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

CHEMICAL ENGINEERING DIVISION

SUMMARY REPORT

JANUARY, FEBRUARY, AND MARCH 1953

Stephen Lawroski, Division Director
C. E. Stevenson, Associate Division Director

May 12, 1953

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CHEMICAL ENGINEERING DIVISION

SUMMARY REPORT

FOR JANUARY, FEBRUARY, AND MARCH, 1953

SUMMARY

Determination of Breeding Gain in the Experimental Breeder Reactor

Dissolution of the large number of samples obtained from the natural uranium blanket material of the Experimental Breeder Reactor after approximately 485,000 kw.-hr. of operation has been completed, and analysis of these samples for uranium consumed and plutonium formed is well along. An attempt is being made to distinguish quantitatively between uranium-238 and uranium-235 fission in the blanket area by determining the ratio of ruthenium-106 to cesium-137 in the fission products.

Separation Methods Applied to Halide Systems

Studies of ruthenium decontamination from chloride solutions by co-precipitation with bismuth showed that magnesium was the most effective of a number of reducing agents. A fresh preformed precipitate of bismuth metal when added to ruthenium tracer in hydrochloric acid also reduced and carried considerable ruthenium. The possibility of extracting niobium out of a hydrochloric acid solution of tetravalent uranium was indicated by distribution ratio studies using hexone as solvent, but zirconium was not separated significantly from uranium under the same conditions. Detailed studies of the rate of uranium dissolution in bromine-ethyl acetate mixture were commenced.

Fluoride Volatilization Process Studies

Measurements of the rate of dissolution of uranium in pure bromine trifluoride at 85°C. have yielded values of 0.36 millimoles/(sq.cm.)(hr.) under static conditions, and 0.57 millimoles/(sq.cm.)(hr.) with rapid stirring, in short time tests. These data are being extended to other temperatures and to bromine trifluoride solutions of other process reagents.

Bromine trifluoride, water, and aqueous potassium bifluoride were not effective in removing activity from coupons of Monel or nickel contaminated during the dissolution of irradiated uranium in bromine trifluoride. Versene at pH 8.5 was only moderately effective for this purpose but was more effective at pH 4.5. Over 99 per cent of the alpha, beta, and gamma activity present on such coupons was removed by two washes with citric acid, aluminum nitrate, aluminum sulfate, or zirconium sulfate solution. Only minor variations in the relative removal of various specific fission products and plutonium were observed.

Refractive indexes at 70°C. were determined for various mixtures of bromine pentafluoride and uranium hexafluoride. The kinematic viscosities of bromine tri- and pentafluorides at 25°C. were determined to be 0.81 and 0.26 centistokes, respectively.

At least 98 per cent of the uranium present in samples of fuel alloys (zirconium-tin-uranium) was volatilized by treatment of the dried residue from concentrated hydrofluoric acid dissolution of the alloy with bromine trifluoride at 125°C. In an experiment with irradiated material, a beta decontamination factor of about 10^5 was noted for the uranium in the distillate.

Construction of equipment for uranium dissolution and decontamination on a pilot-plant scale is well under way.

Processing of Uranium at Elevated Temperatures

Theoretical studies have indicated that substantial uranium decontamination might be effected by fluxing the molten metal with uranium trichloride. It is planned to investigate this and other methods of melt processing in recently-constructed equipment. Studies of zirconium tetrachloride reduction by uranium in LiCl-KCl melts indicate that the dichloride is produced which should be readily reduced to metal and deposit with uranium in an electro-deposition process.

Development of Analytical Methods

The feasibility of thiocyanate colorimetric methods for the estimation of a variety of heavy metals which may be incorporated with fissionable material in reactor fuel alloys was demonstrated. The use of a thiocyanate procedure to elucidate the ionic state of titanium in aqueous solution was also indicated.

A well-type scintillation counter was developed for direct use with liquid or solid samples. The instrument can be applied to beta particle measurements for energies over 1.0 m.e.v. and to counting of gamma rays with energies above 0.05 m.e.v. Limited discrimination in counting sources of mixed energy levels is possible.

Processing of Radioactive Laboratory Wastes

To demonstrate the feasibility of continuous operation of the dry active waste incinerator, a 118-hour run was made. A total of 1150 cu.ft. of active waste was burned. There was no evidence of activity build-up in the gas cleaning components. In another series of tests in which mixed fission product activity was added to the feeds, a maximum decontamination factor of about 10^7 was achieved. This was the product of factors of 100 to 1000 achieved in (1) the combustion zone, (2) the scrubbing components, and (3) the final paper filter.

The optimum flow rate for a mixed bed ion exchange unit used for waste decontamination was determined to be about 2 gal./((cu.ft.)(min.)). A procedure was developed for satisfactory regeneration of laboratory-scale mixed bed columns. The addition of powdered iron to a mixed bed column improved decontamination from ruthenium considerably in processing wastes containing mixed fission products.

I. DETERMINATION OF BREEDING GAIN IN THE EXPERIMENTAL BREEDER REACTOR

(M. Levenson)

In order to determine the plutonium production and uranium consumption patterns in the Experimental Breeder Reactor, fissionable and fertile material in the entire reactor was sampled after 485,000 kw.-hr. of operation. The uranium-235 consumption in the fuel, both by capture and fission, was determined and reported last quarter (ANL-4979, page 11). The effort during this period has been on the determination of the plutonium breeding patterns and uranium consumption in the blankets. Because a large per cent of the power (25 to 30 per cent) is generated in the blankets, it is necessary to determine the ratio of uranium-235 fissions to uranium-238 fissions in order to correct for uranium-235 consumed in that area. This is being done by determining the ratio of ruthenium-106 to cesium-137 in the fission product.

The analysis of reactor operation through chemical methods is essentially complete except for the determination of the plutonium quality pattern. Samples of plutonium from various parts of the reactor have been isolated, and the 239/240 ratio will be determined by mass spectroscopy.

A. Dissolution of Natural Uranium Blanket Samples (W. Seefeldt, A. Shor, P. D. Franson)

Approximately 700 pounds of natural uranium blanket material from over 60 points in the reactor were dissolved and are being assayed for plutonium. Samples were obtained from core rod end sections, inner blanket rods, outer blanket bricks, and from the lower blanket cup. Bricks were sampled both by dissolving completely after sectioning and by obtaining drillings at appropriate points. Results of analyses for plutonium formed will be reported when the data are complete and are reconciled.

B. Determination of Uranium Fissioned in EBR Breeding Blankets (E. H. Turk, R. C. Vogel)

1. Determination of Total Fissions in Breeding Blanket

The uranium destroyed by fission in the inner and outer natural uranium breeding blankets of the EBR has been determined by the cesium-137 radiochemical procedure which was used to analyze the enriched uranium core. This procedure was described in reports ANL-4720, page 21, and ANL-4764, page 39.

Typical data for uranium destroyed by fission in the inner and outer breeding blankets are summarized in Table 1. It will be noted that 0.002 to 0.007 per cent of total uranium was consumed in the inner blanket compared to 0.0006 to 0.0016 per cent consumed in certain of the outer blanket bricks.

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Table 1

URANIUM DESTROYED BY FISSION IN SAMPLES FROMEBR BREEDING BLANKET

Estimated by determination of cesium-137
(ANL-4720, p. 21, and ANL-4764, p. 39).
Samples removed from reactor after 485,000
kw.-hr. of operation.

<u>Type and Location of Samples</u>	<u>Uranium Destroyed by Fission, per cent ($\times 10^5$)</u>
Inner Blanket Rod from Hole No. 247 (12.7 cm. from axis)	68.4
Inner Blanket Rod from Hole No. 283 (15.24 cm. from axis)	40.0
Inner Blanket Rod from Hole No. 325 (17.78 cm. from axis)	26.9
Inner Blanket Rod from Hole No. 343 (17.60 cm. from axis)	23.6
Outer Blanket Brick D-109, Inner Third	15.3
Outer Blanket Brick D-109, Center Third	7.0
Outer Blanket Brick D-109, Outer Third	6.2
Outer Blanket Brick NN, Inner Third	16.0
Outer Blanket Brick NN, Center Third	7.3
Outer Blanket Brick NN, Outer Third	8.5

2. Method Development for Distinguishing Between Uranium-235 and Uranium-238 Fissions

A considerable fraction of the power generated in the EBR is developed from fission occurring in the natural uranium breeding blankets. The question arises as to the distribution of this power between uranium-238 fission and uranium-235 fission as the uranium-235 consumed in this area may constitute a significant fraction of the total amount of uranium-235 destroyed in the reactor.

A radiochemical method, suggested by Steinberg of the Chemistry Division, is being developed to distinguish uranium-238 fission from uranium-235 fission. This method is based on the large differences in the ratio of ruthenium-106 to cesium-137 produced when uranium-235 and uranium-238 atoms undergo fission. This difference results from the fact that the cesium isotope is on a relatively flat portion of the curve relating yield on fission to isotope mass, whereas the ruthenium isotope is at a position on the same

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curve where the yield is rapidly changing with isotope mass and is affected by the mass of the atom fissioning. The $\text{Ru}^{106}/\text{Cs}^{137}$ atomic ratio, based on published fission yields for these two uranium isotopes, should change from 0.4 for uranium-238 to 0.075 for uranium-235, giving quite a sensitive indicator as to the uranium isotope undergoing fission. By measuring the $\text{Ru}^{106}/\text{Cs}^{137}$ ratio for a uranium specimen which has been irradiated with neutrons which have caused both uranium-235 and uranium-238 atoms to fission, it should be possible to determine the fraction of the total fissions which occurred in uranium-235 atoms.

The accuracy of the published fission yields is quoted as only ± 10 per cent; thus results from the method based on the $\text{Ru}^{106}/\text{Cs}^{137}$ ratio from published fission yields could be in large error. To eliminate the need for more accurately determined fission yields, a calibration experiment is being conducted to measure experimentally in a standard manner the cesium-137 and ruthenium-106 radioactivities for three types of uranium fission: (1) fast neutron fission of uranium-235, (2) thermal neutron fission of uranium-235, and (3) fast neutron fission of uranium-238. Irradiations under these three conditions will calibrate the equipment for measuring the radioactivity ratio of $\text{Ru}^{106}/\text{Cs}^{137}$ for the three types of uranium fission. If this ratio is the same for fast and thermal neutron fission of uranium-235, the method should be useful for estimating the relative uranium-235 and uranium-238 fissions in a uranium specimen which has undergone a mixture of the three types of uranium fission referred to above. If the $\text{Ru}^{106}/\text{Cs}^{137}$ ratio is not constant for fast and thermal fission of uranium-235, it may still be used for estimating the 235/238 fission ratio if the $\text{Ru}^{106}/\text{Cs}^{137}$ ratio is known approximately for the neutron spectrum under consideration.

The cesium-137 and ruthenium-106 radioactivities are isolated using carrier techniques and are measured by beta counting using an Amperex 100C Geiger tube. The Geiger tube is mounted in a standard shelf assembly-tube mount. All samples are placed on the second shelf for counting. The ruthenium-106 beta activity is measured by the difference in counting rate of the sample through two separate aluminum absorbers, 164 mg./sq.cm. and 2050 mg./sq.cm. This counting arrangement corrects for any 42-day ruthenium-103 which may be present in the sample. The cesium samples are counted with no added absorber; the cesium activity from the EBR samples will be entirely cesium-137 because the samples have cooled at least 240 days so that the one possible contaminant, 13-day cesium-136, will have decayed out.

The value obtained is the ratio of activities, in ct./(min.)(ml.), due respectively to ruthenium-106 and cesium-137, corrected for background count, chemical yield, and geometry. This differs from the previously-quoted ratio of atoms of ruthenium-106 to cesium-137 resulting from fission by the ratio of the specific activity of these isotopes. Values thus far obtained for the $\text{Ru}^{106}/\text{Cs}^{137}$ activity ratio in uranium samples removed from various parts of the EBR are summarized in Table 2. These values cannot be used to estimate relative fissions in uranium-235 and uranium-238 pending completion of the calibration data. It will be noted, however, that the $\text{Ru}^{106}/\text{Cs}^{137}$ activity ratio found for enriched uranium samples was of the order of 2.2 whereas the ratios found in natural uranium samples ranged from 2.9 to 8.0. Low values for this ratio for natural uranium were found in material obtained from outer blanket areas, suggesting that a relatively greater proportion of the fissions occurring in such areas was of uranium-235.

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Table 2

Ru¹⁰⁶/Cs¹³⁷ ACTIVITY RATIO IN EBR URANIUM SAMPLES

<u>Location Where Sample Obtained</u>	<u>Radial Distance from Reactor Center Line, cm.</u>	<u>Ru¹⁰⁶/Cs¹³⁷ Activity Ratio</u>		
<u>Enriched U Rods</u>				
Hole No. 1	0	2.29		
Hole No. 169	8.8	2.23		
<u>Natural U Rods</u>				
Hole No. 247	12.7	6.95		
Hole No. 283	15.2	6.53		
Hole No. 325	17.8	6.55		
Hole No. 343 -1*	17.6	6.35		
Hole No. 343 -2*	17.6	7.53		
Hole No. 343 -3,4*	17.6	7.92		
Hole No. 343 -5*	17.6	7.09		
<u>Natural U Cup</u>				
Sample No. 1	-	5.77		
Sample No. 2	-	5.80		
<u>Natural U Bricks</u>				
Composite of D-109, D-138, NN, D-160, D-165, and D-186	-	5.62		
		<u>Outer Third</u>	<u>Middle Third</u>	<u>Inner Third</u>
No. D-88			4.79	-
No. D-109		3.46	4.94	5.68
No. NN		3.11	-	5.68
No. D-160		2.91	-	-

*No.'s following dash refer to vertical position
of pellets in fuel rod (-1, at top)

III. SEPARATION METHODS APPLIED TO HALIDE SYSTEMS

(M. Beederman, H. Evans, H. M. Feder, G. Kesser,
R. Larsen, E. Reilly, R. Schablaske)

Studies of methods of recovering and decontaminating reactor fuels after dissolution as chlorides or bromides have included tests of ruthenium decontamination by co-precipitation with bismuth, niobium decontamination by extraction in the presence of tetravalent uranium, and an investigation of the mechanism of dissolution of uranium in bromine-ethyl acetate.

A. Ruthenium Decontamination Studies

Investigation of ruthenium decontamination by co-precipitation with bismuth has been directed toward developing the mechanism of this process in order that conditions may be found for increasing the decontamination factor above the present achievable level of about 500. A study of a variety of reducing agents (chiefly metallic in nature) showed that with a single strike any agent capable of reducing bismuth (and, necessarily, ruthenium) caused appreciable removal of ruthenium, although magnesium appeared to be most efficient, as indicated in Table 10. Hydroxylamine, hydrazine, formaldehyde, formic acid, and sodium azide were incapable of effecting reduction.

Table 10

COMPARISON OF REDUCTANTS IN CO-PRECIPITATION OF RUTHENIUM WITH BISMUTH

Conditions: 0.1 M UCl_4 ; 0.02 M BiCl_3 ;

3×10^5 ct./ (min.) (ml.) of Ru

Tenfold excess of reductant. CO_2 atmosphere.

<u>Reductant</u>	<u>Temperature, °C.</u>	<u>Per Cent Removal of Ru</u>
Mg	95	96.9, 98.5
CrCl_2	95	82
VCl_2	95	80
NaBH_4	95	89
Na(Hg)_x	95	87
Mg	10	90, 91
Al	10	71
U	10	71
Zn	10	63

Since metallic bismuth itself reduces ruthenium chloride in solution in macroscopic concentration to the metal, it was of interest to investigate the action of bismuth on tracer ruthenium concentrations.

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Freshly precipitated bismuth was suspended in 10 ml. of 1.0 M hydrochloric acid at 100°C. Ruthenium tracer was added, and the supernatant solution was examined. In an immediate sample, 36 per cent of the activity had disappeared, whereas after 1 and 3 hours the removal of ruthenium had increased to 61 and 78 per cent, respectively. To remove the possibility that adsorption without reduction was taking place, studies were made on the adsorption of tracer by glass surfaces. Ruthenium chloride tracer solutions, either as received or after refluxing in constant boiling hydrochloric acid, were diluted to various acidities and allowed to percolate slowly through fritted glass discs. Down to 0.1 N acid solutions no perceptible amounts of activity were found to be retained by the surface, indicating that the tracer is not radiocolloidal at acidities higher than this. Further studies will be conducted with metallic bismuth of high specific area in the absence and presence of additional reductant or carrier since such a method promises to eliminate the hydrogen evolution hazard connected with the use of magnesium or other metallic reductants.

Evidence now available shows that ruthenium which has been co-precipitated with bismuth desorbs slowly. After precipitating bismuth with magnesium in the usual way, the supernatant was counted after various times of contact. As shown in Table 11, ruthenium in solution increased in 24 hours to a value about six times that found immediately after precipitation. If more than one strike with bismuth is made, it is obviously advantageous to remove the previous precipitate before continuing.

Table 11

DESORPTION OF RUTHENIUM CO-PRECIPTATED WITH BISMUTH

Conditions: 0.2 M UCl_4 ; temperature, 95°C.

<u>Time, hours</u>	<u>Ru Tracer in Solution, ct./(min.)(ml.)</u>
0 (before precipitation)	31.0×10^4
0 (after pptn. with 40 mg. Bi)	0.27×10^4
1	0.99×10^4
2	1.54×10^4
3	1.57×10^4
24	1.77×10^4

An experiment was devised to determine whether or not co-precipitation of ruthenium was effected mainly by the initial bismuth precipitated. Previous experimentation had demonstrated that when magnesium is added to an

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acid bismuth solution the reduction of bismuth and hydrogen ions is competitive and bismuth is not completely precipitated until the acid is exhausted. To a solution containing 1 millimole uranium(IV), 12 millimoles hydrogen ion, and 0.2 millimole bismuth ion at 100°C., magnesium was added in millimole portions. After each dissolution the precipitated bismuth was removed, and the supernatant counted for ruthenium activity. The results of two sets of experiments are shown in Figure 4, which demonstrates that the initial portions of precipitated bismuth are only slightly more effective in ruthenium removal than subsequent ones.

B. Zirconium-Niobium Decontamination Studies

The stability of tetravalent uranium in halide media and its relative non-extractibility into organic solvents indicate that it may be possible to extract certain fission products away from the bulk constituent. Initial experiments along these lines have been done with zirconium-niobium tracer in secular equilibrium. In these tests 0.2 M uranium tetrachloride solution in 6 and 8 M hydrochloric acid containing zirconium-niobium tracer was equilibrated with hexone and with diluted TBP. Gamma scintillation counting was employed to determine the gamma activity of each phase, and zirconium was determined in the aqueous phases. As shown in Table 12, a niobium separation factor of over 150 was obtained using hexone and 6 M hydrochloric acid. Smaller separation factors were obtained with TBP. The estimated errors (± 10 per cent for the zirconium distribution ratios and ± 20 per cent for the niobium distribution ratios) are not large enough to cast doubt on the attractive possibility of niobium decontamination from uranium(IV) by a few stages of extraction and scrubbing. Decontamination of zirconium in the same process will require the development of a suitable organic-soluble complexing agent.

Table 12

DISTRIBUTION OF U(IV), Zr, AND Nb IN CHLORIDE MEDIA

Conditions: initial UCl_4 , 0.2 M; Zr-Nb tracer,
 10^6 ct./ (min.) (ml.)

Composition	Solvent	Distribution Ratio, organic/aqueous, for:			Separation Factors	
		U	Zr	Nb	Zr/U	Nb/U
6 M HCl	Hexone	<0.01	0.073	1.5	>7	>150
8 M HCl	Hexone	0.13	0.19	50	1.5	380
4 M HCl	30 vol. per cent TBP-Amsco	0.040	0.039	2.5	1.0	62
6 M HCl	30 vol. per cent TBP-Amsco	1.22	0.90	7	0.7	5.7

FIGURE 4.
STEPWISE REMOVAL OF RUTHENIUM BY
PRECIPITATION WITH BISMUTH.

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C. Bromine-Ester Dissolution Studies

Experiments to clarify the rate and mechanism of metal dissolution in bromine-ethyl acetate mixtures have been begun. Only preliminary data are available. They indicate that the reaction of bromine with ethyl acetate alone at reflux temperature is autocatalytic but is not light sensitive. In the presence of uranium the consumption of bromine is apparently second order in bromine, and the reaction with ethyl acetate does not become appreciable until the metal is nearly exhausted. The products of the reaction will be isolated and further characterized.

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IV. FLUORIDE VOLATILIZATION PROCESS STUDIES

Laboratory work during the quarter has been concerned with uranium dissolution kinetics, dissolver decontamination, phase equilibria, analytical methods development, process feasibility demonstrations on STR fuel elements, and corrosion testing. Progress in the laboratory has been seriously hampered by determination that the particular type of silver solder used in much of the existing equipment is attacked sufficiently rapidly by bromine trifluoride as to render its use undesirable in most applications. In addition to corrosion problems, this results in contamination of interhalogen solutions by silver fluoride. Hence, most of the major pieces of apparatus are currently being modified to all-nickel or Monel construction.

The effectiveness of several possible dissolver wash solutions in removing plutonium and fission product fluorides from nickel and Monel coupons has been studied in considerable detail. The distribution of activity between the liquid and vapor spaces of the dissolver has also been determined through coupon contamination measurements. Preliminary measurements on the rate of solution of uranium in bromine trifluoride with stirring have been made. Exploratory studies on the possibility of recovering uranium from STR-type fuel elements through dissolving the alloy in hydrofluoric acid solution and subsequent fluorination with bromine trifluoride have yielded encouraging results. Vapor-liquid equilibrium work on the system bromine trifluoride-bromine pentafluoride is awaiting further tests to assure proper operation of the Othmer still. The determination of the miscibility gap in the liquid-liquid system bromine-bromine trifluoride has been completed. Refractive index measurements on the system bromine pentafluoride-uranium hexafluoride at 70°C. have been finished. The viscosities of bromine trifluoride at 25°C. and 75°C. and bromine pentafluoride at 25°C. have been determined. Qualitative corrosion tests have been made with a variety of silver solders in bromine trifluoride. Preliminary studies of corrosion by aqueous aluminum sulfate solutions on Monel have been made.

Fabrication of process vessels for the pilot plant installation is substantially complete following a period of perfection of welding technique and radiograph analysis. Installation of equipment in the cell area is under way. Instruments, valves, scales, etc., are now on hand, and inspection, cleaning, and calibrating operations are being completed. The panel board is being fabricated, and installation will begin shortly.

Tests have been completed on the heat transfer characteristics of interhalogen vapor condensers fabricated by water coil and metal spraying techniques. A brief investigation was made of the effect of interhalogen and hydrogen halide vapors in air on CWS paper filters.

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A. Laboratory Investigations (D. Fairgrieve, J. Fischer, J. Fudala, F. Linzer, R. Long,* W. Ludewig,** J. Schnizlein, L. Stein, R. Steunenberg, H. Tyler, R. C. Vogel, W. Wade:

1. Uranium Dissolution Studies

a. Experiments in Laboratory-Scale Dissolver

Three dissolutions of irradiated uranium have been carried out in the 2.3-liter laboratory dissolving vessel described in ANL-4979, page 81. As samples obtained from these tests yielded precipitates upon hydrolysis, the fate of plutonium present could not be determined, and more runs are necessary to outline the behavior of plutonium. However, further runs await equipment changes due to difficulties arising from the corrosion of silver-soldered connections in the liquid lines and sampling system. The silver fluoride in the dissolver liquid leads to a precipitate of silver bromide when the samples are hydrolyzed in aqueous solution, making reliable radio-chemical analysis virtually impossible. These lines and the sampling system are now being so modified as to eliminate silver solder in the system.

b. Kinetics of Uranium Dissolution in Interhalogen Systems

The small-scale apparatus for studying the rate of solution of uranium in interhalogens has been put into operation, and some tentative results are available. At $85 \pm 1^\circ\text{C}$. the initial rate of dissolution of uranium metal in pure bromine trifluoride was 0.36 millimoles/(sq.cm.)(hr.) in static tests and 0.57 millimoles/(sq.cm.)(hr.) at a stirring velocity at the metal solution interface of about 3800 cm./min. The reproducibility of the results is approximately 0.03 millimoles/(sq.cm.)(hr.) in both cases. Estimates of the absolute accuracy must await further work. Stirring was found to increase the rate of dissolution and to decrease the amount of fluoride film found on the sample at the end of the run. The solution rates are calculated from the weight loss of the uranium sample during the run. The above results are based on 15-minute exposures.

Work is under way to investigate the effect of the following variables on solution rates: metallurgical character of the uranium, temperature, stirring speed, concentration of bromine in the bromine trifluoride, and time of exposure. The present intention is to measure the rates over a sufficiently small time interval such that the composition of the solution will not be changed appreciably.

c. Preparation of Bromine Monofluoride

The basic chemistry involved in the dissolution of uranium in bromine fluorides is somewhat uncertain. It is believed that some bromine monofluoride may be formed as a product along with bromine. The former compound has never been isolated in pure form. An attempt is being made to

*On loan from University of Michigan on participating institution basis.

**On loan from California Research and Development Corporation.

prepare it by the following reactions:

- (1) $\text{Br}_2 + \text{F}_2$ under mild conditions;
- (2) $\text{Br}_2 + \text{BrF}_3$;
- (3) $\text{Br}_2 + \text{BrF}_5$;
- (4) $\text{KBr} + \text{BrF}_3$;

The compound is reported to be unstable, disproportionating rapidly at room temperature. Each of the above reactions has yielded a small amount of volatile material, but proof of composition awaits further work.

d. Metal Ignition Studies

Apparatus is being constructed for studying reactions of the following materials at elevated temperatures:

- (1) $\text{U} + 2\text{BrF}_3 \longrightarrow \text{UF}_6 + \text{Br}_2$ (or BrF) ;
- (2) $\text{U} + 3\text{F}_2 \longrightarrow \text{UF}_6$;
- (3) $2\text{Al} + 2\text{BrF}_3 \longrightarrow 2\text{AlF}_3 + \text{Br}_2$;
- (4) $2\text{Al} + 3\text{F}_2 \longrightarrow 2\text{AlF}_3$;
- (5) $\text{U} + 3\text{ClF}_3 \longrightarrow \text{UF}_6 + 3\text{ClF}$ (or Cl_2) .

It is known that some of these reactions may become violent under certain conditions, and the purpose of the study is to establish limits on conditions for the safe use of metallic uranium and aluminum in these systems.

2. Dissolver Decontamination Studies

Data have been obtained on the efficacy of various aqueous solutions in removing the residual plutonium and fission product fluorides which are deposited on the dissolver walls when an irradiated slug is dissolved in bromine trifluoride. The experiments described below also clarify the spatial distribution of plutonium and fission products in the dissolver. Although preliminary results were given in the last quarterly report, the entire experiment will be described here for unity.

Coupons of 50-mil Monel, 130-mil Monel, 5-mil nickel, 65-mil aluminum, and 10-mil platinum, each 5/8-inch square, were suspended on a 1/16-inch nickel wire rack in the dissolver during the dissolution of Clinton slug slices in bromine trifluoride. Some coupons were positioned vertically and others horizontally in the first experiment, with less elaborate arrays in later ones. The rack was set on the dissolver bottom such that some coupons were immersed in the dissolver solution while others were in the vapor space.

Three dissolutions were made (Runs 5, 6, and 7) under the conditions shown in Table 13. After each dissolution was complete, the active inter-halogen solution was removed from the dissolver. In Run 5 the entire rack

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of coupons was rinsed with fresh bromine trifluoride while still in the dissolver. In Runs 6 and 7 the rack was removed from the dissolver, and the coupons were rinsed individually to prevent cross contamination. This rinse removed traces of uranium hexafluoride remaining on the coupons.

Table 13

DISSOLUTION CONDITIONS FOR ACTIVE RUNS - MONEL DISSOLVER

Slices of Clinton-irradiated slugs, irradiated 162 days, cooled 300 days, used.

	<u>Run 5⁽¹⁾</u>	<u>Run 6</u>	<u>Run 7</u>
Initial Composition of Dissolver Solution			
Mole Per Cent, BrF ₃	100	100	90
Mole Per Cent, Br ₂	0	0	10
Moles BrF ₃ /mole Uranium ⁽²⁾	19	18	17.8
Uranium Charge, grams	88.7	98.6	101.8
Mean Temperature, °C.	90	95	80
Maximum Pressure, mm. Hg	4750	3000	2760
Reaction Time, hours	5.5	5.5	2.8
F ₂ Added During Dissolution, per cent theoretical	22 ⁽³⁾	0	0
Coupon Washing Procedure in BrF ₃	in dissolver	external	external

(1) Final dissolver solution contained traces of platinum due to dissolution of platinum coupons.

(2) About 400 ml. of BrF₃ at approximately 70°C.

(3) The fluorine was later found to contain 22 per cent non-condensibles, giving rise to the high pressure and preventing further additions of fluorine.

In Run 5 the dissolver solution was sampled; in Runs 6 and 7 both solution and vapor samples were taken. These samples were hydrolyzed in aluminum nitrate solution in preparation for radiochemical analysis. It was found that most of these solutions contained precipitates which would render radiochemical analysis impractical. These precipitates were identified as silver bromide, and appeared to have originated in the corrosion of silver solder by interhalogens.

After the coupons were rinsed with bromine trifluoride, they were counted for alpha, beta, and gamma activity. Gamma scans with a scintillation spectrometer were also conducted. The alpha counting was done on a Bradley Proportional Counter using 90 per cent argon-10 per cent methane gas and operating at 1100 volts.

For beta counting of the 130-mil Monel coupons, a halogen-filled G-M tube (window thickness, 1.4 g./sq.cm.) was used. Due to the high activity, a 1/2-inch lead shield (15.25 g./sq.cm.) with an 0.081-inch diameter hole drilled through was placed on the second shelf, and samples were counted on the third, fourth, or fifth shelf, depending on the activity. Proper geometry factors were obtained by use of a 25.8-mg. uranium standard and by the use of the average of 12 coupons. Some samples of low activity were counted without the lead shield in the usual manner. All values are corrected to top shelf, no absorber.

Gamma activity on the 50-mil Monel coupons was counted on a scintillation spectrometer (single channel pulse analyzer) for both the scan and the integrated value. Due to the high activity of the samples, risers were added so that the distance from the sample to the crystal could be varied. A 1775 mg./sq.cm. carbon absorber was used. Each position was checked with cesium standards, and the proper factors obtained. For the integrated count a 10-volt window was used up to 0.1 m.e.v. For the scans, a 2-volt window was used from 0.01 to 0.82 m.e.v.

a. Distribution of Activity in Dissolver

After the bromine trifluoride rinse in the dissolver of the coupons contaminated in Run 5, they were allowed to dry and were counted. The platinum coupons were not included because in the liquid phase they were dissolved, and when exposed in the vapor space, were badly corroded. Results for the Monel coupons only, tabulated according to coupon position in the dissolver, are given in Table 14 and graphically illustrated in Figure 5. Some general observations from these data may be summarized as follows:

- (1) The liquid phase coupons showed about 100 times the activity of those in the vapor phase. Some of the contamination on the vapor phase coupons may have been caused by rinsing the liquid and vapor coupons in the same bromine trifluoride, or by spray carried into the vapor space during the dissolution. For these reasons it is felt the alpha activity on the vapor-exposed coupons does not necessarily indicate volatile plutonium formation. In Runs 6 and 7 the coupons were rinsed separately so that contamination of coupons exposed to the vapor presumably occurred only by entrainment during dissolution.
- (2) The horizontal coupons appeared to be slightly more active than the vertical ones, but not significantly different.
- (3) No real difference in activity was noted between the upper and lower faces of the coupons in the liquid phase,

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Table 14

DISTRIBUTION OF ACTIVITY ON MONEL COUPONS EXPOSED IN RUN 5

Clinton-irradiated (162 days) slug slices (88.7 g.), cooled 300 days, were dissolved at approximately 90°C. with fluorine added (22 per cent of theoretical) to the initial 400 ml. BrF₃.

Coupon Thickness, (1) mils	Coupon Location			Total Ct./Min. Per Coupon		
	Inches Above Dissolver Bottom	Orientation	Phase	alpha x 10 ⁻³	beta x 10 ⁻⁵	gamma (2) x 10 ⁻⁵
130	0.3	Vertical	Liquid	53	295	-
130	0.75	Horizontal	Liquid	82	332	-
130	1.3	Vertical	Liquid	68	328	-
130	1.8	Horizontal	Liquid	82	401	-
130	2.4	Horizontal	Vapor	2.4	33	-
130	3.3	Vertical	Vapor	0.49	5.1	-
130	3.8	Horizontal	Vapor	0.62	7.0	-
130	4.3	Vertical	Vapor	0.33	3.0	-
130	4.8	Horizontal	Vapor	0.27	2.2	-
130	5.4	Horizontal	Vapor	0.064	0.66	-
50	0.3	Vertical	Liquid	15	-	2.2
50	0.9	Horizontal	Liquid	27	-	2.3
50	1.3	Vertical	Liquid	18	-	1.7
50	1.9	Horizontal	Liquid	16	-	1.4
50	2.5	Vertical	Vapor	0.62	-	0.087
50	3.3	Vertical	Vapor	0.20	-	0.048
50	3.9	Horizontal	Vapor	0.21	-	0.043
50	4.3	Vertical	Vapor	0.14	-	0.026
50	4.9	Horizontal	Vapor	0.11	-	0.024
50	5.5	Horizontal	Vapor	0.15	-	0.026

(1) The 130-mil coupons are about four times rougher than the 50-mil coupons as shown by a Brush surface analyzer.

(2) Total counts divided by two so that counts per side are tabulated.

FIGURE 5.

DISTRIBUTION OF ACTIVITY ON MONEL
COUPONS EXPOSED IN Run No. 5.

130-mil coupons used for alpha and beta
counts; 50-mil coupons for gamma counts

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indicating that settling of active fluorides under these conditions may not be an important factor.

As regards the other metals exposed, the aluminum coupons were somewhat more active, and the nickel foil coupons considerably less active than the Monel ones. These coupons were counted for alpha and gamma activity only. Some correlation was found between activity and surface roughness of the coupons. Data for nickel and aluminum coupons are given in Table 15.

Table 15

DISTRIBUTION OF ACTIVITY ON NICKEL AND ALUMINUM COUPONS

EXPOSED IN RUN 5

Clinton-irradiated (162 days) slug slices (88.7 g.), cooled 300 days, were dissolved at approximately 90°C. with fluorine added (22 per cent of theoretical) to the initial 400 ml. BrF_3 .

Coupon Thickness, mils	Coupon Location			Total Ct./Min. Per Coupon	
	Inches Above Dissolver Bottom	Orientation	Phase	alpha $\times 10^{-3}$	gamma $\times 10^{-5}$ (1)
<u>Nickel Coupons</u>					
5	0.3	Vertical	Liquid	4.8	0.51
5	1.3	Vertical	Liquid	3.6	0.34
5	2.0	Horizontal	Liquid	3.5	0.39
5	2.6	Horizontal	Vapor	0.56	0.091
5	3.3	Vertical	Vapor	0.13	0.022
5	4.3	Vertical	Vapor	0.077	0.015
5	5.0	Horizontal	Vapor	0.021	0.029
<u>Aluminum Coupons</u>					
65	0.3	Vertical	Liquid	75	4.9
65	1.3	Vertical	Liquid	73	5.7
65	2.1	Horizontal	Liquid	18	2.0
65	2.7	Horizontal	Vapor	0.69	0.11
65	3.3	Vertical	Vapor	0.40	0.055
65	4.3	Vertical	Vapor	0.27	0.045
65	5.1	Horizontal	Vapor	0.18	0.028

(1) Total counts divided by two so that counts per side are tabulated.

The gamma scans of the coupons show, unambiguously, only the presence of rare earths, zirconium, and niobium, although indications are

that all the fission products are present on the coupons. Gamma scan plots are given later in the section on decontamination washes.

Assuming that the dissolver walls are contaminated in the same manner as the rough coupons, one can approximate that 10 per cent of the total alpha activity and 30 per cent of the total beta activity should be found adhering to the metal surfaces of the liquid space of the dissolver (based on activity found by nitric acid dissolution of similar irradiated material).

In Run 6 the dissolution was first attempted at 60°C., but when it had not started after 5 hours, the temperature was raised to 95°C. During this run no fluorine was added to the dissolver. In this run Monel and nickel coupons similar to those in Run 5 were used. Readings from a Brush surface analyzer showed that attempts to polish the coupons manually had little effect on their roughness. After the dissolver solution was discharged, the coupons were removed from the dissolver and rinsed individually with bromine trifluoride. They were then counted as in the previous run. The data, given in Table 16, show essentially the same activity distribution as Run 5. General conclusions that may be derived from Run 6 are:

- (1) As in Run 5, the liquid phase coupons show about 100 times the activity of those from the vapor space. Since this ratio holds approximately for alpha, beta, and gamma activity, it is felt that the activity in the vapor space is largely due to splattering effects.
- (2) There was no essential difference between the horizontally and vertically positioned coupons.
- (3) There was no essential difference between nickel and Monel coupons.

Gamma scans of the coupons from Run 6 are essentially the same as those from Run 5. These data are presented in a later section.

In Run 7 only a few coupons were included in the liquid and vapor spaces. Although slightly more activity was found on the coupons, the distribution was the same as in the previous runs. These data are given in Table 17. A pair of previously contaminated coupons were included in the liquid space and were found to increase in activity more than 100 per cent, indicating that continued addition of fission product fluorides occurred on a contaminated surface as well as on a fresh one. The coupons were found to gain approximately 0.7 mg. in weight during the run.

b. Coupon Decontamination Experiments

(1) Comparison of Various Wash Solutions - Total Activity

It is of interest to know the most effective and least corrosive way of washing fission products and plutonium out of the dissolver vessel.

The coupons contaminated during Run 5 were washed up to four times in bromine trifluoride, water, or aqueous solutions of various complexing agents. The washing arrangement consisted of a double hook of nickel

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Table 16

DISTRIBUTION OF ACTIVITY ON COUPONS EXPOSED IN RUN 6

Clinton-irradiated (162 days) slug slices (98.6 g.), cooled 300 days, were dissolved at approximately 95°C., in 400 ml. BrF₃. No fluorine added.

Coupon Thickness, (1) mils	Coupon Location			Total Ct./Min. Per Coupon		
	Inches Above Dissolver Bottom	Orientation	Phase	alpha x 10 ⁻³	beta x 10 ⁻⁵	gamma x 10 ⁻⁵ (2)

Monel Coupons

130	0.7	Vertical	Liquid	51	243	-
130	1.3	Horizontal	Liquid	51	320	-
130	1.7	Vertical	Liquid	75	380	-
130	1.9	Vertical	Liquid	138	967	-
130	2.8	Vertical	Vapor	1.8	15	-
130	3.4	Horizontal	Vapor	0.49	5.0	-
130	3.8	Vertical	Vapor	0.47	5.3	-
130	4.4	Horizontal	Vapor	0.17	0.93	-
130	4.8	Vertical	Vapor	0.40	3.0	-
50	5.0	Vertical	Vapor	0.27	2.1	-
50	0.3	Horizontal	Liquid	53	-	5.4
50	0.9	Vertical	Liquid	51	-	3.8
50	1.3	Horizontal	Liquid	45	-	3.5
50	2.1	Vertical	Liquid	55	-	7.1
50	2.2	Vertical	Liquid	27	-	2.9
50	2.6	Vertical	Vapor	2.7	-	0.34
50	2.7	Vertical	Vapor	0.88	-	0.21
50	2.9	Vertical	Vapor	0.96	-	0.12
50	3.0	Vertical	Vapor	0.92	-	0.11
50	3.4	Horizontal	Vapor	0.20	-	0.035
50	4.0	Vertical	Vapor	0.30	-	0.043
50	4.4	Horizontal	Vapor	0.14	-	0.030
50	5.5	Vertical	Vapor	0.15	-	0.019

Nickel Coupons

125	0.3	Vertical	Liquid	53	402	-
125	1.3	Vertical	Liquid	52	328	-
125	3.4	Vertical	Vapor	0.54	0.57	-
31	0.3	Vertical	Liquid	39	-	4.4
31	1.3	Vertical	Liquid	23	-	2.1
31	2.3	Horizontal	Liquid	8.2	-	0.87
31	2.4	Horizontal	Liquid	3.1	-	0.41
31	4.4	Vertical	Vapor	0.22	-	0.026

(1) The 130-mil coupons were about four times rougher than the 50-mil coupons as shown by a Brush surface analyzer.

(2) Total counts divided by two so that counts per side are tabulated.

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Table 17

DISTRIBUTION OF ACTIVITY ON COUPONS EXPOSED IN RUN 7

Clinton-irradiated (162 days) slug slices (101.8 g.), cooled 300 days, were dissolved at approximately 80°C. in 400 ml. BrF₃. No fluorine added. All coupons exposed vertically.

Material	Coupon Thickness, mils	Coupon Location		Total Ct./Min. Per Coupon		
		Inches Above Dissolver Bottom	Phase	alpha x 10 ⁻³	beta x 10 ⁻⁵	gamma x 10 ⁻⁵
Monel	125	0.3	Liquid	95	565	-
	31	0.3	Liquid	59	-	11
Nickel	125	0.3	Liquid	44	720	-
	31	0.3	Liquid	40	-	8.3
	5	0.3	Liquid	37	-	5.8
Monel	125	4.3	Vapor	0.89	3.3	-
	31	4.3	Vapor	0.26	-	0.075
Nickel	31	4.3	Vapor	0.46	-	0.11
	5	4.3	Vapor	0.24	-	0.049

(1) Total counts divided by two so that counts per side are tabulated.

wire from which a thick Monel coupon (130 mils) and a thin Monel coupon (50 mils) were suspended. This arrangement was rotated rapidly in the wash solution by means of a stirring motor. Each wash continued for 30 minutes at room temperature. Alpha, beta, and gamma counts and gamma scans were made after each wash. Bromine trifluoride, water, and aqueous potassium hydrogen fluoride solutions proved quite ineffective for removal of plutonium and fission product fluorides from Monel as more than a third of the original activity remained. Versene solution at a pH of 8.5 was moderately effective, as the activity levels were reduced to a few per cent of the original values after four washes. Solutions of citric acid, aluminum sulfate, zirconium sulfate, and aluminum nitrate were very effective decontaminating agents, resulting in activity reduction to only a few tenths of a per cent of that found originally. The results of these tests are shown in Table 18 and in Figure 6.

(2) Effect of pH on Versene Wash Solutions

The ionic species present in Versene solutions vary with the pH, being mostly H₂V⁻² at pH 4.5, HV⁻³ at pH 8.5, and V⁻⁴ at pH 11.7, where

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Table 18

EFFECT OF DISSOLVER WASH SOLUTIONS ON CONTAMINATED MONEL COUPONS

Two Monel coupons (130-mil and 50-mil) stirred rapidly through wash solution, 30 minutes per wash, at room temperature. Coupons contaminated in Run 5.

Activity Counted		Coupons Used	Original Activity Level, ct./min.	
α_1		130-mil, rough	$\alpha = (4 \text{ to } 8) \times 10^5$	
α_2		50-mil, smooth	$\alpha = (1 \text{ to } 3) \times 10^4$	
β		130-mil, rough	$\beta = (2 \text{ to } 5) \times 10^7$	
γ		50-mil, smooth	$\gamma = (3 \text{ to } 4) \times 10^5$	

Wash Solution	Concn., M/L	pH	Wash No.	Per Cent Original Activity Left After Wash			
				α_1	α_2	β	γ
BrF ₃	-	-	1	79	106	111	52
H ₂ O	-	-	1	75	100	57	45
KHF ₂	8	0.9	1	46	52	74	55
Versene	0.03	8.5	1	15	5.4	15	4.6
Citric Acid	0.52	1.6	1	0.33	1.5	0.79	1.2
Al ₂ (SO ₄) ₃	0.12	0.5	1	0.24	1.2	0.72	0.73
Zr(SO ₄) ₂	0.23	0.5	1	0.20	0.71	0.86	1.3
Al(NO ₃) ₃	0.23	0.5	1	0.52	0.63	0.41	0.74
BrF ₃	-	-	2	80	97	100	43
H ₂ O	-	-	2	49	66	33	27
KHF ₂	8	0.9	2	34	37	61	41
Versene	0.03	8.5	2	7.6	3.0	5.8	2.3
Citric Acid	0.52	1.6	2	0.24	0.43	0.29	0.36
Al ₂ (SO ₄) ₃	0.12	0.5	2	0.09	0.20	0.51	0.29
Zr(SO ₄) ₂	0.23	0.5	2	0.24	0.51	0.47	0.65
Al(NO ₃) ₃	0.23	0.5	2	0.51	0.54	0.23	0.52
Versene	0.03	8.5	3	4.2	2.0	1.1	1.4
Citric Acid	0.52	1.6	3	0.09	0.28	0.09	0.19
Al ₂ (SO ₄) ₃	0.12	0.5	3	0.04	0.12	0.03	0.08
Zr(SO ₄) ₂	0.23	0.5	3	0.14	0.18	0.12	0.19
Al(NO ₃) ₃	0.23	0.5	3	0.31	0.34	0.11	0.21
Versene	0.03	8.5	4	3.9	1.8	0.80	1.20
Citric Acid	0.52	1.6	4	0.06	0.23	0.06	0.14
Al ₂ (SO ₄) ₃	0.12	0.5	4	0.04	0.14	0.02	0.11
Zr(SO ₄) ₂	0.23	0.5	4	0.10	0.18	0.08	0.18
Al(NO ₃) ₃	0.23	0.5	4	0.32	0.39	0.15	0.23

FIGURE 6.

DECONTAMINATION OF MONEL COUPONS BY DISSOLVER WASH SOLUTIONS.

Coupons exposed during BrF_3 dissolution of irradiated uranium — Run No. 5
Rinsed in dissolver with BrF_3 prior to removal. Successive 30-minute washes at room temp.

Original Activity Levels: a_1 130-mil rough coupons, 4 to 8×10^4 ct./min.
 a_2 50-mil smooth coupons, 1 to 3×10^4 ct./min.
 β 130-mil rough coupons, 2 to 5×10^7 ct./min.
 γ 50-mil smooth coupons, 3 to 4×10^5 ct./min.

DECONTAMINATING SOLUTIONS:

V is the ethylenediamine tetra-acetate group. In the experiments reported above, a pH of 8.5 was employed for comparison with the decontamination procedure used at K-25.¹ The effect of pH on the decontamination power of Versene under these conditions is shown in Table 19. It thus becomes apparent that the more acid wash solution (pH of 4.5) is more effective.

Table 19

EFFECT OF pH ON DECONTAMINATION OF MONEL BY VERSENE

Two Monel coupons (130-mil and 50-mil) stirred rapidly through wash solution, 30 minutes per wash, at room temperature.

<u>Activity Counted</u>	<u>Coupons Used</u>	<u>Original Activity Level, ct./min.</u>
α_1	130-mil, rough	$\alpha = (4 \text{ to } 8) \times 10^4$
α_2	50-mil, smooth	$\alpha = (3 \text{ to } 6) \times 10^4$
β	130-mil, rough	$\beta = (2 \text{ to } 6) \times 10^7$
γ	50-mil, smooth	$\gamma = (3 \text{ to } 7) \times 10^5$

<u>pH</u>	<u>Wash No.</u>	<u>Per Cent Original Activity Left</u>			
		<u>α_1</u>	<u>α_2</u>	<u>β</u>	<u>γ</u>
4.5	1	0.14	0.07	0.19	0.27
8.5	1	4.9	2.4	0.6	4.1
11.7	1	64	66	65	90
4.5	2	0.09	0.06	0.09	0.17
8.5	2	3.7	1.8	0.3	3.3
11.7	2	61	62	65	83

(3) Influence of Concentration in Zirconium and Aluminum Sulfate Wash Solutions

Table 20 indicates the effect of changing the concentrations of zirconium and aluminum sulfate wash solutions on their decontaminating ability. Varying the concentration of aluminum sulfate from 0.1 M to 0.05 M

¹S.T. Benton and R.A. Gustison, Recovery of Plutonium and Fission Products from Reactor Pot Residues of the Chlorine Trifluoride Process, K-817, Sept. 12, 1951.

Table 20

EFFECT OF ALUMINUM OR ZIRCONIUM SALT CONCENTRATION ON
DECONTAMINATION OF MONEL

Two Monel coupons (130-mil and 50-mil) stirred rapidly through wash solution, 30 minutes per wash, at room temperature.

Single Wash

<u>Activity Counted</u>	<u>Coupons Used</u>	<u>Original Activity Level, ct./min.</u>
α_1	130-mil, rough	$\alpha = (3 \text{ to } 13) \times 10^4$
α_2	50-mil, smooth	$\alpha = (1 \text{ to } 5) \times 10^4$
β	130-mil, rough	$\beta = (1 \text{ to } 8) \times 10^7$
γ	50-mil, smooth	$\gamma = (2 \text{ to } 4) \times 10^5$

<u>Wash Solution</u>	<u>Concn., M/L</u>	<u>pH</u>	<u>Per Cent Original Activity Left</u>			
			<u>α_1</u>	<u>α_2</u>	<u>β</u>	<u>γ</u>
$\text{Al}_2(\text{SO}_4)_3$	0.1	0.5	0.15	0.53	0.48	1.2
	0.05	0.5	0.40	0.08	1.2	0.24
	0.01	0.5	0.57	3.3	4.9	24
$\text{Zr}(\text{SO}_4)_2$	0.2	0.5	0.21	0.20	0.58	0.77
	0.1	0.5	0.21	0.06	0.33	0.16
	0.02	0.5	0.11	0.35	0.16	0.07

had no appreciable effect, but poorer decontamination was obtained with a 0.01 M solution. Zirconium sulfate solutions 0.2 M, 0.1 M, and 0.02 M all showed virtually the same decontaminating ability.

(4) Gamma Scans of Coupons During Decontamination Steps

In an attempt to identify the various fission product species remaining on the coupons after the washes, gamma scans were taken with the single channel pulse analyzer (gamma ray spectrometer). Curves for pure fission product species counted with the same carbon absorber of 1775 mg./sq.cm. which was used in counting the coupons are given in Figure 7.

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FIGURE 7.

GAMMA SCINTILLATION SCANS OF SEPARATED FISSION PRODUCTS.
SCANS OBTAINED THROUGH 1775 mg./sq. cm. CARBON ABSORBER.

Examination of all the scans of the Monel coupons prior to washing indicated that the species adsorbed on the various coupons were identical (within the detection capabilities of the gamma ray spectrometer). A strong peak due to niobium-zirconium activities is apparent at 0.73 m.e.v. Typical rare earth peaks appear in the low energy region. The region of intermediate energies shows no conclusive peaks.

From Figure 8, which summarizes the effect of washing with various reagents, it is concluded that very little gamma activity is removed by further bromine trifluoride washes, and that what washing does occur is general in character. Much the same results were noted for the water washes with the exception that ruthenium appeared to be slightly less readily removed than other fission products. This was evidenced by the appearance of a small peak in the 0.5 m.e.v. region on successive washes. The curves for Versene at pH 8.5 also suggested that ruthenium was not so effectively removed as the other fission products. The plot for citric acid was interesting since it indicated that cesium was not being removed effectively, as shown by a peak which developed at 0.66 m.e.v. on successive washes. Cesium, however, presents no real problem since its fission yield is sufficiently low that only very few cesium counts are obtained from the coupon.

The effectiveness of aluminum sulfate, zirconium sulfate, and aluminum nitrate washes was also shown by the gamma scans, but the character of the curves allowed no specific conclusions to be drawn.

(5) Corrosion of Monel by Wash Solutions

If an aqueous wash solution is to be used in removing plutonium and fission product fluorides from the dissolver, it should not only be an efficient decontaminating agent but should also be as non-corrosive as possible. Static corrosion tests allow an estimate of the practicality of a wash solution, but further tests involving cycling between the aqueous wash solution and interhalogen solutions must be done before a wash solution can be considered seriously.

Static corrosion tests of Monel in aqueous aluminum nitrate solutions, previously reported in ANL-4922, page 126, showed a rate of about 6 mils/yr. at room temperature at pH values above 1.5. Corrosion was faster at higher acidities and at higher temperatures. It is felt that aluminum nitrate might be satisfactory, but the rates are high enough at elevated temperatures to warrant investigation of other systems.

It is well known that Monel is attacked seriously by oxidizing acids. Thus, aluminum sulfate, which is not an oxidizing agent, may prove to be superior to aluminum nitrate. Several sources from the literature recommend Monel as a suitable material for handling aluminum sulfate solutions, especially when air is excluded from the system. Preliminary corrosion tests in the laboratory indicate a rate of about 4 mils/yr. over a pH range from 0.03 to 3.2 and aluminum sulfate concentrations of 0.01 to 0.1 M at 25°C. At 70°C. under the same conditions the rate was about 8 mils/yr.

(6) Comments on Decontamination Washing Experiments

A dissolver wash solution will be satisfactory providing it can fulfill the following criteria:

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FIGURE 8.
EFFECT OF DISSOLVER WASHING AGENTS ON GAMMA
SCINTILLATION SCANS OF CONTAMINATED MONEL COUPONS.
SCANS OBTAINED THROUGH 1775 mg./sq. cm. CARBON ABSORBER. 50-mil MONEL
COUPONS CONTAMINATED WITH MIXED FISSION PRODUCT AND PLUTONIUM FLUORIDES
DURING DISSOLUTION OF IRRADIATED URANIUM IN BROMINE TRIFLUORIDE (Run No. 5).

- (a) that it will continue to decontaminate Monel effectively after the residual plutonium and fission product fluorides have been "baked" on the surfaces by distilling the interhalogen solution from the dissolver;
- (b) that aqueous-interhalogen cycling will not create serious corrosion problems; and
- (c) that plutonium can be recovered from the solutions.

When the recovery of plutonium is considered from an economic viewpoint, an additional factor is apparent. If it is desirable to reduce the volume of a washing solution such as aluminum sulfate appreciably, i.e., by a factor of 10, it may be difficult to extract the plutonium from a solution which may be 0.5 M in aluminum sulfate. The extractability of plutonium from aluminum nitrate solution is a distinct advantage which the latter system possesses.

The organic dissolving agents, Versene and citric acid, might be satisfactory as wash solutions, and plutonium may well be extractable from these solutions after concentration and acidification.

It would thus appear desirable to attempt further evaluation of the corrosion of Monel by aluminum nitrate as this is the major debatable point concerning its use. A further point to study is the desirability of a plutonium precipitation step from the wash solution rather than a solvent extraction step.

3. Phase Equilibrium Studies

a. Vapor-Liquid Equilibria in the System $\text{BrF}_3\text{-BrF}_5$

Some vapor-liquid equilibria in the system bromine trifluoride-bromine pentafluoride have been measured at 1 atmosphere pressure. A thermodynamic consistency check on these isobaric data, however, indicated that the Othmer still was not functioning properly. Measurements on the interhalogen system were temporarily discontinued in order to test the Othmer still with known organic mixtures. It had previously been felt desirable to avoid this experiment since residual organic materials tend to form carbonaceous residues when exposed to halogen fluorides.

The Othmer still did not operate properly on either of the systems ethanol-water or toluene-n-heptane. The improper operation appeared to result from poor mixing of the returned condensate with the contents of the boiling chamber. Consequently, the still has been so modified that the condensate is returned to the center of a circulating loop in which heat is added to the boiling liquid. It is hoped that some mixing will occur before

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the condensate reaches the boiling chamber. The modified still is now being rechecked with known organic mixtures.

b. Liquid-Liquid Equilibria in the System Bromine and Bromine Trifluoride

The determination of the miscibility gap in the liquid system bromine-bromine trifluoride has been completed. The experimental procedure was given in ANL-4979, page 88. The solubilities were measured from 9°C. to the consolute temperature at 55.5°C. as a condensed system.

The data are given in Table 21 and Figure 9. The consolute point was found to occur at about 62 mole per cent bromine at 55.5°C. Estimates of the vapor pressures to be expected in this system were made by applying the van Laar equation to the data. The large positive deviations from ideality as indicated by this calculation would partially account for the high pressures which have been observed during the dissolution of uranium in bromine trifluoride. It is also likely that this effect would be increased by the presence of uranium hexafluoride.

Table 21

MISCIBILITY OF BROMINE AND BROMINE TRIFLUORIDE

<u>Temperature, °C.</u>	<u>Composition of Phases in Equilibrium</u>	
	<u>Mole Per Cent Br₂ in BrF₃-rich Phase</u>	<u>Mole Per Cent Br₂ in Br₂-rich Phase</u>
A. Equilibrium approached from a lower temperature:		
16.1	16.2	94.8
25.0	17.7	92.9
35.3	22.2	90.0
39.7	-	88.0
45.8	29.7	84.8
49.5	34.2	82.7
50.8	-	80.0
53.9	46.8	-
B. Equilibrium approached from a higher temperature:		
50.2	35.6	-
49.1	33.6	82.3
47.6	32.2	82.8
42.2	27.1	-
41.3	-	87.9
39.4	24.9	-
31.0	20.6	91.1
28.7	-	91.4
9.0	13.9	95.4
C. Synthetic method (temperature for disappearance of interface on heating mixtures of known composition)		
<u>Composition, Mole Per Cent Br₂</u>	<u>Miscibility Temperature, °C.</u>	
39.6	51.8	
48.4	54.5	
55.6	54.8	
55.7	54.9	
63.6	55.5	
71.1	54.7	
76.9	52.8	

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FIGURE 9.

MISCIBILITY OF BROMINE AND
BROMINE TRIFLUORIDE.

Atmospheric Pressure

Legend:

- Equilibrium approached from a lower temperature.
- Equilibrium approached from a higher temperature.
- Synthetic method — miscibility temperature.

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In this study this system has been regarded as the binary bromine-bromine trifluoride, although it is possible that intermediate species such as bromine monofluoride may be present.

c. Solid-Liquid Equilibria in the System Uranium Hexafluoride-Bromine Trifluoride

The studies on the solid-liquid equilibria in the system uranium hexafluoride-bromine trifluoride are continuing. Indications have been found of the presence of compounds in the solid state in the hexafluoride-rich area. Data for this system will be reported when complete and conclusive evidence is available.

4. Refractive Index of Uranium Hexafluoride-Bromine Pentafluoride Mixtures

Refractive indexes for mixtures of uranium hexafluoride and bromine pentafluoride have been determined as a function of composition using the hollow prism-spectrometer method.² At $70.0 \pm 0.5^\circ\text{C}$. for the sodium D lines, the refractive index was found to obey the equation:

$$n_D^{70} = 1.3275 + 0.0380N - 0.0065N^2 - 0.0010N^3$$

where n_D^{70} = refractive index

N = mole fraction of UF_6 in BrF_5 .

The probable error of a single point was found to be ± 0.002 unit, indicating that the precision of analysis of mixtures by this method would be approximately 0.7 per cent. The absolute error of the measurements, however, is believed to be as large as ± 0.0004 unit. The data from which the equation was derived are given in Table 22.

5. Viscosity of Bromine Fluorides

Rough viscosity measurements were made on bromine trifluoride at 25°C . and 75°C ., and on bromine pentafluoride at 25°C . Determinations were made with a pyrex modified-Ostwald type viscometer which was immersed in a thermostated bath of MFL oil. The viscometer was calibrated with water both before and after the interhalogen measurements. The calibration did not change as a result of contact with the interhalogens. The results are given in Table 23.

6. Recovery of Uranium from Enriched Fuel Reactors

Studies of the recovery of uranium from zirconium-uranium fuel elements are being continued. Preliminary work showed that chlorine trifluoride will not fluorinate a uranium tetrafluoride-zirconium tetrafluoride mixture appreciably under mild conditions. By dissolution of the alloy in concentrated hydrofluoric acid followed by treatment with bromine

²L. Stein and R.C. Vogel, The Refractive Indices of Bromine Trifluoride-Bromine Pentafluoride Mixtures, ANL-4941, December, 1952.

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Table 22

REFRACTIVE INDEXES OF URANIUM HEXAFLUORIDE--
BROMINE PENTAFLUORIDE MIXTURES

Temperature: $70.0 \pm 0.5^\circ\text{C}$.
 Sodium D Lines
 Measured by hollow prism method.

Mole Fraction of UF_6 In BrF_5	Refractive Index n_D^{70}
0.0000	1.3275
0.1684	1.3338
0.3153	1.3388
0.4354	1.3428
0.5134	1.3449
0.5965	1.3477
0.7607	1.3522
0.9069	1.3560
1.0000	1.3580

Table 23

VISCOSITIES OF BROMINE TRIFLUORIDE AND BROMINE PENTAFLUORIDE

Compound	Temperature, $^\circ\text{C}$.	Kinematic Viscosity, centistokes	Absolute Viscosity,* centipoises
BrF_3	25.0 ± 0.1	0.814 ± 0.008	2.28
BrF_3	75.0 ± 0.1	0.45 ± 0.02	1.2
BrF_5	25.0 ± 0.1	0.259 ± 0.003	0.64

*Calculated from density data of Ruff, Braida,
 and Menzel, Z. anorg. allgm. Chem. 206, 63 (1932);
214, 91 (1933); and 202, 49 (1931).

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trifluoride, about 98 per cent of the uranium was volatilized, and good decontamination was achieved.

a. Dissolution in 10 M Hydrofluoric Acid

An alloy of zirconium, tin, and uranium was dissolved completely at 80 to 90°C. in a solution of 10 M hydrofluoric acid, made 0.01 M with nitric acid, to yield a final solution 1.65 M with respect to zirconium, 5.88×10^{-3} M with respect to uranium, and 4×10^{-3} M with respect to tin.

One hundred ml. of the solution, containing 140 mg. of uranium, was placed in a nickel and Monel still. Excess hydrofluoric acid was distilled off, and the last traces of volatile liquid were removed by vacuum distillation. The distillate contained only 0.19 mg. of uranium, indicating that little entrainment of uranium occurred during the distillation.

The dry residue was treated with chlorine trifluoride at about 1.5 atmospheres and room temperature to decompose any traces of water present. A 50-ml. portion of bromine trifluoride was added, and the system was refluxed at 125°C. under atmospheric pressure for 5 hours.

The volatile components were distilled off, leaving a dry residue which was dissolved in a mixture of 100 ml. of 10 M hydrofluoric acid and 100 ml. of 10 per cent aluminum nitrate solution. Analysis of the solution indicated that 74 mg. of uranium were present in the residue. Thus, 48 per cent of the uranium had been volatilized.

b. Dissolution in Concentrated Hydrofluoric Acid

The failure to convert the uranium tetrafluoride completely to uranium hexafluoride was probably due to the occlusion of the minor amount of uranium tetrafluoride in the much larger amount of zirconium tetrafluoride, which is insoluble in the bromine trifluoride. In order to facilitate the contact, and hence the reaction, it might be advantageous to precipitate the uranium tetrafluoride during the dissolution of the fuel element and prior to evaporating the resultant mixture to dryness. The solubility of uranium tetrafluoride in this system has been thoroughly investigated (ANL-4820, page 13). The precipitation of uranium tetrafluoride during the dissolution of the zirconium can be accomplished by dissolving the alloy in 27 M hydrofluoric acid, in which uranium tetrafluoride is only slightly soluble.

In the second experiment, a sample of a Westinghouse alloy whose composition was reported as 93.4 per cent zirconium, 2.4 per cent tin, and 4.2 per cent uranium was used. Analysis of two samples of this material for uranium indicated that 3.34 per cent and 3.40 per cent was present, respectively. A 13.12-gram sample of this alloy was placed in 10 ml. of water to which was slowly added 90 ml. of 27 M hydrofluoric acid. Dissolution of the alloy proceeded rapidly without the application of external heat. After removal of the hydrofluoric acid by distillation and treatment of the residue with chlorine trifluoride, 70 ml. of bromine trifluoride were added to the residue. The mixture was then refluxed for 8 hours at 125°C. under atmospheric pressure.

The volatile products and the bromine trifluoride were distilled off using vacuum to remove the last traces of volatile material. The residue.

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was dissolved as in the previous experiment, the resultant solution being analyzed for uranium. The residue contained 9.8 mg. of uranium. The results may be summarized as follows:

U in sample - 442 mg.
 U in residue - 9.8 mg.
 U volatilized - 97.7 per cent (calculated)

Thus, it is apparent that it is possible to recover uranium from STR fuel elements by employing concentrated hydrofluoric acid as a solvent followed by treatment with bromine trifluoride.

c. Decontamination of Irradiated Uranium

A third experiment was performed in order to test the experimental procedure to be used in carrying an irradiated sample of the alloy through the above treatment. A 0.557-gram sample of the alloy used in the preceding experiment was dissolved in a 25-ml. nickel tube by the addition of 1 ml. of water, followed by 10 ml. of 27 M hydrofluoric acid added in small increments. The solution was evaporated to dryness in the open tube at the boiling point of the solution (about 120 to 125°C.).

A 5-ml. portion of bromine trifluoride was added to the residue in the nickel tube while the latter was immersed in liquid nitrogen. The tube was then closed with a Monel plug and heated to 130 to 140°C. for 62 hours. The tube, with its contents refrozen, was attached to a very small nickel still which was equipped with a nickel Kjeldahl-type trap. The entire still, with the exception of a 25-ml. fluorothene receiver tube, was heated to 125 to 135°C. by means of nichrome wire wrapping. The receiver tube was placed in liquid nitrogen, and the volatile components were distilled into it.

The fluorothene receiver tube, with its contents frozen, was placed in a bomb containing 110 ml. of 10 per cent aluminum nitrate solution and 15 grams of hydrazine hydrochloride. As the solids melted they were slowly hydrolyzed. The resulting solution was made up to 250 ml. volume and analyzed for uranium.

A second portion of 5 ml. of bromine trifluoride was added to the distillation residue, and the above procedure was repeated, yielding a second distillate and hydrolysate.

The residue remaining in the nickel tube was dissolved by adding, in order, the following reagents: 10 ml. of 10 per cent aluminum nitrate solution, 25 ml. of 27 M hydrofluoric acid, and 5 ml. of 30 per cent aluminum nitrate solution. The dissolved residue was analyzed for uranium. The results of treating the alloy as described are summarized as follows:

	Uranium,	
	Grams In Sample	Per Cent of Total Products
In Alloy Sample (0.557 g., 3.37 per cent U)	0.0188	92
In First Distillate	0.0200	97.8
In Second Distillate	0.00005	0.2
In Residue	0.0004	2.0
In All Products	0.02045	100.0

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The poor material balance is undoubtedly due to analytical difficulties. However, only a negligible amount of uranium hexafluoride was present in the second distillate, and the uranium recovery was probably at least 98 per cent.

The fourth experiment using an irradiated sample fuel alloy was performed in the same manner except that no uranium material balance was attempted due to the difficulties involved in hydrolyzing a known sample of the total distillate (a large part of the sample may have been lost). However, analysis of the residue was in concordance with the results of the trial experiment as about the same amount (0.4 mg.) of uranium was found, and beta and gamma decontamination factors of 10^5 or greater than 10^5 were obtained.

The results of the "hot" experiment may be summarized as follows:

Weight of Irradiated Alloy, grams (irradiated 125 days in NRX, cooled 800 days)	0.5057
Uranium in Alloy, per cent	3.8
Uranium in Alloy, grams	0.0192
Uranium in Residue, grams	0.00038

Total Residue Made Up To a Volume of 20 ml.:

Beta Ct./(min.)(ml.)	1.08×10^7
Gamma Ct./(min.)(ml.)	1.56×10^4
Uranium, <u>M</u>	1.6×10^{-5}

Unknown Portion of BrF₃ Distillate Made Up
To a Volume of About 250 ml.:

Beta Ct./(min.)(ml.)	3.0×10^2
Gamma Ct./(min.)(ml.)	none
Uranium, <u>M</u>	6.6×10^{-5}

Beta Decontamination Factor	1.4×10^5
Gamma Decontamination Factor	$> 10^5$

The results of this series of tests are summarized in Table 24, wherein it will be noted that for three tests only about 2 per cent of the original uranium was found in residues from bromine trifluoride treatment following concentrated hydrofluoric acid dissolution of zirconium-uranium alloys.

7. Corrosion Studies

a. Corrosion of Silver Solder by Interhalogens

It has been an established technique to assemble Monel and nickel equipment for laboratory studies by the use of silver solder. In recent experiments requiring the hydrolysis of interhalogen systems for analysis, copious precipitates of silver halides were obtained. The silver was found to arise from corrosion of silver solder. Since the use of silver solder is sometimes hard to avoid, especially in the assembly of valves, it was felt pertinent to investigate the corrosion of silver solder by interhalogens.

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Table 24

SUMMARY OF URANIUM RECOVERY FROM FUEL ELEMENTS BY FLUORINATION

<u>Sample</u>	<u>Uranium, mg.</u>	<u>Dissolving Reagent, M HF</u>	<u>ClF₃ Treatment</u>	<u>Vol. BrF₃, ml., (1) 1st reflux (2) 2nd reflux</u>	<u>Reflux Time and Temp., °C.</u>	<u>Uranium in Residue, mg.</u>	<u>Uranium in BrF₃ Dist. (1) First (2) Second</u>	<u>Uranium Recovery, per cent</u>
<u>Solution:</u>								
1.65 M Zr 4×10^{-3} M Sn 5.9×10^{-3} M U	177	10	70°C. 1.5 atm. 3 hr.	-	-	156	-	6.2
<u>Solution:</u>								
1.65 M Zr 4×10^{-3} M Sn 5.9×10^{-3} M U	140	10	25°C. 1.5 atm. 0.5 hr.	(1) 50	5 hr. 125°C.	74	no anal.	48.0
<u>Alloy:</u>								
94.2% Zr 2.4% Sn 3.37% U (13.12 g.)	442	25	25°C. 1.5 atm. 0.5 hr.	(1) 70	8 hr. 125°C.	9.8	no anal.	97.7
<u>Alloy:</u>								
94.2% Zr 2.4% Sn 3.37% U (0.557 g.)	18.8	25	none	(1) 5 (2) 5	62 hr. 130-140°C.	0.40	(1) 20 mg. (2) 0.05 mg.	98-100
<u>Irradiated Alloy:</u>								
96.2% Zr 3.8% U (0.5057 g.)	18	25	none	(1) 5	48 hr. 130-140°C.	0.38	> 4 mg.*	98

*Large part of sample lost

Preliminary corrosion studies have been completed on eleven types of silver solder made by two manufacturers (Handy and Harman, and American Platinum Works) both directly and as couples with Monel.

The samples were placed in separate 1/2-inch fluorothene test tubes, covered with purified bromine trifluoride, and capped. The samples were placed in an oven regulated at 70°C. Weight losses in 24-hour exposures at 70°C. are tabulated for each type of silver solder in Table 25.

Table 25

CORROSION OF SILVER SOLDERS BY BROMINE TRIFLUORIDE

1/4-inch Monel square with silver solder
on one side. Exposed to BrF₃ at 70°C.

<u>Manufacturer</u>	<u>Type</u>	<u>Time of Exposure, hours</u>	<u>Total Penetration, mils/hr.</u>
Handy and Harman	Easyflo No. 3	24	0.085
	Easyflo No. 45	24	0.075
	Easyflo No. 35	24	0.099
	RT	24	disintegrated
	RT SN	24	0.15
American Platinum Works	35	24	0.077
	40	24	0.086
	45	24	0.29
			(flaked off)
	50	24	0.082
	503	24	0.12
Handy and Harman	Easyflo Brazing Alloy	19-1/2	0.095
		43-1/2	0.065
		115	0.037
American Platinum Works	355	19-1/2	0.010
		43-1/2	0.0056
		115	0.0019
		139	0.0016

Only Easyflo Brazing Alloy and American Platinum Works No. 355 were tested for longer periods. The A.P.W. No. 355 lost weight early in a room temperature test, but after the first day no appreciable additional corrosion was observed. Thus, the weight loss corresponded to about 0.2 mil penetration in the first day, but the over-all average for a 6-day test showed less than 12 mils/yr. penetration rate. Easyflo Brazing Alloy continued to corrode for 5 days and showed a noticeable separation from the Monel coupon. These results are shown photographically in Figure 10.

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Figure 10

CORROSION OF SILVER SOLDERS BY BROMINE TRIFLUORIDE

- A. Samples prepared by coating one side of a Monel coupon with the silver solder being tested.
1. A.P.W. No. 355 couple; original sample
 2. A.P.W. No. 355 couple exposed to BrF_3 6 days at 70°C .
 3. Easyflo Brazing Alloy couple exposed to BrF_3 5 days at 70°C .
 4. Easyflo Brazing Alloy couple; original sample.

- B. Samples consisted of 1/16-inch wire; an unexposed sample is shown for comparison.
5. A.P.W. No. 355 exposed to BrF_3 6 days at 70°C .
 6. Easyflo Brazing Alloy exposed to BrF_3 24 hours at 70°C .

Figure 11 depicts the corrosion occurring at the joint between the spindle and diaphragm of a 1/4-inch Hoke diaphragm valve after 3 days' immersion in bromine trifluoride at room temperature and at 70°C. This joint is soldered with Easyflo No. 45 silver solder. It can be seen that the corrosion of this joint is quite serious.

Further corrosion tests have been planned for A.P.W. No. 355 silver solder at about 125°C. in boiling bromine trifluoride, at the liquid-vapor interface, and in the vapor space.

b. Corrosion of Monel by Aqueous Aluminum Sulfate

Preliminary studies of the corrosion of Monel by aluminum sulfate solutions have been made and are reported in Section 2.b of this report.

8. Laboratory Equipment Development

As a result of the difficulties arising from the use of silver solder in systems containing interhalogens, it has been necessary to re-examine and evaluate all the equipment now being used in the laboratory. In some pieces of apparatus such as the interhalogen purification still take-off manifold, the dissolver sampling system, and the dispensing apparatus, it is necessary to eliminate silver solder completely. In other equipment such as the Othmer still and the small scale rate apparatus where the problem of silver solder corrosion is primarily a mechanical one, minimization of the amount of silver solder may be sufficient.

Modification of the equipment will consist principally of substituting welded joints and flare connectors for those now joined with silver solder. The valves which are now being used are mostly of the 1/4-inch Hoke No. 413 diaphragm type which are assembled with No. 45 Easyflo silver solder. These valves will either be modified so as to present no silver-soldered surfaces to the contents, or will be replaced completely with all-nickel or Monel valves. These modifications are now under way on all the major pieces of apparatus in the laboratory.

B. Pilot Plant-Scale Equipment (M. Levenson, W. Mecham, I. Winsch, R. Liimatainen, N. Levitz, O. J. Du Temple)

The results of steam-to-water heat transfer tests of condensers using sprayed metal thermal bonds are reported, and the effects of halogen gases on CWS paper filters are described.

1. Heat Transfer Tests of Column Condensers

Three distillation column condensers planned for pilot plant use have been fabricated and tested for heat transfer performance with steam on the inner condensing tubes and water through the cooling coils. The thermal path between these tubes and coils is through sprayed metal as previously described in ANL-4979, page 90. The condensers are identical except for the type of spray metal used.

Condenser No. 1 was made of all-aluminum spray metal. Condenser No. 2 had the condenser tubes covered with 1/16 inch of sprayed aluminum,

Figure 11
CORROSION OF SILVER SOLDER ON HOKE DIAPHRAGM VALVE PARTS
BY BROMINE TRIFLUORIDE

Samples consisted of the diaphragm assembly of 1/4-inch Hoke valves (soldered with Easyflo No. 45 silver solder).

7. Original sample.
8. Three days' exposure to BrF_3 at room temperature.
9. Three days' exposure to BrF_3 at 70°C .

and over this the cooling coils were wound and covered with 1/8 inch of sprayed copper. Condenser No. 3 was made similarly of all sprayed copper.

It has been shown in thermal cycling tests that the difference in the coefficients of thermal expansion between aluminum and nickel may result in cracking and breaking the bond between the two metals for equipment of large diameters. In this test, an 8-inch diameter piece was cycled between 20° and 120°C., and cracks impairing heat transfer appeared after about a hundred cycles.

The dimensions of these condensers are smaller than that of the above test piece (4-1/2 inch outside diameter), and cycling conditions will presumably be less drastic. However, it was felt that comparison of the two spray metals in actual heat exchange performance would give important data for possible future designs. Aluminum is significantly lighter and cheaper, while copper has an expansion coefficient almost identical with nickel and Monel and a slightly higher thermal conductivity. The purpose of this test was to compare the three condensers and obtain preliminary heat transfer data.

Cooling water was passed through the wound tubing at velocities up to 21 ft./sec., and steam was admitted to the condensing tubes at pressures up to 30 p.s.i.g. in a similar manner for testing all three condensers. Heat transfer was measured by the temperature rise and rate of flow of the cooling water under steady-state operation.

The data obtained were widely scattered, indicating that a refinement of the test setup is required for final quantitative evaluation of heat transfer performance. The following table gives some comparative data, however.

Table 26

HEAT TRANSFER PERFORMANCE
OF PILOT PLANT CONDENSERS

<u>Condenser</u>	<u>Type of Spray Metal</u>	<u>Maximum Over-all Heat Transfer Coefficient (U), B.t.u./(hr.)(sq.ft.)(°F.)</u>	<u>Maximum Water Velocity, ft./sec.</u>	<u>Transfer Coefficient, U, at 1 g.p.m.</u>
1	Al	270	21.6	170
2	Al-Cu	480	19.4	340
3	Cu	340	12.0	280

Inasmuch as the mixed spray metal Condenser No. 2 gave the highest heat transfer, whereas it is unlikely that this should be the case, it is not possible to give a final evaluation to the two metals. The following points are notable, however.

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- (1) The all-aluminum condenser was poorest.
- (2) The water rate is not controlling above 2 gal./min.
- (3) There was considerable variation in maximum water flow obtainable from a 40 p.s.i. water main, even though the lengths and diameters of the copper tubing cooling coil were specified identically.
- (4) All condensers have sufficient capacity for boil-up rates anticipated with the pilot plant columns.

Final tests will be made on the columns as a whole.

2. Effect of Halide Vapors on CWS Filters

In connection with the design of an adequate ventilation system for the pilot plant, tests were made to determine the effect on standard CWS filters of mixtures of air and volatile halides that might be encountered in operations. Individual mixtures of air with chlorine trifluoride, bromine pentafluoride, hydrogen bromide, and hydrogen fluoride were passed through a single standard CWS filter taped to a steel filter holder and connected in a typical manner to the building ventilation system.

The procedure used was as follows. Air flow was metered with a rotameter and then combined with the halide vapor stream. Halide flow was determined by the loss in weight of the halide container over the time interval. The gas stream was sampled after passing through the filter by absorbing completely a metered portion of the total flow. A 10 per cent potassium hydroxide solution was used in the absorption train; this was subsequently analyzed chemically for halide content. From the above information halide concentrations before and after contact with the CWS filter were calculated. The pressure drop across the filter was measured with an inclined manometer containing monochlorotrifluoroethylene liquid polymer.

Two standard 8 x 8 x 3-1/16 inch CWS filters were used: one for the first run, and another one for the remaining five runs. The last two runs were made after the filter surface had been coated with atmospheric dust by drawing laboratory air through the filter until the pressure drop had increased from 0.13 to 0.17 inch of water. The test data are summarized in Table 27.

Up to Run 5, the attack on the filter was negligible (at least superficially). However, in Run 1 the rubber gasket on the filter face and the sealing tape were severely attacked. Rubber was removed, and the seal made with Teflon tape. The inner walls of the filter support were also corroded considerably. From the consumption of reactive material, it appears: (1) that fluorine atoms are most reactive to the filter material, bromine slightly less so, chlorine least of all; and (2) that hydrogen fluoride and hydrogen bromide are about equally reactive.

For the runs with clean filters, the pressure drop did not change, indicating no dimensional change with exposure. The concentrations of reactive vapor were as high as 170,000 p.p.m. (see Table 27). (For comparison, 4000 p.p.m. is equivalent to a leak of 1/4 lb./min. of BrF₃ into 800 c.f.m. of air. The pilot plant will be ventilated with 6000 c.f.m.)

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Table 27

EFFECT OF CONTACTING CWS FILTERS WITH REACTIVE HALIDES IN AIR

Standard 8 x 8 x 3-1/16 in. CWS filters rated at 15 c.f.m. for 0.6 in. H₂O pressure drop used in tests. Air flow 3.0 to 3.3 c.f.m. (at 70°F. and 1 atm.) corresponding to 10.9 to 11.8 ft./min. superficial velocity.

Test No.	Halide Added to Air	Test Time, min.	Halide Concentration, p.p.m. by wt.				Halogen Loss, per cent		Pressure Drop, inches water	
			F ₂		Cl ₂ or Br ₂		F ₂ Cl ₂ or Br ₂		Initial	Final
			In	Out	In	Out	F ₂	Cl ₂ or Br ₂		
<u>Tests with Filter A (clean)</u>										
1.	BrF ₅	15	50,700	21,400	42,800	26,000	58	39	-	-
<u>Tests with Filter B (clean)</u>										
2.	HBr	25	-	-	170,000	79,000	-	54	0.12	0.12
3.	ClF ₃	20	23,400	10,200	14,600	12,900	56	12	0.12	0.13
4.	HF	30	76,000	39,000	-	-	48	-	0.13	0.13
<u>Tests with Filter B (after loading with laboratory dust)</u>										
5.	HF	30	26,700	8,400	-	-	69	-	0.17	0.15
6.	ClF ₃	30	18,600	6,100	11,600	9,300	67	20	0.15	0.11

For the last two runs, in which the filter was dust-coated, the pressure drop across the filter decreased 35 per cent, indicating strong attack and conversion of some material to gaseous products. Inspection of this filter at the end of the tests revealed general, slightly dark discoloration, with darker pinpoints suggesting local ignition. In addition, the paper spacers were weakened considerably (compared to the original condition), and the filter material itself had been attacked destructively to some extent. Apparently cellulose is attacked more rapidly than asbestos. This filter had been exposed to a total of over 3 pounds of reactive vapor, and probably this figure could be regarded as the exposure-lifetime.

The results of this brief study may be summarized as follows. Exposure of a CWS filter to reactive halogen vapors at concentrations possible in use in the ventilating system of the pilot plant resulted, not in ignition or complete destruction, but in a gradual structural weakening and possible impairment of filtering efficiency. Only small changes in the pressure drop across the filter occurred up to the point where 3 pounds of reactive material had passed through an 8 x 8-inch filter.

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V. PROCESSING OF URANIUM AT ELEVATED TEMPERATURE

(H. M. Feder, N. Chellew, K. Rohde, A. Glassner,
D. C. Hampson, J. Jost,* B. Blumenthal**)

Work on direct methods of processing uranium at elevated temperatures has included completion of equipment for tests involving melting of uranium, studies of electrodeposition of zirconium from molten chloride baths, corrosion tests with fluoride melts, and an investigation of the use of quartz diaphragms as semi-permeable membranes in fused salt baths.

A. Decontamination of Molten Uranium

The metal vacuum system to be used with the experimental uranium melting furnace (ANL-4979, page 95) is essentially complete. Helium will be substituted for argon for the furnace tube internal atmosphere, but this entails no changes in the purification train which has been installed. The top shroud and gas circulating pump for the argon blanketing system are the main items of equipment not at hand. Assembly and testing are expected to be completed in the next quarter.

Theoretical studies have been begun of the decontamination which might be achieved by fluxing molten uranium with suitable salts. These studies are based on the assumption of thermodynamic equilibrium and the tentative assumption that minor metallic constituents and salts will dissolve completely in the corresponding bulk phases. On this basis, calculations indicate that magnesium oxide flux will remove the rare earth metals only, and sodium chloride flux will remove the alkali metals and alkaline earth metals as well. A uranium trichloride flux (0.01 mole/mole uranium) should remove all these and zirconium and niobium as well, leaving molybdenum and ruthenium as chief contaminants. Calculations such as these are expected to aid the interpretation of experimental data on fluxing when this work is undertaken.

B. Decontamination by Molten Salt Electrolysis

Earlier experiments on the electro-refining of contaminated uranium in fused LiCl-KCl eutectic baths (ANL-4922, page 154) indicated severe contamination of the deposit by zirconium and niobium. The mechanism of this reaction is being investigated on a macro scale. Experiments to date reveal that the reduction of zirconium tetrachloride in the eutectic melt by metallic uranium proceeds to form insoluble black zirconium dichloride in the absence of an electric current. Thermodynamically, the further reduction to metallic zirconium on a uranium surface can proceed with only a small applied voltage (about 0.05 volt). It presently appears that this difficulty will be inherent in such a process.

The vacuum furnace tube designed for similar uranium electrode deposition experiments in fluoride melts has been received and is shown in Figure 12. This equipment provides for the use of a 2-1/4 inch I.D. graphite crucible and has a head which will admit three movable electrodes or other components.

*California Research and Development Company

**Metallurgy Division

FIGURE 12
HIGH TEMPERATURE ELECTROLYSIS CELL

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Additional corrosion tests in static molten fluoride baths were carried out. A nickel crucible containing NaF-UF₄ eutectic was held at 700°C. for 53 hours in a good vacuum. No visible corrosion was evident when the crucible was inspected at the end of the test. The cooled salt mixture was analyzed spectroscopically. Iron, copper, manganese, and nickel were found to be below the limits of estimation. Similar tests with pile-grade graphite crucibles (apparent density 1.67, 0.2 to 0.5 per cent ash content) revealed contamination of the salts with aluminum. Iron, calcium, and magnesium were found to be below limits of estimation. Introduction of the aluminum from an outside source is suspected since the aluminum found exceeds by several-fold that present in the crucibles plus original salt mixture.

Molybdenum and tungsten rods are also being tested. Preliminary indications of corrosion stability are good. Nickel has also been tested for its anodic behavior. Corrosion was rapid, indicating that the nickel fluoride coating formed was not sufficiently adherent.

Work has started on a possible method for decontamination of uranium by means of electrochemical oxidation to the volatile hexafluoride in a fused fluoride bath. Equipment fabrication is complete, but experimental results are not yet available.

The use of Z-cut thin quartz crystals as diaphragms permeable only to lithium and sodium ions in chloride melts is being investigated for its possible practical as well as theoretical significance. To date it has been found that the heat stability of these diaphragms is a critical factor; cracking of the crystals may be avoided by heating and cooling only at rates less than 2°C./min. with particular care needed in the beta transition range (537°C.). It has also been found that molten sodium chloride wets fused quartz in the presence of air and cracks the quartz on cooling. In a vacuum this phenomenon does not occur.

VI. DEVELOPMENT OF ANALYTICAL TECHNIQUES

Conditions for the determination of a number of heavy metal ions in solution by colorimetry using the thiocyanate complexes were developed. The application of a well-type scintillation counter to some fission product analyses was investigated.

A. Application of Thiocyanate Colorimetry to the Determination of Heavy Metals (C. E. Crouthamel, C. E. Johnson, B. Hjelte, R. C. Vogel)

Thiocyanate has been employed in the spectrophotometric analysis of many metal ions both in aqueous and mixed aqueous-organic solution. Previous work³ has shown that at relatively high acetone/water ratio the uranyl ion will develop a stable color in the presence of anions which would bleach the color completely in aqueous medium. Recently, increased interest in various alloys of fissionable material and heavy metals for reactor fuel elements has prompted the extension of the thiocyanate-acetone procedure to the determination of many of the other heavy metals. The feasibility of such analytical procedures has been demonstrated for Fe, Co, Nb, V, Mo, Ti, W, Pd, and Bi.

1. Titanium

Of interest from a fundamental view is the possibility that the method may show the presence of various ionic states in solution. A freshly prepared titanic chloride solution made by dissolving anhydrous titanic chloride in 6 M hydrochloric acid at room temperature develops a yellow color in the thiocyanate-acetone medium with an absorbance index of 10,000. However, if the solution is boiled a few minutes in concentrated hydrochloric acid, the absorbance index increases to 17,000. Fuming in concentrated sulfuric acid increases the absorbance index to a maximum of 55,000.

The reactions involved are probably as follows:

In the case of titanic ion there is no shift in the absorbance peak of the thiocyanate complex under any conditions which do not involve the reduction of the titanium. The titanyl ion (TiO^{++}), therefore, either does not react, or if a complex is formed with titanyl ion, it is not colored. Also, in acetone medium there appears to be no tendency in a period of several hours for the absorbance index to change after color development, indicating that the titanyl ion is stable in the acetone medium. Thus, the possibility of estimating the ratio of titanyl or oxygen-containing titanium ion to the non-

³C.E. Crouthamel and C.E. Johnson, Spectrophotometric Determination of Uranium by Thiocyanate Method in Acetone Medium, ANL-4750 (1952).

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oxygen-containing titanium ions and their complexes, which may be expressed as $\frac{\text{TiO}^{++} + \text{TiOCl}^+ + \dots}{\text{Ti}^{++++} + \text{TiCl}^{+++} + \dots}$, in aqueous solutions of titanium suggests itself.

2. Tungsten

Tungsten, as expected, gives ample evidence of its complicated structure in aqueous solutions. Dilute stock solutions were prepared from

$(\text{NH}_4)_6\text{W}_7\text{O}_{24} \cdot 6\text{H}_2\text{O}$. Numerous polyacid salts with up to 12 tungsten atoms per

molecule can be isolated from this system. However, a procedure which will lead to the development of stable reproducible color in thiocyanate-acetone medium was found possible. The tungstate was first boiled in concentrated hydrochloric acid for 5 minutes. The solution was then cooled to approximately 15°C . with tap water, and approximately 100 mg. of granular tin metal added to the concentrated hydrochloric acid. The solution was shaken on a Burrell shaker for about 10 minutes at room temperature, and a distinct wine-red chloride complex of tungsten appeared. The color was developed with the thiocyanate-acetone solution. A sharp peak at 400 mμ with an absorbance index of 14,500 was obtained. The reactions can be inferred as follows:

It has been shown that heating in the presence of both tin metal and concentrated hydrochloric acid does not produce the required reduction product, and very little and erratic color is formed. With no prior boiling in concentrated hydrochloric acid the tin reduction in the cold and in concentrated hydrochloric acid produced very little color. Reduction in oxalic acid, sulfuric acid, and diglycolic acid produced little or no color. Zinc amalgam failed to give the reduction product as did cadmium, lead, and hydroxylamine hydrochloride.

3. Other Heavy Metals

Niobium showed marked aging effects in tartrate solutions. In each case fuming sulfuric acid-hydrofluoric acid mixture returned the niobium to the state which allowed the development of the maximum absorbance index as observed on freshly dissolved solutions of niobium metal, i.e., 38,000.

Palladium showed minor increases in color development after fuming in sulfuric acid. Iron, cobalt, and bismuth developed the same color with

and without fuming in sulfuric or hydrochloric acid. The studies on vanadium and molybdenum solutions are not complete; however, analytical procedures have been worked out which are satisfactory.

B. Scintillation Counting with a Well-Type Crystal

(C. E. Crouthamel, G. Seto, R. C. Vogel)

With the development of the scintillation counter, it appeared possible that a high-efficiency beta and gamma counting assembly could be made for samples regardless of physical form. If a scintillation counter could be thus used it would count betas and weaker gammas and be more efficient than the Shonka ionization chamber.

1. Equipment Characteristics

A well-type sodium iodide-thallium activated crystal was obtained from the Harshaw Chemical Company packaged in a thin aluminum jacket. The well dimensions were 5/8 inch diameter by 1-1/2 inch deep with a flat base. The crystal surrounding the well was 1/2 inch thick at all points. The application of the standard 5819 photomultiplier unit has been described previously (ANL-4922, page 159; see footnote⁴ reference also). An aluminum cap was made to adapt the well crystal to the standard 5819 photomultiplier unit. Also, a special cylindrical lead shield was made for the unit. The lead walls were 1 inches thick and encased in a steel jacket. The crystal was placed 2 inches below the top of the cylinder, which was 14 inches in length. A lead cap 3 inches thick was placed over the crystal when counting.

The counter in general use can be applied to counting beta particles of 1.0 m.e.v. or greater energy. The limitation is the total absorber thickness of the aluminum jacket (250 mg./sq.cm.) plus that of the test tube used to contain the sample. Gamma counting down to energies of 0.050 m.e.v. is feasible, the limitation here being the noise-to-signal ratio in the photomultiplier assembly. In quantitative work the volume of liquid counted must be kept constant. Figure 13 shows the effect of volume changes when using a 10.5-mm. test tube when samples containing cesium-137 were used. The background counting rate is shown in Figure 14. The attenuator settings of 1 to 22 correspond to 22 one-decibel steps with maximum amplification at step one. The linear portion of each curve is the useful range. Statistical fluctuations indicated in Figure 14 were a maximum of ± 3.0 per cent standard deviation. The remaining fluctuations in the background are attributed to instability of the instrument or to spurious pulses in the line voltage. Removal of the lead shield increased the background by approximately a factor of 2 under present counting room conditions. A decade scaler of 1000 was used, and the dead time of the unit as a whole was determined by the split source procedure. The dead time was found to be 3.5 microseconds due to the limitations of the decade scaling circuit. The true counting rates for samples in the range of 50 to 500,000 ct./min. is given by the following formula for the coincidence correction:

$$N_T = N_O + N_O^2(5.83 \times 10^{-8})$$

where N_T = true counting rate, ct./min.

N_O = observed counting rate, ct./min.

⁴C.E. Crouthamel and C.E. Johnson, Application of the Scintillation Spectrometer to Fission Product Analysis, ANL-4924 (1953).

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FIGURE 13.

EFFECT OF SAMPLE VOLUME ON COUNTING
RATE FOR WELL-TYPE CRYSTAL.

Well-type NaI Crystal with 10.5 mm. I.D.
test tube. Cs^{137} solution; no absorber.

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FIGURE 14.

BACKGROUND COUNTING RATE OF WELL-TYPE SCINTILLATION COUNTER.

Numbers adjacent to curves represent
attenuator setting in decibels.

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2. Application to Fission Product Counting

By counting cesium-137, cobalt-60, and Ru-Rh fission product mixtures it was found that the amount of discrimination possible among various energies is limited, but nevertheless useful under specific conditions. The 5819 photomultiplier was not selected as a scintillation spectrometer for high resolution. However, the stability of the instrument is excellent. Standardization was done against glass-sealed tubes containing cesium-137 and cobalt-60 tracer in solution. A typical sealed cesium-137 tracer which was counted every day for 1 month of continuous operation gave 61200 ± 302 ct./min. This represents a standard deviation of about ± 0.5 per cent. The voltage control was obtained by use of a 10-turn Helipot to reset the voltage on a special highly stable negative voltage supply. A resistance voltage divider with the negative high voltage supply was adjusted to reset the voltage to correspond with a portable Leeds and Northrup potentiometer. The standard deviations over a period of 1 month on sealed cesium-137 and cobalt-60 standards were ± 0.30 per cent. The life of the 5819 photomultiplier in continuous operation has been as long as 1 year with no appreciable change in counting characteristics.

It has been found that a bad photomultiplier tube which has been operated over a long period shows a tendency to decrease in counting rate after the counter has been started. The tube will then recover when the activity is removed for some time. To monitor for this effect, a sample counting 50 to 100,000 ct./min. should be checked for 1-minute and 3-minute counts.

The main advantage of the well-type scintillation counter is the ease in preparing samples for counting, and the increased and easily reproduced geometry obtained. It is more difficult to prepare absorbers since they must be cylindrical wells of uniform thickness along the walls and base. Also, all the radiation does not pass through the absorber vertical to the surface. The use of absorbers has been limited to complete removal of beta radiation for use in gamma counting.

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VII. PROCESSING OF RADIOACTIVE LABORATORY EFFLUENTS

(W. A. Rodger, H. G. Swope, P. Fineman)

Processing of laboratory liquid wastes which were above discharge tolerance and of combustible, radioactive solid wastes continued on a routine basis. The incinerator was operated with charges containing added activity to determine the decontamination potential. Optimum conditions for operating and regenerating mixed bed ion exchange columns, and the effect of iron additions, were determined in the laboratory.

A. Routine Processing of Active Wastes (E. Hykan, K. O. Bremer, L. Hays, O. Lovison, L. Marek, W. Pehl)

About 31,000 gallons of over-tolerance laboratory liquid wastes were processed by evaporation (Struthers-Wells evaporator) to a final volume of 750 gallons. A breakdown of the wastes processed is:

1. Over-tolerance retention tank wastes - 15,000 gallons
2. Laboratory collection wastes - 10,700 gallons
3. Incinerator scrub water - 5,300 gallons.

The activity concentrations of unidentified radioactive contaminants varied from 5 to 500 alpha ct./ (min.)(ml.) and from 100 to 10,000 beta ct./ (min.)(ml.). The overhead condensate activity (gross alpha + beta) varied from 0 to 20 ct./ (min.)(ml.). The average over-all heat transfer coefficient obtained in the evaporator was 320 B.t.u./ (hr.)(°F.)(sq.ft.).

The evaporator bottoms (750 gallons) were concentrated to a final volume of 200 gallons of residue containing about 80 to 90 weight per cent solids. Activity in the concentrator feed averaged about 5.0×10^4 ct./ (min.)(ml.), while the overheads averaged about 5 ct./ (min.)(ml.).

The active waste incinerator was operated routinely to process 2700 cu.ft. of active combustible wastes. Approximately 5 per cent of the charged volume was removed as ash. Charging rates varied from 10 to 17 cu.ft./hr.

B. Incinerator Tests (D. C. Hampson, E. H. Hykan, O. Lovison, L. Marek, W. Pehl)

To demonstrate the feasibility of continuous operation of the dry active waste incinerator, a run of 118 hours' duration was made. Except for the replacement of one pump seal, the run was made without incident. A total of 1150 cu.ft. of active wastes were burned. These consisted of 41.7 volume per cent wood, 9.1 volume per cent A.E.C. filters, and 49.2 volume per cent normal laboratory wastes (wastes collected in 1-cu.ft. fiber drums from the various laboratories). The total is equivalent to 1990 cu.ft. of normal laboratory wastes, or about 400 cu.ft. per 24-hour day. Ash receivers were changed every 8 hours. There was no evidence of activity build-up in the gas cleaning compartments.

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Three 8-hour runs were made to determine furnace body and over-all decontamination factors by the charging of known amounts of radioactivity into the furnace with the waste feed. Equal volumes of a solution of mixed fission product activity (to provide a total of about 5×10^{12} disint./min. per run) were added to each charge of combustible feed material. About 80 cu.ft. were burned in each run.

The exhaust air beta activity was well below the maximum permissible level (MPL) for iodine, i.e., 2.2×10^3 disint./min.(cu.m.), and in all runs was less than the natural beta content of intake combustion air. The data for these runs are compiled in Table 28. The maximum over-all decontamination factor was a little over 10^1 , and the decontamination factor across each of the gas cleaning components (furnace, scrubbers, and filters) varied from 60 to 2600 as presented in Table 29.

In Figure 15, the over-all decontamination factor for each of the controlled contamination runs is compared with the total beta activity in the feed material charged for each run. Employing the present gas cleaning compartments and burning feed material which is of a heterogeneous composition, it appears that the maximum decontamination factor attainable is about 2 to 3×10^1 .

The laboratory section of the waste treatment group devoted most of their time during the past quarter to ion exchange studies, although some work was done on the filtration of retention tank wastes and coolant solutions, and two laboratories were cleaned prior to revamping for recovery of special materials.

C. Ion Exchange Studies (E. Anderson, R. Juvinall, W. Kline, A. Schilb)

Investigations were conducted to determine (1) the optimum flow rate through a mixed bed ion exchange unit, (2) a satisfactory method for regenerating a laboratory mixed bed column, (3) decontamination obtained by the addition of powdered iron to a mixed bed column, and (4) comparison of a two-bed ion exchange unit versus a mixed bed for decontamination from mixed fission product activity.

For a mixed bed ion exchange unit, a flow rate of 2 gal./cu.ft.(min.) was optimum for good decontamination.

To regenerate a laboratory mixed bed column the bed was classified as much as possible by recirculating the liquid in the column. Four per cent caustic was then poured through the entire resin bed, and the bed reclassified by recirculation of the distilled water rinse. Nitric acid was used to regenerate the cation portion of the bed.

Cesium and ruthenium are two of the fission products which lower the decontamination factors in either a mixed bed or cation exchanger. As powdered iron removes ruthenium, a comparison was made of the decontamination obtained when iron was added to a mixed bed. About three-fourths of the ruthenium was removed when powdered iron was added.

As it is considerably easier to regenerate a two-bed ion exchange system than a mixed bed, a comparison of the two was made. Decontamination factors were 3 to 10 times greater using the mixed bed system.

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Table 28

INCINERATOR COMBUSTION OF DRY WASTES WITH ADDED ACTIVITY

Fission product activity added was obtained from
solvent extraction of uranium.

Run No.	Beta Activity Balance					Beta Activity, ct./ (min.) (ml.)			Decontamination Factor, $\frac{A + B}{C}$
	In Incoming Air		In Feed	In Exhaust Air		In Furnace Liquid, ~ 300 gal.	In Peabody Scrub Solution, ~ 70 gal.	In Liquid Drained From Ash, ~ 50 gal.	
	total	total		total					
	beta disint./ (min.) (cu.m.)	beta disint./ (min.) (run)	beta disint./ (min.) (run)	beta disint./ (min.) (cu.m.)	beta disint./ (min.) (run)				
	(A)	(B)	(C)						
T-15	195	4×10^5	1×10^7	14	2.8×10^4	Bkgd. (1)	Bkgd. (1)	Bkgd. (1)	2.6×10^2
T-16	116	2.3×10^5	9×10^7	2	4×10^3	14	3	Bkgd. (1)	2.2×10^4
T-17	185	3.7×10^5	3.7×10^9	2.5	5×10^3	1.3×10^3	30	11	7.4×10^5
T-18	166	$\overset{3.3}{\cancel{4.2}} \times 10^5$	1.6×10^{11}	4	$\overset{8}{\cancel{2}} \times 10^3$	2.5×10^4	780	52	2×10^7
219	300	6×10^5	5.8×10^{12}	97	1.9×10^5	6.3×10^4	8.3×10^4	6.2×10^4	3.1×10^7
220	300	7.5×10^5	5.5×10^{12}	105	2.7×10^5	2.6×10^5	6.0×10^4	1.9×10^5	2.1×10^7
221	300	7.0×10^5	5.1×10^{12}	94	2.2×10^5	3.9×10^5	7.0×10^4	2.7×10^5	2.4×10^7

(1) Count not distinguishable from background of counter.

FIGURE 15.

EXHAUST GAS DECONTAMINATION AS A
FUNCTION OF FEED ACTIVITY LEVEL IN
DRY ACTIVE WASTE INCINERATOR.

Table 29

DECONTAMINATION ACHIEVED IN INCINERATOR IN BURNING TESTS
WITH ADDED ACTIVITY

<u>Component</u>	<u>Decontamination Factor</u>
Furnace Body	220
Scrubbers	60
Schreier-Bartolucci	1.2
Pease-Anthony Venturi	50
A.E.C. Filter	2600
Over-all	3.4×10^7

1. Effect of Flow Rate on Capacity of and Decontamination Effected by a Mixed Bed Ion Exchanger

The manufacturer's recommendation for rate of flow through a mixed bed ion exchange unit is 2 gal./ (cu.ft.) (min.). This same recommendation is given for a cation exchanger, but previous work had shown that a flow rate as high as 10 gal./ (cu.ft.) (min.) could be used satisfactorily (ANL-4872, page 161). With a mixed bed exchanger, however, the capacity was found to be somewhat greater at 2 gal./ (cu.ft.) (min.) than at a 5 gal./ (cu.ft.) (min.) rate (340 versus 280 gal./cu.ft.), and the integrated decontamination factors up to total solids breakthrough were about 2.5 times greater at the 2 than at the 5 gal./ (cu.ft.) (min.) rate. It is therefore concluded that for a mixed bed unit, a flow rate of 2 gal./ (cu.ft.) (min.) is nearer optimum.

In the above work the feed used was tap water adjusted to pH 2.5 with nitric acid to which was added about 1×10^5 ct./ (min.) (ml.) of mixed fission products. Duplicate runs were made, the first using 5/8-inch diameter columns containing 3 cu.in. resin (1:2 HCR-H⁺:SAR-OH⁻) and the second set using 3/4-inch diameter columns containing 6 cu.in. mixed resin.

2. Regeneration of a Mixed Bed Ion Exchange Column

It was planned to determine the optimum concentration of sodium hydroxide to be used for regeneration of the anion portion of a mixed bed ion exchange unit and the minimum amount of regenerant solutions, but difficulty was experienced in obtaining consistent results which might permit adequate comparison. A satisfactory regenerating procedure was developed using 4 per cent sodium hydroxide and 6 N nitric acid.

The feed was tap water adjusted to pH 2.5 with nitric acid to which was added about 1×10^5 ct./ (min.) (ml.) mixed fission product activity.

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Efficiency of the regeneration procedure was based on a comparison of capacity after regeneration to the initial capacity prior to regeneration of a 45 cu.in. mixed bed, containing 15 cu.in. cation resin HCR-H⁺ and 30 cu.in. anion resin SAR-OH⁻.

In a series of ten regeneration cycles the bed capacity varied from 35 to 108 per cent of that initially, and averaged 70 per cent of the initial value, with no apparent relation to the volume of regenerants used. These data are given in Table 30. Discussions with the manufacturers and with equipment companies have shown that they do not attempt to regenerate so small a bed and that difficulties in laboratory manipulation are not encountered in larger units. A schematic diagram of the laboratory column appeared in ANL-4922, page 185. The end of the cation inlet tube was reduced from 7/8 inch to less than 1/2 inch to prevent currents of anion resin from developing above this plug and the interface of the resins. The regeneration procedure used was as follows (volumes given are for a 45 cu.in. resin bed contained in a 1-1/2 inch diameter glass column):

- (1) classification by recirculation of residual effluent (500 ml.);
- (2) down-flow treatment by 4 per cent sodium hydroxide through both resins (1380 ml.);
- (3) recirculation of distilled water rinse to reclassify resin (water removed by suction from top of bed) (500 ml.);
- (4) draining of bed to resin interface (50 ml.);
- (5) treatment of cation bed only with 170 ml. of 6 N nitric acid at flow rate of 10 ml./min.;
- (6) down-flow of distilled water rinse (2000 ml. at flow rate of 15 ml./min.); and
- (7) remixing of resin bed by air up-flow and stirring.

Regeneration Cycle No. 10 in Table 30 used the above procedure, and a 98 per cent efficiency resulted. Cycle No. 6, which gave even better results, was classified by hand, but this procedure cannot be recommended where large amounts of radioactivity are involved.

3. Decontamination Obtained on a Mixed Bed Ion Exchanger with Iron Powder

It has been shown in work at both Oak Ridge and Hanford that powdered iron was effective for the removal of ruthenium. Fission product analyses of effluents after passage through ion exchange units at this Laboratory have indicated that if ruthenium and cesium could be removed, decontamination factors could be increased considerably.

To determine if this could be accomplished, two mixed bed ion exchange units were set up, each containing 3 cu.in. of mixed resin (2:1 SAR-OH⁻:HCR-H⁺). To one of these columns was added 1.2 cu.in. (59.3 grams) of finely-divided iron (30 mesh). The feed used was tap water adjusted to pH 2.5 with nitric acid and to which was added solution to a level of about 5×10^4 ct./min. (ml.) beta activity. Flow rate was 13 ml./min., equivalent to 2 gal./cu.ft. (min.). The integrated decontamination factor after the passage of 2.25 liters, equivalent to 342 gal./cu.ft., was 330 for the mixed bed and 2000 for the mixed bed containing iron. In the effluent from the iron-containing bed at this point, almost 80 per cent of the beta activity was attributed to cesium while the remainder was substantially all ruthenium.

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Table 30

REGENERATION OF MIXED BED RESIN COLUMN

Feed: Tap water at pH 2.5 with additive to about

1 x 10⁵ ct./ (min.) (ml.)Column: 45 cu.in. 2:1 SAR-OH⁻:HCR-H⁺

Flow Rate: 2 gal./ (cu.ft.) (min.)

Regeneration Cycle	Volume Regenerant Solution, liters	Capacity to Total Solids Breakthrough After Regen., liters	Regeneration Efficiency, <u>Cap. after Regen.</u> x 100 42
0	0	42.0	-
1	5.9	11.5	27
2	7.2	26.0	62
3	5.9	24.0	57
4	4.9	14.5	35
5	3.9	33.7	80
6(a)	4.6	45.2	108
7(b)	13.1	35.0	83
8	4.5	29.0	69
9	4.6	32.0	76
10(c)	4.6	41.2	98
Average	5.9		70

- (a) Careful classification by hand shaking.
- (b) New backwash system installed. Developed an air leak during operation.
- (c) New acid inlet tube installed. Two classifications of resin bed.

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4. Comparison of Two-Bed Versus Mixed Bed Ion Exchange Resin System

As it is easier to regenerate a two-bed ion exchange system, a study has been made of the capacity and decontamination obtained using a two-bed system versus a mixed bed. The experiment was made using for the two-bed system 3 cu.in. of HCR-H⁺ cation resin in series with 6 cu.in. SAR-OH⁻. A mixed bed resin containing the same amount of the resins was set up to use the same feed. The feed was tap water adjusted to pH 7.0 with nitric acid to which was added about 2.5×10^5 ct./(min.)(ml.) mixed fission products.

Up to the breakthrough of total solids, the decontamination factor for the two-bed system was 1.4×10^3 and for the mixed bed 1.7×10^4 , with capacities of 406 and 356 gal./cu.ft., respectively.

However, if decontamination factors of only 50 are required, 550 gallons more can be passed through the two-bed system per cu.ft. of resin before regeneration is required. With the mixed bed, a decontamination factor of 140 can be obtained with the passage of 610 gal./cu.ft. beyond total solids breakthrough before regeneration is required. These data indicate that there is not much difference in total capacity of the resins whether a two-bed or mixed bed system is used, but decontamination factors are of the order of 3 to 10 times better with the mixed bed system. These data are shown in Table 31.

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Table 31

COMPARISON OF CAPACITY AND DECONTAMINATION OBTAINED FROM
MIXED AND DUAL RESIN BEDS

Feed: tap water adjusted to pH 7.0 with about 2.5×10^5 ct./(min.)(ml.)
 beta activity (PC-1 counter, 62 per cent yield)
 Columns: Two-Bed; 3 cu.in. HCR-H⁺ and 6 cu.in. SAR-OH⁻
 Flow Rate: 2 gal./(cu.ft.)(min.)

	Volume Increment, liters		Volume Increment, gal./cu.ft.		Integrated Decontamination Factor	
	<u>Two-Bed</u>	<u>Mixed Bed</u>	<u>Two-Bed</u>	<u>Mixed Bed</u>	<u>Two-Bed</u>	<u>Mixed Bed</u>
Before Total						
Solids Breakthrough	8.0	7.0	406	356	1.4×10^3	1.7×10^4
After Total						
Solids Breakthrough	11.0	12.0	559	610	44	1.4×10^2
	4.0	4.0	203	203	3.7	15
	2.5	2.5	127	127	4.0	3.4

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