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CHEMICAL ENGINEERING DIVISION
SUMMARY REPORT

October, November, December, 1958

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SUMMARY

I. Fluoride Volatilization Separations Process (pages 20 to 43)

Work has continued on the development of fluoride volatilization processes for recovering uranium and plutonium from spent power-reactor fuels. Additional results are reported on the fluorination rates of uranium and plutonium oxides and fluorides.

The conversion rate of uranyl fluoride to uranium hexafluoride by elemental fluorine was determined as a function of temperature. The temperature dependence of the rate corresponds to an activation energy of 19.5 kcal/mole. Uranium trioxide is fluorinated at a slower rate than the other uranium compounds investigated. The activation energy is 14 kcal/mole.

On exposure to fluorine plutonium dioxide appears to form the tetrafluoride, which, in turn, is converted to plutonium hexafluoride. The over-all rate of plutonium volatilization corresponds roughly to that obtained with plutonium tetrafluoride from Rocky Flats.

The product of the thermal decomposition of plutonium hexafluoride at 200 C is plutonium tetrafluoride, on the basis of weight determinations.

An incidental observation on the self-decomposition of solid plutonium hexafluoride at room temperature gives a rate of 1.1 per cent per day, in agreement with work reported elsewhere.

Experiments on the vapor-phase transfer of plutonium hexafluoride at room temperature showed that the losses do not increase in proportion to the number of transfers or the quantity transferred.

The fluorination of nickel at 600 to 800 C produced films of a higher density than that of crystalline nickel fluoride. Fluorination studies on titanium, platinum, gold, and silver indicated that none of these metals is suitable for use with fluorine at temperatures much above 100 C.

Development work was continued on a high-temperature fused-salt process for the recovery of enriched uranium from zirconium-matrix fuel alloys. The fuel alloy is dissolved by hydrofluorination in a fused sodium fluoride-zirconium fluoride melt at 600 C. The dissolved uranium is then

volatilized as the hexafluoride by passing fluorine through the melt. Fractional distillation of the hexafluoride provides the final purification and decontamination of the uranium.

Installation of a pilot-plant dissolver-hydrofluorinator made of graphite is nearly complete. Graphite is a promising material of construction for this process step.

Design studies have continued with the objective of minimizing corrosive conditions in the fluorinator by frozen-wall salt containment. Preliminary tests on essentially a full scale have demonstrated the feasibility of frozen-wall containment of the molten zirconium fluoride-sodium fluoride salt with sparging. Both radiofrequency induction heating and electric resistance heating have been tried successfully.

Related volatility separations studies of a more fundamental nature have also continued. Vapor-liquid equilibrium data for the system uranium hexafluoride-bromine pentafluoride have been obtained. Slight positive deviations from ideality, but no azeotropes, have been found.

The purification of the Liquid Metal Fuel Reactor (LMFR) core fluid by a fluoride volatility process is being investigated. Laboratory work has been done to demonstrate the extraction of uranium and fission products with molten sodium fluoride-zirconium fluoride mixtures.

II. Fluidization Studies (pages 44 to 63)

Investigations of the effect of process variables on the fluid-bed drying and fluid-bed fluorination steps of the ADF process (see page 46,) for recovery of uranium from low-uranium-zirconium fuel alloys continued. Synthetic feed solutions containing the equivalent of two and five per cent uranium alloys were fed to the six-inch fluid-bed dryer using single and dual feed nozzles. Particle growth continues to be the limiting factor in sustained (over 40 hours) operation of the dryer. Runs were made at 300 and 450 C with a total operating time of about 115 hours. Additional X-ray diffraction studies of dryer products showed the presence of complex mixtures of several species of zirconium fluoride, with zirconium tetrafluoride being the major constituent formed at temperatures near 300 C, while zirconyl fluoride and some zirconium oxide are formed at higher temperatures (450 C).

Fluorinations of fluid-bed dried material conducted in the 2½-inch diameter fluid-bed fluorinator disclosed a number of factors which affect the degree of uranium removal.

1. Preheating the dryer product at 600 C for a period equivalent in length to the fluorination period had an adverse effect on uranium removal - 89 per cent removal in eight hours of fluorination at 500 C, as compared to 98 per cent without the pre-heat step.
2. Increasing the fluorination temperature from 500 C to 600 C increased uranium removal from 61 to 98 per cent for a zirconium fluoride mixture containing precipitated uranium tetrafluoride (3.5 weight per cent uranium alloy equivalent feed). Analysis of two screened fractions, 20 to 40 mesh and 60 to 100 mesh, of this material showed a slightly higher uranium removal from the smaller particles, 97.6 per cent as compared to 96 per cent for the larger size.
3. Increasing the fluid-bed dryer temperature from 240 C to 450 C had an inhibiting effect on subsequent uranium removal: 60 per cent in eight hours at 500 C as compared to 98 per cent for material prepared at 240 C.
4. Results of tests of the reproducibility of uranium removal during fluorination of dryer product showed excellent agreement: 91.8, 91.6, 90.9 and 91.2 per cent removal in four hours at 600 C.

Laboratory fluorinations conducted at 600 C on zirconium fluoride solids to which 10 and 24 moles of sulfur per mole of uranium had been added indicated sulfate addition did not enhance uranium removal - 92 per cent removed in two hours at 600 C.

A three to 25-fold decrease in surface area of the zirconium fluoride powders was found to result during fluid-bed fluorinations, but in several cases uranium removal was high (up to 98 per cent) despite the decreased surface.

Corrosion results of additional specimens inserted in the fluid-bed fluorinator do not substantiate the excessively high vapor-phase corrosion of nickel observed previously (ANL-5924, pages 69 and 70). Preliminary results from corrosion coupons inserted in the bed showed Monel underwent very little dimensional change and slight intergranular attack.

Additional runs in the fluid-bed waste calciner, used to convert liquid wastes to granular solids, indicated that ruthenium decontamination factors from feed through silica gel adsorber of 10^3 to 10^4 can be achieved. Suppression of ruthenium volatilization at higher temperatures (500 C versus 400 C) was confirmed. The average non-volatile decontamination factor from feed through adsorber ranged from 3×10^4 to 1×10^5 , while off-gas samples taken after the condenser showed total decontamination

factors in excess of 10^6 . The most active run to date was made this period without incident, the feed consisting of an 8:1 dilution of ICPP waste. Gross gamma and ruthenium gamma activities in the feed were 2.8×10^7 and 9.8×10^5 cpm/ml, respectively.

Corrosion experiments on sintered stainless steel metal, using conditions simulating those in the fluid-bed waste calciner, were continued. Results showed nitric acid vapors or mixtures of nitric acid vapors with air or nitrogen produced metal corrosion similar to that which occurred in the calciner bayonet-type filter elements at high temperatures.

Mixing studies using a radioactive tracer technique have been completed in the straight-wall fluid-bed column, using 20 to 40 mesh and 140 to 200 mesh copper spheres. Experiments are continuing in the tapered fluid-bed column.

The use of colored feed solutions in the study of factors influencing particle growth in fluid-bed calciners has not produced material with characteristic growth rings suitable for determining the amount of liquid deposited on the particles in each pass through the spray. Experiments using radioactive tracers are being initiated.

III. Reactor Chemistry (pages 64 to 108)

The program to clarify the factors governing the pyrophoric characteristics of uranium, zirconium, thorium, and plutonium has continued with fundamental studies of kinetics and mechanism of oxidation. In air the use of the burning curve and shielded ignition techniques for uranium has not aided the establishment of a specific area dependence in air. However, a partial insight as to the phenomena observed in air was provided by measuring the maximum burning temperature of 8.5-mm cubes in various gas mixtures. The maximum burning temperature decreases as the oxygen content of the oxidizing gas is decreased. In sufficiently dilute oxygen mixtures ignition of 8.5-mm cubes, as such, is not noticeable at all.

Experiments to measure the rate of propagation of burning of strips of metal foil have been initiated. The factors which cause either a sufficiently fast propagation to constitute an explosion or a sufficiently slow propagation to facilitate control of the reaction are believed to be important. The dependence of the rate of propagation on the thickness of foils has been established for uranium in air and oxygen. Although additives to uranium have a very limited effect, additives to zirconium have a pronounced effect on the propagation rate.

A linear correlation has been demonstrated between the shielded ignition temperatures of zirconium alloys and the oxygen consumed in the first minute, as obtained from the isothermal oxidation data. Such a

correlation allows the prediction of ignition temperatures from isothermal oxidation data. The existence of this correlation is important since isothermal experiments are easier to duplicate by various investigators.

Considerations of the relationship of the breakaway phenomena and the initial cubic rate constant of the oxidation of zirconium and its alloys to earlier literature, theories, and mechanism are presented.

IV. Chemical-Metallurgical Processing (pages 109 to 169)

Melt refining, liquid metal extraction, and intermetallic crystallization are now being examined as direct-cycle pyrometallurgical methods of processing nuclear reactor fuels.

Melt refining consists of melting the discharged fuel and holding it molten for a period of time. Decontamination is effected by mechanisms of volatilization and selective oxidation of certain fission product elements. Work was continued on the behavior of iodine in this process. At macro concentrations, virtually complete (99.5 per cent) removal of iodine from purified metal and skull fractions was realized. An important mechanism of iodine removal is reaction with crucible contaminants to produce volatile iodides of calcium, iron, and magnesium. About one-quarter of the iodine was evolved as molecular iodine. The data showed that about 70 per cent of the iodine diffused through the zirconia crucible walls, whose total porosity was about 20 per cent.

No removal of zirconium from a plutonium - "fissium" alloy was realized by melt refining in either lime-stabilized zirconia or magnesia crucibles. A similar result was previously found for uranium - "fissium" alloy. If desired, zirconium removal may be effected through carbide formation.

In connection with the removal of zirconium as the carbide, information has been obtained on the joint solubilities of zirconium and carbon in uranium at 1400 C. The concentrations measured for uranium and carbon provide a tentative liquidus line in the high uranium region in the ternary system zirconium, carbon, and uranium. The values indicate it is possible to remove zirconium by carbide liquation to less than 0.01 weight per cent, although in practice it would be difficult to achieve this removal. Removal of zirconium by carbide liquation from plutonium - "fissium" alloys is to be investigated in the next quarter.

Progress was made in the melting of oxide-coated pins by reduction of the oxide coating, using magnesium in zinc solution. Although calcium is also effective for this purpose, crucible materials which will withstand simultaneous attack by molten calcium and molten uranium have not been found.

Work was continued on the processing of crucible skulls. As an alternative method of removal from the crucible to avoid crucible breakage and physical removal of skull, chemical pulverization by an oxidation-reduction cycle was investigated. After conversion to uranium dioxide the skulls were powdered and easily poured from a crucible. The possibility for effecting some fission product separation, particularly of molybdenum through volatilization of the trioxide exists.

A method proposed for processing uranium to separate the noble metals not removed by melt refining (ruthenium, molybdenum, etc.) is the Pyrozinc process. This process begins with the dissolution of the metal ingot in molten zinc. Uranium forms an intermetallic compound (U_2Zn_{17}) with zinc, that can be separated by fractional crystallization. Zinc may be removed from the uranium-zinc intermetallic compound by vaporization. Uranium in the oxide dross from melt refining may be similarly recovered after dissolution in liquid zinc-magnesium.

A number of supporting laboratory studies relative to the Pyrozinc process are being made. For example, cadmium has been suggested as an alternate to zinc in the Pyrozinc process.

Additional basic data have been gathered to aid in the design of decontamination processes for liquid-metal solutions. These include the solubilities of zirconium, molybdenum, thorium, and niobium in zinc and of plutonium in cadmium measured at 420 to 750 C.

Americium coprecipitates with plutonium from a cadmium solution in accordance with the logarithmic distribution law. The coefficient of the Doerner-Hoskins relation is 0.79.

Provisional values for the activity of cerium in cerium-saturated zinc solutions have been measured by the emf method. The provisional values for the activity coefficients (relative to solid cerium) are 3.4×10^{-10} and 2.0×10^{-9} at 508 C and 549 C, respectively.

Measurements of vapor and decomposition pressures have been made on the uranium-zinc system at low temperatures by means of an effusion cell mounted on a continuous-weighing electromechanical balance. The probable existence of an additional phase at or near UZn_{11} has been revealed by this method. The known phase relations indicate that this new phase must be difficult to crystallize from a melt and that it must decompose incongruently below 550 C.

The separation of fission products from irradiated uranium by extraction with a fused salt of a zinc or cadmium solution of the metal has been further investigated. In the zinc system the separations achieved by conducting all the operations at 477 C are similar to those achieved by dissolution and extraction at 730 C, followed by cooling to below 550 C.

The time cycles appear to be comparable. The former method has a potential advantage in being adaptable to a wider variety of construction materials; the latter method has the potential advantage of adaptability to multi-contact operations. In the cadmium system the separations achieved were only slightly inferior to those obtained in the zinc system. However, the critical separation factor, that between rare earths and plutonium, has an approximate value of 38, which would permit adequate separations by multiple extractions. The favorable corrosion characteristics of cadmium solutions in a variety of ferrous alloys makes this system particularly attractive.

Work continued on application of a zinc-magnesium solution process to recovery and purification of plutonium from blanket material. The process involves dissolution of the uranium blanket material in zinc, crystallization of U_2Zn_{17} on which plutonium is carried, and separation from the supernatant. Separation of plutonium and uranium is effected by addition of sufficient magnesium to destroy the intermetallic compound. Uranium is precipitated as metal while plutonium goes into solution. Results continue to show that the process is feasible.

Solutions of plutonium in 46 weight per cent magnesium-zinc eutectic alloy were found to be stable in both graphite and tantalum crucibles. The stability in graphite contrasts with a previously observed rapid disappearance of plutonium from a magnesium solution.

Dissolution of skulls in zinc-magnesium solutions is also being studied. The percentages of uranium put into solution have thus far been lower than the desired value of around 95 per cent. In the course of this work it was discovered that cerium oxide as well as uranium oxide is being reduced by magnesium in zinc solution. This is undesirable and, unless conditions can be found to prevent it, will necessitate a second separation from uranium and/or plutonium.

Pressure-siphoning (transfer through a dip tube by pressurizing) appears to be an attractive procedure for separating precipitated zinc intermetallic compounds from the supernatant liquor. It is a procedure which can be readily adapted to remote operation.

Corrosion testing of various metals is being carried out in both zinc and cadmium systems. So far only tantalum and tungsten have withstood attack by zinc at 800 C in static tests. A number of metals, including Armco iron and the following steels. AISI 1025, 1040, 1065, 1095, and 410, were resistant to attack by cadmium and cadmium-uranium alloys. The 300 series stainless steels were attacked by preferential dissolution of the nickel. Dynamic tests will be run in the next quarter.

The results of chemical-metallurgical process studies are being applied to design and component testing of facilities for the EBR-II fuel-processing plant

Drawings and specifications to be included in the bid package from the architect-engineer for the Fuel Cycle Facility are being checked.

The design of the 5-ton cranes for the air and argon cells is continuing. The radiation-resistant manipulator is being fabricated and delivery is scheduled for February 1, 1959. The purchase order for the shielding windows in the air and argon cells was awarded. Split and solid (one-piece) types of protective shutters for the shielding windows are being designed. A split-type unit will be constructed for testing in the mock-up facility. A stereo-optical depth perceptor was constructed and tested in the mock-up facility. A Kollmorgen periscope was installed in the wall of this facility.

A mercury-vapor lamp is undergoing gamma irradiation and testing for light output. Insulating materials for electrical conductor cables have also been tested in a gamma field. Natural and synthetic (Hycar) rubber have shown good flexibility after gamma irradiation to 5×10^8 roentgen.

Thirty 10-kilogram ingots of natural uranium-5 per cent "fissium" alloy were produced in the melt-refining furnace. These runs are preliminary to the preparation of the 50 per cent enriched uranium-5 per cent "fissium" alloy being planned. A panelboard for the melt-refining furnace has been designed and is being built.

The construction of the Laboratory and Service Building is about one-third completed. The purchase order for the junior-cave windows was placed. The fume hood for evaporating samples in the junior caves was tested. Its efficiency for removal of perchloric acid fumes varied from 45 to 65 per cent, depending upon the type of water spray nozzle, volume flow rate of air, and water-droplet eliminator used.

Progress is reported on the synthesis and analysis of pure molybdenum disulfide and on the problem of achieving calorimetrically useful combustions in an oxygen bomb prior to the determination of the heat of formation of this compound.

Samples of fluorine have been subjected to volumetric and infrared analyses in preparation for calorimetric combustions in a fluorine bomb. The available sample of highest purity contained 0.54 volume per cent impurities. Hydrogen fluoride, tetrafluoromethane, nitrogen trifluoride and silicon tetrafluoride impurities appear to be readily identifiable in a nickel absorption cell with barium fluoride windows.

Work has begun on the combustion of molybdenum metal in fluorine for the determination of the heat of formation of molybdenum hexafluoride.

V. Routine Operations (pages 170 to 171)

The operation of the radioactive waste-processing facility and the gamma-irradiation facility continued without incident.

I. FLUORIDE VOLATILIZATION SEPARATIONS PROCESS

Work has continued on the development of fluoride volatilization processes for recovering uranium and plutonium from spent power reactor fuels. Additional results are reported on the fluorination rates of uranium and plutonium oxides and fluorides.

The conversion rate of uranyl fluoride to uranium hexafluoride by elemental fluorine was determined as a function of temperature. The temperature dependence of the rate corresponds to an activation energy of 19.5 kcal/mole. Uranium trioxide is fluorinated at a slower rate than the other uranium compounds investigated. The activation energy is 14 kcal/mole.

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Development work was continued on a high-temperature fused salt process for the recovery of enriched uranium from zirconium matrix fuel alloys. The fuel alloy is dissolved by hydrofluorination in a fused sodium fluoride-zirconium fluoride melt at 600 C. The dissolved uranium is then volatilized as the hexafluoride by passing fluorine through the melt. Fractional distillation of the hexafluoride provides the final purification and decontamination of the uranium.

Installation of a pilot-plant dissolver-hydrofluorinator made of graphite is nearly complete. Graphite is a promising material of construction for this process step.

Design studies have continued with the objective of minimizing corrosive conditions in the fluorinator by frozen-wall salt containment. Preliminary tests on essentially a full scale have demonstrated the feasibility of frozen-wall containment of the molten zirconium fluoride-sodium fluoride salt with sparging. Both radiofrequency induction heating and electric resistance heating have been tried successfully.

Related volatility separations studies of a more fundamental nature have also continued. Vapor-liquid equilibrium data for the system uranium hexafluoride-bromine pentafluoride have been obtained. Slight positive deviations from ideality, but no azeotropes, have been found.

The purification of the Liquid Metal Fuel Reactor (LMFR) core fluid by a fluoride volatility process is being investigated. Laboratory work has been done to demonstrate the extraction of uranium and fission products with molten sodium fluoride-zirconium fluoride mixtures.

Discussions were held with K. Oshima from Tokyo, Japan, regarding fluoride volatility processing. A discussion of off-gas scrubbing and ventilation with representatives from HAPO and AEC, Washington, D.C., occurred on October 7, 1958.

A. Plutonium Fluoride Studies (R. K. Steunenberg)

1. Introduction

A possible separations process based on the volatilities of uranium hexafluoride and plutonium hexafluoride was described in the previous quarterly report (ANL-5924, page 24). Briefly, this process consists of dissolving the irradiated fuel in an appropriate aqueous solution, calcining the solution to a mixture of dry oxides, and converting the oxides to the corresponding fluorides. The uranium and plutonium are both volatilized as the hexafluorides. Several potential methods are being considered for the separation, decontamination and purification of the uranium and plutonium fluorides.

In connection with this process, laboratory work was continued on the fluorination rates of uranium and plutonium oxides and fluorides. Pilot-plant studies on certain aspects of this process are being performed by the Fluidization Group (see Section II)..

2. Fluorination Rate of Uranyl Fluoride (M. Steindler, D. Steidl)

The apparatus used in this work has been described in detail elsewhere (ANL-5924, Figure 2). Briefly, fluorine was passed over a nickel reaction boat which contained the uranyl fluoride sample inside a nickel

furnace tube. The off-gases were passed through two cold traps to collect the uranium hexafluoride product and then through limestone traps to dispose of the excess fluorine.

The uranyl fluoride used in the experiments was ground prior to use, and the hygroscopic nature of the solid required storage in a desiccator. The following analyses of the material showed it to be of adequate purity:

	Analyzed	Calculated for UO ₂ F ₂
U	77.0 %	77.3%
F	11.9 %	12.3%
U(IV)	0.05%	0 %
3 UO ₂ F ₂ /U ₃ O ₈	1.11	1.10

The measured variables were temperature, time of exposure to fluorine, initial and final sample weights, and the amount of uranium hexafluoride collected. The average area of the top of the sample that was exposed to fluorine was calculated from the average sample weight, an experimental value of its bulk density (2.18 g/cc), and the geometric configuration of the reaction boat. The reaction rates were based on analyses of the uranium collected in the cold traps.

The experimental results are listed in Table 1. These data were fitted to the equation

$$\log_{10} \text{ rate } [\text{mg U}/(\text{sq cm})(\text{hr})] = 9.9772 - \frac{4232}{T(\text{K})}$$

which expresses the fluorination rate of solid uranyl fluoride as a function of temperature. The temperature dependence of the rate corresponds to an activation energy of 19.5 kcal/mole.

Table 1

FLUORINATION RATE OF URANYL FLUORIDE

		Pressure:		1 atm			
		Fluorine Concentration:		100%			
		Flow Rate		40 to 100 cc/min ^a			
Exp	Initial Weight (mg)	Final Weight (mg)	Temp (C)	Time of Exposure (min)	Area (sq cm)	Uranium Volatilized (mg)	Rate ^b of Uranium Volatilization [mg U/(sq cm)(hr)]
52	980.1	967.2	200	30	1.60	7.8	9.7
53	855.5	823.3	200	60	1.52	22	14.5
20a	817.4	768.3	300	5	c	c	c
20b	768.3 ^c	267.8	300	30	1.32	390	506
26	604.5	24.6	375	10	1.10	440	2400
27	1277.5	3.4	375	15	1.39	910	3640

^aMaintained constant for each experiment.

^b $\log_{10} \text{ rate } [\text{mg U}/(\text{sq cm})(\text{hr})] = 9.9772 - 4232/T(\text{K}); \Delta E^* = 19.5 \text{ kcal/mole.}$

^cResidue from experiment 20a used in experiment 20b. The uranium volatilized in 20b also includes that from 20a. The rate was calculated from the sum of the exposure time.

3. Fluorination Rate of Uranium Trioxide (M. Steindler, D. Steidl)

The apparatus and techniques used in this study were similar to those used in the fluorination of uranyl fluoride. The uranium trioxide was obtained from the Fluidization Group, with the batch designation P-81. The material had been prepared by fluid-bed calcination at 375 C of a 70 per cent uranyl nitrate hexahydrate solution to which 0.08 per cent sulfate had been added. The uranium trioxide product was analyzed as 99 per cent trioxide, 0.13 per cent water, 0.048 per cent sulfate and 0.375 per cent nitrate. An experimentally determined bulk density value of 3.5 g/cc was used in the calculations. The variables observed and the method used to calculate the rates were identical to those used for the fluorination of uranyl fluoride.

The results are given in Table 2. The rate data were fitted by the method of least squares to give the equation

$$\log_{10} \text{rate} [\text{mg U}/(\text{hr})(\text{sq cm})] = 7.4072 - \frac{3140}{T(\text{K})}$$

An activation energy of 14 kcal/mole was derived from the temperature dependence of the rate.

Table 2

FLUORINATION OF URANIUM TRIOXIDE

Pressure: 1 atm
Fluorine Concentration: 100%
Flow Rate: 50 to 95 cc/min^a

Exp	Initial Weight (mg)	Final Weight (mg)	Temp (C)	Time of Exposure (min)	Area (sq cm)	X-ray ^b Result	Uranium Volatilized (mg)	Rate ^c of Uranium Volatilization [mg U/(sq cm)(hr)]
21	740.5	740.7	35	10	1.25	-	-	-
22	740.7	740.0	200	10	1.25	-	-	-
30	658.2	650.4	200	30	1.20	UO ₃ only	4.2	7.0
51	905.0	908.7	200	30	1.34	-	1.2	1.8
29	694.0	658.2	300	10	1.21	-	26	129
28	787.0	694.0	300	30	1.25	-	74	118
23	740.0	618.1	375	10	1.21	-	93	461
24	851.1	623.1	375	30	1.25	-	178	285
25	886.5	618.1	375	10	1.26	UO ₃ only	122	581

^aMaintained constant for each experiment.

^bX-ray data determined by D. S. Flikkema.

^cLog₁₀ rate [mg U/(sq cm)(hr)] = 7.4072 - 3140/T(K); ΔE* = 14 kcal/mole.

Both X-ray examination and visual observations indicated that the solid residue remaining after the fluorinations was at least primarily

unreacted uranium trioxide. Prolonged fluorination at the higher temperatures may produce uranyl fluoride, although no attempt was made to investigate the product of fluorinations under these conditions.

4. Fluorination Rate of Plutonium Dioxide (M. Steindler, D. Steidl)

The experimental methods used in this study have been reported previously (ANL-5875, page 5). The plutonium dioxide was prepared by the pyrohydrolysis of plutonium tetrafluoride at 900 C with steam. The resulting solid had a bulk density of 1.59 g/cc and was used without further analysis. The plutonium tetrafluoride used in the preparation had been analyzed previously and found to have a purity exceeding 99 per cent.

The plutonium hexafluoride formed during the fluorination was collected in two cold traps at -120 C. The solid residue remaining in the reaction boat was reweighed, transferred to a platinum boat and pyrohydrolyzed at 900 C by steam. The resulting hydrogen fluoride was trapped in distilled water and titrated with standard base. The plutonium dioxide formed during the pyrohydrolysis was weighed.

The measured variables were temperature, time, initial and final sample weights, amount of hydrogen fluoride formed during the pyrohydrolysis, and the weight of plutonium dioxide after the pyrohydrolysis.

The results are shown in Table 3. These data indicate overall conversion rates of plutonium dioxide to the hexafluoride comparable to those obtained from Rocky Flats plutonium tetrafluoride. If the logarithms of the rate values are plotted against the reciprocal of the absolute temperature, a slight curvature is apparent in the line, suggesting a change in the relative contributions of two or more reactions to the rate-controlling process.

Table 3

FLUORINATION OF PLUTONIUM DIOXIDE

Pressure 1 atm
Fluorine Concentration 100 %
Flow Rate 65 to 150 cc/min^a

Exp No	Initial Weight (mg)	Final Weight (mg)	Temp (C)	Time of Exposure (min)	Area (sq cm)	PuF ₄ in ^b Residue (wt %)	Pu Volatilized (mg Pu)	Rate of Pu Volatilization [mg Pu/(sq cm)(hr)]	Rate of PuF ₄ Formation ^c in Solid [wt % PuF ₄ /(sq cm)(min)]
104	126.5	128.2	200	30	1.93	7.1	0.1	0.1	0.12
105	114.5	116.0	200	30	1.87	7.1	0.4	0.4	0.13
106	116.6	118.8	200	60	1.88	10.8	0.4	0.2	0.10
97	118.8	130.8	300	5	1.92	9.0	3.4	2.1	9.9
103	74.6	79.7	300	10	1.64	9.0	4.5	2.7	6.1
102	113.4	117.8	375	5	1.87	9.8	9.9	6.3	11.8

^aMaintained constant for each experiment

^bBased on weights and fluorine analyses of the residues, assuming that only PuO₂ and PuF₄ are present

^cCorrected for PuF₆ volatilized

The chemical analyses of the solid material remaining after the fluorination indicate a substantial fluorine content. Insufficient information on plutonium oxyfluorides is available to determine whether or not they were present in the solid residue, and the chemical analyses are incapable of distinguishing oxyfluorides from mixtures of the dioxide and tetrafluoride. The residues from the experiments at higher temperatures were shown by analysis to have a high fluorine content, and on the basis of visual inspection the material appeared to be at least primarily the tetrafluoride.

If it is assumed that the initial reaction is a conversion of plutonium dioxide to the tetrafluoride, and that this is followed by conversion of the tetrafluoride to the hexafluoride, the solid residue is then a mixture of plutonium dioxide and plutonium tetrafluoride. On this basis, the concentration of tetrafluoride in the solid and the rate of conversion of dioxide to tetrafluoride can be calculated from the fluoride analysis. These data are given in Table 3.

If plutonium hexafluoride is formed only from the tetrafluoride, the rate of plutonium volatilization may be compared with that obtained from pure plutonium tetrafluoride (ANL-5875, page 10) by multiplying the exposed area of the solid sample by the plutonium tetrafluoride concentration. The volatilization rates obtained in this way are in good agreement with those obtained from pure plutonium tetrafluoride, indicating that the plutonium dioxide in the mixture acts as a solid diluent until it is converted to the tetrafluoride.

5. Fluorination of a Thoria-Urania Pellet
(M. Steindler, D. Steidl)

A single exploratory experiment to determine the amount of uranium volatilized from a thoria-uranium pellet by fluorination at 375 C and at 600 C was performed. The material had been prepared by the Metallurgy Division in connection with the development of non-metallic reactor fuels. The nominal composition of the pellets was 2.5 weight per cent uranium dioxide and 97.5 weight per cent thorium dioxide, fired to 90 per cent of theoretical density. The pellets were dark, tan-colored right cylinders, 6 mm in diameter and 12 mm long.

A pellet weighing 2.2248 g was placed in a nickel boat and exposed to 100 per cent fluorine at atmospheric pressure and at a flow rate of 85 cc/min. An exposure of five minutes at 375 C volatilized only 1.4 mg of uranium, and no change was evident in the appearance of the pellet. An additional treatment for five minutes at 600 C, however, volatilized 15 mg of uranium. The residue was snow white and of considerably larger volume than the original pellet. Complete bleaching of the material was apparent, except for a small amount of unreacted material in the center of the pellet. The concentration of uranium remaining in the material was 0.79 weight per cent.

It was concluded that at least a substantial fraction of the uranium in such a fuel can be removed by fluorination at 600 C. Better removals would probably be attained by using longer exposures or by grinding the pellets prior to fluorination.

6. Thermal-Decomposition Product of Plutonium Hexafluoride
(L. E. Trevorrow, W. A. Shinn)

In the preceding quarterly report (ANL-5924, pages 37 to 39) the product of thermal decomposition of plutonium hexafluoride at 300 C was identified as plutonium tetrafluoride by measurements of weight change. A similar experiment has been performed in which the decomposition temperature was 200 C.

The plutonium hexafluoride was held in a nickel vessel at 200 C until approximately 60 per cent of the sample had decomposed. The reaction was quenched by cooling the vessel to liquid-nitrogen temperature and the fluorine produced by the reaction was removed by evacuation. The vessel was weighed and then evacuated at room temperature to remove the undecomposed plutonium hexafluoride. A final weighing gave the amounts of solid decomposition product in the vessel.

On the basis of these data, the ratio of fluorine to plutonium in the solid decomposition product was 3.97. In the previous determinations at 300 C ratios of 4.08, 3.95 and 3.96 had been obtained.

The products of thermal decomposition at 200 C as well as at 300 C appear to be plutonium tetrafluoride and fluorine. The quantitative removal of plutonium hexafluoride from the solid decomposition product by evacuation at room temperature indicates that stable addition compounds are not formed from these materials at room temperature.

7. Decomposition of Plutonium Hexafluoride at Room Temperature
(L. E. Trevorrow, W. A. Shinn)

The decomposition rate of plutonium hexafluoride at room temperature has been reported, with relatively good agreement, by at least three other groups^{1,2,3}. The decomposition under these conditions is believed to result from the emission of alpha particles by the plutonium and their absorption by the surrounding material. A confirmation of this rate was obtained incidental to other experiments in the present work.

¹Weinstock, B. and Malm, J. G., J. Inorg. Nucl. Chem., 2 380 (1956).

²Mandleberg, C. J., et al., ibid, 2 358 (1956).

³Florin, A. E., et al., ibid, 2 368 (1956).

A nickel vessel containing a gram of plutonium hexafluoride was allowed to stand at room temperature for 42 days. Initially, about 90 per cent of the sample was in the solid phase. At the end of this period the vessel was cooled in liquid nitrogen, evacuated to remove fluorine and reweighed. The amount of plutonium hexafluoride which had decomposed was calculated from the weight loss on the basis of the reaction

The weight observations were as follows:

Initial weight of PuF_6	1.0739 g
Weight of fluorine produced	0.0555 g
Weight of PuF_6 decomposed (Calc)	0.5156 g

Thus about 48 per cent of the sample decomposed in 42 days, giving a sample arithmetic average rate of 1.1 per cent of the original sample per day. This value is in agreement with the rates reported by other workers of 1.1¹, 1.2², and 1.3 ± 1³ per cent per day.

8. The Vapor-Phase Transfer of Plutonium Hexafluoride at Room Temperature (L. Trevorrow, W. A. Shinn)

Three experiments were conducted to determine the losses incurred during the transfer of gaseous plutonium hexafluoride in vacuum at room temperature. The material was transferred by volatilizing it from a nickel vessel at room temperature to another one at liquid nitrogen temperature.

In two of the experiments a purified sample of plutonium hexafluoride was transferred from a vessel A to another vessel B, then to a third vessel C. Vessels A and C were then weighed to determine the amount transferred out of A and the amount collected in C. Each of the two experiments therefore included two transfers.

In the third experiment the plutonium hexafluoride sample was transferred from A to B, then back and forth between B and C seven times, making a total of eight transfers. In all the transfers the path included about seven inches of 3/8-inch nickel tubing, a nickel diaphragm valve, two Monel bellows valves, and two flare connectors with Teflon gaskets. In all cases the equipment had been well seasoned by previous work with fluorine and plutonium hexafluoride.

The results of the transfer experiments are given in Table 4. A comparison of the first two experiments, with losses of 1.2 and 0.66 per cent, respectively, indicates that the amount of material lost remained approximately constant when the sample size was doubled. In the third

experiment the time required for the manipulations introduced a significant amount of radiation decomposition during the course of the operations. The loss of 1.4 per cent given in Table 4 is corrected for this effect. On this basis, the amount of loss was about the same for eight transfers as it was for two.

Table 4

LOSSES INCURRED DURING THE TRANSFER OF PLUTONIUM
HEXAFLUORIDE VAPOR AT ROOM TEMPERATURE

Apparatus: Seven inches of 3/8-in. diameter nickel tubing, a nickel diaphragm valve, two Monel bellows valves and two flare connectors gasketed with Teflon. The system was pretreated with F_2 and PuF_6 .

No. of Transfers	Plutonium Hexafluoride Balance			
	Transferred from Vessel (g)	Collected in Vessel C (g)	Lost in Transfer (g)	Per Cent Loss
2	1.0868	1.0739	0.0129	1.2
2	2.3600	2.3445	0.0155	0.66
8	1.4275	1.407 ^a	0.020 ^a	1.4 ^a

^aCorrected for radiation decomposition.

B. Pilot-Plant Operations
(W. J. Mecham)

1. Fused Salt Process

In the fused salt process for recovery of uranium from zirconium-uranium alloy fuels, two process steps are involved: (1) the dissolution of the alloy in fused salt at about 600 C with a hydrogen fluoride sparge, and (2) the formation and volatilization of uranium hexafluoride with a fluorine sparge. The corrosion resistances of metals in such systems as would be required have been shown to be probably unsatisfactory for long-term operation without frequent vessel replacement. Consequently, recent studies have been made to avoid or to minimize metal corrosion by means of special designs.

Graphite is unattached in the fused salt-hydrogen fluoride environment and is promising as a material of construction for a dissolver. The installation of a graphite dissolver pilot-plant unit is nearing completion.

In the fluorination step, corrosion of the salt container may be avoided by containing the molten salt in its own solid phase by means of a frozen-wall vessel. Since metal parts other than those in contact with the molten salt may be relatively cool, metals may be usable without severe corrosive attack. Two methods are promising for introducing heat internally to the salt: radiofrequency induction heating and low-voltage electrolytic resistance heating of the salt. Preliminary tests have been completed on both of these systems to show the feasibility of their operation on the pilot-plant scale. Studies are continuing to establish an optimum design.

a. Graphite-Dissolver Installation
(R. W. Kessie, W. J. Mecham)

The graphite-dissolver facility of the pilot plant consists of a dissolver to which uranium-zirconium alloy subassemblies can be charged, lines for transfer of molten salt, and a system for introducing hydrogen fluoride and recovering it from the off-gas. Service facilities have been installed and the installation of process equipment is nearing completion. Dissolution tests are planned in the next quarter.

b. Frozen-Wall Design Studies

(1) Electrolytic Heating and Electrical Resistance Heating Tests
(J. D. Gabor)

Internal heating of a frozen-wall fluorinator may be accomplished by low-voltage electrical power applied to metal resistance heaters or to electrodes in the molten salt. In the former case, an electric current is conducted through a metal, such as Inconel, and the heat generated in the metal is transferred to the salt by conduction. In the latter case an alternating current is conducted through the molten salt by electrodes, and heat is generated directly in the salt due to its electrical resistance. These electrodes, suitable for replacement as necessary, can be of simple design. Preliminary tests were made on a pilot-plant scale with 40 mole per cent zirconium fluoride-60 mole per cent sodium fluoride salt to explore the feasibility of the frozen-wall concept and to test various methods of heating.

The test equipment consisted of a jacketed, open-top, stainless steel vessel cooled by boiling water in the jacket. Heating elements were suspended from above. Two types of heaters were used, both of a hairpin configuration. One pair of elements, used for electrical resistance heating, was fabricated of 1/2-inch schedule 40 Inconel pipe, two feet long, welded to nickel pipe extension leads. The other pair of elements, used for electrolytic heating, was made from 3/4-inch OD nickel tubing, with a 1/8-inch wall. Power was supplied as 60 cycle ac controlled by a

saturable reactor. A thermocouple inside of one of the heating elements determined the control temperature. Nitrogen was used as a sparge gas. Observations and wall measurements were made through the open top. A schematic diagram of the test equipment is shown in Figure 1.

FIGURE 1
SCHEMATIC DIAGRAM OF ELECTRODE HEATER TEST UNIT

In Run E-1 only the Inconel heaters, positioned three inches above the bottom of the vessel, were used. Boiling water was used as the coolant throughout the test. The shape and the uniformity of the frozen wall were strongly influenced by the position of the sparge line. To produce a wall of uniform thickness circumferentially, it was necessary to center the exit end of the sparge line carefully in the vessel. The variation of the vertical cross-sectional shape of the wall with time from start-up was measured at two points on the circumference. The wall was much thinner near the top than at the bottom. This was primarily due to short-circuiting of the electric current near the salt surface, i.e., much of the current passed through the salt near the top rather than through the metal. During the operation the voltage across the heaters (in series) was as high as 19 volts and the current as high as 870 amp. The power input varied from 10 to 16 kw.

FIGURE 2
COMPARISON OF FROZEN-WALL PROFILES
IN ELECTRODE TESTS

In Run E-2 the Inconel heaters were used only for start-up, and the nickel electrodes were used during the test period. All current passed through the molten salt. The lower resistivity of the nickel reduced the tendency for current to flow primarily through the surface of the salt and allowed more uniform introduction of heat into the salt in the vertical direction. The more uniform thickness of the frozen wall during this test can be seen in the comparison between wall measurements made eight hours after start-up for Runs E-1 and E-2 (shown in Figure 2). An important advantage of the nickel electrodes is that they operate at a much lower temperature than do the Inconel heaters. The rate of corrosion of the nickel electrodes would be considerably lower than that of the Inconel heaters.

In Run E-2 the power requirements were 22 volts and 840 amp or 18.5 kw at the beginning while the salt was still being melted. At the end of the test period, after stable conditions had been established, the electrodes operated at 13 volts and 420 amp or 5.5 kw.

The over-all electrical resistance of the frozen wall was found to be above 40,000 ohms. The effective resistance of the molten salt between the electrodes was the order of 0.03 ohm. Resistance measurements can thus be used to indicate the presence of a protective wall, and possibly to measure the minimum wall thickness.

In Run E-3 operation was attempted without water in the jacket. A hard crust appeared at the surface (probably due to relatively high heat loss from the surface compared to the heat input), preventing wall measurements. A resistance check of the salt wall after a few hours of operation showed very low resistance, indicating no protective wall. After cooling the wall with water the measurement again showed the high resistance of solid salt. Cooling of the jacket vessel by natural convection was therefore not suitable for providing a salt wall. Maintenance of a frozen wall by resistance heating is concluded to be feasible where adequate control of the wall temperature can be provided. The electrolytic heating

method is considered to be superior to electric-resistance heating. Designs of improved heaters and an unjacketed vessel for air cooling are under way for additional experiments to establish an optimum design.

(2) Frozen-Wall Induction Heating Tests
(R. W. Kessie)

Induction heating makes possible the minimum number of internal components in contact with the molten salt in a frozen-wall design of the fluorinator. All other components of the container, except transfer lines and sparger, are near room temperature, at which there is no corrosion problem. The large difference in electrical resistivity of the 40 mole per cent zirconium tetrafluoride - 60 mole per cent sodium fluoride salt ($\sim 10^8$ ohm-cm for solid phase and ~ 1 ohm-cm for the liquid phase) allows induction heating of the liquid without significant heat generation occurring in the frozen wall.

Figure 3 is a top view of the experimental frozen-wall vessel. It consists of an alundum crucible, 12 inches OD by 18 inches

high with 1/2-inch thick sides and bottom. The induction coil is wound outside the crucible near the bottom. The cooling coils fabricated of 1/4-inch OD nickel tubing and spaced 1/2 inch apart along the vertical wall, are on the inside wall of the crucible. Water is used as the coolant. The stainless steel secondary vessel used is 20 inches OD by 24 inches high. The annulus between the crucible and secondary is filled with tampered granules of expanded mica, which provide an electrical insulating support for the induction coil.

The radiofrequency source is an electron tube oscillator with a 15-kw output rating. Preliminary experiments with this oscillator and the test assembly were made with 40 weight per cent sulfuric acid (in glass) as a stand-in system in order to estimate coupling of various coils to various sized loads. On the basis of these experiments it was decided to use a five or ten-turn coil directly coupled (no output transformer).

After charging solid salt, the unit was started, using tubular electric resistance heaters to produce a small molten pool, about 4 inches OD by 5 inches high, in the center of the frozen salt. With a molten pool of this size, induction heating alone generated enough heat to enlarge the pool. In plant operation, start-up could be accomplished by transferring molten salt into the unit from the dissolver or other vessel.

Direct observations of the salt wall were made and dimensions measured during operation. The operating conditions for the three runs are shown in Table 5. Thicknesses of the frozen walls are shown in vertical and in horizontal sections in Figure 4. The data were taken after conditions had stabilized for about one hour. Changing conditions from Run I-2 to Run I-3 required about one-half hour for the frozen wall to stabilize. From Figure 4 it can be seen that wall thickness varied inversely with power input. A five-turn coil placed at the bottom of the charge appeared to be the best arrangement for this system. At no time did it appear that molten salt contacted the metal of the cooling coil. Measurements of the electrical resistance across the solid salt wall were taken to confirm this.

In Run I-1 experiments made with and without sparging showed no appreciable effect of sparging on the frozen wall, except in the case where the sparge exit was close to the wall. In this case a local thinning of the wall was observed. Other effects of sparging were noted as follows:

a) With sparging the melt temperature was very uniform (525 C); without sparging, fluctuations (up to 85 C higher) of temperatures were noted. These fluctuations were random with position and time.

Table 5

OPERATING CONDITIONS IN FROZEN-WALL
INDUCTION-HEATED TESTS

Mark 1 Test Assembly
Salt: 40 m/o ZrF_4 - 60 m/o NaF

Run	I-1	I-2	I-3
Plate Input (kw)	10.7	23.0	7.8
Salt Input (kw)	--	5.5	1.25
Efficiency (%)	--	24	16
Wall Resistance (ohm)	2000	--	100,000
Coil Turns	10	5	5
Coil Length (in.)	10	5	5
Coil Current (RF amp)	65	125	95
Frequency (kc)	350	425	415
Minimum Wall Thickness (in.)	$3/16$	$1/8$	$1/2$
Bottom Wall Thickness (in.)	3.75	1.75	1.87
Wall Resistivity (ohm-cm)	--	--	$\sim 10^8$

FIGURE 4
FROZEN-WALL INDUCTION-HEATING TESTS:
CROSS SECTIONS THROUGH FROZEN WALL

VERTICAL PROFILES

TYPICAL HORIZONTAL PROFILES
NEAR COOLING COILS

b) Without sparging, a thin crust was formed at the top of the melt. This crust was not over 1/16-inch thick and was periodically melted and re-formed by convection currents. A small gas sparge was sufficient to remove a crust already formed and keep the molten surface clear of all frozen salt.

Once an initial stabilization had been reached at some power level, the system proved very stable over a wide range of power inputs and corresponding wall thicknesses and did not require adjustments. These tests indicate the feasibility of using induction heating for a frozen-wall fluorinator.

2. Related Volatility Studies

In the fluoride volatility process the final step is the purification of the product, uranium hexafluoride. Distillation has been shown to provide a high degree of separation of uranium from fission products and impurities encountered in processing. Two fundamental studies on the behavior of uranium hexafluoride in volatility separations are being carried out.

a. Vapor-Liquid Equilibrium of the System Uranium Hexafluoride-Bromine Pentafluoride (R. C. Liimatainen)

Considerable experience with the fractional distillation of this system has been reported by investigators both here and elsewhere.^{3a,3b} However, these separations were evaluated on the assumption of ideal behavior in accordance with Raoult's law, since no vapor-liquid equilibria had been published. In previous distillations of mixtures of bromine pentafluoride and uranium hexafluoride, it was found necessary to bubble in a slow, continuous stream of fluorine to keep all of the bromine as bromine pentafluoride; otherwise, corrosion reactions produced lower fluorides and free bromine. The addition of fluorine was also necessary in the current study.

The equilibrium still used in this investigation was of the recirculation type. The vapor was bubbled through the liquid by means of a magnetically actuated piston pump. The flow rate of vapor was indicated by a thermal flowmeter. The temperature was read on a Leeds and Northrup type K-3 precision potentiometer as the millivolt output from calibrated copper-constantan thermocouples. The pressure was indicated on a mercury manometer that was coupled to the still through a null-point transmitter. The samples were hydrolyzed and analyzed by wet chemical methods. For each run the still was maintained under isothermal conditions for at least 12 hours. Figure 5 shows a diagram of the equilibrium still assembly.

^{3a}Mecham, W. J., et al., Chem. Eng. Progress 53 728 (1957)

^{3b}Goodman, E. I., BNL-1217 (1952)

Data obtained on the 70 C isotherm are presented in Table 6. Slight positive deviations from ideality are shown. An x-y diagram of the system at 70 C is presented in Figure 6. Particular attention was paid to the bromine pentafluoride-rich end in order to establish that no azeotrope exists. Data have also been obtained on the 90 C isotherm and are being analyzed. Details of this investigation will be presented in a topical report.

Table 6
VAPOR-LIQUID EQUILIBRIUM DATA FOR THE SYSTEM URANIUM
HEXAFLUORIDE-BROMINE PENTAFLUORIDE

Equipment Description: Recirculation-type equilibrium still. See Figure 6

Mole Per Cent BrF_5		Temp, C, T	Pressure, mm Hg, P	Relative Volatility, α	Activity Coefficients	
Liquid x	Vapor y				BrF_5 γ_1	UF_6 γ_2
2.1	4.2	69.4	1380	2.04	1.44	1.00
9.3	14.8	69.3	1429	1.68	1.19	1.00
19.4	28.0	69.9	1564	1.62	1.17	1.02
22.5	32.0	69.7	1582	1.62	1.17	1.03
23.1	30.7	69.6	1569	1.47	1.08	1.05
40.0	50.2	69.4	1683	1.51	1.11	1.03
40.6	50.4	69.7	1708	1.49	1.10	1.05
46.1	55.9	69.6	1731	1.49	1.09	1.05
57.2	63.8	69.5	1778	1.32	1.03	1.12
67.5	72.2	69.7	1836	1.25	1.02	1.16
78.2	82.8	69.5	1870	1.34	1.03	1.09
80.1	83.3	69.6	1887	1.24	1.02	1.18
88.0	88.4	69.4	1890	1.04	1.00	1.36
88.0	89.1	69.4	1885	1.11	1.00	1.28
92.4	93.0	69.5	1909	1.09	1.00	1.30
92.8	93.3	69.1	1880	1.08	1.00	1.31
93.2	93.7	69.3	1888	1.09	1.00	1.30
93.4	94.9	69.5	1896	1.31	0.97	1.09
93.8	94.3	69.3	1904	1.10	1.01	1.30
94.2	94.3	69.3	1902	1.03	1.00	1.37
96.2	96.8	69.4	1913	1.21	1.01	1.20
98.5	98.6	69.6	1915	1.06	1.00	1.35

FIGURE 6
VAPOR-LIQUID EQUILIBRIUM IN THE SYSTEM
URANIUM HEXAFLUORIDE-BROMINE PENTAFLUORIDE

b. Laboratory Fractionation Column
(R. O. Ivins)

A 1/2-inch diameter, packed laboratory fractionation column is being assembled for fundamental investigations of separations in uranium hexafluoride systems. The first experiments planned are with the system uranium hexafluoride-bromine pentafluoride. A diaphragm pump is to be provided for recirculation of vapor for steady-state runs at various liquid-vapor ratios. Assembly is nearing completion.

C. Liquid Metal Fuel Reprocessing
(J. Fischer)

Laboratory work has been done to demonstrate the extraction of uranium and fission products with molten sodium fluoride-zirconium fluoride mixtures. The variables that affect the extraction process, as it applies to the Liquid Metal Fuel Reactor (LMFR) solution fuel, have been studied.

Laboratory extraction experiments have been conducted with a higher magnesium content (up to 1900 ppm) in the bismuth alloys. In such alloys uranium is extracted rapidly at first, but the extraction is not as complete as it is in the absence of magnesium.

Extraction experiments have been made in a new apparatus from which liquid samples can be taken during the course of experiments. Rates of extraction of uranium from bismuth in the presence of magnesium have been obtained. The enhanced effect that sparging with hydrogen fluoride has on uranium extraction has been demonstrated.

The effect that bismuth trifluoride may have as an oxidant in extracting uranium from bismuth alloys has been tested. Complete extraction of uranium by the fused salt was obtained, but the reaction was slow.

Bismuth pentafluoride has been prepared by the reaction of fluorine with bismuth. Bismuth trifluoride has been prepared by the hydrogen reduction of the pentafluoride. The strong oxidizing power of bismuth pentafluoride has been demonstrated by its chemical reactions. The temperature at the triple point of bismuth pentafluoride has been determined as 151.4 ± 0.5 C.

1. Extraction of Uranium and Fission Products from Bismuth
(M. Adams, N. D. Phillips,* T. Gerding, J. Stockbar)

In the original conception of the fluoride volatility process for the LMFR (ANL-5820, page 34) the fuel was initially treated with fused sodium fluoride-zirconium fluoride saturated with hydrogen fluoride. In more recent work (ANL-5924, page 54) extractions of uranium and fission products were demonstrated using the fused fluoride salt without hydrogen fluoride.

More quantitative work on extractions both with and without hydrogen fluoride is now available. Removal of uranium and fission products, using the salt alone can be accomplished, but both the extent of removal and the rate of removal are increased by sparging the salt with hydrogen fluoride.

In all the recent work a higher content of magnesium has been used in the bismuth synthetic fuels than has been proposed for use in the actual reactor fuel. A higher content of magnesium serves to improve the stability of the uranium solutions toward oxidation. It also increases the rate of dissolution of uranium and other additives, making the alloys easier to prepare.

Data from a series of extractions carried out without hydrogen fluoride sparging in the rocking furnace (described in ANL-5924, page 54) are presented in Table 7. In these experiments 50 grams of synthetic bismuth fuel were sealed in a graphite tube with an equal volume of fused salt (15 grams). The graphite tube was placed in a copper secondary container. The unit was then heated in a furnace which rocked through an angle of about 40 degrees at one cycle per minute.

*Special Scientific Employee on loan from Babcock and Wilcox, Alliance, Ohio.

Table 7

RATE OF EXTRACTION OF URANIUM FROM BISMUTH IN THE PRESENCE
OF MAGNESIUM - ROCKING EXPERIMENTS

Experiments were done in the rocking furnace at 600 C (see ANL-5924, page 54 for a description of the rocking furnace). Fifty grams of bismuth and fifteen grams of salt (equal volumes) were used in each experiment.

Exp No.	Uranium in Original Alloy (ppm)	Magnesium in Original Alloy (ppm)	Time at 600 C (min)	Uranium in the Metal Phase after Extraction (ppm) ^a	Uranium in the Salt Phase after Extraction (ppm)	Material Balance ^b (per cent)
1190	900	1090	5	255	1900	91.7
1566	715	470	15	9	2300	98.0
1548	835	1900	30	49	2900	110
1563	835	1900	60	8	3000	109
1550	835	1900	180	42	2900	109

^aAn experimentally determined blank value of 15 ppm uranium has been subtracted from each uranium determination.

^bMaterial balance = $\frac{\text{U in metal} + \text{U in salt (after extraction)}}{\text{U in Original Alloy}}$

Uranium was extracted rapidly at first, but the extraction was not complete. In the one experiment in which the concentration of magnesium in the bismuth was low, extraction was rapid and more nearly complete. Results showing the rapid extraction of uranium in the absence of magnesium were previously reported (ANL-5924, page 55).

A new apparatus has been constructed to aid in the study of rates of extraction of uranium and fission products under various conditions of sparging with hydrogen fluoride and of concentrations of the constituents. The device consists of a flanged stainless steel tube with a connection to a vacuum system. The tube can be heated by a furnace and the top portion cooled by circulating water through the

attached copper coils. A top flange has been fitted with a thermocouple well, a sparge tube, a stirring shaft with a molybdenum paddle, and a port for sampling the liquid metal. The apparatus is shown in Figure 7.

In operation an alloy of bismuth, uranium, and magnesium is made in a molybdenum cup in the apparatus. A sample is taken of the alloy. The alloy is cooled and, after opening the apparatus, the sodium fluoride-zirconium fluoride salt mixture is added. The temperature is raised to 550 C and stirring is started. Samples of the liquid bismuth are taken by lowering a 4-mm quartz tube through a rubber serum cap on top of the sampling port, through a gate valve and into the liquid metal. The pressure in the quartz tube is reduced by means of a large syringe connected through a short length of rubber tubing. The quartz tube, containing four to ten grams of bismuth, is then withdrawn and the gate valve closed.

The apparatus is equipped with a sparge tube through which argon or hydrogen fluoride can be added. In Table 8 results of some experiments, both with and without hydrogen fluoride, are presented. Uranium can be removed rapidly at first with or without the hydrogen fluoride. Removal is incomplete, even after long contact times, unless hydrogen fluoride is used. When hydrogen fluoride was sparged through the molten salt at rates between 0.1 and 1 gram per minute, the extraction was nearly complete in 15 to 30 minutes.

Table 8

RATE OF EXTRACTION OF URANIUM FROM BISMUTH IN THE PRESENCE OF
MAGNESIUM: WITH AND WITHOUT HYDROGEN FLUORIDE SPARGING

Experiments done at 550 C in the liquid-sampling apparatus (see Figure 7).

Exp No.	Sparge	Magnesium in Original Alloy (ppm)	Uranium Remaining in Alloy After Stirring - minutes (ppm)									
			0	15	30	45	75	90	105	135	195	225
1528	None ^a	2400	1425	235	-	-	-	-	-	-	-	-
1531	None ^a	2820	1325	129	-	-	-	-	-	120	-	127
1552	None ^a	2600	1325	175	-	-	71	-	-	73	75	-
1571 ^b	HF	2390	1355	23	6	4	-	-	5	-	-	-
1586 ^c	HF	1957	1495	4	3	-	-	10	-	-	-	-

^aAn experimentally determined blank value of 15 ppm uranium has been subtracted from the uranium determinations.

^bA stainless steel sparge tube was used for HF introduction. The blank value has not been determined for uranium.

^cA molybdenum sparge tube was used. The blank value for the uranium has not been determined.

A series of experiments, using bismuth trifluoride as an oxidizing agent in place of hydrogen fluoride, was carried out. An amount of bismuth trifluoride, sufficient to supply fluorine for the oxidation of all the

uranium, magnesium, and zirconium present to uranium tetrafluoride, magnesium fluoride and zirconium tetrafluoride, respectively, was added to the salt. Fifty-gram samples of the same bismuth alloy were rocked with 15-gram portions of the sodium-zirconium-bismuth fluoride salt. Uranium removal was a function of time. The extraction was complete after two hours. Data from these experiments are shown in Table 9.

Table 9

RATE OF EXTRACTION OF URANIUM IN THE PRESENCE
OF MAGNESIUM: OXIDATION WITH
BISMUTH TRIFLUORIDE

Experiments done in the rocking furnace at 600 C. Fifteen grams of sodium fluoride-zirconium fluoride salt were used in each experiment. Sufficient bismuth fluoride was added to oxidize all uranium, magnesium, and zirconium present in 50 grams of alloy.

The same original alloy was used in each experiment. It contained 935 ppm uranium, 2700 ppm magnesium, and 350 ppm zirconium dissolved in the bismuth. In each experiment 0.869 gram of bismuth trifluoride was added to the salt.

Experiment No.	Time at 600 C (min)	Uranium in the Metal Phase after Extraction (ppm) ^a	Uranium in the Salt Phase after Extraction (ppm)
1581	15	41	1800
1570	30	34	2600
1583	60	21	2700
1585	120	0	2600

^aAn experimentally determined blank value of 15 ppm uranium was subtracted from each determination.

3. Bismuth Fluoride Chemistry
(E. Rudzitis and W. Gunther)

a. Preparation, Properties, and Reactions of Bismuth
Trifluoride and Bismuth Pentafluoride

Hydrofluorination and fluorination in fused salt media have become important in the development of the volatility process for the reprocessing of reactor fuels in this Laboratory. A knowledge of the chemistry

of the metal fluorides is important to the development of these processes. The properties and reactions of bismuth trifluoride and bismuth pentafluoride are of special importance to the Fused Salt Volatility process for the LMFR and have been under investigation. This work is essentially complete and a topical report is being prepared.

D. Volatility Corrosion Studies

(L. Hays, R. Breyne, W. Seefeldt)

The predominant limiting factor in the use of "L" nickel as a material of construction for the fluorination step of the fused salt dissolution process is the rate at which it is attacked intergranularly. Several experiments have been made to determine the effect of (1) fluorine purification, and (2) lower operating temperature on the corrosion of "L" nickel in this environment.

FIGURE 8
EFFECT OF FLUORINE PURIFICATION AND TEMPERATURE ON
CORROSION OF "L" NICKEL IN FLUORINATED
FUSED FLUORIDE MELTS

The experiments were conducted in the same manner as described in ANL-5896, page 22. Strips of "L" nickel were exposed simultaneously to the liquid phase, interface, and vapor phase. The reference test conditions were fluorine-sparged sodium fluoride-zirconium fluoride (equimolar) at 600 C. The effect of fluorine purification was studied by passing tank fluorine through a bed of sodium fluoride. Operation at lower temperature (475 C) was made possible by the addition of lithium fluoride to the melt. No attempt was made to separate the effects of lower temperature and the presence of lithium salt. Corrosion evaluations included dimensional changes and intergranular attack. Results are shown graphically in Figure 8.

The following conclusions may be drawn from the data:

1. In general, both fluorine purification and operation at 475 C reduce corrosion substantially.

2. The maximum dimensional change was not greatly improved by fluorine purification, but was lower by a factor of three at the lower temperature of 475 C.

3. Intergranular attack was greatly reduced by fluorine purification; the lower operating temperature resulted in a comparable decrease.

4. Interface effects disappeared at 475 C.

5. Vapor-phase effects were evident in the test involving fluorine purification, but absent in greater part at the lower temperature.

II. FLUIDIZATION STUDIES

(A. A. Jonke, N. M. Levitz)

Investigations of the effect of process variables on the fluid-bed drying and fluid-bed fluorination steps of the ADF process, (see page 46) for recovery of uranium from low-uranium-zirconium fuel alloys continued. Synthetic feed solutions containing the equivalent of two and five per cent uranium alloys were fed to the six-inch fluid-bed dryer using single and dual feed nozzles. Particle growth continues to be the limiting factor in sustained (over 40 hours) operation of the dryer. Runs were made at 300 and 450 C with a total operating time of about 115 hours. Additional X-ray diffraction studies of dryer products showed the presence of complex mixtures of several species of zirconium fluoride, with zirconium tetrafluoride being the major constituent formed at temperatures near 300 C, while zirconyl fluoride and some zirconium oxide are formed at higher temperatures (450 C).

Fluorinations of fluid-bed dried material conducted in the $2\frac{1}{2}$ -inch diameter fluid-bed fluorinator disclosed a number of factors which affect the degree of uranium removal.

1. Preheating the dryer product at 600 C for a period equivalent in length to the fluorination period had an adverse effect on uranium removal - 89 per cent removal in eight hours of fluorination at 500 C, as compared to 98 per cent without the pre-heat step.
2. Increasing the fluorination temperature from 500 C to 600 C increased uranium removal from 61 to 98 per cent for a zirconium fluoride mixture containing precipitated uranium tetrafluoride (3.5 weight per cent uranium alloy equivalent feed). Analysis of two screened fractions, 20 to 40 mesh and 60 to 100 mesh, of this material showed a slightly higher uranium removal from the smaller particles, 97.6 per cent as compared to 96 per cent for the larger size.
3. Increasing the fluid-bed dryer temperature from 240 C to 450 C had an inhibiting effect on subsequent uranium removal; 60 per cent in eight hours at 500 C as compared to 98 per cent for material prepared at 240 C.
4. Results of tests of the reproducibility of uranium removal during fluorination of dryer product showed excellent agreement; 91.8, 91.6, 90.9 and 91.2 per cent removal in four hours at 600 C.

Laboratory fluorinations conducted at 600 C on zirconium fluoride solids to which 10 and 24 moles of sulfur per mole of uranium had been added indicated sulfate addition did not enhance uranium removal - 92 per cent removed in two hours at 600 C.

A three to 25-fold decrease in surface area of the zirconium fluoride powders was found to result during fluid-bed fluorinations, but in several cases uranium removal was high (up to 98 per cent) despite the decreased surface.

Corrosion results of additional specimens inserted in the fluid-bed fluorinator do not substantiate the excessively high vapor-phase corrosion of nickel observed previously (ANL-5924, pages 69 and 70). Preliminary results from corrosion coupons inserted in the bed showed Monel underwent very little dimensional change and slight intergranular attack.

Additional runs in the fluid-bed waste calciner, used to convert liquid wastes to granular solids, indicated that ruthenium decontamination factors from feed through silica gel adsorber of 10^3 to 10^4 can be achieved. Suppression of ruthenium volatilization at higher temperatures (500 C versus 400 C) was confirmed. The average non-volatile decontamination factor from feed through adsorber ranged from 3×10^4 to 1×10^5 , while off-gas samples taken after the condenser showed total decontamination factors in excess of 10^6 . The most active run to date was made this period without incident, the feed consisting of an 8:1 dilution of ICPP waste. Gross gamma and ruthenium gamma activities in the feed were 2.8×10^7 and 9.8×10^5 cpm/ml, respectively.

Corrosion experiments on sintered stainless steel metal, using conditions simulating those in the fluid-bed waste calciner, were continued. Results showed nitric acid vapors or mixtures of nitric acid vapors with air or nitrogen produced metal corrosion similar to that which occurred in the calciner bayonet-type filter elements at high temperatures.

Mixing studies using a radioactive tracer technique have been completed in the straight-wall fluid-bed column, using 20 to 40 mesh and 140 to 200 mesh copper spheres. Experiments are continuing in the tapered fluid-bed column.

The use of colored feed solutions in the study of factors influencing particle growth in fluid-bed calciners has not produced material with characteristic growth rings suitable for determining the amount of liquid deposited on the particles in each pass through the spray. Experiments using radioactive tracers are being initiated.

Fluid-bed program discussions were held at ANL with Dr. C. M. Nicholls of Harwell, U. K., and with representatives from Dow Chemical Company, Midland, Michigan, and the Fluor Corporation, Los Angeles, California. Laboratory fluid-bed equipment was discussed with J. Kennelley, Mallinckrodt Chemical Company, St. Louis, Missouri.

Waste calcination was discussed with representatives of Hanford Atomic Power Operations. A feed materials conference held at Paducah was attended on October 21 and 22, 1958.

A. Separation of Uranium from Zirconium-Uranium Fuel Alloys

The term "ADF Process" has been selected to designate the general fuel-recovery process which involves aqueous dissolution of the fuel, drying of the solution to solids, and subsequent fluorination of the fissile elements. Development work is being carried out on an engineering scale to apply the process to enriched uranium-zirconium fuel alloys. Laboratory work is also being done on application of the process to uranium-plutonium fuels (see Section I, page 21). For the zirconium alloys, the process involves dissolution of the alloy in aqueous hydrofluoric acid, followed by conversion of the metal to dry granular solids by spraying the solution into a fluidized bed of granular material. The solids are then fluorinated in a fluid-bed reactor to remove the uranium as the volatile hexafluoride.

1. Fluid-Bed Drying (J. Barghusen, N. Levitz, D. Raue, R. Zeman*)

Additional investigations of operating variables were performed in the six-inch diameter fluid-bed dryer while preparing material for fluid-bed fluorination studies. Two long runs were made to obtain data on the rate of particle growth as a function of feed rate. The uranium-free residue from fluid-bed fluorinations was tried as an alternate starting bed material. The use of dual feed nozzles was investigated.

a. Operating Conditions (See Table 10)

The feed solutions in all the runs contained about 1.4 M zirconium, 6.3 M fluoride, and either 0.03 M or 0.013 M uranium as uranyl fluoride, equivalent to 5 and 2 weight per cent uranium alloy, respectively. Bed temperatures of 300 and 450 C were used. The fluidizing velocity was maintained at 2 ft/sec and the nozzle atomizing pressure was 30 psig. Most of the runs were made with a single 0.040-inch liquid nozzle at feed rates ranging from 50 to 80 ml/min. More recently, two 0.028-inch liquid nozzles were installed to determine the effect of multiple feed points on particle growth and dryer operability. The nozzles were mounted

*Co-op student from Northwestern University, Evanston, Illinois.

at 5.5 and 11 inches above the gas dispersion plate at an angle of 90 degrees from each other. Separate feed pumps maintained a rate of 50 ml/min in each nozzle.

Table 10

SUMMARY OF RUNS MADE IN SIX-INCH FLUID-BED DRYER

Fluidizing Gas Velocity:		2 ft/sec				
Feed Concentration:		1.4 M Zirconium				
Fluoride to Zirconium Mole Ratio:		4.5				
Atomizing Gas Pressure:		30 psig				
Run No.	Starting Bed	U Conc in Feed (w/o alloy equiv)	Feed Rate (ml/min)	Run Time (hr)	Bed Temp (C)	Liquid Nozzle Size (in.)
ZCP-48	ZrO ₂	5	50 to 70	14	450	0.040
ZCP-49, 50	ZrF ₄ ^a	5	80	34	300	0.040
ZCP-51	ZrO ₂	2	50 to 80	14	300	0.040
ZCP-52	Fluorinated Residue	2	50 to 80	15	300	0.040
ZCP-53	ZrO ₂	2	50	22	300	0.040
ZCP-54, 55, 56	ZrF ₄ ^b	2	90 to 100	15	300	0.028 ^c

^aFinal bed from dryer Run ZCP-44.

^bFinal bed from dryer Run ZCP-53.

^cTwo 0.028-inch diameter liquid nozzles used.

The residue from fluid-bed fluorinations was used as starting bed material for one run, while refractory grade zirconium oxide and dryer products were used in the others. A low feed rate (approximately 50 ml/min) was used at the start of a run to precoat the starting bed particles to prevent particle agglomeration. Total operating time for the dryer during this quarter was 113 hours.

b. Operating Performance

Continual particle growth occurred in all the runs; however, no serious operating difficulties were encountered. A small amount of agglomerated material which had apparently formed on the nozzles and then broken off was found in the bed at the end of Run ZCP-52 and again after the subsequent dual nozzle runs. The factors which cause these formations are as yet unexplained.

During Run ZCP-50, as a result of particle growth, the minimum fluidizing velocity for the bed approached and finally exceeded the velocity maintained at the column inlet. This resulted in poor mixing in the zone below the feed nozzle, while the portion of the bed above the nozzle was probably well fluidized because of the additional gases introduced by the nozzle. A temperature spread of 15 degrees developed between the upper and lower portions of the bed as a result of the formation of the two mixing zones. A normal temperature spread is about 3 degrees. Some difficulty was experienced in maintaining a constant feed rate during the first two dual nozzle runs, but the condition was corrected before the last run, ZCP-56, and no additional problems occurred.

c. Evaluation of Dryer Operation

The primary evaluation of a dryer run is made on the basis of the change in the distribution of particle sizes in the bed. If there is no change, the dryer can be run indefinitely; however, all of the operations to date with zirconium fluoride solutions have resulted in continual particle growth in the bed, which precludes runs of long duration. Growth can occur by deposition of solids on single particles and by agglomeration of particles. Microscopic examination of dryer products indicates that the latter mechanism is of minor importance with this feed material. One method of expressing particle growth is in terms of the doubling time, the time required for the initial average diameter to double in value. In Figure 9 is a plot of the ratio d/d_0 versus time for

FIGURE 9
PARTICLE GROWTH WITH TIME IN
SIX-INCH FLUID-BED DRYER

several runs, where d is the volume-average particle diameter at time t and d_0 is the initial volume-average particle diameter. These data indicate that the doubling times range from 15 to 20 hours and are not affected greatly by the feed rate or initial particle size. Initial average particle sizes ranged from 0.09 to 0.26 mm. In these runs feed rates of 50 and 80 ml/min for a single nozzle and a total of 100 ml/min for the dual nozzles were used. The absence of any affect of feed rate on particle growth rate was unexpected and requires further study.

Since continuous particle growth eventually makes the dryer inoperable, some auxiliary means must be provided to counteract the growth. Seed particles of some inert solid may be fed into the bed to act as nuclei for deposition of solids. An alternative scheme is to use "jet grinding" to reduce the particle size by attrition. This scheme will be tested by introducing the sonic air jet directly into the fluidized bed.

d. Properties of Calcined Solids

The results of initial experiments to identify the products of the drying operation were reported in the previous report (ANL-5924, page 87). Additional qualitative results have been obtained from X-ray diffraction studies on material produced in fluid-bed dryer runs and on material specially prepared by spraying zirconium fluoride solutions directly on the wall of the dryer for 10 to 15 minutes. The results of these studies indicate that the materials produced in the dryer are a complex mixture of several species of zirconium fluoride. The data are presented in Table 11.

Table 11

QUALITATIVE RESULTS OF X-RAY DIFFRACTION ANALYSES ON DRIED ZIRCONIUM FLUORIDE^a

X means the compound was present, O means the compound was not.

Sample	F/Zr Mole Ratio in Feed	Drying Temp (C)	ZrF ₄ High-Temp Polymorph	ZrF ₄ Low-Temp Polymorph	ZrF ₄ ·H ₂ O	ZrOF ₂	New Cubic Phase	Unidentified Phase	ZrO ₂
Spray Dried	4.5	300	X	O	X	O	O	X	O
Spray Dried	10.0	300	Only an amorphous material found ^b						
Spray Dried	4.5	450	X	O	O	X	X	X	O
Spray Dried	10.0	450	X	O	O	X	X	X	O
ZCP-31	10.0	300	O	X	O	O	O	O	O
ZCP-38	10.0	300	X	X	O	O	O	O	O
ZCP-39	10.0	450	O	O	O	X	O	O	X

^aData obtained by D. S. Flikkema.

^bChemical composition that of zirconium tetrafluoride.

At 300 C zirconium tetrafluoride is the principal species formed. This material seems to be a mixture of two polymorphic forms. The relative amounts of the two polymorphs present may be a function of the residence time of the material in the dryer. The amorphous material formed in the spray-drying test at 300 C has not been detected in any fluid-bed products, but its chemical composition is that of zirconium tetrafluoride.

At 450 C zirconyl fluoride and zirconium oxide are the predominant species present. The relative amounts present are determined by the gas environment and residence time in the dryer. At a temperature above 400 C, zirconyl fluoride in the presence of water vapor will react to give zirconium oxide and hydrogen fluoride. With a fluoride to zirconium mole ratio of 10 in the feed (free acid 10 M), this reaction takes place only to a limited extent. Chemical analysis of ZCP-39 product (a run made at 450 C) shows that the composition of the product is that of zirconyl fluoride plus a small amount of zirconium oxide. The hydrolysis of zirconyl fluoride is more evident in the product from Run ZCP-48 made at 450 C in a low-fluoride atmosphere (free acid 0.7 M). This product contained only two per cent fluoride, indicating a high percentage of zirconium oxide is present.

Future work will include operations with solutions containing the equivalent of 2 weight per cent uranium-Zircaloy-2 alloy. Runs utilizing dual nozzles will be continued.

2. Recovery of Uranium from Uranium-Zirconium Mixtures by Fluorination in a Fluidized-Bed Reactor (G. J. Vogel, A. Rashinskas, L. Marek)

a. Pilot-Plant Studies

Uranium-zirconium mixtures prepared in a fluid-bed dryer were fluorinated batchwise in the 2.5-inch diameter fluid-bed reactor (see ANL-5789, page 39) to determine the effects of changes in operating conditions in the fluorination and the drying step on uranium removal. Previous data (ANL-5924, page 68) had shown that approximately 99 per cent of the uranium could be removed from material containing the equivalent of 5 and 10 weight per cent uranium alloy by fluorinating for 12 hours at 500 C or 8 hours at 600 C.

In the fluorination runs the dryer product was fluidized with nitrogen, while being heated to the reaction temperature. Fluorine was then added to give a 15 per cent mixture and the fluorination was continued for one or more successive four-hour periods. Samples were taken at the end of each period.

Results of current investigations on factors which affect uranium removal are summarized below and in Tables 12 and 13.

(1) Reproducibility of Results (see Table 12)

In order to determine the reproducibility of uranium removal in fluid-bed fluorination experiments, a batch of dryer product (Run ZCP-50, 5 weight per cent uranium alloy equivalent feed) was blended

Table 12

RESULTS OF REPRODUCIBILITY EXPERIMENTS IN FLUID-BED FLUORINATOR

Equipment: 2½-inch diameter Monel column
 Fluidizing Gas Velocity: ~1 ft/sec
 Fluidizing Gas Composition: 15% Fluorine, 85% Nitrogen
 Run Duration: 8 hours
 Fluorination Temperature: 600 C
 Feed Material: ZCP-50 composite

Fluorination Run No.	Uranium Concentration of Bed, Per Cent Uranium ^a			Per Cent U Removed After Fluorination Time of	
	Before Fluorination	After 4-hr Fluorination	After 8-hr Fluorination	4 hr	8 hr
U-Zr-21	2.18	0.18	0.11	91.8	95.0
U-Zr-22	2.26	0.19	0.17	91.6	92.5
U-Zr-23	2.08	0.19	0.15	90.9	92.8
U-Zr-24	2.17	0.19	0.15	91.2	93.1

^aX-ray spectral analysis, as reported.

Table 13

EFFECT OF OPERATING VARIABLES ON REMOVAL OF URANIUM FROM URANIUM-ZIRCONIUM POWDERS

Equipment: 2½-inch diameter Monel column
 Fluidizing Gas Composition: 15% F₂, 85% N₂
 Fluidizing Gas Velocity: ~1 ft/sec

Fluorination Run No.	Effect Studied	Fluid-Bed Dryer Conditions		Fluorination Temp (C)	Per Cent of Original Uranium Removed After	
		Uranium Concentration in Feed (w/o alloy equivalent)	Temp (C)		4 hr	8 hr
U-Zr-15 ^a	Preheating in Nitrogen at 600 C for 7 hr	5	240	500	88	89
U-Zr-11 ^a	No preheating	5	240	500	88	98
U-Zr-13 ^b	Fluorination temp	3.5	300	500	50	61
U-Zr-16 ^b	Fluorination temp	3.5	300	600	92	97
U-Zr-18 ^c	Drying temp	5	450	500	56	60
U-Zr-11 ^a	Drying temp	5	240	500	88	98

^aStarting material expected to be ZrF₄ with ZrO₂ core.

^bStarting material expected to be primarily ZrF₄ with about 1% Sn.

^cStarting material expected to be ZrO₂ and ZrOF₂.

in a twin-shell blender and then divided into four fractions, each of which was separately fluorinated for eight hours at 600 C with 15 per cent fluorine in the fluidizing gas. Uranium removals for the first four hours showed excellent agreement; 91.8, 91.6, 90.9 and 91.2 per cent; the values are similar to results previously obtained (ANL-5924, page 68). The uranium removal obtained after eight hours of fluorination also showed good reproducibility: 95.0, 92.5, 92.8, and 93.1 per cent, but were not as high as expected from previous experience. Previous eight-hour results with 5 weight per cent material have shown up to 98 per cent uranium removal. One major difference in the feed to the fluorinator for the current series was the higher percentage of large particles, 52 per cent plus 40 mesh size.

(2) Effect of Preheating the Solid

A seven-hour pre-heat in nitrogen at 600 C, which was expected to volatilize residual water and hydrogen fluoride from the dryer product (made from five weight per cent uranium alloy equivalent feed) and leave the material more porous, gave negative results: 89 per cent uranium removal after eight hours of fluorination at 500 C, as compared to 98 per cent without the heating step. However, the four-hour samples in both cases showed equivalent uranium removals, 88 per cent, indicating sintering during the heating step made only a portion of the uranium unavailable for fluorination.

(3) Effect of Fluorination Temperature

A higher fluorination temperature (600 C versus 500 C) gave improved removal of uranium, 97 per cent as compared to 61 per cent in eight hours, for material prepared by drying a solution containing precipitated uranium tetrafluoride (3.5 weight per cent uranium alloy equivalent feed). The feed solution also contained tin, used as a reductant for the uranium prior to precipitation, and the improved removal of uranium may be related to the greater volatilization of stannic fluoride, 60 per cent at 600 C as compared to 8 per cent at 500 C (stannic fluoride bp - 705 C).

To determine the effect of particle size on uranium removal, two size fractions of this material were analyzed for uranium after fluorination. Uranium removals were 96.0 and 97.6 per cent for the 20 to 40 mesh fraction and 60 to 100 mesh fraction, respectively.

(4) Effect of Fluid-Bed Dryer Temperature

A higher fluid-bed dryer temperature, 450 C, instead of 240 C, produced an adverse effect on uranium removal: 60 per cent as compared to 98 per cent for eight-hour fluorinations at 500 C. The dryer

product contained a high percentage of zirconium oxide that may have sintered while being converted to the tetrafluoride, making the uranium less available for fluorination.

(5) Effect of Fluorination on Surface Area

Measurements of surface area have been made by the nitrogen-adsorption method on fluid-bed dryer and fluorination products prepared from feed solutions with uranium contents ranging from 3.5 to 10 per cent alloy equivalent. The data, presented in Table 14, indicate there is a 3 to 25-fold decrease in surface area during fluorination, probably due to sintering. No correlation was found between uranium removal and the surface area before or after fluorination. Evidently other undetermined factors cause differences in uranium removal for materials prepared under various conditions. Nevertheless, for any given batch of material, sintering may account for the decreased rate of uranium removal with time.

Table 14

SURFACE-AREA MEASUREMENTS ON FLUID-BED DRIED AND FLUORINATED MATERIAL

(Fluorination Temp - 600 C)

Dryer Run No.	Fluori- nation Time (hr)	Uranium Alloy Equivalent Feed (w/o)	Surface Area (sq m/g)		Uranium Removal (%)
			Before Fluori- nation	After Fluori- nation	
ZCP-38 ^a	8	3.5	2.6	0.1	95
ZC-103 ^b	6	5.0	3.0	1.2	92
ZCP-42 ^c	12	10.0	4.8	0.9	98

^aContained precipitated UF₄; drying temp 300 C;
F/Zr ratio 10:1.

^bDrying temp 350 C; F/Zr ratio 3.5:1.

^cDrying temp 300 C; F/Zr ratio 3.5:1.

(6) Effect of Sulfate Additive on Uranium Removal

Previous data have indicated that higher concentrations of uranium enhance uranium removal, probably by producing more porous material through which gases could readily diffuse. Therefore, additives such as carbon or sulfate, which would form volatile fluorides, were added to feed solutions to produce this effect. A single laboratory experiment on carbon addition indicated that it did not aid in uranium removal (87 per cent after eight hours, see ANL-5924, page 74). Laboratory fluorination experiments were made on two samples containing three per cent uranium and 24 and 10 moles of sulfur as sulfate per mole of uranium. The solids were fluorinated for two hours at 600 C with 100 per cent fluorine. The results showed about 92 per cent removal of uranium for both samples. This removal of uranium was slightly better than that realized with addition of carbon, but was not sufficiently improved to warrant further study.

Experiments are planned to determine the following:

1. The extent of uranium removal from solids equivalent to a 2 weight per cent uranium alloy.
2. The effect of higher fluorine concentrations up to 100 per cent fluorine in the fluidizing gas.
3. The feasibility of using a static (non-fluidized) bed during fluorination.

b. Corrosion in the Fluidized-Bed Fluorinator
(L. Hays, R. Breyne, W. Seefeldt)

Beginning with Run U-Zr-6B, corrosion specimens of nickel have been inserted into the fluid-bed fluorinator; these have extended through the entire length of the unit. It was reported in ANL-5924, pages 69 and 70, that the first of these specimens, a 1/4-inch OD tube, suffered severe vapor-phase dimensional attack at elevations of 36 and 47 inches, well above the upper surface of the fluid bed. The intergranular attack for specimen 1 (not previously reported) has been superimposed on the dimensional change in Figure 10.

Specimens 2 and 3 consisted of 1/4-inch OD nickel rods. Specimen 4 consisted of two flat strips of nickel, one for corrosion evaluation and the other for analysis of the corrosion film. Exposure conditions and graphical results for rods 2 and 3 are shown in Figures 11 and 12. It will be noted that no extreme corrosion has occurred in either rods 2 or 3 in the vapor phase, though exposures were comparable to those of specimen 1. This would suggest some condition during the exposure of the

FIGURE 10
VERTICAL CONTOUR OF NICKEL CORROSION SUPPORT TUBE
IN FLUID-BED FLUORINATOR
(SPECIMEN 1)

TIME AND TEMPERATURE: 20 HOURS AT 500 C
12 HOURS AT 600 C
BED: URANIUM-ZIRCONIUM FLUORIDES
FLUIDIZING MEDIUM: 15% FLUORINE IN NITROGEN
RUNS: U/Zr-6B TO U/Zr-14
GAS VELOCITY: 1.1 FT/SEC

FIGURE 11
VERTICAL CONTOUR OF NICKEL CORROSION ROD
IN FLUID-BED FLUORINATOR (SPECIMEN 2)

SPECIMEN: NO. 2, 1/4-IN. OD ROD
RUNS: U/Zr-15 TO U/Zr-18
TIME AND TEMPERATURE: 24 HR AT 500 C
8 HR AT 600 C
7 HR AT 600 C (N₂ ONLY)
FLUIDIZING MEDIUM: 15% F₂ IN N₂
BED: URANIUM-ZIRCONIUM FLUORIDE
GAS VELOCITY: 1.1 FT/SEC

FIGURE 12
VERTICAL CONTOUR OF NICKEL CORROSION ROD
IN FLUID-BED FLUORINATOR
(SPECIMEN 3)

SPECIMEN: NO 3, 1/4 INCH OD ROD
RUNS: U/Zr-19 AND U/Zr-20
TIME AND TEMPERATURE: 16 HR AT 500 C
FLUIDIZING MEDIUM: 15% F₂ IN N₂
BED: URANIUM-ZIRCONIUM FLUORIDES
GAS VELOCITY: 1.1 FT/SEC

latter (where high corrosion was observed) that was unique, such as the presence of a minor constituent or of a local metallurgical abnormality. It was noted in specimen 1 that "grain growth" had occurred in the regions of high attack. Perhaps the large grains were present initially and were responsible for accelerated attack, though one would not expect such acceleration unless grain boundaries were weakened through some other effect.

Preliminary evaluations have been made on one of the two strips constituting specimen 4. Exposure time was 32 hours at 600 C. In the region of the specimen ranging from elevation 0 to 32 inches, large regions of local attack were evident. The attack consisted of wide shallow

pits in areas of otherwise undisturbed metal and were generally located under tightly adherent film that was difficult to remove. Pit depth averaged about 1.0 to 1.5 mils. No accelerated attack was observed above an elevation of 32 inches.

During Runs U/Zr-6B to U/Zr-20 (total exposure period of 80 hours) coupons of nickel and nickel-base alloys were exposed in the bed. The results of the evaluations are shown in Table 15. Monel appears to be superior in having low rates of dimensional change and a small amount of intergranular attack. Inconel, though not subject to intergranular attack, did show excessive dimensional change. The normally protective film on Hastelloy B appears not to be protective when in contact with a fluid bed, as evidenced by very high rates of dimensional attack.

Table 15

CORROSION OF COUPONS EXPOSED IN FLUID-BED FLUORINATOR

Location: In bed
 Temperature: As noted
 Fluidizing Gas: 15% F₂ in N₂
 Runs: U/Zr-6B to U/Zr-20
 Coupon Area: 16.4 sq cm

Metal	Coupon	Time at 500 C (hr)	Time at 600 C (hr)	Weight Loss ^a (mg)	Dimensional Change ^b (mils/mo)	Inter- granular Attack (mils)
"L" Nickel	H12	60	20	324.3	7.9	2.4 to 3.8
	H2A			343.9	8.4	
"L" Nickel	H2B ^c	40	8	106.9	4.4	
	H2C			119.6	4.9	
Hastelloy B	BO1 ^c	20	12	2495.8	148	Not Evaluated
	BP1			2583.6	153	
Inconel	LR2	60	20	1356.0	35	None
	LS2			900.9	23	
Monel	MD3	60	20	69.6	1.7	0.4
	ME3			81.8	2.0	

^aAfter defilming in boiling ammonium oxalate.

^bAssuming linear rate of attack.

^cH2B and H2C replaced BO1 and BP1 after first 32 hours of exposure.

Scale removed from the reactor following Run U/Zr-8 was analyzed spectrochemically. An element found in the scale in a quantity not consistent with materials of construction or process feeds was manganese. Additional information is being obtained by analyzing other scales and feed materials, and relating the results to specific runs. The concentrations of minor constituents in the corrosion film are being determined by neutron activation and chemical spectroscopy.

B. Calcination of Reactor Fuel-Processing Wastes

The fluid-bed waste calcination process consists of the conversion of liquid wastes from solvent extraction processes into solids by means of a heated fluidized bed. The calcined wastes, whose volume is lower than the volume of the liquid by a factor of eight, are withdrawn and stored. Prior to atmospheric discharge, the off-gases are treated to remove entrained and volatile fission products. During the past quarter additional tests of the efficiencies of the venturi scrubber and of the silica gel adsorber were performed, using spike feed of from 250:1 dilution to 8:1 dilution. The experimental equipment has been described in a previous report (ANL-5896, page 66).

1. Pilot-Plant Studies

(J. W. Loeding, E. L. Carls, C. Schoffstoll, R. Beck,
W. D. Turner, J. Wehrle)

a. Ruthenium Decontamination Factors

Tables 16 and 17 summarize the data from several spike runs, including extended 85-hour and 21-hour runs, involving various dilutions of ICPP waste at calcination temperatures of 400 C and 500 C. The average factors for the decontamination of ruthenium from feed through adsorber for all of the runs are in excess of 10^3 . The highest average ruthenium decontamination factor, obtained in Run HWC-62 (500 C), was in excess of 10^4 . Nearly all of the ruthenium decontamination was achieved in the adsorber. The absence of ruthenium in the venturi recycle streams during the 500 C runs, as well as the difference between the amount of ruthenium found in the product at the two temperatures, clearly demonstrates the effectiveness of the higher temperature in suppressing volatility of ruthenium. If necessary, considerably higher removal of ruthenium can be achieved by partial condensation of the off-gases, as shown by decontamination factors for total activity of greater than 10^6 obtained from the feed through the condenser.

Table 16

DECONTAMINATION FACTORS OBTAINED IN
WASTE CALCINATION SPIKE RUNS

			<u>Feed</u>		
			<u>Runs 61, 62</u>	<u>Runs 64 to 69</u>	
Dilution of ICPP Waste			250:1	100:1	
Gross γ , cpm/ml			1.1×10^6	3.0×10^6	
Ru γ , cpm/ml			4.9×10^4	1.1×10^5	
<u>Average Decontamination Factors</u>					
<u>Run No.</u>	<u>Bed Temp (C)</u>	<u>Run Duration (hr)</u>	<u>Feed Thru Adsorber</u>		<u>Feed Thru Condenser</u>
			<u>Ru</u>	<u>Non-Volatile</u>	<u>Gross γ</u>
HWC-61	400	6	3.9×10^3	2.9×10^4	2×10^6
HWC-62	500	6	1.7×10^4	7.7×10^4	4×10^5
HWC-64	400	6	6.7×10^3	1.3×10^5	3×10^7
HWC-65	500	6	1.6×10^3	5.0×10^4	4×10^6
HWC-66	400	85	2.8×10^3	5.6×10^4	2×10^7
HWC-69	500	21	8.3×10^3	6.6×10^4	3×10^6

Table 17

PERFORMANCE OF VENTURI SCRUBBER AND SILICA GEL ADSORBER

(For run conditions, see Table 16)

Run No.	Activity Collected, % of Feed				Efficiency for Particulate Removal from Gas %		Ru in Product, % of Feed
	Venturi Scrub Soln		Adsorber		Scrubber	Adsorber	
	Ru	Non-Vol	Ru	Non-Vol			
HWC-61	39.3	0.014	~60 ^b	0.24 average	64 average	98.8 average	5.0
HWC-62	N.D. ^a	0.64	~2.5 ^b				73
HWC-64	32.5	0.64	~60 ^b				5.7
HWC-65	N.D. ^a	0.40	~2.5 ^b				70
HWC-66	23.4	1.73	105	0.19	90.0	98.4	6.2
HWC-69	N.D. ^a	14.2	2.5	0.32	97.8	99.2	c

^aNot detectable - less than 2 per cent of feed.

^bAmount determined by backwash after Run HWC-65. Distribution estimated from Ru content of venturi scrub stream and from backwash data after Run HWC-69.

^cAnalytical results not available.

b. Non-Volatile Decontamination Factors

The efficiencies of removal of particulate radioactivity passing through the sintered stainless steel filters were determined for both the venturi scrubber and the silica gel adsorber. The calciner is equipped with Purolator convoluted stainless steel filters, which are known to be inferior to the original Micrometallic bayonet-type stainless steel filters. That the new filters were in an increasing state of decay was evidenced by the percentage of feed non-volatile activity in the venturi scrubber recycle stream increasing over the six runs from 0.014 to 14.2. The passing of particulate matter by the filters, although unplanned, became advantageous as it allowed the investigation of the efficiency of the equipment in removing non-volatile activity from the calciner off-gas. The particulate removal efficiency of the venturi scrubber ranged from 64 to 98 per cent. The lower efficiency of the scrubber occurred during the earlier runs with essentially new filters, which passed markedly less particulate, as well as that of a smaller size distribution. The amount of non-volatile activity leaving the venturi scrubber varied only slightly from run to run (0.2 to 0.3 per cent) despite the very large (thousand-fold) variation in dust loading of the input gas.

The silica gel adsorber not only removed volatile ruthenium from the off-gas, but also acted as a filter, reducing the amount of non-volatile activity by a factor of about 100, while the combined efforts of the calciner and scrubber reduced the non-volatile activity by a factor of approximately 600. The average non-volatile decontamination factor (as noted in Table 16) from feed through adsorber for all of the runs ranges from 2.9×10^4 to 1.3×10^5 .

Samples of the off-gas taken after the condenser indicated that the decontamination factor for total activity from feed through the condenser was in excess of 10^6 . Gamma-ray spectrometer analysis of samples taken during Run HWC-66 (400 C) indicated that approximately 25 per cent of this activity was due to cerium and 75 per cent due to ruthenium. The presence of cerium in the off-gas is due to the passage of particulate activity from the calciner into the off-gas manifold. The absence of cesium activity suggests that the cesium was leached out by liquid contact either in the scrubber or in the condenser. This is supported by the fact that the solids in the venturi scrub solution were found to contain primarily cesium activity when separated from the liquid by filtration.

The most active run to date, HWC-72 at 400 C, was made with a feed consisting of an 8:1 dilution of ICPP waste. This resulted in a feed with gross gamma of 2.8×10^7 cpm/ml and ruthenium gamma of 9.8×10^5 cpm/ml. Operations were satisfactory and beta-gamma radiation survey meter readings of condensate and off-gas samples taken during the

run were about the same as those detected in 100:1 dilution runs. Assuming correspondingly low analytical results from these effluent streams, the decontamination factors may be higher by a factor of ten than those reported for previous runs.

c. Silica Gel Adsorber Regeneration

During this series of spike runs the silica gel adsorber was regenerated three times. All three backwashes were done by spraying water intermittently into the top of the adsorber and allowing it to drain through the silica gel. Each incremental volume of water was equal to approximately 0.25 bed volume of the silica gel. The temperature of the adsorber was maintained at approximately 70 C during the backwashes. In all cases 1.75 bed volumes of water were sufficient to remove better than 99 per cent of the removable ruthenium, the first 0.5 bed volume removing 96 per cent or better. The adsorber was backwashed after Run HWC-65, at which time it contained activity from the first four spike runs. Total ruthenium activity removed amounted to an average value of 31 per cent of the ruthenium fed to the calciner for the four runs. Because HWC-62 and HWC-65 were 500 C runs and because of the absence of ruthenium in the venturi scrub solution for these runs, the bulk of the ruthenium is undoubtedly attributable to the 400 C runs, HWC-61 and HWC-64. Results from later backwashes led to estimated values of 2.5 per cent for the 500 C runs and 60 per cent for the 400 C runs. The next backwash, performed after the extended 85-hour run (HWC-66), yielded 105 per cent of the ruthenium fed to the calciner during this run, giving a material balance of 135 per cent. Evidently some of the ruthenium had accumulated from previous runs and was not completely removed in previous regenerations of the silica gel.

d. Venturi Scrubber Recycle Stream Acidity

An analysis of data from the runs which utilized the venturi scrubber system has been made in an attempt to determine the cause of deviations from a previously reported steady-state level of 4.8 M acid in the recycle stream. The acidity of the recycle stream is dependent upon the partial pressures of nitric acid and water vapor in the vapor phase above the liquid stream. If the operation of the scrubber were such that complete conversion of the oxides of nitrogen to nitric acid in the vapor phase could be effected, the equilibrium acid molarity of the recycle stream would be about 12 M. Since the physical characteristics of the scrubber are such that complete conversion is not attained, the steady-state acidity level of nitric acid in the recycle stream will be below this value. Experimental data have shown that with the nominal operating conditions as stated in the previous reports, the steady-state acid molarity of the recycle stream varies between 4.6 M and 5.1 M for the majority of the runs. Deviations from this range are due to fluctuations

of one or more variables, such as temperature, pressure, and composition of off-gas from the calciner. One of these variations or a combination of them has been observed in several runs in which disparities in recycle acid concentration have been noticed. For example, calculations indicate that the lower average feed rate during Run HWC-66 (about 10 per cent less than that of previous runs) was sufficient to account for the observed rise in scrub solution acid molarity from 4.7 M to 7.5 M.

e. Equipment Changes

Modifications in the existing equipment have been initiated to accommodate a new filtering and blowback head similar to that previously described (ANL-5858, page 45). There are provisions in the head for up to ten filters which may be automatically blown back in any desired sequence. Testing of this head, prior to installation, is being performed currently. Installation will proceed in the near future.

f. Future Work

Additional work regarding the suppression of ruthenium volatilization at low bed temperatures by the addition of a catalyst to the feed for the waste calciner is contemplated.

Work on the fluid-bed calcining of a concentrated Hanford Purex Waste is also contemplated. Feasibility studies will be started following equipment changes.

2. Corrosion Studies

(W. B. Seefeldt, R. Breyne, L. Hays)

A program to determine the nature, cause, and methods of prevention of the corrosion that was observed in the sintered stainless steel (type 316) filters of the pilot-plant calciner has been instituted. Experimental equipment to simulate calciner operation was constructed. This was described in ANL-5924, page 83.

Results of the first few runs previously reported were not conclusive - corrosion patterns defining the cause of the attack did not evolve. The apparatus was revised after Run WC-8 because difficulties were experienced with some equipment items. A new preheater, consisting of a coil of type 309 stainless steel tubing in a furnace, was substituted for the old unit, and the line between the preheater and the specimen furnace was also heated.

Further efforts were made to determine qualitatively the severity of corrosion of sintered stainless steel by nitrogen or air at 550 C. The results are shown in Table 18. In Run WC-9, the specimen

Table 18

**RESULTS OF CORROSION TESTS OF SINTERED STAINLESS STEEL TYPE 316
EXPOSED TO SIMULATED OFF-GASES OF WASTE CALCINATION PROCESS**

ΔP across test section: 6 to 8 inches of water
 Specimen pretreatment: Degreased in acetone and ethyl alcohol
 Temperature: 550 C
 Vapor Composition: 3 M HNO₃ vaporized into gas indicated

Run No.	Duration of Run (hr)	Gas	Gas Rate (l/min)	Acid Rate (ml/min)	Metallography and Comments
WC-9	134 ^a	N ₂	2.7	1	General corrosion observed at 100X; attack was greater than that in Run WC-4, but less than that observed in fractured filter from pilot-plant unit.
WC-10	24	None	-	1	Slight corrosion observed at 100X.
WC-11	141	Air	2.55	1	General corrosion observed through entire section, though not quite as severe as in Run WC-9

^a Specimen was exposed to acid vapors without nitrogen for additional 25 hours due to exhaustion of nitrogen during week end test.

was exposed to nitric acid vapors in nitrogen for 134 hours. During an additional 26 hours, exposure only to acid vapors occurred when the nitrogen supply became exhausted over a week end. Metallographic evaluation revealed severe general corrosion easily observable at a magnification of 100X; this corrosion penetrated the entire cross section. The severity was greater than that seen in Run WC-4 (see ANL-5924, page 83). To ascertain the relative amount of corrosion caused by the inadvertent exposure to nitric acid vapors alone, Run WC-10, in which the nitrogen gas was omitted, was made. Twenty-six hours of exposure resulted in slight general attack. From this, one can conclude that the attack in Run WC-9 resulted in greater part from the 134 hours of exposure to the nitrogen-acid vapor mixture. In addition, it appears that the acid alone is capable of corroding the stainless steel in a comparable manner at this temperature.

In the subsequent run (WC-11) the nitrogen was replaced with air. Exposure was for 141 hours at 550 C. General corrosion was observed through the entire section, although it was not quite as severe as with the nitrogen diluent.

Control of the equipment and of the operating variables was good during these runs. It can be qualitatively concluded from these results that 3 molar nitric acid vapors diluted with air or nitrogen at 550 C can cause the type of attack observed in the fractured bayonet filters of the pilot-plant unit. Temperatures of this magnitude were observed in the filter chamber of the pilot-plant unit only in those runs in which carbon monoxide gas was employed to destroy the nitric acid. Under normal conditions the temperature of the filter chamber is approximately 300 C. Future efforts will be directed to the effect on corrosion of operation at a lower temperature (400 C), and the effect of substitution of part of the diluent (nitrogen or air) with carbon monoxide.

C. Fundamental Studies

1. Mixing Studies in Straight and Tapered Fluidized Beds (H. Littman)

Several series of runs dealing with a radioactive tracer study of solids mixing in the straight wall fluid-bed column (described in ANL-5858, pages 51 and 53) using dry air at room temperature as the fluidizing medium have now been completed. Bed heights of 16 and 32 inches were used for each of the two size fractions of copper spheres, -20 to +40 and -140 to +200 mesh. Investigations also included the effect of gas velocity and counter location. Similar sets of runs will be made in the tapered column and the data will then be evaluated. A mathematical solution to describe the mixing in the tapered bed will be sought. Evaluation of data is underway and a topical report is in preparation.

2. Factors Influencing Particle Growth in a Fluid-Bed Calciner (B. Lee)

A study of the mechanism of particle growth during operation of the fluid-bed calciner is underway. Efforts have been made to determine the amount of feed liquid deposited on each particle during a single traverse through the spray zone. Colored feed solutions, containing potassium permanganate as coloring agent, were sprayed onto particles of sodium carbonate. Particles from runs of various duration were mounted in Lucite and examined microscopically, but no clear growth rings were observed. Future work will include studies with radioactive tracers in an attempt to determine the fraction of particles contacted by the spray and the amount of liquid deposited on the particles as a function of operating time for very short periods of operation.

III. REACTOR CHEMISTRY

The program to clarify the factors governing the pyrophoric characteristics of uranium, zirconium, thorium, and plutonium has continued with fundamental studies of kinetics and mechanism of oxidation. In air the use of the burning curve and shielded ignition techniques for uranium has not aided the establishment of a specific area dependence in air. However, a partial insight as to the phenomena observed in air was provided by measuring the maximum burning temperature of 8.5-mm cubes in various gas mixtures. The maximum burning temperature decreases as the oxygen content of the oxidizing gas is decreased. In sufficiently dilute oxygen mixtures ignition of 8.5-mm cubes, as such, is not noticeable at all.

Experiments to measure the rate of propagation of burning of strips of metal foil have been initiated. The factors which cause either a sufficiently fast propagation to constitute an explosion or a sufficiently slow propagation to facilitate control of the reaction are believed to be important. The dependence of the rate of propagation on the thickness of foils has been established for uranium in air and oxygen. Although additives to uranium have a very limited effect, additives to zirconium have a pronounced effect, on the propagation rate.

A linear correlation has been demonstrated between the shielded ignition temperatures of zirconium alloys and the oxygen consumed in the first minute, as obtained from the isothermal oxidation data. Such a correlation allows the prediction of ignition temperatures from isothermal oxidation data. The existence of this correlation is important since isothermal experiments are easier to duplicate by various investigators.

Considerations of the relationship of the breakaway phenomena and the initial cubic rate constant of the oxidation of zirconium and its alloys to earlier literature, theories, and mechanism are presented.

A. Metal Oxidation-Ignition Kinetics

(J. G. Schnizlein, H. A. Porte, P. J. Pizzolato, J. D. Bingle, D. F. Fischer, L. W. Mishler, P. Martin, C. A. Bayens,* L. Leibowitz, and R. C. Vogel)

1. Uranium Ignition Studies

a. Specific Dependence Upon Area of Uranium in Air

The effect of specific area on the ignition temperature for uranium and certain uranium alloys in oxygen has been reported (ANL-5858, page 55, and ANL-5924, page 91). A series of experiments was also completed in an effort to observe a specific dependence upon area in air.

*Cooperating Institution Student from Detroit University.

Samples of Battelle-base uranium and alloys of 1 atom per cent aluminum and 1 atom per cent copper were run as 8.5-mm and 3.5-mm cubes and as 10-mil foil. Argonne-base uranium was run as 8.5-mm and 3.5-mm cubes. Many of the burning curves were very complex, due to the previously reported (ANL-5924, page 93) tendency for samples to thermocycle rather than ignite spectacularly, and no conclusion could be reached with respect to a specific dependence upon area.

Because of this difficulty in determining the ignition temperature of uranium in air, using the burning-curve method, an attempt was made to obtain ignition temperatures by the plunging technique. This is the method that has been successfully employed to determine the ignition temperature of zirconium foils in air and oxygen. It consists of rapidly inserting the foils into a heated furnace under a blanket of flowing helium, and then, as soon as the sample has reached an equilibrium temperature, admitting the air or oxygen. It is a "go" or "no-go" type of experiment, that is, the metal either ignites or it does not. A series of such runs can therefore pin down the ignition temperature quite accurately.

However, when used with 0.25-mm (10-mil) uranium foils, this method had about the same success as the burning-curve technique. With oxygen there was a sharp distinction between the "go" and the "no-go" runs, but when air was used, no such difference was observed. The foils would heat somewhat and then immediately the temperature would drop back to the original value. Examination of the samples after these runs revealed them to be still predominantly metal covered with a heavy oxide coating. These "used" samples showed definite ignitions in subsequent runs in oxygen, thereby demonstrating that they had not been completely consumed when run in air.

Figure 13 shows runs in oxygen and runs in air for 10-mil Battelle-base uranium foil, and the difference between experiments in the media is apparent. Figure 14 compares runs in air for one atom per cent copper and one atom per cent aluminum alloys of uranium with the Battelle-base metal at various temperatures. The one atom per cent aluminum alloy seems to rise to slightly higher temperatures than the other two metals when air is admitted at 450 C, but at higher temperatures the difference is negligible.

b. High-Temperature Oxidations of Uranium in Air

Hanford investigators have been studying the oxidation of uranium at elevated temperatures. Because these temperatures are in the region in which we have been investigating the ignition of uranium, a series of experiments was conducted, both to determine the agreement with the Hanford data and also to see if there was any fundamental difference from our burning-curve data.

A brief description of the Hanford runs⁴ is presented here: "Tests have shown that after an immediate, moderate temperature increase when the air is admitted, the temperature drops quickly to a level somewhat above the furnace temperatures. At temperatures between 400 and 700 C, the reaction proceeds linearly for a period of time until a definite, sharp, large temperature peak occurs. This peak lasts only a few minutes, but is repeated in a cyclic manner until the sample is entirely consumed..... At 700 C and above, the temperature increases immediately....."

⁴Private communication, R. K. Hilliard, General Electric Co., Hanford Atomic Products, Richland, Washington.

Essentially, our experiments were shielded ignition tests in which the temperature of the sample was followed until it was completely consumed. Most of the runs were carried out in the quartz ignition apparatus (ANL-5924, page 89), although a few were done using the regular burning-curve apparatus, in which the air is somewhat preheated, for comparison purposes. Figure 15 shows the first 45 minutes of runs with initial sample temperatures of 500, 620, 700, and 800 C. These runs tend to follow very closely the description of similar experiments at Hanford. Also, it is evident that they show essentially the same characteristics as the burning-curve experiments in air - a tendency to thermocycle rather than to ignite spectacularly.

Table 19 compares the times to cyclic burning for these runs with those reported by Hanford. Maximum temperatures reached during the runs are also recorded.

In addition, two runs of a similar type were done on the Stanton thermobalance with an initial temperature of 500 C. The first was done to determine the approximate rate of oxidation and the second to record the temperature trace of the sample during the run. Since, with this apparatus, it was not possible to weigh the sample and record its temperature at the same time, it was necessary to do two runs. Figure 16 shows a combined graph of weight gained versus time for the first run and the sample temperature versus time for the second run. The weight-gain plot indicates a fairly linear oxidation rate of 1.04 mg/(sq cm)(min) until the run was terminated at 60 minutes. However, at approximately seven minutes and twenty minutes there are brief increases in this rate to about

Table 19

URANIUM OXIDATION IN AIR AT ELEVATED TEMPERATURES

2300 cc/min Air

Sample Size: Hanford - 3/4 in. by 1/4-in. diameter cylinders
 Quartz app - 1-cm cubes

Starting Temp (C)	Time to Cyclic Burning (min)		Maximum Temperature Reached (C) (No Hanford data available) Quartz Apparatus
	Hanford	Quartz Apparatus	
400	180		
500	80	120	596
620	28	31	946
700	0	13	1086
800		0	{ 1101 1330 ^a >1400 ^b >1400 ^a
		0 ^a	
		0 ^b	
1000		0 ^a	

^aBurning-curve apparatus, 1-cm cube, 6000 cc/min in air.

^bBurning-curve apparatus, 8.5-mm cube, 6000 cc/min in air.

2 mg/(sq cm)(min). It can be seen that there are two small humps at almost exactly the same times on the temperature trace plot. This plot also shows that very high-temperature humps began to occur in the second run at about the same time that the first run had been terminated. The different heat-balance characteristics for each apparatus may explain why these high-temperature excursions occurred on the Stanton thermobalance run while the 500 C runs in the quartz apparatus and the ignition apparatus showed much smaller temperature increases during the cyclic portion of the runs.

c. Maximum Burning Temperatures

It has been shown in the preceding sections of this report that there were some apparent differences between the ignition of uranium in oxygen and in air. Chief among these differences seemed to be the tendency of samples to thermocycle in air at rather moderate temperatures, while in oxygen the sample temperature rose above the range of the thermocouples being used and appeared to remain there until they were consumed. A series of experiments was run, utilizing a rhenium-tungsten thermocouple capable of recording 2200 C in a non-oxidizing atmosphere, to determine whether the maximum temperature that the samples reach after ignition (the burning temperature) is related to this difference and also to determine the relation of this burning temperature to gas composition. The thermocouples were coated with Sauereisen adhesive cement to protect them as much as possible from the oxidizing atmosphere.

Burning-curve-type experiments were performed using 8.5-mm cubes of Argonne-base uranium in oxygen, in oxygen-helium mixtures, and in oxygen-nitrogen mixtures. Figure 17 shows one such typical run from which it can be seen how both the ignition temperature and the maximum burning temperature have been determined. One can also see from this figure that the thermocyclic phenomenon still is present even though the sample temperature rises to 1660 C. In fact, there is evidence that the sample goes through these temperature cycles even in pure oxygen, where the maximum burning temperature is 2150 C or higher, although the thermocouples usually failed after a short time above 2000 C.

In all of these experiments a constant flow rate (1200 cc per min) of oxygen was used in the gas mixture to give assurance that the decrease of the maximum burning temperature with decreased oxygen percentage was not caused by the lack of oxygen. This means that for the experiments with low oxygen composition the total flow of gas was quite high. Neither the maximum burning temperature nor the ignition temperature was found to be affected by the larger total flow rates of gas. For example, in the case of a 30 per cent oxygen-70 per cent helium mixture, doubling the total flow rate from 4000 to 8000 cc/min gave an almost identically shaped burning curve, including the thermocyclic phenomenon.

In Figure 18 is plotted the maximum burning temperature versus gas composition, combined with the plot of ignition temperature shown in Figure 24 of ANL-5924. From it one can see that there is no sharp distinction between ignition in oxygen and the phenomenon observed in air. There seems rather to be a gradual lowering of the burning temperature with decreased oxygen content. When the burning temperature approaches the ignition

temperature, it is obvious that the ignition becomes much less of a spectacular phenomenon. When the two temperatures coincide, then ignition, as such, is not noticeable at all.

Additional experiments in oxygen have shown that the one atom per cent aluminum and two atom per cent copper, while having, respectively, much lower and much higher ignition temperatures than pure uranium, have approximately the same maximum burning temperatures as pure uranium.

d. Uranium Powder Ignition in Oxygen

It has been postulated that, in addition to the ignition temperature of uranium being a function of the ratio of area to mass, there also may be a total mass dependence, especially in considering uranium powders. Anderson and Belz⁵ have reported such a total mass dependence for zirconium powders. They observed that a 1-gram sample of zirconium powder ignited at a higher temperature than 2 grams of the same powder. They also theorized on probable causes for total mass dependence.

⁵Anderson, H. C. and Belz, L. H., J. Electrochem. Soc. 100 240 (1953).

In an attempt to see whether the uranium powder obtained from our hydriding experiments (ANL-5896, page 83) gave any indication of such a total mass dependence, burning curves were run in oxygen on three samples of this powder which had different total weights. The data obtained from these runs are tabulated below:

<u>Weight of Sample</u>	<u>Observed Ignition Temp (C)</u>
0.307	120
0.464	130
0.913	125

It is quite evident that no indication of a total mass dependence is apparent from these experiments.

e. Uranium Burning Propagation Rate Studies

In addition to understanding the factors influencing the ignition temperature of a metal, it would be useful to understand the factors influencing and controlling the rate of burning propagation. If the propaga-

tion rate is sufficiently fast the ignition would constitute an explosion, whereas a slow propagation rate would indicate a greater ease in controlling or stopping the reaction. Foil strips of pure uranium metal, as well as certain uranium alloys, were used to determine the propagation characteristics of uranium burning in oxygen and air.

The apparatus which was designed and employed for the propagation studies is shown in Figure 19. A centimeter scale, with aluminum pins extending above each centimeter mark, was used to measure the distance traveled by the ignition front; this scale rests in two slots in the evaporating dish. The purpose of the dish is to catch any particles of the burning sample that might fall. The sample is held above and parallel to the scale by the

brass nut and bolt mount which is suspended by a heavy copper wire from a steel rod clamped to the ring stand. The resistance wire igniter, mounted on a piece of transite, is approximately six centimeters away from the nut and bolt assembly and is positioned either against or attached to one end of the sample - depending on the operating conditions. All of this equipment is enclosed in a sealed Lucite box lined with asbestos, except for the

front. The box is provided with a gas inlet and outlet. The back side of the box is a hinged door that can be secured with a wing nut. The edges of the opening in back are lined with rubber insulation to make it leak-tight.

The Lucite box and its contents are illuminated by two 500-watt photoflood lamps. The complete reaction is recorded by a Fastax camera to establish what occurs. The film speed is adjusted to suit the duration of the event by controlling the power input to the camera motors. Utilizing the timing device of this camera and the centimeter scale within the Lucite box, the number of centimeters that the burning progresses during one second (the velocity of the propagation) may be determined.

A series of experiments has been carried out, using the propagation apparatus described above, on uranium and certain uranium alloys. Six-centimeter lengths of various foils were ignited at one end in both oxygen and air, and the rate of propagation of the burning along the center 4-cm length of the sample was determined from films of the event taken with the Fastax camera. The variables studied thus far include sample thickness, surface preparation, and additive effects.

In air, there are two separate "fronts" that appear to move along the sample as the burning progresses from one end to the other. These are illustrated in Figure 20, which shows the sample after the burning has propagated part of the way along it. The first of these fronts we have called the "oxidation front," since it appears to mark the point where the sample begins to oxidize extensively due to the heat from the burning a short distance away. The oxidation front is quite distinct compared to the second front, which we have labeled the "ignition front." This front marks the point where the sample has been ignited and is glowing due to the burning of the metal. In some cases it is impossible to define clearly this ignition front due to the fact that it is too indistinct on the film of the event. In experiments where both fronts are apparent, they progress at approximately the same rate.

In oxygen, however, only the ignition front is visible (see Figure 21), undoubtedly because of the higher speed of propagation and the increased light emission from the burning sample.

Figure 22 presents a typical plot of the propagation rates of both the oxidation and ignition fronts for a 10-mil Battelle-base uranium foil in air. In a similar manner rates were determined for each of the other samples run. The preliminary data thus obtained are summarized in Table 20. In addition, Figure 23 shows a log-log plot of sample thicknesses vs propagation rates for these data. Straight-line relationships can be seen for samples both in oxygen and air. It should be emphasized, however, that the 1.73-mm thick strip did not propagate when ignited in air. Perhaps there is a critical burning propagation rate of approximately 0.1 cm per sec.

FIGURE 20
BURNING OF URANIUM IN AIR

A OXIDATION FRONT B IGNITION FRONT

FIGURE 21
BURNING OF URANIUM IN OXYGEN

Table 20

URANIUM BURNING PROPAGATION RATES

Samples were 3 mm wide and 6 cm long and were polished with 600 grit SiC, unless otherwise noted.
(Each run listed separately.)

Thickness (mm)	Metal	Burning Propagation Rates		Average Distance Between Fronts (cm)
		Oxidation Front (cm/sec)	Ignition Front (cm/sec)	
		<u>In Air</u>		
0.03	Uranium ^a	<u>-b</u>	1.71	<u>-b</u>
0.13	BMI Base	0.509	0.519	0.53
0.13	Uranium ^a	0.553	0.549	0.40
0.13	Uranium ^a	0.585	0.571	0.52
0.13	Uranium ^a	0.512	0.506	0.47
0.23	ANL Base	0.355	0.354	0.67
0.25	BMI Base	0.341	<u>-b</u>	<u>-b</u>
0.25	BMI Base	0.363	0.363	0.65
0.25	BMI Base ^{c,d}	0.291	0.292	0.72
0.25	Uranium ^a	0.386	0.386	0.60
0.25	1 a/o Al	0.327	0.346	0.62
0.25	1 a/o Cu	0.319	<u>-b</u>	<u>-b</u>
0.48	ANL Base	0.241	0.237	1.00
1.00	Uranium ^a	0.125	<u>-b</u>	<u>-b</u>
1.73	ANL Base (as cast) ^e	- - - - -	Did Not Propagate	- - - - -
		<u>In Oxygen</u>		
0.03	Uranium ^a		24.5	
0.13	BMI Base		5.78	
0.13	Uranium ^a		6.04	
0.13	Uranium ^a		5.33	
0.23	ANL Base		2.99	
0.25	BMI Base		3.10	
0.25	BMI Base ^d		2.10	
0.25 ^f	BMI Base ^g		1.28	
0.25	Uranium ^a		3.75	
0.25	1 a/o Al		3.24	
0.25	1 a/o Cu		2.83	
0.48	ANL Base		1.46	
0.48 ^f	ANL Base ^g		0.54	
1.00	Uranium ^a		0.972	
1.73	ANL Base (as cast) ^e		0.634	
3.40	ANL Base (as cast) ^e		0.293	

^aUranium foil obtained from Special Materials Division, ANL; not further characterized at present.

^bThe front is not clearly defined on film of the event.

^cWedge-shaped strip varying in width from 2.0 to 7.6 mm over that portion of the sample used in determining propagation rates.

^dUnpolished.

^eLength of sample only 3.5 cm.

^fOriginal thickness before previous ignition in air.

^gPreviously ignited in air.

Equations expressing the relationships shown in Figure 23 are as follows:

$$\text{In air: Rate} = \frac{0.137}{B^{0.696}}$$

$$\text{In oxygen: Rate} = \frac{0.890}{B^{0.801}}$$

where B is sample thicknesses in mm and Rate is the burning propagation rate in cm per sec.

A number of conclusions can be drawn from the work thus far:

1. The propagation rate in oxygen is about 10 times the rate in air. This is probably due to the much higher burning temperature in oxygen.
2. Duplicate samples indicate satisfactory reproducibility. The average deviation is less than five per cent from the mean.
3. A dependence of the propagation rates upon sample thickness, both in oxygen and in air, has been established.
4. The one percent aluminum and one per cent copper alloys show very little difference in propagation rates from the base metal, both in air and in oxygen. (It will be remembered that the ignition temperatures in oxygen for these three foils are the same.)
5. Ignition propagates somewhat faster, both in oxygen and in air, using polished samples rather than unpolished ones.
6. Samples which had ignited and burned in air contained enough metal at the conclusion of the runs so that they could be re-ignited in an oxygen atmosphere.

Work is now under way to determine the effect of gas contaminants and also metal surface contaminants on the propagation characteristics of uranium.

2. Uranium Isothermal Studies

a. Microscopic Observations

As previously reported (ANL-5924, page 95) the progress of the oxidation of a uranium sample was followed visually, using the microscope, while the oxygen consumption was measured by means of the volumetric apparatus. Study by this hot-stage microscopic technique has been limited to magnifications of about 200 times by the requirement of a long-working distance objective. It was felt that the information obtained in this earlier work might possibly be supplemented by microscopic examinations at higher magnification.

In order to accomplish this, the oxidation of an electro-polished uranium sample in the volumetric apparatus at 200 C in 200 mm of oxygen was interrupted at intervals and the sample removed for microscopic examination. So that the same field might be relocated each time the sample was examined, one face of the cube was marked initially by means of a platinum wire embedded in the surface.

From this experiment it appears that the interruptions in the oxidation, involving evacuating the reactor, cooling of the sample, handling in the laboratory atmosphere, reheating, etc., caused no change in the characteristic two-stage oxidation. However, there is a noticeable effect on the manner in which the oxide surface changes during the reaction. Although there was some growth of the oxide nuclei which formed very early, i.e., during heat-up in vacuum, the principal observable change under these conditions seems to be a gradual over-all roughening of the surface by an increase in the number of oxide nuclei.

Study of the oxide film after transverse sectioning revealed layers similar to those previously reported (see ANL-5789, Figure 17). The relative thicknesses of these layers suggested that the discontinuities are associated with the interruption in the oxidation. This layering effect may account for the somewhat different way in which the surface is changed during oxidation when interruptions in the reaction are involved.

Experiments were carried out to determine which operation or combination of operations involved in such interruptions is responsible for the observed discontinuities in the oxide layer. The oxide coating produced in an oxidation in which the interruption entailed only evacuation of the reactor was examined in transverse section; there was no evidence of layering attributable to the interruption. When the interruption entailed cooling the sample to room temperature as well as evacuation of the reactor, the resulting oxide film consisted of two layers (see Figure 24). The relative thicknesses of these layers were such that the discontinuity was clearly associated with the interruption.

FIGURE 24
SECTION OF OXIDIZED URANIUM SAMPLE SHOWING
INTERFACE IN OXIDE COATING RESULTING FROM AN
INTERRUPTION OF THE REACTION

A further experiment indicated that the observed layering effect is caused by the cooling and/or reheating of the sample alone. In this experiment the interruption involved cooling the sample to room temperature and reheating to 200 C, while maintaining 200 mm of oxygen pressure. Examination of the oxide film in transverse section again revealed the presence of two layers whose relative thicknesses show definitely a connection with the interruption.

b. Oxidation in Activated Oxygen

In exploring various factors which might influence the course of uranium oxidation, two runs were carried out at 200 C in 20 mm oxygen pressure, during which a Tesla coil was used to produce a discharge in the gas. Although there was poor quantitative agreement between the two runs, it was clear that the rate of oxidation was increased markedly over a control run, by the application of the discharge. The average rates of oxygen consumption, in $\mu\text{g}/(\text{sq cm})(\text{min})$, for the early stages of these runs were 0.3 for the control and 2 and 8 for the two Tesla-coil runs.

Other workers have observed similar effects of activated gases or heterogeneous chemical reactions. Tiapkiha and Dankow⁶ found an enhanced oxidation of silver resulting from an electric discharge in oxygen. A similar increase in oxidation rate was found in the more detailed

⁶ Tiapkiha, V. V. and Dankow, P. D., Doklady Akad. Nauk. SSSR. 59, 1313 (1948).

work of Natarova.⁷ Law⁸ found that application of a Tesla coil to the gas phase increased adsorption rates in a number of systems, including oxygen on copper, magnesium, and aluminum. Fryburg⁹ and Dravnieks¹⁰ both used oxygen activated in a Woods discharge tube in studying rates of metal oxidation. Fryburg found oxygen atoms to be some four hundred times more effective in causing oxidation of platinum. Dravnieks found copper to be influenced in a complex way by the oxygen atoms, with the effect on oxidation rate depending on temperature. For a number of other metals he found no marked effect.

In view of these findings and of our interest in elucidating the mechanism of the uranium oxidation, as well as exploring factors which may be of concern in metal-ignition problems, further experiments of this kind will be carried out. Ionization of the gaseous atmosphere is a phenomena which will be encountered with irradiated materials. Electric discharge and photoactivation equipment is currently being assembled to provide more refined means of activation.

3. Zirconium Ignition Studies

a. Shielded Ignition Studies

(1) Apparatus Modification

The shielded-ignition apparatus has been rebuilt entirely of quartz, instead of mullite and Pyrex, to eliminate leakage, decrease the volume of the system and facilitate replacement of damaged reactor tubes. A complete description of the apparatus and procedure was reported previously (ANL-5896, pages 93 to 98).

Because this modification caused the ignition temperature of a few alloys to be lowered as much as 20 degrees, the ignition temperatures of all the alloy foils were redetermined in both oxygen and air. The revised ignition temperatures are reported, together with values for several additional zirconium alloys and titanium, in Table 21. Repeated tests indicate a reproducibility within 5 degrees. In cases for which the dependence of ignition temperatures upon flow rate in air was examined (see following section), the lowest ignition temperature obtained is reported. In almost every case the ignition temperatures in air were the same (within experimental error) as those in oxygen.

⁷ Natarova, R. I., Zhur. Fit. Khim. 32, 79 (1958).

⁸ Law, M. J. D., J. Electrochem. Soc. 104, 439 (1957) and 105, 103 (1958).

⁹ Fryburg, G. C., J. Chem. Phys. 24, 175 (1956).

¹⁰ Dravnieks, A., J. Am. Chem. Soc. 72, 3761 (1950).

Table 21

SHIELDED-IGNITION TEMPERATURES OF ZIRCONIUM
AND ZIRCONIUM ALLOYS IN OXYGEN AND IN AIR

All alloys and pure titanium were 0.13-mm (5-mil) foils; pure zirconium as noted.
Flow rates for oxygen ignitions: Helium, 5200 cc per min; followed by oxygen, 3050 cc per min.
Flow rates for air ignitions: Helium, 1900 cc per min; followed by air, 4660 cc per min.
For conversion to linear flow rates: 1 cc per min = 0.20 cm per min.

Alloy Composition (Atom Per Cent)	Oxygen Ignition Temperature (± 5 C)	Air Ignition Temperature (± 5 C)	Isothermal Data ^a at 700 C in 200 mm Oxygen	
			Cubic Rate Constant, k $10^7(\mu\text{g}/\text{sq cm})^3/\text{min}$	Weight Gained First Minute ($\mu\text{g}/\text{sq cm}$)
Pure Zr (0.94 mm)	935	>1000	1.6, 0.97 ^b	236, 175 ^b
Pure Zr (0.28 mm)	833	849	1.6, 0.97 ^b	236, 175 ^b
Pure Zr (0.13 mm)	786	784	1.6, 0.97 ^b	236, 175 ^b
Pure Zr (0.025 mm)	665	641	1.6, 0.97 ^b	236, 175 ^b
0.91 Ni	792	794	1.5	245
3.60 Cu	784	800	0.78	195
1.76 U	765	766	4.1	284
1.84 V	763	764	Parabolic	332
3.60 Sn	759	767 ^c	1.2	205
2.15 Al	739	740 ^c	12.0	452
3.62 Al	753	754	8.0	546
1.08 Ti	694	698 ^c	69.7	624
2.12 Ti	634	632 ^d	251.	946
4.16 Ti	529	531	Parabolic	1400
14.9 Ti	372 ^e	374 ^d	^f	^f
Pure Ti	922	980	0.12	132

^a Isothermal studies of bulk samples were presented in ANL-5924, pages 101 to 105.

^b Isothermal run in air at 700 C and 1 atm.

^c Helium flow, 1450 cc per min.

^d Helium flow, 960 cc per min.

^e Helium flow, 1900 cc per min; oxygen flow, 2150 cc per min.

^f Ignition occurred when isothermal oxidation of bulk sample attempted at 700 C.

(2) Gas Flow-Rate Dependence

It has been shown previously that the flow rate of oxygen has little influence on ignition temperatures in oxygen. Most experiments were conducted with a protective flow rate of helium of 5200 cc per min, followed by an oxygen flow rate of 3050 cc per minute (620 cm per min linear velocity).

In contrast, the ignition temperatures in air were changed as much as twenty degrees Centigrade by varying the flow rates of both the helium and air. The lowest ignition temperatures in air were obtained with low flow rates of helium (960 to 1900 cc per min) and an intermediate flow rate (4700 cc per min) of air. The effect of various flow rates of helium and air upon the ignition temperatures of the

Table 22

THE EFFECT OF FLOW RATE ON THE AIR-IGNITION TEMPERATURE OF THE 3.60 ATOM PER CENT COPPER ALLOY OF ZIRCONIUM

0.13-mm (5-mil) foils;
protective helium flow followed by air.

Helium Flow Rate (cc/min) ^a	Air Flow Rate (cc/min) ^a	Air Ignition Temperature (C)
960	1400	806
960	3370	797
960	5490	798
960	7990	797
960	10300	802
1900	4660	800
4700	1400	812
4700	3370	799
4700	5490	799
4700	7990	799
8450	1400	830
8450	3370	812
8450	5490	812
8450	7990	817

^aVolume flow rate of 1 cc/min is equivalent to a linear flow rate through the reactor of 0.20 cm/min.

3.60 atom per cent copper (0.13-mm foil) is shown in Table 22. A partial study of the effects of flow rates on the ignition temperature of 4.16 atom per cent titanium (0.13-mm foil) and pure zirconium (0.03-mm foil) indicate the same general dependence.

(3) Surface Preparation
Dependence

The effect of surface preparation on ignition temperature in air was studied for the 0.13-mm (5-mil) foil of the 14.9 atom per cent titanium alloy. Foil in the "as received" condition produced the highest ignition temperature, 406 C; dry polishing with 600-grit silicon carbide paper produced an intermediate ignition temperature, 388 C; wet polishing with 600-grit silicon carbide paper produced the lowest ignition temperature, 374 C.

Therefore, all samples were prepared by wet polishing.

(4) Correlation of Ignition Temperatures with Isothermal
Data

A correlation of the ignition temperatures of zirconium alloy in oxygen has been attempted with several quantities extracted from isothermal rate data. Except for the nickel and copper, all of the alloys from which foils were made exhibited breakaway phenomena when oxidized at 700 C and 200 mm of oxygen. However, an apparent correlation could be seen between breakaway weights and ignition temperatures as reported in ANL-5896, page 97. A fair degree of correlation was obtained with initial cubic rate constants, but unfortunately the few alloys which oxidized according to the parabolic rate law could not be compared in this manner. A good correlation was found between ignition temperature and oxygen consumed in the first minute as calculated from the isothermal data (see Table 21). Figure 25 demonstrates that an inverse relationship was found. Since it was experimentally observed in the shielded ignition experiments that the foils which did ignite did so within the first few seconds after the oxygen was admitted, it is reasonable that at high temperatures the very initial rates of oxidation are most important in determining whether or not an ignition will take place.

Although isothermal rate data in air were obtained only for pure zirconium, the agreement of that one point with the correlation indicates the probable applicability of this correlation to studies in air. It may be recalled that the ignition temperatures of the alloys in air are very similar to those obtained in oxygen.

This relationship allows the prediction of ignition temperatures of new alloys from isothermal rate data. This is particularly important in that the conditions of an ignition experiment may be difficult to duplicate from investigator to investigator, but methods for obtaining isothermal rate data are comparatively easy to reproduce.

(5) Ignition Temperature Dependence on Specific Area

The ignition temperature of zirconium is dependent on the specific area of the metal. Previous studies of this effect (ANL-5896, pages 98 to 99) have been extended and a new relationship established.

As was expected, pure zirconium foil showed a decreasing ignition temperature with decreasing foil thickness, since the specific area (surface area per gram) increases with decreasing thickness. A plot of ignition temperature versus log specific area is illustrated in Figure 26. Included with the data from this work are data of other investigators found in the literature. A good straight line can be drawn through the points of the Anderson and Belz¹¹ powder data, Gulbransen and Andrew¹²

¹¹ Anderson, H. C. and Belz, L. H., J. Electrochem. Soc. 100, 240 (1953).

¹² Gulbransen, E. A. and Andrew, K. F., J. Metals 9, 394 (1957).

0.13-mm (5-mil) foil datum, Hayes and Roberson¹³ 1.6-mm (63-mil) sheet datum, and the points of this investigation on 0.025, 0.13, 0.28 and 0.94-mm (1, 5, 10, and 37-mil) zirconium metal foils. The slope and intercept of the line yield the relationship

$$T_{\text{ig}} = 1070 - 208 \log A/m$$

where T_{ig} is the ignition temperature (C) and A/m is the specific area (sq cm per gram).

The datum reported by Garibotti, Green and Baldwin¹⁴ on 0.76-mm (30-mil) sheet appears high. This may possibly be due to contamination of the surface prior to the experiment.

DeHollander's¹⁵ point appears to fall far below the line. The datum was obtained in air, using a technique in which lathe turnings, wrapped around a thermocouple, were thrust into a furnace. Ignition was defined by a flow of the sample and an inflection in the temperature-time curve. It was observed that only when the furnace temperature was above 750 C would ignition occur. Thus, if the ignition temperature was defined as 750 C instead of 400 C as reported, the point would be in very good agreement with the ignition temperature line in the figure. This emphasizes that the ignition temperature is not an intrinsic property of a metal but must be defined in terms of the experiment.

¹³ Hayes, E. T. and Roberson, A. H., J. Electrochem. Soc. 96, 149 (1949)

¹⁴ Garibotti, D. J., Green, H. M. and Baldwin, W. M., Jr. AECU-3013 (1955)

¹⁵ DeHollander, W. R., BW-44989 (1956).

Table 23

ELECTRICAL HEATING IGNITION EXPERIMENTS IN OXYGEN

Specimen Size: 11 x 3.0 x 0.13 mm
 Oxygen Flow Rate: 1400 cc/min

Run No.	Variac Setting	Heating Time (msec)	Ignition Occurrence	Heating Rate (cal/msec)	Energy (cal)	Calc Temp (C)
<u>0.91 a/o nickel-zirconium foil</u>						
55,57	55	66.2	Yes	0.058	3.84	1502
58,59	50	65.2	No	0.047	3.08	1220
75,77	80	32.1	Yes	0.126	4.03	1608
78,80	75	32.6	No	0.106	3.44	1375
61,63	75	53.5 ^a	Yes	0.103	5.50	1845 (56% melted)
83,84	55	82.0 ^a	Yes	0.053	4.33	1765
<u>14.9 a/o titanium alloy foil</u>						
68,69	35	66.7	Yes	0.023	1.51	702
64,65	30	66.7	No	0.017	1.15	558
70,71	55	31.7	Yes	0.049	1.55	722
72,73	55	32.1	No	0.045	1.45	680

^aHeating continued until sample failure.

The temperatures listed in the table were calculated for the center mm of the specimens assuming that no heat losses occurred during the heating process. Calculations have shown that there is negligible conductive heat loss from the center of the specimen up to times of the order of 100 msec. Because of the difficulty of estimating the coefficients under these experimental conditions, corrections for heat losses by convection and by radiation were not applied.

In runs 61, 63, and 83, 84, electrical heating was continued until the 0.91 atom per cent nickel alloy specimen failed. More energy was applied in these runs than was required in runs 55, 57 and 75, 77, where heating was stopped before specimen failure occurred.

The ignition temperatures obtained by this method for the 0.91 atom per cent nickel and the 14.9 atom per cent titanium were in the same relative order as by the shielded tests, but were approximately 85 per cent greater than the shielded-ignition temperatures. There is no apparent dependence of ignition energy upon heating rate over the range

of heating rates from 0.02 to 0.13 cal per millisecond. Further work would be required to confirm these findings and also to determine the minimum heating rates necessary to ignite the various alloys.

c. Zirconium Burning Propagation Rate Studies

Exploratory experiments with various alloy foils showed considerable variations of the ability of a sample to ignite and to continue burning in room atmosphere after one end was ignited with a torch. Some alloys which had shown the lowest shielded-ignition temperatures could be ignited with a luminous flame and would continue to burn to complete consumption. All alloys could be ignited with an oxygen-gas flame. Some of them, which had shown the highest shielded-ignition temperatures, would not continue to burn in air when removed from the flame. Those alloys with intermediate shielded-ignition temperatures showed varied behavior strongly dependent on sample thickness, sample width, and type of flame used to ignite them.

More refined experiments were conducted in the apparatus described in the earlier section on uranium burning propagation studies. Marked differences of rates of propagation along 1-mm wide strips have been shown for a few alloys in both air and oxygen. The dependence on the width of a sample has been verified with an experiment on a wedge-shaped, 0.13-mm (5-mil) strip of 2.12 atom per cent titanium alloy. The sample width varied from 0.5 to 5.0 mm over its length of 6 cm. The ignition was observed to cease at the point where the sample was approximately 3 mm wide.

Additional studies of the effects of additives, sample width, and sample thickness are in progress.

4. Zirconium Isothermal Oxidation Studies

a. Discussion of Isothermal Oxidation of Zirconium and Its Alloys

The oxidation data for a series of zirconium-base binary alloys at 700 C in 200 mm oxygen were reported previously (ANL-5924, pages 101 to 105). Considerations of the relationship of these data to earlier literature, theories, and the mechanism of the cubic rate oxidation and the breakaway phenomena are discussed below. It is believed that if an additive element is soluble in alpha zirconium, a prediction can be made with respect to the effect that this element will have on the oxidation rate of zirconium. Therefore, through the correlation of ignition temperatures with isothermal rate data previously established, it may be possible to predict from the binary metal phase diagrams the effect of additive elements, if they are soluble in alpha zirconium, on the ignition temperature.

(1) Literature and Theoretical Considerations

The general characteristics of the oxidation of zirconium and zirconium-base alloys were (1) an initial stage in which the rate of oxygen consumption decreased with time and (2) a certain oxide thickness at which the film lost its protective properties, leading to a faster, essentially linear rate of oxidation. For pure zirconium and most of the alloys studied, the initial rate was cubic, although a few of the alloys showed an initial parabolic rate.

Several studies have been made to determine the mechanism of the formation of oxide film on zirconium. By employing inert markers it has been observed^{16,17} that the oxidation proceeds by oxygen (anion) migration through the oxide film toward the metal-metal oxide boundary. In another study¹⁸ it was reported that anodic oxidation of zirconium at room temperature under low electric fields also proceeds by anion migration through the zirconium dioxide.

Consideration of the size of oxygen ions shows that they are too large to occupy interstitial positions in the zirconium oxide lattice. Therefore, it may be concluded, at least in thin films without cracks, that anion diffusion takes place by lattice defects or holes.

Thermoelectric power measurements* on films of pure zirconium and zirconium-tin alloys gave negative thermoelectric powers.¹⁷ Thus, it may further be concluded that these films were anion-deficient semiconductors (n-type).

According to the Wagner-Hauffe semiconductor approach to alloy oxidation, foreign ions of lower valency than zirconium should increase the rate of oxidation, since they create more lattice defects. Conversely, ions of higher valency than zirconium should reduce the concentration of oxygen ion defects and thus decrease the oxidation

¹⁶ Chirigos, J. and Thomas, D. E., WAPD-53 (1952).

¹⁷ Mallett, M. W. and Albrecht, W. M., J. Electrochem. Soc. 102, 407 (1955).

¹⁸ Flint, O., and Varley, J. H. O., Nature Lond. 179, 145 (1957).

* To determine the type of conduction (electrical) in a semiconductor it is necessary to make thermoelectric power measurements. If the current is carried exclusively by electrons, then the thermoelectric power will be negative, whereas the thermoelectric power must be positive if the current is carried by positive holes.

rate. Although this theory was derived for parabolic oxidation, it is not necessarily limited to this oxidation rate law, since it has been found to apply to zinc, which follows a logarithmic rate law.¹⁹

A few attempts have been made to give a theoretical basis for the cubic rate equation. Mott^{20,21} derived a cubic rate equation based on the premise that diffusion of cation vacancies is rate controlling, where the number of vacancies is proportional to the number of negative ions per unit surface area and to a linear field set up by the ions. Engell, Hauffe, and Ilschner²² derived a similar equation based on the migration of positive holes and the diffusion of lattice vacancies. Both of these derivations were based on p-type oxide films. A different approach has been taken by Uhlig,²³ who recently derived a cubic rate equation based on electron flow from the metal as the controlling step in the oxidation process. This equation would be applicable for films up to several thousand angstrom units, where the space charge in the oxide is important.

An attempt to explain the cubic oxidation of titanium has been made by Kofstad and Hauffe.²⁴ They suggested that, in view of the high solubility of oxygen in titanium, the cubic rate law could be interpreted in terms of diffusion of oxygen through the outer layer of oxygen-enriched titanium. Since zirconium also has a high oxygen solubility, it is probable that the cubic oxidation of zirconium and titanium follow a similar mechanism.

Thus, it is not altogether surprising that the oxidation of zirconium, which ostensibly proceeds by inward diffusion of oxygen, does not obey the simple parabolic rate law, because the kinetics of oxidation are complicated by oxygen dissolution in the outer layer of zirconium metal.

(2) Correlation of Isothermal Rate Data with Theory

A condition that must be met if the Wagner-Hauffe theory is to apply is that the metal which is added to the zirconium share in the film formation, but must not give rise to the formation of a new phase. This condition has on occasion been expressed in terms of the

¹⁹ Vernon, W. H. J., Akeroyd, E. I., and Stroud, E. G., *J. Inst. Metals* 65, 301 (1939).

²⁰ Mott, N., *Trans. Faraday Soc.* 36, 472 (1940).

²¹ Cabera, N. and Mott, N., *Report on Prog. in Physics* 12, 163 (1949).

²² Engell, H., Hauffe, K. and Ilschner, B., *Z. Electrochem.* 58, 478 (1954).

²³ Uhlig, H. H., *Acta Metall.* 4, 541 (1956).

²⁴ Kofstad, P., and Hauffe, K., *Werkstoffe und Korrosion* 7, 642 (1956).

solubility of the added metal oxide in zirconium dioxide. However, it is thought that a more appropriate way of expressing this condition is in terms of the original state of the added metal in alpha zirconium before oxidation. Thus, if the added metal is in true solution in the metallic state, it is unlikely that segregation into two distinct oxide phases will occur on oxidation, even if the added metal oxide is insoluble in zirconium dioxide. This statement should be true for reasonably dilute alloys and for temperatures sufficiently low so that the metal ion mobilities in the oxide phase are low. For the problem under immediate consideration both of these conditions are true.

In the case of a metal insoluble in alpha zirconium, the situation that probably exists in the alloy is that agglomerates of the second metal are randomly situated throughout the zirconium. Then when oxidation occurs these islands of alloying metal produce agglomerates of alloying metal oxide which tend to remain as a separate oxide phase. Since solubility equilibrium does not have an opportunity to be established in the oxide phase in experiments under the conditions of this study, it is believed that solubility data for the oxide systems are not germane.

In Table 24 are presented data for the alloy systems that were studied in this program and that are in the category of the additive metal being reasonably soluble (greater than one atom per cent). It is to these systems that the Wagner-Hauffe theory should be applicable. In columns two, three and four of Table 24 are presented the ratios of cubic rate constants for the alloy to that for zirconium. In column seven the predicted effects of the additive by the theory of Wagner-Hauffe are indicated and column eight shows the observed effect. The last column indicates whether or not there is agreement with the predicted effect. Only in the case of lead does the theory disagree with the experimental data. Lead is an exceptional additive in that its Goldschmidt ionic radius is 52 per cent greater than that of zirconium. All of the other additives considered in this table have ionic radii less than that of zirconium. The oxide of lead most likely formed, PbO , is also the thermodynamically most unstable additive oxide of the series by many kilocalories. Therefore, for these two reasons lead can be considered unique.

The agreement of experimental results with predicted results is actually better than six examples out of seven. The phase diagrams in the literature indicate that copper, beryllium, cobalt, nickel, iron, chromium, silicon, platinum, vanadium, molybdenum, tungsten, uranium, and carbon are relatively insoluble in alpha zirconium at 700 C. These alloys, therefore, should not necessarily follow the predictions of the valence effect of Wagner-Hauffe theory. In the thirteen cases cited ten do not follow the prediction and only three (molybdenum, vanadium, and iron) follow the prediction. Of these three, the first two additive oxides are somewhat volatile and thus not typical. The other (iron) shows an increased rate of oxidation which follows the prediction despite the very low solubility in zirconium.

Table 24

PREDICTION OF INITIAL OXIDATION BEHAVIOR OF ZIRCONIUM ALLOYS

Consideration restricted to (a) initial rate of oxidation at 700 C in 200 mm oxygen and (b) zirconium alloys used experimentally whose solubility is greater than 1 a/o in alpha zirconium at 700 C.

Alloying Element	Ratio ^{a,b}			Solubility in Alpha Zr at 700 C, (a/o)	Oxidation Number ^d Most Likely in Oxide	Effect of Additive on Initial Oxidation Rate		Agreement with Prediction
	1 a/o ^c	2 a/o ^c	4 a/o ^c			Predicted by Wagner-Hauffe Theory	Observed	
Al	8.8 B	7.5 B	5.0 B	1.6	3	Increase	Increase	Yes
Hf	0.88	0.88	0.88	miscible	4	No change	Essentially no change	Yes
Ti	4.4 B	157 B	P B	miscible	2	Increase	Increase	Yes
Sn	0.58B	0.69B	0.75B	2	4	No change	Essentially no change	Yes
Pb	0.69B	1.0 B	0.50B	3	2	Increase	Essentially no change	No
Nb	3.7 B	P B	4.3 B	3	2	Increase	Increase	Yes
Ta	P	P	P B	5	2 ^e	Increase	Increase ^f	Yes

^aRatio of the cubic rate constant of the alloy compared to that of pure zirconium, except symbol "P" indicates oxidation followed parabolic rate law rather than cubic. In these cases the oxygen consumed per unit time is greater than for pure zirconium for the period of the experiment.

^bSymbol "B" indicates breakaway phenomenon during period of observation.

^cNominal concentrations. For exact concentrations see ANL-5924, pages 103 and 104.

^dPredicted from thermodynamic data.

^eExperimentally demonstrated that TaO formed when Ta reacts with ZrO₂ at 1700 C. (Chupka, W. A., Berkowitz, J. and Ingram, M. G., J. Phys. Chem. 26, 207 (1957).

^fThe oxidation of tantalum alloy follows the parabolic, rather than the cubic, rate law. However, the extent of oxidation during the initial oxidation is greater than that for pure zirconium for the same time interval.

Among the additives studied that were soluble in zirconium, none increased the oxidation resistance as the theory would predict, because none had oxidation numbers higher than four. Five additives which were not studied: technetium, rhenium, ruthenium, osmium, and iridium, have oxidation numbers greater than four, but of these only ruthenium has been found to have an appreciable solubility in α -zirconium. The solubilities of the other four are unknown.

It therefore seems appropriate to look among the metal additives not soluble in zirconium, for which the Wagner-Hauffe theory does not apply, for the additives which might increase oxidation (and therefore ignition) resistance. In seeking to explain the effects of additives on the oxidation rate which will not follow the Wagner-Hauffe theory it is necessary to consider the properties of the individual oxides concerned. These properties might be preferential oxidation relative to zirconium, protective nature of the oxides, diffusion rates of ions in the oxides, and electrical conductivities of the oxides.

(3) Breakaway Phenomenon

After a period many of the alloys studied have exhibited an acceleration in the oxidation kinetics. This so-called "breakaway"

or "transition" has previously been observed^{14,17,25,26,27} to occur during the oxidation of zirconium and zirconium alloys. The interpretation given to the breakaway has been that, since the volume ratio of zirconium dioxide to zirconium is 1.5, the oxide grows under compressive strain, and at a certain film thickness the oxide cracks to release the compression energy that leads to the breakaway.

In some recent work²⁵ it has been shown that the breakaway is actually associated with a phase transformation in the zirconium dioxide film. Electron-diffraction studies showed that the initial film formed on zirconium is actually the cubic polymorph of zirconium dioxide. After a period of oxidation this transforms to the tetragonal and finally to the monoclinic (stable) form of zirconium dioxide. The breakaway was said to occur when the transformation from tetragonal to monoclinic took place.

Some work along this line has been conducted in these studies. Examination by electron diffraction of the pre-breakaway oxide films formed on pure zirconium, the 1.42 atom per cent aluminum alloy, and 3.60 atom per cent tin alloy has revealed the presence of the cubic polymorph of zirconium dioxide in every case. After the breakaway the 1.42 atom per cent aluminum, 3.54 atom per cent tantalum, 3.60 atom per cent tin, and the 3.52 atom per cent uranium alloys were examined by X-ray diffraction, and in every case monoclinic zirconium dioxide was observed. These results would tend to confirm the conclusion that the breakaway is associated with a polymorphic transformation in the zirconium dioxide film.

Undoubtedly these polymorphic transformations are brought about by several interrelated effects that change in relative importance with different impurities in the metal. For pure zirconium the following, oversimplified process may take place. Initially, a thermodynamically unstable film of cubic zirconium dioxide is formed. The film grows under large compressive strain and, since it is extremely adherent to the metal substrate, it is protective in nature. At a critical thickness the compressive strains become too great and must be relieved by transformation of the oxide film to the tetragonal, and finally the monoclinic, form. Coincident with the last transformation the film loses its protective properties and a faster rate of oxidation ensues.

²⁵ Korobkov, I. I., Ignatov, D. V., Yevstyukhin, A. I., and Yemelyanov, V. S., A/CONF.15/P/2054, Second United Nations International Conference on Peaceful Uses of Atomic Energy, Geneva, 1958.

²⁶ Kendall, L. F., Wheeler, R. B., and Bush, S. H., Nucl. Sci. and Engr. 3, 171 (1958).

²⁷ Gulbransen, E. H. and Andrew, K. F., J. Metals 10, 281 (1958).

When certain metallic impurities that are soluble in zirconium are added, the oxidation process produces a film that consists of the additive metal oxide dispersed in cubic zirconium dioxide. If the ionic radius of the additive ion is sufficiently different from the ionic radius of zirconium, the zirconium dioxide lattice will be distorted. This will decrease the stability of the cubic form, thereby causing the polymorphic transformation to occur at a lower thickness of film than in pure zirconium.

As an extension of this reasoning, a general rule, that appears useful in predicting the occurrence of the breakaway phenomenon, was formulated. This rule is that a breakaway will occur when the Goldschmidt ionic radius of the additive element differs by 15 per cent or more from the ionic radius of zirconium.

In the case of additives predicted to follow the Wagner-Hauffe theory, all seven additives (19 out of 21 alloy compositions) follow the rule. These are alloys of aluminum, hafnium, titanium, tin, lead, niobium, and tantalum (see Table 25). Tantalum, which is predicted to show a breakaway phenomenon, does so only in the highest concentration. It is quite likely, however, that the one and two atom per cent runs were not carried out long enough to observe the breakaway phenomenon. If breakaway can be assumed to occur later, than the agreement is shown for all of these 21 alloys.

When metallic impurities that are insoluble in zirconium are added, the oxidation film consists of cubic zirconium dioxide and separate agglomerates of the additive metal oxide. Under certain conditions the separate oxide agglomerates may interfere with the adhesion of the film to the metal; this would, in turn, cause polymorphic transformation in the zirconium dioxide film and thus bring about faster oxidation rates. The additives that are insoluble in alpha zirconium do not follow the Wagner-Hauffe theory for oxidation of alloys. However, these insoluble additives show good agreement with the rule relating the occurrence of breakaway with additive ionic radius. Of the thirteen insoluble additives, ten follow the rule: four in all three concentrations, four in the two and four atom per cent concentrations, one in the one and two atom per cent concentration, and one in the four atom per cent concentration (see Table 25). From the trend of breakaway time versus additive concentration in the case of uranium and silicon (ANL-5924, pages 103 and 104) it is possible that the runs on the lower concentrations of these additives were not carried out long enough to observe a breakaway. This agreement with the rule predicting breakaway is particularly remarkable, since the factors causing breakaway are probably different for the insoluble and soluble additive systems.

Table 25

PREDICTION OF BREAKAWAY PHENOMENA OF ZIRCONIUM ALLOYS
FROM IONIC RADII OF ADDITIVES

Breakaway predicted if ionic radius of additive in its oxide
is more than 15% different from zirconium ionic radius.

Additive Element	Solubility ^a (a/o of Additive in Zirconium at 700 C)	Breakaway Phenomena Observed			% Difference Ionic Radius of Additive from Zr ⁴⁺ Radius ^c	Breakaway Phenomena Predicted from Ionic Size	Agreement of Experiment with Theory
		1 a/o ^b	2 a/o ^b	4 a/o ^b			
Al	1.6	Yes	Yes	Yes	-34	Yes	Yes
Hf	miscible	No	No	No	- 3.4	No	Yes
Ti	miscible	Yes	Yes	Yes	-21	Yes	Yes
Sn	2	Yes	Yes	Yes	-15	Yes	Yes
Pb	3	Yes	Yes	Yes	+52	Yes	Yes
Nb	3	Yes	Yes	Yes	-21	Yes	Yes
Ta	5	No	No	Yes	-22	Yes	Yes ^d
Cu	<0.26	No	No	No	+10	No	Yes
Be	<0.4	No	No	No	-61	Yes	No
Co	<1	No	No	No	- 5.8	No	Yes
Ni	<1	No	No	No	-10	No	Yes
Fe	<0.02	No	No	No	- 4.6	No	Yes
Cr	<0.5	No	No	No	-26	Yes	No
Si	<0.3	No	Yes	Yes	-55	Yes	Yes ^d
Pt	<1	No	Yes	Yes	-40	Yes	Yes ^d
V	<1	Yes	Yes	No ^e	-25	Yes	Yes
Mo	<0.2	No	Yes	Yes	-22	Yes	Yes ^d
W	<0.25	No	No		-22	Yes	No
U	<0.3	No	No	Yes	+21	Yes	Yes ^d
C	Carbide	No	Yes	Yes	-77	Yes	Yes ^d

^aIt is assumed that the metals soluble in alpha zirconium (i.e., Al, Hf, Ti, Sn, Pb, Nb, and Ta) will follow the Wagner-Hauffe law.

^bNominal concentrations. For exact concentrations see ANL-5924, pages 103 and 104.

^cGoldschmidt ionic radii used for additive oxide ion most likely to form from thermodynamic considerations. Ionic radius of zirconium taken as 0.87Å.

^dFor these cases the breakaway phenomena occurs for alloys of higher concentration but not for those of lower. From the trend of break time vs additive concentration in the case of uranium, tantalum, and silicon, it is possible that the runs were not carried out long enough to observe a breakaway (ANL-5924, pages 103 and 104).

^eThe kinetic data do not show the breakaway phenomenon. However, X-ray diffraction data indicate the monoclinic form at the end of the experiment, suggesting that the kinetic breakaway, defined as deviation from the initial rate law, may not coincide with polymorphic transformation.

In order to understand better the mechanism of growth of oxide film on zirconium, more information concerning the nature of the film must be obtained. To accomplish this electron diffraction studies of oxide films are being continued.

b. Oxidation of Zirconium-Titanium Alloys

The oxidation of the one, two, and four atom per cent titanium alloys at 700 C showed that the addition of small amounts of titanium greatly increased the oxidation rate of zirconium (ANL-5924, pages 99 to 104). The extension of this study to alloys of higher titanium content and pure titanium required that the oxidation be conducted at a lower temperature, 500 C, because the 14.9 and 49.9 atom per cent titanium alloys ignited when run at 700 C. The accumulated data at 500 and 700 C are listed in Table 26. At 500 C the oxidations were in 760 mm oxygen, while at 700 C the oxidations were in 200 mm oxygen. It has previously been shown (ANL-5789, page 72) that the oxidation of zirconium is relatively insensitive to oxygen pressure.

Table 26

OXIDATION OF ZIRCONIUM-TITANIUM ALLOYS

Dimensions of specimens:

Pure Zr, 1.08 Ti, 2.12 Ti and 4.16 Ti - Parallelepipeds 1 x 1.5 x 2 cm

Pure Ti, 3.74 Ti, 14.9 Ti, and 49.9 Ti - Cylindrical discs 1.7 cm in diameter, 0.5 cm thick

Alloy Composition (Atom Per Cent)	Log -Log Slope (1/n)	Weight Gained in First Minute ($\mu\text{g}/\text{sq cm}$)	Breakaway Time (min)	Breakaway Weight ($\mu\text{g}/\text{sq cm}$)	Linear Rate ($\mu\text{g}/(\text{sq cm})(\text{min})$)	Total Weight at 400 min ($\mu\text{g}/\text{sq cm}$)
At 500 C in 760 mm oxygen						
Pure Zr ^a	0.32	38	No Breakaway Observed			259
1.08 Ti	0.38	72	150	580	1.8	1035
3.74 Ti	0.39	160	17	631	18.0	7078
4.16 Ti	0.46	145	17	625	24.1	10100
14.9 Ti	0.25	971	7	1672	101.	40670
49.9 Ti	0.56	220	51	1990	22.6	10215
Pure Ti	0.21	38	No Breakaway Observed			159
At 700 C in 200 mm oxygen						
Pure Zr	0.33	236	No Breakaway Observed			1770
1.08 Ti	0.37	624	370	6215	9.3	3175
2.12 Ti	0.39	946	365	9468	13.0	5625
3.74 Ti	0.41	1550	115	10200	11.6	23140
4.16 Ti	0.44	1400	200	14450	30.2	12500
14.9 Ti	-	-	Ignition Occurred			-
49.9 Ti	-	-	Ignition Occurred			-
Pure Ti	0.30	132	-	195	-	470

^a200 mm oxygen instead of 760 mm

The values of the log-log slope indicate considerable variations of the initial rate law for oxidation. Therefore, initial rate constants are not comparable. The weight gained in the first minute increased with increasing titanium content up to 14.9 atom per cent and then decreased for the 49.9 atom per cent alloy at both temperatures. At 500 C no breakaway

phenomena were shown for pure zirconium or pure titanium, but was shown for the alloys; the breakaway times decreased with increasing titanium content up to 14.9 atom per cent and then increased for 49.9 atom per cent titanium. The breakaway weights increased with increasing titanium content at both 500 and 700 C. Both the linear rates after breakaway and the total weight gain after 400 minutes at 500 C increased to a maximum at 14.9 atom per cent and decreased for the 49.9 atom per cent titanium alloy.

B. Metal-Water Reactions

(L. Baker, M. Kilpatrick,* R. C. Liimatainen, C. H. Smith, R. Warchal, W. A. Rodger, and R. C. Vogel)

The experimental program to determine rates of reaction of molten reactor fuel and cladding metals with water is continuing. The principal laboratory-scale method involves the rapid melting and dispersion of metal wires in a water or steam environment by a surge current from a bank of condensers. Preliminary work with aluminum was described in the previous quarterly report (ANL-5924, pages 105 to 107). The method of energy calibration, however, was unsatisfactory because of the low electrical resistivity of aluminum. Runs with zirconium, which has a more favorable resistivity, are reported in the following paragraphs.

The experimental program to determine the reaction rates of molten fuel and cladding metals with water during nuclear transients using the TREAT reactor is also continuing. Progress has been mainly on construction and procurement of equipment.

1. Laboratory Studies

Runs made with Zircaloy-2 and zirconium wires of 0.060-inch nominal diameter are summarized in Table 27. The runs were made in the 75-cc stainless steel reaction cell described in ANL-5896, page 104. Normally, 35 cc of degassed water were added to the cell; the runs were made in vacuum at room temperature. In three runs, the cell was pressurized with 3 atm of argon gas. The sample weight was the difference between the initial weight of wire and the weights of the shielded ends remaining in the electrode mounts. Sample weight in the case of runs in which the wire remained intact had to be estimated from the length of the oxidized portion of the sample.

The procedure for measuring the energy imparted to the sample during a run was also described in ANL-5896, page 104. The measured energy was used to obtain the initial temperature, using thermodynamic data. The calculated temperatures are estimated to be accurate within ± 100 C. The calculated temperatures are consistent with the appearance of the residue. Samples were observed to remain intact when the energy

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calculations indicated a temperature below the melting point. Samples remained in one piece up to an energy corresponding to about 50 per cent melted, although they were severely deformed. At higher energies, the residue was in the form of approximately spherical particles that decreased regularly in size with increasing energy.

Table 27

PRELIMINARY RUNS: CONDENSER-DISCHARGE METHOD

Zirconium wire specimens, nominal diameter: 0.060 inch

Run	Sample Weight (g)	Energy Input (cal/g)	Calc Temp, C, and Comp.	Hydrogen Yield		Initial Rate of Pressure Rise (atm/sec)	Appearance of Residue
				(cc, NPT)	(% Theo)		
23 ^a	0.337	127	1500, solid	-	1.2	2.6 ^a	Wire intact
13	0.285	137	1600, solid	5.6	3.9	-	Wire intact
22	0.293	150	1800, solid	6.1	4.2	1.2	Wire intact
24	0.310	158	1840, 5% liq	9.0	5.9	1.0	Wire deformed
28 ^a	0.344 ^b	174	1840, 30% liq	-	-	8.0 ^a	Wire deformed
27 ^a	0.344 ^b	183	1840, 50% liq	-	-	6.6 ^a	Wire deformed
25	0.326 ^b	190	1840, 60% liq	12.7	8.9	-	Large particles
26	0.305 ^b	203	1840, 80% liq	13.3	7.9	2.1	Large particles
14	0.259	217	1900, liq	10.4	8.2	-	Wire deformed
15	0.288	218	1900, liq	12.8	9.0	-	Large particles
18	0.300	233	2100, liq	17.9	12.1	6.5	Large particles
16	0.255	284 ^c	2700, liq	21.4	17.1	13.6	Coarse particles
20	0.284	275	2600, liq	33.3	23.8	Spike ^d	Coarse particles
19	0.270	276	2600, liq	56.8	42.7	Spike	Fine particles
17	0.301	296	2900, liq	67	45	Spike	Fine particles
21	0.298	313	3100, liq	54.9	37.4	Spike	Fine particles
11	0.256	501	3850, 10% vap	84	67	-	Powder, 25 μ

^aApproximately 3 atm argon present initially.

^bSpecimens were fabricated from Crystal Bar Zirconium, 60 to 61 mils diam; all others were Zircaloy-2, 54 to 57 mils diam.

^cRun is located out of order in table since hydrogen yield, pressure transient and appearance indicated a less energetic run.

^dVery rapid pressure rise.

Hydrogen yield was determined by passing the contents of the cell, following a run, through a series of liquid nitrogen traps to remove the water. The quantity of hydrogen was determined by collecting the gas in a known volume by means of a Toepler Pump and measuring the pressure with a manometer. Data on hydrogen yield were checked by measurements of the weight gain of the specimen when a quantitative recovery of the sample was possible. It was assumed that the only reaction to occur was

The values of hydrogen yield determined by the volumetric method are shown in Table 27. The hydrogen yield is also shown in Table 27 as a percentage of a theoretically completed reaction in accordance with Equation 1.

Oscillograms of pressure vs time were obtained for most of the runs, using a quartz crystal pressure transducer. Two distinct types of traces were obtained. Runs made at low energy showed a slowly rising pressure, while runs made at high energy showed very rapid pressure rise. Typical pressure-time curves are shown in Figures 28 and 29. The low-energy runs showed a linear initial rate. Values of the measured initial rates are given in Table 27.

The data on hydrogen from Table 27 are plotted as a function of energy in Figure 30. A regular increase in the extent of reaction occurs up to an apparently critical temperature of 2600 C. Runs at higher initial temperatures showed a very rapid rise of pressure and an enhanced yield of hydrogen. It seems significant that no sharp change in the reaction rate occurred on passing through the melting point. It might be tentatively supposed that the critical temperature corresponds to an ignition point. Ignition occurs when the rate of heat generation by reaction exceeds the rate of heat loss; both are determined to a large extent by the particle size. Precise methods to measure the particle sizes of residues are currently under development. Data, on particle size, together with auxiliary data on rates of heat loss determined from runs using platinum samples, will facilitate a thorough analysis of the data according to the principles outlined in ANL-5896, page 108.

Rates of pressure rise are plotted as a function of energy input in Figure 31. It is apparent that runs made in the presence of argon showed abnormally high rates of pressure rise.

2. In-Pile Testing in the TREAT Reactor

The construction of the autoclave that will be used in static tests previously described in ANL-5896, page 111, is completed (see ANL-5924, Figure 28, page 107 for a diagram of the high-pressure autoclave), and it has been pressure-tested hydraulically to 4000 psi with no indication of leakage. There was no observed increase in the diameter of the vessel (to within 0.0005 inch) during the 4000-pound test. The autoclave assembly was Freon leak tested to 100 psi and no leaks were observed. A leak rate of less than 10^{-9} cc/sec was observed using helium at 400 psi.

A meeting was held with the Metallurgy Division to discuss the fabrication of the fuel pins to be used in this investigation. The first series of test specimens (144 pins) are to be cylinders each 0.2 inch in diameter and 1 inch long. Fuel pins of natural uranium and 20 per cent enriched uranium-235 are to be fabricated, and all the clad fuel pins will have a cladding thickness of 0.02 inch. A summary of the fuel pins to be fabricated is as follows:

Core Material	Clad or Can Material
U	None (12 pins)
U (18 w/o)-Al (82 w/o)	None (12 pins)
	Al (12 pins)
U (93.5 w/o)-Zr (5 w/o)-Nb (1.5 w/o)	None (12 pins)
	Zircaloy-2 (12 pins)
UO ₂	Stainless steel (6 pins)
	Zircaloy-2 (6 pins)

Fabrication of the fuel pins will start at the end of February.

The average response time (time required for a thermocouple to reach 63 per cent of its final value in a step temperature change) of a 24-gage bare chromel-alumel thermocouple was found to be 50 milliseconds.

Experiments on the behavior of a pressure transducer (consisting of a piezoelectric crystal in a stainless steel mounting) in a gamma-radiation field were conducted. An artificial pressure was applied to the transducer in the form of an electric charge from the calibrator. A charge of 0.531 volt remained constant for three minutes in the absence of radiation; the estimated period in this case is approximately 1000 hours.

A second experiment checked the stability of the output voltage in a 10-r/hr gamma field from cobalt-60. The output changed with time in the following manner:

<u>Time (min)</u>	<u>Output (volt)</u>
0	0.530
20	0.531
40	0.532
90	0.540

The last experiments were conducted in a radiation field having an intensity of about one million roentgens per hour (Gamma Irradiation Facility at the Argonne National Laboratory). The average period obtained was 41 seconds.

The experiments in the TREAT reactor will take place in from a fraction of a second to about five seconds, depending upon such factors as fuel enrichment. In TREAT, it is estimated that, in a typical transient, the maximum dose rate would be about 700 times that used here. Assuming that the period is inversely proportional to the intensity of the radiation, then the period of the pressure transducer would become approximately 40 milliseconds. Under these conditions, a change in the output voltage from a quartz crystal pressure transducer could not necessarily be interpreted as a change in pressure. Shielding the pressure transducer with an inch of lead would cut down the radiation by approximately a factor of ten. Preirradiating the quartz crystal for 10 minutes would be helpful if the flux in the subsequent experiment were independent of time. However, in the TREAT reactor, the intensity will approximately increase exponentially with time. Similar experiments on radiation stability will be conducted on magnetic reluctance-type and strain gage-type pressure transducers.

C. Reactor Decontamination Studies (W. B. Seefeldt)

The present studies, which are a cooperative effort between the Reactor Engineering and Chemical Engineering Divisions, are being made to determine the feasibility of decontaminating the auxiliaries of a boiling water reactor in the event of rupture of a fuel element. The primary aim of this work is the removal of the activity deposited in situ, so that direct maintenance may be possible. A secondary, though important, objective is the study of the type and quantity of activity adsorbed and the rate at which buildup of these adsorbed activities occurs.

Four sources of material will be used for the decontamination studies:

- (1) samples of various metals that have been placed in each of two locations in the Experimental Boiling Water Reactor (exit steam line and the condenser);
- (2) portions of the EBWR system that are removed for experimental purposes;
- (3) samples of metal that have been contaminated in a loop designed to simulate operating conditions in a boiling water reactor; and
- (4) samples contaminated in laboratory autoclaves.

1. Laboratory Static Tests (S. Vogler, H. Tyler)

The immediate purpose of the autoclave experiments is to introduce fission product activity onto type 304 stainless steel and to use this contaminated metal to measure the effectiveness of various decontaminating reagents. To do this, a stainless steel liner containing 2 grams of irradiated natural uranium and 100 ml of deionized water is placed inside an autoclave and heated for approximately six days at 600 psi and 486 F. At the completion of a test the contents are removed and the liner rinsed with distilled water. The liner is then cut into strips for use in decontamination studies. The autoclave was described in the previous report (ANL-5924, page 109).

a. Activity Identification

Several of the contaminated samples were examined in the 256-channel gamma scintillation spectrometer in an effort to identify nuclides responsible for the activity. Major peaks were observed at 150, 500 and 750 kev and minor peaks at 32, 590, 1500, 2050 and 2400 kev. Some of the nuclides which have peaks at these values include cerium-141, cerium-praeseodymium-144, ruthenium-103, ruthenium-rhodium-106, antimony-124, and zirconium-niobium-95.

b. Activity Deposition as a Function of Liner Pretreatment

An autoradiograph of the first autoclave liner heated with irradiated uranium indicated that the activity had deposited in a very irregular and spotty fashion in the vapor space. A series of experiments was run to determine if variation of the pretreatment of the stainless steel liner would result in a more even deposition of the radioactivity. The following pretreatments were used:

- (1) The liner was degreased with acetone, and rinsed with water, concentrated nitric acid, and deionized water.
- (2) The liner was degreased with acetone, scrubbed with Tide and water, rinsed with water, concentrated nitric acid, and deionized water.
- (3) The liner was degreased with acetone, scrubbed with Tide, rinsed with water, etched with a nitric acid-hydrofluoric acid solution and rinsed with deionized water.
- (4) The cleaning treatment as in (2) followed by an oxide film-forming pretreatment in 600 psi saturated water for one week.

The autoradiographs of a sample of each of these liners showed the deposition of the radioactivity still to be irregular and spotty.

c. Decontamination of Adsorbed Activity as a Function of Liner Pretreatment

The decontamination obtained from each of these samples was compared, using a caustic-permanganate solution as the decontaminating reagent. A sample (~1 inch square) of each of the liners was counted for beta activity on a proportional counter and for gamma activity with a single channel scintillation spectrometer. Each specimen was then treated with approximately 100 ml of the decontaminating solution, with heating and stirring. After rinsing and drying, the metal specimen was again assayed for beta and gamma activities, and the decontamination factor* for both beta and gamma activities was determined.

The results are given in Table 28. Each of the reported values is the average of at least two results, with a fair agreement in most cases.

It is difficult to explain the variation in decontamination with liner pretreatment, although there seems to be a trend towards better decontamination with an etched liner or one that has been preoxidized.

$$\text{*Decontamination factor} = \frac{\text{activity before treatment}}{\text{activity after treatment}}$$

It is planned to use the preoxidized liner as the reference for future contamination experiments. This is consistent with reactor operation, as all reactors operating under pressure will immediately develop such an oxide coating before being exposed to appreciable amounts of activity due to fission products.

Table 28

DECONTAMINATION OF STAINLESS STEEL TYPE 304
FROM MIXED FISSION PRODUCT ACTIVITY

Activity deposited by heating irradiated uranium metal in deionized water at 600 psi and 486 F for approximately 6 days.

Initial β and γ activities: ca 10^4 cpm

Vessel Pretreatment ^a	Decontamination Factor			
	Alkaline Permanganate ^b		Turco ^c	
	β	γ	β	γ
1	44	21		
2	11	8	12	10
3	51	54	70	32
4	67	46	24	29
4	162 ^d	59 ^d		

^aSee Text

^b 3% KMnO_4 } Heat for 1/2 hour at 95 C.
 20% NaOH }
 10% ammonium citrate - heat for 1/4 hour at 85 C.

^cTurco 4501 - heat for 1/2 hour at 130 to 140 C; rinse.
 Turco 4502 - 0.24 g/cc - heat for 1/2 hour at 100 to 105 C.
 25% HNO_3 - one-half hour at room temperature.
 (The Turco reagents are proprietary compounds.)

^dThe alkaline-permanganate treatment was repeated a second time before the ammonium citrate reagent.

d. Other Decontamination Studies

In addition to the alkaline permanganate reagent, the efficiencies of several other liquid reagents were tested in scouting experiments. Soaps and wetting agents were relatively ineffectual. It was found that 10 per cent phosphoric and sulfuric acids containing inhibitors gave fair decontamination factors of 15 to 25 at 85 to 90 C in one-half hour exposures;

metal losses were 0.01 mil. Decontamination factors of ~ 200 were achieved with ceric sulfate in 10 per cent sulfuric acid, but at the expense of high corrosion. A successful reagent for reactor systems probably must be used in the presence of mild steel, which would make the mineral acids unattractive.

Other reagents, involving the use of sulfamic acid, ethylene diamine tetraacetic acid, hydrazine, and hydrogen peroxide, were tested and found to give modest decontamination results.

e. Vapor-Phase Decontamination

The decontamination of reactor systems with aqueous decontaminating reagents calls for the circulation of large volumes of liquid. Vapor-phase decontamination, if feasible, would involve smaller volumes of solution and would lead to better access to crevices and remote locations. Several preliminary experiments were performed to study vapor-phase decontamination.

The first tests were tried with water and nitric acid. The apparatus was arranged in such a manner that the liquid in a glass flask was allowed to boil, with the rising vapor passing over the metallic specimens. These were condensed and returned to the boiler. It was also noticed that vapor condensed on the metallic specimens. The chosen concentrations of nitric acid resulted in vapors containing approximately 32 and five weight per cent nitric acid.

The specimens used were obtained from a stainless steel liner which had been pretreated according to procedure (3) on page 100 and contaminated in the autoclave as previously described. The irradiated uranium used in the autoclave test was cooled approximately two months. The metal specimens used for the decontamination tests were each $5/8$ inch by 1 inch. At the completion of the experiment the samples were re-counted, and several of the samples were also counted in the 256-channel scintillation spectrometer, in order to identify the residual activities.

The results of these experiments are given in Table 29. Decontamination factors as high as 33 were obtained in exposure for one hour to condensing vapors of nitric acid, with the more concentrated acid being somewhat more effective. Repeated exposures for one hour increased the decontamination factor to as high as 46. Weight losses with the more dilute nitric acid were approximately 0.4 mg per one-hour exposure, which is equivalent to a penetration of 0.003 mil.

Table 29

VAPOR-PHASE DECONTAMINATION OF STAINLESS
STEEL PLATES WITH NITRIC ACID

Original activity: $\beta \sim 2 \times 10^4$ cpm
 $\gamma \sim 6 \times 10^4$ cpm
 Plate: 5/8 in. x 1 in.
 Time: 1 hr per exposure

HNO ₃ Weight Per Cent	Decontamination Factor ^b					
	β			γ		
	Pretreatment ^a			Pretreatment ^a		
	1	2	Total	1	2	Total
0	1.2	-	-	1.7	-	-
	1.3	-	-	1.7	-	-
32	15	1.8	28	10	1.7	17
	12	2.1	24	8	1.9	16
65	10	2.2	22	14	1.5	21
	33	1.4	46	28	1.5	42

^aSee text, page 102.

^bDecontamination factor = $\frac{\text{Activity before treatment}}{\text{Activity after treatment}}$

Examination of the scintillation spectrometer scans brought out the following points:

- (1) The full distribution of fission products is present after the decontamination cycle with distilled water.
- (2) After the decontamination cycle with concentrated nitric acid, the bulk of the residual activity was found under a peak at 360 kev. A second scan eight days later showed a decrease in peak height of approximately one-half, which was accepted as confirmation for iodine-131, which has a half-life of eight days and a photopeak at 364 kev.
- (3) After the first treatment for one hour with the more dilute nitric acid, the bulk of the activity was represented by peaks at 495 and 360 kev. Minor peaks were also noticeable at 75, 160, 640, 760 and 1580 kev. After a second exposure with the less concentrated

nitric acid, the major peak heights were decreased by a factor of two. A half-life measurement of the 360-kev peak gave a value of eight days, which is undoubtedly due to iodine-131. The 495-kev peak probably represents ruthenium activity.

- (4) Apparently the decontamination of the iodine was somewhat less than the other nuclides, so that the iodine-131 photopeak became relatively more prominent after a decontamination experiment.

These tests with nitric acid vapors were intended to explore the feasibility of the procedure. Other vapor-phase reagents will be tested in future work.

2. Evaluation of Reactor Specimens (S. Vogler, H. Tyler)

During the operation of the EBWR with defected fuel* (second defect test), metal samples were placed in the reactor steam line ahead of the steam dryer, and in the condenser. The samples in the condenser were removable immediately after reactor shutdown; those in the steam line were not removable for several days. In the second defect test the reactor was in operation for approximately 15 weeks, during which time it logged 51,214 megawatt hours before shutdown at 11:38 on November 7, 1958.

a. Steam-Line Specimens

The steam-line specimens were counted 10 days after reactor shutdown, so that short-lived nuclides, such as fluorine-18, copper-64, and manganese-56, would not be detectable even if originally present. There were eight different metal specimens in the steam line and a sample of each was counted in a single-channel scintillation counter using a 3-in. x 3 in. sodium iodide-thallium activated crystal as the sensing element. In addition, these specimens were analyzed with the 256-channel gamma scintillation spectrometer.

The metal samples present in the steam line are listed below.

- (1) Structural steel ASTM A113
- (2) AISI-4140
- (3) 13 per cent chrome steel
- (4) Chrome-molybdenum steel (carbon, 0.45 max; manganese, 0.70 to 1.00; silicon, 0.20 to 0.35; chromium 1.0 to 1.5; molybdenum, 0.45 to 0.65; vanadium, 0.15 minimum).

*The defected fuel was uranium oxide canned in stainless steel with the cladding intentionally punctured by drilling a small hole.

- (5) Low carbon steel
- (6) 13 per cent chrome non-hardening steel
- (7) X8001 - Aluminum with one per cent nickel
- (8) A198 - Aluminum with one per cent nickel and 0.1 per cent titanium.

The results with the single-channel scintillation counter indicate that approximately the same amount of gamma activity adsorbs on all of the steel specimens, but that approximately twice as much gamma activity is adsorbed on the aluminum alloys.

The gamma scintillation spectrometer scans indicated peaks at the following energies: 0.145, 0.25, 0.50, 0.82, 1.17, 1.33, 1.63 and 2.6 Mev. The peak heights have been compared among the various metals to indicate any selectivity of adsorption of the activated corrosion products on the metals in the steam line. The results given in Table 30 confirm the fact that approximately twice as much activity is adsorbed on aluminum as on steel. The peaks observed indicate that cobalt-58 and cobalt-60 are the principal adsorbed activities. The following peaks are attributed to these isotopes:

cobalt-58	0.511, 0.81, 1.35, 1.62 Mev
cobalt-60	1.17, 1.33, 2.50 Mev.

The relative peak heights indicate that the activity of cobalt-58 is roughly 50 times that of cobalt-60. The probable source of cobalt-58 is an (n, p) reaction on nickel-58; the cobalt-60 may be from an (n, γ) reaction on cobalt-59.

Two other peaks at approximately 0.3 and 0.15 Mev were observed. The higher peak might indicate the presence of chromium-51, which has a 0.32-Mev gamma. This nuclide has been observed as a neutron-activated corrosion product in water reactors. Further confirmation would depend upon chemical separation.

b. Condenser Specimens

There were five different specimens in the condenser:

- (1) Stainless steel 304
- (2) Mild steel
- (3) Copper
- (4) A198 - aluminum containing one per cent nickel and 0.1 per cent titanium
- (5) X8001 - aluminum containing one per cent nickel.

These specimens were degreased by soaking in acetone and then air dried. They were removed promptly from the reactor and counting began approximately two hours after shutdown.

Table 30

COMPARATIVE GAMMA ENERGIES OF EBWR
STEAM-LINE SAMPLES

Reference: 0.82-Mev peak on sample 8
taken as 100

Time of Reactor Operation: 15 weeks

Total Power: 51,214 mwh

Counting Time: 10 days after shutdown

Geometry: ~50 per cent

Photopeak Energy (Mev)	Relative Peak Heights								Gamma Activity, cpm $\times 10^{-5}$
	0.145	0.25	0.5	0.82	1.17	1.33	1.63	2.6	
Sample No. ^a									
1	-	-	15	44	0.81	2.9	0.33	0.14	1.63
2	2.0	2.6	14	39	0.60	2.5	0.30	0.08	1.46
3	2.6	2.2	20	58	0.91	3.5	0.20	0.15	2.12
4	1.8	2.6	16	44	0.55	2.7	0.28	0.13	1.70
5	1.6	1.8	13	36	0.71	2.4	0.38	0.10	1.47
6	2.0	1.2	16	46	0.66	2.8	0.28	0.10	1.70
7	1.2	2.0	35	87	0.50	5.8	0.55	0.35	3.23
8	1.0	2.2	34	100	0.60	5.5	0.50	0.35	3.20

^aFor identification, see text.

The major peaks observed were at 0.51 and 0.82 Mev. Because previous experience had indicated the presence of short-lived isotopes, counting was continued daily in order to observe any decay. The 0.510-Mev peak decayed rapidly. The half-life of the rapidly decaying portion of this peak was determined graphically. Two of these plots are shown in Figures 32 and 33. The half-life of the shorter-lived component was found to range from 1.5 to 2.3 hours, which encompasses the known half-life of fluorine-18 of 1.87 hours. Fluorine-18 has been noticed repeatedly in the EBWR steam cycle. Because of the short half-life, this activity was not observed in the "first defect test" because of the greater lapse of time from reactor shutdown to the first counting.

The relative peak heights of the 0.82 and 0.51 - Mev peaks (after decay of the fluorine-18) agree quite well with the ratio obtained from the response curve of pure cobalt-58. Because of the much lower levels of activity present in the condenser, the cobalt-60 observed in the steam line samples was not detected in the condenser samples. The copper-64 activity observed on the specimens in the condenser after the first defect test was not observed during this test.

The total counting rate for each specimen at two different times has been tabulated in Table 31 in order to give a semi-quantitative measure of the absorption of each of the active nuclides. These results show that the aluminum alloys showed the greatest adsorption of fluorine-18 by a factor of approximately 10 over the specimen showing the next largest adsorption. The counting rate after 72 hours (fluorine-18 decayed out) is caused by cobalt-58. The stainless steel shows a very low adsorption of both the fluorine-18 and the cobalt-58.

Table 31

ADSORPTION OF ACTIVITY ON METALLIC SPECIMENS
PLACED IN THE STEAM CONDENSER DURING
THE EBWR SECOND FUEL-DEFECT TEST

Coupon Dimensions: $3/4 \times 1\frac{1}{2} \times 1/16$ in.

<u>Material</u>	Counting Rate of Activity under 0.510-Mev Peak (cpm per sample) after	
	<u>0 hr</u>	<u>72 hr</u>
Stainless Steel 304	210	100
Mild Steel	780	70
Copper	380	130
A198	6040	250
X8001	6890	180

3. Loop Tests
(C. Bally, D. Grosvenor, W. B. Seefeldt)

The installation of the loop that simulates the operation of a boiling water reactor is complete; installation of instrumentation is in progress. A schematic diagram of the loop together with general operational philosophy was presented in ANL-5858, pages 66 and 67.

IV. CHEMICAL-METALLURGICAL PROCESSING

Melt refining, liquid metal extraction, and intermetallic crystallization are now being examined as direct-cycle pyrometallurgical methods of processing nuclear reactor fuels.

Melt refining consists of melting the discharged fuel and holding it molten for a period of time. Decontamination is effected by mechanisms of volatilization and selective oxidation of certain fission product elements. Work was continued on the behavior of iodine in this process. At macro concentrations, virtually complete (99.5 per cent) removal of iodine from purified metal and skull fractions was realized. An important mechanism of iodine removal is reaction with crucible contaminants to produce volatile iodides of calcium, iron, and magnesium. About one-quarter of the iodine was evolved as molecular iodine. The data showed that about 70 per cent of the iodine diffused through the zirconia crucible walls, whose total porosity was about 20 per cent.

No removal of zirconium from a plutonium-"fissium" alloy was realized by melt refining in either lime-stabilized zirconia or magnesia crucibles. A similar result was previously found for uranium-"fissium" alloy. If desired, zirconium removal may be effected through carbide formation.

In connection with the removal of zirconium as the carbide, information has been obtained on the joint solubilities of zirconium and carbon in uranium at 1400 C. The concentrations measured for uranium and carbon provide a tentative liquidus line in the high uranium region in the ternary system zirconium, carbon, and uranium. The values indicate that it is possible to remove zirconium by carbide liquation to less than 0.01 weight per cent, although in practice it would be difficult to achieve this removal. Removal of zirconium by carbide liquation from plutonium "fissium" alloys is to be investigated in the next quarter.

Progress was made in the melting of oxide-coated pins by reduction of the oxide coating, using magnesium in zinc solution. Although calcium is also effective for this purpose, crucible materials which will withstand simultaneous attack by molten calcium and molten uranium have not been found.

Work was continued on the processing of crucible skulls. As an alternative method of removal from the crucible to avoid crucible breakage and physical removal of skull, chemical pulverization by an oxidation-reduction cycle was investigated. After conversion to uranium dioxide the skulls were powdered and easily poured from a crucible. The possibility for effecting some fission product separation, particularly of molybdenum through volatilization of the trioxide, exists.

A method proposed for processing uranium to separate the noble metals not removed by melt refining (ruthenium, molybdenum, etc.) is the Pyrozinc process. This process begins with the dissolution of the metal ingot in molten zinc. Uranium forms an intermetallic compound (U_2Zn_{17}) with zinc, that can be separated by fractional crystallization. Zinc may be removed from the uranium-zinc intermetallic compound by vaporization. Uranium in the oxide dross from melt refining may be similarly recovered after dissolution in zinc-magnesium.

A number of supporting laboratory studies relative to the Pyrozinc process are being made. For example, cadmium has been suggested as an alternate to zinc in the Pyrozinc process.

Additional basic data have been gathered to aid in the design of decontamination processes for liquid metal solutions of fuels.

The solubility of zirconium in zinc is given by the equations

$$\log (w/o \text{ Zr}) = 9.418 - 7752/T \quad (420 \text{ to } 545 \text{ C})$$

and

$$\log (w/o \text{ Zr}) = 4.310 - 3521/T \quad (545 \text{ to } 750 \text{ C})$$

The two regions correspond to the solid phases ZrZn_{14} and ZrZn_6 ; the observed peritectic decomposition temperature of the zinc-rich phase agrees with the value obtained by thermal analysis.

The solubility of molybdenum in zinc is given by the equations

$$\log (w/o \text{ Mo}) = 2.757 - 3630/T \quad (420 \text{ to } 550 \text{ C})$$

$$w/o \text{ Mo} = 0.022 \quad (550 \text{ to } 730 \text{ C}).$$

A peritectic decomposition of an intermediate phase (b.c.c., $a_0 = 3.10 \text{ \AA}$) to molybdenum and a saturated solution occurs at about 550 C.

The solubility of thorium in zinc is given by the equation

$$\log (a/o \text{ Th}) = 6.007 - 6385/T.$$

The equilibrium solid phase is $\text{Th}_2\text{Zn}_{17}$ and its solubility appears to be given by the above equation up to its melting point.

The solubility of niobium in zinc has been measured from 450 to 750 C. The zinc-rich eutectic contains 0.075 weight per cent niobium. The solubility rises to 0.22 weight per cent at 750 C; it does not fit an Arrhenius-type equation. Metallographic evidence suggests that intermediate phase(s) exist in this system.

The solubility of plutonium in cadmium is given by the equations

$$\log (w/o \text{ Pu}) = 6.217 - 4100/T \quad (330 \text{ to } 404 \text{ C})$$

and

$$\log (w/o \text{ Pu}) = 3.456 - 2240/T \quad (404 \text{ to } 550 \text{ C}).$$

The results suggest the peritectic decomposition of the cadmium-richest phase at 404 C.

Americium coprecipitates with plutonium from a cadmium solution in accordance with the logarithmic distribution law. The coefficient of the Doerner-Hoskins relation is 0.79.

The binary eutectic valley in the zinc-rich system with uranium and ruthenium is reported. The saturation concentrations of ruthenium are higher than were previously reported.

Preliminary exploration of the zinc-rich corner of the ternary system zinc-magnesium-uranium reveals that the solubility of uranium is decreased slightly by additions of magnesium up to about 10 atomic per cent, increased slightly by further additions to about 26 atomic per cent magnesium, and then decreased precipitously by further additions of magnesium. Metallographic studies and the solubility data suggest that the field of primary crystallization shifts abruptly from U_2Zn_{17} to metallic uranium in the vicinity of 26 atomic per cent magnesium.

Provisional values for the activity of cerium in cerium-saturated zinc solutions have been measured by the emf method. The provisional values for the activity coefficients (relative to solid cerium) are 3.4×10^{-10} and 2.0×10^{-9} at 508 C and 549 C, respectively.

Measurements of vapor and decomposition pressures have been made on the uranium-zinc system at low temperatures by means of an effusion cell mounted on a continuous-weighing electromechanical balance. The probable existence of an additional phase at or near UZn_{11} has been revealed by this method. The known phase relations indicate that this new phase must be difficult to crystallize from a melt and that it must decompose incongruently below 550 C.

The separation of fission products from irradiated uranium by extraction with a fused salt of a zinc or cadmium solution of the metal has been further investigated. In the zinc system the separations achieved by conducting all the operations at 477 C are similar to those achieved by dissolution and extraction at 730 C, followed by cooling to below 550 C. The time cycles appear to be comparable. The former method has a potential advantage in being adaptable to a wider variety of construction

materials; the latter method has the potential advantage of adaptability to multi-contact operations. In the cadmium system the separations achieved were only slightly inferior to those obtained in the zinc system. However, the critical separation factor, that between rare earths and plutonium, has an approximate value of 38, which would permit adequate separations by multiple extractions. The favorable corrosion characteristics of cadmium solutions in a variety of ferrous alloys makes this system particularly attractive.

Work continued on application of a zinc-magnesium solution process to recovery and purification of plutonium from blanket material. The process involves dissolution of the uranium blanket material in zinc, crystallization of U_2Zn_{17} on which plutonium is carried, and separation from the supernatant. Separation of plutonium and uranium is effected by addition of sufficient magnesium to destroy the intermetallic compound. Uranium is precipitated as metal while plutonium goes into solution. Results continue to show that the process is feasible.

Solutions of plutonium in 46 weight per cent magnesium-zinc eutectic alloy were found to be stable in both graphite and tantalum crucibles. The stability in graphite contrasts with a previously observed rapid disappearance of plutonium from a magnesium solution.

Dissolution of skulls in zinc-magnesium solutions is also being studied. The percentages of uranium put into solution have thus far been lower than the desired value of around 95 per cent. In the course of this work it was discovered that cerium oxide as well as uranium oxide is being reduced by magnesium in zinc solution. This is undesirable and, unless conditions can be found to prevent it, will necessitate a second separation from uranium and/or plutonium.

Pressure-siphoning (transfer through a dip tube by pressurizing) appears to be an attractive procedure for separating precipitated zinc intermetallic compounds from the supernatant liquor. It is a procedure which can be readily adapted to remote operation.

Corrosion testing of various metals is being carried out in both zinc and cadmium systems. So far only tantalum and tungsten have withstood attack by zinc at 800 C in static tests. A number of metals, including Armco iron and the following steels: AISI 1025, 1040, 1065, 1095 and 410, were resistant to attack by cadmium and cadmium-uranium alloys. The 300 series stainless steels were attacked by preferential dissolution of the nickel. Dynamic tests will be run in the next quarter.

The results of chemical-metallurgical process studies are being applied to design and component testing of facilities for the EBR-II fuel-processing plant.

Drawings and specifications to be included in the bid package from the architect-engineer for the Fuel Cycle Facility are being checked.

The design of the 5-ton cranes for the air and argon cells is continuing. The radiation-resistant manipulator is being fabricated and delivery is scheduled for February 1, 1959. The purchase order for the shielding windows in the air and argon cells was awarded. Split and solid (one piece) types of protective shutters for the shielding windows are being designed. A split-type unit will be constructed for testing in the mock-up facility. A stereo-optical depth perceptor was constructed and tested in the mock-up facility. A Kollmorgen periscope was installed in the wall of this facility.

A mercury vapor lamp is undergoing gamma irradiation and testing for light output. Insulating materials for electrical conductor cables have also been tested in a gamma field. Natural and synthetic (Hycar) rubber have shown good flexibility after gamma irradiation to 5×10^8 roentgen.

Thirty 10-kilogram ingots of natural uranium-5 per cent "fissium" alloy were produced in the melt-refining furnace. These runs are preliminary to the preparation of the 50 per cent enriched uranium-5 per cent "fissium" alloy being planned. A panelboard for the melt-refining furnace has been designed and is being built.

The construction of the Laboratory and Service Building is about one-third completed. The purchase order for the junior cave windows was placed. The fume hood for evaporating samples in the junior caves was tested. Its efficiency for removal of perchloric acid fumes varied from 45 to 65 per cent, depending upon the type of water spray nozzle, volume flow rate of air, and water droplet eliminator used.

Anodic dissolution of uranium dioxide was not achieved in molten chloride baths. The addition of fluoride to these baths appears to be a promising route to such dissolutions.

Progress is reported on the synthesis and analysis of pure molybdenum disulfide and on the problem of achieving calorimetrically useful combustions in an oxygen bomb prior to the determination of the heat of formation of this compound.

The rotational energy of the oxygen bomb has been found to be 0.64 calorie per minute and the energy input during a standard firing cycle has been found to be 1.9 calories.

Samples of fluorine have been subjected to volumetric and infrared analyses in preparation for calorimetric combustions in a fluorine bomb. The available sample of highest purity contained 0.54 volume per cent impurities. Hydrogen fluoride, tetrafluoromethane, nitrogen trifluoride and silicon tetrafluoride impurities appear to be readily identifiable in a nickel absorption cell with barium fluoride windows.

Work was begun on the combustion of molybdenum metal in fluorine for the determination of the heat of formation of molybdenum hexafluoride. It is necessary that nickel and Monel parts be seasoned by exposure to this gas and to fluorine in order to minimize unwanted side reactions.

A. Laboratory Studies
(H. M. Feder)

1. Separations by Recrystallization from Liquid Metals
(I. Johnson)

The basic process being studied consists of

- (1) dissolution of the irradiated metal in a solvent metal,
- (2) crystallization of the actinide metal(s) as an inter-metallic compound, and
- (3) removal of the solvent metal from the intermetallic compound by volatilization or leaching.

The basic process may also be extended to include a hot filtration to remove insolubles, and a liquid metal-fused salt or liquid metal-liquid metal fission product extraction step.

Fundamental information is being collected on systems containing zinc, cadmium, and mercury as the solvent metals so that an optimum choice of the solvent will be possible.

a. Phase Studies

The separation of uranium and plutonium from fission product elements may be accomplished by crystallizing from the molten solvent the intermetallic compound formed from the uranium and the solvent. Such separations may be limited by any of three factors:

- (1) The solubility of the fission product element is exceeded as the temperature is lowered. The solubilities must therefore be measured.

- (2) The solubility of the fission product element is never exceeded, but it coprecipitates with uranium by solution in the intermetallic lattice. The results reported in previous quarterlies (ANL-5896 and ANL-5924) indicate that only the lanthanide and actinide metals have been found to coprecipitate with uranium from a zinc solution.
- (3) The solubility of the fission product element is never exceeded and it does not coprecipitate. The separation is then only limited by the completeness with which the mother liquor is removed from the crystallizate after washing.

Studies of the solubilities of niobium, zirconium, molybdenum, and thorium in zinc are reported below. Additional studies of the solubility of ruthenium in the uranium-zinc system have been made. The solubility of plutonium in cadmium has been measured.

An alternate method for the decomposition of the uranium-zinc intermetallic compound is by leaching with a magnesium-rich alloy. Data are reported for the solubility of uranium in the magnesium-zinc system.

(1) Niobium-Zinc
(A. E. Martin and R. J. Uhle)

The niobium-zinc system has apparently never been examined before. The solubility of niobium in zinc was determined in the temperature range 450 to 750 C by our usual technique of taking filtered liquid samples of saturated solutions at a series of temperatures. The solubilities, shown in Figure 34 on an Arrhenius-type plot, fall on a smooth curve except for points at the lower temperatures, where little change with temperature is exhibited. These data are in fair agreement with those obtained at the same time by Knighton.²⁸

Metallographic examination of the ingot obtained in this experiment revealed the presence of a eutectic structure. This information, coupled with the solubility data, indicates that there is a eutectic in the zinc-niobium system at about 0.075 weight per cent niobium.

Experiments are under way to determine whether there are intermediate phase(s) in this system. The metallographic examination suggests that this is the case.

²⁸Knighton, J. B., American Smelting and Refining Co., private communication.

(2) Zirconium-Zinc
(A. E. Martin and C. Wach)

The solubility of zirconium in zinc was studied in the temperature range 430 to 730 C by our usual technique of taking filtered liquid samples of saturated solutions at a series of temperatures.

Data are shown in the usual form in Figure 35. Also shown are the sampling data obtained by Knighton (ANL-5759, pages 118, 119), the curve obtained by Gebhardt²⁹ by thermal analysis, and a composite line given by Chiotti et al.³⁰ The line given by the latter is based mainly on their own data from measurements of vapor pressure at higher temperatures, thermal analysis, and metallographic examination, but also partly on Knighton's and their own liquid sampling results. The peritectic reaction at 545 C reported by Gebhardt²⁹ and also by Iowa State College³⁰ is not indicated by the composite line.

Our data fall on two well-defined lines that intersect at about 554 C, in fair agreement with the reported peritectic. Our data also agree well with Knighton's. Our data are in fair agreement with the composite line³⁰ above the peritectic temperature; below 545 C the composite line is based on only one sampling experiment and a metallographic estimation of the eutectic composition. Finally, our data are in poor agreement with Gebhardt's, which had been obtained only by thermal analysis.

²⁹Gebhardt, E., Z. Metallkunde 33 355-7 (1941).

³⁰Iowa State College Newsletter (Sept. 1958).

According to the phase information compiled at Iowa State College,³¹ the two compounds richest in zinc are ZrZn_{14} and ZrZn_6 ; the first decomposes peritectically at 545 C, the second decomposes at 750 C.

In view of these observations, it is clear that our lower solubility line, from 420 to 554 C, represents the equilibrium of ZrZn_{14} with a zirconium-saturated melt. The solubility is given by the equation

$$\log (w/o \text{ Zr}) = 9.342 - \frac{7692}{T} .$$

The upper solubility line, extending from 554 C to 750 C, represents the equilibrium of ZrZn_6 with a zirconium-saturated melt. This solubility is given by the equation

$$\log (w/o \text{ Zr}) = 4.310 - \frac{3521}{T} .$$

³¹Chiotti, P., ISC-759 (July 1956).

(3) Molybdenum-Zinc
(A. E. Martin and C. Wach)

Earlier work on this system is very sketchy. Hansen³² reports that no additional phase is formed by molybdenum and zinc at high temperatures, and he dismisses a report of an additional phase formed at lower temperatures by ascribing it to a probable impurity of iron.

The solubility of molybdenum in zinc was determined by our usual technique in the temperature range 422 to 730 C. A stirring rod of pure metal served as the primary source of molybdenum, but additional metal was also added in powder form.

The solubility results, shown in Figure 36 in the usual log solubility versus $1/T$ form, fall on two lines which intersect at about 550 C. This temperature is thus indicated as a peritectic temperature in the zinc-molybdenum system, a conclusion that has been confirmed in two ways. A slight thermal arrest was obtained at this temperature on cooling a zinc melt to which had been added some clippings of molybdenum sheet. More conclusive evidence was obtained by holding molybdenum rods in molten zinc overnight at a series of temperatures. Rods held at temperatures below 550 C were coated with metallic layers of an additional phase, while those held above this temperature were not. The lower solubility line, from 420 to 550 C, therefore represents the equilibrium between an intermetallic compound of zinc and molybdenum and a molybdenum-saturated melt. This solubility is described by the equation

$$\log (w/o \text{ Mo}) = 2.757 - \frac{3630}{T} .$$

³²Hansen, M., Constitution of Binary Alloys, McGraw-Hill Book Co., (New York 1958) p. 981.

The upper solubility line, from 550 to 730 C, presumably represents the equilibrium between molybdenum metal and a molybdenum-saturated melt. This solubility is practically constant at 0.022 weight per cent molybdenum.

The X-ray diffraction patterns of crystals formed during the cooling of saturated melts and of crystals formed on the surface of molybdenum rods immersed in molten zinc for five days at 450 C were found to be identical. The pattern is b.c.c., with a_0 approximately equal to 3.10 Å. Work is in progress to establish the composition and structure of the intermetallic compound.

(4) Thorium-Zinc
(A. E. Martin and R. J. Uhle)

The solubility of thorium in zinc was determined by our usual technique of taking filtered samples of saturated solutions. The results are shown in Figure 37 in a log solubility versus $1/T$ plot for the temperature range 445 to 705 C. The data fall fairly well on a straight line over the entire range, so that the solubility can be represented by the equation

$$\log (a/o \text{ Th}) = 6.007 - \frac{6385}{T}$$

At thorium concentrations less than about 0.50 weight per cent, where it is approximately true that weight per cent thorium equals 3.55 times the atomic per cent of thorium, this solubility can also be given by the expression

$$\log (w/o \text{ Th}) = 6.557 - \frac{6385}{T}$$

Figure 37 also includes solubility data obtained at Iowa State College³³ by thermal analysis of alloys up to the composition $\text{Th}_2\text{Zn}_{17}$, the most zinc-rich of the four phases in the zinc-thorium system.

³³Iowa State College Newsletter (July 1958).

It is apparent that an extension of our solubility line to these high concentrations checks very well with their data. Our solubility data thus represents the equilibrium between $\text{Th}_2\text{Zn}_{17}$ and a thorium-saturated melt.

(5) Plutonium-Cadmium and Plutonium-Amercium
Cadmium

(I. O. Winsch, P. Nelson, R. C. Paul)

Measurements were made of the solubility of plutonium in cadmium as a function of temperature by the usual sampling technique. The solubility was found to increase from 0.3 per cent at 330 C to nearly four per cent at 500 C.

The experiments were done by charging 58 grams of plutonium and 1368 grams of cadmium in a mild steel crucible within an induction-heated furnace (ANL-5602, page 122). The experiments were carried out under an inert atmosphere of helium. The molten cadmium was agitated with a motor-driven stirrer throughout the experiment, except while sampling. Equilibrium was approached from both higher and lower temperatures. Separate samples taken at the same (or close) temperatures indicate the reproducibility to be about one per cent in this experiment. Americium concentrations were determined in the original plutonium and in all samples so that appropriate corrections could be applied to the alpha count. Ameri-

cium analyses were performed by means of an anion exchange separation of americium and plutonium, followed by alpha counting of a direct plate of the americium fraction. The accuracy of the americium analysis is ± 10 to 20 per cent.

Table 32

PLUTONIUM AND AMERICIUM
CONCENTRATIONS IN
CADMIUM SOLUTIONS
AT 330 TO 550 C

Charge 58.4 g plutonium
 0.01 g americium
 1368.5 g cadmium

(Samples were obtained in the order shown)

Temp (C)	$1000/T$	Solution Concentrations	
		Plutonium (w/o)	Americium (μm)
333	1.65 ₀	0.274	0.88
404	1.47 ₇	1.400	2.33
470	1.34 ₆	2.97	6.32
554	1.20 ₉	4.07	6.6
505	1.28 ₅	3.76	6.6
446	1.39 ₁	2.18	4.0
399	1.48 ₈	1.26	3.16
351	1.60 ₃	0.435	1.17
332	1.65 ₃	0.279	0.825
330	1.65 ₈	0.270	0.825
399	1.48 ₈	1.28	3.29
472	1.34 ₂	2.85	5.06
552	1.21 ₂	4.10	6.9
547	1.22 ₀	4.10	7.0
557	1.20 ₅	4.02	7.4

The data are tabulated in Table 32 and plotted in Figure 38. The concentrations measured above 550 C were those which would have resulted from complete dissolution of the charge; they presumably represent unsaturated solutions.

The sharp change in slope of the solubility curve at about 404 C indicates a probably peritectic transformation

at this temperature. Work is in progress to determine the nature of the phases formed in the plutonium-cadmium system. If this system is exactly analogous to the cerium-cadmium system, the phases expected are PuCd_{11} and PuCd_6 .

Equations representing the solubility of plutonium in cadmium are

$$\log (w/o \text{ Pu}) = 6.217 - \frac{4100}{T} \quad (330 \text{ to } 404 \text{ C})$$

and

$$\log (w/o \text{ Pu}) = 3.456 - \frac{2240}{T} \quad (404 \text{ to } 500 \text{ C}).$$

The americium contents of the plutonium-saturated solutions have been treated as a case of coprecipitation of americium with plutonium. The Doerner-Hoskins plot for this coprecipitation is shown in Figure 39. The value of λ for the coprecipitation of americium with plutonium is 0.790.

(6) Ruthenium-Uranium-Zinc
(I. Johnson and K. E. Anderson)

The solubility of ruthenium in a zinc solution also saturated with uranium is significantly lower than its solubility in the absence of uranium.²⁹ The exact solubility of ruthenium is of some importance for the processing of uranium alloys containing several per cent of ruthenium, because it determines the minimum allowable crystallization temperature for separation.

A zinc ingot containing 0.042 weight per cent ruthenium and 1.5 weight per cent uranium from a previous solubility experiment was remelted and held at 700 C for five hours to achieve saturation. This solution was cooled slowly and filtered samples were taken at about 25 C intervals. The ruthenium concentrations in solution are shown in Figure 40. It may be seen that the ruthenium concentration decreases slowly as temperature is lowered, until about 500 C is reached. Below this (peritectic) temperature the concentration sharply decreases. The low-temperature portion of this curve for the ruthenium-uranium-zinc system appears to be identical with that found in the ruthenium-zinc system.

The same melt was subsequently reheated and held for about a half hour at each successively higher temperature prior to sampling. The results of this experiment are also shown on Figure 40. The ruthenium concentrations achieved do not quite reach the values found in the cooling experiment.

(7) Uranium-Zinc-Magnesium
(A. E. Martin and R. J. Uhle)

In order to establish the effect of magnesium on the solubility of uranium in zinc, uranium concentrations were measured in a series of saturated zinc-magnesium alloys by our usual technique. The

results of these determinations are shown in Figure 41 in the usual log solubility versus $1/T$ form, and in Figure 42 as a plot of isothermal liquidus lines in the ternary system. The data indicate relatively minor effects of as much as 26 atomic per cent magnesium on the solubility of uranium. Between 26 and 40 atomic per cent magnesium a sharp drop in the uranium solubility occurs. In terms of primary fields of crystallization on the ternary diagram, the data suggest a shift in composition from one field to another. In this system the shift suggested by the metallographic evidence is from the field of primary crystallization of U_2Zn_{17} to that of uranium.* This interpretation will be checked by X-ray diffraction examination of the crystalline materials precipitated to the bottoms of the ingots.

Additional data on solubility have been sought at higher contents of magnesium, but inconsistent results were obtained. In the hope that a different experimental approach might clarify the situation, an isothermal experiment was conducted by incremental addition of magnesium to uranium-saturated zinc at 675 C. The results of this run should indicate more clearly the transition between the fields of crystallization.

*If this be true then the maxima in Figure 42 should be drawn as cusps rather than rounded. This has not been done because of uncertainty in their location.

b. Thermodynamic Studies

In any reaction in which a metallic element is transferred to or from a liquid-metal solution, the activity of the element in the liquid-metal solution will be of importance in determining the position of the equilibrium. For example, if the fuel to be dissolved occurs in part as an oxide, then a reaction of importance might be

in which magnesium dissolved in zinc is used as a typical reductant. In this case the equilibrium condition is determined by the equation

$$0 = \Delta F^\circ + RT \ln \frac{a_{\text{U}}}{a_{\text{Mg}}^2} ,$$

where a_{U} and a_{Mg} are the respective activities of the uranium and magnesium in the zinc solution. These activities must be known as functions of concentration and temperature if this relation is to be used in practical computations. In this example the relatively low activity coefficient of uranium in molten zinc (and hence its low activity at moderate concentrations) is a significant part of the driving force for this reaction.

Studies are under way to determine the activities (and activity coefficients) of several metals of importance in liquid zinc and cadmium solutions. The activity of uranium dissolved in zinc solutions has already been studied by the emf method (ANL-5924, page 132).

(1) Cerium-Zinc System (I. Johnson and R. M. Yonco)

A cell similar to the one used for the uranium-zinc system was set up. One electrode was metallic cerium and the other electrode was a saturated solution of cerium in liquid zinc. At the temperatures of operation the phase diagram of the system indicates that the saturated solution is in equilibrium with a CeZn_{11} intermetallic phase. The electrolyte was a dilute solution of anhydrous CeCl_3 in potassium chloride-lithium chloride eutectic mixture. The emf developed by this cell was 0.7138 volt at 508 C and was 0.6836 volt at 549 C. An attempt to obtain a value at 600 C failed when the cell developed an internal short. This was caused by the formation of a mass of the cerium-zinc intermetallic phase between the two electrodes. While the voltages obtained can only be considered as provisional, they do permit an estimate of the activity of cerium in zinc solution. These values of the activity, when combined with the known solubility of cerium in zinc, allow the activity coefficients to be estimated as 3.4×10^{-10} at 508 C and 2.0×10^{-9} at 549 C.

(2) Uranium-Zinc System
(C. L. Rosen and P. Bergland)

Uranium-zinc alloys are being studied by the effusion method in order to clarify certain parts of the phase diagram and to determine the thermodynamic properties of the intermediate phases in the system.

FIGURE 43
CONTINUOUS WEIGHING VACUUM EFFUSION APPARATUS

The effusion apparatus shown in Figure 43 is a modification of the one described in ANL-5858, page 82. It consists of an effusion cell suspended within a furnace from one arm of a continuously recording balance. The weighing is accomplished by repelling a magnetic core with a solenoid having a linear force-current relationship. The balance is a null-point instrument. The null position is determined by means of a linear variable differential transformer (LVDT). The core of the LVDT is rigidly attached to the balance

beam and, as the beam shifts from its null position, a voltage (whose phase depends upon the direction of the shift from the null position) is induced in the secondary of the LVDT. This voltage is amplified and drives a reversible two-phase motor that varies the current in the solenoid to return the balance to its null-position.

It can be shown from thermodynamic considerations that at a given temperature every stable phase field in a binary phase diagram has associated with it a unique volatility or range of volatilities. As one proceeds with effusion of a mixture, one traverses the phase diagram from the volatile-rich side to the volatile-poor side. In the present experiments three different volatilities have been exhibited by uranium alloys at each of the temperatures tested. A typical experimental result is shown in Figure 44. Figure 45 shows the comparison with pressures measured by a dew-point method³⁴ and those calculated from emf measurements.

The fact that the effusion experiments indicate the existence of another intermetallic phase of the approximate composition

³⁴Chiotti, P., Klepfer, H. H. and Gill, K. J., Journal of Metals: Trans. AIME, 209, 51 (1957).

UZn₁₁, which was not found at higher temperatures (Chiotti³⁴ and ANL-5924, page 132), suggests that this phase decomposes peritectically below 550 C.

Future work will include a variation of the orifice size and an improvement of temperature measurement and control in order to increase the precision of the vapor-pressure measurements. Similar measurements on the uranium-cadmium system are in progress.

c. Liquid Metal-Fused Salt Separations (M. Ader, J. Pavlik)

(1) Zinc System

The feasibility of removing certain fission products from irradiated fuels dissolved in liquid zinc has been demonstrated (ANL-5896, page 135, and ANL-5924, page 41) by tracer-level experiments in which decontamination was accomplished by molten salt extraction at about 725 C, followed by cooling below 500 C to crystallize intermetallic compounds of the actinide elements.

The highly corrosive nature of zinc strongly limits the choice of materials of construction, although graphite and certain refractories are possibilities (see pages 160 to 162 for data on corrosion tests). However, the corrosion of various ferrous alloys by molten zinc is greatly decreased below 500 C, particularly in the presence of certain

inhibitors such as aluminum. Interest in this possibility prompted an experiment (MA-Zn-69) in which dissolution, extraction, and precipitation all took place at 477 C. In this experiment irradiated uranium metal was allowed to react with molten zinc containing 0.2 weight per cent magnesium in a covered, but not air-tight, tantalum crucible. A flowing atmosphere of argon was used to reduce oxidation by air. A 30 weight per cent lithium chloride-70 weight per cent potassium iodide flux was also employed. The mixture was stirred vigorously for seven hours at 477 C, after which the unreacted uranium was removed and stirring was continued for two hours.

An iodide-containing flux was desired as a possibly useful variant of the all-chloride fluxes hitherto employed. A cursory search of the literature revealed no stable, low-melting (<500 C), all-iodide flux that could be prepared quickly from common reagents. However, the lithium chloride-potassium iodide system was found to yield a suitably low-melting eutectic. A phase diagram was obtained by thermal

analysis and is shown in Figure 46. The eutectic composition lies between 35 and 37.5 mol per cent potassium iodide (68 to 70 weight per cent) and has a melting point of 429 ± 4 C. The thermal analysis gave no indication of formation of an intermediate phase.

The distributions of specific elements in experiment MA-Zn-69 are given in Table 33. The plutonium and fission products were present in trace amounts due to growth and decay in the irradiated uranium, and were analyzed radiochemically. Uranium was analyzed colorimetrically or fluorimetrically, magnesium by EDTA titration. The data are expressed in percentages so as to show the fraction of each element present in a given phase relative to the amount in the irradiated uranium which reacted with zinc. The uranium consumed was determined by difference by removing the unreacted uranium, cleaning it in sulfuric acid, and weighing. A discussion of the results follows:

Magnesium: The magnesium concentration remained close to the nominal concentration throughout the experiment, indicating little or no oxidation by air had occurred.

Table 33

DISTRIBUTION OF ELEMENTS RESULTING FROM REACTION OF
IRRADIATED URANIUM WITH ZINC - 0.2 WEIGHT PER CENT
MAGNESIUM AT 477 C UNDER 30 WEIGHT PER CENT
LITHIUM CHLORIDE - 70 WEIGHT PER CENT
POTASSIUM IODIDE FLUX

(Experiment MA-Zn-69)

Composition: 2.27 kg Zn - 0.20 w/o Mg, 0.0567 kg U,
0.20 kg 30 w/o LiCl - 70 w/o KI
Uranium: Irradiated 1686 d, cooled 533 d, 95 ppm Pu
Conditions: Material of construction, tantalum; flowing
argon atmosphere
Procedure: Phases agitated vigorously for 7 hr at 477 C;
unreacted U removed and phases agitated
additional 2 hr
Sampling: Samples drawn through grade 60 porous graphite
into quartz glass tubing

Stirring Time (hr)	Magnesium in Zinc Phase (w/o)	Per Cent of Elements in Solution ^a						
		U	Pu	RE ^b	Zr	Ru	Sr	Cs
		Zinc Solution						
1.1	0.20	13	14	9	17	14	-	-
3	0.20	6.2	7.1	5.6	40	43	1.2	2.2
5	0.20	0.34	0.53	0.51	50	67	0.15	0.4
6	0.21	0.37	0.53	1.1	54	79	0.04	0.4
8	-	-	-	0.46	-	89	0.01	0.4
9	0.21	0.41	0.69	0.42	64	88	0.01	0.5
Flux Solution								
3	-	0.006	0.08	9.2	0.1	0.01	39	28
5	-	0.006	0.14	15	0.1	0.01	62	43
7	-	0.006	0.18	21	0.3	0.19	86	61
8	-	-	-	24	-	0.02	100	76
9	-	0.006	0.18	20	0.1	0.02	76	60

^aBased on analysis of irradiated uranium control.

^bRare earth beta activity composed of Ce¹⁴⁴, Pr¹⁴⁴, Pm¹⁴⁷, Y⁹⁰.

Uranium: The values of 0.34 to 0.41 per cent of the uranium found in the metal phase from the fifth to ninth hour of stirring correspond approximately to the solubility of uranium in zinc at 477 C, i.e., approximately 0.01 weight per cent. However, the analyses at the end of the first and third hours indicate uranium concentrations greater by 40 and 20 times. These high concentrations may be due to supersaturation or to formation of precipitate particles too fine to be filtered by grade 60 porous graphite (average pore diameter = 33 microns). (Microscopic examination of ingots formed by reaction of zinc with uranium below 500 C revealed the presence of crystals very much smaller than those formed by cooling solutions of uranium in zinc.) The contamination of the early samples by unfiltered particles is supported by the observation that the percentages of plutonium, rare earths, zirconium, and ruthenium in these samples at 1.1 hours are all close to that of uranium. After three hours of stirring the percentages of zirconium and ruthenium in the melt samples continued to increase while the percentages of plutonium and the rare earths decreased, because the latter coprecipitate with uranium. Apparently five hours of aging were required for all of the precipitate particles to grow to a filterable size. The rate of reaction and precipitation with uranium at temperatures below 500 C is considerably slower than at 725 C or higher, but for practical purposes the additional time is partly offset by that required to crystallize uranium by cooling.

The amount of uranium extracted into the flux phase was negligible and in line with results obtained in previous experiments.

Plutonium and Fission Products: Zirconium and ruthenium were not appreciably extracted by the lithium chloride-potassium iodide flux and probably did not coprecipitate with uranium. Strontium and cesium were well extracted by the flux and coprecipitation was also probably negligible. The lack of a complete material balance for these elements seems to indicate that the presence of accidental scavengers has not been fully eliminated. About 0.2 per cent of the plutonium and 20 per cent of the rare earths were extracted by the flux, the remainder being coprecipitated with uranium. The fission product results may be summarized by stating that these elements were finally distributed in approximately the same manner as in a previous experiment in which irradiated uranium was dissolved in zinc-0.13 weight per cent magnesium under Dow 230 flux at 742 C and cooled to 456 C.

The data do not give any clear indication that the presence of iodide in the flux caused a significantly greater degree of plutonium-cerium separation above that obtained with chloride fluxes.

(2) Cadmium System

Interest in cadmium as a solvent for reprocessing irradiated fuels has led to a study of the behavior of plutonium and fission products with respect to

- (1) distribution between cadmium-magnesium-uranium solutions and molten salts, and
- (2) coprecipitation with the intermetallic compound UCd_{11} .

In Experiment MA-Cd-68 irradiated uranium was dissolved in cadmium-0.23 weight per cent magnesium solution at 470 C under molten lithium chloride-potassium chloride eutectic flux. The mixture was held in a covered, but not air-tight, mild steel crucible. A flowing atmosphere of argon, in addition to the magnesium metal and flux cover, was used to suppress air oxidation. After seven hours of vigorous stirring, during which samples of both metal and flux phases were withdrawn, magnesium was added to increase its nominal concentration to 1.9 weight per cent. The mixture was stirred for an additional 16.5 hours and was sampled again. Coprecipitation was next studied by cooling the mixture at a rate of 0.3 to 0.5 C/min, with stirring, and sampling the metal phase at several temperatures.

Experimental details and distributions of specific elements are given in Table 34. The data are expressed in percentages so as to show the fraction of each element present in a given phase relative to the amount in the irradiated uranium specimen dissolved. The first two parts of the experimental data, (I) and (II), show distributions at 470 C between the flux and metal solutions containing 0.23 and 1.90 weight per cent magnesium, respectively. Part III gives data used to interpret the coprecipitation behavior of fission elements. A discussion of the results follows.

Magnesium: The magnesium concentration remained constant at about 0.23 weight per cent during seven hours of stirring, and at 1.90 weight per cent during 16.5 hours of stirring, indicating that oxidation by air was negligible.

Uranium: The uranium disc (1.1-inch diameter x 5/32-inch thick) dissolved completely after a little more than three hours of agitation; approximately 75 per cent dissolved within the first hour. The disc was suspended vertically in the liquid metal with one face about 1/8 inch from the edge of a one-inch square paddle rotating at 1500 rpm.

The percentages of uranium extracted by the flux were 0.1 and 0.2 per cent, respectively, in Parts I and II of this experiment. Although the extraction of uranium by the flux is quite small, it is significantly greater than any extractions from zinc solutions which have been encountered.

Plutonium and Fission Products: Approximately 0.3 per cent of the plutonium was extracted by the flux in both Part I and Part II of the experiment.

Table 34

DISTRIBUTION OF ELEMENTS AT 470 C BETWEEN LITHIUM CHLORIDE-POTASSIUM CHLORIDE EUTECTIC AND: (I) CADMIUM - 0.23 WEIGHT PER CENT MAGNESIUM - 1.7 WEIGHT PER CENT URANIUM; (II) CADMIUM - 2 WEIGHT PER CENT MAGNESIUM - 1.7 WEIGHT PER CENT URANIUM; (III) DURING PRECIPITATION OF URANIUM BY COOLING

Nominal Compositions: (I) 2.72 kg Cd-0.25 w/o Mg - 1.7 w/o U;
0.20 kg LiCl-KCl eutectic
(II) 2.76 kg Cd-2.0 w/o Mg - 1.7 w/o U;
0.20 kg LiCl-KCl eutectic

Uranium: 48 g; irradiated 1686 d, cooled 525 d,
100 ppm Pu

Conditions: Material of construction, mild steel; flowing
argon atmosphere

Procedure: See text

Sampling: Samples drawn through grade 60 porous graphite
into quartz tubing

	Liquid Phase Sampled	Hr Stirring at 470 C	Mg (w/o)	Per Cent of Elements in Solution ^a							
				U	Pu	RE ^b	Zr	Nb	Ru	Sr	Cs
Part I	Metal	1	0.234	74	-	-	-	-	-	-	-
	Metal	2	-	80	-	-	-	-	-	-	-
	Metal	3	0.232	92	95	79	71	61	57	0.81	43
	Metal	5	0.236	99	-	-	-	-	-	-	-
	Metal	7	0.235	97	105	77	63	40	33	0.55	16
	Flux	3	-	1.39 ^c	0.18	13.7	1.5	2	0.72	114	55
	Flux	7	-	0.10	0.34	10.4	1.5	2	0.34	94	61
Part II	Metal	16.5	1.90	90	98	79	41	12	8.5	0.10	2.4
	Flux	16.5	-	0.17	0.32	9.0	1.7	3	0.49	89	74
Part III		Temp (C)									
	Metal	450	-	91	99	81	50	21	16	0.19	4.3
	Metal	430	1.95	69	83	35	44	26	18	0.28	4.7
	Metal	405	-	45	60	5.3	56	42	36	3.3	10
	Metal	383	-	33	47	2.3	59	56	46	2.1	11
	Metal	363	-	29	38	2.0	56	61	49	3.4	12
	Metal	338	2.07	24	36	2.0	54	66	54	0.63	10

^aBased on analysis of irradiated uranium control.

^bRare earth beta activities: Ce¹⁴⁴, Pr¹⁴⁴, Pm¹⁴⁷, Y⁹⁰.

^cQuestionable result.

The Doerner-Hoskins plot for the coprecipitation of plutonium with UCd_{11} , shown in Figure 47, yields a coefficient, λ , with a value of 0.75.

Approximately 10 per cent of the rare earths was extracted by the flux in Parts I and II of this experiment. The separation factor for plutonium and rare earths, $\frac{(\text{RE}) \text{ salt}/(\text{RE}) \text{ metal}}{(\text{Pu}) \text{ salt}/(\text{Pu}) \text{ metal}}$, has a value in this system of about 38. This may be compared with separation factors of 48 to 59 in the zinc system. If the plutonium-rare earth data represent equilibrium values, separation factors of this magnitude indicate the possibility that plutonium-rare earth separations could be achieved by multi-batch or counter-current multi-stage operation. Additional experimentation will be re-

quired to determine the mechanism of this extraction, its reversibility and its kinetics.

Coprecipitation of the rare earths with UCd_{11} is shown in the Doerner-Hoskins plot of Figure 47. The coefficient, λ , has the unusually large value of ~ 3.6 . Such a large coefficient is surprising, but not unreasonable, because uranium and the rare earths form isostructural cadmium compounds of the type MCd_{11} . The deviation of the last two points from the drawn curve may be due either to radioactive contamination of the weakest beta-counting samples or to the fact that the mixture of activities in the rare earth fraction is partially fractionated by the coprecipitation.

Extraction of zirconium, niobium and ruthenium into the flux was small throughout Parts I and II of this experiment. For all three elements there occurred a slow diminution of activity in the metal phase which was reversed during the subsequent cooling. These data show that coprecipitation of these elements with UCd_{11} is not taking place; rather, they suggest a scavenging effect involving a phase other than the liquid metal or fused salt.

Strontium and cesium were strongly extracted by the flux, with the former extracted more completely and rapidly than the latter. The concentrations of strontium and cesium in the metal phase prior to precipitation of UCd_{11} were low and, therefore, not at a favorable

level to determine whether coprecipitation of these elements took place; the trend of the data, however, does not support such a conclusion.

In summary, it appears that fission product separation processes based on cadmium as a solvent and employing fused salt extractions and precipitation by means of an intermetallic compound will operate as effectively as with zinc as a solvent. Future studies of extraction will be done with an apparatus having a cleaner atmosphere and with more attention given to purity of the fused salt. Higher concentrations of plutonium and cerium or other fission products will be used to avoid the confusing side-effects that sometimes occur at trace-level concentrations.

d. Electrolytic Separations
(J. Wolkoff)

As a preliminary to an investigation of fission product separation processes involving electrolytic deposition into liquid metal cathodes, a short study of the problem of anodic dissolution of uranium dioxide has been undertaken. The motive for this study was the fact that at least part of the melt-refining dragout may be present as the oxide, and its dissolution poses a greater problem than the dissolution of metal.

Sintered pellets of uranium dioxide were used for the dissolution tests. They were pressed at 32 tsi and sintered at 1400 C. The salt bath chosen for the first tests was the ternary eutectic of CaCl_2 - BaCl_2 - NaCl (mp 450 C).

The tests made to date are summarized in Table 35. In general, simple immersion of the pellet in the bath for an interval was tried, followed by attempted anodic dissolution. The pellet was held on a graphite anode tray.

Table 35

TESTS FOR DISSOLUTION OF SINTERED URANIUM DIOXIDE PELLETS

Exp No.	Temp (C)	Treatment	Time (hr)	Initial Salt Bath Composition	Remarks
0-3	500	Simple contact between pellet and salt bath	5.3	CaCl_2 - BaCl_2 - NaCl eutectic, ^a plus 2.6 w/o U as chloride ^b	No tendency to dissolve
	500	Pellet resting on graphite anode during electrolysis	6.9	CaCl_2 - BaCl_2 - NaCl eutectic, ^a plus 2.6 w/o U as chloride ^b	No tendency to dissolve
0-4	700	Pellet resting on graphite anode during electrolysis	7.2	CaCl_2 - BaCl_2 - NaCl eutectic	No tendency to dissolve
0-5	700	Simple contact between pellet and salt bath	4.3	CaCl_2 - BaCl_2 - NaCl eutectic, plus 10 w/o cryolite	No tendency to dissolve
	700	Pellet resting on graphite during electrolysis	1.9	CaCl_2 - BaCl_2 - NaCl eutectic, plus 10 w/o cryolite	Pellet partly dissolved

^aEutectic composition 50 w/o CaCl_2 , 29 w/o BaCl_2 , 21 w/o NaCl .

^bValence state of U not known, probably mixture of U^{+3} and U^{+4} .

Uranium dioxide did not dissolve in the pure chloride eutectic at 500 C or 700 C. An attempt to solubilize uranium dioxide in the fused salt by the addition of a low concentration of uranium chloride, according to the reaction

was made in Experiment 0-3. No effect was noted. The addition of 10 weight per cent cryolite to the eutectic in Experiment 0-5 gave a clear indication of anodic attack at the pellet-graphite contact line.

2. Thermochemistry of Inorganic Substances

a. Chemical Studies (E. Greenberg)

The sample of synthetic molybdenum disulfide described in the previous quarterly report (ANL-5924, page 145) was exhausted in preliminary noncalorimetric combustion experiments. An additional 10-gram quantity has been kindly donated by the Climax Molybdenum Company. In order to supplement the supply of synthetic molybdenum disulfide a quantity of this material is being prepared according to a procedure developed at the Climax Molybdenum Company.³⁵ Two small trial quantities have been prepared and the synthesis of a 50-gram quantity is in progress.

A 100-gram sample of natural molybdenum disulfide has been prepared by purifying some material donated by the Climax Molybdenum Company. The purification procedure was similar to that described by McBride.³⁶ Preliminary determinations of moisture by the Karl Fischer method indicate that the sample contains about 0.42 per cent water. The material is currently being analyzed for molybdenum and sulfur.

b. Rotating Bomb Calorimeter (R. L. Nuttall, D. R. Fredrickson)

The rotating bomb calorimeter has been tested further and used to obtain (a) the firing-energy correction and (b) the rotational-energy correction. Also, a series of preliminary calorimetric combustions of molybdenum disulfide has been carried out. The glass bomb was completed and has been used to observe full-scale reactions. Combustion techniques for burning molybdenum disulfide were first tried in the glass bomb.

Table 36 is a summary of the experiments to determine ignition energy. The bomb was set up exactly as in a benzoic acid run (without benzoic acid and cotton thread) and fired 20 times. The purpose of the

³⁵Bell, R. E. and Herfert, R. E., J. Amer. Chem. Soc., 79, 3351 (1957).

³⁶McBride, J. J., Low Temperature Heat Capacities of Layer and Chain Type Crystal Structures, University of Michigan Doctoral Thesis (1956).

experiment was to calibrate by calorimetric means the measuring unit for ignition energy that was read with each firing. In Table 36, column two lists the resistance rise in ohms of the calorimeter thermometer. Column three is the dial calibration of the measuring unit for ignition energy. Column four gives the average amount of energy for each firing.

Table 36

SUMMARY OF IGNITION ENERGY EXPERIMENTS

<u>Number of Firings</u>	<u>ΔR</u>	<u>$(\Delta R/\text{Full Scale})10^4$</u>	<u>Cal/Firing</u>
20	0.001043	1.10	1.8 ₃
20	0.001221	1.34	2.1 ₅
20	0.001090	1.17	1.9 ₀

Rotational energy was determined by setting up the bomb in the usual manner and observing the change of resistance with time, without rotation, and with rotation. Table 37 summarizes the rotational energy experiments.

Table 37

SUMMARY OF ROTATIONAL
ENERGY EXPERIMENTS

<u>$R/\text{sec} \times 10^7$</u>	<u>Energy, Calories/ minute</u>
3.10	0.65 ₄
3.20	0.67 ₅
2.89	0.60 ₅
2.90	0.61 ₂

$$\text{Avg} = 0.63_6 \pm 0.01_7$$

Several trial combustions were made in the glass bomb to find the best conditions to burn molybdenum disulfide to molybdenum trioxide and sulfur trioxide. A new technique, in which the sample pellet is suspended on an imbedded wire, seems to work rather well. However, the conversion to sulfur trioxide was poor. Combustions using higher pressures of oxygen resulted in more complete conversion to sulfur trioxide, but the maximum feasible pressure is limited. As higher pressures of oxygen are used, the temperatures attained in the reaction increase. Eventually, temperatures high enough to melt the platinum suspension wire and to spoil the run are attained.

A series of seven calorimetric runs, using the suspended wire technique, was made. Conditions were varied from experiment to experiment. Conversion of sulfur to sulfur trioxide varied from 37 per cent at six atmospheres to 80 per cent conversion at 10 atmospheres. High pressures could not be used. As a solution to this problem a suspension wire melting at higher temperatures was sought. A platinum-10 per cent rhodium alloy wire did not prove to be satisfactory. Two experiments with rather heavy pure iridium wire were tried. The iridium wire did not melt and its use may be successful. Further experimentation with this metal awaits receipt of some finer wire, as a heavy wire causes certain mechanical problems.

All of the suspended wire experiments were performed with the bomb assembled in the inverted position. Sodium hydroxide solution was placed in two 6-ml crucibles inside the bomb. After the combustion the bomb was rotated to dissolve the molybdenum trioxide and sulfur trioxide in the caustic solution. The net reaction in the bomb is thus

c. Fluorine Bomb Calorimetry
(J. L. Settle and L. Stein*)

Construction of the full-scale train for bomb charging, discharging and analytical purposes has continued. It is expected that this will be completed and in operation in January, 1959.

An apparatus for the analysis of fluorine was constructed and used to analyze two tanks of fluorine. A half-pound cylinder of commercial fluorine in routine use was found to contain impurities to the extent of 1.61 volume per cent. A half-pound cylinder of Pennsylvania Salt Company "high-purity" fluorine which was on hand was found to contain 0.54 volume per cent of impurities.

In the procedure used in this analysis fluorine is admitted to one atmosphere of pressure to a Pyrex bomb containing approximately 50 grams of mercury. The surface coating of fluoride formed on the mercury prevents immediate reaction, so the initial pressure in the bulb can be accurately measured. After shaking the bomb to promote the complete reaction, the residual pressure is measured with an oil manometer.

An infrared gas-absorption cell made of nickel, with barium fluoride windows attached to it by Araldite Cement, was evacuated and filled to a pressure of 420 mm mercury of fluorine from the half-pound cylinder in routine use. A Beckman Model 1R4 Spectrophotometer was used to obtain a scan of the infrared absorption peaks of this material. The major

*Cooperating Staff Member, Chemistry Division, ANL.

impurities detected by this method were hydrogen fluoride and carbon tetrafluoride. A peak arising from the absorption by a small amount of nitrogen trifluoride and/or silicon fluoride was also present.

Work was begun on the problem of analyzing the molybdenum hexafluoride produced by the fluorine combustion of molybdenum:

Nickel and Monel appear to be the only metals which may be satisfactorily used as containers for handling and storing molybdenum hexafluoride. Even these materials must be "seasoned" and brought to constant weight by prefluorination with molybdenum hexafluoride and elemental fluorine before quantitative transfers of molybdenum hexafluoride can be accomplished. After being seasoned, the lines and vessels must be protected from moisture, because the protective coating is hygroscopic.

Various physical methods will be employed for the determination of the products of reaction between molybdenum and fluorine. These may include the following:

- (1) Quantitative transfer of condensible gases from the bomb to a weighing bulb to establish the material balance between the amount of molybdenum consumed in the reaction and the amount of molybdenum hexafluoride produced.
- (2) Measurement of the equilibrium vapor pressures and vapor densities of the product gases and comparison with accepted values for pure molybdenum hexafluoride.
- (3) Use of infrared absorption to identify volatile impurities in the molybdenum hexafluoride.

Molybdenum hexafluoride may also be analyzed chemically by dissolving it in excess water with care to avoid the loss of any hydrofluoric acid. This solution may then be analyzed for molybdenum and fluorine by conventional methods.

d. High-Temperature Enthalpy Calorimeter
(R. L. Nuttall and E. D. West*)

The design of the calorimeter is complete and the detail drawings have been finished, checked and sent to the shops for construction.

*Consultant from National Bureau of Standards.

For proper design of the calorimeter it was desirable to know the thermal resistance across a "sandwich" consisting of an aluminum ring between two stainless steel rings. A test apparatus was set up and measurements made with a $3\frac{1}{4}$ -inch OD, $2\frac{1}{2}$ -inch ID, 0.010-inch thick aluminum ring held between type 304 stainless steel rings by twenty-four 6-40 machine screws. The measured coefficient of heat transfer across this sandwich was about $0.01 \text{ watt cm}^{-2}\text{deg}^{-1}$ and did not change appreciably after cycling between 25 C and 500 C.

B. Semi-Works Studies of High-Temperature Processes (L. Burris, Jr.)

1. Melt-Refining Studies

(N. R. Chellew, G. A. Bennett, V. G. Trice, Jr.,
A. Schneider, J. Schilb, W. H. Spicer, L. F. Dorsey)

The melt-refining process consists simply of melting the fuel in a zirconium oxide crucible and holding it molten for a period of several hours at a minimum temperature of 1300 C. During this time purification from fission products is effected primarily by:

- (1) vaporization of the noble gases and other volatile elements such as cesium, and
- (2) selective oxidation of the highly electropositive elements, such as the rare earths, and their removal in a reaction layer which forms along the crucible walls.

The noble metals are not removed except in a small side stream of material (called "drag-out") This side stream, consisting largely of the crucible skull remaining after pouring the purified material, must be processed for removal of the noble metals and also for recovery of the fissionable materials. The noble metals will build up to equilibrium concentrations which are dependent on the percentage of "drag-out" material. The resulting alloys are "fissium" alloys *

*The alloy composition chosen for the initial EBR-II loading is:

molybdenum	2.46 w/o
ruthenium	1.96
rhodium	0.28
palladium	0.19
zirconium	0.10
niobium	0.01
uranium	remainder

a. Behavior of Fission Elements in Melt Refining
(N. R. Chellew, J. Schilb)

(1) Iodine Behavior

In experiments previously reported (see ANL-5924, pages 122 to 124), conducted with macro concentrations of iodine, it was shown that

- (a) isotopic mixing of fission product iodine and inert iodine added as uranium triiodide takes place rapidly;
- (b) more than 98 per cent of the iodine at EBR-II concentrations in synthetic fuel is removed from ingot and skull fractions by holding the fuel molten in a zirconia crucible for three hours at 1400 C; and
- (c) a primary mechanism of removal was formation and volatilization of alkaline earth iodides.

Recently completed studies were aimed at obtaining further information on the volatilization of this fission element.

The reaction of uranium triiodide with lime-stabilized zirconia was studied first to determine whether iodine volatilization is affected by the crucible constituents. Approximately three grams of uranium triiodide were charged to a zirconia crucible, covered with a close fitting zirconia cover, which was then inserted into a long Vycor tube. The assembly used is pictured in Figure 48A. The charge, containing about 1900 milligrams of iodine, was resistance heated under an atmosphere of helium for three hours at 1300 C. The unheated upper portion of the Vycor tube served as a condenser for volatilized material. After the furnace had cooled, the crucible and contents were removed from the Vycor tube. Inspection of the

tube showed that material had sublimed and deposited on inner walls in those regions where the temperature was 600 C or less. Three temperature zones, which contained distinct bands of condensate, were separately treated with acid to recover volatilized material for identification. Techniques used in the analyses of the sublimates were fluorophotometric for uranium, colorimetric for iodine, and spectrochemical for 31 additional elements which included several "fissium" constituents plus those believed to be present as contaminants in lime-stabilized zirconia and Vycor. Analyses of elements found in highest concentration are presented in Table 38 on a gram-atom basis.

Table 38

MATERIAL VOLATILIZED DURING ZIRCONIA-URANIUM
TRIIODIDE HEAT

Run I-72E

Crucible: Pressed zirconia,^a porosity ~20 per cent
 Charge: 3029 mg uranium triiodide
 Conditions: Atmosphere, helium; temperature, 1300 C;
 time, 3 hr
 Apparatus. See Figure 48A.

Collector ^b Temp (C)	Element Concentration ^c (gram atoms x 10 ⁶)						
	I	Ca	Fe	Mg	U	Zr	Al, Ti or HF
30 to 250	1379	7	36	4	13	55	<20
250 to 425	2041	50	716	493	13	3	<10
425 to 1300	2230	998	18	8	1	5	<12

^aComposition given by Norton Company for stabilized zirconia (w/o):

CaO, 5.0; SiO₂, 0.7; Fe₂O₃, 0.2; Al₂O₃, 0.5; TiO₂, 0.3;
 HfO₂, < 2.0; ZrO₂, balance.

^bWall temperature of upper portion of Vycor tube.

^cEstimated accuracy of analyses: Uranium and iodine, ±5% (relative); others, factor of two.

Examination of various element concentrations indicate that:

- (a) 40 per cent of the iodine collected was condensed in a zone at a temperature of above 425 C, about 90 per cent as CaI₂;

- (b) 36 per cent of the total iodine collected deposited in the zone between 250 and 425 C, primarily as FeI_2 and MgI_2 (ratio of FeI_2 to MgI_2 was approximately 2 to 1); and
- (c) the remainder of the sublimate was nearly pure iodine.

Minor amounts of uranium, zirconium, aluminum, and hafnium were found. Other than sublimation of molecular iodine apparently produced by decomposition, the results show that reaction with the crucible contaminants to produce volatile iodides is an important mechanism in iodine removal. This conclusion is consistent with data on the vapor pressure of the iodides.

An experiment to obtain additional quantitative data on iodine volatilization was made in an induction furnace. A charge containing 210 ppm of iodine was prepared by placing uranium triiodide and uranium containing iodine-131 tracer (obtained by irradiation of unenriched uranium in the CP-5 reactor in a thermal flux of 10^{12} n/(sec)(sq cm) for 72 hours) in a hole drilled in "fissium" metal and covering with a lid of the same alloy. The material was held in zirconia at a temperature of 1400 C for three hours under a helium atmosphere in an assembly (see Figure 48B) designed to collect totally the material that would condense above a temperature of about 250 C. Iodine-bearing activity present in the condenser and crucible was recovered by treatment with acid. Representative fractions of the skull and ingot were obtained by separate dissolution of outer and inner portions of the liquated alloy. Results of this experiment (Run I-74A) are given in Table 39, along with data from a previous experiment similarly conducted with the exception that the volatilized fraction contained primarily activity evaporated from the melt surface (Run I-67A, ANL-5924, page 125).

A comparison of the total iodine recovered (see Table 39) in these experiments shows that roughly 70 per cent of the iodine removed in melt refining was evaporated through the walls of the crucible, whose total porosity was about 20 per cent. For both experiments the retention of iodine in ingot and skull fractions was less than 0.5 per cent.

(2) Barium and Strontium Studies

An investigation of the fate of EBR-II levels of barium and strontium in melt refining of "fissium" alloys is in progress. About 700 ppm of each of these elements will be generated in each pass of fuel through the reactor (2 per cent of total atoms fissioned, 15 days cooled) containing initially 50 per cent U^{235} . An earlier study of strontium behavior (ANL-5560, page 75) conducted with irradiated material containing about 100 ppm of homogeneously distributed strontium isotopes had shown that at

1200 C the removal of this element from the ingot was essentially quantitative (0.03 per cent remaining in ingot). The mechanism of removal appeared to be preferential oxidation and incorporation into the skull and crucible. Percentages of strontium and barium in vaporized and condensed fractions were small. The present experiments were designed to give more detailed information on the volatilization of these elements during melt refining.

Table 39

DISTRIBUTION OF IODINE^a IN MELT-REFINING EXPERIMENTS

Crucible:	Pressed zirconia; porosity ~20 per cent			
Atmosphere:	Helium			
Total Melt Time:	180 minutes			
Temperature:	1400 C			
Apparatus:	See Figure 48B			
	Run I-67A		Run I-74A	
	Wt (g)	% I ¹³¹ Activity ^b	Wt (g)	% I ¹³¹ Activity ^b
Charge				
"Fissium" ^c	316.1	100	182.3	100
Irradiated Uranium	3.7		3.7	
Uranium Triiodide	0.3202		0.0634	
Ingot	298.3	0.2	147.0	< 0.1
Skull ^d	19.4	0.2	39.0	< 0.1
Crucible	--	1.2	--	1.7
Volatilized	(from melt surface)	16.7	(from melt surface + crucible walls)	84.8
Total Recovered		18.3		86.5

^aIodine level in experimental charges (ppm): Run I-67A, 615; Run I-74A, 210.

^bEstimated accuracy of values listed, $\pm 10\%$ (relative).

^c"Fissium" composition (w/o): Mo, 2.4; Ru, 1.9; Zr, 1.0; Ce, 0.7; Rh, 0.3; Pd, 0.2; U, remainder.

^dSkull separated by top pouring in Run I-67A and acid etching in Run I-74A.

In two experiments charges containing about 1000 ppm of barium or strontium and 145 ppm of iodine were prepared by placing the metal plus uranium triiodide in holes machined in "fissium" blocks. The charges were heated in zirconia crucibles under a helium atmosphere to a temperature of 1400 C for three hours in the assembly pictured in

Figure 48B. The crucible and charge were removed from the tantalum tube and the inner walls and heat shields were treated with acid to recover volatilized material. Analyses of barium and iodine or of strontium and iodine volatilized in the tests are given in Table 40.

Table 40

VOLATILIZATION OF BARIUM, STRONTIUM AND IODINE
BY MELT REFINING

Charge: ^a	Run I-77E - "Fissium," 207.4 g + Barium, 0.2219 g + UI ₃ , 0.0398 g
	Run I-80E - "Fissium," 282.6 g + Strontium, 0.2735 g + UI ₃ , 0.0675 g
Atmosphere:	Helium
Total Melt Time:	180 minutes
Temperature:	1400 C
Apparatus:	See Figure 48B

		Weight (mg)		
	Element	Charged	Volatilized ^b	Per Cent Volatilized
Run I-77E	Ba	221.9	2.7	1.2
	I	24.5	18.7	76
Run I-80E	Sr	273.5	3.1	1.1
	I	41.5	19.3	47

^aFinal w/o composition of charges were:

Mo, 2.5; Ru, 2.0; Ce, 0.6; Zr, 0.4; Rh, 0.3; Pd, 0.2;
Nb, 0.01; I, Ba, Sr (see table); U, remainder.

^bAnalytical technique: Flame-spectrophotometric for barium and strontium and colorimetric for iodine, estimated accuracy of values listed, $\pm 10\%$ (relative).

Approximately one per cent of the alkaline earth elements was volatilized, presumably as iodides, in each experiment. The boiling points of barium iodide and strontium iodide have been estimated to be 1575 and 1725 C, respectively, with a probable error in estimation of ± 100 C.³⁷ The vapor pressures of their oxides are considerably lower than one atmosphere at similar temperatures. An excess of iodine collected of 50 to 75 per cent over that accountable for in sublimed barium and

³⁷Quill, L. L., Chemistry and Metallurgy of Miscellaneous Materials, National Nuclear Energy Series, IV - 19B, 197, (1950).

strontium iodides is indicative that reaction of iodine with crucible impurities and subsequent volatilization may have occurred. Analyses of ingot and skull fractions of the liquated ingots will be reported as the information becomes available.

(3) Behavior of Zirconium in Plutonium "Fissium" Alloy

Analytical data on the behavior of zirconium during melt refining of a 19.7 weight per cent plutonium-"fissium" alloy in lime-stabilized zirconia and magnesia crucibles are reported in Table 41. No significant removal of the zirconium was realized with either crucible material. Procedures followed in these melts were previously described in ANL-5759, page 96, and ANL-5789, page 85.

Table 41

BEHAVIOR OF ZIRCONIUM IN MELT REFINING PLUTONIUM-"FISSIUM" ALLOY

Alloy Composition, w/o:	U, 68.7 to 68.8; Pu, 19.7 to 20.0; Ru, 5.3; Pd, 3.1; Mo, 1.5; Ce, 0.14; Zr (see table)			
Temperature:	1300 C			
Melt Time:	120 min in Zirconia; 70 min in Magnesia			
	Run I-27A Pressed Zirconia Crucible		Run I-28A Pressed Magnesia Crucible	
	Wt (g)	Zr ^a (w/o)	Wt (g)	Zr ^a (w/o)
Charge	353.2	1.04	372.9	0.92
Melt Sample Halfway Through Run	-	1.05	-	1.07
Ingot	343.8	1.02	334.8	1.04

^aConcentrations determined by spectrophotometric technique; estimated accuracy, $\pm 5\%$ (relative).

(4) Zirconium Removal as Carbide

Laboratory Studies

A study of the uranium-zirconium-carbon system was continued. In the experimental procedure zirconium turnings and outgassed graphite powder, or these materials plus high-purity zirconium powder, were added to holes drilled in uranium blocks. Ratios of carbon-to-zirconium concentrations were varied from 0.11 to 12.6 for the charges which contained from 0.08 to 0.72 weight per cent carbon and 0.04 to 1.60 weight per cent zirconium. The materials were induction heated in beryllia crucibles under one-third atmosphere of helium to an equilibrium temperature of 1400 C for 24 to 25 hours and quenched. Less than five minutes was required for solidification. Stirring of the molten charge was minimized by the use of a heavy wall (50-mil) tantalum susceptor.

FIGURE 49
JOINT SOLUBILITY OF ZIRCONIUM AND CARBON
IN MOLTEN URANIUM AT 1400C

Ingots sections from all melts revealed the presence of liquated inclusions in a top zone and an inclusion-free area at the bottom containing only precipitated carbide (see typical photomicrograph, ANL-5924, Figure 34). Samples of the metal free of inclusions were analyzed for carbon and zirconium. The results plotted in Figure 49 show a tentative liquidus line in the high uranium region of the ternary system. The accepted accuracy for the analyses reported are ± 10 per cent relative. Concentrations reported for Run 78A are believed to be high in zirconium and/or carbon because of occluded solid solution in the metal submitted for analysis.

The data indicate that it is possible to remove zirconium by carbide liquation to less than 0.01 weight per cent at 1400 C. With 0.02 to 0.05 weight per cent zirconium in equilibrium with solid solution, the carbon content of the liquated metal will be reduced to 600 ppm or less. A comparison of the amounts of zirconium charged to that in uranium solution (liquated phase) showed a removal of 97 ± 2 per cent of the element. Although the composition of the solid phase has not been determined for the individual experiments, the preliminary analytical data and observations are consistent with a mechanism of zirconium removal involving a very slow liquation of zirconium carbide and uranium carbide together in solid solution from the molten metal.

Semi-Works Studies

(V. G. Trice, W. H. Spicer)

The study of the removal of zirconium as the carbide was concluded with two runs in which "fissium" was liquated for five hours at 1400 C in contact with a 3 x 0.5-inch disc of dense graphite (Type AGR). Zirconium removals were 37 per cent of an initial 1.0 per cent and 50 per cent of an original 0.40 per cent, which compares favorably with those obtained in graphite-coated crucibles (~50 per cent in five hours). However, the carbon contamination was considerably higher, being as much as 1200 ppm as compared with the usual 300 ppm. Ingot yields were also adversely affected by formation of a large reaction mass adhering to the disc. In an earlier experiment utilizing a porous graphite disc a similar reaction mass, which on analysis proved to be principally uranium carbide with a lesser amount of zirconium carbide, was observed.

Subsequent efforts in this program will be directed towards evaluating the graphite treatment for the removal of zirconium from plutonium-"fissium" (a simulated fuel composed of 20 per cent plutonium, 75 per cent uranium, and five per cent alloy constituents). The principal question concerns the effect of the graphite treatment on plutonium losses. During the past quarter a glove-box enclosure was added to the vacuum-melting furnace. Various other minor modifications in equipment were also made to facilitate the handling of plutonium alloys. Runs will start in the next quarter.

b. Melt Refining of Irradiated Fuel
(V. Trice)

A small tilt-pour bell-jar type of vacuum-melting furnace has been designed and constructed for the melt refining of batches of irradiated fuel weighing up to one kg. During the next quarter it will be fitted out and tested prior to installation in the Chemical Engineering Division's Senior Cave. Initially this furnace will be used to verify laboratory findings and to extend the knowledge of the fate of certain fission product activities in the melt refining of spent fuel of the EBR-II type.

Fuel for these experiments is being irradiated in the CP-5 reactor. The first loading of 200 grams of 10 per cent enriched uranium-"fissium" has been irradiated for three months. The reactor is currently down for repairs but is expected to be back in operation in mid-1959. The first loading will be removed from the reactor after an additional month of irradiation. A second irradiation facility has been constructed and will be installed in the reactor to increase the rate of production of irradiated fuel.

c. Melting of Sodium-Coated Pins
(G. A. Bennett, L. F. Dorsey)

Melting of sodium-coated pins is more difficult than the melting of uncoated pins. This is attributable, not to the sodium coating, but to an oxide coating which is present or which is easily formed on pins from exposure to air or from oxygen present in the sodium. Investigation of chemical methods for reduction of the oxide coating was continued.

Calcium Reduction

Although calcium is an effective reducing agent for uranium dioxide, nearly all experiments using calcium have been unsuccessful because of crucible failures. Zirconia, magnesia, and beryllia are attacked by the molten calcium-uranium system. Crucibles that might withstand chemical attack, such as thoria and alumina, have failed because of thermal shock. The use of calcia or calcia-lined graphite crucibles is to be tried.

In the experiments involving calcium reduction a difficulty was encountered because of the pyrophoric nature of the calcium and sodium films deposited on interior surfaces of the furnace. Oxidation of the calcium film before opening the furnace and the use of minimum amounts of calcium were necessary to prevent spontaneous ignition.

Reduction with Magnesium in Zinc Solution

Reduction of uranium dioxide with magnesium in zinc solution has been shown to occur (ANL-5924, page 140), and this method is therefore being investigated as a means of reducing the oxide coating on fuel pins. A series of experiments have been carried out in which sodium coated pins in a metal basket were submerged for two hours in zinc-magnesium alloys of varying compositions. The pins were then removed, drained, and subsequently melt refined at 1400 C. Small batches of pins (200 to 300 grams) have been dipped in 1, 3, 6, and 10 weight per cent magnesium-zinc alloys. Wetting of the pins to produce bright adhesive coatings of magnesium-zinc alloy, with no trace of uranium oxide, have been achieved with the 1 and 10 weight per cent alloys at temperatures of 550 and 625 C, the only compositions tried at elevated temperatures. At lower temperatures (450 to 500 C) wetting was incomplete for all alloy compositions.

The two batches of coated pins were then melted and held at 1400 C for one hour. Several pin shells still existed for the batch coated with the one per cent magnesium alloy. Very few were present for the batch coated with the 10 per cent alloy. This approach seems promising and will be pursued. It will be necessary to determine the extent of uranium loss to the coating solution, and to investigate further the effect of magnesium concentration on the quality of the uranium product of the melting operation.

d. Oxidation-Reduction Treatment of Melt-Refining Skulls
(V. G. Trice, W. H. Spicer)

An oxidation-reduction cycle has been successfully demonstrated as a means of chemically removing "fissium" skulls from melt-refining crucibles. In the melt-refining process the principal residue is the dross remaining in the zirconia crucible. This dross consists of an oxide reaction layer adhering to and, on occasion, penetrating the crucible walls plus a film of unpoured metal. Removal of this dross from the fragile ceramic crucible poses a problem. Mechanical removal requires breakage of the crucible and presents problems of remote handling. In the case of a dross which penetrates the crucible walls, mechanical removal is even more difficult. Chemical removal with liquid metal solvents has been investigated but is an unsatisfactory procedure because of the porosity and frequently poor integrity (caused by cracks produced during the melt-refining process) of the zirconia crucibles. An oxidation-reduction cycle provides an expansion-contraction sequence which breaks the dross from the walls of the crucible and renders it into a powder which may be poured from the crucible.

The dross consists principally of uranium metal and various oxides, including uranium dioxide. The oxidation-reduction cycle is effected by the reactions

The results of a series of six powdering experiments are presented in Table 42. In each case the dross was broken down into a powder that could be poured from a crucible. Initiation of the highly exothermic oxidation reaction was achieved at temperatures as low as 200 C, but a higher ignition temperature of 800 C provided better control of the reaction. Low-temperature ignition was followed by an extreme temperature excursion which resulted in fracture of the crucible. Oxidation was conducted with pure oxygen at pressures of 100 to 500 mm. Reduction was carried out with hydrogen at a pressure of approximately 300 mm.

Special note is made in Table 42 of the presence of cerium in several of the skulls. Cerium, being the most reactive constituent of "fissium," forms an oxide on the crucible walls. In most cases where cerium was present, the melt did not penetrate the crucible walls. Hence, the powdering process had no noticeable effect on the crucible. With melt penetration of the crucible, however, the crucible was undercut or spalled to the depth of penetration.

Table 42

SUMMARY OF OXIDATION-REDUCTION DROSS POWDERING RUNS

Run	Material	Conditions	Results
1	"Fissium" (without cerium) skull in zirconia crucible	O ₂ oxidation for 1 hr at 800 C H ₂ reduction for 1 hr at 800 C	Skull powdered Product could be poured from crucible Crucible integrity maintained
2	"Fissium" A ^a (with cerium) skull in graphite-coated zirconia crucible	O ₂ oxidation for 1 hr at 800 C H ₂ reduction for 1 hr at 800 C	Skull powdered Product could be poured from crucible Crucible integrity maintained
3	"Fissium" A (with cerium) skull in zirconia crucible Crucible also contained 3 x 0.5 in graphite disc Disc mechanically removed before run	O ₂ oxidation initiated at 200 C H ₂ reduction for 1 hr at 600 C	Ignition at 200 C followed by extreme temperature excursion Maximum temperature attained not known but certainly exceeded 1000 C Crucible cracked Product was a pourable powder
4	"Fissium" A (with cerium) skull in graphite-coated zirconia crucible	O ₂ oxidation initiated at 300 C H ₂ reduction for 1 hr at 600 C	Ignition at 300 C followed by extreme temperature excursion Crucible cracked Product was a pourable powder
5	"Fissium" (without cerium) skull in zirconia crucible	O ₂ oxidation initiated at 200 C H ₂ reduction for 1 hr at 600 C	Ignition at 200 C followed by extreme temperature excursion Crucible cracked Product was a pourable powder
6	"Fissium" A (with cerium) skull Crucible contained 3 x 0.5 in graphite disc Crucible was cracked before run	O ₂ oxidation for 1 hr at 800 C H ₂ reduction for 1 hr at 800 C	Skull powdered Product was pourable Large mass of material adhering to graphite disc was not powdered Disc was not consumed
6A	Graphite disc and adhering reaction mass from Run 6	O ₂ oxidation for 1 hr at 800 C H ₂ reduction for 1 hr at 800 C	Approximately one-third of reaction mass was powdered Unburnt portion probably UC plus some ZrC Graphite disc was not consumed

^a"Fissium" A is an alloy containing uranium plus 7.5 w/o Mo, 0.5 w/o Zr and 0.6 w/o Ce

A beneficial by-product of the oxidation-reduction cycle is the possibility of the removal of molybdenum and ruthenium as volatile oxides. Atomics International is investigating this technique as a means of partially decontaminating irradiated uranium dioxide fuels.³⁸ Molybdenum trioxide (MoO₃) has a vapor pressure of about one mm at 800 C. Ruthenium tetroxide (RuO₄) melts at approximately 25 C and boils at about 150 C (at 760 mm), but it is an unstable compound which has a significant rate of decomposition at temperatures as low as 100 C (see ANL-4463, page 68). The decomposition product is the relatively non-volatile ruthenium dioxide.

³⁸Sinizer, D. I., et al., "The Processing-Refabrication Experiment (PRE) for Irradiated UO₂," NAA-SR-2778. (1958).

In preliminary qualitative experiments, the removal of molybdenum as the volatile trioxide was demonstrated. In several experiments oxidized "fissium" dross was held for two hours at 800 C and 40 microns pressure. A white powder, which during the hydrogen reduction was reduced to a black powder, collected on the relatively cooler crucible cover. X-ray spectral examination of the powder showed it to be rich in molybdenum, thereby indicating that the volatile material was the yellow-white trioxide of molybdenum. No concrete evidence of ruthenium volatilization has been observed.

To extend further the investigation of fission product removal from melt-refining residues as volatile oxides, a small tube furnace has been designed and constructed. It consists of a reaction vessel in series with condensation zones for molybdenum trioxide and ruthenium tetroxide. A series of quantitative experiments has been planned. In initial experiments thin biscuits of "fissium" were successfully powdered by an oxidation-reduction cycle at 800 C. For subsequent experiments a special alloy spiked with 40-day ruthenium-103 has been prepared to facilitate the investigation of ruthenium removal.

e. Equipment Development

(1) Testing of Susceptor Materials
(G. A. Bennett and L. F. Dorsey)

The promising preliminary performance of a silicon carbide-silicon nitride-impregnated graphite (Type CS) induction heating susceptor in a sodium atmosphere was reported in the previous quarterly (ANL-5924, page 153). The impregnation of these susceptors was carried out by the National Carbon Co. Their stability in a sodium atmosphere contrasts with repeated failures of unimpregnated graphite susceptors in a sodium atmosphere.

Additional use of this susceptor material has since been made, including about a dozen runs in the presence of sodium. No deterioration or chemical attack has been observable. A second impregnated susceptor has been put into use and appears to have the same excellent characteristics as the first.

(2) Portable Scintillation Detector Head
(A. Schneider and J. Schilb)

In studies of the pyrometallurgical reprocessing of fuel, it is often useful to follow, during the experiment, the fate of individual fission products by radiochemical methods. Such methods can be applied to experiments containing either irradiated uranium or synthetic "fissium" alloys to which radioactive tracers have been added. Equipment, consisting

of a portable scintillation detector head, a single-channel pulse height analyzer and the usual electronic accessories, was built for this purpose. The performance of this equipment was tested in an area of moderately high background activity (20 mr/hr) with a source simulating a mixture of fission products and emitting gamma rays ranging from 320 to 1330 kev. It was possible to identify and estimate the concentrations of the following components of the radiation source: chromium-51, cesium-137, cobalt-60, and krypton-85. The resolution for the 661-kev peak of cesium-137 was 11 per cent.

2. Development of Liquid Metal Solution Processes

Various processes which involve purification of uranium or plutonium by selective crystallization, distillation, or by extraction of impurities into molten metals or salts, are now under development.

a. Development of Processes for Recovery of Plutonium from EBR-II Blanket Material

The objective of a process for EBR-II blanket material is the isolation of plutonium in sufficient purity for reconstitution of core material. Fission product removal is not particularly important. In the previous quarterly (ANL-5924, page 154) it was pointed out that the blanket alloy had been changed from the relatively low melting 5 weight per cent chromium alloy to 3 weight per cent molybdenum alloy. It has since been changed again to beta-randomized uranium containing no alloying agent.

(1) Application of Pyrozinc-Magnesium Process to Blanket Materials

(I. O. Winsch, P. Nelson, J. DeKany, R. Paul, R. Beck)

In the pyrozinc-magnesium process for blanket materials (see schematic diagram in Figure 51, ANL-5896) zinc is used to dissolve blanket material. On cooling, U_2Zn_{17} precipitates and carries down plutonium. After a separation of the excess zinc from the uranium and plutonium compounds, enough magnesium is added to the U_2Zn_{17} - Pu_2Zn_{17} concentrate to form a 54 weight per cent zinc - 46 weight per cent magnesium eutectic. Addition of magnesium to high concentrations decomposes the intermetallic uranium and plutonium compounds. Plutonium is soluble in the eutectic, while uranium is only slightly soluble and settles out. A separation of the eutectic phase from the insoluble uranium is made, after which distillation is employed to separate the plutonium from the magnesium and zinc.

In reporting this work in the previous quarterly, several inconsistencies in plutonium behavior were pointed out, one of which was the partial disappearance of plutonium from the 46 per cent magnesium-zinc eutectic solution on cooling. This same phenomenon occurred in a fourth run completed in the past quarter (see Table 43 and Figure 50),

Table 43

RESULTS OF PYROZINC-MAGNESIUM PROCESS

Equipment described in ANL-5896, page 165

Experiment 4^a

Charge: 1% Pu-U Alloy - 70.4214 g

<u>Step</u>	<u>Per Cent of Charge</u>		
	<u>U</u>	<u>Pu</u>	<u>Decanted Phase</u>
Dissolution at 800 C to produce ~ 3.5 w/o solution	102	100	--
Precipitate by cooling to 450 C-- Supernatant sample (Values adjusted for 100% phase separation)	0.2	3.3	--
Decanted zinc	0.2	2.1	65.0
Mg addition--mixing at 800 C Supernatant sample	8.1	89.5	--
Cooling to 450 C to precipitate uranium-- Supernatant sample (Values adjusted for 100% phase separation)	2.3	41.8	100
Decanted Zn-Mg Eutectic, 450 C	1.9	34.0	81.5
Zn-Mg Wash--mixing at 800 C	6.6	65.0	--
Cooling to 450 C and decantation - Values adjusted to 100% phase separation	2.5 3.4	46.8 64.6	72.5 100
Heel	78.5	11.7	--
Samples	1.8	4.1	--
Material balance on decanted phase plus heel	84.9	98.7	--

^a Previous experiments described in ANL-5924, page 155, and ANL-5896, pages 163 to 165.

roughly one-half disappearing from solution. However, all of the missing plutonium was recovered in the succeeding wash. It has been postulated that a portion of the uranium is precipitated as metastable U_2Zn_{17} , which carries down a portion of the plutonium.

Complete dissolution of the charge was effected as indicated by the good material balances for plutonium and uranium in the dissolution step. As in previous runs, the plutonium was effectively carried on the U_2Zn_{17} precipitate. A Doerner-Hoskins coefficient, λ , having a value of 0.63 would account for the plutonium remaining in solution. The over-all material balance for plutonium was very good (98.7 per cent), but the material balance for uranium was poor (85 per cent). This may be due to low results from an analysis for the uranium content of the final heel.

A different processing scheme for the blanket in which the material will be dissolved in a cadmium-magnesium alloy, will be tried in the next quarter. The cadmium will then be distilled away, leaving a magnesium phase in which plutonium is soluble but uranium is highly insoluble. Cadmium is being used instead of zinc to avoid corrosion problems.

(2) Stability of Solutions of Plutonium in Molten
Zinc-46 Weight Per Cent Magnesium Eutectic Alloy
Held in Graphite and Tantalum Crucibles
(I. O. Winsch, R. Paul)

Two experiments were conducted to determine the stability of plutonium solutions in molten zinc - 46.5 weight per cent magnesium alloy held at 800 C in graphite and tantalum containers.

In the first experiment 530 grams of a zinc-magnesium eutectic containing 0.29 gram of plutonium and 0.17 gram of uranium was held in a tantalum crucible at a temperature of 800 C for a period of six hours. Mixing was provided by means of a motor-driven tantalum agitator. Three samples of the molten alloy were taken at two-hour intervals during the experiment.

In the second experiment 779 grams of a zinc-magnesium eutectic containing 0.14 gram of plutonium and 1.7 grams of uranium were charged to a graphite crucible. The melt was held at 800 C for a period of two hours, with constant agitation, after which time a sample of the molten alloy was taken. After sampling, the alloy was poured from the crucible into a copper mold. The poured ingot was then recharged to the graphite crucible and reheated to 800 C. The mixing, time, sampling, and pouring procedures were repeated so that a total of three samples were obtained.

As shown in Table 44, the analytical results of both experiments are very encouraging, indicating no apparent decrease in the

Table 44

STABILITY OF SOLUTIONS OF PLUTONIUM IN MOLTEN
MAGNESIUM-ZINC EUTECTIC ALLOY HELD AT 800 C
IN GRAPHITE AND TANTALUM CRUCIBLES

Composition of Alloy Solution: 46 w/o Mg; 54 w/o Zn

Time (hr)	Graphite		Tantalum ^a
	Pu (cpm/g)	U (w/o)	Pu (cpm/g)
0 (charge)	1.25×10^7	0.030	3.94×10^7
2	1.22×10^7	0.032	3.92×10^7
4	1.23×10^7	0.033	3.90×10^7
6	1.28×10^7	0.032	4.17×10^7

^aUranium solubility was exceeded so uranium analyses are invalid.

plutonium concentration of the zinc-magnesium alloy in either container material. The behavior of plutonium in this eutectic alloy held in graphite is considerably different from its behavior in a magnesium solution. Loss of plutonium from a magnesium solution held in graphite at 900 C occurred fairly rapidly (65 per cent decrease in plutonium concentration after six hours - ANL-5820, page 121). The uranium concentration in the graphite experiment also remained constant, but the uranium analyses in the tantalum experiment were erratic. The variations in uranium concentration in the latter case were undoubtedly caused by the fact that the uranium solubility was exceeded in the solution, and variable amounts of the solid uranium phase were removed in the samples taken.

(3) Solubility of Molybdenum in Magnesium
(P. Nelson and R. Paul)

An experiment to determine the solubility of molybdenum in magnesium, since molybdenum was at this time a constituent of the blanket alloy, was performed. Magnesium was agitated in contact with molybdenum at 1000 C. The molybdenum was present in the form of platelets measuring 0.1 x 0.1 x 0.01 inch. The analyses of samples taken between temperatures of 680 to 1000 C indicate that less than 2×10^{-4} weight per cent molybdenum dissolved in the magnesium.

This indicates that any molybdenum present in plutonium-bearing magnesium-zinc phases produced in the blanket processes under consideration would separate out in the course of the subsequent zinc distillation and be separable from the plutonium if desired.

(4) Vapor-Liquid Equilibrium for Zinc-Magnesium System
(P. A. Nelson, R. A. Beck and R. C. Paul)

Some of the Pyrozinc processes which are being considered for blanket processing require separation of zinc from magnesium by distillation. The vapor pressure of zinc is 8 to 10 times that of magnesium at distillation temperatures, indicating easy separation of the two components. However, a departure from ideality might lower the relative volatility to the point where several distillation stages would be required to obtain sufficient separation of the components. Operability of a remote process involving recycled streams would be facilitated by efficient separations. Therefore, work is in progress to obtain vapor-liquid equilibrium data.

b. Recovery and Purification of Uranium from Crucible Skulls

(R. D. Pierce, J. C. Hesson, A. Schneider, E. F. Johnston)

The Pyrozinc process is being investigated for processing skulls from the melt-refining process to recover the fissionable material and separate it from noble metals and from the fission product-bearing dross. The skull material, amounting to about 10 per cent of a melt-refining charge, provides the bleed stream for the noble metal fission products in the melt-refining process. Therefore, a fairly high separation of noble metals is required in order to control their concentrations in recycled fuel. The process consists of dissolution in a zinc-magnesium alloy (magnesium being present to reduce uranium and plutonium oxides) followed by selective crystallization of the U_2Zn_{17} or Pu_2Zn_{17} intermetallic compounds. The crystals are separated from the zinc solution containing the noble metals and uranium and plutonium are recovered by heating to decompose the intermetallic compounds and volatilize the zinc.

Three modes of attack have been considered for dissolving the uranium in skulls from experimental melt-refining runs:

- (1) treatment of the skull in the original zirconia crucible,
- (2) removal of the skull by breaking the zirconia crucible,
or
- (3) removal of the skull by chemical means.

Investigation of the latter procedure was reported on page 148. Direct treatment in the crucibles has been discarded because zirconia crucibles are somewhat porous to zinc. The bulk of the experiments have been performed with skulls that were removed by breaking the crucibles. The zirconia crucibles that have been previously used in melt-refining runs are easily broken. The skull may be readily separated from crucible fragments. The skulls are then charged to a graphite filter crucible and heated with zinc containing magnesium as a reducing agent for any oxidized uranium. The melt is held at 800 C to permit reaction and dissolution. At the completion of the run the zinc solution is filtered through a graphite frit. The residue is recontacted with fresh zinc solution to achieve washing and further extraction of uranium.

Runs have been made with zinc containing 0, 2, and 6 per cent magnesium. Every contact has failed to achieve the desired extraction of about 95 per cent of the uranium. A material balance showed that as much as one-third of the uranium from the skulls is unaccounted for by the chemical analyses of the extracts and residue. Although this discrepancy prevents evaluating the recoveries precisely, sufficient uranium has been

left in the residue after each run to show that the extraction efficiency was low. Efficiencies achieved appear to be in the range of 60 to 90 per cent. The runs have been plagued with agitator failures that have prevented an evaluation of the effect of mixing on the extractions. A heavier mixer has been installed and satisfactory stirring is expected in subsequent runs.

In order to understand better the character of the crucible skulls a few have been broken and separated into a "button" of nearly solid uranium alloy and scale containing the bulk of the oxidized metals. These portions were sampled and analyzed. The one chemical analysis completed gave these results:

	Total Uranium in Fraction (%)	$\frac{U_{As\ Metal}}{U_{Total}}$
Scale	78	0.89
Button	86	0.94
Average	80	0.90

The content of metallic uranium was obtained from the ruthenium analysis by assuming that the ratio of metallic uranium to ruthenium in the skull was equal to that of the original charge.

As described previously on page 148, complete oxidation of the skull has been carried out to produce a powder that can be dumped from the crucible. Work has been initiated to develop a process to recover uranium from the powder. In preliminary experiments the oxide has been contacted with zinc-magnesium solutions. Uranium reduction has been extremely slow, even with vigorous stirring, probably because the zinc solution did not wet the particles. Somewhat better results were obtained when the oxide was introduced through a salt flux above the zinc.

Reduction of Cerium Oxide. The Pyrozinc experiments have revealed that the cerium present as oxide in crucible skulls is also reduced by magnesium in zinc solution. Even uranium in zinc solutions containing no magnesium will reduce cerium oxide. This results from the very low activity coefficient of cerium in zinc solution ($\sim 10^{-8}$). Subsequent separation of uranium and cerium during recrystallization has not been possible because of nearly quantitative coprecipitation.

The usefulness of the Pyrozinc process depends largely on the ability to reduce selectively the oxides of uranium and plutonium while the fission products deposited in the skull (mainly rare earth oxides) are retained in a state in which they are insoluble in zinc or are later separable from the uranium. The previously described behavior of cerium oxide and the low recovery yields of uranium obtained during actual processings of skulls have pointed out the necessity for a more detailed study of chemical reactions occurring in liquid metals.

c. Phase Separation of Precipitated Zinc Intermetallic Compounds from Zinc Supernatant Solution
(J. C. Hesson, R. D. Pierce)

In the liquid metal purification processes conceived to date, it is important to achieve good separation of the crystallized intermetallic compounds from the supernatant liquid metal. The degree of separation often controls product losses and the decontamination effected. A variety of separation procedures have been considered and tested in varying degrees. These are listed and evaluated in Table 45.

At the present time, pressure-siphoning (transfer through a dip tube by pressurizing) appears to be one of the most promising procedures. Experimental results for this procedure will be described in greater detail. Five runs were made using a bottom-loading furnace, as shown in ANL-5668, Figure 39, page 99. Intermetallic crystal cakes and zinc charges varying in weight from 4 to 14 kg were loaded into the center vessel, and zinc was loaded into the charge vessel. After melting, the zinc was readily transferred from the charge vessel to the center vessel by pressure-siphoning. At 500 C the zinc was pressure-siphoned from the intermetallic crystal layer to the zinc receiver vessel. The crucibles in the charge vessel and in the center vessel could be raised and lowered with respect to the siphon tube.

Conditions of the phase-transfer operations were as follows:

<u>Run</u>	<u>Procedure</u>
1	Zinc siphoned from above crystal interface
2	Siphon tube (5/16-inch ID) pushed well below crystal interface
3	Same as 2
4	"20C" (140 micron - effective filtration 30 microns) carbon filter frit inserted into end of tube which was pushed into bed
5	A $4\frac{3}{8}$ -inch-diameter tantalum disc perforated with 168 1/16-inch holes fixed on a rod was used to compress crystals as crucible was raised. Siphon tube opening was just above disc.

Table 45

EVALUATION OF METHODS FOR SEPARATING U_2Zn_{17}
INTERMETALLIC CRYSTALS FROM SUPERNATANT ZINC SOLUTIONS

<u>Method</u>	<u>Number of Tests</u>	<u>Results</u>	<u>General Comments</u>
1) Differential pressure filtration through porous frit or screen ^a	>10	Efficiently separates phases when working properly; filter cakes containing as high as 15 to 20% U have been produced.	Efficient separation of phases. Not readily adaptable to remote operation because of difficulty in removing intermetallic from frit. Premature filtration can take place. End of filtration uncertain. Zinc vapors in flowing inert gas create problems of gas disposal and result in line plugging. Pressure sealing between chambers is difficult.
2) Supernatant removal by pressure siphoning	5	Efficient transfer of zinc supernatant even through open pipes inserted into cake. Cakes have ranged from 10 to 15% U.	Good efficiency of separation and ease of remote operation make this an attractive procedure. Handling of cake poses problems. Separation vessel could be moved to retort furnace.
3) Settling of crystals on removable dish		Separations have been poor. Cakes have been of fair uranium content (10 to 15%)	Not attractive because of poor efficiency. Close tolerances required make construction and remote operation impractical.
4) Settling of crystals into removal screen	2	Because zinc drainage can occur, filter cakes are more concentrated in U than for procedure No. 3.	Suffers from same disadvantages as No. 3.
5) Pouring of crystal slurry into screen basket	2	Neither run successful. Fine 50 mesh, 3-mil Ta screen not wet in first run and filtration did not occur. Screen broke in second.	Eliminates need for close tolerances required with (2) and (3). Requires slurry transfer and subsequent dumping of screen.
6) Decantation of supernatant	~6	Supernatant free of intermetallic. Because of interlocking character of crystals, cake does not shift appreciably during pouring. In many cases, separation of supernatant liquid from cake has been poor.	Fairly attractive if removal of supernatant solution could be improved. Connections to tiltable, closed separation vessel operated remotely and at high temperature could pose problems.
7) Freeze elongated ingot and break or cut near crystal interface	1	The crystals settled to the lower 2 inches of a 10-inch long ingot. Might be problem of some crystals adhering to crucible wall and not settling.	Remote operation would be difficult.
8) Freeze cake area and pour off overlying zinc	not tried	--	No advantage over (7), plus increased problems of temperature control.

^aApparatus described on page 127, ANL-5820.

No evidence of transfer of U_2Zn_{17} intermetallic crystals was found in the sectioned ingots of the zinc siphoned from the crystals of runs one to four. For the fifth run a slight amount of the intermetallic was transferred in the siphoned zinc. The crystals were small and possibly were broken from the larger crystal masses by the compression.

The intermetallic crystals in the filter cake form an interlocking mass and act as their own filter. In the second and third runs the dip tube and thermocouple well left impressions in the crystal bed as the crucible was lowered after the zinc separation. In this respect the crystal bed is similar to moulding sand.

In the fourth run the carbon filter caused very slow zinc siphoning and only about one-fifth of the zinc was transferred before the filter plugged. In view of the filtering action of the crystal bed, a fine porosity filter in the siphon tube is not considered necessary. A coarse filter may, however be beneficial.

It is estimated that the filter cakes contain 10 to 15 per cent uranium. The compressed cake produced in Run 5 appears to have a slightly higher concentration of intermetallic. Samples from the ingots and cakes of the third and fifth runs are being analyzed for uranium content.

Additional runs are planned in which the effects of siphon tube at bottom of the filter cake, coarse filter at end of siphon tube, and moderate amount of cake compression will be studied.

d. Corrosion in Liquid Metal Systems

(I. O. Winsch, J. P. DeKany, H. W. Lavendel, J. Pavlik)

A program to test the corrosion by liquid metals was initiated in order to find suitable container materials for the handling of molten zinc-magnesium-uranium alloys and cadmium-magnesium-uranium alloys. Initial static experiments have been designed to screen a number of materials. The criterion of rejection in these tests is the inability of a material to resist attack while exposed to the particular liquid metal alloy for 100 hours at the test temperature. The tests results were evaluated on the basis of metallographic and spectrographic analyses.

The materials to be tested were in the form of coupons, approximately $1/2$ inch x 1 inch x $1/8$ inch. The tests were performed by sealing the test coupons in capsules, 1 inch OD x $2\frac{1}{4}$ inches high, containing the corrosive media. The capsules were fabricated from material considered to be resistant to attack by the corrosion system. Mild steel was selected as the capsule material for the molten cadmium alloy systems. Tantalum was used as the capsule material for the liquid zinc

alloy tests, since after 200-hour tests at 750 C spectrographic analysis revealed less than 0.1 per cent tantalum dissolved in pure molten zinc and less than 0.2 per cent tantalum dissolved in liquid zinc - 46 per cent magnesium eutectic alloy.

Prior to containment in capsules, the coupons were cleaned in two acidic solutions, first in a 20 per cent sulfuric acid bath for five minutes in order to "break" any scale on the sample, and second in a 20 per cent nitric acid for five minutes which removed the broken scale. A coupon along with 75 grams of cadmium or zinc alloy was loaded into a cylindrical capsule. Caps were then welded on the capsules in an inert gas atmosphere.

The loaded capsules were placed in a large resistance-heated furnace and held at test temperature: 750 C for the zinc alloy tests and 550 C for the cadmium alloy tests, for 100 hours. After the 100-hour period, the capsules were removed and sectioned for examination.

(1) Molten Cadmium Tests

Corrosion tests were performed upon the following materials: 1025 steel (low carbon), 1040 steel (medium carbon), 1065 steel (medium-high carbon), 1095 steel (high carbon), 310 and 304 stainless steels (austenitic), 410 stainless steel (martensitic), Armco iron, and tantalum, in order to evaluate their resistance to molten cadmium.

The metallographic and spectrographic examination did not disclose signs of corrosion with any of the tested materials, with the exception of the 300 series stainless steels. The corrosion of the latter materials consisted of a preferential dissolution of nickel from the stainless steel, as indicated by the presence of 0.01 to 0.03 per cent nickel in the cadmium phase and an interfacial diffusion layer between the steel and cadmium phases.

(2) Molten 2 Per Cent Uranium-Cadmium Solution

The same materials as tested with pure cadmium were also evaluated in contact with molten 2 weight per cent uranium-98 weight per cent cadmium alloy.

The same results as above were obtained for pure cadmium.

(3) Molten Zinc

The corrosion resistance of the following materials: mild steel spray-coated with Colmonoy 6 alloy (chromium, nickel alloy), tungsten, titanium, and vitallium alloy (64 weight per cent cobalt, 5 weight per cent molybdenum, 27 weight per cent chromium, 2 weight per cent iron, 2 weight per cent nickel) were evaluated in a pure zinc medium.

With the exception of tungsten, all of the above materials dissolved completely in the zinc. Metallographic examination of the tungsten revealed no attack by the zinc.

Mild steel spray-coated with Colmonoy 6, and titanium were also corrosion tested in 46 weight per cent magnesium - 54 weight per cent zinc (eutectic composition) alloy. In this case the materials were severely attacked, but did not dissolve completely. This would seem to indicate that the presence of magnesium at high concentrations in the zinc inhibits the corrosiveness of the zinc.

(4) Future Tests

A series of tests employing the same corrosion coupons as used in the previous cadmium tests will be conducted in a medium of cadmium-magnesium-uranium. The zinc tests will be continued, utilizing the following materials: nitrided steels, tungsten, several tungsten alloys, thermenol, and several ceramic materials.

C. Fuel-Processing Facilities for EBR-II (J. H. Schraidt)

1. Process Auxiliaries and Building

Descriptions of the Fuel Cycle Facility (formerly designated the Process Building) are given in previous quarterly reports, ANL-5789 and ANL-5820. The H. K. Ferguson Company, Cleveland, Ohio, is the architect-engineer.

About 130 drawings are needed in the "bid package" for the Fuel Cycle Facility. Thus far six drawings have been approved; 44 have been approved with exceptions, and 73 are in their preliminary stages. Some additional drawings may be required to show necessary details. Sixty-five divisions of specifications are needed to complete the bid package for the Fuel Cycle Facility. Of these, 16 divisions have been approved with exceptions, and 37 are in their preliminary stages.

a. Cranes and Manipulators (J. Graae)

The design of the 5-ton cranes for the argon cell was reviewed with Paceco (Pacific Coast Engineering Company). Several changes, in order to provide the features outlined in our specifications and to provide clearances adequate for removal of trolleys, have been requested.

The bridge for the radiation-resistant manipulator is nearing completion in the General Mills shop. The toggle-switch control box has been received and has been wired to operate the General Mills articulated manipulator in our mock-up facility. All design work for the prototype manipulator being fabricated is essentially completed. Shop assembly and testing are scheduled for completion during January, 1959, and delivery for February 1, 1959.

b. Shielding Windows and Shutters
(T. W. Eckels, J. Graae)

The purchase order for 31 shielding windows for the Fuel Cycle Facility has been placed with Pittsburgh Plate Glass Co. The final drawings on the shielding windows and their liners are being revised, following a meeting with Pittsburgh Plate Glass Company in mid-December, 1958. Rather extensive shielding calculations have been necessary as a result of the reduced glass area in the mid-section of the window (hour-glass shape). These calculations are being made both at Argonne and by Pittsburgh Plate Glass. A satisfactory shielding design has not yet been attained.

Detail design of the shutters for the cell-shielding windows will be done by Argonne, and the shutters will be purchased as a separate bid package. The shutters are closed when the windows are not used for observations. The architect-engineer will incorporate on his drawings the information necessary for installation of the shutter rails and the electrical wiring. Both one-piece and split-type shutters are being designed. The split type is required where there is not sufficient wall space on either side of the shielding window for a one-piece shutter. This situation exists at the windows in the central control room of the argon cell. A split shutter will be built and tested in the mock-up facility.

c. Optical Viewing Devices
(T. W. Eckels)

The stereo-optical depth perceptor (ANL-5820, page 135) was mounted on an adjustable stand and is being tested in the mock-up facility. It has proved useful for certain non-routine manipulator operations. Since it is easily moved from one window to another, it is planned to have five or six more made. The present model utilizes a pair of commercially available 7 x 50 binoculars and an adjustable mirror system to focus on objects from five to about 30 feet away from the observer.

A standard Model 301 Kollmorgen wall periscope adapted for a wall five feet thick was installed in the mock-up facility. The image quality and viewing capabilities are excellent. Shielding modifications to this periscope are being studied to make it satisfactory for use in the air cell.

d. Cell Lighting
(L. F. Coleman, T. W. Eckels)

A prototype 1000-watt luminaire and its wall mount have been designed for remote installation. Delivery of eight units being constructed by the Central Shops is expected early in 1959. These lamps will be mounted and tested in the mock-up facility at the spacing and height planned for the argon cell. Machinable ceramic stock has been ordered for making up radiation-resistant insulators in the wall mount and luminaire. Better evaluation of fuel processing component operation should be possible with the proper level of lighting.

For an accelerated irradiation test, a mercury vapor lamp (General Electric, Type H400A1) of small diameter is being irradiated in the 4-inch diameter urns of the Argonne Gamma-Irradiation Facility.

2. EBR-II Fuel Processing Mock-Up Facility

a. Manipulator Removal Blister
(J. Graae, D. C. Hampson)

The manipulator removal "blister" will provide a means for handling the manipulators and cranes within the argon cell. The motors in the manipulator "blister" (ANL-5924, page 169) have been tested by picking up an 8000-pound load. The efficiency of the gear reducer was low (30 per cent), probably due to the increased viscosity of the oil caused by the low (35 to 40 F) ambient temperature of the unheated "blister" enclosure which is located on the roof of the Chemical Engineering Division building. An oil of lower viscosity will be installed in the gear case and the unit tested when the ambient temperature is higher. This condition points out the necessity of some sort of heater for the "blister" mechanism for the EBR-II installation in Idaho.

b. Melt-Refining Furnace Testing
(D. C. Hampson, M. A. Slawewski)

The 50 per cent enriched uranium - 5 per cent "fissium" alloy which will be used in the fabrication of the fuel pins for the initial loading of the EBR-II reactor will be prepared in the Mark IV furnace. About 80 to 100 10 - kilogram ingots will be needed for the fabrication of some 10,000 fuel pins. The nominal composition of the alloy in weight per cent is: uranium, 95; molybdenum, 2.46; ruthenium, 1.96; palladium, 0.19; rhodium, 0.28; zirconium, 0.10; and niobium, 0.01.

Thirty 10-kilogram ingots of natural uranium - 5 per cent "fissium" alloy have been produced in the Mark IV furnace. The preparation of the fuel alloy in the melt-refining furnace is serving to train personnel, to test operating procedures and equipment, and to accumulate data on alloy compositions, crucible life and process yields. Analytical results of the first five runs are complete, except for niobium. These results and incomplete results from the next 10 runs indicate that the ingots are homogeneous and that, with the exception of zirconium, the inactive fission elements are alloying quantitatively. About 70 per cent of the zirconium goes into solution.

Two types of samples were used to determine the ingot composition, protrusion samples and section samples. Two small protrusions are cast on the base of the ingot, and horizontal sections were taken from the top, middle, and bottom of the ingot. In the course of selecting the type of analysis that is best suited to the EBR-II fuel, three types of analyses were made: wet chemical, X-ray spectrographic, and emission spectrographic. The results of these analyses showed that the protrusion samples are representative of the ingot composition. The analysis of the protrusions agreed with the average of the analysis of the slices of the body of the ingots and in general produced a smaller spread of analytical data. This is probably a result of the quick freezing of the protrusions, which prevented any segregation due to fractional solidification.

The results of the runs made to prepare the 30 10-kilogram ingots of natural uranium - 5 per cent "fissium" can be summarized as follows:

(1) Yield

- (a) The average yield for a liquation of three hours at 1400 C is 97 per cent (no cerium in these runs).
- (b) The addition of cerium (a stand-in for the total rare earth produced by fission in the fuel) reduces this yield to 93 per cent.
- (c) The yield is increased by raising pouring temperatures, as indicated below, for $3\frac{1}{2}$ -hour liquations at 1390 C:

<u>Run</u>	<u>Pour Temp (C)</u>	<u>Yield (%)</u>
DL- 8	1200	95.3
DL- 9	1300	96.1
DL-10	1380	96.3

- (d) Longer liquation times reduce the yield. The average yield for a three-hour or less run was 97.3 per cent. The average yield for four-hour runs was 96.4 per cent.

(2) Degassing of Crucibles

New pressed zirconia crucibles were used for each run. These crucibles were used "as received" or degassed at 10^{-3} mm pressure for several hours at temperatures between 600 C and 1500 C. The degassing of the crucibles does not appear to have any significant effect on the yield of the melt. Indications are that degassing improves the resistance of the crucibles to thermal shock. This is being investigated further.

(3) Crucible Life

All of the crucibles give evidence of some degree of cracking due to the heating or cooling (at a rate of 10 C/min). One crucible leaked metal to the susceptor after about two hours at 1400 C, reducing the yield of this run to 80 per cent. All other crucibles held the metal during the entire cycle

b. Melt-Refining Equipment

(A. A. Chilenskas, G. J. Bernstein, L. F. Coleman,
D. C. Hampson)

The fabrication of the Mark V version of the furnace is almost complete and it should be installed and tested in the early part of the next quarter. A control console for the melt-refining furnace is being constructed for testing with the Mark V furnace. Instruments and control components have been ordered and wiring diagrams and panel layouts have been prepared. Construction of the console by the Division's instrument group has begun.

A layout has been started of the melt-refining operation equipment to be installed in the argon cell. This layout will include information concerning floor space allocation, equipment location, and electrical and gas-line layout. Also included will be equipment itemization and designation as to supplier and installer (i.e., by the contractor or by Argonne). The new Mark V furnace and auxiliary equipment will be installed in the mock-up facility according to this layout.

Volatile fumes, such as due to sodium, cesium, and iodine, are released during the melt-refining operation. A Mark II fume trap (ANL-5896, page 175, Figure 54) containing a rechargeable sorbent material has been designed to collect these volatiles. The fume trap has been designed to permit remote charging and discharging of the sorbent bed and to increase the collection efficiency for sodium. Fabrication of the fume trap has been completed. It will be tested with sodium and iodine in the mock-up facility furnace.

c. Material Testing
(G. J. Bernstein, L. F. Coleman)

A number of manufacturers of electric cables have submitted samples of elastomers and proposed designs for a 54-conductor cable to be used in supplying power to the six argon-cell manipulators. Retention of flexibility, mechanical strength and electrical resistance under irradiation are the desired qualities. Several natural and synthetic (Hycar) samples have shown good flexibility after radiations up to 5×10^8 r. Electrical characteristics have not yet been determined. At present it appears that a Hycar formulation 1042, containing an anti-rad,* Antiox 4010,** will be suitable for the outer jacket. The conductor insulation will probably be linear polyethylene or natural rubber containing Antiox 4010.

Testing of dc motors in a high-purity dry argon atmosphere has continued. Commutators of two prototype motors have been rhodium plated in an effort to alleviate sparking. No marked improvement has been noted. The tests will be continued with a number of manufacturer-recommended grades of brushes.

d. Sample-Container Closure Device
(P. Fineman, D. C. Hampson)

A machine for simultaneous remote capping of two sample containers is being designed. It will be used primarily in the argon cell and will be operated with the General Mills manipulator. A prototype is to be built for testing in the mock-up facility. The caps will be stored in a dual holder, each magazine containing 24 caps. The holders will be loaded outside the air and argon cells, brought into the argon cell, inserted in the capping machine, and discharged when empty. The sample containers to be capped with this machine will be of aluminum, 3 inches

*A compound to inhibit radiation damage.

**N,N'-cyclohexyl-phenyl-para-phenylene-diamine made by Bayer Farben Fabriken, Germany, whose distributor is Haftone, Inc., New York, New York.

in length by 3/4-inch outside diameter and 0.025-inch in wall thickness. The caps will be made of tin plate. These are normally used as an inner seal for 1-inch screwneck containers (e.g., varnish cans). When pressure tested, an aluminum container capped with this type of closure began to leak at 14 psig, and the cover remained on at 26 psig. Purchase requisitions have been placed for the caps and aluminum containers.

3. Laboratory and Service Building (P. Fineman)

Building construction is about one-third complete, including the laying of the exterior walls of pumice block, the placement of concrete for footings and walls, and the installation of services - heating and ventilating, electrical, plumbing and process piping.

Aggregate for the concrete in the low-level counting room Number 1 was supplied from Illinois and sent to Idaho in closed cars. The natural radioactivity count of Illinois aggregate is about five to 10 times lower than Idaho aggregate.

The purchase order for the six glass shielding windows for the junior caves was placed with the Pittsburgh Plate Glass Company, the qualified low bidder. The design of the metal frames for the windows was reviewed and our comments were sent to the glass manufacturer. Drawings showing the installation of the assembled window were prepared by the architect-engineer, H. K. Ferguson Company. These have been examined and our comments returned to them.

The laboratory furniture offered and the design of the waste liquid evaporator submitted did not meet specifications. The general contractor was asked to resubmit the two items for our approval.

A fume hood for evaporating samples in the junior caves was tested by the Industrial Hygiene and Safety Division. Its operation is based on scrubbing of the fumes with water in an exhaust pipe equipped with three spray nozzles, one above the other. The scrub water is recirculated through the nozzles via a pump. The efficiency of fume removal which varied randomly from 45 to 65 per cent, was determined by evaporating samples of perchloric acid and nitric acid and contacting the resulting fumes with water (see Table 46). Hollow cone, solid cone, and fog nozzles were used in these tests. The nozzles can be oriented in such manner that the liquid and gas flows are either parallel or counter to each other. The air flow volume was varied from 39 to 157 cfm. Two water droplet eliminators were tested - stainless steel mesh and fiberglass (100 to 200 μ diameter). The fiberglass appears to be slightly better than the stainless steel mesh.

Table 46

SUMMARY OF RUNS TO DETERMINE FUME-SCRUBBER EFFICIENCY

Spray Nozzle Flow Rate: 60 degree hollow cone 1.5 gpm
 full cone 1.5 gpm
 fog nozzle 0.05 gpm

Mist Eliminator: (Operated dry)

Runs 1 through 9: York mesh stainless steel (304)
 demister, 5 in diameter x 4 in
 thick at 12 lb/cu ft

Runs 10 and 11: Fiberglas, 100 to 200 μ diameter,
 at 4.6 lb/cu ft

Run Series	Test Fumes (Acid)	Air Flow (cfm)	Static Pressure (in. water)	Fume Removal Efficiency ^a	Test Conditions	
					Nozzle	Scrub Solution Flow ^b
1	Perchloric	164	2.5	59	2 hollow cone	Parallel
2	Perchloric	121	1.0	45	2 hollow cone	Parallel
3	Perchloric	39	0.06	58	2 hollow cone	Parallel
4	Perchloric	157	2.6	50	3 hollow cone	Parallel
5	Nitric	157	2.6	62	3 hollow cone	Parallel
6	Nitric	157	2.6	56	1 fog (top) 2 hollow cone (bottom)	Counter Parallel
7	Perchloric	157	2.6	45	1 fog (top) 2 hollow cone (bottom)	Counter Parallel
8	Perchloric	157	2.6	49	1 full cone (top) 2 full cone (bottom)	Parallel Counter
9	Perchloric	120	2.6	46	1 full cone (top) 2 full cone (bottom)	Parallel Counter
10	Perchloric	114	2.3	64	1 full cone (top) 2 full cone (bottom)	Parallel Counter
11	Perchloric	128	2.8	65	1 full cone (top) 2 full cone (bottom)	Parallel Counter

^a Average of runs in each series.

^b Direction relative to gas flow.

V. ROUTINE OPERATIONS (H. G. Swope)

A. Waste Processing

1. Operations

(J. Harast, K. Bremer and F. Testa)

The total volume of liquid wastes processed from October through December, 1958, was 52,750 gallons. Of this amount 29,000 gallons were evaporated 10,100 gallons were filtered, 5,900 gallons were flocculated, 7,500 gallons were treated by cation exchange, and 250 gallons were stabilized by absorption into vermiculite. All of the wastes processed through the cation exchange unit were from the EBWR.

A summary of the wastes processed for the year 1958 is shown in Table 47.

Table 47

SUMMARY OF RADIOACTIVE LIQUID WASTES PROCESSED DURING THE YEAR 1958

Gallons of Wastes Treated as Shown

1958 Quarterly Period	Evaporation							Absorption into Vermic- ulite					Totals
	Reten- tion Tanks	Decon Soln	Gamma Facility Water	Cam- Cool Cutting Water	D-34 Sludge	Misc	Concen- tration ^a	Ion Ex- change	Filtra- tion	Floccu- lation		Misc	
January - March	500	16,610	2,135	2,655	-	2,798	1,123	-	4,480	5,360	493	5,063	41,517
April - June	6,140	20,527	1,425	1,350	2,100	2,133	1,350	-	520	2,760	398	68	39,077
July - September	1,220	12,373	1,233	2,565	1,310	2,771	1,201	8,000	8,000	900	845	-	40,421
October - December	2,580	15,670	340	1,115	2,590	5,173	1,710	7,520	10,140	5,900	245	-	52,989
Totals - Gal	10,440	65,180	5,133	7,685	6,000	13,175	5,699	15,520 ^b	23,140	14,920	1,981	5,131 ^c	174,004
%	6.00	37.43	2.95	4.42	3.15	7.57	3.27	8.94	13.30	8.58	1.14	2.95	100.00

^a Principally evaporator bottoms.

^b Includes 14,020 gal from EBWR, 1,500 from retention tanks.

^c Principally by decay.

2. Laboratory

(H. G. Swope, C. Ryberg and M. Jones)

The work on the absorption of various strong acids and bases into vermiculite at room temperature has now been completed. With the exception of concentrated sulfuric acid and glacial acetic acid, all concentrated acids required dilution or at least partial neutralization. It would appear that the absorption of the above type of wastes into vermiculite is not a completely satisfactory method of handling this type of waste.

B. Gamma-Irradiation Facility

(H. G. Swope, J. Harast, R. Juvinall, J. Gates, B. Kullen, N. Ondracek and D. Anthes)

The year 1958 was the third full year of operation of the Argonne High-Level Gamma-Irradiation Facility. Table 48 summarizes 1958 work.

Table 48

SUMMARY OF IRRADIATIONS PERFORMED IN RACK M-1 OF THE ARGONNE HIGH-LEVEL GAMMA-IRRADIATION FACILITY DURING 1958

1958 Quarterly Period	No. of Samples ^a				Total Day Units (Rads ^b)				Total Night Units (Rads ^b)			
	QMC	Ind	Educ Inst	ANL	QMC	Ind	Educ Inst	ANL	QMC	Ind	Educ Inst	ANL
January - March	2,594	283	62	103	3,211	390	75	641	67	2,466	152	3,565
April - June	1,589	149	219	60	1,981	339	229	398	193	2,833	749	2 197
July - September	1,725	72	23	92	2,368	190	113	533	18	2,235	887	2,135
October - December	1,256	132	60	106	1,790	229	127	806	27	1,890	1,032	3,083
Totals	7,164	636	364	361	9,350	1,148	544	2,378	305	9,424	2,820	10,980

^aEquivalent to a No. 2 sized can.

^b1 unit = 2×10^6 r.

A total of 8,525 samples were irradiated in 1958 as compared to 11,139 in 1957; day units were 13,420 and 12,899 and total night units were 23,529 and 16,688 in 1958 and 1957, respectively. In addition, 3,141 special dosimetry samples were run during the year.

Rack M-2, which is capable of holding samples as large as 20 inches in diameter and 29 inches high, was used almost as much in 1958 as in 1957 (12 samples). Because of the design of this rack the flux is about 50,000 r/hr.