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Chemistry-Separation Processes for

ARGONNE NATIONAL LABORATORY
P. O. Box 299
Lemont, Illinois

CHEMICAL ENGINEERING DIVISION
SUMMARY REPORT

January, February, and March, 1956

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CHEMICAL ENGINEERING DIVISION

SUMMARY REPORT

for January, February, and March, 1956

SUMMARY

I. Direct Cycle Boiling Reactor Entrainment Studies (pages 9 to 16)

Measurement of radioactive carry-over was made on Borax III operating at 300 psig and at power levels ranging from 4 to 14 mw. Decontamination factors of from 1.5×10^4 (at 4 mw) to 6×10^3 (at 14 mw) were obtained. These data are in essential agreement with those predicted by previous laboratory experimental work.

II. Solvent Extraction — Study of Dispersion and Coalescence
(pages 17 to 21)

A continuous flow chamber for the study of mass transfer under conditions in which interfacial area may be measured has been installed. Additional light transmittance data have been obtained extending the presently available area—light transmittance correlations to 25 per cent o/w dispersions.

III. Fluoride Volatilization Separations Processes (pages 22 to 73)

Development work has continued on a fused salt process for the recovery of decontaminated uranium from enriched reactor fuels. Most of the laboratory effort during the quarter has been directed toward an evaluation of corrosion and a search for suitable materials of construction. Additional data were obtained on the corrosion of nickel in a sodium fluoride-zirconium fluoride melt sparged with bromine pentafluoride. The effect of a hydrogen fluoride sparge was also determined, and found to be more severe than was expected.

The study of an all-volatility separations process for uranium-plutonium alloys was continued. Further information on the formation and thermal decomposition of plutonium hexafluoride on nickel packing has been obtained.

In the feed materials area, uranium tetrafluoride produced from ore concentrate was fluorinated in a fixed-bed reactor to produce volatile uranium hexafluoride. Bromine pentafluoride vapor and fluorine gas proved equally effective for this purpose.

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Further work is reported on the behavior of fission product fluorides in fluoride volatilization processes. The anomalous behavior of fission product tellurium has been re-examined in a series of experiments with active tellurium. The radiochemical reduction of tellurium hexafluoride was confirmed, and it was shown that the reduced form is converted back to the volatile hexafluoride by bromine trifluoride.

Corrosion data were obtained on nickel-base alloys and other metals in bromine trifluoride solutions containing uranium hexafluoride. The corrosion rates of nickel, Monel, Inconel and copper in fluorine gas at elevated temperatures were also measured to allow an intelligent selection of the material of construction for the preparation of plutonium hexafluoride.

The initial series of five pilot plant runs was completed. These runs were made to demonstrate a process for the recovery of decontaminated uranium hexafluoride from irradiated natural uranium fuel elements. Batches of uranium metal (up to 22 lb) were dissolved in about 200 lb liquid bromine trifluoride at about 120 C and at pressures up to 3 atmospheres. Dissolution times as short as 8 hours were demonstrated using slugs 1.35 inches in diameter. Uranium hexafluoride of about 99 per cent purity and decontaminated to activity levels below that of normal uranium was obtained by batch distillation in 2-inch diameter packed columns. Decontamination factors from gross beta and gross gamma of about 10^5 were demonstrated with the activity levels used.

The head end dissolution facilities for testing the fused-salt dissolution of zirconium-uranium fuel alloys has been assembled and leak tested.

IV. Chemical Metallurgical Separation Processes (pages 74 to 109)

The results of a melt-refining experiment with 0.4 per cent burn-up EBR fuel pins are reported. The distribution of fission elements was found to be similar to that found in earlier reported experiments at much lower fission element concentrations. The corrosive attack of molten uranium on pure alumina crucibles has been shown to produce an interfacial layer of nearly pure uranium dioxide and an equivalent amount of aluminum in uranium solution.

In the search for low melting stable oxide slags, a composition in the lime-beryllia system melting at 1385 C has been found. X-ray evidence for a previously unreported compound in this system is presented.

Study of the protective coating of tantalum with tantalum boride was continued. At 1275 C the corrosive attack by molten uranium was less than 50 microns after 50 hours.

The speed of extraction of plutonium from molten uranium by liquid magnesium in an unstirred system is materially increased by thorough outgassing of the experimental components; it is evident that foreign materials at the interface present a significant resistance to plutonium transfer.

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Work was continued in the semi-works on the development of slagging techniques and on the testing of equipment components. Several methods of purifying the inert argon cell atmosphere have been tested. The removal of oxygen by converting it to water which is then removed in a drier appears promising. Further studies have been conducted on the extraction of plutonium from uranium with magnesium and on the subsequent distillation of magnesium to recover the plutonium.

V. Fluidization Studies (pages 110 to 126)

The design of the multistage, fluidized-bed, green salt pilot plant was essentially completed and fabrication of the equipment components has been started. Experimental work was continued in the bench-scale reactor to establish the optimum operating conditions for the green salt process. A comparison between dissociated ammonia and undissociated ammonia for reduction of uranium trioxide was made. The rate of the reduction reaction was found to be somewhat higher when the ammonia was pre-dissociated before feeding to the reactor. In the hydrofluorination step the use of an increasing temperature gradient from the top stage to the bottom stage, greatly reduced the solids residence time required for conversion of uranium dioxide to uranium tetrafluoride. In one run a residence time of three hours was sufficient for 98 per cent conversion to green salt.

The production of crude green salt from uranium ore concentrate was carried out on a kilogram scale with satisfactory results. Size reduction of the ore pellets to a fluidizable powder was readily achieved by jaw crushing the material to pass 40-mesh sieve.

Design work on the shielded calciner for radioactive wastes was continued and fabrication of the calciner and auxiliaries was started.

A fundamental study of the fluidization of mixtures of solid particles of two widely separated sizes was advanced. "Phase diagrams" relating gas velocity to bed composition were prepared for binary mixtures of five different systems. These "phase diagrams" appear in many respects to be analogous to, and have the properties of, vapor pressure diagrams for binary liquids.

VI. Reactor Chemistry -- Metal Oxidation and Ignition (page 127)

The equipment described in previous quarterly reports have been set up and preliminary runs made.

VII. Analytical Research and Services -- Direct Assay of Molybdenum and Ruthenium in Ternary Alloys with Uranium by X-ray Emission (pages 128 to 134)

New procedures are described for quickly determining the concentration of molybdenum and ruthenium in non-radioactive alloys representative of high burn-up reactor fuels by the method of X-ray emission analysis.

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VIII. Routine Operations (pages 135 to 136)

Operation of the gamma irradiation facility and the radioactive waste processing building is described.

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I. DIRECT CYCLE BOILING REACTOR ENTRAINMENT STUDIES

(A. J. Shor)

Measurements of radioactive carryover were made on the Borax III boiling reactor. The reactor was operated at 300 psig and data were taken at different power levels ranging from 4 to 14 mw. Isokinetic samples were obtained from the steam leaving the reactor vessel, and direct samples were taken of the reactor water and turbine condensate. Decontamination factors, representing the ratio of beta-gamma activity in the reactor water to the activity carried in the steam or condensate were determined on samples permitted to decay for 20 to 30 hours. The principal activity at that time appears to be 15-hour Na^{24} which serves as an indicator of the liquid droplet entrainment. The decontamination factors showed a variation with power level and ranged from about 1.5×10^4 at the 4-mw levels to 6×10^3 at 14-mw level. These data are supported by previous laboratory experiments at atmospheric pressure and in the range 150 to 600 psia at comparable steam velocities and power densities.

A. Experimental Procedure

1. Sampling

A description of the locations of the sampling stations for the reactor and steam cycle has been reported previously (ANL-5529, pages 9 to 12). Samples were taken from the steam line leaving the reactor, from the discharge lines of the steam separator and from the condensate leaving the condenser hotwell. The steam samples were removed at isokinetic rates, throttled to about atmospheric pressure, and condensed. Care was taken to prevent knockout of moisture in the sampling process. The reactor water sample was obtained directly from a continuously circulating loop, run through a heat exchanger and throttled to atmospheric pressure. No flashing of the water was permitted.

During the test period the reactor was operated for about three days at each of four different power levels. Initially, samples were taken at the 12-mw level until a steady condition was achieved. Then the power was decreased to 8 mw and observations were made to determine the length of time required to reach a new steady condition by following the entrainment. The power was decreased further to 4 mw for about 2 1/2 days and finally samples were taken at 14 mw.

Samples were removed at approximately 8-to 12-hour intervals. Four-milliliter aliquots of overhead samples were evaporated on small aluminum dishes for low level counting, while 200- μ aliquots were used for reactor water analysis. The samples were counted in a proportional beta-gamma counter.

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2. Samples Analysis

The reactor water was deionized and varied in specific resistance between 5×10^5 to 2×10^5 ohm-cm. It was maintained at a pH of 5 to 6 during the tests. The activation products dissolved in the water were derived from natural impurities, from corrosion products of the reactor and steam system, and from dissolved gases initially present in the water. Decay curves for the reactor water samples (log activity vs time) exhibited considerable curvature for about the first twenty hours decay. However, in the interval between 20- and 30-hours decay, the principal activation product appeared to be 15-hour Na^{24} .

The activity in the steam and condensate was derived from the reactor water droplets carried as entrainment and from volatile activation products. These were continually being swept out of the reactor in the boiling process. Thus, the decay curves for the steam showed a similar but not identical decay scheme as a result of some partition of activation products between the reactor water and condensate. However, after about 20 hours decay of the steam and condensate samples, the rates of decay were constant with slopes characteristic of Na^{24} . Therefore, a decay interval between 20 to 30 hours was chosen as that most representative of the activity associated with decontamination factors based on droplet entrainment.

Figure 1 shows a semi-log plot of a set of data obtained at the 4-mw operating level. Although the steam and condensate decay curves show similar curvature, the marked differences in the rates of decay in the 1- to 20-hour interval between the reactor water and the condensate is readily apparent. However, after about twenty hours decay, all these curves approach the slope of 15-hour Na^{24} . An attempt to analyze the decay of the steam and condensate curves by subtracting out the Na^{24} contribution also leads to complex curves which appear to decay, at least in the interval of 4 to 10 hours, with a half-life of about 100 minutes. Figure 2 shows a semi-log plot of a set of data obtained at the 14-mw operating level. The decay range from 20 to 80 hours is covered. In the interval 20 to 50 hours the decay rates show half-lives of about 15 hours. After about 50-hours decay, the slope begins to change so that the steam and condensate appear to decay at a slower rate than the reactor water. An explanation for the differing decay rates of the reactor water and the steam will require a more thorough analysis of the activation products. This is being attempted by study of the gamma energy spectrum. The presence of volatile activation products which are carried out of the reactor water with the steam is considered a possible cause of the differing decay rates. For example, it was apparent when drawing a sample of steam and reactor water simultaneously that the condensed steam showed a higher activity than the reactor water. Rather crude radiation survey instruments were used in this test. However, the activity in the steam rapidly decayed with about a 7-second half-life indicative of N^{16} . Similar effects could occur in reference to longer-lived volatile activities.

B. Decontamination Factors

Figure 3 shows the variation of decontamination factors with time and power level based on the steam and condensate samples. After about one day

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FIGURE I.
DECAY CURVES FOR A SET OF SAMPLES
OBTAINED AT 4 MW FROM THE BORAX III
REACTOR USING PROPORTIONAL BETA-GAMMA COUNTING.

FIGURE 2.
DECAY CURVES FOR A SET OF SAMPLES
OBTAINED AT 14 MW FROM THE BORAX III
REACTOR USING PROPORTIONAL BETA-GAMMA COUNTING.

FIGURE 3.
DECONTAMINATION FACTORS FOR STEAM AND
CONDENSATE BORAX III REACTOR.

following a change in power and for the duration of the test, the decontamination factors show little fluctuation. A trend can be seen at different power levels; for 14 and 12 mw the decontamination factor averages about 6×10^3 while at the 4- and 8-mw levels the decontamination factors are about 1.5×10^4 . These numbers lie in the range of 20- to 30-hours decay so that the decontamination factors principally represent the reactor water to steam Na^{24} activity ratio and are indicative of the droplet carryover. Referring to the data at 12 mw, it is noted that the decontamination factors based on steam samples taken before and after the moisture separator check very closely.

Decontamination ratios based on steam and reactor water samples permitted to decay for about 40 days do not exhibit any noticeable trend with power level but lie in the range 1×10^3 to 2×10^3 . A mechanism for this behavior based on a partition of activities resulting from relatively volatile long-lived activities has been mentioned. The attempt to identify the radioactive species in the reactor may lead to further light on the partition mechanism.

Figure 4 shows a graph of the decontamination factors obtained in the Borax III tests vs the velocity of the steam in the free space above the boiling interface. Also shown are data obtained in a high pressure loop and in a laboratory scale entrainment study apparatus as reported in ANL-5422, pages 8 through 16 and ANL-5333, pages 7 through 10, respectively. The Borax III data are represented by vertical lines indicating the range of decontamination factors at the specified power level. The intersecting horizontal lines represent average values. The factors are based on the 20- to 30-hour decay samples shown in Figure 3. It is seen from the graph that between the power levels of 4 to 14 mw and corresponding steam velocities in the reactor free space between 0.3 to 1.0 ft/sec, no sharp break in the decontamination factor curve occurs. Similar conclusions can be stated for this range of steam velocities for data previously reported and in part repeated here. The hollow circles represent a set of data taken by isokinetic sampling in a high pressure boiling loop at different power levels and pressures. Although the data scatter widely, they exhibit a similar trend in the range of free steam velocities observed. The graph of decontamination factors obtained at one atmosphere in a small scale experimental apparatus shows a similar trend. The three curves are displaced in respect to the range of decontamination factors observed. This displacement may be accounted for in part by wall effects in the experimental apparatus. The diameter of the cylindrical boiler was about 3 inches in the atmospheric runs, and was about 5 inches in the boiling loop experiments. The diameter of the reactor vessel was 4 1/2 feet. Thus, considering the probable range and direction of the droplets leaving the boiling interface, it is reasonable to expect that in the smaller vessels a greater portion of the droplets were impinged on the walls.

C. Conclusion

It has been found, based on short-term operation, that the decontamination factors obtained on the Borax III reactor vary between 6×10^3 to 1.5×10^4 corresponding to reactor power levels ranging from 4 to 14 mw. These decontamination factors refer to primary droplet entrainment

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FIGURE 4.
DECONTAMINATION FACTOR vs
STEAM VELOCITY.

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without the use of special steam separators and correspond to steam of greater than 99.9 per cent quality.

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II. SOLVENT EXTRACTION — STUDY OF DISPERSION AND COALESCENCE

(W. A. Rodger, V. G. Trice, Jr., L. F. Dorsey)

Work has continued on the investigation of mass transfer in a continuous-flow mixing chamber. The mixing chamber has been installed and tests of the sampling device and the light probe for interfacial area measurements have been completed.

Additional light scattering data have been obtained to extend the presently available correlations to 25 per cent dispersions. New probes for use in the mixing chamber have been designed, constructed, and calibrated.

A. Mass Transfer Studies

The essential features of the mixing chamber for use in mass transfer studies are shown in Figure 5. The chamber is a six-inch right cylinder supplied with the necessary auxiliaries to provide for sampling, introduction and discharge of fluids, measurement of temperature and light transmission, and mixing of the contents. The vessel is fitted with a six-bladed flat blade impeller and four baffles each 1/10 the diameter of the vessel.

The influent streams are individually introduced, the heavy phase above the light phase below the impeller. The contents of the vessel are discharged through two ports, one near the top and one near the bottom, to reduce adverse effects on the mixing pattern. The effluents then pass through a baffle to the sampling zone.

Sampling techniques were developed on the assumption that an entirely satisfactory sampler would have to incorporate some sort of discriminator which would force the device to sample selectively the desired phase of an emulsion. This is necessary because the calculation of mass transfer coefficients is based on the composition of the liquids in the chamber. Therefore, contact of the phases after the sample is withdrawn must be eliminated or at least held to a minimum in order to prevent erroneous results.

A series of tests were made to determine the adaptability of fritted tip filters to the selective sampling of emulsions. The performance of the fritted filters is believed to be due to differences in the wetting characteristics of the two phases for the fritted filter. The system isobutanol-water, which was chosen for the initial mass transfer studies, was used in testing the fritted tip samplers. This system was by no means the best choice for demonstrating selective sampling because of the polar characteristics of isobutanol. Tests were made at the expected operating pressure range of 5 to 15 psi with an organic to aqueous flow ratio of 1:1.

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FIGURE 5.
CONTINUOUS-FLOW AGITATED CHAMBER.

A. Discharge Line
B. Sampler
C. Thermometer

D. Inlet-Light Phase
E. Impeller & Shaft
F. Inlet-Heavy Phase
G. Light Probe

It appears that it will be possible to obtain samples of either phase containing less than 10 per cent of the opposite phase. Upon continued use, the efficiency of the samplers appears to improve.

Although the fritted tip samples do not show absolute phase discrimination, they do have advantages over bulk sampling by syringe or other means. Probably most important is the time required for sampling. The fritted tip samples are obtained at the rate of 15 ml in 10 to 30 seconds in the form of one primary phase with a small amount of the contaminating phase as a separate layer. Bulk samples obtained by syringe must be transferred to a container and the phases permitted to separate before the desired phase may be withdrawn. Bulk sampling is definitely inferior to fritted tip sampling because after sampling the phases are in contact for a longer period of time with more interfacial area available for mass transfer.

B. Light Transmittance Studies

The interfacial area of the emulsion in the mixing chamber will be determined from light transmittance correlations similar to those described in ANL-5512. The transmitted light is conducted from the point of measurement to the light detector by means of a light probe.

The light probe which has been used is a platinum-coated glass rod. A total of fourteen glass probes have been made following standardized procedures. Without exception, substitution of probes had no effect on the reproducibility of light transmittance data. However, the glass probes were fragile and frequently subject to damage. Therefore, probes of a more rugged design were developed for use in the mixing chamber.

Two probes of a new design were tested. These probes were similar in that both consisted of 3/8-inch stainless steel tubing with thin quartz windows cemented in place at each end. However, the inside surfaces of one probe (Probe 1) were plated and polished to give a bright, highly reflective surface, and for the other probe (Probe 2), the inside surfaces were painted a dull flat black.

The stainless steel probes are compared with each other and with the standard glass probe in Figure 6. As shown by Figure 6B and 6D, transmittance readings for the stainless steel probes are independent of the wavelength of incident light (red light for 1P-41 and yellow light for 1P-42 phototube) and the type of phototube employed. This is not the case for the standard glass probe, Figure 6A indicating that the glass probe absorbs more yellow than red light with the net effect that for given conditions the phototube detects a higher percentage transmittance for red than yellow light. Figure 6C compares the polished stainless steel probe with the standard probe and shows that a higher percentage of the incident light is conducted by the glass probe. The inference is that the platinum coating on the glass rod is a better reflector than

FIGURE 6. RESPONSE CHARACTERISTICS OF LIGHT PROBES.

the polished stainless steel. As expected, the same conclusions apply to the stainless steel probe with the flat black surface which, as may be seen from Figure 6E, conducts less light than the polished stainless steel probe. In summary, Figure 6 shows that the reflectivity of the interior probe surfaces affects the response characteristics and that the calibration of new probes by comparison with the standard probe is desirable.

The selection of the proper probe depends on the operating conditions. For most applications, a calibrated stainless steel probe would be preferable because of its durability. Because of the limitations of the detector electronic circuit, the best operating range is in the region of measured $\ln I_0/I$ of 1.0 to 5.0. The restriction limits the use of the nonreflecting stainless steel probe (2) while at the same time creates for it an important role for systems where $\ln I_0/I$ falls between 0.2 and 1.0 as measured with the standard glass probe.

During the next quarter the work to extend further the light transmittance correlations will be continued. Also, some mass transfer data will be obtained on the system isobutanol-water.

III. FLUORIDE VOLATILIZATION SEPARATIONS PROCESS

Development work has continued on a fused salt process for the recovery of decontaminated uranium from enriched reactor fuels. The zirconium-matrix alloy of the STR type is dissolved in a fused mixture of sodium fluoride and zirconium fluoride by hydrofluorination at 500 to 600 C. Bromine pentafluoride or fluorine can then be passed through the melt, volatilizing the uranium as the hexafluoride. The final purification and decontamination are accomplished by fractional distillation.

Most of the laboratory effort during the quarter has been directed toward an evaluation of corrosion and a search for suitable materials of construction. Additional data were obtained on the corrosion of nickel in a sodium fluoride-zirconium fluoride melt sparged with bromine pentafluoride. The effect of a hydrogen fluoride sparge was also determined and found to be more severe than was expected. For the purpose of engineering design, the heat liberated by the dissolution reaction was calculated.

The study of an all-volatility separations process for uranium-plutonium alloys was continued. Further information on the formation and thermal decomposition of plutonium hexafluoride on nickel packing has been obtained.

In the feed materials area, uranium tetrafluoride produced from ore concentrate was fluorinated in a fixed-bed reactor to produce volatile uranium hexafluoride. Bromine pentafluoride vapor and fluorine gas proved equally effective for this purpose. A few additional data on the recovery of uranium from magnesium fluoride slags produced in the reduction of the tetrafluoride to metal are presented.

Further work is reported on the behavior of fission product fluorides in fluoride volatilization processes. The anomalous behavior of fission product tellurium has been re-examined in a series of experiments with active tellurium. The radiochemical reduction of tellurium hexafluoride was confirmed, and it was shown that the reduced form is converted back to the volatile hexafluoride by bromine trifluoride.

Corrosion data were obtained on nickel-base alloys and other metals in bromine trifluoride solutions containing uranium hexafluoride. The corrosion rates of nickel, Monel, Inconel and copper in fluorine gas at elevated temperatures were also measured to allow an intelligent selection of the material of construction for the preparation of plutonium hexafluoride at 550 C.

The initial series of five pilot plant runs was completed. These runs were made to demonstrate a process for the recovery of decontaminated uranium hexafluoride from irradiated natural uranium fuel elements. Batches of uranium metal (up to 22 lb) were dissolved in about 200 lb liquid bromine trifluoride at about 120 C and at pressures up to 3 atmospheres. Dissolution

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times as short as 8 hours were demonstrated using slugs 1.35 inches in diameter. Uranium hexafluoride of about 99 per cent purity and decontaminated to activity levels below that of normal uranium was obtained by batch distillation in 2-inch diameter packed columns. Decontamination factors from gross beta and gross gamma of about 10^7 were demonstrated with the activity levels used.

The head end dissolution facilities for testing the fused-salt dissolution of zirconium-uranium fuel alloys has been assembled and leak tested.

Recent work was presented at the Raw Materials Meeting in Cincinnati, January 12 to 13. On January 26 and 27 conferences were held with J. T. Long, G. I. Cathers and S. H. Stainker of Oak Ridge National Laboratory. On February 8, in conjunction with the group working on fluidization, a meeting was held with representatives of industrial organizations interested in the production of uranium tetrafluoride, hexafluoride or trioxide for the Commission. This meeting has been followed by a series of more information meetings.

G. Strickland, R. Johnson, and W. J. Johnson of Brookhaven National Laboratory visited Argonne for an exchange of information from February 13 to 16. Mr. R. A. Gustison of the Electrometallurgical Division of Union Carbide and Carbon visited on March 2 to obtain information on the use of bromine trifluoride as a fluorinating agent. N. J. Hawkins and J. W. Coddling of Knolls Atomic Power Laboratory exchanged information with us on the preparation and properties of plutonium hexafluoride on January 5 and 6.

A. Laboratory Investigations

1. Processing of Enriched Uranium Reactor Fuels (R. K. Steunenberg, S. Vogler)

The principal effort has been directed toward corrosion studies and is reported in Section A-2.

The dissolution of zirconium by hydrogen fluoride in the fused fluoride medium evolves a significant amount of heat. This quantity was calculated in order to establish the dissolver heat load. The following reaction was used as the basis for the calculation at 1000 K:

The result obtained was $\Delta H = -180$ kcal/mole, using values for the heats of formation at 298 K, and the change in heat content as given by Quill.¹

¹Quill, L. L., The Chemistry and Metallurgy of Miscellaneous Materials — Thermodynamics, NNEs IV-19B, McGraw-Hill (1950)

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2. Corrosion Investigations

a. Fused Salt Processing of Enriched Uranium Reactor Fuels (W. Seefeldt, S. Vogler, R. Breyne, L. Hays)

The evaluation of nickel in fluorinated and hydrofluorinated fused salts was continued. The apparatus and methods of evaluation used were described in ANL-5494, pages 33 and 34. Embrittlement of the nickel occurred in a long run at high hydrogen fluoride sparge rates. Alternate materials of construction are being tried for this step. A test of nickel in stagnant melt was also made. All testing was done in melts equi-molar in sodium fluoride and zirconium tetrafluoride.

1. Corrosion During the Bromine Pentafluoride Sparge

A series of runs (36 through 44 in Table 1) at 600 C, in which either nickel fluoride was added to the melt or uranium hexafluoride to the sparge, completed the work with bromine pentafluoride sparging. Data from most of these runs are fragmentary and are shown in Table 1. Further data will be reported after more complete evaluation. Plugging of the inlet sparge tube about two inches from the gas exit together with high rates of attack at that point continued. The typical appearance of a sectioned sparge tube is shown in Figure 7. The sections are 0.5 in. apart. The sections are arranged in the clockwise direction beginning with the lowest section nearest the center. The increased accumulation of material in sections one through four and the reduction in wall thickness is quite apparent. This phenomenon does not occur at 700 C. Further work on this plugging problem is necessary. The addition of nickel fluoride to the melt (Runs 36 through 38) did not increase the rate of liner attack appreciably. Evaluation on the effect of uranium hexafluoride addition to the sparge at 600 C has not yet been made.

2. Corrosion During the Hydrogen Fluoride Sparge

Data for hydrogen fluoride sparge runs are also presented in Table 1. Efforts to lengthen runs and increase sparge rates with hydrogen fluoride in Run 51 resulted in serious embrittlement of both liner and sparge tube. The nickel liner is shown in Figure 8. The average sparge rate was 38 g/hr. Although the run length was 117 hours, some evidence suggests that liner failure may have occurred after 60 to 70 hours of exposure. Wall thicknesses at the failed sections were not substantially reduced; failure was due to general weakening by embrittlement. It is apparent that a

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Table 1

RESULTS OF CORROSION STUDIES IN FUSED NaF-ZrF₄ SPARGED WITH BrF₅ OR HF

Material: "A" Nickel Melt Weights: 300-350 gm
 Fused Salt: Equimolar NaF-ZrF₄ Liner Area: 1.62 in.²
 All melts used with HF were prefluorinated except in runs 45 through 47

Run	Exposure Time (hr)	Sparge Gas	Additives to		Sparge Rate (g/hr)	Dimensional Change, (mil/day) ^a										Location of Max Attack		
			Sparge Gas	Melt		Liner Wall		Sparge Tube		Impingement Plate Holes			Avg Plate Thickness	Avg Plate OD	Sparge Tube Length	Liner ^b Wall	Sparge ^c Tube	
						Max	Inter-face	Below Plate	Above Plate	Min	Max	Avg						
36	9	BrF ₅		NiF ₂ ^d	{ 16.4								{ 0	{ 1.2				
36A	11	BrF ₅		NiF ₂ ^d														
37	52	BrF ₅		NiF ₂ ^d	12	0.3	0.5	2.8	1.4				0		0	0.5		
38	5	BrF ₅		NiF ₂ ^d	34.4	{ 4.8	4	3.2	22				{ 0	0	0	0.5		
38A	10	BrF ₅		NiF ₂ ^d	97.3													
39-41		BrF ₅		NiF ₂ ^d	{ Evaluations to be made													
42-44		BrF ₅	10% UF ₆															
45	14	HF			9	3.5	0	<5.2	<1.7	1.7	5.2	<0.9	<0.9	<52	0			
46	53	HF			7.6	1.1	0	1.8	< .46	1.8	3.2	1.4-1.8	0.9	<14	1.5			
47	120	HF			3.6	0.32 (0.2 typ.)		0.3-2	0.3	1.1	3.2	1.6			0	0.5		
48	23	HF			26.1	{ 0.38 (1.4 typ.)							{ 1.3-2	1.3	1			
48A	13	HF			41.5													
49	65	HF			7.7											<0.2	<0.4	
50	86	HF			5								<0.14	0.14				
51	117	HF			38													

^aAssumes linear rate of attack over exposure period.^bInches above bottom of liner.^cInches above impingement plate.^d16.5 g

FIGURE 7

SECTIONS OF TYPICAL BrF_5 SPARGE TUBE
USED IN FLUORIDE MELT AT 600 C

Each section is 0.5 in. apart. Sections are arranged in clockwise direction beginning with the lowest section nearest the center. Note the build up of plugging material in sections one through four and the corresponding reductions in wall thickness.

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FIGURE 8

EMBRITTLMENT OF NICKEL LINER AND SPARGE TUBE
DURING HYDROFLUORINATION OF MELT

(Run 51 - see Table 1 for operating conditions)

rapid flow of hydrogen fluoride through a melt is required for this severe embrittlement to occur. The metal in the failed liner immediately above the melt level appeared sound. The mechanism by which this failure occurs is not clear.

Preceding Run 51, six other runs with HF sparge had been made, three with melt that had been prefluorinated (Runs 48 through 50), and three that had not been. Severe embrittlement was not encountered. Pre-fluorination is accomplished by sparging the melt with 15 to 30 grams of bromine pentafluoride for one hour at 600 C; this treatment fluorinates and removes oxygen, sulfur, and other impurities. The following evidence suggests that melt purification is helpful in reducing attack during the hydrogen fluoride sparge: (1) the rate of attack on the liner used in Runs 48, 48A, and 49 (melt prefluorinated) was only a small amount greater than that in Run 47 (melt not prefluorinated) even though the sparge rate was substantially greater, and (2) rates of attack on the impingement plates in Runs 48 and 48A with high sparge rates and those in Runs 45 and 46 at low sparge rates were comparable.

Alternate materials of construction for the hydro-fluorination step are now being examined. Tests are presently planned on various forms of graphite, copper, nickel and nickel alloys that are more resistant to intergranular attack (low-carbon nickel, Inconel, "D" nickel), nickel-molybdenum alloys, alumina and alumina-coated metal. Metals will be evaluated for intergranular attack and weight changes, refractories for wall thickness changes. Some preliminary data (weight losses only) are shown in Table 2. A single test of nickel in a stagnant, unsparged melt was made at 600 C. The results are shown in Table 3. It appears that the rate of attack decreases with time.

Since the above corrosion tests indicated excessive attack on nickel when hydrogen fluoride is passed through a sodium fluoride-zirconium fluoride melt at 600 C, it was necessary to determine whether significant impurities were present in the reagents. Both the melt and the hydrogen fluoride were analyzed.

A 100-gram sample of the hydrogen fluoride was distilled from the main supply into a 250-ml nickel vessel. The electrical conductivity and infrared spectra were determined on samples from this vessel. The specific conductance was found to be 2.9×10^{-3} reciprocal cm-cm, corresponding to a purity of 99.95 per cent.

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Table 2

PRELIMINARY WEIGHT LOSS^a DATA ON COUPON TESTS IN
HYDROFLUORINATION MELT AT 600 C

Melt: equi-molar NaF-ZrF₄
 Sparge Gas: HF
 Sparge Rate: ca. 300 gms/hr
 Melt Weight: 400 gms
 Time: 50 hours
 Liner Area: 1.62 in.²

<u>Coupon Material</u>	<u>Area, dm²</u>	<u>Wt. Loss, mg</u>	<u>Rate of Attack^b (mils/day)</u>
"A" Nickel	0.16	235.5	3.1
		323.6	4.3
"I" Nickel	0.16	337.9	4.5
		301.3	4.0
Inconel	0.10	174.3	3.7
		162.6	3.4

^aPrimary method of evaluation will be for inter-granular attack. The test will be continued until the "A" nickel (control) is embrittled severely, at which time the other metals will be evaluated.

^bAssumes uniform attack.

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Table 3

CORROSION OF NICKEL IN STAGNANT EQUI-MOLAR NaF-ZrF₄ AT 600 C

Each weight loss shown represents one coupon.
 Coupon Area: 0.10 dm²

Time		Weight Loss (mg)	Δ Weight Loss (mg)	Rate (mils/month)
Wet Ground Coupons	14 days	69.9	69.9	0.67
	28 days	65.7	-4.2	very low
As-Rolled and Degreased	14 days	60.8	60.8	0.58
	28 days	97.8	37.0	0.35

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The measured impurity in this case was water. The infrared spectrum* was similar to that obtained from the highest purity hydrogen fluoride available. In particular, absorption due to sulfur dioxide was totally absent.

The major impurity found in zirconium fluoride has been oxygen. A previous determination had indicated 2.5 weight per cent of oxygen. If this is assumed to be zirconium oxide, it is present to the extent of 12 mole per cent (ANL-5494, pages 25 to 28). Further analyses are tabulated in Table 4.

The differing results on the same batch of zirconium fluoride may be due to inhomogeneity in the samples. Although it is not certain what effect oxygen has on the corrosion, it has been shown that it is removed by sparging the melt with bromine pentafluoride.

Both batches of the zirconium tetrafluoride were examined spectrographically to detect possible cationic impurities. The major ones found were: hafnium, 2.5 per cent; aluminum, 0.1 per cent; iron, 0.1 per cent. In the General Chemical Company sample, 0.3 per cent titanium and 0.08 per cent yttrium were also found. No other impurities were detected in excess of 0.1 per cent.

b. Interhalogen Systems at 125 C; Bromine Trifluoride-Uranium Hexafluoride
(J. G. Schnizlein, R. K. Steunenberg, H. D. Tyler)

A series of corrosion tests on metals and alloys commonly used with halogen fluoride solutions was reported previously in ANL-5290, pages 57 to 60. In these studies corrosion rates were measured in pure bromine trifluoride and in solutions of bromine and bromine pentafluoride in bromine trifluoride. These data have recently been extended to include solutions of uranium hexafluoride in bromine trifluoride.

The same testing procedures were employed as in the previous tests. The metals investigated were nickel, welded nickel, Monel, welded Monel, K-Monel, Inconel, Duranickel, Incoloy, aluminum, stainless steel (types 304 and 347) and mild steel. Specimens of these metals were located in the liquid, interface and vapor regions of a boiler, in which a solution of uranium hexafluoride in bromine trifluoride was refluxed at 125 C. At the end of the test period analyses for uranium indicated about 5 mole per cent uranium hexafluoride in the solution.

In order that the complete data will be available in one place, these results are summarized along with the previous ones in Table 5. Nickel, Monel and Inconel were found to be the best of the metals tested for bromine trifluoride service, their corrosion rates being extremely low.

*Courtesy of R. M. Adams, Chemistry Division

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Table 4

OXYGEN CONTENT OF ZIRCONIUM FLUORIDE
FROM VARIOUS SOURCES

Method: Oxygen evolution upon treatment
 with bromine trifluoride, according
 to the method of Katz and Hoekstra^a

Material	ZrO ₂ in ZrF ₄ (mole per cent)
NaF-ZrF ₄ obtained from ORNL and used in corrosion tests	3.3
ZrF ₄ from General Chemical Company	12.3
ZrF ₄ same material as above, analyzed 5 months later	15.6

^aHoekstra, H. R., and Katz, J. J., Analytical Chemistry
25, 1608-12 (1953)

Table 5

CORROSION IN INTERHALOGEN SYSTEMS AT 125 C

Coupons: 1-3/8 in. x 1-3/8 in. x 1/16 in. initially polished with fine steel wool and scouring cleanser paste, washed, degreased and dried at 110 C.

Supports: Insulating Teflon spacers.

Fluoride Film Removal: 1 M $\text{Al}(\text{NO}_3)_3$, 0.05 M sulfamic acid, pH 0.5.

Metal	Time of Exposure (Weeks)	Penetration in mils per year ^a											
		Pure BrF_3^b			10% BrF_5 - 90% BrF_3			10% Br_2 - 90% BrF_3			10% UF_6^c - 90% BrF_3		
		Vapor	Interface	Liquid	Vapor	Interface	Liquid	Vapor	Interface	Liquid	Vapor	Interface	Liquid
Nickel	11	+ ^d	+	+	+	0.006	0.012	+	0.002	0.004	0.008	0.018	0.008 ^e
Welded Nickel	11	+	0.0004	+	0	0.012	0.005	+	0.001	0.006	0.007	+	0.0008
Monel	11	+	+	0.005	+	0.025	0.029	+	0.020	0.024	0.004	0.003	0
Welded Monel	11	+	+	0.005	0.004	0.029	0.018	+	0.015	0.033	0.005	0.002	0
K Monel	11	0.0002	0.003	0.007	0.009	0.031	0.036	0.008	0.025	0.034	0.005	0.004	0.004
Inconel	11	0.0005	0.010	0.027	0.0008	0.045	0.046	+	0.029	0.041	0.020	0.011	0.015
Duranickel	4	0.12	0.28	0.30	0.23	0.30	0.26	0.30	0.37	0.37	0.05	0.02	0.009
Incoloy	4	1.3	3.2	3.6	1.4	1.5	1.7	0.74	1.0	0.9	0.7	1.2	2.5
Aluminum ^e	4	0	0.71	0.70	0.19	0.10	+ ^f	0	0.17	+ ^d	+	+	+
Magnesium ^g	4	- ^h	-	+	-	-	+	-	-	+	-	-	-
Stainless Steel (Type 304)	1	2.8	3.6	3.4	5.3	6	6.9	1.3	2.0	2.0	2.5	2.9	4.1
Stainless Steel (Type 347)	1										2.4	3.3	5.6
Mild Steel	1	4.9	7.7	7.8	11	16	19	2.7	4.9	4.1	6.8	5.2	9.0
Nicloy-9	1	-	74	-	-	160	-	-	27	-	-	-	-

^aIn cases when the corrosion rate is of the order of less than 0.1 mil penetration per year, the actual numbers carry little significance. They have been included in these data to emphasize the fact that the test demonstrates high resistance, that is, a corrosion rate of 0.001-mil penetration per year for metal A and 0.002-mil penetration per year for metal B does not necessarily mean that A is twice as good as B, but that both metals are entirely satisfactory for service.

^bThe exposure time for pure BrF_3 to nickel through Inconel was 20 weeks instead of 11.

^cInitial UF_6 concentration in liquid. Removing and replacing samples necessitated some loss of UF_6 so the final UF_6 concentration was 5.1 mole %.

^d+ indicates a weight gain less than 1 mg.

^eConcentrated HNO_3 wash used to remove fluoride film from aluminum.

^fWeight gain 7.8 mg total.

^gNo method devised for film removal without attack of coupon. Weight changes are of the same order of magnitude as Duranickel, so penetrations should be of the same order of magnitude.

^h- indicates no measurement made.

Duranickel, Incoloy, aluminum, magnesium, mild steel and the stainless steels are adequate for most purposes. Their corrosion rates are sufficiently high, however, that they will tend to contaminate the solutions with corrosion products. Nicloy-9 is not recommended for use in these systems.

These corrosion studies will be reported in detail, along with the performance of silver solders, corrosion by aqueous wash solutions and the effects of a aqueous-interhalogen cycling procedures in a separate topical report.

c. Corrosion of Metals in Gaseous Fluorine at Elevated Temperatures
(M. J. Steindler, R. C. Vogel)

A study of the corrosion of certain metals in a stream of gaseous fluorine at elevated temperatures has been initiated in order to evaluate materials of construction suitable for the high temperature preparation of plutonium hexafluoride. Nickel, Monel, Inconel and copper coupons have been exposed to elemental fluorine at temperatures between 550 C and 750 C.

The apparatus used in this study, shown in Figure 9, consists of a nickel tube surrounded by a one-inch tube furnace. Commercial high purity (99.5 per cent min) fluorine was used without further purification. A Fluorolube bubbler served to indicate approximately the flow rate of gas over the coupon. Temperatures were measured by an external thermocouple which also controlled the current to the furnace through a suitable controller.

In a typical experiment, the coupon was cleaned by treatment with nitric acid or aqua regia, weighed and introduced into the furnace tube. The system was flushed with helium during the warming period and after the system had attained the desired temperature, fluorine was substituted for the helium stream. Flow rates employed ranged from 40 to 100 ml/min. At the conclusion of the experiment, helium was substituted for fluorine, the sample cooled to room temperature and carefully removed. Measurements obtained were weight gain of the coupons, weight loss of coupons in those cases where the film was easily removable, and film thickness of the corrosion layer. The latter data were obtained by mounting specimens in bakelite using standard metallographic procedures. The data obtained on samples of nickel, Inconel, Monel and copper are shown in Table 6. All data have been extrapolated linearly to obtain corrosion rates in terms of inches per year.

There exist few reliable data in the literature on the corrosion of metals in gaseous fluorine.^{2,3,4} Most of the existing data have been briefly summarized in Table 7.

^{2a} Landan, R., and Rosen, R., Ind. Eng. Chem., 39, 281 (1947)

^{2b} Landan, R., Corrosion, 8, 283 (1952)

³ Meyers, W. R., and DeLong, W. B., Chem. Eng. Progress, May 1948

⁴ BNL-176; Progress Report of the Reactor Science and Engineering Department, January 7: + March 31, 1952

FIGURE 9

APPARATUS FOR THE STUDY OF CORROSION
OF MATERIALS IN GASEOUS FLUORINE.

Table 6

CORROSION OF METALS IN ELEMENTAL FLUORINE AT ELEVATED TEMPERATURES

Experiments carried out in equipment shown in Figure 9

Material ^a	Temp (C)	Exposure Time (Hours)	Area (in ²)	Weight Change (g)	Film Thickness (in x 10 ³)	Corrosion Rate, mils/yr	
						From Weight Changes	From Film Thickness
Nickel	550	6.20	1.71	0.0005	- ^b	4	-
Nickel	650	5.28	1.71	0.0057	0.6	59	314
Nickel	750	4.07	1.71	0.0265	1.2	350	816
Monel	650	6.00	1.61	0.0040	-	40	-
Monel	750	6.12	1.49	-0.423	7.54	2,900	3,460
Inconel	550	5.00	1.54	0.1686	7.83	3,200	4,780
Inconel	650	5.60	1.48	0.3998	11.0	7,000	6,000
Inconel	750	4.65	1.47	1.1184	50.9	24,000	33,450
Copper	550	2.42	0.52	0.0014	-	110	-
Copper	650	4.83	1.21	0.0252	-	430	-
Copper	750	5.75	1.10	0.0474	-	750	-

^aWeight gain data for nickel converted to penetration by assuming nickel fluoride alone is formed. Film thickness data converted to penetration by assuming the theoretical (X-ray) density of nickel fluoride. Weight gain data for Monel converted to penetration by assuming an average atomic weight for Monel of 60.145. Film penetration measurements converted to penetration rates by assuming a copper fluoride-nickel fluoride film density of 4.51. Penetration rates for Inconel were calculated from weight gain and film thickness data assuming no chromium to be present in the corrosion film.

^bFilm too thin to measure adequately.

Table 7

CORROSION OF METALS IN GASEOUS FLUORINE AT ELEVATED TEMPERATURES
ACCORDING TO DATA AVAILABLE IN LITERATURE

<u>Material</u>	<u>t (C)</u>	<u>Reference</u>	<u>Penetration (in./yr) x 10³</u>
Nickel	500	2a and 2b	72
Nickel	500	3	61.2
Nickel	600	3	348
Nickel	600	4	0.065
Nickel	650	3	192
Nickel	700	2a and 2b	1200
Nickel	700	3	408
Monel	500	2a, 2b, 3	24
Monel	600	3	720
Monel	600	4	0.116
Monel	650	3	960
Monel	700	2a and 2b	240
Monel	700	3	1800
Inconel	500	3	744
Inconel	600	3	2040
Inconel	600	4	5.93
Inconel	650	3	1560
Inconel	700	3	6120
Copper	500	2a and 2b	2400
Copper	500	3	1440
Copper	600	3	11880
Copper	700	2a and 2b	36000
Copper	700	3	34800

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1. Nickel — Samples of nickel were etched prior to exposure to fluorine with nitric acid containing small amounts of sodium chloride. In all cases a uniform, adherent corrosion film was obtained. In general, the data obtained are in reasonable agreement with literature values. Brookhaven⁴ has reported values which are consistently lower than those obtained elsewhere. The reasons for this discrepancy are not clear. Meyers and DeLong³ carried out experiments using fluorine from a small electrolytic cell and the fluorine supply was believed to contain appreciable quantities of oxygen. This impurity probably had a more severe effect on copper than on nickel but the extent of corrosion of nickel by oxygen in the presence of fluorine is difficult to evaluate. Metallographic examination of the nickel specimen showed no unusual features attributable to the corrosion process.
2. Monel — Samples of Monel were treated with nitric acid containing small amounts of sodium chloride prior to exposure to fluorine. In Experiment 4 of Table 6 the film on Monel was too thin to measure and Monel, in Experiment 5, produced a film which flaked off rapidly but only on exposure to air. Metallographic examination of the Monel coupons showed no unusual features of the corrosion process.
3. Inconel — Inconel coupons were treated with aqua regia prior to exposure to fluorine. Except for Experiment 8 of Table 6 the films were relatively uniform and adherent. The film thickness measurement for Inconel in Experiment 8 represents an average of several measurements (75 mils max; 29 mils min). This film flaked off easily even with careful handling of the specimen. The most reliable value for the corrosion rate of this specimen is that obtained by weight loss measurement.

Examination of the film obtained on Inconel in Experiment 6 using X-ray fluorescence measurements revealed a marked decrease in chromium content of the film compared to the chromium content of the untreated metal. It has been calculated that a 91 per cent (± 4 per cent) depletion of chromium has occurred within the upper 3 mils of the corrosion film. The red volatile substances collected in the Fluorolube bubbler would indicate that the loss of chromium is due to formation of the volatile CrF_4 , CrF_5 , or CrF_6 . Metallographic examination of the Inconel samples revealed no void formation or extensive intergranular attack indicating that the volatilization of chromium does not take place at a rate very different from the rate of reaction of the iron and nickel components of Inconel. In view of these observations,

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penetration rates of Inconel were calculated from both weight gain and film thickness data assuming no chromium to be present in the corrosion film.

The data obtained in these experiments are in moderately good agreement with those obtained elsewhere with the exception of those data obtained at Brookhaven.⁴

4. Copper — Samples of copper were treated for one second in clean, concentrated nitric acid prior to exposure to fluorine. Exposure of copper samples to fluorine led to relatively small rates of corrosion of copper but excessive quantities of nickel fluoride from the furnace tube were produced. It is believed that contact of the nickel furnace tube with the copper specimen in some fashion enhanced the rate of corrosion of nickel while retarding that of copper. The rates of corrosion of copper at comparable temperatures observed by other workers are considerably higher than those reported here. Additional investigation of this effect is planned although the exclusion of oxygen in the present experiments may account for a large portion of the differences in the observed rates of corrosion. In the absence of further data, both copper and nickel appear to have comparable rates of corrosion in gaseous fluorine.

The data on the rate of corrosion of copper will be extended to insulated specimens and a brief examination of calcium fluoride and alundum under the same conditions is contemplated. Finally a comparison of rates obtained both in the presence and absence of plutonium is contemplated.

3. Fission Product Fluoride Investigations
(R. K. Steunenberg)

- a. Tellurium Fluoride Studies
(J. Fischer, G. Redding)

Tellurium is found in the form of the highly volatile hexafluoride in the fluoride volatility process for the recovery of uranium as uranium hexafluoride from various fuel elements. The possible formation of a non-volatile compound from the reaction of tellurium hexafluoride with either bromine trifluoride or bromine pentafluoride, as postulated by Page,⁵

⁵Page, W. R., A Continuous Flow Pilot Plant for the Separation of Bromine-Fluorine Compounds and Light End Fission Product Fluorides from Uranium Hexafluoride, BNL-174, March 1952

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was discussed in ANL-5529, page 45. Evidence was given to show that no non-volatile compound was formed due to a reaction of tellurium hexafluoride with either bromine, bromine trifluoride or bromine pentafluoride.

One explanation for past references to a non-volatile tellurium compound in interhalogen media may be found in erroneous or misinterpreted radiochemical data. The use of total gamma activity in tracer experiments may be misleading if the tracer activity is not well defined especially when the decay schemes are complex and the gamma activity is in the energy range where internal conversion is possible. Two of the major long-lived radioactive isotopes of tellurium found in fission products and irradiated tellurium are $\text{Te}^{127\text{m}}$ and $\text{Te}^{129\text{m}}$. These nuclides decay in the following manner.

It has been shown that the internal conversion of the gamma rays is practically complete.^{6,7}

The occurrence of non-volatile reduced fractions in radioactive tellurium hexafluoride had been found by R. R. Williams, Jr.⁸ to be prevalent to the extent that about fifty per cent of the atoms of $\text{Te}^{129\text{m}}$ undergoing gamma transitions resulted in separation of Te^{129} as a non-volatile component. Because their conversion ratios are high, only a small fraction of the gamma rays from $\text{Te}^{127\text{m}}$ and $\text{Te}^{129\text{m}}$ are observed. A mixed sample of $\text{Te}^{127\text{m}}$ and $\text{Te}^{129\text{m}}$ in secular equilibrium undergoes beta decay with a half-life intermediate between 33.5 and 115 days, depending upon the relative proportions of the two nuclides. However, when internal conversion causes a chemical reaction leading to separation of Te^{127} and Te^{129} the separated species decay with a half-life intermediate between 9.3 hours and 72 minutes, depending on the relative proportions of the two nuclides. Therefore, beta counting can be

⁶Cooper, E. P., Phys. Rev., 61, 1 (1952)

⁷Helmholz, A. C., Phys. Rev., 60, 415 (1941)

⁸Coryell and Sugarman, Radiochemical Studies: The Fission Products, Book 1, McGraw-Hill, 1951, page 220

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used as a measure of the tellurium present. The half-life characteristics of the beta decay can be used as an indication of whether the metastable species have been separated from the non-metastable species through a chemical reaction induced by internal conversion.

- (1) Preparation of Materials -- Clinton-irradiated (28 days) tellurium was cooled for twenty-one days in order to allow the tellurium-131 to decay to iodine-131. The tellurium activity was then separated from the iodine and xenon activity in a manner similar to the preparation of tellurium tracer used by Glendenin.⁹

Radioactive tellurium hexafluoride was prepared by direct fluorination of the radioactive tellurium. The details of the preparation and purification will be published in a separate topic report.

- (2) Apparatus -- The apparatus has been described in ANL-5529, page 45. It was modified so that a twenty-five-ml Fluorothene tube was attached to the 304-ml gas-measuring vessel with only one valve and a short line intervening. The close proximity of the Fluorothene tube to the gas-measuring vessel was necessary to insure quantitative condensation of the tellurium hexafluoride into the Fluorothene tube, which could be cooled with liquid nitrogen. It was found that long lines and extra valves acted to impede the flow of tellurium hexafluoride at low pressures. A second Fluorothene tube was attached close to the first to form a simple distillation apparatus. The nickel lines and valves were heated to 75 C in order that bromine trifluoride could be transported from one part of the apparatus to another without condensation except in a liquid-nitrogen-cooled receiver.

- (3) Experimental Results -- Partial Reduction of Tellurium Hexafluoride Due to Internal Conversion -- The radiochemical separation of Te^{129} by the reduction of tellurium hexafluoride to a non-volatile species was observed by Williams⁸ to occur at tellurium hexafluoride pressures of 5 to 10 mm. Using the growth of the beta activity in the volatile fraction after separation, he computed that 45 to 55 per cent of the gamma transitions resulted in tellurium hexafluoride reduction. In the following experiments it is demonstrated that similar results are obtained at higher pressures.

⁹Coryell and Sugarman, Radiochemical Studies: The Fission Products, Book 3, McGraw-Hill, 1951, page 1613.

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An experiment was carried out to determine the activity of the tellurium before separation of nuclides through internal conversion. Radioactive tellurium hexafluoride was condensed from a 304-ml nickel vessel at about 25 C and about 250 mm into a 25-ml Fluorothene tube which was cooled with liquid nitrogen. The sample was hydrolyzed and the beta activity per gram of tellurium, as shown in Table 8, was obtained. The counting data for elapsed time in days after hydrolysis is shown for Sample 1. Sample 2 is a duplicate hydrolysis. Sample 3 is a similar hydrolysis of tellurium hexafluoride to which 3 ml of bromine trifluoride were added. The deviation of this sample from the others is within the experimental error. These values were used as standards for indicating the secular equilibrium beta counts per quantity of tellurium hexafluoride.

In order to determine to what extent Te^{127} and Te^{129} separations in tellurium hexafluoride at higher pressures occur, a known amount of tellurium hexafluoride was condensed into a fluorothene tube, the tube was heated to 25 or 75 C and time was allowed for Te^{127} and Te^{129} growth as indicated in Table 9. The volatile fraction was condensed into another tube and the non-volatile residue was dissolved with several portions of hot 3 M hydrochloric acid, made up to a known volume and sampled for counting. The counts per minute were obtained at intervals and plotted in Figure 10 against elapsed time after the separation. It can be seen from the rapid decay of the non-volatile fractions that they are mainly a mixture of Te^{127} and Te^{129} rather than that of a secular equilibrium mixture of Te^{127m} and Te^{129m} . This indicates that decomposition due to internal conversion has actually taken place. The curves were extrapolated to zero time to obtain the counts of reduced Te^{127} and Te^{129} in the non-volatile fraction at the time of separation of the volatile tellurium hexafluoride and the reduction product.

The counts per minute per gram of tellurium in the 25-ml tube after separation are compared with the counts per minute per gram of tellurium before separation in Table 9. The ratio of the former to the latter multiplied by one hundred is the per cent of Te^{127} and Te^{129} separated by the reduction of tellurium hexafluoride as a result of the internal conversion of the gamma rays. One sample was allowed to grow at 75 C and was separated at this temperature in order to compare it with a similar growth and separation in the presence of bromine trifluoride. The amount of Te^{127} and Te^{129} separation appears to be dependent on the growth time. The per cent separation for the longest growth time is of the same order of

03:12:04:03:03

Table 8

TOTAL BETA ACTIVITY IN HYDROLYZED
RADIOACTIVE TELLURIUM HEXAFLUORIDE

<u>Sample No.</u>	<u>Time in Days After Hydrolysis of Sample</u>	<u>Sample Weight, Grams of Te</u>	<u>Beta Counts per Min per Gram Te</u>
1	0	0.535	5.2×10^7
	3		4.7×10^7
	8		4.5×10^7
	11		4.4×10^7
2	1	0.522	5.3×10^7
3 ^a	12	0.485	4.9×10^7

^aSample No. 3 contained 3.0 ml of bromine trifluoride

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Table 9

SEPARATIONS OF TELLURIUM-127 AND -129 DAUGHTERS IN TELLURIUM HEXAFLUORIDE

Sample No.	Growth Time (Hours ^a)	Temp (C)	Wt of Sample (Grams of Te)	Calculated Pressure (mm Hg)	Initial Activity TeF ₆ Before Separation (Beta Counts/(min)(g Te))	Non-Volatile Fraction ^b After Separation (Initial Beta Counts/(min)(g Te))	Per Cent Daughter Separation
4	76	25	0.314	1810	5.16×10^7	1.78×10^7	34
5	65	25	0.304	1770	3.85×10^7	1.15×10^7	30
6	21	25	0.289	1710	5.05×10^7	3.08×10^6	6
7	17	75	0.300	2480	4.71×10^7	1.23×10^6	2
7a ^c						4.34×10^7 ^c	

^aTime tellurium hexafluoride stored in vessel.^bCounts obtained by extrapolation to time of separation.^cVolatile fraction of Sample No. 7 after separation.

FIGURE 10
Te 127 + Te 129 DAUGHTER BETA DECAY.

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magnitude as Williams'⁸ results. Sample 7a is the volatile fraction of Sample 7, hydrolyzed and counted 48 hours after the separation. The beta counts, considering two-days decay, agree within experimental error with the value before separation.

After 1472 minutes, Sample 4 decayed to 620 counts per minute. This activity may be attributed to the 9.3-hour activity of Te^{127} since the 72-minute activity of Te^{129} would have been dissipated by this time. The information was used to obtain the decay curve of Te^{127} shown as a broken line in Figure 11. The Te^{127} activity was subtracted from the total activity at various times to obtain the Te^{129} activities shown in Table 10 and plotted on Figure 12. The half-life of 74 minutes for Te^{129} obtained from the graph agrees with the literature values^{10,11} indicated in Table 10. These experiments show conclusively that tellurium hexafluoride is decomposed by internal conversion of the gamma rays.

- (4) Separation of Tellurium Activity from Bromine Trifluoride and the Effect of Bromine Trifluoride on the Separation of Te^{127} and Te^{129} — It was desirable to see what extent of separation of Te^{127} and Te^{129} would occur in bromine trifluoride and to determine what activity would remain behind in a partial or total volatilization of bromine trifluoride when mixed with radioactive tellurium hexafluoride.

Samples 8 and 9, containing tellurium hexafluoride and bromine trifluoride in the amounts shown in Table 11, were completely distilled at 75 C from a Fluorothene tube in which beta growth was allowed for the time indicated. The beta counts per minute per gram of tellurium after separation were compared with similar counts before separation, which were obtained from the standard hydrolyzed tellurium hexafluoride. Sample 8 had no activity remaining. Sample 9, which had a longer growth time, had only a small percentage of the activity remaining and it decayed in a manner similar to the separated daughter activity. This indicates that bromine trifluoride is capable of oxidizing the reduced tellurium fragments about as fast as they are formed as a result of the internal conversions. It also proves that no non-volatile compound is formed between bromine trifluoride and tellurium hexafluoride.

Samples 10 and 11 contained similar mixtures of tellurium hexafluoride and bromine trifluoride in

¹⁰Hollander, J. M., Perlman I., and Seaborg, G. T., Rev. Mod. Phys. 25, 469 (1953)

¹¹Day, M. C. Jr., Eakins, G. W., and Voight, A. F., Phys. Rev. 100, 796 (1955)

FIGURE II
Te 127 + Te 129 DAUGHTER BETA DECAY.

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Table 10

DECAY OF TELLURIUM-127 AND -129 SEPARATED
FROM TELLURIUM HEXAFLUORIDE

Time After Separation (Minutes)	Te-127 + -129 (Beta Counts/min) Observed	Te-127 (9.3 hr) (Beta Counts/min) Calculated	Te-129 (Beta Counts/min) By Difference
0	5.60×10^3	3.87×10^3	1.73×10^3
50	4.81	3.65	1.16
100	4.16	3.43	0.73
150	3.67	3.22	.45
200	3.30	3.04	.26
250	3.02	2.84	.18
300	2.78	2.67	.11

Half-Life Te-129 74 minutes (See Figure 11)

Literature Value Te-129 72, 70⁸, 74⁹

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FIGURE 12
Te 129 DAUGHTER BETA DECAY.

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Fluorothene tubes. Fifty per cent of the bromine trifluoride was distilled out of the tube with essentially no reflux. Only a very small fraction of the activity was found in the hydrolyzed residue. This indicates that tellurium activity can be separated by distillation from bromine trifluoride and that there is no stable complex formation in the liquid.

- (5) Residual Tellurium Activity from Uranium Hexafluoride — Tellurium Hexafluoride Mixtures — A mixture of tellurium hexafluoride and uranium hexafluoride as shown for Sample 12 in Table 11 was completely distilled from a Fluorothene tube. The residual activity is small and it decays out in the same manner as the separated tellurium daughter activity. From this it can be assumed that no non-volatile complex or compound is formed from the components of the mixture.

b. Fission Product Volatilization Studies
(L. E. Trevorrow)

Experiments have been done to help fill in gaps in existing knowledge on the volatility of fission products from bromine trifluoride solution. It is of particular interest to determine whether difficulties will be encountered in the volatility processing of high burn-up and short-cooled fuels. Individual metals or alloys were dissolved in bromine trifluoride, and the volatile products were distilled from the mixture under reduced pressure at 80 C. The work was done in an electrically heated nickel apparatus which allowed the reactions to be carried out in vacuo or in a helium atmosphere. Temperature changes accompanying the reactions were followed using a recording potentiometer with an Inconel-Constantan needle thermocouple. Pressure changes in the system were indicated by the usual Helicoid Monel Bourdon gages.

"Fissium" alloy* is a synthetic alloy of a composition corresponding to 2 per cent total atom burn-up and 15 days cooling. It was dissolved in bromine trifluoride. It reacts at roughly the same rate as pure uranium. Reaction rates for some of the other materials were in the order niobium > molybdenum > ruthenium > "fissium." This order may hold for these metals only in the particular forms used in this set of experiments. The niobium and molybdenum samples were pieces of sheet metal. The ruthenium sample was a pellet prepared from 80-mesh powder.

The results of experiments on niobium, ruthenium, molybdenum and iodine are given in Table 12.

*An alloy prepared by the Sylvania Electric Products, Inc., by powder metallurgy techniques from natural uranium and inactive fission product elements was used in this work.

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Table 11

TELLURIUM ACTIVITY FOUND IN RESIDUES AFTER VOLATILIZATION

Partial or complete volatilization of mixture of
bromine trifluoride and tellurium hexafluoride.

Sample No.	Growth Time in Tube (Hours)	Mixture	Per Cent Volatilized	Temp	Before Separation β Counts/(min)(g Te)	Time After Separation (Hours)	Non-Volatile Fraction After Separation β Counts/(min)(initial g Te)	Per Cent Activity Remaining
8	17	1.01 g TeF_6 6 g BrF_3	100	75	4.67×10^7	1	0	0
9	64.5	0.91 g TeF_6 6 g BrF_3	100	75	4.52×10^7	0	1.86×10^4	0.041
						1	1.61	
						1.2	1.34	0.002
						7.1	8.6×10^3	
10	2	0.95 g TeF_6 6 g BrF_3	50	75	4.52×10^7	21.5	6.26×10^4	0.14
						45	3.81×10^4	0.084
11	2	0.95 g TeF_6 12 g BrF_3	50	75	4.30×10^7	88	$>4 \times 10^2$	>0.0009
12	2	0.93 g TeF_6 10.0 g UF_6	100	75	4.48×10^7	2	4.26×10^4	0.095
						16.5	5.0×10^3	0.011

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Table 12

DISTILLATION OF INDIVIDUAL METALS

<u>Element</u>	<u>Initial Amount, g</u>	<u>Residue, g</u>	<u>Distillate, g</u>
niobium	0.360	0.354	0.00747
ruthenium	0.474	0.475	0.0004
molybdenum	1.15	no weighable residue	
iodine	0.876	no weighable residue	

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It is seen that niobium and ruthenium distill to a small extent whereas molybdenum and iodine apparently distill completely. Both ruthenium and niobium left a large amount of residue in the still pot when distilled to dryness. Both residues were analyzed chemically. The ruthenium residue was not easily identified, but the niobium residue appears to be BrF_2NbF_6 , a compound prepared by other workers.¹² Following is the comparison of analytical and theoretical percentages:

Analysis: Nb, 29.6%; Br, 24.8%; F, 47.5%

Theoretical: Nb, 29.6%; Br, 24.6%; F, 46.8%

4. Preparation, Handling and Thermal Stability of Plutonium Hexafluoride
(M. D. Adams, R. C. Vogel, D. V. Steidl)

Experiments have been carried out on the decomposition of plutonium hexafluoride in a heated packed zone both with a thermal gradient through the zone and in a uniformly heated zone.

In all the experiments, conditions for the preparation of plutonium hexafluoride were the same. Plutonium tetrafluoride was weighed into a nickel boat which was placed in a 0.625-inch (ID) furnace tube. Helium was passed through the apparatus while the furnace was brought to 500 C and the 0.625-inch (ID) packed tube was heated to the desired temperature. Fluorine was then substituted for helium. After a predetermined time the fluorine was turned off and helium passed through the apparatus again until it was cool enough to disassemble.

In the previous quarterly report (ANL-5529, page 39) some data from the first experiments and a drawing of the first apparatus were given. Several further experiments have been carried out in this equipment and the information obtained is shown in Table 13.

A significant result of these experiments is the discovery that the decomposition product of plutonium hexafluoride can, under the unusually low temperature condition of these experiments, apparently be refluorinated. This effect is shown in Figure 13. The amount of plutonium found in each section is represented by a bar graph. Temperature is indicated on the right vertical axis. In shorter experiments the largest amount of plutonium is found in the first part of the packing. In longer experiments, however, most of the plutonium is found in the last packing sections. It seems evident that

¹²Gutmann, V., and Emeleus, H. J., J. Chem. Soc. 1046 (1950)

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Table 13

DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE IN A PACKED ZONE WITH A THERMAL GRADIENT

Plutonium hexafluoride prepared by passing fluorine gas at 500 C over plutonium tetrafluoride. Zones 1, 2, 3 and 4 prepared from nickel wool (except in experiment 25 where copper was used). Section 1 was 3 inches long; 2, 3, and 4 were 1.5 inches. Zone 5 is a vertical unpacked section. Zone 6 is a cold trap.

Furnace tube and packed tube diameter -- 0.625 inch.

Decompositions were carried out in a fluorine atmosphere.

Equipment is shown in ANL-5529, page 40.

Exp No.	Time (min)	Pu Used (mg)	Fluorine Flow Rate (cc/min)	Site of Deposition (Zone)	Estimated Temperature (C)	Per cent of Original Pu	Material Balance (%)
15	60	15.2	50	1	325	3.87	25.5
				2	200	6.27	
				3	140	7.70	
				4	100	7.46	
				6	-196	0.2	
21	15	19.35	77.5	1	350	5.4	45.3
				2	220	4.2	
				3	125	3.5	
				4	100	3.3	
				5	25	26.5	
				6	-196	2.8	
25 ^a	5	17.0	135	1	360	68.5	108.2
				2	225	8.77	
				3	140	0.64	
				4	100	0.0	
				5 and 6	-	30.17	
29	15	12.5	29	1	290	9.3	44.1
				2	250	9.2	
				3	160	4.6	
				4	100	3.9	
				5	25	7.6	
				6	-196	10.5	

^aTube packed with copper wool rather than nickel wool.

FIGURE 13
INFLUENCE OF TIME AND TEMPERATURE
ON THE SITE OF PLUTONIUM DEPOSITION

Apparatus shown in ANL 5529, page 40

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at 250 C in an atmosphere of fluorine the decomposition product of plutonium hexafluoride can be refluorinated. Since the highest flow rate used is about 70 cm per min it does not seem likely that entrainment of the plutonium tetrafluoride significantly influences these results.

One run (Experiment 25) in this series was carried out using copper wool in place of nickel. In this case practically all the plutonium was stopped in the first section of packing.

After the experiments had been carried out using a temperature gradient, a series was started using a uniform temperature throughout the packed zones. For experiments of this type another furnace tube was constructed (Figure 14) following approximately the same plan as the previous unit. The packed section was 10 inches instead of 7.5 inches long and heat for the packing was supplied by a coil of asbestos-covered Nichrome wire wound around the tube.

Experiments 33, 37 and 41 at 120, 180 and 240 C respectively, were carried out in this apparatus. The packing was not prefluorinated. Data from them are presented in Table 14. It is significant that deposition of plutonium is least at the highest temperature, 240 C. This may support the earlier findings which indicated the decomposition product could be refluorinated.

As a supplement to this type of experiment, the effect of prefluorination on the deposition was studied at the same temperatures.

Fluorine was passed through the apparatus after heating the packed section 50 to 100 C higher than the temperature at which the experiments were to be run. Plutonium tetrafluoride had been previously loaded into the furnace tube but this was not heated. After 30 minutes or longer, helium was substituted for the fluorine. The furnace tube was heated and the packing section temperature adjusted to the desired range. Helium was then cut off and fluorine again passed through the apparatus as in the previous experiments.

In all these experiments most of the plutonium hexafluoride passed through the zones and reached the cold trap, zone 6, or decomposed in the vertical tube, zone 5, just beyond the packed section, which could not be heated to as high a prefluorination temperature. The data are shown in Table 14.

Decomposition of plutonium hexafluoride is obviously influenced by the prefluorination and the greater amounts of deposition obtained in previous experiments may be due more to chemical reaction of the plutonium hexafluoride with the nickel packing than to thermal decomposition.

Another apparatus will be constructed in the near future which will allow plutonium hexafluoride to be passed through a packed section in a choice of helium, fluorine, or mixed helium and fluorine atmospheres. Prefluorination studies can then be made under more favorable conditions on packing and construction materials.

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FIGURE 14

APPARATUS FOR STUDY OF DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE
IN A UNIFORMLY HEATED PACKED ZONE

Table 14

DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE IN A UNIFORMLY HEATED PACKED ZONE

Plutonium hexafluoride prepared by passing fluorine gas at 500 C over plutonium tetrafluoride.

Zones 1, 2, 3 and 4 are all 2.5 inches long and are packed with nickel wool. Zone 5 is a vertical unpacked section and zone 6 is a cold trap. Apparatus shown in Figure 14.

Decomposition is carried out in a fluorine atmosphere.

Fluorination time, 12 minutes.

Experiment Number	33	45	37	47	41	49
Prefluorination Conditions,						
Time, min	-	75	-	30	-	30
Temperature	-	210	-	250	-	350
F ₂ flow rate during PuF ₆ preparation and decomposition, cc/min	124	41	68.3	83	70.4	48.2
Starting Amount of PuF ₄ , mg	10.99	10.6	13.87	15.1	13.65	17.0
Material Balance, %	86.0	96.1	75.9	75.1	59.8	83.2
Temperature of Zones 1, 2, 3 and 4	125	120	180	180	240	240
	<u>(% of Plutonium Found in Each Zone)</u>					
<u>Site of Decomposition, Zone Number</u>						
1	10.1	7.0	16.0	9.4	3.0	1.1
2	8.9	1.0	10.7	0.4	2.1	0.2
3	10.6	0.9	2.4	0.3	2.0	0.3
4	13.7	1.6	9.0	0.6	7.4	0.2
Total 1, 2, 3 and 4	43.3	10.5	38.1	10.7	14.5	1.8
5	38.7	45.3	31.4	25.4	} 45.3	36.7
6	4.0	40.3	6.4	39.1		44.7

5. Processing of Feed Materials
(R. K. Steunenberg)

a. Ore Concentrates
(O. Sandus, W. A. Shinn)

Further fixed bed fluorination studies were carried out on uranium tetrafluoride which was produced from South African Rand ore concentrate by hydrogenation and hydrofluorination in a fluidized bed reactor. Liquid bromine trifluoride, bromine pentafluoride vapor and gaseous fluorine were used as the fluorinating agents with a fixed bed reactor. The resulting uranium hexafluoride was collected along with the interhalogen in cold traps. In the case of fluorine, the excess was not condensed. The contents of the cold traps were hydrolyzed with 6 M nitric acid for uranium analyses. The residues from the fixed bed were dissolved in aqua regia and also analyzed for uranium.

The results of these experiments, indicated in Table 15, show that the uranium was readily volatilized by all of the fluorinating agents used. These results are comparable to those reported in ANL-5529, page 43, in which the ore concentrate was treated with liquid bromine trifluoride.

b. Uranium-Magnesium Fluoride Slags
(O. Sandus, W. A. Shinn)

Uranium-magnesium fluoride slag from Mallinckrodt was treated with bromine pentafluoride vapor in a fixed bed at 500 C. The amount of the uranium volatilized as the hexafluoride is indicated in Table 16, along with comparison data reported previously (ANL-5529, page 44) on the treatment of this material with liquid bromine trifluoride. The excessively high material balances on the bromine pentafluoride experiments are not understood; they may have been caused by analytical errors or by faulty sampling. From the analyses of the residues, the experiments with liquid bromine trifluoride and with bromine pentafluoride vapor gave substantially the same results. Ninety-five per cent or more of the uranium was volatilized from the slag.

It is believed that the remaining 2 to 5 per cent of the uranium can probably be volatilized by further grinding of the slag. No further work on this problem is anticipated at the present time.

B. Pilot Plant Operations

(W. J. Meham, R. C. Liimatainen, R. W. Kessie, J. I. Thigpen*,
H. Brown, A. Freeman, F. Gast, W. Pehl, K. Pelletier)

During this quarter the initial series of five pilot plant runs was completed. These runs were made to demonstrate the recovery and decontamination

*Special Scientific Employee on loan from Hercules Powder Company.

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Table 15

TREATMENT OF ORE-PRODUCED UF_4 WITH BrF_3 , BrF_5 , AND F_2 IN A FIXED BED REACTORMaterial: UF_4 ^a produced from ore concentrate^b in a fluidized bed reactor

Exp No.	Fluorinating Agent	Wt of Sample (g)	Temp (C)	Time (hr)	BrF_3 (ml)	Flow Rate (g/hr)	U Volatilized (Relative %)	U in Residue (Relative %)	Material Balance (%)
1	BrF_3	0.1915	25 ^c	~2 1/2	5		99.8	0.2	102.1
2	BrF_3	0.1844	125	2	5		99.9	0.1	98.9
3	BrF_5	0.1832	500	2		6.8	100.0	0.04	91.7
4	BrF_5	0.1939	500	1		3.6	99.8	0.2	92.4
5	F_2	0.2088	500	2		~0.8	100.0	0.03	101.1
6	F_2	0.2384	500	1		~0.6	100.0	0.02	95.3

^aAssayed 93.7% as UF_4 .^bSouth African Rand ore, concentrated by ammonium diuranate-ion exchange process, Lot Number 6, assayed 83% as U_2O_8 . The main constituents other than uranium oxides are: NH_3 , 1.72%; SiO_2 , 2.06%; total Fe, 0.3%.^cHeated to 125 C to obtain overhead samples.

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Table 16

TREATMENT OF U-MgF₂ SLAG WITH BrF₃ AND BrF₅

Material: Mallinckrodt slag, reject, ground,
assaying 5.9% U.

Exp No.	Fluorinat- ing Agent	Wt of Sample (g)	Temp (C)	Time (hr)	BrF ₃ (ml)	BrF ₅ Flow Rate (g/hr)	U Volatilized (Relative %)	U in Residue (Relative %)	Material Balance %
1	BrF ₃	1.2962	125	6 1/2	5		95.5	4.5	78.6
2	BrF ₃	1.1749	125	6	5		96.5	3.5	96.9
3	BrF ₅	2.9678	500	2		4	97.7	2.3	171.5
4	BrF ₅	3.2273	500	1		4	98.5	1.5	200.5

of uranium hexafluoride from natural uranium fuel elements. Dissolution, recovery and decontamination data for the complete series are presented.

The head end equipment for use in testing fused-salt dissolution of zirconium-uranium fuel alloys has been installed and leak tested.

1. Process Runs in Existing Pilot Plant

The existing interhalogen pilot plant was designed to dissolve 10-kg batches of natural uranium fuel and to decontaminate the uranium hexafluoride product of the dissolution by fractional distillation. The equipment has been described previously in ANL-4922, page 137.

Although it is possible to use any of a number of process schemes, the current series of tests followed the operations of the flowsheet in Figure 15.

a. Dissolutions

The results of the five dissolutions completed to date are summarized in Table 17. In each run, two to six slugs of uranium metal were charged to the dissolver through a 2-inch plug valve. Bromine trifluoride dissolver solution was then introduced in a quantity sufficient to insure that the slugs were covered with liquid at all times. The temperature of the dissolver was next raised to start the reaction. A small amount of water cooling was used when necessary to control the temperature.

The first three runs were made with inactive uranium. The slugs used were commercial-grade normal uranium (as-rolled, not heat treated) and were 1.35 inches in diameter and 4 inches long, unclad and weighing approximately 1.75 kg each. The last two runs contained activity from Clinton-irradiated slugs.

In Run D-1, the dissolver was operated as a closed system, with no product take-off during dissolution. The bromine trifluoride charged to the dissolver initially contained about 7 mole per cent bromine pentafluoride* and no uranium hexafluoride. The initial rate was extremely slow, so that it was necessary to raise the temperature to 132 C in order to obtain a reasonable dissolution rate.

In Run D-2, the initial dissolver solution contained 2.9 mole per cent uranium hexafluoride. The reaction rate was sufficiently high that above 60 C no additional heat had to be supplied to maintain the desired temperature. In Run D-3, six slugs were used with a dissolver solution containing 2.4 mole per cent uranium hexafluoride.

*The "as received" purity of the bromine trifluoride used.

FIGURE 15

PROCESS STEPS IN VOLATILITY PILOT PLANT RUNS

Key to Process Steps

Step

Process Operation

- I Uranium slugs charged, decanned with an aqueous solution, and the dissolver dried.
- II Bromine trifluoride dissolver solution added, reaction products removed overhead at constant pressure.
- III Bromine trifluoride regenerated from bromine with fluorine gas in dissolver.
- IV Dissolver solution fractionated to recover reagents and UF₆ product.
- V Aqueous wash solution used to remove fission products from dissolver.

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Table 17SUMMARY OF DISSOLUTIONS

Run No.	Dissolver Charge		Mole % UF ₆ in Soln		Dissolution Time (Hours)	Temp (C)	Pressure (psia)
	Uranium (lb)	Solution (BrF ₃ , BrF ₅ , UF ₆) (lb)	Initial	Final			
D-1	7.7 ^a	182	0.0	2.5	31	125→132	20→45
D-2	7.6 ^a	167	2.9	5.0	8	110→122	38
D-3	22.8 ^a	168	2.4	3.0	9	120	30
D-4	8.4 ^a	233	3.7	5.1	9	120	40
D-5	5.2 ^b	200	2.3	3.7	8	120→140	25→50

^aSlugs 1.35 inches diameter.^bSlugs 1.10 inches diameter.

Data for these three runs were presented in more detail in the previous quarterly (ANL-5529, pages 52 to 57). The uranium hexafluoride concentrations in Table 17 are slightly lower than those presented in the report of last quarter. All the present values are obtained from analytical results, while some of the previous ones were estimates.

Run D-4 was a 2-slug run similar to the above, but with a "hot spike" of four slices of irradiated uranium slugs. Run D-5 was a 2-slug run using irradiated Clinton Slugs. These were de-canned in the dissolver with a 10 weight per cent sodium hydroxide—20 weight per cent sodium nitrate solution. The aqueous-interhalogen changeover was accomplished without difficulty by purging and evacuating the heated dissolver.

Data on the overhead material collected during dissolution are given in Table 18. In Run D-5 no material was taken overhead because the relatively small amount of uranium metal was not sufficient to change the uranium hexafluoride composition of the dissolver solution substantially. Differences in fractions of material taken overhead are attributed to the differences in uranium hexafluoride concentration in the dissolver.

At the end of each dissolution, any material taken overhead was returned to the dissolver and fluorinated by sparging with fluorine gas. The fluorination was continued at between 20 C and 70 C until the dissolver solution showed no red color of free bromine.

b. Decontamination in Run D-4

The active material used in Run D-4 was 1017-day Clinton-irradiated uranium, which had been cooled 348 days. The reported plutonium content was 0.086 g plutonium/kg uranium. Four slices of this material was charged to the dissolver together with two inactive uranium slugs. A fifth slice was dissolved in nitric acid and analyzed for activity. This result was used to determine the activity in the dissolver solution, as given in Table 19.

After the D-4 dissolution was complete, a liquid inter-halogen sample was taken of the dissolver solution. The activity per gram of this sample is given in Table 19 in terms of the per cent of the total activity per gram in the dissolver. The discrepancy can be attributed to either the low solubility or surface adsorption of fission products fluorides in the dissolver.

The activity analyses of the material taken overhead during the dissolution in Run D-4 is also given in Table 19. This material was then returned to the dissolver, fluorinated, and distilled overhead in three fractions at a pressure of 30 psia with vapor take-off. The activity levels in the dissolver overhead material as reported in Table 19 show total activities well below those of the daughters of natural uranium at secular equilibrium, which are approximately 80 beta ct/(min)(mgU) and 4.5 gamma ct/(min)(mgU).

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Table 18

OVERHEAD COLLECTED DURING CONSTANT PRESSURE DISSOLUTION

<u>Run No.</u>	<u>Amount Collected^a (Wt % Dissolver Charge)</u>	<u>UF₆ Content (Wt %)</u>	<u>Interhalogen Composition</u>
D-2	5.7	29.5	BrF _{1.9}
D-3	26.0	66.8	BrF _{1.4}
D-4	1.5	40.6	BrF _{3.8}

^a Collected in dissolver column overhead receiver.
Process Step IIb of Figure 15.

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Table 19

DECONTAMINATION OF DISSOLVER SOLUTION IN RUN D-4

Fission Product Activity of 1017-day Clinton-irradiated Uranium
(330 g) cooled 348 days

Process Step ^a	Process Activity	Amount of Activity ^b		
		Plutonium Alpha	Gross Beta	Gross Gamma
Ia	Total Activity Charged to Dissolver ^c , ct/(min)(mgU)	1.6×10^2	1.4×10^4	5.6×10^3
Dissolver Sample	Per Cent of Dissolver Activity in Liquid Sample ^d	60	22	80
IIb	Activity Overhead During Dissolution ^e , ct/(min)(mgU)	0.5	22	1
IV b-1	Distillate From Dissolver First Cut ^f , ct/(min)(mgU)	0.2	14	0.8
IV b-2	Second Cut ^g , ct/(min)(mgU)	-	12	0.4
IV c	Third Cut ^h , ct/(min)(mgU)	-	1	0.2

^aProcess steps refer to flow diagram, Figure 15.

^bActivity uncorrected for approximately 1-week growth of uranium daughters. Natural uranium at (daughter) equilibrium has approximately 80 beta ct/(min)(mgU) and 4.5 gamma ct/(min)(mgU).

^cBased on nitric acid dissolution and analysis of one slice of batch charged.

^dLiquid interhalogen sample taken immediately after dissolution.

^e3.2 lb taken overhead, 63 wt per cent UF_6 . This was ~6 per cent of total UF_6 .

^f21.3 lb taken overhead, 85 wt per cent UF_6 . This was ~5 per cent of total UF_6 .

^g12.5 lb taken overhead, 68 wt per cent UF_6 . This was ~25 per cent of total UF_6 .

^h201 lb taken overhead, 4.3 wt per cent UF_6 . This was ~25 per cent of total UF_6 .

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c. Decontamination in Run D-5

The active material charged to the dissolver in Run D-5 was 1217-day Clinton-irradiated uranium which had been cooled 197 days. The two slugs were aluminum clad, and together weighed 2.34 kg. The reported plutonium content was 0.162 g plutonium/kg uranium. No separate slice was available for independent analysis. The activity in the dissolver during Run D-5 was therefore taken to be equal to the activity removed in the aluminum nitrate decontamination washes used* at the end of the run. The ability of this solution to solubilize fission product fluorides has been demonstrated in earlier tests, reported in ANL-5039, pages 43 through 53. Comparison of the plutonium washed out with the reported plutonium content of the irradiated slugs indicated a removal efficiency of 85 per cent. Removal efficiencies of this order for all major fission products were found to be consistent with the approximate fission product activity expected in uranium of the given irradiation conditions and cooling time. After dissolution and fluorination in Run D-5, a liquid sample of dissolver solution was taken with the results given in Table 20, indicating less activity in the dissolver solution than expected from the activity charged.

The dissolver solution was then distilled overhead** with the results shown in Table 20. The fission product activities in this overhead material are well below the natural uranium daughter activities at secular equilibrium. Plutonium decontamination appears to be of the order of 10^3 . This material was then charged to the still pot of the purification column.

d. Further Decontamination in the Purification Column

The results of further decontamination by distillation overhead in the purification column are stated in Table 21. The distillation*** was stopped when bromine color appeared in the product. At this point the column was shut down, the still pot contents transferred out, and the material which had been taken overhead was transferred back to the still pot. The contents of the column were then fluorinated and the distillation repeated. The overhead fractions consist of uranium hexafluoride with about 1 wt per cent bromide impurity and with total activity levels well below those of natural uranium. The total beta and gamma counts were measured from one to two weeks after separation and include the activity of uranium daughters that have grown in during this period. The evaluation of fission product decontamination factors for the process requires discrimination between fission product and uranium daughter activity. Presently available counting data indicate that, when the uranium daughter activity

*Three washes and a water rinse were actually used; the total removal is reported.

**Process step IV b, Figure 15

***Process step IV d and e, Figure 15

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Table 20

DECONTAMINATION OF DISSOLVER SOLUTION IN RUN D-5

Fission Product Activity of 1217-day Clinton-irradiated Uranium
(2.34 kg) cooled 197 days

Process Step ^a	Process Activity	Amount of Activity ^b		
		Plutonium Alpha	Gross Beta	Gross Gamma
Ia	Total Activity Charged to Dissolver ^c , ct/(min)(mgU)	3.4×10^3	4.4×10^5	3.7×10^5
Dissolver Sample	Per Cent of Dissolver Activity in Liquid Sample ^d	42	36	29
IV b-1	Distillation From Dissolver First Cut ^e , ct/(min)(mgU)	4.3	30	2.9
IV b-2	Second Cut ^f , ct/(min)(mgU)	0.7	25	1.5
IV c	Third Cut ^g , ct/(min)(mg soln ^h)	-	0.7	0.1

^a Process steps refer to flow diagram, Figure 15.

^b Activity uncorrected for approximately 10-day growth of uranium daughters.

^c Assumed equal to activity removed from dissolver in aqueous wash, process step V b (Figure 15).

^d Sample taken 12 hours after dissolution.

^e 5.8 lb taken overhead, 88.0 wt per cent UF_6 . This was ~20 per cent of total UF_6 .

^f 17.4 lb taken overhead, 99.2 wt per cent UF_6 . This was ~80 per cent of total UF_6 .

^g 178 lb taken overhead, 0.4 wt per cent UF_6 . This was ~1 per cent of total UF_6 .

^h Based on total solution rather than uranium because of the low uranium content.

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Table 21

ADDITIONAL DECONTAMINATION IN PURIFICATION COLUMN IN RUN D-5

(Process Steps IV d and e, Figure 15)

A. Still Pot Charge

1. Total weight = 49.9 lb
2. Weight % UF_6 = 22.5
3. Weight % interhalogens = 77.5 (BrF_3)
4. Total Activity:
 - 4.4 gamma ct/(min)(mgU),
 - 36.0 beta ct/(min)(mgU)

B. Operating Conditions, Average

1. Temp column = 80 C
2. Total pressure = 40 psia
3. Boil-up rate = 35.2 lb/hr (UF_6)
4. Reflux ratio = 45/1

Operating Time (hours)	Amount Overhead (lb)	Composition (Weight % Br)	Overhead Line Sample	
			Activity ct/(min)(mgU) ^{a, b}	
			Gross Beta	Gross Gamma
4.0	5.8	2.50	19.2	1.1
5.0	6.8	1.21	17.0	0.8
12.5	10.4	1.86	16.4	0.8
13.8	11.3	1.60	22.5	0.9

(Repeat Distillation after Fluorination)

2.3	2.3	11.70	18.3	1.0
3.3	3.7	4.40	22.0	0.7
3.9	5.0	3.90	13.2	0.6
7.3	5.5	1.30	12.7	1.3
8.8	6.3	0.50	22.6	1.3
10.7	7.4	0.34	22.4	1.0
13.0	8.6	0.09	20.0	1.2

^a Natural uranium has approximately 80 ct beta/(min)(mgU) and 4.5 ct gamma/(min)(mgU) with the counting instruments used.

^b The plutonium activity charged to this step was too low to permit reliable determination of additional decontamination

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grown in is subtracted from that of the process samples, the net fission product gross beta and gamma activity is an order of magnitude (or more) lower than the total values reported in Table 21. Pending more accurate low-level counting calibrations, the over-all fission product decontamination factors in Run D-5 are estimated at $\sim 2 \times 10^5$ for gross fission product beta activity and $\sim 2 \times 10^6$ for gross fission product gamma activity.

e. Other Column Operations

Preliminary fractionations of uranium hexafluoride-bromine trifluoride mixtures at 2 to 3-atmosphere pressures have yielded overhead uranium hexafluoride with as little as 0.018 weight per cent bromide impurity. However, no substantial product cut of this purity has been obtained, because of the appearance of free bromine color in the overhead as the distillation was continued. Also, substantial quantities of finely divided solid (mostly nickel fluoride) were observed in the still pots. This material has been largely flushed out with bromine trifluoride washes. Subsequent fractionations will show definitely whether this is the result of process corrosion. Most likely the solid was due to non-recurring corrosion involved with start-up of the columns, which had previously held organic and aqueous solutions.

A preliminary fractionation of a uranium hexafluoride-bromine pentafluoride mixture has shown the equivalent of 25 theoretical plates in the 16-foot packed (Helipak) column. The data and operating conditions are summarized in Table 22. No elemental bromine contamination was evident from color observations of the overhead product in this mixture.

Further fractionation tests are to be made.

f. Operating Difficulties

In the previous quarterly, it was indicated that a number of valve failures had occurred, but that the incidence of failures had declined. There have been no valve failures in this period. However, at the end of the D-5 dissolution, a leak was observed* at a nozzle entering the top of the dissolver. The dissolver distillation operations were finished at slightly below atmospheric pressure, and from pressure indications it was observed that this leak was very small under this condition. After the decontamination of the dissolver, it was observed that the leak (now large in a pressure test) was a crack in a piece of 2-inch Monel pipe welded to the top of the dissolver. Repair of this leak is being made. This failure is attributed to metallurgical defects rather than to processing conditions. Another process run with higher levels of shorter cooled activity is under consideration.

*Visual observation made while monitoring the radiation during the distillation step.

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Table 22

BATCH DISTILLATION OF A URANIUM HEXAFLUORIDE-BROMINEPENTAFLUORIDE MIXTUREColumn

Packed Length, 16 ft; ID 1.75 in.; Packing: Helipak 3019

Charge

Total Still Pot Charge: 67.3 lb

UF₆ Content of Charge: 37 (wt) per cent (balance BrF₅)

Operating Conditions

Pressure: 50 lb/sq in abs

Still Pot Temperature: 90 C

Column Temperature: 80 C

Boil-up Rate: 22 lb/hr (BrF₅)

Reflux Ratio: 27/1 (L/D)

Pressure Drop: 25 inches of water (16 ft column)

Start-up Time: 4 hours

Separation Resultsof Grab Sample

<u>Overhead During Distillation</u>		<u>Still Pot Composition (wt % UF₆)</u>	<u>Height Equivalent to a Theoretical Plate (inches)</u>
<u>Cumulative Amount (lb)</u>	<u>Composition (wt % UF₆)</u>		
6.4	0.236	37.1	-
16.8	0.037	40.0	8.3
27.1	0.058	62.9	7.7
32.6	0.093	71.3	8.0

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2. Construction of Fused Salt Dissolution Facility

The equipment and lines for the head end facility for testing the fused salt dissolution of zirconium-uranium fuel alloys have been installed, together with all electrical furnaces and instrumentation. The system consists of a salt melting and transfer vessel, a dissolver eight inches in diameter and seven feet high, and a small packed tower on the off-gas line connecting the dissolver with the purification columns in the existing pilot plant. Freeze valves are located in the molten salt transfer lines between the melting tank and the dissolver and between the dissolver and the removable waste salt container. Other lines connect with vessels in the existing pilot plant for supply of halogen vapor. Nickel and Monel are used throughout as materials of construction. This system has been found leak tight in a freon test (including the copper gaskets on the top flanges of the three major pieces of equipment). The system is ready for insulation of lines, instrumentation checks and shakedown operations.

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IV. CHEMICAL METALLURGICAL SEPARATION PROCESSES

The results of a melt-refining experiment with 0.4 per cent burn-up EBR fuel pins are reported. The distribution of fission elements was found to be similar to that found in earlier reported experiments at much lower fission element concentrations. The corrosive attack of molten uranium on pure alumina crucibles has been shown to produce an interfacial layer of nearly pure uranium dioxide and an equivalent amount of aluminum in uranium solution. The kinetics of the reaction are discussed.

In the search for low melting stable oxide slags, a composition in the lime-beryllia system melting at 1385 C has been found. X-ray evidence for a previously unreported compound in this system is presented.

Study of the protective coating of tantalum with tantalum boride was continued. At 1275 C the corrosive attack by molten uranium was less than 50 microns after 50 hours.

The speed of extraction of plutonium from molten uranium by liquid magnesium in an unstirred system is materially increased by thorough outgassing of the experimental components; it is evident that foreign materials at the interface present a significant resistance to plutonium transfer.

Work was continued in the semi-works on the development of slagging techniques and on the testing of equipment components. Several methods of purifying the inert argon cell atmosphere have been tested. The removal of oxygen by converting it to water which is then removed in a drier appears promising. Further studies have been conducted on the extraction of plutonium from uranium with magnesium and on the subsequent distillation of magnesium to recover the plutonium.

Information exchange on chemical metallurgical separations processes were held with K. C. Dewalt, M. L. Feldman, H. M. Ogle and L. S. Moody of the General Electric Company on March 13, with A. A. Smith, J. B. Knight and H. E. Howe of American Mining and Smelting on February 15, with S. J. Yosim of Atomics International on March 3 and with R. S. Newburg of Atomics International on March 26 and 27.

A. Laboratory Studies (H. M. Feder)

1. Melt Refining

- a. Melt Refining of High Burn-Up Materials
(N. Chellew, M. Ader, M. Beederman, C. Cushing, J. Schilb,
D. Finucane, J. Bingle, C. Seils)

Analytical results of the melt-refining experiment employing 0.4 per cent total atom burn-up material (see ANL-5529, page 63) are given

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in Table 23. In addition, the fission element concentrations in the skull and ingot fractions relative to their concentrations in the unrefined starting material are tabulated in Table 24.

The over-all results of the experiment may be summarized as follows:

- (1) Violent agitation or splattering of molten metal because of gas evolution was not seen during melting in a helium atmosphere. This observation was later supported by the absence of splatter marks inside the melt crucible, by the recovery of 99.5 per cent of the original weight charged to the crucible, and by the absence of mixed fission product activity on the zirconium getter coupon suspended about 3 inches above the melt. Motion pictures taken during the melting operation showed that just prior to melting and coalescence (mp about 1154 C) the individual fuel pins did not swell to any large extent.
- (2) The distribution of fission elements after melting was similar to that found in earlier experiments made with material of the order of 0.004 per cent burn-up. No surprising changes due to fission product concentration were found.
- (3) Recovery of refined uranium was 5 to 11 per cent lower than obtained in earlier experiments employing low burn-up materials. Furthermore, the form and appearance of the skull differed from those previously obtained. Whether the poorer uranium recovery is characteristic of high burn-up materials or is due to experimental limitations — e.g., geometry of crucible, size of charge — is uncertain and cannot be answered by this one experiment.

Dissolution of skull, ingot, and unrefined (control) metal was effected by means of 10 M nitric acid - 1 M hydrofluoric acid - 0.5 M aluminum nitric solution to give clear, residue-free solutions.* The skull was dissolved in two steps to give outer and inner fractions containing 68 and 32 per cent, respectively, of the total skull uranium. Inspection of the analytical results in Tables 23 and 24 reveals that the

*This is in contrast to the action of the same solvent on synthetic uranium-fission product alloys made by powder metallurgical techniques (Sylvania "fission") and ingots derived therefrom. These leave insoluble residues (primarily ruthenium) that are subsequently dissolved in alkaline hypochlorite solution.

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Table 23

DISTRIBUTION OF MATERIAL AFTER MELTING - RUN PB-1A

Charge: 7 EBR fuel pins; wt, 75.90 g; 1.8 w/o Zr in U enriched to 15%;
0.4% total atom burn-up; irradiated 93 days, cooled 318 days.

Crucible: Magnesia bottom-pour double crucible arrangement, previously
outgassed.

Conditions: 3 hr 50 min at 1200 C, 10 min at 1243-1253 C before pour;
flowing helium atmosphere, 110 ml/min

Dissolution: 10 M HNO_3 - 1 M HF - 0.5 M $\text{Al}(\text{NO}_3)_3$ solution; skull dissolved
in two fractions.

Fraction ^a	Per Cent of Starting Material									
	Uranium	Pu	Rare Earths	Sr	Ru	Cs	Te	Nb ^b	Zr	Mo ^c
Outer Skull	10.12		65.2	4.11	10.3	0.07	111.	10.0	16.1	
Inner Skull	4.70		0.5	0.02	4.7	0.0002	0.3	5.4	4.4	
Ingot	85.48		10.2	0.03	88.9	0.0009	2.0	94.7	85.9	81.4
Unaccounted	-		24.1	95.8	-	99.9	-	-	-	

^aUnaccounted values obtained by difference; dashed entries indicate recoveries analytically exceeding 100 per cent.

^bNiobium values corrected for decay and growth from zirconium.

^cSpectrophotometric analysis.

Table 24

FISSION ELEMENT CONCENTRATION FACTORS AFTER MELTING-RUN PB-1A

Charge: 7 EBR fuel pins; wt, 75.90 g; 1.8 w/o Zr in U enriched to 15%;
0.4% total atom burn-up; irradiated 93 days, cooled 318 days.

Crucible: Magnesia bottom-pour double crucible arrangement, previously
outgassed.

Conditions: 3 hr 50 min at 1200 C, 10 min at 1243-1253 C before pour;
flowing helium atmosphere, 110 ml/min

Dissolution: 10 M HNO_3 - 1 M HF - 0.5 M $\text{Al}(\text{NO}_3)_3$ solution; skull
dissolved in two fractions.

$$\text{Concentration Relative to Control} = \frac{\text{cpm/mg U in Fraction}}{\text{cpm/mg U in Control}}$$

Fraction	Per Cent Uranium	Pu	Rare Earths	Sr	Ru	Cs	Te	Nb ^a	Zr
Outer Skull	10.12	-	6.4	0.41	1.00	0.007	10.9	0.99	1.59
Inner Skull	4.70	-	0.11	0.0048	0.99	0.00003	0.069	1.15	0.93
Ingot	85.48	-	0.12	0.00032	1.04	0.00001	0.024	1.11	1.00

^aNiobium values corrected for decay and growth from zirconium.

distribution of fission elements within the skull was not homogeneous. The concentration of each element in the inner skull was equal to or closely approximated that in the ingot; and, except for ruthenium and niobium, this concentration differed significantly from that found in the outer skull. It may be concluded that at least one-third of the uranium which was retained in the skull was of the same composition as the ingot.

By means of the scintillation spectrometer, the zirconium getter coupon and the furnace sight glass were scanned for surface gamma activity. These parts were about three inches and 29 inches above the melt respectively. On both parts, cesium-137 was identified as the major constituent. A small amount of an unidentified gamma activity of 0.7 to 1.4-Mev energy was also present. In addition, a gamma activity of 0.87-Mev energy on the zirconium coupon was resolved into a clear peak. This activity has been tentatively identified as Mn^{54} (0.85-Mev gamma, no beta, 310-day half-life). Its source is presumed to be the fast (n,p) reaction on the iron impurity present in the fuel pins. No appreciable beta activity above 2-Mev energy was found. This finding suggests that appreciable volatilization of strontium, yttrium, cerium, praseodymium, and ruthenium did not occur.

Comments regarding the behavior of individual fission elements in this experiment and comparison with behavior in earlier experiments follow:

Ruthenium, Niobium and Molybdenum — The results indicate that significant removal of these elements occurs neither at low or high initial concentrations of the individual elements nor at low or high concentrations of accompanying fission product elements.

Zirconium — The removal of this element by melt refining appears to decrease as its original concentration increases. In the present experiment essentially no zirconium was removed at an initial concentration of 1.8 weight per cent. Previous experiments have indicated that zirconium removal at much lower initial concentrations is almost entirely a result of the presence of small amounts of carbon in uranium and the consequent formation and liquation of insoluble zirconium carbide.

Tellurium — Very low retention of tellurium in melt-refined uranium containing a high concentration of other fission product elements has been observed and discussed previously (ANL-5333, page 48). Formation and liquation of a stable, insoluble rare earth telluride was hypothesized. The retention of only 2 per cent tellurium in Run PB-1A (Table 23) is in accord with this hypothesis. Appreciable loss of tellurium from the melt by volatilization of the metal or of some inter-metallic compound of tellurium may be ruled out because all the original tellurium can be accounted for in the dross and ingot.

Cesium — The removal of this element in Run PB-1A was quantitative to 0.001 per cent, and greater than that obtained in any previous experiment made with uranium having a lower initial cesium concentration. This observation is in accord with earlier observations

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that cesium removal increases as its initial concentration increases (ANL-5255, page 43). In previous experiments with less highly irradiated uranium, synthetically spiked with macro amounts of ruthenium, palladium, zirconium and cerium, the removal of cesium was markedly impeded (ANL-5333, page 49). Since this was not the case in Run PB-1A, it may be concluded that at high initial cesium concentration no significant retention is caused by the presence of other fission elements.

Strontium — The removal of this element was quantitative to 0.03 per cent in Run PB-1A. However, unlike cesium, the mechanism of strontium removal is preferential oxidation and incorporation of the oxide into the dross and crucible. The retention of most of the 96 per cent of unaccounted strontium activity in the magnesia crucible is indicated by its non-volatilization and by the observation that acid washings of the furnace tube did not yield enough total beta activity to account for more than approximately 5 per cent of the missing strontium. Strontium removal does not appear to be seriously affected either by high initial strontium concentration or high initial concentration of other fission products.

Rare Earths — The behavior of the rare earths in Run PB-1A was similar to that observed in experiments with synthetic uranium — fission product alloys. Rare earth distribution is definitely affected by increasing initial rare earth concentration in the direction of increasing its retention in the ingot. Most of the 24 per cent of rare earth unaccounted for should be found in the magnesia crucible because the furnace tube washings do not account for the missing activity and volatilization of rare earth activity is ruled out by the absence of cerium and praseodymium activities on the zirconium getter coupon suspended above the melt during the experiment.

Plutonium — Data on this element for Run PB-1A are not available.

b. Control of Dross in Melt Refining
(N. Chellew, C. Cushing, J. Schilb, D. Finucane)

Fifteen experimental melts of high purity uranium have been made as part of a general study of the mechanism of dross formation in melt refining. The general procedures and standard conditions in these experiments were as previously described (ANL-5529, page 64). Measurements of some or all of the following were made for each experiment: weight, thickness and composition of dross and composition of ingot. In addition, specimens of dross and crucible were examined visually under a stereoscopic microscope.

The nature of the dross was first established. Specimens of dross and crucible were mounted in lucite and polished with 600-mesh silicon carbide paper. The dross was found to consist of a reaction layer uniformly thick over the entire wetted crucible area (Figure 16). Two types of irregularity are evident, namely, voids at the alumina-dross boundary and

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FIGURE 16

PHOTOMICROGRAPH OF DETACHED REACTION LAYER

Run 34E: 2 hr at 1300°C; Metal separated by top pouring;
Sample mounted in lucite; Dark areas are voids.

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metallic inclusions. The metallic inclusions in the dross are concentrated mainly at the dross-molten metal interface and occasionally form a continuous layer over it. Such patches of retained uranium metal result from incomplete pouring of the molten metal. Preliminary evidence that the dross consists mainly of uranium dioxide has been previously reported (ANL-5255, page 15). X-ray diffraction patterns were made of dross samples which were powdered and loaded into capillaries in an inert atmosphere dry box. Only the characteristic pattern of uranium dioxide was obtained. Chemical analysis of typical dross samples are given in Table 25. It is evident that the aluminum concentration is unimportant and that the over-all composition conforms closely to that expected from a mixture of uranium dioxide (theoretical oxygen content = 11.8 per cent) with about twelve per cent of included uranium metal.

The source of the dross-forming oxygen was established by the analyses for aluminum shown in Table 25. Comparison of the recovered aluminum and oxygen with the theoretical mole ratio of aluminum to total aluminum plus oxygen in alumina, 0.40, indicates that within the combined errors of measurement the alumina is the sole significant source of oxygen in these experiments. Because greater than 96 per cent of the aluminum recovered is found in the metal phase and less than two per cent of the oxygen recovered is found there, the equation

may be said to describe the over-all corrosion reaction nearly quantitatively. Further evidence that side reactions, such as with impurities in the helium atmosphere, play only a minor role is provided by the analyses shown in Table 26.

The corrosion data from all experiments to date are summarized in Table 27. In these experiments the thickness of the oxide layer was found to vary from 87 to 184 microns and its weight from 1.85 to 5.89 grams. For the purposes of comparison with more accurate results to be obtained later, an average weight fraction of twelve per cent occluded uranium in the dross was assumed in calculating columns six and seven of Table 27.

In Experiment 25E, the entire oxide layer was covered with a layer of unpoured metal approximately 100 microns thick. A correction to the measured dross weight was applied for this.

In six standard experimental melts maintained at 1200 C for 120 minutes, the oxide layer formed to an average extent of 0.053 gram per cm², with all the variations being within the estimated probable errors of measurement. It may be seen from the result of Run 40E that the surface attack is independent of total area. No significant variation in corrosion between 20 and 270 minutes is apparent. This bespeaks a very rapid initial reaction and subsequent protection of the substrate by the reaction layer.

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Table 25

DISTRIBUTION OF ALUMINUM AND OXYGEN IN URANIUM MELT-REFINING EXPERIMENTS

Crucible: Morgan Triangle RR recrystallized alumina

Charge: Normal uranium containing 6 ppm oxygen and <14 ppm aluminum

Run	Melt Information	Element	Concentration in				Mole Ratio in Recovered Material Al/Al + O
			Dross		Ingot		
			Per Cent	Gram	Per Cent	Gram	
34E	{ Time at 1300 C, 2 hr Dross Wt, 5.00 g Ingot Wt, 514.08 g	Oxygen ^a	11.0	0.550	0.0006	0.003	-
35E	{ Time at 1300 C, 2 hr Dross Wt, 5.68 g Ingot Wt, 528.95 g	Aluminum ^b	0.50	0.028	0.135	0.715	0.44
		Oxygen ^a	9.9	0.563	0.0018	0.009	
36E	{ Time at 1300 C, 4 hr Dross Wt, 6.13 g Ingot Wt, 557.50 g	Aluminum ^b	0.40	0.025	0.140	0.780	0.43
		Oxygen ^a	10.4	0.638	0.0006	0.003	

^aAnalytical precision, $\pm 10\%$ relative.^bAnalytical precision, $\pm 3\%$ relative.

Table 26

IMPURITIES OF INGOT AFTER MELT REFINING

Crucible: Morgan Triangle RR alumina

Melt Conditions: Temp, 1200 C; Time, 120 min; atmosphere,
purified helium

	<u>Concentration, ppm</u>		
	<u>C</u>	<u>O</u>	<u>N</u>
Charge Material	30	11 12	10
Ingots, Run 20E	31 30	16 16	10
Ingots, Run 24E	50 50	14 13	10

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CORROSION OF ALUMINA BY MOLTEN URANIUM AND URANIUM ALLOYS

Crucible: Morgan Triangle RR recrystallized alumina, previously outgassed at 800 C.
 Charge: Uranium containing 30 ppm carbon, 12 ppm oxygen, <10 ppm nitrogen.
 Conditions: Helium atmosphere; 1200 C melts heated to 1300 C in ~15 minutes for separation of dross by top pouring technique

Run No.	Charge	Melt Conditions			Weight of UO ₂ Found, Grams ^b	Grams of UO ₂ per cm ² of Alumina Wetted ^a
		Temp, C	Time, Min	Crucible area Wetted, Cm ²		
20E	Uranium, 512.85 g	1200	120	45.6	1.85	0.041
24E	Uranium, 516.25 g	1200	120	44.2	2.23	0.050
25E	Uranium, 554.29 g	1200	120	48.4	2.90 ^c	0.060
26E	Uranium, 512.17 g	1200	120	44.8	3.01	0.067
28E	Uranium, 548.34 g	1200	120	46.9	2.23	0.047
40E	Uranium, 1282.2 g	1200	120	95.4	5.27	0.055
						Average 0.053 ± 0.007 ^d
22E	Uranium, 526.82 g	1200	270	45.8	2.51	0.055
21E	Uranium, 544.05 g	1200	30	46.9	2.15	0.046
38E	Uranium, 512.51 g	1130-1340	21	43.8	2.54	0.058
34E	Uranium, 519.08 g	1300	120	44.6	4.40	0.099
35E	Uranium, 534.63 g	1300	120	45.8	5.00	0.109
36E	Uranium, 563.63 g	1300	240	49.3	5.39	0.109
30E	Uranium - 8.6 a/o Chromium, ^e 550.31 g	1200	120	47.6	4.40	0.092
32E	Uranium - 8.6 a/o Aluminum, ^e 718.73 g	1200	120	62.0	5.89	0.095
33E	Uranium - 1.5 a/o Thorium, ^e 575.38 g	1200	120	49.3	4.77	0.097

^aSee text, page 81.

^bA metal button formed at crucible pouring lip was removed prior to obtaining weight of uranium dioxide. Metallographic examination of the buttons showed them to be essentially 100 per cent uranium.

^cCorrected for measured volume of metal adhering to dross. See text, page 81.

^dAverage deviation.

^eNominal composition.

At 1300 C the initial reaction proceeds to about twice the extent of the reaction at 1200 C and again apparently becomes very slow. Each of the three alloying elements, chromium, aluminum and thorium, caused promotion of the corrosion reaction to about the same extent. This was surprising because of the chemical differences in their behavior. The mechanistic significance of these facts will be further pursued using the analysis of the ingot for aluminum as a more precise measure of the corrosion reaction.

Crucible undercutting could be measured only at the melt line using the non-wetted surface of the crucible as a reference line. Irregularities and tapering of the undercut made these measurements difficult and unreliable with respect to determination of the reacted alumina volume. The measured depth of crucible undercutting varied from one-third to slightly in excess of the thickness of the oxide layer. No correlation between this depth of undercutting and the total extent of reaction was obtained, even though the total undercut volume must show such a relation. The factors controlling the uneven penetration of high purity alumina will be further studied.

c. Search for Stable Oxidic Slags
(M. Ader, J. Bingle)

The lime-beryllia system is being investigated in an effort to find a oxidic slag melting below 1450 C which is stable toward reaction with uranium. A eutectic of approximately 65 weight per cent (45.3 mole per cent) calcium oxide has been reported to melt at 1405 C.¹³

The freezing point ranges of several lime-beryllia melts of nominal composition 45.2 to 54.3 mole per cent calcium oxide was found to be approximately the same. The most reliable freezing point found thus far is 1385 C for the composition 54.3 mole per cent lime-45.7 mole per cent beryllia.

X-ray diffraction analysis has shown that the lime-beryllia system is not a simple eutectic system. A powder sample from a melt prepared by heating a mixture of 50.2 mole per cent calcium carbonate and 49.8 mole per cent beryllium oxide in platinum to over 1400 C gave an X-ray pattern (CuK α radiation) containing many more lines than present in a physical mixture of lime-beryllia. The pattern obtained clearly indicated the presence of the face-centered cubic calcium oxide structure, the absence of the hexagonal beryllia structure, and the presence of a new face-centered cubic structure with lattice constant $a = 14.012 \pm 0.001 \text{ \AA}$. Approximately 100 lines belonging to the latter structure were successfully indexed. The lattice constant for calcium oxide calculated from the same pattern, $a = 4.808 \text{ \AA}$, compares favorably with a recent literature¹⁴ value of $4.810 \text{ \AA}$.

¹³ Geller, R. E., et al., Journal of Research of the National Bureau of Standards, 36, 297 (1946)

¹⁴ Swanson, H. E., and Tatge, E., NBS Circular 539, Vol. I, page 44

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The composition of the new compound is uncertain but can be limited to a narrow range. Geller¹³ reports that compositions between CaO and CaO:BeO contained CaO as the primary phase, and compositions between CaO:1.5 BeO and BeO contained BeO as the primary phase. The intensity of the calcium oxide lines in our X-ray pattern supports the first observation. Thus, the composition of the compound is limited to greater than 50 and less than 60 mole per cent beryllia, e.g., 3 CaO:4 BeO. A phase diagram study by means of X-ray analysis will be made within the range of interest to determine the composition of the compound(s) formed. It is also intended to prepare the pure compound to determine its density and, thereby, the number of molecules per unit cell. Attempts to separate the compound from excess calcium oxide by flotation have not been successful.

2. Magnesium Extraction Studies

a. Extraction of Plutonium from Molten Uranium (E. Greenberg, M. Nathans, K. Anderson)

Recent extraction runs confirm earlier experiments (ANL-5494, Table 13 and ANL-5529, Table 15) which indicated the slowness of approach to equilibrium in static equilibrations. The data are reported in Table 28.

In Run 25, the capsule was heated and shaken in the same manner as in Run 22 (ANL-5529, pages 70 to 73). The longer equilibration period, with shaking, resulted in a distribution coefficient increase from 0.14 to 0.20.

It is possible that the slowness of approach to equilibrium in the static experiments is due to a high interfacial resistance caused by an oxide layer or other material at the interface. Therefore, in Runs 26 and 27, all of the crucible and capsule components (except the charge itself) were outgassed in vacuum at 800 to 900 C prior to their use in equilibration experiments in order to see if such treatment was effective in promoting equilibrium conditions. The partition obtained in Run 26 was significantly higher than average of static Runs 18, 23 and 24 conducted with components not vigorously outgassed. The result for Run 27 appears to be at variance with all previous results and work is in progress to check this.

The accumulated data indicate a limiting value of about 0.20 for the distribution coefficient. Agitation of the melt, and degassing of the crucible and capsule components appear to be effective in promoting equilibrium. It is planned that future experiments will be carried out using an induction heater in order to achieve stirring during the liquation period.

b. Extraction of Fission Products from Uranium Alloys (G. R. B. Elliott)

A study of the distribution of fission products between magnesium and uranium-chromium or uranium-iron alloys has been undertaken.

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Table 28

RESULTS OF PLUTONIUM PARTITION EXPERIMENTS

All equilibrations were conducted in high purity alumina crucibles,
with graphite caps, inside sealed steel capsules

Run No.	Weight of Uranium (g)	Weight of Magnesium ^a (g)	Charged Pu ^b (mg)	Temp (C)	Time at Temp (hr)	Final Pu in U (wt %)	Final Pu in Mg (wt %)	Total Pu Recovered (mg)	K ^c (apparent)	Remarks
18 ^d	46.29	20.69	-	1169	5	0.038	0.034	25	0.091	Static Equilibrations
23 ^d	26.3	22.97	-	1180	9	0.82	1.20	496	0.15	
24	33.7	20.6	-	1180	4.5	0.833	1.35	566	0.17	
22 ^d	45.30	20.20	-	1169	1.5	0.29	0.40	213	0.14	Crucible shaken. See Text, p. 86.
25	37.9	5.23	-	1168	5	0.481	0.950	233	0.20	
26	15.4	12.6	145	1186	4.3	0.390	0.703	150	0.18	Static equilibrations using degassed crucibles and capsules.
27	10.5	12.1	101	1184	4.3	0.169	0.660	99	0.40	

^aHigh purity sublimed magnesium was used throughout.

^bThe plutonium was initially in the uranium phase.

^cThe definition of K (apparent) is mole fraction of Pu in Mg/mole fraction of Pu in U.

^dPreviously reported in ANL-5529, page 72.

The initial program will concern the distribution of macro amounts of the individual fission products (either inactive or pile activated) between the immiscible phases. The equipment for this study is under construction. Details of its operation will be reported later.

c. Extractions from Powdered Uranium
(R. Nuttall, J. Settle)

Experiments have been made in which uranium, containing fission products, was converted to a powder and mechanically suspended in liquid magnesium. The liquid phase sampled by removing portions through a filter. These samples and the unfiltered remainder are being analysed to determine how much and at what rate the various fission products appear in the liquid magnesium. Only preliminary results are available.

In the first experiment 13 grams of powdered Sylvania "fissium" were suspended for two hours in 10 grams of magnesium at 700 C. The extraction of palladium appeared to be quantitative. The uranium, ruthenium and zirconium contents in the magnesium phase were 0.5, 6 and less than 4 per cent, respectively, of the initial amounts.

In a second experiment a slice of Clinton slug (about 72 ppm plutonium) weighing 36 grams was powdered and suspended in 70 grams of magnesium for three hours at 700 C. About eighty per cent of the plutonium was extracted into the magnesium phase, and the extraction of cerium was quantitative.

3. Container Material Studies
(C. L. Rosen, R. V. Sweezer)

a. Tantalum Borides

Molten uranium was held at 1275 degrees in tantalum boride-coated crucibles for 50 hours for an examination of their corrosion. A similar tantalum crucible not boride-coated was subjected to the same treatment for comparison. The preparations and results are given in Table 29. At the end of the experiment the tantalum crucible was completely corroded away while no definite evidence of attack on the borided crucibles was microscopically visible. This establishes a corrosion rate of approximately one mil per hour for tantalum and less than one mil per day for the borided material at 1275 C.

Further experiments were conducted to find a suitable suspending medium for fine boron powder that will enable one to apply the boron as a liquid suspension at room temperature. The vehicle must be completely vaporizable to leave a thin, smooth, and uniform coating of elemental boron. An acetone suspension (ANL-5529) has been found to produce a coating that can be converted to a tantalum boride. However, its viscosity is too low and its vapor pressure too high to permit quantitative and reproducible uniform coating to a predetermined thickness. At present an oil suspension is being tested. Prolonged vacuum evaporation

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Table 29

CORROSIVE ATTACK OF URANIUM ON BORIDED AND NON-BORIDED TANTALUM

Crucibles: 0.060-inch thick walls

Corrosion Conditions: Temperature 1275 C; pressure 10^{-4} mm Hg; time, 50 hours

No.	Crucible Preparation		Corrosion
	Method	Weight of Boron in Coat, mg	
C1	Heated 20 min in contact with boron powder at 1750 C; vacuum heat treated 5 hours at 1900 C	32.9	No measurable attack. Slight discoloration of boride layer below uranium level
C3	Heated 7 min in contact with boron powder at 1350 C; vacuum heat treated 5 hours at 1900 C	16.2	
C6	Vacuum heat treated 5 min at 1900 C, boron deposited from vapor only	0.2	Completely corroded below uranium level
X	Tantalum control; no pre-treatment	none	Completely corroded below uranium level

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of the vehicle is required but the coating meets the above requirements provided that the original surface is scrupulously cleaned prior to application of the suspension.

b. Ruthenium Borides
(C. L. Rosen, D. S. Flikkema, R. V. Sweezer)

The system ruthenium-boron has been reinvestigated by sintering stoichiometric mixtures of ruthenium and boron powders. The compounds found by Buddery and Welch¹⁵ were identified as Ru_2B , RuB , Ru_2B_3 , RuB_2 . The tentative assignment of compounds found in this investigation is listed in Table 30.

4. Separation Processes Based on Uranium Halides

a. Reaction of Uranium with Metal Halides
(M. Beederman)

Possible separation process applications have been indicated for the reaction of uranium with molten zinc chloride (ANL-5494, page 55). In the reaction

uranium trichloride in solution and metallic zinc are formed. A physical separation of the fused salt phase from the metallic phase may be effected by filtration or decantation. It is anticipated that some of the fission product elements such as the platinum group metals and molybdenum will be incorporated in the metal phase.

Experiments have been performed to investigate this reaction. The apparatus consists of a medium porosity Pyrex glass frit sealed to a Pyrex tube with inlets for argon and vacuum. The assembly was charged with a mixture of zinc chloride and potassium chloride and was heated in a tube furnace to 400 C. A constant flow of argon was maintained. A rapid reaction results upon adding a pellet of fission alloy (1 to 2 grams) to the fused mixture. After reaction ceased a vacuum was drawn and the fused salt was filtered from the zinc metal and any fission product elements incorporated in the zinc. The separated phases are being analyzed for their constituents.

b. Iodide Vaporization and Thermal Decomposition
(G. R. B. Elliott)

A paper study on the applicability of deBoer type processes for uranium or plutonium recovery or purification has been completed. These

¹⁵Buddery, J. H., and Welch, A. J. E., Nature, 362 (1951)

Table 30

PHASES IN THE RUTHENIUM-BORON SYSTEM

<u>Ru:B</u> <u>Stoichiometry</u>	<u>Firing</u> <u>Temp</u>	<u>Phases Present</u>			<u>Tentative</u> <u>Assignment</u>
		<u>Major</u>	<u>Minor</u>	<u>Questionable</u>	
4:1	1275 C	Ru	I		
2:1	1400 C	I	Ru		RuB + Ru
1:1	1250 C	I		Ru	
1:2	1400 C	II		Ru	RuB ₂
2:5	1400 C	III			
1:3	1400 C	III			
1:4	1400 C	III			Ru ₂ B ₅
1:10	1400 C	III			
1:12	1400 C	III			

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processes do not appear satisfactory for use with plutonium. Although the deBoer process is interesting as a possible purification method in special situations such as U^{235} recovery from EBR-II, the pressure of other more urgent problems will prohibit a development program along these lines at this time.

c. The Solubility of Uranium Hydride in Fused Salts
(G. R. B. Elliott)

The solubility of uranium hydride in molten alkali metal halides is of interest in connection with possible process applications. Solubility in the lithium chloride-potassium chloride eutectic just above its melting point was measured and found to be very small.

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

1. Study of Fuel Purification on a Kilogram Scale
(G. Bennett, J. Jones)

Fuel purification studies were continued on a kilogram scale using Sylvania fission* diluted with an equal weight of natural uranium. Two experiments were made in the past quarter to determine the effect of charge size on fission product decontamination and ingot yield. The experimental procedure described in ANL-5529, page 73 was followed in all cases. Results of these experiments and some experiments on crucible re-use presented in the previous quarterly report and for which analytical data had been unavailable are given in Table 31.

The re-use of crucibles apparently had little effect on cesium and zirconium removal, but the retention of cerium in the ingot was increased by crucible re-use, being as high as 51 per cent on the third use of a crucible (Run 22). Results obtained with fission must be considered as qualitative only. The high concentrations of oxygen (500 to 1000 ppm), nitrogen (120 ppm), and carbon (100 ppm), which were reported in ANL-5494, page 70, will influence fission product removals and may make the removals of some elements insensitive to experimental variations. For example, zirconium may be largely removed through carbide formation with the carbon impurity.

As noted in the previous quarterly (ANL-5529, page 75), ingot yields suffer when high liquation temperatures (1400 C) are employed (Runs 17, 18, and 24). Ingot yields with 5-kg charges were no better than those obtained with 2-kg charges which average 91.6 per cent.

2. Metal Recovery from Slags

It has been pointed out previously (ANL-5494, page 63) that in the melting of Sylvania fission, a tough, brittle, porous slag, somewhat

*Uranium in which fission products have been dispersed by powder metallurgy techniques in concentrations equivalent to about 2 per cent burn-up of total fuel atoms.

Table 31

SEMI-WORKS KILOGRAM-SCALE MELT-REFINING RUNS

Charge: 2 kilograms of metal comprised of equal quantities of Sylvania fissium and natural uranium to give fission product concentrations equivalent to 1 per cent burn-up

Crucible: Magnesia

Run	Use	Crucible History		Liquation		Per Cent Recovery in Ingot	Per Cent Fission Product Retention		
		From Previous Run	Time Lapse (days)	Conditions Time (hr)	Temp (C)		Cesium	Cerium	Zirconium
17	1	-	-	1	1400	87.9	26	< 6	< 44
18	1	-	-	2	1400	86.6	< 9	< 6	< 44
24 ^a	1	-	-	2	1400	87.3	-	< 6	35
25	2	24	4	2	1400	91.1	25	< 18	37
19A	1	-	-	0.5	1200	95.6	25	< 12	< 11
19B	2	19A	1	0.5	1200	95.6	19	23	< 11
9	1	-	-	0.5	1200	93.4	15	< 12	< 11
20	2	9	62	0.5	1200	91.3	7	26	11
13	1	-	-	0.5	1300	89.9	31.7	< 6	< 11
21	2	13	48	0.5	1300	89.2	22	18	23
22	3	21	2	0.5	1300	96.4	30	51	< 33
Charge: 5 kg									
28	1	-	-	2	1300	91	(no data available)		
29	1	-	-	2	1200	91	-	3	32

^aAlumina crucible used.

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resembling petroleum coke in appearance, is formed on the surface. Considerable uranium is retained in this slag and adheres to the reaction layer formed along crucible walls. Attempts have been made to consolidate this uranium in a button using a procedure described in HW-38912.¹⁶ This procedure was reported to cause coalescence of uranium in small pieces or turnings, which would normally be retained in an oxide skin or shell. The procedure involves the use of calcium as a uranium oxide reductant, and a flux of barium chloride which is used to dissolve the calcium oxide.

To date, six experiments have been made using 25- to 50-gram charges of unpoured skull material from previous oxidative slagging runs. Calcium, in approximately 25 per cent excess over that required for complete reduction assuming the oxide as UO_2 , has been the reducing agent. Either calcium or barium chloride, in a quantity approximately equal to the amount of oxide formed assuming complete reaction, has been the fluxing agent. Iodine (0.15 mole iodine per mole of uranium) has occasionally been used as a booster.¹⁷ The samples were heated to approximately 1200 C in the induction furnace and held at this temperature for 15 to 30 minutes.*

These efforts have met with variable success. However, definite coalescence of the uranium has occurred in some instances, in which 80 to 90 per cent of the uranium charge has been isolated as a small button or a hard metallic uranium structure from the bottom of the crucible.

Three attempts have also been made to separate the uranium from the slag layer as it is being formed, by adding the reducing and fluxing agents to the surface of the melt. Due to the corrosive nature of the reactants and the high vapor pressure of calcium, application of this technique is difficult. In one run in which this was tried, a pour was not obtained, but the heavy slag layer, characteristic of fissium melts, was missing. In the second run, a pour was obtained but the metal yield was not significantly improved (92.7 per cent).

Inasmuch as the type of slag obtained in the melting of irradiated material is not yet known, this work will be subordinated to other high temperature problems.

3. Effect of Inert Atmosphere Purity on Ingot Yield (A. A. Chilenskas, F. Mertes)

In the previous quarterly report (ANL-5529, page 78) experiments were reported which showed the effect on ingot yield of various concentrations of air in the inert argon blanketing gas. Additional experiments were made

¹⁶ DeHollander, W. R., "The Melting of Small Pieces of Uranium Metal," HW-38912

¹⁷ Smith, C. F., "Uranium Metallurgy, Chapter 2 of Metallurgy, Los Alamos Technical Series," Volume 10, LA-1223

*In one run, a highly exothermic reaction occurred, which carried the temperature considerably higher. This did not appear to effect coalescence.

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in the past quarter to determine the effect of the nitrogen impurity alone. Two scouting runs were also conducted to ascertain the effect of exposing a large surface area of uranium to the atmosphere, such as will be encountered in practice when 1/8-inch diameter fuel pins are melted.

The experimental conditions for all the atmosphere contamination runs were identical with the exception of atmosphere composition. The 1300-gram charge consisted of approximately equal weights of Sylvania fission (1-3/8 in. OD rod) and 1-5/16 in. OD natural uranium rod. The fission portion of each charge was composed of one slice from three different bars to minimize the impurity variation of the fission from one charge to another. The charge, the magnesia crucible, and other system components were first degassed under vacuum (1 to 10 microns of mercury) to 600 C. Subsequent heating, melting, and retention at 1200 C for 3 hours were conducted under flowing argon or helium atmosphere. The contaminant gas was pumped into the flowing inert stream with a calibrated syringe pump.

The results of all the air* and nitrogen contamination experiments are plotted on Figure 17. The ingot yield, in general, decreases as the concentration of contaminant gases in the argon is increased. The results of the experiments performed under purified helium and purified argon, and plotted as zero per cent added contaminant, scatter considerably, but indicate that for this system no significant change in yield would be expected in extrapolating the argon contaminants to near zero. The insensitivity of yield at near zero impurity concentrations in argon using fission may be largely due to impurities already present in this material (oxygen, nitrogen, and carbon, and fission product powders).

In general the effect of nitrogen is similar to that of air upon the yield, and it appears that high nitrogen concentration cannot be tolerated any more than high air concentration. It should be noted that the permissible impurity concentration presently being considered for the main cell atmosphere (0.1 per cent oxygen and 5 per cent nitrogen) is considerably higher than that shown to be compatible with high yield by Figure 17. Therefore, consideration should be given to separating the atmosphere blanketing the melt-refining process from the main cell atmosphere.

In order to ascertain the effect fuel rod size might have on the melting and coalescing characteristics of the charge, two experiments were performed on which the charge consisted of 1/8-inch rods or 1/8-inch plus 3/16-inch rods of natural uranium. In an argon atmosphere having 0.2 per cent air as impurity, a yield of 87 per cent was obtained from a charge of 520 grams. It was observed that oxide shells of many of the rods were present after pouring and that drainage from these shells may have been incomplete. With no added air contamination of the argon, these shells were not present and the yield was about 94 per cent. It is felt that these yields are lower than would be expected from a charge consisting of 1-5/16 in. rods and that the surface-to-volume ratio of the metal is indicated to be an important variable.

*The results of the air contamination of argon studies are plotted in Figure 19, ANL-5529, page 79.

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FIGURE 17
URANIUM INGOT YIELD AS A FUNCTION
OF AIR AND NITROGEN CONCENTRATION IN ARGON

4. Control of Volatile Fission Products (J. Wolkoff)

Work continued on the development of apparatus to trap volatilized fission products, such as cesium and iodine, within the furnace. The multi-plate crucible cover described in the last quarterly report (ANL-5529, page 82) was used to collect material volatilized from a 1:1 Sylvania fissium-uranium charge held molten at 1190 C for two hours. Spectrographic analyses were obtained on the material scraped from successive plates in the stack, and those elements found in significant amounts are given in Table 32.

The presence of the relatively non-volatile elements such as barium and strontium on the cooler plates and furnace walls was considered to indicate the formation of a fume (also confirmed by observation). In an attempt to determine whether the fume resulted from poor atmosphere or was inherent in the use of fissium which has a high oxygen impurity content of about 1,000 ppm, a run was made in an induction-heated vacuum furnace that allowed vacuum degassing and a stringent atmosphere purge. The condensing surface in the cover was modified as shown in Figure 18. High purity crucible grade magnesia packing was utilized as a packing material.

Despite the improved atmosphere control, a small amount of fume escaped and collected on surrounding cold surfaces of the furnace. Spectrographic analyses of this fume showed cadmium and cesium to be major constituents.

Work with fissium has now been terminated since quantitative analyses of the inactive fission products require excessive analytical time. The work will continue using a pure fission element, such as cesium, to develop methods of trapping it as a pure metal or as a cesium oxide fume. Final testing of the methods developed will be made with irradiated material.

5. Design and Testing of Components for Pilot Plant (G. J. Bernstein, V. N. Thelen)

a. Development of Top-Pour Crucible

Nine additional runs were made in the past quarter in continuing the evaluation of the top pouring method for plant use. A description of the equipment is given in ANL-5466, page 63. The same crucible was used for the first six runs in which 4-kg charges of uranium and fissium equivalent to 1 per cent burn-up of fuel were melted in an alumina-coated graphite crucible. Crucible performance was satisfactory until a crack was discovered following the sixth use. Ingots were of good appearance and yields ranged from 89.8 to 98.4 per cent with an average of 94.0 per cent (see Table 33). There was a slight tendency toward increased yields on repeated use.

A set of three runs were made in which a slip-cast MgO liner was substituted for the alumina coating on the graphite crucible. A hairline

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Table 32

MAJOR CONSTITUENTS OF MATERIALVOLATILIZED FROM MOLTEN FISSION

Element	Concentration in Scrapings (per cent — order of magnitude)				
	Plate 1 (700-800 C)	Plate 2 (600-700 C)	Plates 3-6 (400-600 C)	Plates 7-11 (200-400 C)	Furnace Walls (25 C)
Aluminum ^a	>>1	>1	>1	0.1	0.1
Barium	>>1	>>1	1	0.5	0.5
Magnesium ^a	>>1	>1	0.5	0.05	<0.02
Strontium	>>1	>1	0.02	0.5	0.3
Cesium	5	(not determined)	0.5	0.2	Very strong
Cadmium	<0.1	<0.1	0.3	<0.1	10
Cerium	<0.1	<0.1	<0.1	--	--

^aNot constituents of fission but present in crucible or furnace materials

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FIGURE 18
CRUCIBLE AND COVER FOR TRAPPING
VOLATILIZED FISSION PRODUCTS.

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Table 33

SUCCESSIVE TOP-POUR CRUCIBLE RUNS IN SAME CRUCIBLE

Alumina-coated graphite crucible. Four kg of fissium corresponding to 1 per cent burn-up of fuel. Melting time: 1 hour; liquation time: 2 hours at 1200 C

<u>Run No.</u>	<u>Pouring Temp, C</u>	<u>Per Cent Pour</u>
19	1300	91.2
20	1315	93.5
21	1325	89.8
22	1320	98.4
23	1310	95.7
24	1360	94.8

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crack developed near the spout of the MgO liner following the third use. The metal charge consisted of ingots from previous 1 per cent burn-up equivalent runs with the addition of some Sylvania fissium. Yields ranged from 93.5 to 97.9 per cent (Table 34).

b. Development of Bottom-Pour, Fusible-Leg Crucibles

Attention was centered principally on testing a large graphite crucible which has been designed for use in the pilot plant. The crucible itself is 6 1/2 inches OD by 8 inches deep, the fusible-leg appendage on the bottom being 4 inches long. Preliminary tests indicated that good coupling could be achieved for induction heating. Radiant heat loss without the use of reflectors or insulation was excessively great.

This crucible was coated with alumina using commercial coating equipment which incorporates a flow of powdered alumina through an oxy-hydrogen torch. The fusible leg was coated by splitting the leg and then pressing it into a sleeve on the bottom of the graphite crucible. This crucible has been used to melt a charge of 10 kilograms of uranium with a pour yield of 96 per cent.

c. Testing of Bell Jar Furnace

A possible design for the pilot plant is one in which the melting crucible is placed under a metal bell jar. The bell jar, consisting of a two-foot length of 24-inch steel pipe closed at one end, is placed upon a 3/4-inch thick steel plate to provide closure. In this design, no seal is planned between the pipe and the plate except that provided by the machined surfaces. The bell jar is operated under reduced pressure to prevent loss of volatile fission products to the cell proper.

Freon leak tests showed that no detectable leakage occurred at the lowest measurable negative head (0.1 inch water). Freon was readily detectable at an equivalent positive head. Tests with argon and air revealed that at a pressure differential of 1 inch of water, leakage would be less than 1 cfm at room temperature or with the crucible at 1300 C within the bell jar.

6. Extraction of Plutonium by Liquid Magnesium
(I. O. Winsch, W. H. Spicer)

Further studies have been conducted in the semi-works on the extraction of plutonium from uranium with magnesium and on the subsequent distillation of the magnesium to recovery the plutonium. This is a possible procedure for processing core or blanket materials to recover the plutonium.

a. Magnesium Extraction Studies

Preparation of Plutonium Alloys Several additional uranium-chromium-plutonium alloys (5 wt per cent chromium, tracer plutonium) and one uranium-plutonium alloy have been prepared in the Vycor tube furnace described

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Table 34

TOP-POUR CRUCIBLE RUNS USING MgO LINER

Melting time: 1 hr; Liquation time:
1 hour at 1200 C

<u>Run No.</u>	<u>Ingot Charge (grams)</u>	<u>Sylvania Fissium (grams)</u>	<u>Pour Temp (C)</u>	<u>Per Cent Yield</u>
25	2993	1060	1320	93.5
26	3086	1102	1310	96.8
27	4065	None	1300	97.9

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in ANL-5529, page 89. Chromium is used to lower the melting point of the uranium metal and thus make it possible to operate at temperatures at which the vapor pressure of magnesium is less than 1 atm, and to reduce difficulties with materials of construction. The chromium-uranium eutectic occurs at 5 wt per cent chromium (melting point of 860 C). The alloys have been fairly homogeneous except for a slightly higher plutonium concentration on the top of the ingots. A summary of the alloys prepared to date is shown in Table 35. In the preparation of these alloys, alpha activity was not detected outside of the alumina crucibles containing the melts.

Extraction of Plutonium with Magnesium Three extraction runs have been completed to date using the alloys of Runs 1, 2 and 3 of Table 35. Agitation was imparted to the melt by rocking the crucible for a period of one-half hour over a temperature range of 920 to 1000 C. After this period, the melt was allowed to cool to 820 C, at which temperature the magnesium extract was poured into a copper mold.

The results of the magnesium extraction experiments, as shown in Table 36, indicate distribution coefficients of between 0.14 and 0.20, which are comparable to those reported by the laboratory section (see page 86 of this report).

Chromium analyses were obtained on the separated magnesium extracts from two runs. The concentrations of chromium found were 0.02 and 0.033 wt per cent chromium in magnesium. The value of 0.02 wt per cent is an average of analyses of an interior sample (0.0134 wt per cent) and a surface sample (0.0275 wt per cent).

A batch extraction unit having a capacity for contacting 5 kg of uranium with 5 kg of magnesium is being fabricated and should be in operation within six months.

b. Magnesium Distillation Studies

In two previous magnesium distillation runs, a uranium-aluminum alloy (8 per cent uranium) was used to determine the extent of entrainment which might occur. Analytical results on these runs (Runs 7 and 8 reported in ANL-5529, page 87) indicate uranium or aluminum entrainment did not occur to any great extent (less than 0.02 wt per cent of either in distillate).

Distillation Runs 9 and 10 were complete using the magnesium-plutonium extracts from extraction Runs 1 and 2 (Table 36) as the still pot charges. "Burping" of the magnesium-plutonium melt during Run 9 resulted in alpha contamination of the condenser and magnesium distillate. An analysis of the distillate showed it contained 34 per cent of the total 7 mg of plutonium originally present in the charge.

In Run 10, a baffle was placed over the still pot to de-entrain any liquid particles in the vapor. In this run, only 0.5 per cent of the 7 mg in the charge of the plutonium was found in the magnesium distillate.

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Table 35

SUMMARY OF PLUTONIUM ALLOYS PREPARATION

<u>Run No.</u>	<u>Nominal Chromium Conc (per cent)</u>	<u>Alloy Wt (grams)</u>	<u>Total Plutonium in Ingot (mg)</u>	
			<u>Based on Body Analyses</u>	<u>Based on Top Surface Analyses</u>
1	5	612.4	10.4	11.7
2	5	595.2	11.0	16.8
3	5	503.1	107	130
4	0	175.0	1575	1575
5	5	262.0	2000	---

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Table 36

MAGNESIUM EXTRACTION OF PLUTONIUM FROM URANIUM-CHROMIUM ALLOYS

Run No. ^a	Charge			Magnesium Extract			U-Cr Phase	Pu	Pu Material	Distribution
	Wt Alloy (g)	Wt Pu (mg)	Wt Mg (g)	Mg Poured (g)	(%)	Pu Conc (mg)	Pu Conc (mg)	Extracted (%)	Balance (%)	Coefficient (mole fraction basis)
1	612.4	10.4	616.7	602.6	98.5	7.13	4.65	68.5	113.0	0.154
2	593.2	11.1	562.6	528.0	94.0	6.9	3.88	62.0	97.5	0.190
3	501.8	105.0	507.0	475.8	93.8	61.0	42.5	58.0	99.0	0.142

^aAlloys of same Run No. of Table 35 used.

An attempt to provide an accurate plutonium material balance was made by adding to the still pot a uranium-iron (11 per cent iron) alloy, which melts at about 725 C. It was hoped that the plutonium would transfer into the uranium phase as the distillation proceeded. However, examination of the still pot residue showed that only a small portion of the uranium-iron alloy had melted. All of the magnesium had distilled, but because of difficulties in heating the distillate transfer lines, only a small portion of the distillate was found in the receiver. The major portion of the magnesium remained in the condenser.

A new distillation unit has been fabricated and will be used for future magnesium distillation studies.

7. Inert Gas Purification
(A. A. Chilenskas, I. G. Dillon, F. Mertes)

In the study of the various systems proposed for the inert gas purification for the EBR-II fuel processing cell, the choice of system is highly influenced by the purity requirements of the inert gas and the estimate of the air leakage rate into the cell.

The maximum allowable concentrations of oxygen and nitrogen in the argon cell atmosphere have been tentatively set at 0.1 and 5 per cent, respectively. The air inleakage rate for this cell is, of course, unknown. An estimate of 0.01 cu ft/min has been made based upon the lineal feet of gasketed surfaces and on data of leakage rates through or past various static and movable seals obtained by Heywood, et al at Knolls Atomic Power Laboratory.^{18,19,20}

It should be noted that the cell gas purity requirements as specified above refers to the main cell atmosphere in which the bulk of the fuel elements fabrication work will take place. The purity requirement for the inert atmosphere blanketing the melt refining operation is suggested as being much higher by the atmosphere contamination studies (see page 94). It will probably be desirable, therefore, to make furnace atmospheres independent of the main cell atmosphere.

The work done thus far has been directed toward finding systems for the removal of oxygen and nitrogen from the main cell gas.

a. Removal of Oxygen from Argon

A system for the removal of oxygen from argon has been proposed (Figure 19) and certain components have been tested. The nitrogen removal

¹⁸Heywood, et al. "Static Seal Tests," KAPL-501

¹⁹Heywood, et al, "Static Seal Studies," KAPL-974

²⁰Heywood, et al, "Control Rod Gas Seals," KAPL-1161

FIGURE 19

A POSSIBLE SYSTEM FOR THE REMOVAL OF OXYGEN FROM ARGON

- Basis: (1) Air inleakage rate 0.01 cfm
 (2) Cell volume 24,000 cu ft
 (3) Oxygen tolerance level 0.1% (1000 ppm)
 (4) Nitrogen tolerance level 5.0% (50,000 ppm)

system shown in Figure 19 has been included for completeness only.

The cell gas first enters the pre-drier which removes any moisture in the cell gas. The oxygen content is then determined by converting it to water and measuring the dew point. Based on this analysis, hydrogen is added to the bulk gas stream at slightly less than the stoichiometric amount needed to convert the oxygen to water vapor. The gas then passes through a catalyst chamber, where combination of the hydrogen and oxygen occurs, and then through a drier where the water vapor is removed. A dew point analysis of the exit stream can then be used to check the efficiency of the oxygen removal system and to periodically test for the presence of hydrogen.

Preliminary testing of the oxygen removal system components, consisting of the pre-drier, drier, and catalyst, has been completed. "Molecular Sieves, Type 4A" have been used as a drying agent in tests in which argon containing 1.9 per cent moisture was dried to a moisture content of less than 3 ppm. A breakthrough loading of 21.7 per cent, i.e., 21.7 grams water/100 grams dry "molecular sieves," was achieved with no increase in effluent gas moisture content while loading. The "molecular sieves" were regenerated satisfactorily using service compressed air passing through the column at 300 C.

A "Deoxo Catalytic Purifier," which is a commercial unit used for oxygen removal from hydrogen, has been tested at room temperature for catalyzing the reaction between hydrogen and oxygen to form water. The tests were performed with amounts of hydrogen both less than and in excess of the stoichiometric amount required for complete oxygen to moisture conversion. The results of the tests show that complete conversion of oxygen occurs when an excess of hydrogen is used and that the per cent conversion achieved when less than the stoichiometric amount is used corresponds to the per cent hydrogen introduced.

Additional tests are being performed on oxygen removal from argon using liquid NaK (eutectic) at room temperature with the purpose of developing an alternate system to the one proposed or as an auxiliary to the main cell gas system. An auxiliary system could be used, for example, in a purification scheme for the argon blanketing the melt refining operation where it may be desirable to reduce oxygen concentration to a very low value. Preliminary tests have shown that the oxygen content in argon can be reduced from 900 ppm to 14 ppm by the use of NaK in a bubbler system. Methods of de-entraining NaK from the gas stream are now being sought.

b. Nitrogen Removal from Argon

Some nitrogen removal methods which have been discussed in the literature and may be applicable here are: (1) solid calcium at 650 C, (2) lithium in lithium amalgam at room or slightly elevated temperatures, and (3) magnesium in the liquid phase at 900 C or vapor phase at 1000 C. An additional method of nitrogen removal consists of a simple cell gas purge and replacement of the purged gas with tank argon.

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A few experiments to study nitrogen removal in dynamic, one-pass systems were completed. The systems liquid 30 per cent magnesium in lithium at 350 C, liquid lithium at 200 C, and "molecular sieves at -76 C were tested. No significant nitrogen removal was obtained with any of them. Consideration is now being given to the study of nitrogen removal by the use of apparatus which will permit multipass gettering and static nitriding and denitriding rate studies.

8. Design of a Pilot Plant for Processing EBR-II Fuel by
a Pyrometallurgical Process
(D. C. Hampson, R. Malecha)

Work is continuing on the design of the process cell and equipment for processing EBR-II fuel. A flowsheet showing the materials handling functions has been made. This flowsheet shows the pieces of equipment necessary for the core processing and for the introduction, removal and internal routing of the metal, containers and other components. The types of manipulations necessary, i.e., special purpose or general purpose manipulators, are indicated. In addition the services required for each piece of equipment are shown.

A pictorial representation of the flowsheet is being made to aid in determining space requirements. This will also be used in planning the window locations and the location of the services.

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V. FLUIDIZATION STUDIES

(A. A. Jonke)

The design of the multistage, fluidized-bed, green salt pilot plant was essentially completed and fabrication of the equipment components has been started. Experimental work was continued in the bench-scale reactor to establish the optimum operating conditions for the process. A comparison between dissociated ammonia and undissociated ammonia for reduction of uranium trioxide was made. The rate of the reduction reaction was found to be somewhat higher when the ammonia was pre-dissociated before feeding to the reactor. In the hydrofluorination step the use of an increasing temperature gradient from the top stage to the bottom stage, greatly reduced the solids residence time required for conversion of uranium dioxide to uranium tetrafluoride. In one run a residence time of three hours was sufficient for 98 per cent conversion to green salt.

The production of crude green salt from uranium ore concentrate was carried out on a kilogram scale with satisfactory results. Size reduction of the ore pellets to a fluidizable powder was readily achieved by jaw crushing the material to pass a 40-mesh sieve.

Design work on the shielded calciner for radioactive wastes was continued and fabrication of the calciner and auxiliaries was started.

A fundamental study of the fluidization of mixtures of solid particles of two widely separated sizes was advanced. "Phase diagrams" relating gas velocity to bed composition were prepared for binary mixtures of five different systems. These "phase diagrams" appear in many respects to be analagous to, and have the properties of, vapor pressure diagrams for binary liquids.

Meetings on Industrial Participation In Feed Materials Production were attended at Cincinnati in January and at Oak Ridge in February. On February 8 a meeting held at Argonne to discuss the development work in this Division on feed materials processes was attended by 18 industrial representatives.

A. Green Salt Process

(E. Petkus, N. Levitz, M. Jones, M. Deerwester)

Work during the past quarter was concentrated on completing the design of the green salt pilot plant and beginning the installation of equipment. In addition experimental work was continued in the bench-scale reactor to establish the optimum operating conditions for the process.

1. Uranyl Nitrate Denitration

Two uranyl nitrate denitration runs were made during this period to produce uranium trioxide for subsequent reduction and hydrofluorination

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experiments. During these runs it was noted that the porous stainless steel filters in the disengaging section of the reactor had become partially plugged, as evidenced by an unusually high pressure drop across the filters (about 15 psig). The plugging was of such a nature that it was not possible to clean the filters satisfactorily by blowback with air. They were therefore removed and cleaned by boiling in dilute (2 M) nitric acid and by reverse flow of acid through the pores. This treatment reduced the pressure drop to a low value though not equivalent to that of new filters.

Inasmuch as the filters had been in operation for several hundred hours and under a wide variety of experimental conditions, eventual plugging was not surprising. The occasional use of high blowback gas velocities to clean the filters probably contributed to the plugging. Experimental evidence on the filtration of fluid catalyst²¹ has shown that high blowback velocities tended to lodge fine particles permanently in the filter pores, causing an increase in the initial pressure drop across the filters. However, when the blockback rate used was 50 per cent of the throughput rate, no increase in initial pressure drop occurred through several thousand cycles of filtration and blowback.

One disadvantage in the use of porous filters is that the large filter area required represents a considerable capital investment. In the pilot calciner a filter area of about 1/4 sq ft/(lb)(hr) of uranium trioxide was used. It is apparent that an alternative, low cost method for dust separation would be highly desirable for a plant-scale installation. Accordingly it was decided to investigate the use of an internally mounted cyclone separator.

A 3-inch diameter cyclone was installed inside the disengaging section of the calciner in place of the porous filters, as shown in Figure 20. A tube (dip-leg) extends from the bottom of the cyclone into the fluidized bed to return the separated dust particles. A small filter bank is used for final clean-up of the gas, although in a production plant this might be accomplished in the nitric acid absorption tower.

This technique for dust separation had been tested previously in the original 3-inch diameter fluidized-bed calciner (see ANL-5254, page 98), but was abandoned because of operating difficulties resulting from the small scale of the equipment. In these early experiments the cyclone dip tube had an inside diameter of only 5/8 inch; consequently, the tube frequently became plugged with solids, making the cyclone inoperable. In the present instance the inside diameter of the dip-leg was enlarged to 1 1/8 inches to preclude plugging.

²¹ Pall, D. B., Ind. Eng. Chem. 45, 1197 (1953)

1/2

FIGURE 20
FLUIDIZED-BED CALCINER WITH
INTERNALLY-MOUNTED CYCLONE SEPARATOR
AND SEPARATE FILTER CHAMBER.

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Some preliminary tests have been made to check the operability of the dust separator, but no denitration runs have yet been made with the altered equipment. In the preliminary tests made under simulated run conditions, the dip-leg did not become plugged, and the cyclone appeared to operate satisfactorily. In future runs the efficiency of the cyclone will be determined by measuring the amount of dust passing through to the filter chamber.

2. Reduction

Present practice for the production of uranium dioxide in existing plants calls for the use of either dissociated ammonia or pure hydrogen as the reductant. The use of undissociated ammonia has been considered and investigated in laboratory experiments at various sites,^{22,23} the general conclusion being that the rate of the reduction reaction was somewhat slower when the ammonia was not pre-dissociated. However, these experiments were conducted with the ammonia flowing over a small sample of uranium oxide, and the results may not be directly extrapolable to the case in which the gas passes through a bed of the oxide as in a fluidized bed. Since many of the heavy metals, including uranium, act as catalysts for ammonia synthesis, it was thought that dissociation would occur in the fluidized bed, and that this might increase the rate of reduction.

In order to compare the reduction rates with dissociated and undissociated ammonia two runs were made in the 3-stage fluidized bed reactor under essentially identical conditions except that in one case pure ammonia was used and in the other case a mixture of 75 per cent hydrogen and 25 per cent nitrogen, simulating "cracked" ammonia was used. The results of the two runs are given in Table 37, the average per cent conversion to uranium dioxide being 96.0 for undissociated ammonia and 96.2 for the hydrogen-nitrogen mixture.

Since the conversion was very high in both cases it was not possible to draw a firm conclusion from the results of these two runs. Two additional runs were therefore made at a higher feed rate, so that the conversion would be lower and the results more meaningful. As shown in Table 38 the run made with undissociated ammonia gave very erratic results, the percentage conversion varying from 59 to 86, and averaging 73.6 per cent. Mechanical operability in this run was poor, as evidenced by irregular discharge of product, though no reasons have been found to account for the difficulties. The run with hydrogen-nitrogen mixture gave fairly uniform conversion, averaging 84.0 per cent.

From the results given in Tables 37 and 38 it can be concluded with reasonable certainty that the reaction rate with undissociated

²² Kuhlman, C. W., MCW-217

²³ Goldbeck, C. G., NYO-2043, page 14

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Table 37

COMPARISON OF DISSOCIATED AND UNDISSOCIATED AMMONIA
FOR REDUCTION OF UO_3 IN FLUIDIZED BED

Equipment: 3-inch diameter, 3-stage reactor

Operating Equipment:

Starting Bed	UO_2 (>80% reduced)
Static Bed Depth	4 inches (each stage)
Bed Temperature	575 C
Feed Material	UO_3 from Run 74
Feed Particle Size	minus 40 mesh
Feed Rate	3.3 lb/hr
Inlet Gas Velocity	0.5 ft/sec at 575 C, 1 atm
Solids Retention Time	4 hr (average)

Time After Start (hr)	Conversion (Percentage UO_2)	
	Run 30 Undissociated NH_3	Run 31 Dissociated NH_3 ^a
1.7	95.0	93.1
3.4	96.7	96.5
5.1	97.1	96.1
6.8	<u>94.4</u>	<u>96.0</u>
Average (last 3 samples) ^b	96.0	96.2

^aMixture of 75% H_2 and 25% N_2

^bFirst sample omitted since steady-state not yet attained

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Table 38

COMPARISON OF DISSOCIATED AND UNDISSOCIATED AMMONIA
FOR REDUCTION OF UO_3 IN FLUIDIZED BED

Equipment: 3-inch diameter, 3-stage reactor

Operating Conditions:

Starting Bed	UO_2 (>80% reduced)
Static Bed Depth	4 inches (each stage)
Bed Temperature	575 C
Feed Material	UO_3 from Run 78
Feed Particle Size	minus 40 mesh
Feed Rate	4.8 lb/hr
Inlet Gas Velocity	0.5 ft/sec at 575 C, 1 atm
Duration of Run	6.5 hr
Solid Retention Time	2.8 hr (average)

<u>Time After Start</u> <u>(hr)</u>	<u>Conversion (Percentage UO_2)</u>	
	<u>Run 32</u> <u>Undissociated NH_3</u>	<u>Run 33</u> <u>Dissociated NH_3^a</u>
1	86.0	77.3
2	74.4	89.0
3	83.3	85.0
4	72.8	81.6
5	58.5	80.4
6	<u>79.0</u>	<u>83.9</u>
Average (last 5 samples) ^b	73.6	84.0

^aMixture of 75% H_2 and 25% N_2

^bFirst sample omitted since steady-state not yet attained

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ammonia is at least no higher than with dissociated ammonia and is probably slightly lower. Since the cost of cracking the ammonia is very small, no important advantage is to be gained by eliminating this operation.

3. Hydrofluorination

In previous multistage hydrofluorination runs the bed temperature on each of the three stages was maintained at 450 C, in order to eliminate the temperature variable for comparison of multistage runs with single stage runs. Under these conditions the results showed that two passes through the reactor with a total solids retention time of about 8 hours were required to reduce the unconverted uranium dioxide (AOI) to 1.9 per cent or less. During this quarter a run was made in which a temperature gradient was maintained between the top and bottom of the reactor; that is, the top stage was at 400 C, the middle stage at 500 C, and the bottom stage at 600 C. The results summarized in Table 39 show that the AOI was approximately 1.0 per cent after a single pass through the reactor with an average solids retention time of about 3.9 hours. Thus the solids retention time was less than half that required in previous runs to achieve the same degree of conversion to uranium tetrafluoride.

At the termination of the run, samples from each of the three stages were analyzed to determine the extent of conversion. The results given in Table 39 show that most of the reaction occurred in the top stage (16.7% AOI), and that the material in the second stage (1.6% AOI) was already sufficiently converted to meet the specification of 1.9 per cent maximum AOI. Thus a solids residence time of less than 3 hours was sufficient to achieve the required results in this run.

It is also interesting to note that some reduction of uranium from the hexavalent to the tetravalent state occurred during the hydrofluorination run due to the incorporation of about 10 per cent hydrogen in the inlet gas. The feed to this run contained about 96 per cent uranium dioxide, the remainder being oxides of hexavalent uranium, which after hydrofluorination would be converted to uranyl fluoride. The results in Table 39 show that the uranyl fluoride concentration (water soluble content) was 2.1 per cent in the top stage, 0.4 per cent in the middle stage and 0.1 per cent in the bottom stage. To meet the specification for metal grade uranium tetrafluoride (UO_2F_2 1.0% min, 2.5% max) it will be necessary to decrease the amount of reduction in either the hydrofluorination step or the reduction step.

4. Reduction and Hydrofluorination of Uranium Ore Concentrate

Bench-scale experiments on the production of crude green salt from Rand ore concentrate in a 1-inch diameter, fluidized-bed reactor were described in the previous report (ANL-5529, page 99). One additional batch run was made during this quarter in the 3-inch diameter reactor, primarily for the purpose of preparing crude green salt for laboratory-scale experiments on the fluorination of the tetrafluoride to uranium hexafluoride.

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Table 39

SUMMARY OF MULTISTAGE HYDROFLUORINATION RUN 22Equipment: 3-inch diameter, 3-stage reactorOperating Conditions

Starting Bed	UF ₄ from Run 20B (1.8% AOI)
Static Bed Depth	4 inches (each stage)
Bed Temperatures	top 400 C, middle 500 C, bottom 600 C
Feed Material	UO ₂ from Runs 30 and 31
Feed Particle Size	minus 40 mesh
Feed Rate	1.8 lb/hr
Inlet Gas Composition	64% HF, 10% H ₂ , 26% N ₂
Inlet Gas Velocity	0.45 ft/sec at 600 C, 25 psig
HF/UO ₂ Mole Ratio	2.1 times stoichiometric
Duration of Run	9 hr
Solids Retention Time	3.9 hr (average)

<u>Hours After Start</u>	<u>Product Composition (%)</u>		
	<u>UO₂</u>	<u>UO₂F₂</u>	<u>UF₄</u>
1.5	1.2	0.1	98.0
3.0	0.6	0.2	98.5
4.5	1.0	0.1	98.4
6.0	1.3	0.2	97.8
7.5	0.8	0.1	98.2
9.0	0.8	0.1	99.2

Composition of Solids in Each Stage at End of Run

<u>Stage</u>	<u>UO₂</u>	<u>UO₂F₂</u>	<u>UF₄</u>
Top	16.7	2.1	75.5
Middle	1.6	0.4	95.9
Bottom	0.7	0.1	99.1

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For this run, 2.8 lb of the ore, which had been crushed and screened between 40 and 325 mesh, was charged to the reactor, giving a static bed depth of 9.2 inches. The reduction was performed at 575 C for 2 hours using 3 parts hydrogen to 1 part nitrogen at a velocity of 0.35 ft/sec. The product was hydrofluorinated at 450 C with 50 per cent hydrogen fluoride in nitrogen at a velocity of 0.35 ft/sec. After 1.5 hours of hydrofluorination with 1.5 times the stoichiometric amount of hydrogen fluoride, the AOI was 4.3 per cent. Hydrofluorination was continued for an additional hour using a total of 2.5 times the stoichiometric amount of hydrogen fluoride, at which time the analysis of the product was as shown in Table 40.

Table 40

ANALYSIS OF CRUDE GREEN SALT PREPARED

FROM RAND ORE CONCENTRATE

<u>Analysis</u>		<u>Calculated</u>	
Total U	75.2 %	UF ₄	87.2 %
U (+4)	68.7 %	UO ₂ F ₂	8.4 %
AOI	2.9 %	UO ₂	<u>2.9 %</u> *
		Total	98.5 %

*Maximum value, since AOI may consist partly of impurities.

In this, as well as in previous experiments, the ore concentrate, which was received in the form of pellets about 1/4 inch in diameter, was crushed and screened to obtain a particle size suitable for fluidization. The crushing operation, in which a small jaw crusher was used, produced a large fraction of fine particles smaller than 325 mesh. This fine material, which constituted roughly 40 per cent of the crushed ore, was screened out and rejected from the foregoing experiments, because it was feared that the large percentage of fines would cause channelling and poor fluidization. Subsequent tests in a glass column showed, however, that the inclusion of the fine particle fraction appeared to improve rather than impair the fluidization quality. This unexpected behavior is believed to be due to the low bulk density (1.2 g/cc) of this material as compared to high density uranium trioxide (about 4.0 g/cc) on

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which previous experience was based. The significance of the fluidization tests is that the Rand ore concentrate pellets can be reduced to a fluidizable size merely by crushing the material to pass through a 40 mesh sieve.

5. Green Salt Pilot Plant

Major design work on the green salt pilot plant was completed during this quarter and fabrication of the components has been started. A schematic drawing of the pilot plant is shown in Figure 21. Uranium trioxide from the existing denitration reactor will be fed to the top of the 4-stage, 5-inch diameter, stainless steel reduction column. Each stage of this reactor will have a bed depth of about 10 inches and a freeboard of approximately 14 inches. Bed support will be provided by perforated plates having cone-shaped holes for gas distribution. The solids will be heated by tubular electric heaters bonded to the outer wall by sprayed copper metal.

The uranium dioxide product will overflow into a standpipe from which it will be fed by screw feeder to a gas lift, transporting it to the top of the hydrofluorination reactor. The latter will be similar in design to the reduction heater but will contain 5 stages, 6 inches in diameter, constructed of Monel. Off-gases from the two reactions will be filtered in separate chambers containing porous metal filters. Installation of the pilot plant is scheduled for completion by the end of the next quarter.

One of the problems encountered in the design of bench-scale and pilot-scale facilities involving solids handling is the continuous metering of small quantities of granular solids. Standard commercial equipment, such as rotary valves, screw feeders, and rotating tables, are available only in large sizes handling quantities of solids which are usually too large for experimental studies. To solve this problem several types of miniature solids feeders have been developed, as shown in Figure 22. The modified Jabsco pump has been in use for the feeding of uranium oxides to the 3-inch diameter multistage reactor. The pump has a six-vaned rubber impeller and was found to have a capacity of about 23 ml/rev. For uranium oxide feed rates of 2 to 4 lb/hr the impeller was revolved at 1/6 to 1/3 rpm by means of a Graham variable speed transmission. The chief limitation of this feeder is that it cannot be used at elevated temperatures because of the rubber rotor.

The rotating drum feeder consisted of a 4-inch ID stationary outer shell and an 8-vaned drum rotor. The vanes were approximately 1/8 inch high and the overall length of the shell was about 8 inches. A clearance of about 1/16 inch was maintained between the vanes and the shell wall. The test model was constructed of Lucite but it could be easily fabricated from metal to handle hot solids. In tests with sand the feeder gave satisfactory steady operation.

The most satisfactory solids feeding devices were found to be the miniature screw feeders. These are very compact and can be easily constructed from an ordinary wood drill or auger, together with pipe

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FIGURE 21

SCHEMATIC DIAGRAM OF FLUIDIZED-BED
GREEN SALT PILOT PLANT.

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FIGURE 22
SOLIDS METERING DEVICES.

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fittings and a simple packing gland. The capacities of several auger sizes between 9/16 and 1 inch diameter have been determined and are listed in Table 41. The 9/16-inch screw feeder has been tested with both sand and uranium trioxide and was found to give steady, reproducible feed rates.

Table 41

CAPACITIES OF MINATURE SOLIDS FEEDERS

<u>Type of Feeder</u>	<u>Solids Rate (ml/rev)</u>
Modified Jabsco Pump (Model 903)	23
Rotating Drum	40
Screw Feeders:	
9/16" Drill in 1/2" Pipe	1
3/4" Drill in 3/4" Pipe	3
7/8" Drill in 3/4" Pipe	4.2
1" Drill in 1" Pipe	6

B. Calcination of Reactor Fuel Processing Wastes
(J. Loeding)

Work continued on the design of the shielded fluidized-bed calciner for the experimental processing of radioactive wastes. Fabrication of the reactor and some of the auxiliary components has been started. Installation of this unit is expected to begin during the next quarter.

C. Fundamental Studies
(H. Katz, T. Cannon)

Studies of particle size distribution in partially fluidized beds of mixed particle size have been continued with a view toward defining more precisely the relationship between size distribution and gas velocity on the one hand, and the state of the bed, whether fixed or fluidized, on the other.

A considerable amount of effort was devoted to improvement of the experimental apparatus and technique. Investigation showed that the configuration of the bed is highly dependent on the uniformity of air distribution. Thus, in order to obtain reproducible data, the sintered disk must be perfectly clean and horizontally aligned, and the column

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must be vertically aligned and precisely centered over the disk. An improved apparatus was therefore constructed using a 2-inch diameter lucite column mounted in a frame which permitted easy removal of the column and disk, and replacement in the manner described.

It was also found that complete removal of gelatine from the disk was very difficult and incomplete removal resulted in non-uniform air distribution. Because of this, several attempts were made to freeze beds to which water instead of gelatine had been added. This was not too satisfactory because of the difficulty in cutting the bed. Attempts were also made to add water to the bed, allow it to drain, and cut without freezing, but the bed did not remain sufficiently firm during cutting. The technique finally adopted was to add just enough water to wet the entire bed, and then remove most of the water by means of an aspirator connected to the bottom of the column. Using this technique, the bed remains firm and cuts easily, and the gelatine removal and filtration steps are eliminated.

Additional data were obtained in this manner for the two systems of binary particle size mixtures on which preliminary data were previously reported, and for three other systems. Complete data for the 20 to 40, 140 to 200 mesh system are shown in Figure 23 and for the 40 to 60, 140 to 200 mesh system in Figure 24. The curves in these two figures are representative of the type of data obtained for the various systems studied. In contrast to the behavior of uniformly sized particles, which fluidize at a well-defined minimum velocity, it was found that for mixtures of particles of two sizes, the transition from fixed to fluidized state occurs over a range of gas velocities. Starting with a fixed bed of a homogeneous binary mixture of any given composition, fluidization begins at a gas velocity represented by the lower curve and is complete at a gas velocity represented by the upper curve. In the region between the two curves the lower portion of the bed will be fixed and the upper portion fluidized. Figures 23 and 24 therefore represent "phase diagrams" relating gas velocity to bed composition, which define the three zones corresponding to the fixed bed, the fluidized bed, and a mixture of fixed and fluidized beds.

The resemblance of these curves to a temperature composition diagram for liquid-vapor equilibrium is apparent. Preliminary calculations indicate that tie lines may be drawn and the lever rule applied to obtain the relative weights of the fixed and fluidized sections. Thus, this type of plot may be used to predict the behavior of a bed of any mixture of the two particle sizes involved at any given flow rate, in a manner exactly analogous to the use of a phase diagram, using flow rate as the variable analogous to temperature.

The reason for the unusual shape of the upper curve in Figure 23 is not yet clear but it may be due to the fact that the minimum void fraction for these binary mixtures occurs at a composition of about 55 to 60 per cent of the coarse component (see ANL-5529, page 104). Thus the velocity required for complete fluidization of mixtures of this composition would be lower than might be expected in the absence of the

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FIGURE 23

"PHASE DIAGRAM" RELATING BED
COMPOSITION TO GAS FLOW RATE FOR
BINARY PARTICLE MIXTURES.

Mixtures of 40-60 and 140-200 Mesh Glass Beads

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FIGURE 24

"PHASE DIAGRAM" RELATING BED
COMPOSITION TO GAS FLOW RATE FOR
BINARY PARTICLE MIXTURES.

Mixtures of 20-40 and 140-200 Mesh Glass Beads

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void fraction variation. The dotted portion of the upper curve in Figure 24 may actually show unusual curvature also. What was thought to be scatter of the data in some of the other systems studied now appears to be due to this unexpected shape in the curves. Some additional data on these systems, and on other systems using very narrow particle size cuts, is planned in an effort to determine the cause of this type of behavior. Also, work is in progress on the development of the liquid-vapor analogy as a possible basis for correlation of these curves.

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VI. REACTOR CHEMISTRY — METAL OXIDATION AND IGNITION

(H. Porte, J. G. Schnizlein, R. C. Vogel)

The program directed toward the study of spontaneous ignitions of uranium, thorium, zirconium, and plutonium is proceeding as outlined in ANL-5494, pages 104 to 109.

The vacuum system, furnace assembly and volumetric apparatus have been assembled to measure oxidation rates of metals and have all performed reasonably satisfactorily. Three preliminary runs have been completed.

The oxidation of the polished uranium cubes at 200 C and 200 mm O_2 although initially different (i.e., the first 50 min) showed essentially a constant rate of about 5 micrograms per square centimeter per minute up to 280 min.

Comparison with literature data presented in ANL-5494, page 107 shows this to be comparable with the lowest rates observed by other investigators.

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VII. ANALYTICAL RESEARCH AND SERVICES — DIRECT ASSAY OF MOLYBDENUM AND RUTHENIUM IN TERNARY ALLOYS WITH URANIUM BY X-RAY EMISSION

(D. S. Flikkema and R. V. Schablaske)

It has been found possible to determine quickly the concentration of molybdenum and ruthenium in non-radioactive alloys representative of high burn-up reactor fuels by the method of X-ray emission analysis. Preliminary steps of chemical dissolution and separation are not required. These ternary alloys, up to five weight per cent molybdenum and ruthenium, are being studied (ANL-5529, page 66) because they are considered to represent the equilibrium alloys which will result from cycling through the sequence of uranium fuel operations. It also appears that the equilibrium alloy may be used for the original fuel of the fast reactor to obtain uniform behavior from start-up.

The procedure involves sampling of the ingot by slicing with a silicon carbide wheel at the plane of interest and reducing this surface to the flatness and finish obtained by a five-minute grinding and polishing operation. In the X-ray spectrograph the flat surface is examined for the intensity of its molybdenum and ruthenium K-emission lines with counting times of one to eight minutes for each line. A calibration plot of intensities in counts per second against chemically determined weight percentages is determined and is used for subsequent analyses. Results have been obtained to within ± 2 per cent, relative, in the range 0.7 to 3.8 weight per cent molybdenum and to within ± 10 per cent, relative, in the range 0.9 to 4.6 weight per cent ruthenium.

The chemical method used for ruthenium involves separation of the ruthenium as the volatile tetroxide and subsequent colorimetric determination. Molybdenum is separated from the uranium by ether extraction and ion exchange and is determined by a thiocyanate spectrophotometric method (ANL-5224). Dissolution and chemical analysis of one sample for ruthenium and molybdenum require about one day as compared with about five minutes for surface preparation and one to eight minutes counting time for each emission line of interest in the direct method discussed here. Both chemical methods are stated as reliable to two per cent.

A. Experimental Procedure and Results

The X-ray equipment used is the Norelco spectrograph modified for spectrometric determination of uranium in solution (ANL-5529, page 121), and provided with a topaz analyzing crystal whose interplanar spacing, d , is 1.356 angstroms. The Norelco specimen holder is fitted with a removable aluminum plate having a circular aperture under which the flat specimens are held with a spring clip. The aperture is made to be seven-eighths of an inch or other convenient diameter to insure a constant

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viewing area with specimens of varying size. A Buehler No. 435 silicon carbide wheel is used to cut slices from the alloy ingots. Grinding and polishing to the flatness desired is finished on 20 micron silicon carbide paper.

To obtain solid specimens which would be suitable as known for the initial calibration and also as relatively permanent standards, slices were taken from ingots which had been prepared for other studies and shown to be reasonably homogeneous (ANL-5529, page 66). Both top and bottom surfaces of these slices were polished and then examined in the spectrograph. The line intensities from both surfaces and from selected areas on any one surface varied at most 1.1 per cent for a given slice, with maximum average variation of 0.7 per cent, indicating that the alloys were very suitable. Adjacent slices were then taken for chemical analysis as noted in the following diagram.

The tungsten target primary tube was operated at 50 kilovolts peak and 50 milliamperes, the 50-kilovolt peak setting giving optimum signal to background ratio. A collimator having parallel plates four inches long spaced 0.005 in. apart (ratio 800 to 1) was used between the topaz crystal and a krypton-filled Geiger counter detector. Under these conditions, the results given in Table 42 were obtained. Figure 25 is a calibration plot of intensities in counts per second plotted against chemically determined weight percentages based on the data of Table 42.

B. Discussion of Results

The choice of analyzing crystal is dictated by the wave lengths of the relevant emission lines of molybdenum, ruthenium, and uranium which are

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Table 42

TYPICAL CALIBRATION DATA IN TERMS OF X-RAY LINE INTENSITY vs
WEIGHT PER CENT OF MOLYBDENUM AND OF RUTHENIUM IN TERNARY
ALLOYS WITH URANIUM

<u>Specimen</u>	<u>Composition</u> <u>Weight Per Cent</u>		<u>Counts/second at indicated 2θ angles</u> <u>^a25,600 counts taken</u>			
	<u>Ru</u>	<u>Mo</u>	<u>RuKβ</u>	<u>MoKβ</u>	<u>RuKα</u>	<u>^bUβ_3 + MoKα</u>
			24.35°	26.95°	27.47°	30.35°
Unalloyed Uranium			35	46	38	195
1E	0.883	0.716	44	61	76	237
2E	1.54	1.32	53	72	113	271
5E	2.95	2.76	69	103	168	358
11E	4.62	3.21	85	110	238	384
16E	3.13	3.79	70	120	179	412

^aFor the lowest ratio of total to background counting rate obtained with MoK α , 25,600 counts would permit a probable error of 3.5 per cent; this number of counts at the highest ratio found gives a probable error of 0.6%.

^bThe intensity at 30.35° minus the intensity from unalloyed uranium at 30.35° is considered to be the molybdenum contribution to the intensity at this angle.

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FIGURE 25

TYPICAL PLOT OF X-RAY INTENSITY vs. WEIGHT PERCENTAGE FOR THE DIRECT ASSAY OF MOLYBDENUM AND RUTHENIUM IN TERNARY ALLOYS WITH URANIUM.

characterized in Table 43. Even though the reflection angles from the lithium fluoride analyzer are below the angle (about 22 degrees, as defined by the instrument geometry) at which the fluorescent beam begins to span it fully, the intensities from this analyzer are greater than from the topaz crystal (ANL-5529, page 129). However, the lithium fluoride rocking angle of about 0.3 degrees, i.e., the two-theta angular range over which Bragg reflection occurs for a particular wave length because of crystal structure imperfection, precludes cleanly resolving $\text{MoK}\beta$ from $\text{RuK}\alpha$ and $\text{MoK}\alpha$ - $\text{UL}\beta_3$ from $\text{UL}\beta_1$; accordingly the dispersion and resolving power of the topaz analyzer are required to get both molybdenum and ruthenium quantitatively, as described, in the concentration range of interest. The line resolution achieved is shown by the linear ratemeter scan of Figure 26, obtained from a surface-finished slice containing 3.2 per cent molybdenum and 4.6 per cent ruthenium.

From preliminary study it appears that, up to about four weight per cent of the alloying constituents molybdenum and ruthenium, the presence of one does not disturb the analysis for the other beyond a reproducibility limit of two to three per cent. To maintain these levels of reliability at higher concentrations probably would require a more complicated resort, such as establishing a family of working curves. Also at the low end of the concentration range a systematic study of fixed ruthenium concentrations with variable molybdenum concentrations may give a clue for improving the ± 10 per cent reliability of the ruthenium determination.

Other factors affecting the precision of this "surface analysis" or areal method have not been evaluated experimentally. The degree of surface flatness and finish needed for a given level of precision is not known, but the operation selected as a starting compromise is simple and quick enough. Again, for cases of heterogeneity in the specimen surface, a more representative and reproducible analysis is possible by rotating the specimen in its own plane to integrate out the non-uniformity of the exciting beam. When a background of gamma radiation is present, the relatively sharp energy discrimination permitted by a proportional counter can be exploited.

Table 43

REFLECTION ANGLES FROM LITHIUM FLUORIDE AND TOPAZ ANALYZINGCRYSTALS FOR MOLYBDENUM, RUTHENIUM AND URANIUM X-RAYEMISSION LINES

<u>Emission Line</u>	<u>Wavelength (Angstroms)</u>	<u>2θ Angle Lithium Fluoride (2d = 4.028A^o)</u>	<u>2θ Angle Topaz (2d = 2.712A^o)</u>
RuK β	0.572	16.33 ^o	24.35 ^o
UL γ_1	0.615	17.57	26.21
MoK β	0.632	18.03	26.95
RuKa	0.644	18.37	27.47
MoKa	0.710	20.31	30.35
UL β_3	0.710	20.31	30.35
UL β_1	0.720	20.60	30.79

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FIGURE 26

X-RAY SPECTROGRAM OF AN URANIUM ALLOY
CONTAINING 3.2 PERCENT MOLYBDENUM
AND 4.6 PERCENT RUTHENIUM

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VIII. ROUTINE OPERATIONS

(H. G. Swope)

A. Waste Processing Operations
(J. F. Harast, K. Bremer, L. Marek, R. Kufrin)

The total volume of liquid wastes processed was 28,000 gallons. Of this amount, 24,000 gallons were evaporated, 2,500 gallons were flocculated after adjusting the pH to 12, 620 gallons were sludge from the metallurgical waste treatment plant, which were dewatered on a vacuum filter, 240 gallons were oil and coolant wastes which were absorbed in vermiculite and 130 gallons were very radioactive wastes which were put into concrete.

B. Gamma Irradiation Facility
(J. F. Harast, A. C. Rashinskas, J. B. Roll, T. E. Emmering,
B. Tani, K. Clark)

A total of 1483 samples were irradiated during this quarter as shown below.

Number of Samples Irradiated

	<u>Quartermaster Food and Container Institute</u>	<u>Industry</u>	<u>Educational Institutions</u>	<u>ANL</u>
January, 1956	155	145	0	12
February, 1956	152	237	0	15
March, 1956	<u>433</u>	<u>320</u>	<u>0</u>	<u>14</u>
Total	740	702	0	41

Four new fuel rods from the MTR were received on January 27, 1956 and four more on March 12, 1956. At present the intensity in the various positions within the rack varies from 0.5 to 2×10^6 r/hr.

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C. Dosimetry
(R. Juvinall)

Cadmium sulfide crystals (Clairex CL-1 photocell) have been studied for possible use in the continuous measurement of gamma intensity in the irradiation facility.

Preliminary results have indicated that this method checks the ferrous-ferric chemical dosimetry within ± 10 per cent, in the range studied of 400,000 to 2.5 million roentgens per hour.

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