performed in the 12-inch-diameter calciner.

All three materials were received in an "as-crushed" condition. The materials were screened and the fraction smaller than 16 Tyler mesh screen and greater than 92 Tyler mesh was used as the starting bed. The resulting material had a mass median particle diameter of 0.4 to 0.5 mm. All three candidate materials were tested under operating conditions in the 12-inch-diameter calciner for approximately 24 hours. Results indicated that all three materials are suitable for use as startup beds. In general, the materials had low attrition resistance and produced a greater amount of fines than alumina calcine, but had good solubility in nitric acid scrub solutions. Because of this high solubility, any fines elutriated were readily dissolved in the scrubbing solution and thus could be recycled to the feed system without difficulty. Due to its lower cost and local availability, dolomite was selected for a five-day test to study the long-term effects of its use as a startup bed material.

The five-day run using dolomite confirmed the results of the 24-hour test. A simulated acidic aluminum nitrate waste was fed at a rate of 22 l/hr to duplicate the vapor space velocities encountered in the Waste Calcining Facility. The total operating time was 112 hours, which allowed approximately one bed turnover to occur. The bed height remained at six inches above the nozzle during the entire run, and control of the mass median particle diameter was obtained by adjusting the nozzle air ratio. The fines elutriation rate was 100 percent of the theoretical solids production rate for the first 15 hours, but by the end of the run it had dropped to normal levels associated with alumina calcine ($\approx$ six percent of the theoretical solids production rate). By the end of this test the bed was essentially 100 percent alumina calcine.

In addition to the five-day run, several tests were made simulating the NaK heating period in the WCF using dolomite as the starting bed material. High fines rates were again observed but the elutriated material was easily handled by the scrubbing system due to the high solubility of the dolomite in the nitric acid scrubbing solution.

Dolomite has been selected as a startup bed material for the WCF. The mineral is crushed and screened to -16 +30 Tyler mesh screen size with a mass median particle diameter of 0.45 mm. The WCF was successfully started up using a dolomite starting bed on March 24, 1967.

2.4 Valveless Feed Control for the WCF

(P. E. LaMont; Development Engineering Section)

Suspended solids in the feed to the WCF calciner have caused occasional plugging of the flow control valves in the feed system. A proposal has been made to remove the valves and to control the feed flow rate with a fluid vortex amplifier used as a vortex restrictor. Studies are currently underway to test a commercial vortex amplifier in a mocked-up feed system.

2.41 Vortex Restrictor Description. A vortex restrictor is essentially a right circular cylindrical chamber into which the main fluid stream enters radially through a large port in the wall of the cylinder, and the controlling streams enter tangentially through tiny ports also in the wall of the cylinder.

Figure 21 is a cut-away view of a vortex restrictor. The combined fluids exit axially through a small port on the end of the cylinder. The tangential jets generate a vortex which is confined inside the chamber. By increasing the control stream flow rate, the pressure drop across the vortex is increased due to the greater angular and radial accelerations of the fluid and greater friction loss; because of the greater pressure drop, the main stream flow rate decreases. When the pressure drop across the vortex is significant compared to the overall pressure drop in the system, the flow rate can be controlled. In conventional applications, the main and controlling streams are both the same fluid, usually air. In the calciner feed control system, the main stream is the liquid waste and the controlling stream is air. This eliminates dilution of the feed by the control fluid. Performance is highly dependent upon chamber dimensions. In test run to date, a one-inch-diameter commercial model was used. Although tests are not yet conclusive, the results indicate that the pressure drop across the two-phase vortex is stable with respect to time.

Fig. 21 Cut-away view of vortex restrictor.

2.42 Simulated Feed System Tests. The vortex restrictor can be operated in two basic ways. Air from the two-phase outlet stream can be disengaged below the restrictor, or the two-phase outlet stream can be fed directly to the nozzle without the air being disengaged. Figure 22 is a schematic drawing of the test system showing both methods of operation. The overall head in the test system was the same as in the WCF feed system, and a full-scale calciner feed nozzle was used. Both water and aluminum nitrate solution were metered. For testing purposes, the range of control desired was from 90 to 20 gallons/hour net flow of liquid.

The results of the preliminary tests using a disengaging pot to separate the air from the liquid indicate that the liquid flow rate can be adjusted from greater than 90 to less than 20 gallons/hour. A greater head between the restrictor and the constant head tank requires a greater quantity of air for a given liquid flow rate. The restrictor was tested on levels from five to eight feet below the constant head tank; air rates up to 11 scfm were needed to reduce the flow to less than 20 gallons/hour. Once the air rate was set, the liquid rate remained essentially constant, confirming the formation of a stable two-phase vortex.

Fig. 22 Schematic diagram of apparatus for testing vortex restrictor operation.

The predictable nature of the response is particularly desirable in remote installations. In this system, the restrictor position and disengaging pot configuration must be chosen correctly so that the liquid will drain from the disengaging pot to the nozzle at all flow rates. Foam accumulation in the disengager pot has been a problem.

Tests using the nonvented system indicate that performance is dependent upon orientation and location of the vortex restrictor. When the restrictor is separated from the nozzle by a combination of horizontal and vertical runs of pipe, large pressure and flow fluctuations occur which are characteristic of two-phase flow. When the restrictor is separated from the nozzle by a minimum of pipe, cycling is reduced to a tolerable level and satisfactory flow control is obtained. A performance curve for the nonvented system is shown in Figure 23. The steep slope at low air flow rates and the shallow slope at high air flow rates are typical of both vented and nonvented performance curves.

Fig. 23 Vortex restrictor performance curve.

2.43 Future Studies. The rates of corrosion and erosion of the vortex chamber are unknown at present. It is planned to construct a restrictor of stainless steel for installation in a test loop which will be run unattended for long periods. Simulated aluminum and zirconium wastes will be used in the tests. A flowmeter and controller will be installed in the loop to test restrictor performance as a control element.

2.5 Corrosion-Erosion Testing of Materials Used in WCF Construction (T. K. Thompson, S. J. Horn; Development Engineering Section)

In anticipation of the Waste Calcining Facility operating with zirconium waste feedstock late in 1967, a recirculating test loop has been designed and constructed to study the combined corrosion and erosion properties of a synthetic,

zirconia bearing, acidic scrub solution. The composition of this solution is based on results obtained in pilot plant calcination of simulated zirconium waste in the 12-inch-diameter calciner. The solution is made by mixing fines from the pilot plant runs with a nitric acid solution.

Materials of construction for the test apparatus, with the exception of the silicon carbide spray nozzle, are the various stainless steel alloys that exist in the WCF scrub system, namely Types 304, 304L, and 347. A flow sheet of the test unit is shown in Figure 24. The pump is a Hazleton double volute, centrifugal slurry pump.

Fig. 24 Schematic diagram of corrosion-erosion test loop.

The first operating period comprised a total of 463 hours of operating time at 29°C and 12.5 psia. The average composition of the synthetic scrubbing solution used during this period is given below:

H^+	2.5 M
NO_3^-	2.5 M
Zr^{++}	0.5 g/l
Al^{+3}	0.4 g/l
F^-	0.13 g/l
Undissolved Solids	0.07 g/l

A comparison of pertinent operating parameters of the WCF and the corrosion-erosion loop test is given in Table XVIII.

TABLE XVIII
COMPARISON OF WCF AND TEST OPERATING CONDITIONS

Parameter	Test Value	WCF Value [a]
Scrub Flow Rate Through Ceramic Spray Nozzle	15.8 gpm	15.8 gpm
Scrub Flow Rate to Venturi Scrubber	0.40 gpm/orifice	2.645 gpm/orifice
Velocity of Scrub Solution on Orifice at Operating Conditions	18.3 ft/sec	17.3 ft/sec
Air Flow Rate Through Venturi Scrubber	60 scfm	709 scfm
Velocity of Air in Throat of Venturi Scrubber at Operating Conditions	242 ft/sec	245 ft/sec

[a] WCF data obtained from ICPP Waste Calcining Facility Safety Analysis Report, IDO-14620, Figure V-3, Page V-8.

At the end of the operating period, the test loop was dismantled and various components were measured for corrosion. Each piece was cleaned in boiling 35 percent HNO₃, water rinsed, acetone washed, air dried, and weighed. Corrosion rates, based on weight loss, for various components are given in Table XIX. No metal loss could be measured at the throat or orifices of the venturi scrubber although weight loss indicated some general corrosion of the equipment (Table XIX). The control valve was a dual-plug design constructed of Type 316 stainless steel. Measurement of the plugs and seats revealed an approximate 0.001-inch decrease in the outside diameter of the top plug whereas the lower plug diameter remained unchanged. The top seat increased in inside diameter by 0.0006 inch and the bottom seat increased by 0.0001 inch.

TABLE XIX

CORROSION-EROSION TEST RESULTS

Equipment Item	Corrosion-Erosion Rate (mils/month)
Silicon Carbide Spray Nozzle	0.03
Venturi Flowmeter (304)	0.08
Venturi Scrubber (304L)	0.31
Reducing Section (347-304-347)	0.00
3/4-inch ELL in Spray Nozzle Leg (347)	0.05
Pump Impeller	0.01

2.6 Model for Transient Particle Size Distribution in Fluidized Bed Calciner (B. R. Dickey, E. S. Grimmer; Development Engineering Section)

Mathematical modeling of the transient particle size distribution within the fluidized bed calciner[1] has continued during the year. The model's greatest potential is in predicting the response of the particle size distribution within the fluidized bed to changes in the feed rate, feed density, fluidizing gas velocity, and gas density. Correlation of the nozzle air-to-liquid feed ratio (NAR) in terms of a pseudo seed addition rate is required before the validity of the model can be established by comparison with actual plant data.

The form of the equations previously stated[1,19] and the computer program based on these equations are cumbersome and require excessive computer time. A more efficient computational algorithm for determining the transient response can be derived as follows. The cumulative weight fraction in the fluidized bed as a function of particle size and time is given by the following partial differential equation[19]:

$$\frac{\partial^2 W_f}{\partial L^2} + \left[\frac{A_c k_e(L)}{W_B g(L)} + \frac{P}{W_B g(L)} - \frac{3}{L} \right] \frac{\partial W_f}{\partial L} = \frac{S}{g(L) W_B} \frac{\partial W_s}{\partial L} - \frac{1}{g(L)} \frac{\partial^2 W_f}{\partial L \partial t} \quad (1)$$

where

W_f = cumulative weight fraction, dimensionless

A_c = cross-sectional area of the bed, ft²

W_B = weight of the bed, grams

$$g(L) = \left(\frac{2F}{\rho_s} \right) \frac{(a + bL)}{\sum_{i=1}^{\infty} S_i (a + bL)}, \quad \text{ft/hr}$$

$k_e(L)$ = rate constant for elutriation, g/ft²-hr

P = product rate, g/hr

S = seed addition rate, g/hr

L = particle diameter, cm

t = time, hr.

Equation (1) can be simplified by defining new quantities and making a change of the dependent variable; thus let

$$\begin{aligned}\phi_f &\triangleq \frac{\partial W_f}{\partial L} \\ K(L) &= \frac{A_c k_c(L)}{W_B g(L)} + \frac{P}{W_B g(L)} - \frac{3}{L} \\ \psi_s &= \frac{\partial W_s}{\partial L}\end{aligned}$$

Equation (1) then becomes

$$\frac{\partial \phi_f}{\partial L} + K(L)\phi_f = \frac{S \psi_s}{g(L) W_B} - \frac{1}{g(L)} \frac{\partial \phi_f}{\partial t} \quad (2)$$

Since the growth rate $g(L)$ is dependent on the total surface area of the particles in the bed, a small ΔL is required in the range of small particles sizes. However, a small ΔL increases the machine computation time. A variable size ΔL satisfies both the criteria for calculation of an accurate surface area and a reasonable computation time.

Finite differencing Equation (2) for the case where the increment ΔL increases linearly with L yields

$$\frac{2\phi_{m+1} - 2(1-k^2)\phi_m - 2k^2\phi_{m-1}}{2k^{m-1}(k+1)\Delta L_1} + K(L)\phi_m = \frac{S\psi_{s,m}}{g(L)W_B} - \frac{1}{g(L)} \frac{[\phi_{m,t+\Delta t} - \phi_{m,t}]}{\Delta t} \quad (3)$$

Equation (3) can be simplified and rearranged to give the following set of equations:

$$\begin{aligned}K_2\phi_{2,t+\Delta t} + 2\phi_{3,t+\Delta t} &= \frac{\beta_2 S\psi_2}{g(L)W_B} + \frac{\beta_2 \phi_{2,t}}{g(L)\Delta t} \\ -2k^2\phi_{m-1,t+\Delta t} + K_m\phi_{m,t+\Delta t} + 2\phi_{m+1,t+\Delta t} &= \frac{\beta_m S\psi_m}{g(L)W_B} + \frac{\beta_m \phi_{m,t}}{g(L)\Delta t}\end{aligned} \quad (4)$$

$$(m = 3, 4, \dots, M-2)$$

$$-2k^2\phi_{M-2} + K_{M-1}\phi_{M-1} = \frac{\beta_{M-1} S\psi_{M-1}}{g(L)W_B} + \frac{\beta_{M-1} \phi_{M-1,t}}{g(L)\Delta t}$$

where

$$\beta_m = 2k^{m-1}(k+1)\Delta L_1$$

$$K_m = \beta_m \left[K(L) + \frac{1}{g(L)\Delta t} \right] - 2(1-k^2)$$

M = designation of the largest particle size

m-1, m-2 = one and two particle sizes smaller, respectively, than particle size m.

Equation (4) is in the form of a tridiagonal matrix and can be readily solved for the unknowns, $\phi_m, t + \Delta t$, by a calculational procedure based on Gaussian elimination. Any change in the factors affecting the particle size distribution is reflected in a change in the scalar quantities K_m, β_m, S, W_B , and $g(L)$. A revised digital computer program, based on the system of Equations (4), was written in FORTRAN for the IBM-7040.

The transient particle size distribution calculated by the new procedure yielded the same results as the earlier method and the computer time was decreased by a factor of eight. Use of the model in predicting the particle size response to disturbances or arbitrary changes within the plant calciner will depend on the ability to correlate the effect of the NAR on the particle size distribution.

3. PROPERTIES OF SOLID CALCINED WASTE

3.1 Volatility of Minor Constituents from Calcine (M. E. Jacobson; Chemistry Section)

After converting the highly radioactive aqueous wastes at the Idaho Chemical Processing Plant to granular solids in the Waste Calcining Facility, the solids are stored underground in large stainless steel bins. The center-line temperature of the calcine may be as high as 700°C during storage due to radioactive decay of the contained fission products. The distribution of the constituents that are volatile in the heated calcine changes during the period of high heat generation, with migration occurring from the hot zone to a cooler zone.

To determine what constituents migrate from the higher temperature regions during long-term heating, volatility experiments were run using radioactive calcine from the WCF. In these experiments, two-gram samples of WCF calcine were placed in small, open alumina tubes and inserted into combustion tube furnaces. Temperatures were controlled at 525, 700, and 800°C for one year. Samples of the solid calcine were removed after six months and after one year, and fission product content, mercury content, and crystallinity of the alumina were determined. The results are given in Tables XX and XXI.

As expected, no volatilization of Sr-90 and Ce-144 occurred. Cesium began to volatilize somewhere between 700 and 800°C, which agrees with the results obtained previously [20] in short-term experiments. Ruthenium apparently

TABLE XX

VOLATILITY OF MINOR CONSTITUENTS FROM WCF
CALCINE DURING LONG-TERM HEATING
(Percent Volatilized)

Temperature (°C)	Cesium-137		Ruthenium-106		Mercury	
	6 month	12 month	6 month	12 month	6 month	12 month
525	0	0	---	54	25	93
700	0	0	64	82	93	>97
800	77	86	99	99	>96	>96

TABLE XXI

CRYSTALLINITY OF WCF ALUMINA CALCINE DURING LONG-TERM HEATING

Temperature (°C)	6 months	12 months
525	<10% gamma	50-70% gamma
700	25-40% gamma	50-70% gamma
800	alpha present	35-40% alpha

volatilized appreciably at 525°C during long-term heating. Mercury volatilized appreciably at all three temperatures although the effect of time was apparent only at 525°C.

The X-ray diffraction data indicated that amorphous alumina calcine stored at 700°C or lower temperatures formed gamma-Al₂O₃ consistently with no tendency to form any alpha-Al₂O₃. At 800°C, however, crystalline alpha-Al₂O₃ was formed. The effect of time on the formation of both crystalline species is apparent to some extent in the data shown in Table XXI. Phase data cited in the literature[21] suggest that if the heating period is sufficiently long at or below 700°C to form gamma-Al₂O₃, this crystalline form will remain stable up to nearly 900°C. If the heating period at or below 700°C is short and a temperature of 800°C or higher is obtained relatively soon, the alpha-Al₂O₃ will undoubtedly predominate.

Based on the results of these one-year experiments, the following conclusions relative to long-term storage of alumina calcine in bins have been made:

- (1) Essentially no cesium volatilizes at 700°C or lower temperatures, but significant amounts volatilize at 800°C or higher.

- (2) Appreciable quantities of ruthenium volatilize at temperatures as low as 525°C.
- (3) The originally amorphous alumina will convert to either gamma or alpha crystalline alumina depending on the temperature. Gamma alumina will be the only crystalline form at 700°C or lower, while alpha alumina will be the predominant crystalline form at 800°C or higher.
- (4) Neither strontium nor cesium is volatilized during storage at 800°C or lower temperatures.

3.2 Corrosive Effects of Zirconia Calcine in Storage

(D. W. Rhodes, C. A. Zimmerman; Chemistry Section)

The calcining of zirconium fuel processing waste, containing fluoride, is planned in the near future. Presently available storage facilities are constructed of Type 304 stainless steel. Long-term corrosion tests have been initiated to evaluate the corrosion of the present material, as well as alternate materials of construction for future zirconium calcine storage vessels, in contact with this calcined waste product. The construction materials under test are Types 304, 304L, 316ELC, 347, and 405 stainless steels, carbon steel, and Type 6061 aluminum alloy. Tests are being conducted at 200°C (the expected maximum container wall temperature during storage) in a stainless steel vessel filled with zirconia calcine and supported in a tube furnace. The test specimens are separated and electrically insulated from each other by glass spacers. These materials will be examined initially for corrosion attack after an exposure of one year.

4. HEAT TRANSFER STUDIES AFFECTING THE CALCINATION PROCESS AND STORAGE OF THE CALCINED PRODUCT

4.1 Heat Transfer from Horizontal Tube Bundles to Fluidized Beds of Solids (J. C. Petrie; Process Engineering Section)

Criteria for the design of internal heat exchangers for fluidized beds are not presently available in the literature. Over the past several years, however, numerous applications of internal heat transfer in fluidized beds have been made at the Idaho Chemical Processing Plant in connection with the development and application of the waste calcination program. The purpose of this section, then, is to present correlations of these data and to indicate their applicability to design of heat exchangers for use in beds of fluidized solids.

Data for heat transfer from horizontal tube bundles to fluidized beds in the ICPP plant[18] and pilot plant calciners[22, 23] have been correlated with dimensionless moduli. A comparison of this correlation with one for heat transfer to a single horizontal tube from a fluidized bed[24] shows good agreement, indicating that the individual tubes are not significantly affected by others within the bundle.

4.11 Data Correlation For Nonfinned Heat Exchanger Tubes. A Summary of the data used is given in Table XXII. The correlation best fitting the ICPP data for heat transfer from the various nonfinned heat exchangers to fluidized beds is shown in Figure 25 and can be represented by

$$N_{Nu_t} = 14 \left(\frac{G}{G_m} \right)^{1/3} (N_{Pr})^{1/3} \left(\frac{Dt}{Dp} \right)^{2/3} \quad (1)$$

TABLE XXII

SUMMARY OF FLUIDIZED BED HEAT TRANSFER DATA

Calcliner Unit	Bed Temperature (°F)	Heat Transfer Coefficient (Btu/hr-ft ² -°F)	Particle Diameter (ft x 10 ³)	Nusselt No. $\frac{hD}{k}$	Effectiveness Factor for Finned Surfaces (Dimensionless)	Brandt No. $\frac{c_p \mu}{k}$	Reduced Fluidizing Velocity (G/G _m)	Tube-to-Particle Diameter Ratio (Dt/Dp)	Vreedenberg's Parameter $\frac{GD_t \mu}{D p^3 \rho g}$
Two-foot-square pilot plant calcliner (Run No.)									
37	570	95	1.71	220		0.680	2.45	36.8	0.062
32B	750	72	1.91	145		0.680	1.47	32.7	0.033
30	750	116	1.07	242		0.680	3.45	58.4	0.153
29	750	110	1.30	220		0.680	0.45	50.0	0.076
07	750	87	1.13	170		0.680	1.13	37.3	0.091
23	750	86	2.16	173		0.680	2.05	27.5	0.039
23	930	90	2.27	166		0.680	2.05	27.5	0.039
21	750	53	2.41	105		0.680	1.62	25.9	0.028
21	750	72	1.48	145		0.680	3.72	42.5	0.114
Twelve-inch-diameter pilot plant calcliner (Run No.)									
09	750	125	1.94	174		0.680	2.22	21.5	0.033
12A	930	150	1.41	190		0.690	2.82	29.6	0.072
12B	930	125	1.14	158		0.690	4.21	36.5	0.118
14A	930	150	1.16	208		0.690	4.97	35.9	0.123
14B	750	115	1.61	141		0.680	2.61	25.9	0.050
15	750	156	1.20	221		0.680	4.65	34.7	0.120
16	750	98	1.99	136		0.680	2.46	20.9	0.036
17	750	115	1.57	160		0.680	3.88	26.5	0.075
18	570	92	1.40	148		0.680	3.31	29.7	0.070
Four-foot-diameter plant Calcliner (Run No.)									
H-)	750	67	1.61	214		0.680	2.18	77.7	0.106
Finned tube experiments plain tubes (Run No.)									
10	270	73	1.74	229		0.691	3.06	35.9	0.455
11	276	49	1.74	153		0.691	2.03	35.9	0.402
13	278	58	1.63	181		0.691	3.96	38.3	0.440
14	279	43	1.63	136		0.691	1.71	38.3	0.390
Finned tube experiments -- 5 fins/inch (Run No.)									
1	290	20	1.74	63	0.24	0.691	3.06	35.9	0.455
2	287	10	1.74	34	0.16	0.691	2.03	35.9	0.402
4	314	28	1.63	105	0.42	0.691	2.56	38.3	0.440
5	313	19	1.63	60	0.36	0.691	1.71	38.3	0.390
Finned tube experiments -- 11 fins/inch (Run No.)									
19	304	20	1.74	63	0.24	0.691	3.06	35.9	0.455
20	294	8	1.74	25	0.12	0.691	2.03	35.9	0.402
22	310	24	1.63	75	0.35	0.691	2.56	38.3	0.440
34	308	11	1.63	35	0.24	0.691	1.71	38.3	0.390
Tests for maximum in heat transfer (Run No.)									
1	561	255	0.84	420		0.680	9.20	61.6	0.345
2	585	186	0.84	240		0.680	6.50	61.6	0.207
3	484	202	0.84	343		0.680	7.10	61.6	0.267
4	540	208	0.84	353		0.680	5.90	61.6	0.239
5	552	219	0.84	372		0.680	4.40	61.6	0.167
6	538	92	0.84	150		0.680	2.50	61.6	0.094
7	586	238	0.84	381		0.680	9.60	61.6	0.360
8	485	240	0.84	414		0.680	6.30	61.6	0.309
9	588	230	0.84	360		0.680	4.80	61.6	0.182
10	618	220	0.84	342		0.680	3.70	61.6	0.139
11	540	158	0.84	264		0.680	1.70	61.6	0.065

Fig. 25 Correlation of heat transfer data from in-bed heat exchangers.

where

N_{Nu_t} = Nusselt number based on the tube diameter, dimensionless actual fluidizing air mass velocity

G/G_m = calculated minimum fluidizing air mass velocity reduced fluidizing air mass velocity ratio, dimensionless

N_{Pr} = Prandtl number of the fluidizing air, dimensionless

D_t/D_p = ratio of tube diameter to particle diameter, dimensionless.

The exponents in Equation (1) were rounded to the given values from a linear regression analysis of a least squares fit of the data using an IBM-7040 computer. In this analysis, the Nusselt number divided by the Prandtl number to the 1/3 power was treated as a function of the particle Reynold's number, the reduced fluidizing air mass flow ratio, and the tube-to-particle-diameter ratio. The particle Reynold's number was dropped from the final form of the data correlation because of its insignificant contribution. The exponent on the particle Reynold's number was only 0.06 in the linear regression analysis.

The maximum deviation of the data from Equation (1) is 43 percent. The Prandtl number of the fluidizing gas raised to a conventional exponent was included in the correlation even though the validity of this exponent could not be proved due to the small variation in Prandtl numbers during these tests. Fluid

properties were arbitrarily determined at a "film" temperature, defined as the arithmetic average between the bed temperature and the surface temperature of the horizontal tubes.

The reduced fluidizing mass velocity is defined as the ratio of actual fluidizing air mass velocity divided by the calculated minimum fluidizing air mass velocity. The minimum fluidizing air mass velocity was calculated by the following formula presented by Leva[25]:

$$G_{\min} = 1.40 \times 10^5 \frac{D_p^{1.85} \rho (\rho_s - \rho)^{0.914}}{\mu^{0.88}} \quad (2)$$

where

$G_{\min}$ = minimum fluidizing mass velocity, lbs/hr-ft²

D_p = average particle diameter, ft

ρ = density of fluidizing air, lbs/ft³

ρ_s = particle density of solid, lbs/ft³

μ = viscosity of fluidizing air, lbs/ft-hr.

This formula agrees best with experimental values for minimum fluidizing air mass velocities determined in the 12-inch-diameter pilot plant calciner. Several formulas are available for predicting minimum fluidization mass velocities; all are similar to Leva's but use different constants and exponents [26]. Table XXIII compares experimental minimum fluidizing mass velocities for two beds of different particle sizes with the various formulas available for calculating minimum fluidization mass velocities. The experimental data were determined by plotting pressure drop versus fluidizing air flow rate and selecting the velocity where the pressure drop becomes nearly constant as the minimum fluidizing air mass velocity [1]. As shown by the data in Table XXIII, experimental minimum fluidization mass velocities for beds typical of those at ICPP agree best with values calculated by Leva's formula. Therefore, all of the minimum fluidization mass velocities used in this study were calculated from Equation (2).

TABLE XXIII

MINIMUM FLUIDIZATION MASS FLOW RATES

	$G_{\min}$ (lbs/hr-ft ²)	
	Bed No. 1	Bed No. 2
Theoretical Correlation[26]	137	121
Frantz's Correlation[26]	29	28
Leva's Correlation[25]	87	78
ICPP Data	71	68

In the correlation represented by Equation (1), the reduced fluidizing mass velocity replaces the conventional Reynold's number for definition of the flow characteristics. By data analysis, it was found that the Nusselt number depended much less on the particle Reynold's number than on the reduced fluidizing air mass velocity. The reduced fluidizing mass velocity (G/G_m) is felt to be more useful than a Reynold's number in fluidized bed work because the lower limit of G/G_m is unity, and the magnitude of G/G_m depicts a degree of fluidization better than any other single parameter.

A maximum in heat transfer rates as a function of fluidizing mass velocity or G/G_m , is expected[27]. However, no maximum was found in the Nusselt number as a function of G/G_m although the maximum G/G_m was slightly greater than 9. The predicted maximum must occur at some still higher value of G/G_m .

Data from both triangular and square pitch tube bundles were included in the correlation given in Equation (1); no significant difference is evident, further indicating that heat transfer from each tube is independent of that from its neighbors.

4.12 Conclusions. Heat transfer rates from multiple horizontal tubes to fluidized beds can be predicted by a dimensionless correlation of easily defined terms. The correlation shows that the heat transfer coefficient is inversely related to the particle diameter and the tube diameter and is directly related to the reduced fluidizing mass velocity. The reduced fluidizing mass velocity replaces the conventional Reynold's number normally appearing in heat transfer correlations.

Comparison of this correlation with a previous correlation for heat transfer from a fluidized bed to a single horizontal tube is reasonably good. This indicates that for tube-to-tube separations exceeding 43 particle diameters, there is no significant influence of other tubes within the heat exchanger. Data from heat exchangers having both triangular and square pitch tube arrangements were correlated by the same equation, further indicating independent heat transfer from the tubes.

Results of this study showed a continued increase in heat transfer coefficient with the one-third power of the gas velocity up to the test limit of a reduced fluidizing air mass velocity of 9; the expected maximum apparently occurs at some still higher mass velocity.

4.2 Transfer of Heat from Finned Tubes to a Fluidized Bed (E. S. Grimmer, W. A. Freeby; Development Engineering Section)

The capacity of the fluidized bed waste calcination process -- as well as that of many other fluidized bed processes -- is limited by the rate at which heat can be transferred to the bed. With in-bed heating bundles, the controlling resistance to heat transfer is nearly always that on the bed side of the tubes. Increasing the heat transfer area on the bed side of the tubes by use of fins is, therefore, a logical means of increasing heat transfer rates. However, considerable development work is indicated in this area to evolve combinations of fin design and fluidized bed operating parameters which lead to optimum performance. Initial testing has been performed and the results are promising; additional testing is continuing.

Fundamentally, the goal is to determine combinations of conditions in which there is adequate fluidizing action in the spaces between the fins so that the actual surface heat transfer coefficient will be reasonably high, and at the same time have enough fins of reasonable length so that the actual area is large. Radial fins on horizontal tubes appeared to offer the best chance for success, and testing to date has been limited to this type. Principal equipment parameters are, then, number of fins per unit length of tube, fin height, tube diameter, and tube spacing. In limited testing to date, fin spacings ranging from 5 to 11 fins per inch have been used with fin heights of 0.4 inch, tube diameters have ranged from 5/8 to 3/4 inch, and tube center-line spacings have been about 2-1/4 inches [1,28].

The most significant bed operating parameters are believed to be particle size and reduced mass velocity; limited testing has been done with mass median particle diameters around 0.5 mm and with reduced mass velocities ranging from 1.5 to 15.

Conclusions from the recent limited testing may be summarized as follows:

- (1) Radial fins are effective in giving high rates of heat transfer to fluidized beds without plugging or other operating problems.
- (2) Limited testing of finned tube bundles has given overall heat transfer coefficients, based on the bare tube areas, of over 800 Btu/hr-ft²-°F; this is over five times that obtainable from bare tubes under comparable conditions. Heat transfer coefficients based on actual fin area, have been up to 50 percent of those for bare tubes, indicating good penetration of the fluidized bed particles into the spaces between the fins.
- (3) Heat transfer rates from finned tubes are better for smaller particles and for higher fluidizing velocities over the limited ranges tested.
- (4) Heat transfer rates were found to increase with increases in fluidizing velocity up to a reduced fluidizing velocity (G/G_m) of 10; further increases in G/G_m resulted in decreased heat transfer rates.
- (5) Additional testing, now underway, is necessary before the optimum combinations of finned tube design parameters and fluidized bed operating conditions can be defined.

4.3 Heat Dissipation from Buried Radioactive Sources

(B. R. Dickey, D. E. Black; Development Engineering Section)

The study of heat transfer from buried radioactive heat sources in the soil [1,29] has been extended to include the case of transient temperatures within a container of buried waste. The boundary value problem for the transient temperatures within a large-diameter source and the surrounding medium is described by the following equations:

$$\frac{\partial^2 T_1}{\partial r^2} + \frac{1}{r} \frac{\partial T_1}{\partial r} + \frac{\partial^2 T_1}{\partial z^2} + \frac{q''(r, z, t)}{k_c} = \frac{1}{\alpha_1} \frac{\partial T_1}{\partial t} \quad (1)$$

for

$$(0 \leq r \leq R_B, d < z < D)$$

and where

$$q'' = 0 \text{ for } z < d \text{ and } z > D$$

and

$$\frac{\partial^2 T_2}{\partial r^2} + \frac{1}{r} \frac{\partial T_2}{\partial r} + \frac{\partial^2 T_2}{\partial z^2} = \frac{1}{\alpha_2} \frac{\partial T_2}{\partial t}$$

for

$$(r \geq R_B \text{ and any } z) \quad (2)$$

and the boundary conditions

$$(a) \quad T_1(r, z, 0^+) = T_2(r, z, 0^+) = T_s$$

$$(b) \quad T_1(r, 0, t) = T_2(r, 0, t) = T_s$$

$$(c) \quad \lim_{z \rightarrow \infty} T_1(r, z, t) = \lim_{z \rightarrow \infty} T_2(r, z, t) = T_s$$

$$(d) \quad \lim_{r \rightarrow \infty} T_2(r, z, t) = T_s$$

$$(e) \quad T_1(R_B, z, t) = T_2(R_B, z, t)$$

$$(f) \quad k_c \frac{\partial T_1}{\partial r}(R_B, z, t) = k_s \frac{\partial T_2}{\partial r}(R_B, z, t)$$

$$(g) \quad T_1(0, z, t) = \text{Finite}.$$

Finite sine transformations of Equations (1) and (2) with respect to the independent variable Z followed by a finite difference approximation results in the following system of equations which must be solved at each time step for a given n :

$$-\phi_1 \bar{u}_{1,t} + \psi_1 \bar{u}_{2,t} = -\beta_1 \bar{u}_{1,t-\Delta t} - Q_1(n)$$

$$\phi_m \bar{u}_{m-1,t} - \phi_m \bar{u}_{m,t} + \sigma_m \bar{u}_{m+1,t} = -\beta_m \bar{u}_{m,t-\Delta t} - Q_m(n)$$

$$(\text{for } m = 2, 3, \dots, M1-2)$$

$$\phi_{M1-1} \bar{u}_{M1-1,t} - \phi_{M1-1} \bar{u}_{M1-1,t} + \sigma_{M1-1} \bar{u}_{M1-1,t} = -\beta_{M1-1} \bar{u}_{M1-1,t-\Delta t} - Q_{M1-1}(n)$$

$$\begin{aligned}
\bar{\phi}_{M1+1} \bar{u}_{M1-1,t} - \bar{\phi}_{M1+1} \bar{u}_{M1+1,t} + \sigma_M \bar{u}_{M1+2,t} &= -\beta_{M1+1} \bar{u}_{M1+1,t-\Delta t} \\
\phi_m \bar{u}_{m-1,t} - \phi_m \bar{u}_{m,t} + \sigma_m \bar{u}_{m+1,t} &= -\beta_m \bar{u}_{m,t-\Delta t} \\
(\text{for } m = M1+2, M1+3, \dots, M-2) \\
\phi_{M-1} \bar{u}_{M-2,t} - \phi_{M-1} \bar{u}_{M-1,t} &= -\beta_{M-1} \bar{u}_{M-1,t-\Delta t} \quad (3)
\end{aligned}$$

where

- T_1, T_2 = Temperature within solidified waste and soil, respectively, °F
 T_s = Initial soil temperature, °F
 r, Z = Radial and axial dimensions in cylindrical coordinates, ft
 q'' = Heat generation rate within solid waste, Btu/hr-ft³
 k_c, k_s = Thermal conductivities of solid waste and soil, respectively, Btu/hr-ft-°F
 d, D = Depth beneath the soil surface of the top and bottom of the heat source, respectively, ft
 R_B = Radius of the vessel containing the solid waste, ft
 t = Time, hours
 $\bar{u}_{m,t}$ = Transformed temperature at point m at time t , °F
 $M1$ = Outermost nodal point in region $0 < r < R_B$, integer
 M = Outermost nodal point in radial direction, integer
 c = Mesh size multiplier (a constant)
 L = That depth at which an increase, ΔL , results in a negligible change in the calculated temperature, ft
 n = Finite transform parameter, integer
 m = A nodal point in the radial direction, integer

$$Q_m(n) = \frac{q''}{k_c n} \left[\cos\left(\frac{n\pi d}{L}\right) - \cos\left(\frac{n\pi D}{L}\right) \right] \left[\frac{c^{2m-2} + c^{2m-3}}{2} \right] [\Delta r_1]^2$$

$$\bar{\phi}_{M1} = \phi_{M1} \left[\frac{c^2}{(1-c^2)} \right]$$

$$\phi_{M1-1} = \text{the quantity } \phi_{M1-1} - \left(\frac{\sigma_{M1-1} c k_c}{c k_c + k_s} \right)$$

$$\bar{\sigma}_{M1-1} = \text{the quantity } \frac{\phi_{M1+1} c k_c}{c k_c + k_s}$$

$$\bar{\phi}_{M1+1} = \text{the quantity, } \phi_{M1+1} - \left(\frac{\phi_{M1+1} k_s}{c k_c + k_s} \right)$$

$$\phi_1 = \text{the quantity } \left[4.0 + \beta_1 + \left(\frac{n\pi\Delta r_1}{L} \right)^2 \right]$$

$$\beta_m = \left[\frac{c^{2m-2} + c^{2m-3}}{2\alpha\Delta t} \right] [\Delta r_1]^2$$

α = thermal diffusivity of calcine or soil (depending on context), ft²/hr.

The system of Equations (3) was solved by the method of Thomas [30]. For the case of the solidified waste, the mathematical model was not validated by experimental data; however, based on the results from the simulated element [29], the calculated temperatures should reasonably approximate the actual temperatures in and surrounding the bin. The approach to steady state for a bin of specified size and internal heat generation rate is shown in Figure 26. Because of the large capacitance of the system, approximately two months are required for the steady temperatures to be reached. The system of Equations (3) can also be used to calculate the temperature as a function of position and time in a solidified waste in which the heat generation is decaying at a specified decreasing rate, as shown in Figure 27 for a theoretical MTR fuel waste cooled three years.

The mathematical models proposed thus far are strictly applicable to a solidified waste which may be considered as a uniform heat source. At sufficiently high temperatures, the heat generating fission products would migrate into the thermally cooler regions of the calcine. These moving heat sources further complicate any mathematical description of the transient temperatures within the solidified waste. A study is underway to develop mathematical models for (a) predicting temperatures within a waste subjected to fission product migration and (b) calculating temperatures in a cylindrical vessel which is being filled

Fig. 26 Calculated transient temperatures in a buried cylindrical bin filled with solidified waste.

Fig. 27 Calculated transient temperatures in a buried cylindrical bin filled with unsolidified waste (theoretical MTR waste cooled three years).

with calcine. Diffusivity data for the various fission products, as required by the model, will be determined.

4.4 Storage of Calcine at Elevated Temperatures (B. R. Dickey; Development Engineering Section)

Calcined wastes generated in the WCF during the first operating campaign are stored in cylindrical bins 10 feet in diameter and 20 feet high, contained in a concrete vault buried in the earth. Air flowing by natural convection within vertical, cylindrical annuli removes a portion of the decay heat while the remainder is transferred to the vault wall by thermal radiation and convection.

Calcine from current operations is being stored in cylindrical bins 12 feet in diameter and 40 feet high within a buried concrete vault. Heat is removed by conduction to the bin wall followed by convection and thermal radiation to the vault wall. These first and second generation bins were designed on the basis of maximum center-line temperatures of 400 and 700°C, respectively. These limitations on maximum permissible temperatures result in added costs for storage facilities because of the required spacing of cooling surfaces for heat removal.

If the calcine could be stored at center-line temperatures near or at the fusion temperature of alumina (2000°C), the greater thermal conductivity would permit a marked increase in the size of the storage container. This high temperature storage concept is based on the assumption that migrating or volatile fission products will condense within the cooler portions of the calcine. A mathematical study is now underway to determine the effects of fission product migration on temperatures within a stored mass of calcine.

If wastes are to be stored at high temperatures (the present study will indicate the theoretical practicality) there are several major problem areas which must be investigated:

- (1) The behavior patterns of migrating fission products must be determined experimentally. This involves the determination of the interrelationships between the fission product distribution and the temperature profiles for any proposed geometry.
- (2) The significance of the corrosion to the containment vessel at the higher temperatures must be determined.
- (3) Problems in the area of high temperature measurement for extended periods of time and the possibility of chemical reaction of the stored wastes with thermocouple materials must be studied.

Fluor Corporation conducted a conceptual design of a high-temperature storage facility in 1959-60. A cylindrical vessel, 12 feet in diameter and approximately 15 feet high, was to be filled with radioactive calcine having a rate of heat release of approximately 2.5 Btu/lb-hr. The project was abandoned because of (a) the large mass of calcine involved together with the many unknowns concerning fission product migration and volatilization, (b) uncertain loads on the off-gas cleanup equipment, (c) problems in high temperature measurement for extended periods of time, and (d) unavailability of calcine with a sufficiently high rate of heat generation.

4.41 Current Study Objectives. The current study involves, for the purpose of calculation, the situation where the central core of the stored mass is in a molten state. This assumption, however, is not a prediction that any melting would ever occur in stored calcine; fission product migration at lower temperatures may be sufficient to prevent fusion in a reasonable sized storage bin.

The major objectives of the calcine meltdown study are (a) the acquisition of data on the migration of fission products within solidified waste as a result of melting the central core, (b) determination of the experimental temperature profile in both the melt and the solid, and (c) development of adequate mathematical models for predicting the transient and steady state temperatures within the solid and melt, together with the movement of the "melt-line".

Design of any experimental equipment requires an analysis of the heat transfer characteristics of the reasonable geometries for the calcine containment vessel. The following cases were considered in the current mathematical study:

- (1) Solid cylinder of finite length with perfectly insulated ends.
 - (a) Cylinder in a medium of constant temperature.
 - (b) Cylinder insulated on vertical surfaces.
- (2) Solid cylinder of finite length; heat loss at ends, and placed in a medium of constant temperature.

- (3) Hollow cylinder of finite length with specified heat flux at the inner surface; heat loss at ends, and placed in a medium of constant temperature.
- (4) Solid sphere of calcine.
 - (a) Placed in a constant temperature medium.
 - (b) Insulated sphere in a constant temperature medium.
- (5) Hollow sphere placed in a constant temperature medium; specified flux at the inner surface.
- (6) Parameters included in the analysis of each of the above cases were heat generation rate, thermal properties of the calcine, heat transfer coefficients, and the physical dimensions of the container.

Each of the above cases was evaluated by solving the applicable differential equation using the appropriate boundary conditions. Thus, for a cylinder, the temperature is given by

$$\frac{d^2 T}{dr^2} + \frac{1}{r} \frac{dT}{dr} + \frac{q''}{k_c} = 0$$

and the boundary conditions for the particular problem. For a sphere, the temperature is given by

$$\frac{d^2 T}{dr^2} + \frac{2}{r} \frac{dT}{dr} + \frac{q''}{k_c} = 0$$

and the appropriate boundary conditions, where:

T = temperature, °F

r = radial distance, ft.

q'' = heat generation rate, Btu/hr-ft³

k_c = thermal conductivity of calcine, Btu/hr-ft-°F

4.42 Results of Current Study. Calculation of temperatures within the solid cylindrical and spherical containers of calcine resulted in the following conclusions:

- (1) Calcine decay heat (based on current values) alone cannot supply enough heat to melt the center of the calcine mass unless the container is very large ($R > 5$ feet).

- (2) If high-efficiency insulation is used, the melting point of the calcine can be reached; however, the temperature drop through the calcine would be small. Fission product migration studies require a significant temperature drop through the calcine.

Since heat generation rates within existing calcine are too low to ensure self-melting within a mass of reasonable size, consideration is being given to melting through the use of internal resistance heaters or by induction heating. If possible, the outer surface of a cylindrical mass of calcine will be maintained at a constant temperature much less than the melting temperature, to provide both an adequate driving force for fission product migration into the "thermally" cold calcine and a convenient boundary condition for the mathematical model. Results of laboratory studies which elucidate the mechanisms of fission product migration will be incorporated into the mathematical model.

4.5 Heat Transfer Across Vertical Cylindrical Air Gaps

(J. C. Petrie; Process Engineering Section)

(B. R. Dickey; Development Engineering Section)

Correlations have been developed from results of experimental tests for determining the rate of heat transfer from a constant temperature cylindrical heat source surrounded by a concentric shroud; ie, the situation that would exist if shrouds were used around calcine storage bins. The air gap between the source and shroud was open at each end, allowing a net flow of air through the system. The apparatus used to obtain the data has been described previously [1], and a tabulation of the data and heat transfer rates is shown in Table XXIV. A complete discussion of the experimental results and the methods of calculation has been published in IN-1110[33]; results are summarized here.

The rate at which heat is transferred by free convection across a completely enclosed air gap has been previously correlated in terms of an effective thermal conductivity as a function of the Rayleigh number [31,32]. The net heat transferred by conduction and natural convection in the current study was determined by subtracting the heat transferred by radiation from the total heat leaving the source. Calculation of the radiative heat transfer from the source to the shroud was complicated, since the temperature increased with height along the shroud. Details of these calculations are given in IN-1110[33].

A comparison of the effective thermal conductivities determined in this study with the effective conductivities for the case of a completely enclosed annulus is shown in Figure 28. The pseudo-effective thermal conductivity across an annulus open at the ends is approximately 1.2 times that of a completely enclosed air space. Correlations for natural convective heat transfer from vertical, cylindrical surfaces are valid in the presence of nearby surfaces down to an annular spacing of at least 0.35 inch.

TABLE XXIV

HEAT BALANCE AT THE SURFACE OF THE HEATED CYLINDER

Source-to-Shroud Annular Spacing (inches)	Total Heat Input, Q_T (Btu/hr)	Source Wall Temperature (°F)	Radiation Heat Transfer Q_R		Natural Convection Heat Transfer Q_C	
			(Btu/hr)	(%)	(Btu/hr)	(%)
0.35	170	120	26	15	144	85
	360	201	95	26	265	74
	680	209	129	22	551	78
	760	225	178	24	582	76
2.7	360	145	103	29	257	71
	990	240	325	33	665	67
	1710	325	617	36	1093	64
	2210	370	845	38	1365	62
	3010	460	1309	43	1701	57
	3720	520	1758	47	1962	53
6	360	140	103	29	257	71
	550	175	182	33	368	67
	680	195	236	35	444	65
	1020	238	375	37	645	63
	1360	275	500	36	860	64
	1710	305	630	37	1080	63
12	170	110	61	36	109	64
	360	135	115	32	245	68
	680	181	248	36	432	64
	1090	220	385	34	705	66
	1360	245	490	35	870	65
	1710	275	624	36	1096	64
Heat Transfer Without a Shroud	550	125	365	66	185	34
	1020	160	670	66	350	34
	1590	190	1020	64	570	36
	2390	240	1500	63	890	37
	3420	300	2130	63	1290	37

Fig. 28 Effective thermal conductivities across annular spaces as a function of the Rayleigh number.

5. ADDITIONAL WASTE MANAGEMENT STUDIES

5.1 Removal and Recovery of Mercury from WCF Feed (M. W. Wilding; Chemistry Section)

In the future, it may be desirable to operate the WCF at higher calcination temperatures, in which case much of the mercuric oxide in the alumina bed may volatilize and be collected in the scrubbing solution stream. The mercury would be converted to soluble mercuric nitrate in the scrubbing solution and be recycled to the calciner, thus producing a buildup of mercury in the system. To prevent this, the mercury should be removed from the waste before calcination.

Laboratory studies indicate that it may be possible, and economically desirable, to reclaim mercury from waste solutions for reuse. An 85 percent solution of hydrazine hydrate, when added to synthetic aluminum nitrate waste [1.0M HNO_3 , 1.6M $\text{Al}(\text{NO}_3)_3$, 0.02M $\text{Hg}(\text{NO}_3)_2$, and 0.09M NaNO_3] at a 1.0 volume percent level, reduced essentially all of the mercuric ion in solution to the metal after three hours of boiling. At one volume of hydrazine hydrate per 100 volumes of waste solution, approximately eight cents worth of hydrazine would be used in processing the approximately 22 cents worth of mercury in one gallon of waste. The mercury could then be reused as a catalyst for the dissolution of aluminum alloy fuels.

5.2 Waste Blending Study

(G. E. Lohse, J. L. Lockard; Process Engineering Section)

Wastes in storage at the ICPP vary in activity depending on the type of fuel from which the waste originated, the fuel irradiation time in the reactor, and the time since the fuel was discharged from the reactor. For economic reasons, the facility for storing solids calcined in the WCF was designed to contain solids having a heat generation rate of up to 0.4 Btu per hour per pound. To avoid wasting storage space by producing low heat generating waste, and to avoid damage by producing wastes that are too hot, it is frequently necessary to blend old and new waste to obtain solids with the desired heat generation rate. As future commitments are realized, numerous changes in ICPP and WCF processing schedules are anticipated; consequently, a FORTRAN-IV program has been written to update schedules rapidly. Currently, the program is being used to give a preliminary estimate of the activity level of the liquid waste that will remain after the termination of the current WCF campaign, and also to optimize the processing availability of the WCF, as blending of future with current wastes is achieved. The activity level of future blends could influence the design of the next solids storage facility. Ultimately the program may be used to guide the filling of the liquid storage tanks as well.

The program consists of the main routine and four subroutines for reading all the input data, for computing the blends, for indexing and sequencing tanks according to the heat generation rates and processing availability, and for determining the volume of liquid waste calcined, the volume and heat generation rate of the solids produced, and the chemical composition of the waste. The program has the capacity of 200 blending combinations from four different blending stocks, but it is limited to a total of 30 different tanks and ten heat generation decay curves.

III. REACTOR TECHNOLOGY SUPPORT

1. LOFT ASSISTANCE PROGRAM

The Chemical Technology Branch has several development studies underway in support of the Loss-of-Fluid Test (LOFT) at the National Reactor Testing Station. The LOFT project is the field duplication of a loss-of-coolant or maximum credible accident for a water-cooled reactor. As envisioned throughout this reporting period, this test consists 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.

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-monitor for the containment atmosphere, (d) the evaluation of plateout samplers, and (e) the design construction, and operation of a fission product generation and containment unit to assist in evaluating the results of the preceding studies as well as to provide general support for the LOFT program. Progress in each of these areas is reported although all are continuing programs and none has reached a state permitting final conclusions to be stated.

1.1 LOFT Coating and Elastomer Evaluation and Decontamination Studies (B. J. Newby, T. L. Evans, R. G. Butzman; Chemistry Section)

Studies are continuing to evaluate coating materials for the interior of the Loss-of-Fluid Test (LOFT) containment building and to develop decontamination methods for these coated surfaces. The ideal coating system for LOFT would have the following characteristics:

- (1) Be typical of coatings existing in present and future reactor containment buildings
- (2) Be resistant to conditions that might exist in the LOFT containment buildings
- (3) Be sufficiently elastic to be able to contract and expand with its substrate as surfaces are heated and cooled
- (4) Contain a primer that can be applied over structural steel by the vendor and can be covered with the finish coat later at a more convenient time when the steel is in place in the LOFT containment building
- (5) Be a coating system that can be decontaminated from radioactivity.

Studies have been performed to find coating systems having these characteristics [a].

[a] The experimental evaluations of protective coatings and reagents reported here were done to obtain information on the performance of these materials in the specific applications and environments listed. Any conclusions as to the relative merits of the materials apply only to the specific conditions mentioned. The fact that some materials were observed to be superior or inferior to others in these tests does not imply any general finding of superiority or inferiority.

1.11 Coatings Typical of those in Existing Containment Buildings. An informal and limited survey of the practices in selection and specification of coatings for the interior of power reactor containment buildings revealed that up to now little consideration has been given to the interaction of fission products released in a nuclear accident with the protective coating used. Since the protective coatings have been largely selected on the basis of general industrial criteria, eg, durability, appearance, and light reflectance, typical practice was found to involve a wide range of high quality coating systems. No national or industry-wide standards are in use and, thus, several coating systems could be considered typical. Therefore, for the present study it has been assumed that a coating system having contamination and decontamination characteristics at about the midpoint of the spectrum of values experienced with the most common of the durable protective coatings would be representative of those used in the industry. For the LOFT experiment, of course, a coating with the best decontamination characteristics possible is desired.

1.12 Coatings Resistant to LOFT Containment Building Environment. Coating systems applied to the interior surfaces of the LOFT containment building should be resistant to pressurized steam, gamma radiation, and solutions that might be sprayed on the coating system to decontaminate it. Some results of these tests have been reported previously [1,16]; more recent results are summarized in Table XXV. Coatings were considered to have the following:

- (1) Satisfactory chemical resistance to a reagent if the reagent produced little or no effect on a coating submerged at 60°C for five days
- (2) Questionable resistance if the coating was markedly affected between one and five days of submergence

TABLE XXV

RESISTANCE OF COATINGS TO DECONTAMINANTS AND ENVIRONMENTAL
CONDITIONS PRESENT DURING THE LOFT EXPERIMENT

Test Number	Finish Coat	Primer	Finish Coat Generic Type	Substrate	100 Wt % HNO ₃ (60°C)	2 lb/gal Turco Alkaline Rust Remover (60°C)	1 lb/gal Turco Alkaline Rust Remover (60°C)	1/2 lb/gal Turco Alkaline Rust Remover (60°C)	Resistance to Pressurized Steam (30 psig and 133°C) (3 days)	Radiation Resistance (dose rate of 2 x 10 ⁶ R/hr at 45°C for Total Dose of 1 x 10 ⁶ R)
1	Chemfast MP White (Converter Catalyst Number 46802)	Chemfast E.P. Primer	Epoxy	Carbon Steel	U(a)	S(a)	S	S	S	S
2	Chemfast MP White (Converter Catalyst Number 46802)	Chem Zinc	Epoxy	Carbon Steel	U	S	S	S	S	S
3	Chemfast MP White (Converter Catalyst Number 46802)	RB 1370 Zinc Rich	Epoxy	Carbon Steel	U	Q(a)	S	S	U	---
4	Chemfast MP White (Converter Catalyst Number 46802)	None	Epoxy	Concrete	U	S	S	S	S	---
5	Chemfast MP White (Converter Catalyst Number 46802)	None	Epoxy	Concrete	U	S	S	S	U	---
6	Phenoline 368	Phenoline 368	Modified Phenolic	Carbon Steel	U	S	S	S	S	S
7	Tanclene	Aluminum Primer	Epoxy	Carbon Steel	U	S	S	S	U	S
8	Tanclene	Aluminum Primer	Epoxy	Aluminum	U	U	U	S	S	---
9	Tanclene	Phenoline 368	Epoxy	Carbon Steel	U	G	G	S	S	S
10	Epoxy 3-303-90	None	Epoxy	Carbon Steel	U	Q	S	S	S	S
11	Chemfast OK-1055	Chemfast E.P. Primer	Epoxy	Carbon Steel	U	S	S	S	S	S
12	Chemfast OK-1055	Devron 600	Epoxy	Carbon Steel	U	S	S	S	U	S
13	Phenoline 302	Phenoline 300	Modified	Carbon Steel	S	S	S	S	S	S
14	Plasite 7155	Plasite 7155	Modified Phenolic	Carbon Steel	U	Q	S	S	S	S

(a) S = Satisfactory
Q = Questionable
U = Unsatisfactory

(3) Unsatisfactory resistance if the reagent produced a marked effect in less than one day of submergence.

Coatings were also considered to have a (a) satisfactory resistance to pressurized steam if exposure at 30 psig (133°C) for three days produced little or no effect on the coating and (b) satisfactory resistance to radiation if a beta-gamma dose rate of about 2×10^6 R/hr at 45°C, continued for a total dose of 10^9 R, had little or no effect on the coating.

The resistance of a coating to physical and chemical tests may depend upon the substrate, primer, or converter (curing) catalyst used. Comparison of tests 7 and 8 of Table XXV indicates the influence of the substrate on the resistance of the coating system to chemicals. In this case the basic reagents probably diffused through the coating and reacted with the aluminum. Tests 1 and 3 demonstrate the dependence of the chemical resistance of coatings on the primer where either primer might be regarded as acceptable for ordinary use. The influence of the converter catalyst on resistance to pressurized steam, again a choice between apparant equals, is shown by tests 4 and 5. Tests 7 and 8 illustrate the dependence of this property on substrate. Comparison of tests 2 with 3, 11 with 12, and 7 with 9 illustrates the dependence of steam resistance on the primer.

Phenoline 302 passed all the tests satisfactorily. Most of the coatings tested, however, would be adequate as a covering material for the inside of the LOFT containment building if resistance to the exposure conditions was the only consideration.

1.13 Elasticity of Coatings. Currently it is planned to have elastomer joints in the interior concrete surfaces of the LOFT containment building to allow the concrete surfaces to expand and contract with the outer steel shell of the building. Coatings applied over these joints must be sufficiently elastic to expand and contract with the elastomer without suffering damage. Since coated elastomers must be resistant to conditions that might exist in the building, a polyurethane, an epoxy, and a silicone rubber sealant were tested for their resistance to these conditions. The former two elastomers failed when exposed to 1×10^9 R. The bond between concrete and the polyurethane and silicone rubber elastomers had a tendency to fail under certain conditions but seemed to be satisfactory when covered with coatings. The epoxy elastomer was quite mobile at elevated temperature. When coatings were applied over these elastomers, the coatings cracked and peeled when the systems were heated and cooled. The silicone rubber elastomer was more suitable under conditions that might exist in the containment building than the other two systems. Incorporating woven glass fabric into coatings applied over the silicone elastomer allowed the coatings to expand and contract with the elastomer, when heated and cooled, without cracking and peeling. Figure 29 shows the failure of a coating containing no glass fabric when applied over two concrete blocks held together by a silicone elastomer and autoclaved for 24 hours at 30 psig and 133°C; also shown is the unaffected appearance of the same coating containing glass fabric applied over the same system and autoclaved for 72 hours at 30 psig and 133°C. The latter system was quenched every 24 hours placing additional strain on the coating.

Fig. 29 Effect of pressurized steam on coatings with and without woven glass fabric applied over a silicone rubber elastomer.

1.14 Primers for Structural Steel. It is desirable that structural steel in the LOFT containment building be coated with a primer by the vendor and coated with a finish coat when the rest of the containment building is painted. Since these steel components will be primed by the vendor before the final LOFT coating system can be selected, the primer used on the steel must be compatible with a variety of finish coatings. A primer is required that can remain uncovered for a long time interval before applying the finish coat, yet without adversely affecting adhesion between the primer and finish coats. Coating systems containing a number of primers supposedly meeting the latter requirement, wherein the primers were covered with a variety of finish coatings after the primers had been cured for a short time and for a year, are being tested for their resistance to chemical reagents, radiation, and pressurized steam. Results of testing systems containing a finish coating applied over a primer cured for a short time are shown in Table XXVI. Systems consisting of finish coats over their usual primers were tested to show how systems containing these finish coats should have reacted to the tests.

The Phenoline 368 primer was recommended for use on the steel components in the LOFT containment because of its fine compatability and good

TABLE XXVI

EFFECT OF PRIMERS ON COATING SYSTEMS SUBJECTED TO CONDITIONS PRESENT DURING THE LOFT EXPERIMENT

Finish Coat	Finish Coat Generic Type	Primer	Primer Generic Type	Chemical Resistance				Resistance to Pressurized Steam (30 psig and 133°C for 3 days)	Radiation Resistance (dose rate of 2 x 10 ⁶ R/hr at 45°C for total dose of 1 x 10 ⁵ R)
				3M HNO ₃ (60°C)	2 lb/gal Turco 4502 (60°C)	1 lb/gal Turco Alkaline Rust Remover (60°C)	1/2 lb/gal Turco 4521 (60°C)		
Amercoat 66	Epoxy	Amercoat 66[a]	Epoxy	U[b]	S[b]	S	S	S	S
Amercoat 66	Epoxy	Amercoat 71	Epoxy	U	S	S	S	S	S
Amercoat 66	Epoxy	Chemfast E.P. Primer	Epoxy	U	S	S	S	S	S
Amercoat 66	Epoxy	Catha-Coat Formula 300	Chemically cured zinc silicate	U	S	S	S	S	S
Amercoat 66	Epoxy	Carbo Zinc 11	Self cured zinc silicate	U	S	S	S	S	S
Amercoat 66	Epoxy	Phenoline 368	Modified Phenolic	U	S	S	S	Q	S
Phenoline 300	Modified Phenolic	Phenoline 300[a]	Modified Phenolic	---	---	---	---	U	S
Phenoline 300	Modified Phenolic	Amercoat 71	Epoxy	U	S	S	S	U	S
Phenoline 300	Modified Phenolic	Chemfast E. P. Primer	Epoxy	U	U	Q	Q	U	S
Phenoline 300	Modified Phenolic	Catha-Coat Formula 300	Chemically cured zinc silicate	Q	S	S	S	U	S
Amercoat 33HB	Vinyl	Amercoat 86[a]	---	U	U	S	S	U	S
Amercoat 33HB	Vinyl	Amercoat 71	Epoxy	Q	S	S	S	U	S
Amercoat 33HB	Vinyl	Chemfast E.P. Primer	Epoxy	U	U	S	S	U	S
Amercoat 33HB	Vinyl	Catha-Coat Formula 300	Chemically cured zinc silicate	U	U	U	U	U	S
Devco SX-1661	Chlorinated Rubber	Chemfast E.P. Primer [a]	Epoxy	U	U	Q	S	U	S
Devco SX-1661	Chlorinated Rubber	Amercoat 71	Epoxy	U	U	S	S	U	S
Devco SX-1661	Chlorinated Rubber	Catha-Coat Formula 300	Chemically cured zinc silicate	U	U	U	U	U	S
Devran 600	Epoxy	Devran 600[a]	Epoxy	U	S	S	S	U	S
Devran 600	Epoxy	Amercoat 71	Epoxy	U	S	S	S	S	S
Devran 600	Epoxy	Chemfast E.P. Primer	Epoxy	U	Q	S	S	S	S
Devran 600	Epoxy	Catha-Coat Formula 300	Chemically cured zinc silicate	U	Q	S	S	U	S
Phenoline 368	Modified Phenolic	Phenoline 368 [a]	Modified Phenolic	U	S	S	S	S	S

[a] The usual primer for this system.

[b] S = Satisfactory

Q = Questionable

U = Unsatisfactory

performance with Phenoline 368 and Amercoat 66 finish coats. Amercoat 71 was shown to be a very versatile primer compatible with a wide range of different finish coats.

1.15 Contamination-Decontamination Behavior of Coatings. During this report period, mixed fission product behavior was obtained for coated carbon steel, and stainless steel surfaces contaminated in the Contamination-Decontamination Experiment (CDE) Run 2. A description of the CDE equipment and operating conditions during CDE Run 2 is given in the previous annual report[1]. Surfaces in CDE Run 2 received a higher deposition of activity than did those contaminated in CDE Run 1. Some fission products not detected on deposition coupons contaminated in CDE Run 1 were detected on coupons contaminated in CDE Run 2, and their behavior was studied. Table XXVII shows the fission products found on deposition coupons contaminated in CDE Run 2, their relative abundance immediately after contamination, and decontamination factors obtained by a conventional decontamination method. As in CDE Run 1, greater than 90 percent of the activity found on the coupons contaminated in CDE Run 2 came from iodine-131. Coupons contaminated in CDE Run 2 were decontaminated by spraying them first with 2 pounds/gallon Turco 4502 at 80°C for 10 minutes using a spraying System Nozzle 1/4 GG SS 6.5 at a pressure of 30 psig, rinsing with water, spraying with 1/2 pound/gallon Turco 4521 under conditions identical to those used with Turco 4502, and rinsing with water. Although the iodine-131 decontamination factors obtained from coupons contaminated in CDE Run 2 were as poor as those obtained from coupons contaminated in CDE Run 1, the decontamination factors obtained for other fission

TABLE XXVII

CONTAMINATION-DECONTAMINATION BEHAVIOR OF MATERIALS CONTAMINATED
IN CDE RUN 2 [a]

(Zero decay time unless otherwise indicated)

Material	Gross Gamma Activity at 10 cm and 16 day decay time		I-131		Te-132		I-132		Te-99		Mo-99		Ba-140		La-140		Ru-103		Cs-137	
	Contamination in cts/100 sec (x 10 ⁵)	Decontamination Factor (D.F.)	Contam. in d/min/gpl (x 10 ⁴)	D.F.	Contam. in d/min/gpl (x 10 ⁴)	D.F.	Contam. in d/min/gpl (x 10 ⁴)	D.F.	Contam. in d/min/gpl (x 10 ⁴)	D.F.	Contam. in d/min/gpl (x 10 ⁴)	D.F.	Contam. in d/min/gpl (x 10 ⁴)	D.F.	Contam. in d/min/gpl (x 10 ⁴)	D.F.	Contam. in d/min/gpl (x 10 ⁴)	D.F.	Contam. in d/min/gpl (x 10 ⁴)	D.F.
Amercoat 66	4.4	2.8	10.3	4.5	7.5	33	5.8	45	2.7	18	5.5	40	3.6	440	3.2	960	1.8	146	2.0	---
Phenoline 302	1.6	9.4	4.3	7.7	8.5	236	3.0	62	2.3	52	4.4	105	4.4	125	6.5	281	3.8	103	4.0	26
Carboline Epoxy 150	4.6	5.9	4.8	4.9	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Devran 600	3.6	5.6	6.0	5.3	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Mobile Polycote	2.1	5.7	3.7	5.6	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Plasite 7155	3.4	8.0	5.7	7.0	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Contam Affix Perm	6.0	3.8	10.2	3.7	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Devco SX-1661	1.9	3.8	3.1	3.6	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Carboglas 1600	2.3	5.3	3.8	5.0	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Carboline B-15	6.3	2.9	10.8	2.9	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Stainless Steel 304	0.46	900	0.13	200	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Carbon Steel	3.7	280	6.0	312	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---

[a] Decontamination Conditions: Sprayed with 2 1/2 gal Turco 4502 at 80°C for ten minutes followed by spraying with 1/2 10/gal Turco 4521 at 80°C for ten minutes.

products were much better. The decontamination reagent system used in CDE Run 2 (Turco 4502 - Turco 4521) was more effective for fission products other than iodine than the system used in CDE Run 1 (nitric acid - Turco Alkaline Rust Remover). The effectiveness of the Turco 4502-Turco 4521 combination in removing iodine-131 from coupons contaminated in CDE Run 2 was tested against the effectiveness of 2 pound/gallon Turco 4502-1/2 pound/gallon oxalic acid and also 2 pound/gallon Turco 4502-1/2 pound/gallon RD16F (a decontamination reagent manufactured by General Dynamics). While there was not much difference in the effectiveness of the three different combinations in removing iodine, Turco 4502-oxalic acid was slightly more effective than Turco 4502-Turco 4521 which in turn was slightly more effective than Turco 4502-RD16F. The time that a coating is allowed to cure (between 10 days and 7-1/2 months) was found to have little effect on its contamination-decontamination behavior.

Currently there appear to be four alternate methods for decontaminating the inside coated surfaces of containment buildings:

- (1) Spray surfaces for a short time with an effective decontamination reagent combination and obtain the remaining decontamination needed by taking advantage of iodine-131 decay.
- (2) Use pressurized steam.
- (3) Use chemically strippable coating systems.
- (4) Corrode coated surfaces away by prolonged spraying with an effective decontamination reagent combination.

(1) Use of Short Spraying Time plus Iodine-131 Decay. It has been calculated that the inside of the LOFT building must be decontaminated by a factor of 10³ in order to gain limited access into the building after the LOFT experiment. A decontamination factor of no more than 10 (see Table XXVII) could be obtained by spraying coated surfaces with the best decontamination reagent combination. The remaining decontamination needed could be obtained by relying on fission product decay if time needed to obtain decontamination was

not important. As seen in Table XXVII, iodine-131 has the longest half life of the major fission products that were released in CDE Run 2. To obtain an iodine-131 decontamination factor of 10^3 would take 80 days. Iodine-131 has been found as the major fission product on coated coupons 120 days after being contaminated in the CDE.

(2) Use of Pressurized Steam. Previous work[16] has shown that pressurized steam (at 40 psig and 140°C) effectively removed molecular iodine from certain organic protective coatings contaminated at 40°C and atmospheric pressure in the presence of moisture. This remains a potential mode of decontamination for the interior of the containment building.

(3) Use of Chemically Strippable Coating Systems. The concept of strippable and corrodible coating systems is illustrated in Figure 30. Such systems would consist of a permanent base coating containing glass cloth to protect the substrate (concrete containing silicone rubber expansion joints) and an expendable outer coat which can be removed along with the contamination. In the strippable coating system the outer coating would be removed by stripping (rapid dissolution) with a chemical reagent; in the corrodible coating system the outer coating would be corroded away by spraying with decontaminating reagents for long periods of time.

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Fig. 30 Enlarged view of an expansion joint and coating system in the LOFT containment wall.

The top coat (strippable coat) should (a) be impermeable to fission products that will be present in the containment (especially to iodine), (b) be typical of conventional coatings in its contamination properties, (c) be readily removable with a solvent, and (d) be fairly resistant to steam. Systems recommended by manufactures and by our own experience as having the desired characteristics were scoped in the laboratory using molecular iodine as the contaminant; systems giving the best results were studied further in the CDE using mixed fission product contamination. A total of 21 different strippable coatings was studied. In both the laboratory and the CDE, coatings were contaminated in the presence of steam at about 22 psig and allowed to remain in the presence of fission products and steam for 24 hours during which time the steam pressure decayed from 22 to 5 psig. Coupons were then sprayed for ten minutes at various temperatures with a number of stripping reagents, or sprayed a short time with a reagent, the reagent allowed to remain on the coupon for about ten minutes, and then rinsed off with water at 80°C. The system giving the best results was Turco 5302 coating over Amercoat 66 undercoat; this was stripped with isophorone at 70°C for ten minutes. The Turco 5302 coating will be studied in more detail. Many of the strippable coatings studied had the desirable characteristics of being typical of conventional coatings in their contamination properties, being readily removed with the appropriate reagent, and being sufficiently resistant to steam. None of the strippable coatings studied, however, were sufficiently impervious to iodine penetration. It might be possible to improve this characteristic by using thicker coatings or by incorporating a material into

the coatings that will react with iodine. However, developments of the latter sort are not within the scope of the present program.

(4) Use of Corrodible Coating Systems. Coatings (together with fission products) can be corroded or removed from their substrate in a controlled manner by alternately spraying with an alkaline permanganate reagent and an organic complexing reagent, sodium bisulfite, or Turco Alkaline Rust Remover (for periods of from 1/2 to 4 hours with each reagent) at 80°C, continued for long periods of time (4 to 16 hours total spraying time). The coatings come off as small particles (the larger particles being of the order of 1/16 inch across their longest dimension) and can also be removed (although more slowly than if sprayed) if solution can be made to run over the surface. This process is not entirely an erosion process since spraying the coatings with water at 80°C for greater than 16 hours does not erode away surfaces of the coatings tested. Thus, a decontaminable coating system applicable to LOFT might consist of a permanent undercoat with woven glass fabric embedded in it to protect the substrate, and a corrodible outer coating that can be removed along with contamination. Coatings that respond well to removal by corrosion with an alkaline permanganate reagent alternated with another reagent are Phenoline 302, Phenoline 368, Epoxy S-303-50, and Plasite 7155.

The corrodible coating systems suffer from the same weakness inherent in the strippable coating systems; in both systems iodine can penetrate through the removable coating and contaminate the permanent undercoat. In the corrodible system, however, a layer of the undercoat can be also removed for further decontamination without damaging the undercoat system remaining beyond repair. Also, the best corrodible coatings tested seem to be more impervious to iodine penetration than do the best strippable coatings.

Iodine decontamination factors of the order of 10^2 have been obtained by alternately spraying a system consisting of Phenoline 302 over Amercoat 66, containing embedded woven glass fabric, with 2 pounds/gallon Turco 4502 and 1/2 pound/gallon oxalic acid for 1/2-hour periods until a total spraying time of four hours was used. This system was contaminated in the laboratory in the presence of steam simulating CDE operating conditions. Studies will be continued to select a corrodible coating and a permanent undercoat for a corrodible coating system, and to determine whether Turco 4521, Turco Alkaline Rust Remover, oxalic acid, or sodium bisulfite would be the best reagent to be used in combination with an alkaline permanganate reagent.

A modified version of the corrodible coating system offering merit consists of (a) spraying a thixotropic stripping reagent (such as Turco EPO-GON Thick or Turco Jet Strip 5292) on a corrodible coating system; (b) allowing the reagent to remain on the coating system for a short time; and (c) rinsing off the reagent, a layer of coating, and fission products with hot water. It was however, difficult to control coating removal with the two Turco stripping reagents mentioned. If the reagents were allowed to remain on the coatings sufficiently long to obtain acceptable decontamination ($DF > 10$), the reagents would penetrate to the substrate and remove large sections of undercoat and corrodible coating; if the reagents were allowed to remain on the coating only a short time to control coating removal, poor decontamination was obtained ($DF \approx 2$). The reagents also left a slime on the coatings which might prevent repainting.

The use of decontamination reagents in a thixotropic form, while potentially valuable because of the possibility of reducing waste volumes, would require additional development work.

1.2 The Penetration of Iodine Into Protective Coatings (R. R. Hammer, B. J. Newby; Chemistry Section)

Under loss-of-coolant accident conditions in a pressurized water reactor, short lived fission products may be released to the atmosphere of the reactor containment building. The behavior of iodine under these conditions is of prime importance since it may represent more than 90 percent of the nonrare gas fission products released from the reactor vessel. In the course of the evaluation program for the protective coatings for LOFT [1] (Loss-of-Fluid Test), it was discovered that iodine, released as I_2 in experimental studies, penetrated deeply into all of the protective coatings studied. In order to determine the impact of this penetration on the feasibility of decontamination of the protective coatings after a loss-of-coolant accident, quantitative data for the amount of penetration as a function of depth were obtained [a]. From other decontamination studies it was learned that the penetration of iodine was, at least in part, reversible [b]. Because of the importance of the phenomenon of penetration to both the contamination and decontamination aspects of the loss-of-coolant accident, it appeared desirable to fit the experimental data for the penetration to a mathematical model so that extrapolation of the data would be possible. This was done earlier with reasonable success using a few sets of experimental data on two different coatings and a simple analytical approach. Using the solution of Fick's second law for unidirectional diffusion in a semi-infinite solid, diffusivities of the order of 10^{-9} cm²-sec⁻¹ were calculated [c].

Recent studies on the penetration of iodine into protective coatings characteristic of those used in reactor containment buildings have been reported in IN-1095 [34] with the following generalized findings:

- (1) Penetration of iodine occurs with the four types of paint coatings tested: epoxy, vinyl, chlorinated rubber, and phenolic
- (2) The degree of penetration is associated with the temperature of the coating and its physical state.

The previous model for unidirectional diffusion in a semi-infinite solid adequately describes the penetration of iodine into these coatings to thicknesses as great as 0.25 mm. Differences in exposure times of from 6 to 150 minutes, and in storage times between exposure and examination of from one to 312 hours, did not affect the observed diffusivity values by more than a factor of three. In general, the diffusivity increased with temperature, with two coatings showing sharp increases in diffusivity as their softening points were passed. The scale up of activity on protective coatings from laboratory studies to CDE gave calculated results for two coatings in CDE Runs 1 and 2 in good agreement with the measured values.

[a] See page 76 of Reference 1

[b] See page 77 of Reference 1

[c] See page 80 of Reference 1

1.3 Contamination-Decontamination Experiment

(L. T. Lakey, D. E. Black, W. A. Freeby, W. P. Palica; Development Engineering Section)

The Contamination-Decontamination Experiment was installed to augment the Loss-of-Fluid Test Assistance Studies being conducted at the ICPP. 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 and 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 a simulated containment shell. 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 the LOFT.

Four tests have been made in the CDE to date. Contamination of coupons for coating and decontamination studies was emphasized in the first two runs; emphasis was shifted to testing of the LOFT plateout and gas-particulate capsule samplers in the third and fourth runs. The latter two tests were conducted in the CDE during the current fiscal year; Run 3 was made in October, 1966 and Run 4 in March, 1967. A description of the CDE and a summary of the current year's results are summarized in the following sections.

1.31 Description and Operation of Equipment. The CDE, as shown in Figure 31, contains two major elements: an induction furnace for melting the fuel pin

Fig. 31 Schematic flow sheet of the Contamination-Decontamination Experiment.

and a simulated containment vessel. Nozzles, sampling devices, and other test equipment are provided in the containment vessel for inserting coupons to be contaminated, for sampling the containment atmosphere and condensate, and for decontaminating the vessel. The equipment comprising the induction and containment vessel systems was described previously [1] except that the induction furnace and the furnace coupling system were redesigned after Run 3 to eliminate stresses resulting from misalignment and by molten fuel particles spattering on the quartz furnace. In Runs, 1, 2, and 3, the fuel pin was placed in a 200-gram bed of powdered UO_2 inside the quartz tube for melting. Beginning with Run 4, a quartz sleeve and boat were used to hold the fuel pin inside the furnace tube. About 20 grams of powdered UO_2 are placed in the boat before the fuel pin is loaded. The sleeve prevents the molten fuel from contacting the furnace tube, and the boat reduces the amount of UO_2 bed material needed. Guides and stops are built into the various furnace assembly pieces so they can be assembled remotely. The furnace coupling system, shown in Figure 32, was made more rigid to prevent misalignment and the consequent mechanical stresses on the furnace tube when the couplings were being tightened remotely. The coupling system was designed so that the inlet section of the transport line can be moved horizontally through a distance of 26 inches to enable the furnace to be loaded and coupled to the transport line remotely with manipulators.

Fig. 32 Furnace assembly system as modified for CDE Run 4.

The fission product aerosols are generated by melting Zircaloy-clad fuel pins (9/16-inch diameter by 3-1/2 inches long) containing enriched UO₂ pellets. The fuel pins are encased in aluminum jackets to reduce the temperature of the pins during irradiation. Following irradiation in the Materials Testing Reactor, a fuel pin is transported to the ICPP Hot Pilot Plant where the aluminum jacket is dissolved in caustic. The fuel pin is then inserted into the quartz furnace tube and melted by induction heating. During the meltdown, steam is passed over the fuel pin to carry the fission products into the simulated containment vessel where the environmental conditions and atmospheric composition are adjusted to match the anticipated LOFT containment building conditions. After melting of the fuel pin is complete, the containment vessel is isolated, and the temperature of the containment vessel atmosphere is gradually reduced to ambient temperature over a 24-hour period to match the expected decay of the LOFT containment building temperature. During this period, samples of the containment atmosphere and condensate are collected intermittently. At the end of this period, the containment vessel is vented, and the plateout coupons and other sample devices are removed. The test equipment and cell are then decontaminated in preparation for the following run.

1.32 Conduct of Tests. The principal operating conditions for Runs 3 and 4 are compared in Table XXVIII. Operation of the test equipment and facilities was generally satisfactory, and only minor problems were encountered in containing the fission products within the hot cell and in decontaminating the test equipment following each test. During Run 3, shortly after the melting stage of the run was concluded, the quartz furnace tube failed, blowing sintered fuel and bed material out of the quartz tube and into the cell. The containment vessel was immediately isolated. No contamination was released to the operating areas, and the run was continued on schedule. The confinement of activity to the cell and filtering system demonstrated the adequacy of the safety features of the facility. To prevent recurrence of the failure in future runs, a more rigid assembly for holding the furnace tube was designed to minimize mechanical stresses on the tube during and following assembly. The furnace tube was changed to prevent any spattering of molten fuel on the outer quartz wall. The operation of the new furnace and assembly fixture was satisfactory for Run 4.

Numerous coupons were contaminated in Runs 3 and 4 for the LOFT coating selection and decontamination studies described in Section III-1.1. Containment atmosphere was drawn through four gas-particulate sampling cartridges and two of the LOFT gas-particulate capsule samplers during both runs. The evaluation effort on these samplers is being performed under the direction of the ICPP Analytical Branch and is reviewed in the ICPP Analytical Report^[35], along with the development effort on analytical methods. Other results from the two runs are summarized in the following sections.

1.33 Fission Product Behavior. The percentages of various fission product nuclides that were released from the fuel pins during meltdown are given in Table XXIX for the first four CDE runs. The release values were obtained by dividing the quantity of each nuclide found in the containment vessel and transport line by the total amount of each nuclide present in the fuel pin, as determined by the RSAC curie code^[36]. The release values do not include the fission products found in the quartz furnace; analysis of solutions used to leach the furnace tube indicate the fission product plateout on the tube is very low. The release percentages are in relatively good agreement though several meltdown parameters

TABLE XXVIII

COMPARISON OF OPERATING CONDITIONS FOR CDE RUNS 3 AND 4

Condition	Run 3	Run 4
Fuel Element:		
Diameter (inches)	9/16	9/16
Length (inches)	3-1/2	3-1/2
Cladding	Zircaloy-2	Zircaloy-2
Meat	UO ₂ pellets	UO ₂ pellets
Total uranium (grams)	70.2	69.9
Enrichment (percent)	8	8
Fuel element burnup (MWd/Tonne)	740	440
Irradiation flux level (n/cm ² -sec)	6.8 x 10 ¹²	8.6 x 10 ¹²
Total activity in fuel element at reactor shutdown (curies)	7100	7800
Iodine-131 activity in fuel element at reactor shutdown (curies)	41.5	39.9
Cooling time until fuel element meltdown (hours)	7	9.75
Time after start of heating until initial melting occurred (minutes)	4	7
Time fuel pin was molten (minutes)	20	25
Composition of transport gas over fuel	steam and 3% argon	steam and 3% argon
Velocity of transport gas over fuel element (ft/sec)	1.85	1.57
Furnace and containment vessel pressure during meltdown (psig)	22	22
Containment atmosphere temperature during meltdown (°F)	218	224
Composition of containment atmosphere during meltdown	50% air and 50% steam	50% air and 50% steam
Number of sampling systems installed:		
Raw gas sample bombs	2	2
Gas-particulate cartridges	4	4
Gas-particulate capsules	2	2
Plateout capsules	2	2
Plateout coupons (ambient temperature)	156	170
Plateout coupons (heated)	16	0
Plateout coupons (cooled)	16	0
Continuous sampler-monitor	1	1
Deposition tube (heated)	1	1
Deposition tube (ambient temperature)	1	1

TABLE XXIX

FISSION PRODUCTS RELEASED FROM FUEL [a]

Fission Product	Percent Released			
	CDE-1	CDE-2	CDE-3	CDE-4
Sr-89	<0.01	0.05	0.02	---
Zr-Nb-95	Trace	Trace	0.1	0.001
Mo-99	2.5	4.0	8.0	6.5
Ru-103	<0.01	0.07	0.7	0.2
I-131	15.0	17.0	17.0	23.0
Te-132	7.0	9.5	16.0	22.0
Cs-137	11.0	13.0	21.0	8.0
Ba-140	---	0.04	0.04	0.16
Uranium	---	---	0.26	---

[a] Determined by dividing the fission products found in the containment vessel, reactor vessel, and furnace outlet line by the total amount of each fission product present (RSAC Curie Code). Does not include fission products found in the quartz furnacc.

were varied, eg, meltdown rate, transport gas velocity, and burnup. There appears to be a trend toward a higher release with each succeeding run.

The fission product and fuel accountability data are shown in Table XXX for the first four CDE runs. The accountability, particularly of the nonvolatile fission products, shows a general improvement with each succeeding run, though the accountabilities of the volatile (greater than 15 percent release from fuel) fission products, I-131, Te-132, and Cs-137, were still low in Run 3. The low values can be attributed, at least in part, to losses following the furnace break. The accountabilities for the various nuclides are based on a fuel pin inventory calculated with the RSAC curie code.

The distribution of the various nuclides transported from the furnace in Run 3 is shown in Table XXXI. Comparable data for Runs 1 and 2 are not shown because data on the fission product activities in the containment atmosphere and transport line were not obtained. From the tabulation for Run 3, it appears that deposition in the transport line is small; the maximum plateout found in the transport line was six percent (Cs-137). The ratios of the nuclide fractions plated out in the containment vessel (sum of activities in decontamination solutions and activities on samplers) with those found in the containment condensate vary from nuclide to nuclide as expected; however, the variations do not follow a pattern expected from knowledge of their general behavior. For

TABLE XXX

FISSION PRODUCT AND MATERIAL ACCOUNTABILITY

Nuclide	Percent Recovered			
	CDE-1	CDE-2	CDE-3	CDE-4
Sr-89	27	140	137	112
Zr-Nb-95	27	18	90	116
Mo-99	11	4 ^[a]	66	101
Ru-103	18	14	100	74
I-131	31	28	19	57
Te-132	7	9	26	22 ^[c]
Cs-137	84	23	27	93
Ba-140	36	74	89	83
Ce-141	55	10	91	47
Uranium (Fuel and Bed)	98	101	85 ^[b]	107
Zirconium (Cladding)	103	98	---	---

[a] Fuel residue solution analyzed too late to obtain reliable data.

[b] Based on the U-235 recovered from the fuel pin residue.

[c] Not reported in the fuel residue sample.

TABLE XXXI

DISTRIBUTION OF FISSION PRODUCTS TRANSPORTED
FROM THE FURNACE -- CDE RUN 3

	Percentage of Total of Each Nuclide							
	Sr-89	Zr/Nb-95	Mo-99	Ru-103	I-131	Te-132	Cs-137	Ba-140
Containment Condensate	6.80	97.17	51.71	9.40	54.37	29.05	60.42	4.03
Containment Decontamination Solutions	92.49	2.78	42.83	84.10	37.03	64.24	30.07	91.37
Deposition Samples	0.12	0.05	0.60	0.46	3.93	0.53	0.29	0.58
Containment Atmosphere	[a]	[b]	3.37	4.90	3.65	3.81	3.06	2.24
Transport Line	0.59	[b]	1.49	1.14	1.02	2.37	6.16	1.78

[a] Analysis not obtained.

[b] Activity too low to be detected.

example, Sr-89 and Ba-140 should appear higher in the condensate than they do because of their solubilities. Conversely, the insoluble Zr-Nb-95 should plate out to a greater extent. Presence of the fission products on undissolved solids in the liquid samples and nonrepresentative samples are suspected as the reasons for the unusual behavior indicated by the analyses.

1.34 Particulate Concentration and Composition. Three unirradiated fuel pins were melted during cold tests made prior to CDE Run 4. During one of the cold tests, a sample of the containment atmosphere was drawn through a Millipore Type AA filter and analyzed by X-ray fluorescence and emission spectrometry to determine the composition of the particulates. A sample of the particulates plated out on the outlet end of the quartz furnace was also obtained. The results, shown in Table XXXII, indicate that the tin in the Zircaloy cladding is preferentially volatilized. Both silicon (from the quartz furnace) and zirconium show little volatilization. Additional tests of this type are planned.

TABLE XXXII

COMPOSITION OF PARTICULATES RELEASED FROM CDE FUEL

<u>Component</u>	<u>Containment Concentration</u> <u>μg/ft³</u>	<u>Plateout Sample</u> <u>μg</u>
Tin	690	800
Uranium	570	175
Silicon	11	20
Zirconium	< 1	< 1

1.35 Rare Gas Content of Fuel. The fuel pin that was melted during CDE Run 4 was dissolved in an apparatus that quantitatively trapped the krypton and xenon. The dissolution was conducted in such a manner that the gases from dissolution of the UO₂ core were collected separately from those from dissolution of the Zircaloy cladding.

The quantities of the two gases found in the UO₂ were 0.02 standard cc of krypton and 0.14 standard cc of xenon. The amounts of gas in the cladding were less than the detectable limit of 0.001 standard cc. This indicates that the gases were bound in the UO₂ lattice.

1.36 Decontamination of Facility. The CDE equipment and cells require decontamination following each run. Though decontamination is done primarily to permit repeated tests, it also affords an opportunity to obtain practical experience on the relative effectiveness of decontaminants and to test equipment and decontamination procedures on a large scale. The decontamination equipment installed in the CDE include:

- (1) Sprays in the containment vessel
- (2) Flushing connections to critical lines and equipment
- (3) Cell sprays

- (4) Three 100-gallon mixing tanks in which the decontaminating solutions are prepared
- (5) Waste storage tanks in which the waste solutions are collected
- (6) A system for sampling the decontamination solutions.

From the experience gained from the four runs, in which the order of application of the various decontaminating solutions has been varied and the procedures have been changed, the following method of decontamination has evolved:

- (1) Remove all samples
- (2) Remove the fuel residue and other "hot" items that can be removed remotely
- (3) Spray the containment vessel through the in-vessel sprays and flush the condensate system lines and the transport line
- (4) Wash the cell interior with cell sprays
- (5) Enter the cell and remove remaining "hot" items manually
- (6) Enter the cell and wash walls and equipment using a portable decontamination unit (pump, tank, hose, and spray nozzle)
- (7) Enter the cell and complete cleanup by mopping, brushing, etc.

The procedure has proved to be quite effective. Following a normal test run, this procedure reduces the general radiation levels in the cell from ≈ 100 R/hr to less than 1 mR/hr and can be completed in about one week. The solutions (which include water washes and several commercial products) and the order of application are being varied to evaluate their relative effectiveness on each of the fission product isotopes. More test data are needed to complete this comparison; however, it appears that the soluble strontium and cesium isotopes are removed preferentially by the water washes.

The furnace failure in Run 3 caused many particulates to be blown into the cell. Many of these particulates had to be located with hand-carried radiation instruments and then be picked up with sticky paper.

1.4 Continuous Sampler-Monitor for the Containment Building Atmosphere (R. E. Schindler; Development Engineering Section)

A Continuous Sampler-Monitor (CSM) is being developed for use in sampling the containment building atmosphere to determine the fission product concentrations during the Loss-of-Fluid Test. The CSM, for which a schematic flow sheet is shown in Figure 33, would use a scrubber located in the containment building to sample the atmosphere continuously and to separate the fission products into two streams which flow separately through the containment wall to radiation monitors and samplers located outside the building. The scrubber, located in the containment atmosphere to avoid problems with fission product plateout on long sampling lines, washes nearly all of the condensible fission products out of the atmosphere sample into a liquid stream, leaving essentially only rare gas fission products in the gas stream. The scrubbing of the atmosphere

Fig. 33 Schematic flow sheet of Continuous Sampler-Monitor.

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sample allows the condensible and ingestible fission products (primarily iodine) to be monitored apart from the more active but less hazardous (less ingestible) rare gases. The radiation monitors and sampling stations are located outside the containment building where the background radiation is moderate and the equipment is accessible. Gross gamma monitors on each sampling line will provide a continuous record of the gross condensible and rare gas fission product activities in the containment atmosphere. Samples taken from each stream will be analyzed for the major isotopes using spectrum stripping techniques which are being developed by the Nuclear Physics Section. The Continuous Sampler-Monitor will provide useful data on the time and rate of events during the meltdown, eg, the time fission products first reach the containment atmosphere, the rates of increase (or decrease) of fission product concentration, and peak fission product concentrations.

A spray scrubber, such as the one shown in Figure 34, offers a simple and potentially effective means of scrubbing condensible fission products from the containment atmosphere sample. The sample enters through a port in the side of the scrubber, then passes upward through the spray and a de-entrainment device. Iodine, the fission product of greatest concern, can be released in at least four forms: elemental iodine vapor, hydrogen iodide, organic iodides, and iodine adsorbed on particulate matter. Owing to their known ability to react rapidly with the inorganic iodine vapors (elemental iodine and hydrogen iodide), caustic scrubbing solutions have been used in the CSM scrubber. The ability of

a spray scrubber to scrub elemental iodine vapor with a caustic solution was demonstrated in previously reported [1] tests. Currently reported activities include laboratory evaluations of the scrubber performance on fine particles and organic iodides, testing of the CSM in the Contamination-Decontamination Experiment, evaluation of materials for the scrubber, and development of techniques for analyzing samples taken with the CSM.

1.41 Evaluation of the CSM Spray Scrubber for Particulates Scrubbing. Since a portion of the fission product activity in the LOFT containment atmosphere is expected to be in the particulate form, the effectiveness of the Continuous Sampler-Monitor (CSM) in scrubbing particulates from an atmosphere sample was studied. A fluorescein dust with a size range of 0.05- to 0.7-micron diameter was used to test the performance of the CSM spray scrubber on particles under a number of conditions. From these, it was found that the scrubber will effectively scrub the particles larger than 0.2-micron diameter, but most of the finer particles pass on through. Thus, the performance of the CSM spray scrubber on particulate fission products will depend strongly on the size distribution of the particulates released.

(1) Experimental Apparatus. The experimental equipment used to evaluate the CSM spray scrubber is shown schematically in Figure 35. A fluorescein dust with a mass median diameter of 0.43 micron was produced by atomizing a fluorescein solution with a pneumatic atomizing nozzle and allowing the resulting spray to dry. The air and liquid flows to the atomizing nozzle were metered to obtain reproducible size distributions of the dust. The particle size distribution shown in Figure 36 was obtained from electron microscope photographs of two samples of the fluorescein dust. The particles ranged in size from 0.05 to 0.7 micron in diameter.

The spray scrubber (Figure 35) consisted of a piece of "Pyrex" pipe with a spray nozzle placed in one end. To evaluate the effect of various design parameters on the scrubber performance, tests were made using four swirl

Fig. 34 Spray scrubber.

Fig. 35 Schematic flow sheet of apparatus for fluorescein dust scrubbing test.

pressure-atomizing nozzles (Delavan nozzles sizes were 0.50 gph-90°, 0.75 gph-70°, and 1.00 gph-70°, and a Spraying Systems nozzle size was 0.60-1/4 LNN) placed either spraying upward in the bottom of the scrubber or down from the top of the scrubber. The scrubbing chambers were 12- or 18-inch sections of 1-1/2- or 2-inch-diameter "Pyrex" pipe. Water supplied at a pressure of 500 psi was used as the scrubbing liquid for all the tests.

The air containing dust was passed upward through the scrubber at several flow rates. The scrubber performance was measured by collecting samples, with glass fiber filters, of the fluorescein dust in the air entering and leaving the scrubber as shown in Figure 35. The volume of air passing through each filter was measured with a wet-test gas volume meter. A colorimetric method of analysis was used to measure the quantity of fluorescein on each filter. To obtain a material balance on the scrubber, samples of the fluorescein solution leaving the scrubber were taken; however, most of them proved to be too dilute for an accurate analysis.

(2) Results. The spray scrubber removed 98 to 99 percent of the fluorescein dust fed into it in all but a few of the tests. The experimental scrubbing efficiencies varied from a low of 95.3 percent to a high of 99.53 percent; however, the majority was between 98 and 99 percent.

Random errors (on the order of two percent) in the experimental data mask the effect of the operating parameters on scrubbing efficiency. The effects of chamber diameter, chamber length, and spray direction are too small (less than one percent) to be observed. A small decrease -- about half a percent -- in scrubbing efficiency can be observed when the air flow is increased from 200 ml/min to 600 ml/min. Slight differences in performance could also be observed with different spray nozzles.

Fig. 36 Particle size distribution of fluorescein dust.

(3) Discussion. The most noticeable feature of the results is that none of the experimental parameters had a strong effect on scrubbing efficiency. The published literature on the impaction of particles on spray drops offers an explanation[37]. The impaction efficiency of spheres, ie, the ratio of the effective cross section to the actual cross section, is a function of $\sqrt{\Psi}$, where

$$\sqrt{\Psi} = D_p \sqrt{C \rho_p V / 18 \mu D_c}$$

D_p = diameter of the particle

C = Cunningham slip correction

ρ_p = density of the particle

V = relative velocity between particle and collector

μ = viscosity of the gas

D_c = diameter of the collector.

The impaction efficiency, η , which is shown in Figure 37 as a function of $\sqrt{\Psi}$, rises sharply as $\sqrt{\Psi}$ goes from 0.15 to 1. Outside of this narrow range, changes in $\sqrt{\Psi}$ have little effect.

Equation (1) shows that scrubbing by the impaction mechanism is optimized by using a spray with the highest possible drop velocity and the lowest possible drop size. This is achieved for swirl pressure atomizing nozzles by operating small spray nozzles at high pressure [38]. The spray scrubbing tests were conducted operating the smallest available nozzles at a pressure of 500 psi. Delavan nozzles of the type used are reported to produce sprays with a mass median diameter of about 70 microns at 100 psi pressure; higher atomizing pressures produce finer sprays[38].

Some impaction efficiencies, taken from the curve of Ranz and Wong[37], for the conditions [a] of the spray scrubbing tests are tabulated in Table XXXIII for various drop and particle sizes. The impaction efficiencies in Table XXXIII are low for particles smaller than 0.2 micron but appreciable for larger particles.

The particle size distribution shown in Figure 36 reveals that 98 percent of the fluorescein is contained by the particles larger than 0.2-micron diameter. This fraction, 98 percent, agrees with the measured scrubbing efficiencies. It

Fig. 37 Impaction efficiencies of spherical collectors.

[a] $v = 190$ ft/sec (70 percent of the velocity from a frictionless nozzle at 500 psi), $\rho_p = 0.8$ g/ml, $c = 1$.

TABLE XXXIII

IMPACTION EFFICIENCIES OF SPRAY DROPS

Particle Diameter, Micron	0.6	0.4	0.3	0.2	0.15	0.1
70 micron drop	0.8	0.6	0.4	0.15	0.02	0.0
50 micron drop	0.83	0.73	0.55	0.22	0.05	0.0

thus appears that the cut-off of impaction efficiency with decreasing particle size is the effect which controls the measured scrubbing efficiencies. Under the conditions of the experiments, the scrubber removes all the dust larger than 0.25 micron, a varying fraction of the dust between 0.15- and 0.25-micron diameter, and very little of the dust smaller than 0.15-micron diameter. In more general terms, the cut-off conditions of the spray scrubber are an impaction efficiency of 0.2 or a value of $\sqrt{\Psi}$, as defined in Equation (1), of 1/3.

Equation (1) also shows that dense particles are relatively easier to scrub. For example, if the spray scrubber will remove fluorescein particles down to 0.2-micron diameter, it will scrub particles down to 0.075-micron diameter for ZrO_2 ($\rho_p = 5.6$), 0.07-micron diameter for SnO_2 ($\rho_p = 7.0$), and 0.055-micron diameter for UO_2 ($\rho_p = 11.0$).

The particulates released by molten UO_2 are usually extremely fine. Particle sizes reported^[39] by ORNL range down to less than 0.01 micron. Particles of this size will probably pass through the CSM scrubber; however, condensation of steam on the fine particles can enhance scrubbing by producing drops large enough to be scrubbed. For example, saturated steam at 230°F contains enough water to form 5 micron drops if condensed uniformly on a particle cloud containing 10^7 particles/cm³ (an estimate for LOFT based on the agglomeration data of Gussman^[40]). The effectiveness of the CSM spray scrubber for removing fine particles will, thus, depend strongly on whether steam condenses on the particles. Unless moisture condenses on them to form larger particles, the fine particles and the fission products adsorbed on them will probably pass through the scrubber.

(4) Conclusions -- Spray Scrubbing of Particles.

- (1) A spray scrubber can effectively scrub fluorescein dust particles larger than 0.2-micron diameter when scrubbing low air throughput at a spray pressure of 500 psi.
- (2) The scrubbing of particles larger than 0.2 micron is unaffected by a number of design and operating parameters (in the ranges studied): scrubbing chamber size, spray direction, air throughput, and nozzle size and make.
- (3) Particle sizes reported by ORNL for fission product releases from molten fuels are mostly in size ranges smaller than the particles which the spray scrubber has been observed to collect. Unless steam condenses on these fine particles, a major share will probably penetrate the scrubber.

1.42 Evaluation of the CSM Spray Scrubber for Adsorption of Methyl Iodide Vapor. Laboratory tests indicate that the scrubbing efficiency of the CSM spray scrubber for methyl iodide is considerably lower than that observed for molecular iodine. An average scrubbing efficiency of about one-third was observed when scrubbing methyl iodide with a caustic thiosulphate mixture at temperatures from 37 to 75°C with gas flow rates of around 200 cc/minute.

A series of screening tests performed by Hammer [1] using a bubbler-type scrubber revealed a number of solutions which react with methyl iodide. These included oxidizing acid mixtures, mercury salts, and some reducing agents. The caustic thiosulphate mixture was chosen from these solutions because it is a basic solution which reduces iodine to a soluble form.

(1) Experimental Method. The scrubbing tests were conducted by passing tracer methyl iodide through a scrubber which was set up in a constant temperature bath as shown in Figure 38. The scrubbing efficiency was determined by measuring the quantity of methyl iodide in the scrubbing solution and in the gas which passed through the scrubber. An independent check on the scrubbing efficiency was obtained by measuring the average concentration of methyl iodide in a small side stream of the carrier gas entering the scrubber. Both gas and liquid streams passed through warming coils in the temperature bath to allow them to reach the desired temperature before reaching the scrubber. The scrubber body consisted of a one-foot section of 1-1/2-inch-diameter Pyrex pipe, and the spray nozzle was a 0.50 gph-90° nozzle operated at 400 psi pressure. The flow of scrubbing solution from the nozzle was about 45 cc/minute. Gas throughput rates varied from 170 cc/minute to 650 cc/minute; however, most of the flow rates were around 200 cc/minute. Three different scrubbing solutions were used: a 0.5 M NaOH - 0.5 M Na₂S₂O₃ mixture, a 0.5 M NaOH - 1.0 M Na₂S₂O₃ mixture, and water.

Fig. 38 Schematic flow sheet of apparatus for the methyl iodide scrubbing test.

The scrubbing tests were carried out by vaporizing tracer level methyl iodide ($\text{CH}_3\text{I}^{131}$) into the helium carrier gas flowing into the scrubber. A small bed of charcoal impregnated with triethylenediamine was used to collect the methyl iodide not removed by the scrubber. During the first run, the charcoal bed was backed up by a liquid nitrogen cold trap to determine the penetration of methyl iodide through the charcoal; no penetration, however, was detected. The scrubbing solution was allowed to drain from the scrubber into a collection bottle which was vented to the scrubber.

(2) Results. The measured scrubbing efficiencies varied from 18 to 63 percent and averaged 35 percent; interpretation of the data was complicated by data point scatter. The discrepancies in the material balance on the methyl iodide entering and leaving the scrubber averaged 30 percent.

The strongest observable effect was the decrease in scrubbing efficiency with increasing gas flow rate. In a series of consecutive runs under the same conditions (other than gas flow rate), the scrubbing efficiency dropped from 35 percent at a gas flow of 185 cc/minute to 7 percent at a gas flow of 650 cc/minute. No significant effect of temperature could be observed over the range from 37 to 75°C. No significant difference could be observed between the 0.5 M and 1.0 M $\text{Na}_2\text{S}_2\text{O}_3$ solutions; however both thiosulphate solutions scrubbed appreciably better than water.

(3) Discussion. The probable reason for the difference between the performance of the spray scrubber and the bubbler scrubber used by Hammer[1] is the difference in contact time between gas and liquid. The spray drops travel to the wall of the spray scrubber in a millisecond while a bubble takes about a second to pass through a bubbler scrubber. Only a reagent which reacts very rapidly can remove methyl iodide in such a short contact time. Much of the scrubbing probably takes place in the fine drifting mist formed in the center of the spray cone (this mist comprises about one percent of the spray liquid) and in the liquid on the sides of the scrubber.

1.43 Performance of the Continuous Sampler-Monitor During CDE Run 3. The results of testing the Continuous Sampler-Monitor scrubber during CDE Run 3 confirm previously determined performance characteristics. The scrubber performs well on inorganic iodine vapors and large particulates, but poorly on fine particulates (presumably less than 0.1 micron) and organic iodides. The scrubber performance was evaluated by measuring the iodine content of the gas stream leaving the scrubber at three times during the CDE run. In the period shortly after the meltdown, about one-half of the airborne iodine penetrated the scrubber, apparently adsorbed on a fine particulate which was composed of Zircaloy cladding fumes. During the middle of the run, the scrubber removed the iodine from the gas stream almost completely. Near the end of the run, iodine penetration rose again, presumably because of an increase in the organic iodide fraction of the gas sample.

(1) Experimental Setup. The CSM was installed, as shown schematically in Figure 39, to allow sampling of the gas and liquid effluent streams flowing from the scrubber. A sample of the condensible (iodine) and particulate fission products in the gas stream was taken by diverting the gas stream for a measured time interval through a sampler consisting of a glass fiber filter and a bed of charcoal (impregnated with triethylenediamine) in series. The scrubbing liquid

Fig. 39 CSM schematic flow sheet for CDE Run 3.

samples were drawn from the liquid effluent line before the liquid reached the collection tank. Moisture collecting in the gas line was collected in a sump and sampled.

The CSM scrubber which was placed inside the containment vessel consisted of a vertical Teflon cylinder containing a spray nozzle in the bottom and a porous Teflon filter, used as a de-entrainment device, at the top. The atmosphere sample enters through a port in the side of the scrubber and passes up through a spray of scrubbing liquid composed of a 0.5 M sodium hydroxide - 0.5 M sodium thio-sulphate mixture. The scrubbing liquid reaches the scrubber through a line of sufficient length to allow the liquid to warm to the containment temperature before being sprayed into the scrubber. Thus, there was little or no condensation in the scrubber.

The CSM scrubber was operated for about 30 minutes during each of the three sampling periods and shut off between sampling periods. The first sample was taken about one hour after the start of the meltdown (1/2 hour after isolation); the second and third samples were taken 5 and 25 hours, respectively, after meltdown.

(2) Scrubber Performance. The data on the CSM performance provided by the laboratory studies were used in interpreting the results of the CDE Run 3 tests. Based on these studies, the CSM scrubber was expected to perform well on inorganic iodine (HI and I₂) and large particles, but not on organic iodides and very fine particles. The actual results confirm these observations.

(3) Iodine Distribution. A relative distribution of I-131 for each of the three sampling periods was calculated from the quantities of I-131 found in the scrubbing solution samples, the gas line filters, and the gas line charcoal beds. The percentages listed in Table XXXIV were calculated by converting the quantity of I-131 in each sample to a common basis (a unit volume of gas sample) and then dividing by the total of the three samples. The scrubber was operated in the same manner during each sampling period; hence, the observed differences in scrubber performance can be attributed to differences in the nature of the CDE atmosphere at the time of sampling.

TABLE XXXIV

RELATIVE DISTRIBUTION OF IODINE-131 IN THE SCRUBBER-FILTER SYSTEM
(Percentage)

<u>Hours After Meltdown</u>	<u>1</u>	<u>5</u>	<u>25</u>
Scrubber solution	46	99.7	87
Gas line filter	11	0.01	0.02
Charcoal bed	43	0.3	13

During the first sampling period, about half of the fission product iodine penetrated through the scrubber and was collected by the particulate filter and charcoal trap. Since the scrubber removes the inorganic iodine, most of the iodine found in the filter and charcoal at the end of the first hour after meltdown must have penetrated the scrubber either adsorbed on fine particles or as organic iodides. Iodine which is carried through the spray reversibly adsorbed on fine particles might then desorb and migrate through the filter to the charcoal bed. The one-day delay between the time the sample was taken and the time the sample was packaged allowed ample time for loosely adsorbed iodine to migrate across the 1/8-inch gap from the filter to the charcoal. A comparison with the quantity of iodine on the charcoal in the other two samples suggests that much of the iodine in the first sample charcoal arrived by this mechanism rather than as an organic iodine.

During the second sampling period five hours after meltdown, the CSM scrubber performed very well by scrubbing out 99.7 percent of the collected iodine. The airborne iodine must have been almost entirely inorganic iodine for the scrubber to have worked so well. Apparently, the copious particulate observed during the earlier sampling period had either been washed out by the condensing stream or coagulated to a scrubbable size. The 0.3 percent of the iodine found in the charcoal could have come from either inorganic iodine which passed through the scrubber, organic iodides, or desorption of iodine which had plated out in the gas sampling line during the previous sampling period. The good performance of the scrubber during this sampling period shows that it was functioning properly and that it can effectively scrub a favorably composed atmosphere sample.

During the last sampling period, which was 25 hours after meltdown, iodine again penetrated the scrubber in quantity, appearing in the charcoal bed but not on the filter. This "penetrating" iodine is probably composed of organic iodides

which formed late in the run and constitutes a very small fraction of total iodine released from the fuel.

(4) Total Airborne Iodine. The total amount of iodine-131 airborne in the containment atmosphere (calculated from the total of that found in the scrubbing solution and the gas stream) is listed in Table XXXV for each of the three sampling periods as a percentage of the fuel pin inventory (33 curies of iodine-131). Maypack samples taken at about the same time as the one-hour and 25-hour samples contained more iodine than the corresponding CSM samples. The one-hour CSM sample agreed within 25 percent with those from the Maypack samplers, but the CSM sample taken after 25 hours contained only one-third as much iodine as the corresponding Maypack samplers [35].

TABLE XXXV

PERCENT OF IODINE-131 INVENTORY AIRBORNE IN CONTAINMENT

Hours After Meltdown	1	5	25
Percent Airborne Iodine	3.75	0.70	0.26

(5) Nature of the Particulate. The particulate matter which was collected on the filter during the first sampling period was analyzed by emission spectroscopy. A trace of tin (a minor component of the Zircaloy cladding) was detected, but no uranium was found even though the Maypack filters collected large quantities of uranium. Apparently most of the uranium particles were scrubbed out while tin particles passed through the scrubber.

(6) Fission Product Plateout. The extent of plateout of activity on surfaces of the sampling system was determined by removing sections of tubing and other surfaces after the CDE run and measuring the fission products on them. The quantity of I-131 lost in the sampling lines upstream of the sampling points was calculated from the analysis of the tubing samples. The overall iodine balance tabulated in Table XXXVI was prepared by estimating the total quantity of iodine passing the sampling points during the three sampling periods, adding the plateout to obtain a total sample, then calculating the relative iodine distribution.

The plateout of iodine appears to represent a significant loss of iodine only in the case of the gas line. About ten percent of the total iodine penetrated the scrubber (probably during the first sampling period) and plated out in the gas sampling line before reaching the gas sampler. The iodine plateout in the liquid sampling line represents only a small fraction of the total iodine sample; however, its buildup over the run may still require intermittent decontamination for an on-line gross

TABLE XXXVI

RELATIVE DISTRIBUTION OF IODINE-131 THROUGHOUT SYSTEM, INCLUDING LINE PLATEOUT
(Percentage)

Scrubbing Solution	48
Gas Stream	41
Gas Line Plateout	10
Liquid Line Plateout	0.15
Condensate in Gas Line	0.15
Teflon Mist Collector	1.3

gamma monitor. The iodine lost by plateout could represent about a ten percent error in the numbers presented in Tables XXXIV and XXXV -- primarily in those for the first sampling period. An error of this magnitude will not affect any conclusions reached about the scrubber performance.

(7) Other Fission Products. The CSM samples were not analyzed until many of the fission products had decayed away; however, a complete set of data was obtained for Te-129, Cs-137, and Ru-103, as well as I-131. The distribution of these fission products was about the same as for iodine-131, except for Ru-103 which penetrated the spray and plated out in the sampling lines to a much greater extent than any other fission product.

(8) Conclusions. The following conclusions can tentatively be drawn from the CSM data for CDE Run 3:

- (1) The CSM scrubber, as currently designed, will remove inorganic iodine vapors and large particles but will not be efficient for scrubbing fine particulates or organic iodides.
- (2) Shortly after meltdown in CDE, half the airborne iodine in the containment atmosphere was in a form which penetrated the scrubber -- probably adsorbed on fine particulates but possibly also as organic iodides.
- (3) The fine particulate which penetrated the scrubber consisted of tin fumes from the Zircaloy cladding -- presumably with a diameter of less than 0.2 micron.
- (4) The fine particulate had washed out of the atmosphere or coagulated within five hours after meltdown.
- (5) Twenty-five hours after meltdown, a significant fraction (greater than 13 percent) of the residual airborne iodine was organic, but this constitutes less than one percent of the iodine released from the fuel.

1.5 Fission Product Sorption on Materials of Construction for the CSM (M. R. Fox; Chemistry Section)

In an attempt to find a material of construction for the Continuous Sampler Monitor (Section III-1.4) with low fission product retention, 18 coupons of uniform dimensions of six different materials were contaminated in the Contamination-Decontamination Experiment (Section III-1.3). The materials tested were Type 304 stainless steel, Type 6061 aluminum, Teflon-TFE, Kel-F, Kynar, and Pyrex glass. Each sample was analyzed for the four isotopes, I-131, Te-132, I-133, and Mo-99, by gamma-ray spectroscopy. These isotopes were chosen because of their ease of analysis by gamma-ray spectroscopy, because of their high volatility, and because of their abundance (high yields).

The coupons were hung adjacent to each other on horizontal rods in the containment vessel. This was done in order to detect concentration gradients along the rods and to determine, approximately, a value for these gradients. After exposure, the coupons were examined for activity without decontamination.

The results of the analyses are listed in Table XXXVII and indicate (by the agreement of analyses of three samples of each of the materials) that concentration gradients of these four isotopes along the rods holding the coupons are nearly zero; therefore, in this particular region of the containment vessel, good mixing was attained. Thus, the variation in activities observed between material types cannot be ascribed to variations in concentrations of these isotopes in the atmosphere.

TABLE XXXVII

TOTAL ACTIVITY ON COUPONS TESTED FOR FISSION PRODUCT SORPTION (dps)

<u>Material</u>	<u>I-131</u> <u>(x 10⁻⁶)</u>	<u>Te-132</u> <u>(x 10⁻⁶)</u>	<u>I-133</u> <u>(x 10⁻⁶)</u>	<u>Mo-99</u> <u>(x 10⁻⁶)</u>
Stainless steel	41	11	130	4.0
304	46	15	150	7.4
	39	13	120	6.3
Average	42	13	130	5.9
Aluminum	23	5.2	65	2.2
6061	21	5.5	61	2.7
	18	8.6	49	3.6
Average	21	6.4	58	2.9
Kel-F	13	13	47	4.9
	13	13	35	5.5
	20	14	33	5.8
Average	15	13	38	5.4
Kynar	20	11	54	4.6
	21	11	54	4.9
	19	7	52	3.2
Average	20	9	54	4.2
Teflon-TFE	10	3.7	28	1.6
	12	4.3	32	1.8
	14	6.0	37	2.6
Average	12	4.7	33	2.0
Pyrex	3.5	8.0	5.7	3.4
	3.6	8.0	6.0	3.7
	3.6	7.0	6.0	3.0
Average	3.6	7.7	5.9	3.4

In general, the results indicate that, of the materials tested, stainless steel has the highest retention of these isotopes. On the average the activity on the stainless steel coupons was 2.1 times the average activity on the other materials (excluding Pyrex which retained the least activity of any). There were no significant differences in the retention of these isotopes by Kel-F, Kynar, Teflon, and aluminum. The fact that aluminum retains these fission products to the same extent as the organic polymers Kel-F, Kynar, and Teflon would indicate that the mechanism of isotope retention is not predominately a chemical one.

Of the materials tested, Pyrex has the most desirable isotope retention behavior. Its average retentive ability is a factor of 3.7 below that of Kel-F, Kynar, Teflon, and aluminum and a factor of 7.8 below that of stainless steel.

The CSM is currently constructed of Teflon-TFE. If this material should prove to be objectionable (eg, deterioration at high radiation levels), the results of this test will be reconsidered in the selection of a new material of construction.

1.6 Evaluation of LOFT Plateout Capsules

(W. A. Freeby, D. P. Wright; Development Engineering Section)

The fission product behavior in the LOFT containment building following the core meltdown will be determined largely through analyses of atmospheric and plateout samples taken with the LOFT capsule samplers. Two of the atmospheric and two of the plateout capsule samplers were tested in both CDE Runs 3 and 4. Results of the plateout capsule testing are reported in the following paragraphs, and the results of testing of the atmospheric (or gas-particulate) capsule are reported elsewhere [35].

The LOFT plateout capsule sampler (Figure 40) consists of a five-inch-diameter aluminum sphere containing a fixture for holding two 3/4-inch-diameter painted coupons. After a predetermined exposure period in the LOFT containment building, the coupons (held in aluminum cups) are retracted into the capsule. The capsules are then removed from the building for disassembly and analysis of the coupons.

The capsule samplers tested in the CDE were mounted on a rack as shown in Figure 41. In each of the tests performed, the plateout capsule samplers were exposed to the fission product aerosol for a 24-hour period in the CDE, and then closed. Following closure of the plateout capsules, the support rack and capsules were removed from the containment vessel and disassembled remotely in the CDE cell. The coupons were then placed in acetate cups for transfer to an adjoining hot cell. There, the coupons were sealed in plastic bags and transferred to a sample storage area.

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Fig. 40 LOFT plateout capsule assembly.

The primary objective of the testing of the plateout capsules in the CDE to date is to determine if the data obtained from the plateout capsules are meaningful. To accomplish this, the effects of numerous variables (storage, handling, water immersion, capsule orientation, temperature, and condensation) are being studied. Since only two plateout capsules can be tested in each CDE run, other deposition samplers have been installed to augment the capsule evaluation. Two of the plateout capsules were installed for test in CDE Run 2; however, mechanical problems prevented them from operating. The improved units tested in CDE Runs 3 and 4 operated satisfactorily. The results of tests made to date are summarized in the following paragraphs.

Fig. 41 Capsule support rack for CDE containment vessel.

1.61 Variation of Fission Product Deposition on Coupons Contained Within Same Capsule. The fission product activities on the capsule coupons from CDE Runs 3 and 4 are listed in Table XXXVIII. The activities on coupons from the same capsule compare reasonably well, with the maximum variation from an average value for any one capsule being less than 50 percent. However, somewhat more variation is apparent between analyses on coupons from different capsules. Non-homogeneity of the containment vessel atmosphere may be contributing to this latter variation.

TABLE XXXVIII

COMPARISON OF FISSION PRODUCT DEPOSITION ON CAPSULE COUPONS

Nuclide	Activity, dps/cm ²			
	CDE Run 3		CDE Run 4	
	Upper Capsule	Lower Capsule	Upper Capsule	Lower Capsule
I-131	5.66 x 10 ⁶	2.60 x 10 ⁶	3.45 x 10 ⁶	2.12 x 10 ⁶
	7.14 x 10 ⁶	6.20 x 10 ⁶	3.09 x 10 ⁶	2.56 x 10 ⁶
Te-132	2.19 x 10 ⁶	1.53 x 10 ⁶	4.32 x 10 ⁴	4.32 x 10 ⁴
	1.20 x 10 ⁶	1.54 x 10 ⁶	[a]	1.08 x 10 ⁵
Mo-99	2.02 x 10 ⁶	1.13 x 10 ⁶	[b]	---
	1.60 x 10 ⁶	1.26 x 10 ⁶	---	---
Ru-103	4.07 x 10 ⁴	1.19 x 10 ⁴	---	---
	2.96 x 10 ⁴	2.09 x 10 ⁴	---	---
Cs-137	1.07 x 10 ⁴	6.55 x 10 ³	---	---
	7.90 x 10 ³	6.51 x 10 ³	---	---
Ba-140	9.60 x 10 ³	6.32 x 10 ³	---	---
	[a]	7.73 x 10 ³	---	---
Sr-89	1.66 x 10 ³	8.48 x 10 ²	---	---
	1.44 x 10 ³	3.53 x 10 ²	---	---

[a] Only one coupon analyzed.

[b] Analyses for Mo-99, Ru-103, Cs-137, Ba-140, and Sr-89 in Run 4 not available.

1.62 Effect of the LOFT Capsule on Fission Product Deposition. The presence of the spherical LOFT plateout capsule may affect the amount of fission deposited on its sample coupons. To determine the extent of this effect, numerous painted coupons in Teflon cups were attached to the capsule support structure, adjacent to, but outside of the capsules. These samples were exposed in CDE Runs 3 and 4. The exterior coupons and the coupons from the capsules were removed and packaged at the same time using identical procedures.

The activities on the capsule and exterior coupons are compared in Table XXXIX. The effect of the capsule on fission product deposition appears to be small, though the activities on the exterior coupons are generally higher than

TABLE XXXIX

COMPARISON OF FISSION PRODUCT DEPOSITION ON COUPONS INSIDE AND OUTSIDE
OF CAPSULES FOR CDE RUNS 3 AND 4

Nuclide	Average Deposition on Plateout Coupons Inside Capsules dps/cm ² [a,b]		Average Deposition on Plateout Coupons Mounted on Support Rack dps/cm ² [a,b]	
	Upper Capsule	Lower Capsule	Upper Location	Lower Location
<u>Run 3</u>				
I-131	6.40 x 10 ⁶	4.40 x 10 ⁶	6.43 x 10 ⁶	5.54 x 10 ⁶
Te-132	1.70 x 10 ⁶	1.54 x 10 ⁶	6.37 x 10 ⁶	1.66 x 10 ⁶
Mo-99	1.81 x 10 ⁶	1.20 x 10 ⁶	5.60 x 10 ⁶	8.2 x 10 ⁵
Ru-103	3.52 x 10 ⁴	1.64 x 10 ⁴	8.77 x 10 ⁴	2.47 x 10 ⁴
<u>Run 4</u>				
I-131	3.27 x 10 ⁶	2.34 x 10 ⁶	3.60 x 10 ⁶	3.17 x 10 ⁶
Te-132	4.32 x 10 ⁴	7.6 x 10 ⁴	2.73 x 10 ⁵	5.18 x 10 ⁵
Mo-99	---	---	1.44 x 10 ⁵ [c]	3.28 x 10 ⁵ [c]
Ru-103	---	---	---	---

[a] Values reported are arithmetic average of two analyses.

[b] Values for Run 3 calculated back to time of reactor shutdown; values for Run 4 calculated back to end of fuel-pin meltdown.

[c] Only one value reported.

those on the capsule coupons. Possible reasons for the observed differences are shielding of the coupons by the capsule, shorter exposure period for the capsule coupons, and migration of fission products within the capsules. The shielding effect appears most probable. Though the exterior coupons were exposed to the containment atmosphere for several hours longer than coupons in the capsule, the fission product concentrations in the containment vessel had greatly decreased in the later stages of the exposure. Preliminary data on migration of fission products within the capsule make migration an unlikely possibility. Additional comparisons of this type are planned for future CDE runs.

1.63 Effect of Coupon Orientation on Fission Product Deposition. To determine the effect of surface orientation on fission product deposition, the surfaces of painted coupons were oriented in various directions (facing up, down, or sideways) and attached to three levels (top, middle, or bottom) of the capsule support rack in the containment vessel. The major isotopes found on each coupon contaminated in CDE Run 4 are listed in Table XL with the corresponding orientation of the coupon. It appears that only the coupons with the surfaces facing up show substantial deviation from the average deposition found on

TABLE XL

EFFECT OF COUPON ORIENTATION ON FISSION PRODUCT DEPOSITION[a]
FOR CDE RUN 4

Coupon Location	Orientation	Coupon Activity, dps/cm ²		
		I-131	Te-132	Mo-99
Top level	Facing up	9.9 x 10 ⁶	4.32 x 10 ⁶	1.95 x 10 ⁶
Top level	Facing down	4.14 x 10 ⁶	3.27 x 10 ⁵	1.49 x 10 ⁵
Top level	Facing to side	3.90 x 10 ⁶	2.04 x 10 ⁵	1.12 x 10 ⁵
Middle level	Facing up ^[b]	3.26 x 10 ⁶	2.23 x 10 ⁵	9.90 x 10 ⁴
Middle level	Facing down	4.25 x 10 ⁶	2.18 x 10 ⁵	1.27 x 10 ⁵
Middle level	Facing to side ^[c]	3.40 x 10 ⁶	1.67 x 10 ⁵	1.22 x 10 ⁵
Bottom level	Facing up	9.76 x 10 ⁶	3.69 x 10 ⁶	1.34 x 10 ⁶
Bottom level	Facing down	3.35 x 10 ⁶	2.73 x 10 ⁵	1.51 x 10 ⁵
Bottom level	Facing to side ^[c]	4.30 x 10 ⁶	3.79 x 10 ⁵	1.72 x 10 ⁵

[a] Three-quarter-inch-diameter aluminum coupons painted with Amercoat-66.

[b] Believed to be in error -- orientation was probably "downward".

[c] Average of 4 to 6 coupons located in a vertical position. The coupons were either facing or perpendicular to the CDE containment vessel wall at distances of 10 and 17 inches from the wall.

all surfaces. The coupons facing up show deposition levels of iodine two times higher than the other coupons. For particulates (Te-132, Mo-99), the deposition levels were up to ten times higher on the upward facing coupons.

A survey, shown in Table XLI, of the activities on the controlled temperature coupons contaminated in Runs 2 and 3 was made to obtain an independent check on the orientation data from Run 4. The controlled-temperature sampler, shown in Figure 42, uses 1-1/2 x 3/4 x 3/16 inch coupons oriented in various directions. With the exception of the iodine, the activities on these coupons exhibit the same general trend, although not as pronounced, as those on the capsule coupons in Run 4.

1.64 Effect of Temperature and Condensation on Fission Product Deposition. The studies on deposition of fission products on heated and cooled, controlled temperature coupons [1] were continued in Run 3. The procedure used was similar to that used in Runs 1 and 2 except that smaller temperature differences between the containment atmosphere and the coupons were maintained. In Run 3, the average temperature differences between the heated and cooled coupon surfaces

TABLE XLI

EFFECT OF ORIENTATION ON FISSION PRODUCT DEPOSITION ON CONTROLLED TEMPERATURE COUPONS[a] FOR CDE RUNS 2 AND 3

Run	Sampler	Coupon Orientation	Activity, dps/coupon			
			I-131	Mo-99	Te-132	Ru-103
2	Hot	Facing up	9.6×10^{10}	1.1×10^9	1.1×10^9	1.1×10^6
		Facing down	8.5×10^{10}	0.8×10^9	1.4×10^9	0.3×10^6
2	Cold	Facing up	6.3×10^{10}	2.7×10^{10}	3.2×10^{10}	4.0×10^8
		Facing down	4.2×10^{10}	2.2×10^{10}	1.8×10^{10}	8.0×10^8
3	Hot	Facing up	2.2×10^9	2.3×10^9	1.5×10^9	1.3×10^7
		Facing down	2.3×10^9	0.4×10^9	0.2×10^9	0.05×10^7
		Facing to side	2.0×10^9	0.6×10^9	0.14×10^9	0.5×10^7
3	Cold	Facing up	2.8×10^9	2.2×10^9	1.2×10^9	9.0×10^6
		Facing down	2.8×10^9	2.5×10^9	0.4×10^9	7.0×10^6
		Facing to side	2.5×10^9	1.5×10^5	0.6×10^9	10.0×10^6

[a] 1-1/2 x 3/4 x 3/16 inch carbon steel coupons coated with Amercoat-66.

were +4 and -4°F, respectively, compared with the average containment temperature. In Run 1, these differences were +130 and -35°F, respectively, while in Run 2 the differences were +30 and -30°F, respectively. In Figure 43, the data obtained in Run 3 are compared with the deposition data obtained with the controlled temperature coupons from Runs 1 and 2. Though the plots are based upon a limited amount of data, the difference in deposition behavior exhibited by the iodine over that of the particulate fission products, Te-132 and Ru-103, is apparent. Iodine is plated (or absorbed) preferentially on the noncondensing or hot surface while the particulate fission products are deposited more on the condensing or cool surface. Mo-99 and Ba-140 data, though not shown on the figure, follow a pattern similar to that of Te-132 and Ru-103. The plots also indicate that the variation in fission product behavior is small for the small temperature differences ($\approx 5^\circ\text{C}$) expected between the plateout capsule coupons and the LOFT containment wall.

1.7 Studies of Unirradiated Fuel Pin Meltdown Residues

(M. R. Fox; Chemistry Section)

An unirradiated Zircaloy-2 clad UO_2 fuel pin, similar in design and construction to those being used in the hot CDE runs, was melted by induction heating in a flowing steam atmosphere in the CDE furnace. Post-melt fuel studies were made by X-ray powder methods, optical metallography, and microprobe analyses. The purpose of these studies was to develop an understanding of the behavior of this system under these conditions. Such areas as oxide formation and reduction of UO_2 by Zr as well as the gross appearance and behavior of the residue were investigated. The data presented in this report must be considered as being preliminary inasmuch as this has been the first study of a meltdown under the conditions described.

Fig. 42 Controlled-temperature sampler.

1.71 Experimental Conditions. The arrangement of the fuel pin and induction furnace is shown in Figure 44. Steam flowed from left to right through the quartz furnace tube and into the CDE containment vessel during meltdown at a rate of 1.75 feet/second. The steam contained about two percent argon which was introduced as purge gas in instrument lines.

The fuel pin was about 50 percent submerged in a bed of UO_2 powder. This bed was used to prevent direct contact between the molten UO_2 from the fuel pin and the quartz furnace tube. Molten UO_2 wets quartz glass and upon cooling causes the glass to fracture. The UO_2 bed does not become molten since it is in a cooler part of the furnace. The fuel-pin residue was sectioned (perpendicular to the pin axis) for study by microprobe analyses and optical metallography.

Fig. 43 Effect of temperature and condensation on fission product deposition.

Fig. 44 CDE induction furnace showing fuel pin in center of induction coil.

1.72 Results. Since about 50 percent of the pin was embedded in the UO_2 powder, only the upper 50 percent was exposed to the flowing steam atmosphere. Most of the effort spent during this examination was in studying this upper portion.

Probably the most important observation is that the cladding of Zircaloy-2 on the upper half of the pin did not melt, but was completely oxidized to ZrO_2 (melting point of Zircaloy-2 is 1850°C). The oxidized Zircaloy-2 retained much of the original integrity of the cladding. It did fail by cracking, but not to the extent that might be expected.

The UO_2 in the fuel pin showed much evidence of having been molten (melting point 2830°C). This temperature was reached in approximately three minutes corresponding to a heating rate of $16^\circ\text{C}/\text{sec}$. The oxide ZrO_2 (melting point 2690°C), which formed from the metal-water reaction, had not melted significantly, even though it was in direct contact with molten UO_2 . The reasons for

this stability are (a) heat loss from cladding by radiation, (b) cooling of cladding by the flowing steam, (c) failure of the ZrO_2 to "couple" to the field of the induction furnace.

The appearance of metallic inclusions in the cladding- UO_2 boundary region was also observed. They were tentatively identified as a uranium-zirconium alloy. According to Martin and Mrazek[41] when UO_2 is heated above approximately 1500°C it has a tendency to become deficient in oxygen. When this substoichiometric mixture is cooled, metallic uranium is formed. Another possible explanation for the occurrence of metallic uranium is dependent upon the fact that at high temperatures UO_2 and ZrO_2 have almost identical free energies of formation[42].

For example,

$$\Delta F_f (\text{UO}_2, 2000^\circ\text{K}) = -178 \text{ Kcal and}$$

$$\Delta F_f (\text{ZrO}_2, 2000^\circ\text{K}) = -172 \text{ Kcal.}$$

This, then, would make possible the reaction

This possibility would be further enhanced if at least one of the constituents were molten (as was the situation in this experiment). In support of this latter postulate is the fact that the metallic uranium was found to always be accompanied by metallic zirconium in our observations. The UO_2 matrix surrounding these Zr-U inclusions contained Zr up to an estimated 18 weight percent. This matrix is probably a UO_2 - ZrO_2 solid solution.

The lower half of the fuel pin which was not oxidized by the steam, had undergone complete melting. That is, both the fuel and the unoxidized cladding in this region had liquified and had mixed thoroughly in the UO_2 bed.

1.73 Conclusions. The physical stability of the cladding which results from the rapid formation of ZrO_2 could alter the fission product release factors under accident conditions. The skin of ceramic ZrO_2 covering the fuel might keep the individual fuel pins, and therefore the core, somewhat intact and serve as a diffusion barrier and as a chemical trap for fission products volatilized from the fuel. The effect of the stability of the cladding should be studied further.

1.8 High Temperature Properties of Materials (R. R. Hammer; Chemistry Section)

A report, IN-1093[43], has been issued which reviews the physical properties of UO_2 , ZrO_2 - UO_2 solid solutions, ZrO_{2-x} , and Zircaloy-4. Recommended, measured, and extrapolated values for these properties are given. The properties covered include transition temperatures, heat capacities, heat contents, vapor pressures, thermal conductivities, and thermal expansion. The temperature ranges and materials covered were selected for use in the analysis of a loss-of-coolant accident.

2. OTHER REACTOR TECHNOLOGY SUPPORT PROGRAMS

2.1 A new Process for Uranium Aluminide Manufacture Employing Fluidized Bed Techniques

(E. S. Grimmett, R. K. Ballard; Development Engineering Section)

A method has been developed for producing uranium aluminide (UAl_3) in a fluidized bed reactor using uranyl nitrate and aluminum as starting materials. Uranium aluminide compounds have properties which make them desirable as fuels in test reactors, or even power reactors. This process eliminates several of the steps normally used in the manufacture of uranium aluminide compounds and lends itself particularly well to an on-site fuel cycle.

2.11 Uranium Aluminides as Reactor Fuels. There are three uranium aluminide compounds of interest to the reactor engineer. These compounds, along with some of their important properties, are shown in Table XLII. UAl_3 has been made by the fluidized bed process, and it is probable that UAl_2 and UAl_4 can be made as well.

TABLE XLII

PROPERTIES OF URANIUM-ALUMINIDES

<u>Compound</u>	<u>Theoretical Density g/cm³</u>	<u>Uranium Content g/cm³</u>	<u>Melting Point °C</u>	<u>Crystal Structure</u>
UAl_2	8.14	6.64	1590	Face Centered Cubic
UAl_3	6.80	5.08	1350	Face Centered Cubic
UAl_4	6.06	4.16	730	Orthorhombic

Gibson and deBoisblanc [44] proposed that uranium aluminide compounds be used with powdered aluminum to make uranium-rich fuel elements by powder metallurgy techniques. When used in reactors operating with high heat fluxes and power densities, such as the Engineering Test Reactor and the Advanced Test Reactor, these fuels offer advantageous properties not available in other fuels. Some of the advantages of such fuels are as follows:

- (1) Good control can be obtained over the amounts of uranium and boron present in fuel plates by using this technique.
- (2) A remarkable ability to retain fission gases has been shown by UAl_4 , the compound to which the other aluminides convert when used in an aluminum matrix.
- (3) Fuel plates made by this powder metallurgy technique are very stable.
- (4) The estimated thermal conductivities of these compounds are about eight times those of uranium oxides.

The uranium aluminide compounds UAl_2 and UAl_3 have relatively high melting points and high thermal conductivities. These properties make these compounds attractive for use instead of UO_2 in clad tube-type fuel elements. Without the aluminum matrix, these compounds would not convert to the lower melting UAl_4 .

2.12 Process Steps Carried Out In Fluidized Bed Reactor. UAl_3 has been produced at this laboratory from starting materials of uranyl nitrate and aluminum powder by using fluidized bed techniques. No metallic uranium is handled anywhere in the process, and the product leaves the process in its desired size and shape.

In the studies made to date, the product has consisted primarily of well-defined spherical particles of relatively pure UAl_3 . Presumably, UAl_2 or UAl_4 can be produced equally as well by adjusting the aluminum-to-uranium ratio in the first step. The conversion is based on four consecutive chemical reactions:

These reactions are carried out in four consecutive steps in a fluidized bed reactor.

The first step is basically a calcining operation in which a uranyl nitrate solution is converted to the trioxide (UO_3). A starting bed of spherical aluminum particles (-250 +325 mesh) is charged to the reaction vessel. The bed is fluidized with air and the temperature brought to 350°C . An aqueous solution of uranyl nitrate is sprayed through an atomizing nozzle into the hot bed of fluidized aluminum particles where it decomposes to UO_3 as it is deposited on the particles. The laminar oxide coating is built up until the desired weight ratio of uranium to aluminum is attained.

In the second step, the uranium trioxide is reduced with methanol to uranium dioxide so that, during the subsequent chlorination step, undesirable side reactions can be minimized. Other reductants could be used, but with methanol the reaction takes place readily at a low temperature of 350°C . During this step the bed is fluidized by argon gas which is mixed with methanol vapors in a vaporizer-preheater. When the reduction reaction is completed, the bed consists of discrete spheres of aluminum cores surrounded by a uniform coating of uranium dioxide.

Experiments being conducted at the present time indicate that the addition of small amounts of boron (0.5 parts boron to 100 parts uranium) to the uranyl

nitrate feed enhances the formation of an amorphous form of UO_3 . The amorphous form of UO_3 reacts readily with carbon tetrachloride and can be chlorinated directly without being first reduced to UO_2 . Since the boiling point of boron trichloride is 12.5°C , it presumably vaporizes during the chlorination step. Its exact fate, however, is not known. If this new approach is successful, the second step in the process can be eliminated and, thus, the cost of producing uranium aluminide by this process will be reduced further.

Chlorination of the uranium oxide to uranium trichloride takes place in the third step. The bed temperature is again held at 350°C , and carbon tetrachloride is introduced into the bed as a vapor mixed with the argon fluidizing gas. As with the methanol, the carbon tetrachloride is metered as a liquid into a vaporizer-preheater. During this step the feed rate of the carbon tetrachloride must be carefully controlled because the reaction between the carbon tetrachloride and uranium oxide is highly exothermic.

After all of the uranium oxide has been converted to uranium trichloride, the fourth step is begun by raising the temperature of the bed to 600°C , with argon gas used as the fluidizing medium. At this temperature, the uranium trichloride coating reacts with the aluminum core to form UAl_3 and volatile aluminum chloride. The bed now consists of hollow, nearly spherical particles of pure UAl_3 . These particles probably can be densified by passing them through a plasma arc flame. Although tests on uranium aluminide particles have not been conducted, aluminum oxide particles of similar size and porosity have been passed through a plasma arc flame, resulting in a final density greater than 90 percent of theoretical.

2.13 Pilot Plant Equipment. Exploratory studies have been conducted on all four steps of this process on a pilot plant scale. The pilot plant equipment included both two- and four-inch-diameter fluidized bed reaction vessels. A flow diagram of the process using the four-inch-diameter fluidized bed reaction vessel is shown in Figure 45.

The reaction vessel is made from stainless steel and is four inches in diameter by four feet high. Heat is supplied to the vessel by an induction heater whose coils are positioned around the lower part of the insulated vessel. Spherical particles of aluminum are charged into the vessel through a hopper located in the top of the vessel; any portion of the bed can be removed from the bottom of the vessel through a discharge pipe which passes through the fluidizing gas distributor plate. Uranyl nitrate solution and atomizing gas are metered into the vessel through a two-fluid atomizing nozzle placed below the surface of the fluidized bed of particles. The fluidizing gas, either argon or air, enters the vessel through the distributor plate at the bottom of the vessel. Prior to entering the reactor vessel, the fluidizing gas passes through a heated vaporizing chamber where either methanol or carbon tetrachloride is introduced at a controlled rate and mixed as a vapor with the fluidizing gas.

The off-gas from these four steps passes first through a cyclone where the bulk of the entrained fines are removed and, if desired, returned to the fluidized bed. Next, the off-gas passes through a venturi scrubber using water as the scrubbing agent, which removes condensable by-products and water from the off-gas. This is followed by a high-efficiency filter which removes any dust from the

Fig. 45 Schematic flow sheet of apparatus for fluidized bed production of UAl_3 .

off-gas before the gas is discharged from the system. An off-gas recycle loop is provided to reduce argon consumption during the reduction, chlorination, and high temperature conversion steps of the process. The loop includes an absorber to remove any residual acid fumes before the gas reenters the reaction vessel.

2.14 Advantages of Process in Closed-Loop Fuel Cycles. Due to the direct use of uranyl nitrate solution as feed material and to the compactness of the processing equipment, use of the fluidized bed process leads to less costly fuel cycles by eliminating several steps from the conventional cycle. Several advantages are apparent in this abbreviated cycle:

- (1) Costs are reduced by eliminating from the fuel cycle the necessity of converting the uranium to the metal. This eliminates many of the presently required processing and handling steps.
- (2) Because the fluidized bed process produces the uranium aluminide in an ideal spherical form, no further grinding or sizing is required. No large amounts of off-sized product must be returned to the process.
- (3) Uranium aluminide particles ready for use by the fuel fabricator can be produced at an aqueous chemical processing plant by investing in only a small amount of additional equipment.

- (4) General health and radiation hazards are reduced by minimizing cross-country shipments of radioactive materials. (At the present time facilities for different steps of the fuel cycle are located at different sites.)
- (5) Chemical reprocessing costs can be reduced because product specifications could be established by the reprocessor to meet only those required by his particular fuel fabrication operation.
- (6) Any reject material created in the process is directly and automatically re-introduced into the process. For example, the fines from the cyclone are automatically returned to the reactor vessel, and the scrub solution from the venturi scrubber is recycled back to the uranyl nitrate feed stream. With the present processes, recycle of reject material involves many material handling problems.
- (7) The process has the inherent flexibility for custom manufacture of a wide variety of spherical particle-type fuels. This includes many types of fuel materials, as well as possible additions of burnable poisons. The fluidized bed technology developed for this process appears adaptable to the production of many other types of reactor fuel materials such as oxides, carbides, silicides, nitrides, and other binary fuel compounds.

2.2 Removal of Boehmite Coating from ATR Fuel Elements (C. A. Zimmerman; Chemistry Section)

A chemical cleaning procedure for the removal of boehmite (α monohydrate of alumina) coating from the aluminum clad surfaces of ATR fuel elements was proposed since the accumulated oxide of low thermal conductivity could shorten the service life of the fuel elements. This procedure consisted of a one-hour immersion in boiling 1.0 M phosphoric acid - 0.4 M chromium trioxide solution to be followed by a three minute immersion in boiling three molar nitric acid if the phosphate - chromate surface film formed in the first step could not be tolerated in reactor operation. Table XLIII shows the proposed test reactor fuel cycle with film removal between irradiation periods. In general, test reactor fuel elements are moved from one core position to another in the middle of their irradiation life.

TABLE XLIII

TEST REACTOR FUEL CYCLE

Element Fabrication	
First Irradiation	
Film Removal	} Additional Steps if Film Removal is Required
Conditioning in Nitric Acid	
Storage in Basin	
Second Irradiation	
Reprocessing	

Results of laboratory investigation of aluminum corrosion losses in solutions of various concentrations of the cleaning reagents are reported in Table XLIV. All of these appeared acceptable from a corrosion point of view. The 1M phosphoric acid - 0.4M chromium trioxide solution is generally preferred for oxide removal.

TABLE XLIV

CORROSION OF TYPE 6061-0 ALUMINUM BY PHOSPHORIC ACID-CHROMIUM TRIOXIDE SOLUTION

	Corrosion (Mils per Exposure Period)			
	One Hour Exposure		Two Hour Exposure	
	80°C	Boiling	80°C	Boiling
0.5M H_3PO_4 - 0.2M CrO_3	0.009	0.012	0.004	0.010
1.0M H_3PO_4 - 0.4M CrO_3	0.008 ^[a]	0.009 ^[b]	0.019	0.026
1.0M H_3PO_4 - 0.2M CrO_3	0.009	0.011	---	---
1.0M H_3PO_4 - 0.6M CrO_3	0.005	0.011	---	---

[a] Average of two determinations.

[b] Average of twelve determinations.

All others were single measurements.

Removal of the boehmite coating using phosphoric acid - chromium trioxide solution leaves a phosphate - chromate surface film. The amount of phosphorus that could be introduced to the reactor cooling water by this film is very small but could possibly accumulate during reactor operation. Table XLV lists the phosphorus content of films as determined by actual dissolution of the films in boiling 3M nitric acid and analytical determination of the dissolved phosphorus. The phosphate-containing film can be removed from the aluminum surface by a three-minute treatment in boiling three-molar nitric acid. Aluminum loss due to this short treatment is not severe as shown in Table XLVI.

TABLE XLV

PHOSPHORUS CONTENT OF FILM DEPOSITED ON 6061-0 ALUMINUM

Primary Exposure	Phosphorus Removed
One Hour in Boiling Solution as Follows:	Five Minutes in Boiling 3M HNO_3 :
1.0M H_3PO_4 - 0.2M CrO_3	1.9×10^{-5} gram per in ²
1.0M H_3PO_4 - 0.4M CrO_3	2.5×10^{-5} gram per in ²
1.0M H_3PO_4 - 0.6M CrO_3	2.7×10^{-5} gram per in ²

TABLE XLVI

CORROSION OF TYPE 6061-0 ALUMINUM BY BOILING 3M NITRIC ACID

Prior Specimen Treatment	Corrosion (Mils per Exposure Period)	
	Three Minute Exposure	Five Minute Exposure
One Hour Exposure in a Boiling Solution:		
1.0M H_3PO_4 - 0.4M CrO_3	0.134 ^[a]	0.188 ^[a]
1.0M H_3PO_4 - 0.2M CrO_3	---	0.185
1.0M H_3PO_4 - 0.6M CrO_3	---	0.184
1.0M H_3PO_4 - 0.4M CrO_3	0.187 ^[b]	---

[a] Average of two specimens.

[b] Specimen previously exposed in reactor loop.

Two specimens of Type 6061-0 aluminum which had been exposed in a reactor loop to build a boehmite film (1.0 and 0.75 mil thick as determined by Dermatron measurements) were cleaned by the phosphoric acid - chromium trioxide treatment. One of these specimens was then treated with three-molar nitric acid to remove the phosphate - chromate coating. The two specimens were then subjected to an accelerated basin storage corrosion test by exposure for approximately 180 hours in 65°C distilled water that was aerated daily. The specimen that retained the phosphate - chromate coating showed very slight calculated corrosive attack and developed no coating of aluminum oxide. The specimen from which the phosphate - chromate coating was removed suffered a calculated corrosive attack of 0.16 mil and developed a coating of approximately 0.3 mil of bayerite (β trihydrate of alumina). Identification of the boehmite and bayerite forms of alumina was done by X-ray diffraction analysis which was also used to confirm the removal of boehmite from these specimens.

These tests have demonstrated the successful removal of boehmite from aluminum surfaces and the high probability of passivity of the surface under subsequent fuel storage conditions. The rate of accumulation of boehmite in a second exposure in a reactor environment after cleaning and simulated storage was no greater than originally.

IV. NEW MODULAR PILOT PLANT LABORATORIES (S. J. Horn; Development Engineering Section)

Since 1953, chemical engineering development studies for the ICPP have been performed in a converted warehouse building, several miles removed from the processing plant. This laboratory-pilot plant building has a gross floor area of 12,000 square feet, of which only about one-half has been actually used for experiments. The balance of the building has been used for offices, shops, rest rooms, storage, and to house utilities generating equipment such as air compressors, water treating equipment, steam generators, etc.

Since the building was not originally designed as a pilot plant, facilities for the disposal of liquid wastes and the ventilation of experiments have been inadequate. As a consequence, general deterioration of the building and accelerated attack of the experimental apparatus has occurred. In addition to these faults, the design of the building has meant that experiments were installed by assembling the appropriate components and piping, along with the supporting structure, inside the building. As a consequence, these experiments have tended to become permanent installations, regardless of the fact that the experiments would likely have a finite, and probably short, lifetime.

When the general condition of the area had reached a point where extensive renovation could no longer be avoided, it was estimated that the cost of repairing the laboratory would nearly equal the cost of constructing new facilities. This led to the design of new chemical engineering laboratories which are now under construction. The new development laboratories were designed around two basic criteria: (a) to provide as clean an environment as practicable and (b) to use laboratory space as efficiently as practicable. It was felt that these criteria would be best met by employing a module concept in the design of experiments.

The basic feature of a modular experiment is that the experimental apparatus is assembled within a structural framework which serves both to support the entire experiment and to define its external dimensions. In general, the module would be a rectangular parallelepiped having standardized external dimensions. An experiment module can be completely built in a centralized shop area where most fabrication needs are readily available. When completed, the module is tested and calibrated in the shop before it is transported to the laboratory building. After the module has been transported to the laboratory building and installed, final connections to utilities and instrument consoles are made. In this manner, a minimum of construction activity occurs in the laboratory, and new experiments are put into operation with a minimum of interference with experiments already in operation. The reverse procedure is of equal importance. If laboratory space is needed, a temporarily idle experiment can be disconnected and the entire module removed and stored, essentially intact, for future use.

Two laboratory buildings have been designed for these modular experiments. One laboratory was designed for experiments which are tall, compared to the floor area occupied. Typical of such experiments are pulse columns and dissolvers. The second laboratory design is for experiments which do not require much overhead clearance. A High-Bay Laboratory has been designed and built and is presently being outfitted with experiment modules. The Low-Bay Laboratory has been designed and construction is in progress. Both buildings have cement block walls, reinforced concrete floors with a protective coating, and a built-up metal deck roof.

While the use of modular experiments is not unique to these facilities, the concept is so novel that essentially no design guidelines exist for either the laboratories or the experiment modules. The ICPP laboratories have a number of common design features. Among these are a minimum ventilation rate of five complete building changes per hour, adequate drainage for all liquid wastes, a centralized utilities distribution system, and a separate off-gas system which is connected to the plant off-gas system. Similarly, those utilities and reagents available from the main ICPP systems will be supplied by these systems.

1. THE HIGH-BAY LABORATORY

The High-Bay Laboratory has overall inside dimensions of 32 x 46 feet with an overall free height inside of 36 feet. A 35- x 10-foot block of three offices occupies the central portion of the building, dividing it into two parallel bays. The roof of the office block is reinforced and serves as a control mezzanine from which all experiments are operated. An open, stainless steel lined trench is provided for liquid wastes, and air is exhausted from the building through three roof exhaust fans.

Experimental modules are lowered into the laboratory through one of five roof hatches, each having an opening of 10 x 9-1/4 feet. The laboratory can be considered to be divided into eleven module spaces. However, one space is occupied by the fire protection sprinkler system and entrance door, and the space at the end of the office block is occupied by a permanent feed preparation system. In addition, one additional corner space is kept free for a second exit, leaving eight module spaces for ready use. While it is not likely that all eight modules will be in operation simultaneously, all spaces could be occupied by operable experiments.

Installation of modules in the High-Bay Laboratory has proved to be relatively easy, even with winds of up to 15 mph. The average time required to install the four modules now in the laboratory was approximately one hour. The minimum elapsed time from when the module was lying on the transporting truck bed to when it was in position in the laboratory was one-half hour. Figures 46 through 49 show a sequence of installation of modules.

2. THE LOW-BAY LABORATORY

The Low-Bay Laboratory, scheduled for completion in the Spring of 1968, adjoins both the existing CPP-637 laboratory-office building and the recently completed High-Bay Laboratory. Upon completion of the Low-Bay Laboratory, the three laboratory buildings will be interconnected by a utilities tunnel in such a manner that utilities, process solutions, or instrument lines can be run from any laboratory building to the other. As a consequence, the extensive feed preparation system in the High-Bay Laboratory can be used to prepare special reagent solutions and feed them to an experiment in the High-Bay Laboratory, the Low-Bay Laboratory, or a CPP-637 laboratory.

Fig. 46 Experimental module being lifted outside of high-bay laboratory.

Fig. 47 Experimental module over open roof hatch of high-bay laboratory.

The Low-Bay Laboratory has basic internal dimensions of 105 x 30 feet, with a free inside height of 14 feet. The laboratory has space for twenty 8- x 10-foot modules, and each module space has its own ventilation air supply and exhaust duct. Each module space is provided with a connection to each of the utilities lines and to the drain system. Experiment modules are rolled into the laboratory on wheeled bases.

The liquid waste system for this laboratory is buried under the floor and consists of a stainless pipe manifold; each module drain is capped except when in use. The ventilation system is designed to minimize contamination of the laboratory atmosphere with corrosive vapors; portions of an experiment can be enclosed in a shroud and connected to the ventilation exhaust duct to maintain adequate ventilation. In addition, the general flow of air, from the center of the laboratory to the walls, is designed to maintain a properly directed flow of ventilation air.

3. ADVANTAGES OF THE MODULAR PLAN

The modular concept for pilot plant experiments is felt to be the most efficient and flexible means of installing and operating such experiments for the following reasons:

Fig. 48 Experimental module being lowered into high-bay laboratory.

Fig. 49 Two experimental modules in place in high-bay laboratory.

- (1) Lower costs in fabricating experiments since the construction work is done in the shops. This results in more efficient use of construction equipment and more efficient scheduling of craftsmen.
- (2) Standardized design criteria for the experiment modules.
- (3) More efficient utilization of laboratory space because of compact module design, elimination of most shop activity in the laboratory, and minimum interference with operating experiments.
- (4) Extreme flexibility; the modules can be removed and stored, rebuilt and replaced, or salvaged.

V. ORGANIZATION CHART *

INC-B-11070

* ABBREVIATED CHART SHOWING THE RELATIONSHIP OF THE CHEMICAL TECHNOLOGY BRANCH WITHIN THE CORPORATION ORGANIZATION.

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