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MOUND LABORATORY
Operated By
MONSANTO CHEMICAL COMPANY
MIAMISBURG, OHIO

Central File No. 56-12-29

MONTHLY TECHNICAL ACTIVITIES REPORT
THROUGH DECEMBER 15, 1956

BY

J. F. Eichelberger and D. L. Scott

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PRODUCTION PROGRAM

These projects are concerned with the production of alpha and neutron sources, and with the disposal of radioactive wastes Work is being done to improve present methods and processes.

Six polonium-beryllium neutron sources, two alpha sources and five plutonium-beryllium neutron sources were shipped this month.

One alpha source and two plutonium sources were for other AEC sites

The amount of alpha activity discharged to the river was reduced during this period while the beta activity was increased The volume of effluent discharge water was slightly lower than the preceding month

Data for the Waste Disposal Operations are given in Table I

TABLE I

DISCHARGE VOLUME	358,600	GALLONS
TOTAL ALPHA ACTIVITY	2.22	MILLICURIES
TOTAL BETA ACTIVITY	17.06	MILLICURIES
ACTIVITY DENSITY		
ALPHA	1.9	CTS/MIN/ML
BETA	13.9	CTS/MIN/ML

NUCLEAR RESEARCH AND DEVELOPMENT

CHEMISTRY AND METALLURGY

Chemical and metallurgical studies applicable to the weapons program are being made. These studies are directed towards the production of several radiochemically pure elements and of a chemically pure plastic material.

Ionium Project

The ionium project is directed toward the development of a process for the extraction of ionium from partially processed raffinates from the Mallinckrodt Uranium Refinery.

The acquisition of partial analytical data on the combined final products from previous ionium pilot plant runs has permitted the shipment of ten grams of ionium as a nitrate solution to Brookhaven National Laboratory on November 23, 1956. Two one-gram samples of ionium as a nitrate solution have also been bottled for shipment to Battelle Memorial Institute and to the New York Operations Office, respectively. Shipment of these latter two samples is being withheld until complete analytical data have been obtained.

Because of the high uranium content of Final Product No. 7, it has been decided to reprocess the material by using it to enrich Mallinckrodt feed, the arrival of which is pending. Approximately 2.5 grams of ionium were lost as the result of a leak in the two-gallon polyethylene storage bottle; the total ionium content is now 50.47 grams, of which 1.92 grams were taken for analytical samples.

The combined aqueous raffinates of Hot Run No. 9 (Final Product No. 7) are being precipitated with 50 per cent caustic solution to reduce the volume for subsequent disposal. The supernatant liquors will be assayed for ionium content, and if the alpha count is low enough will be discharged to Waste Disposal.

The organic raffinate from Hot Run No. 9 is being stripped with water in an attempt to reclaim ten grams of ionium. The resulting thorium nitrate solution is being precipitated with ammonium hydroxide to reduce volume. The hydroxide precipitate will be dissolved in nitric acid, and the solution will be used for feed make up. The supernates of the hydroxide precipitations will be discharged as waste if they are sufficiently depleted of ionium.

The stripped organic raffinate of Hot Run No. 9, together with approximately 210 gallons of stripped organic from previous operations, will be poured over sawdust in 30-gallon steel drums, which will in turn be inserted inside 55-gallon steel drums, also filled with sawdust. The double drum units will be turned over to the Health Physics Department for disposal. Disposition of used organic solvents has presented quite a problem. It was decided that burial at Oak Ridge National Laboratory probably was the best and safest means. It is of interest to note that laboratory studies have shown sawdust to be a better absorbent than vermiculite in this problem.

Further modifications of the small mixer settler units were made. A tube of smaller inside diameter was used between the feed weir and the mixer to obtain better mixing; however, the flow rate was lowered below the minimum required. It is hoped that a suitable compromise can be obtained between the length and the inside diameter of the tube which will permit an adequate flow of feed and still produce better mixing characteristics.

A compact, four-stage, belt-driven stirrer unit is nearly complete.

Protactinium Project

> *The Albuquerque Operations Office has authorized the production of a gram of protactinium-231 from the unprocessed Sperry-Filter Press residues from Mallinckrodt which remain after the isolation of the first gram*

Strip Experimentation. - Experiments were conducted to determine the efficiency of various solutions in stripping protactinium from the organic extract obtained from the Mallinckrodt raffinate residue. Two liters of feed were extracted with a 50-50 mixture of diisobutylcarbinol (DIBC) and Amsco solvent. Ten milliliters of the resulting extract was mixed for five minutes with one milliliter of each of the strip solutions listed in Table I. Samples from each of the two phases were gamma counted at the 300 Kev peak. The stripping efficiency is reported in terms of the per cent of the protactinium found in the aqueous strip solution. Further experiments with dilute solutions of $TiCl_4$ and $TiCl_3$ will be conducted.

TABLE I

STRIP SOLUTION	PROTACTINIUM RECOVERED IN AQUEOUS STRIP SOLUTION *per cent*
3% H_2O_2	69.7
10% H_2O_2	60.1
20% H_2O_2	74.0
30% H_2O_2	65.7
H_2O	67.8
20% $TiCl_3$	--
2% $TiCl_3$	94.6
10% $TiCl_4$	0.8
SATURATED $SnCl_2$	65.6
SATURATED CuCl	63.2
0.05 *M* NH_4Cl	66.5
0.1 *N* HCl	63.7

To determine the extent to which iron was removed by water from the organic raffinate of Column 3, shown in Figure 1, a five milliliter sample of this liquid, stripped of 93.7 per cent of the protactinium, was treated with an equal volume of water. Tests showed no residual iron present in the treated organic.

Column Development - The 50-gallon, glass-lined, steam-jacketed pressure kettle has been installed in GP 1-B. A digestion of Mallinckrodt raffinate residue from drum No. 44 was made by adding 72 pounds of residue to 200 pounds of 66° Baume sulfuric acid preheated in the kettle at 109°C and 30 psi steam pressure for one hour. During the addition, the temperature rose rapidly to a maximum of 148°C, and fumes of SO_3 and NO_2 were evolved. After two hours

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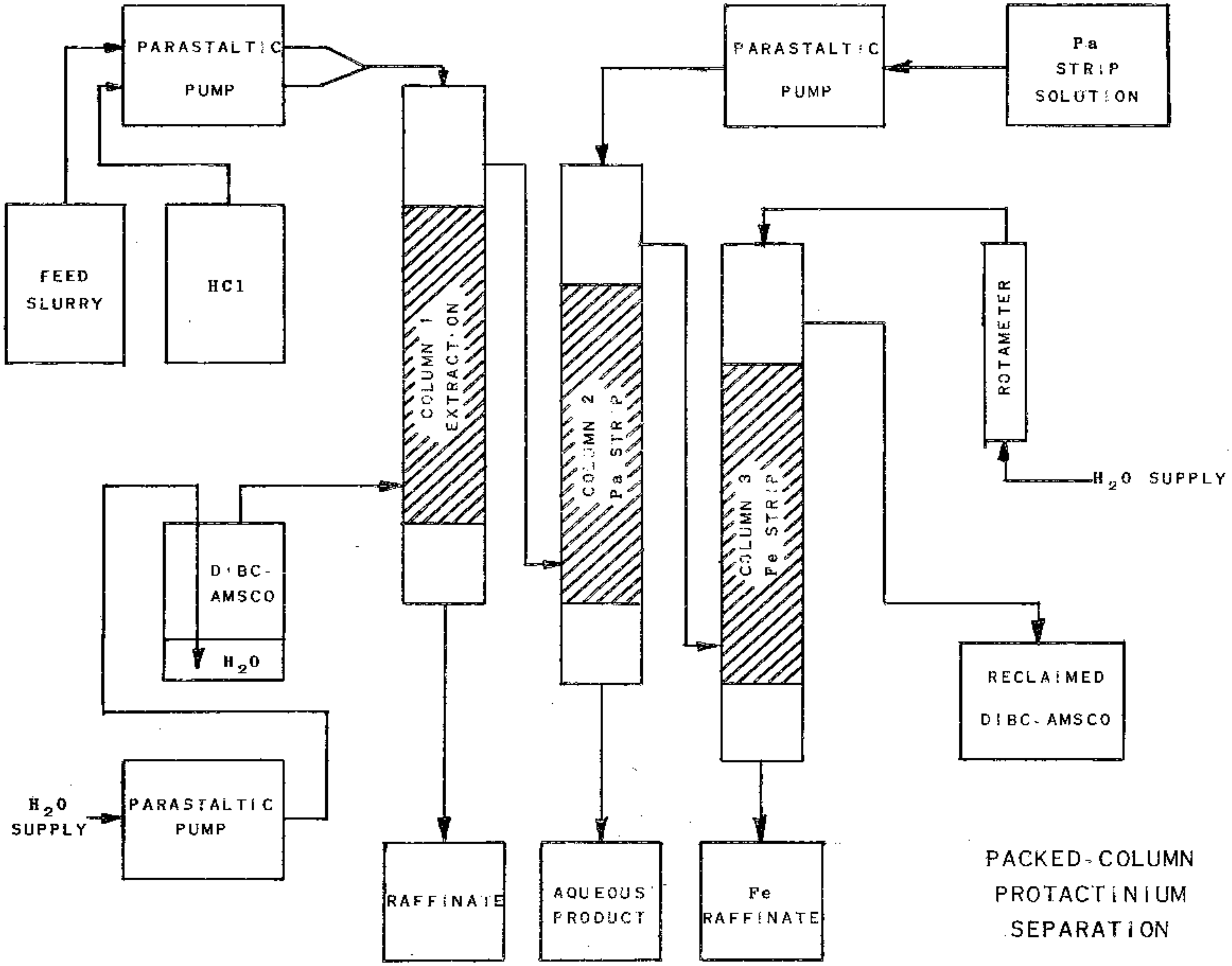

PACKED-COLUMN
PROTACTINIUM
SEPARATION

FIGURE 1

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the steam was turned off and the temperature fell to 116°C. The digested slurry cooled overnight to 37°C and rose again to 69°C when a volume of water equal to the original volume of acid (49.3 liters) was added.

Equal volumes of the digested slurry and concentrated hydrochloric acid were shaken together, and 31 milliliters of this mixture was extracted four times with 7.5 milliliters of pre-equilibrated 50-50 DIBC/Amsco. After the last extraction, the supernate was separated from the solids, and the solids were redigested with sulfuric acid at fuming temperature for one hour. Water and hydrochloric acid were added, and this slurry was equilibrated twice with four milliliter portions of organic. The results of these extractions are listed in Table II.

TABLE II

EFFICIENCY OF EXTRACTION OF 50-GALLON DIGESTION OF MALLINCKRODT RESIDUE

SAMPLE	ACTIVITY AT 300 KEV *cts/min*	Pa IN ORGANIC* *per cent*	PER CENT OF TOTAL 300 KEV COUNT
1ST EXTRACT	59.4	18.9	12.6
2ND EXTRACT	200.6	64.0	42.4
3RD EXTRACT	32.6	10.4	6.9
4TH EXTRACT	1.6	0.5	0.3
1ST SUPERNATE	51.6	—	10.9
1ST SOLIDS	334.7		
5TH EXTRACT	17.1	5.5	3.6
6TH EXTRACT	2.3	0.7	0.5
2ND SUPERNATE	12.5	—	2.6
2ND SOLIDS	95.1		20.1

*THESE PERCENTAGES, AS IN THE LAST REPORT ARE BASED ON 100% OF THE Pa BEING IN THE ORGANIC PHASES AFTER TWO DIGESTIONS AND SIX EXTRACTIONS

These data show that 93.8 per cent of the protactinium was obtained in a single digestion and four extractions. Again, it may be noted that the protactinium was not readily extracted into the organic phase in the first extraction; however, by digesting so that an increase in temperature occurred, the amount of protactinium in the first extraction was increased by about 15 per cent. In addition, the digested slurry was more fluid that obtained by a 100-degree digestion, and the nitrates were decomposed.

It is apparent that iron has a larger distribution coefficient in these solutions than protactinium since the first extractions contain more iron than later ones. All of the iron is extracted by the organic solvent. The raffinate supernates give a negative test for iron, and the last organic extracts also give a negative test.

The three small columns set in GP-1B have been completed and two runs have been made through the extraction column. A flow sheet of this equipment is shown in Figure 1. The slurry feed was stirred continuously and pumped through glass and Tygon lines. The lines were kept small so that the linear velocity was high and no sanding-out occurred. The feed and hydrochloric acid were pumped through Tygon lines with the same Sigmamotor pump and these streams joined and mixed through a Y tube. The organic was pumped by displacement with water since Tygon becomes hard in contact with the organic solvent, and the hydrochloric acid in the organic solvent would have corroded the stainless steel pumps. The columns were filled with $\frac{3}{8}$ inch beryl saddles which were supported above the horizontal marks shown on the columns in the diagram with glass and Teflon. This enabled closer control of the interface when the column was run with the organic as the continuous phase with the interface at the bottom. The columns were staggered vertically with a one-foot drop between each so that the organic flowed through the system by gravity. Each column was five feet long with about 3½ feet of packing.

The first run through the columns utilizing the raffinate obtained from the preparation of the organic product for strip experiments showed that the slurry readily flowed through the packing. The second run was made through Columns 2 and 3, and utilized the organic left from the strip experiments. The flow rates were found to be in error so the pumps were re-calibrated.

The third run was made through Column 1 only. The feed was part of the 50 gallons prepared in the pressure kettle. An organic-to-feed ratio of 0.25/1 was used so that the data could be compared to the small-scale experiments on the same feed. Total through-put through the column was 1.5 gal/hr (0.6 gal/hr each of feed and hydrochloric acid and 0.3 gal/hr of 50-50 DIBC Amsco). The column was run for 3½ hours with organic as the continuous phase, and samples were collected of the aqueous raffinate and of the organic extract at the intervals shown in Table III. The samples were prepared and counted in the same manner as in all of the previous experiments.

TABLE III

RESULTS OF EXTRACTION COLUMN RUN PPP-3

TIME FROM START-UP *hr*	ACTIVITY* AT 300 KEV ORGANIC *cts/min*	AQUEOUS SUPERNATE *cts/min*	SOLIDS *cts/min*	Pa IN ORGANIC** *per cent*
0.5	129.4	237.8	209.3	35.2
1.0	129.8	208.5	194.3	38.4
1.5	127.5	223.5	207.8	36.3
2.5	144.9	205.5	165.8	41.4
3.5	133.1	207.8	178.5	39.0

*ON THE BASIS OF A 5 G SAMPLE.

**ASSUMING ALL OF THE 300 KEV COUNT REMAINING IN THE SUPERNATE IS PROTACTINIUM.

By comparing these data with the laboratory data on the same feed it is concluded that the 3½ feet of packing is equivalent to more-than-one but less-than-two stages. The overall distribution coefficient between the organic and aqueous phases for protactinium in this experiment is approximately 2.5, which gives an extraction factor of 0.62. It was decided to increase the extraction factor to 1.2 in the next column run.

The fourth run was made with the extraction column only and the feed, acid, and organic flow rates were all held at 0.5 gal/hr. The run was interupted by a clogged feed line which had to be replaced with larger-bore glass tubing, however, the data are given in Table IV.

TABLE IV

RESULTS OF EXTRACTION COLUMN RUN PPP-4

TIME FROM START UP *hr*	ACTIVITY* AT 300 KEV ORGANIC *cts/min*	 AQUEOUS SUPERNATE *cts/min*	 SOLIDS *cts/min*	Pa IN ORGANIC** *per cent*
0.5	120.7	186.0	192.8	39.4
1.0	196.1	174.8	203.3	52.9
1.5	181.0	207.0	191.3	46.6

*BASED ON A 5 G SAMPLE.

**ASSUMING ALL OF THE 300 KEV COUNT REMAINING IN THE SUPERNATE IS PROTACTINIUM.

A ten-foot column, two inches in diameter is being set up in GP-1B. Experiments with this column will give the height required and the expected through put of a large production column to be placed in HH-Building. It is believed that the production column will be about 15 feet high and four inches in diameter.

Experiments will be conducted on the boil-down of the aqueous strip product for the second concentration step, since protactinium and iron are the only major components. If the boil down experiments are successful, some consideration will be given to a two column operation where no attempt will be made to partition between the iron and protactinium after extraction; rather, both elements will be stripped from the organic phase and the iron will be separated later. It is believed that this may cut protactinium losses.

Source Analysis. - Five samples of residues containing protactinium have been received from Great Britain. The samples are identified by the name "Ethereal Residues", and bear the reference numbers AB14072 A1 through A5.

Preliminary analysis of two of the samples has been completed. The samples are found to contain 1.7 parts per million of protactinium, which is ten times the concentration found in the average raffinate residue obtained from Mallinckrodt Chemical Works. This value is an estimate based on the gamma counting rate at 300 Kev of the protactinium recovered and concentrated from the British samples as compared with the counting rates at the same energy of several samples prepared from a known weight of protactinium. A more reliable figure will be obtained by alpha-counting after gamma analysis of all five samples has been completed. It is anticipated that the estimate will have to be revised downward slightly, because the standard gamma sources are approximately seven years old and contain significant amounts of decay products.

The British samples are similar in appearance to the Mallinckrodt raffinate residues, and a rough gamma analysis indicates that they are also radiochemically similar However, the principal gamma peak was in the 85 to 95 Kev region rather than at 68 Kev, indicating that ionium has not been concentrated in the British samples. The 27 Kev peak of protactinium is evident but not prominent.

The samples are quite solid as compared with the Mallinckrodt material, and do not disintegrate readily in cold, concentrated hydrochloric acid. After having been heated for one hour with twice the sample weight of concentrated hydrochloric acid, the weight of the wet, centrifuged residue is about 30 per cent of the weight of the original material

The procedure used for determining the protactinium is a modification of the method of analysis used for the Mallinckrodt material. When the Mallinckrodt samples were heated at approximately 90°C for one hour in contact with twice the sample weight of concentrated hydrochloric acid, the residue contained about 90 per cent of the protactinium. When the British samples were treated in the same manner the residue contained only about 10 per cent of the protactinium When titanium carrier was added to the supernate from the hydrochloric acid treatment of the Mallinckrodt samples and the mixture heated, a precipitate of hydrated titanium oxide appeared within ten minutes, and this precipitate carried the remaining protactinium from solution. In the case of the British samples, however, no precipitate appeared after an hour, and it was necessary to add phosphoric acid to the solution in order to obtain a precipitate, with or without added titanium. This precipitate carried the dissolved protactinium

Once the precipitate of titanium oxide appeared however the treatment of the samples was identical with that previously used The precipitates were digested with hot concentrated sulfuric acid, and were then made nine normal in sulfate and six normal in hydrochloric acid. They were extracted with diisobutylcarbinol (DIBC) until the aqueous phase had no significant counts at 27 and 300 Kev on the pulse height analyzer.

The DIBC fractions were combined and were then stripped by allowing them to stand over one-tenth their volume of 30 per cent hydrogen peroxide for about 16 hours. This procedure which relied solely on the decomposition of the hydrogen peroxide for agitation, produced an aqueous phase containing between 95 and 98 per cent of the protactinium previously in the organic phase. The aqueous phase was again adjusted to the proper acidity with sulfuric and hydrochloric acids and re-extracted. The cycle was repeated until all of the protactinium had been concentrated into a single sample of less than three milliliters. When the concentrated product was counted, it contained 97 per cent of the sum of the counts obtained at 300 Kev from all of the DIBC fractions.

An effort was made to recover all traces of protactinium, particularly from the residue which was insoluble in hot, concentrated hydrochloric acid. Hydrofluoric acid attack on the residue, both hot and cold resulted in the recovery of only 0.5 per cent additional protactinium. The residue was treated several times with hot Versene solution (tetra-sodium salt of ethylene diamine tetraacetic acid) to leach out radium and thorium isotopes, since in previous work it had been found that Versene treatment selectively extracted radium and thorium, leaving protactinium quantitatively in the insoluble residue No additional protactinium was found in the residue The Versene solution was acidified to pH 4 with concentrated phosphoric acid, and the resultant precipitate was scanned Prominent peaks were found at 80, 150, and 275 Kev, but none at 27 Kev. The precipitate was digested with sulfuric acid and extracted with DIBC, but no evidence of additional protactinium was found.

It is interesting, and may be useful, to speculate as to the reason for the difference in protactinium concentration between the Mallinckrodt samples and the British samples. The Mallinckrodt uranium refining process may be briefly summarized as follows: The uranium ore is digested with nitric acid, and barium and iron salts are added to remove sulfate and vanadium ions. After filtration, the acidity is adjusted, and the solution is extracted with diethyl ether. The acid concentration of the aqueous phase drops as nitric acid is extracted with the uranium, and a precipitate appears in the aqueous raffinate. This precipitate comprises the raffinate residue which has been the source of protactinium produced at Mound. It is assumed that the British process is similar, and that the "Ethereal Residues" correspond to the Mallinckrodt raffinate residues. The principal constituent of the Mallinckrodt raffinate residues is ferric phosphate, which precipitates as a result of the decrease in acidity. It is reasonable to assume that maintenance of the acidity either by makeup acid or by the use of a higher initial acid concentration would tend to keep ferric phosphate and many other phosphates in solution. However, thorium, niobium, zirconium, and titanium phosphates in particular, are quite insoluble even at moderately high nitric acid concentration. If these phosphates precipitated, carrying protactinium, and the more soluble phosphates passed through filtration, the protactinium concentration of the raffinate residue would be enhanced by a factor which would depend entirely on the amount of iron and other cations which failed to precipitate as phosphates.

The fact that it was not possible to obtain a titanium carrier precipitate without the addition of phosphoric acid tends to confirm the hypothesis that the reason for the protactinium enrichment of the "Ethereal Residues" is connected in some way with the phosphate concentration.

Analysis of the other three samples is continuing, and it is expected that a complete report, including spectrographic analyses, will be available next month.

Plutonium Urinalysis

> *Present methods for determining the amount of plutonium in human urine give unsatisfactory results. A study directed towards adaptation of the present successful procedure for actinium-thorium urinalysis to the recovery and determination of plutonium is being made.*

A number of experimental variations of the method currently used to determine thorium and actinium have been made in an effort to obtain plutonium yields of 90 per cent or greater.

In the control procedure, a 24-hour urine sample is made ammoniacal, and the resultant calcium and magnesium phosphate precipitate is separated from the supernatant liquid by centrifugation. The precipitate is redissolved in nitric acid, and the solution is evaporated to a low volume to destroy residual organic material. The solution is diluted, radiochemically pure cerium is added, and cerium phosphate is precipitated by adjusting the acidity. The cerium phosphate, which carries the plutonium, is mounted and alpha-counted.

A series of 24-hour urine samples was run by the control procedure, and the average plutonium yield was approximately 70 per cent. It was found that the principal loss of plutonium occurred in the initial concentration step involving the precipitation of calcium phosphate at pH 10 or greater. Several experiments were carried out in order to determine the reason and remedy for this loss. Results indicated that:

1. Addition of cerium carrier prior to the calcium phosphate precipitation did not significantly affect the yield;
2. Precipitation of the calcium phosphate at pH 8 instead of pH 10 reduced the yield to 40 per cent;
3. Precipitation of the calcium phosphate from homogeneous solution by heating the urine to decompose the urea improved the yield to 80 per cent;
4. Addition of five milliliters of sulfur dioxide-saturated water to the urine prior to calcium phosphate precipitation did not affect the yield significantly;
5. Stirring for one hour with 10 grams of hydroxylamine hydrochloride at pH 0.5 followed by calcium phosphate precipitation reduced the yield to 50 per cent; and;
6. Stirring for one hour with 30 grams of potassium iodide at pH 1 to 2 followed by calcium phosphate precipitation improved the yield to 84 per cent.

It is possible that some of the results may be better than the reported figures indicate. There is some evidence that the plutonium spike solution used in these experiments may have hydrolyzed to some extent, so that the losses may be more apparent than real. The more promising of the experiments reported above will be repeated with fresh spike solution. In particular, the precipitation from homogeneous solution and the reduction of plutonium (VI) by potassium iodide may, in combination, produce the desired yield of 90 per cent or better.

Plastics Project

This project is immediately directed toward developing a satisfactory process for the blending of diallyl phthalate powder and filler into a plastic whose physical and chemical properties are suitable for the molding operations at Mound Laboratory. When this process has been satisfactorily developed, a search for materials and processes which will provide superior physical and chemical properties will be instituted.

Filler Evaluation - A sample of Johns-Manville of Canada asbestos floats 7RF-1 was stirred with water in the hydraulic separator and 57 per cent of essentially nonfibrous material was removed. Much of the finer magnetite was apparently also removed. The dried fibers were much cleaner, but adhering magnetite could still be observed under the microscope. It is possible that an additional separation by magnetic means would result in a useable product, although the yield would be low.

Fiber-Frax is a fibrous, high-temperature, thermal insulation. It is believed to be a blown, synthetic aluminum silicate. The fibers are very fine and relatively short. A mass appears to be very white, but it does contain large pieces of sintered material, and close examination reveals a small amount of other foreign material, some of which is black. Microscopic examination showed that many of the fibers have a small, solid, transparent sphere attached to one end. These spheres are much larger in diameter than are the fibers to which they are attached. A preliminary experiment showed that many of these spheres could be removed by stirring a suspension of the material in water. Since Fiber-Frax costs one dollar per pound and, since the loss in weight caused by removing the spheres would be large, the cost of a purified Fiber-Frax would be quite high.

Four additional samples of asbestos have been obtained from Hill Brothers Chemical Company. Two of these, No. 20 and No. 35, appear to be far cleaner than any other sample of asbestos floats. Both samples, however, contain visible magnetite.

Mr. John V. Harte and Mr. W. C. Streib of Johns-Manville visited Mound Laboratory in conjunction with our inquiries concerning asbestos. They felt that there was no commercial asbestos which would meet our requirements, but felt that a custom processor might be able to produce a suitable grade. They recommended the Cellulo Company of Sandusky, Ohio.

We have found Mr. Peter P. Mellio of the Cellulo Company to be most cooperative. He has sent us two samples of asbestos which are white, and which appear to be nearly free of nonfibrous material. The fibers are silky and fine but there is a significant percentage of fibrous *sticks*.

Sample No. 10 is an acid-washed, Arizona asbestos and is a standard commercial product sold as a filtering medium. The maximum fiber length is about 0.25 inch, and the iron content is less than 0.08 per cent. Sample No. 100 is the No. 10 material which has been subjected to additional grinding and screening. The fiber length has been reduced to approximately one-half of that for sample No. 10. It still contains a significant amount of fibrous *sticks*. It is felt that the mechanical working during processing may be more effective in breaking-up these fibrous *sticks* than it was in breaking up the larger less fibrous *sticks* in the Colorado, acid-washed asbestos.

Product Formulation - The remaining 13 lots of formulation B9 have been milled on the differential rolls. A fairly wide spread of flow times was obtained. Mill runs B9-2, B9-3, and B9-4 were sent to Cumberland Engineering Company for experimental grinding tests. A pigment, or blend of pigments was milled into each of the remaining lots of B9. The pigments milled-in surprisingly rapidly and a uniform dispersion was obtained during milling in all cases.

The Esterline-Angus recording wattmeters have arrived, but installation is awaiting the availability of Engineering Division manpower. The need for instrumental assistance in determining the end-point of the milling operation has now been amply demonstrated.

Seven small formulations have been made this month. These were all mixed by hand in a large beaker. The sum of the weights of the filler and of the prepolymer was two pounds, and the weight of monomer, of stearate, and of catalyst, was two per cent of the prepolymer weight in each case. Other pertinent details of these runs are given in Table V.

TABLE V

DIALLYL PHTHALATE FORMULATIONS

BATCH NO.	FILLER USED	RATIO FILLER TO PREPOLYMER	RATIO ACETONE TO PREPOLYMER	REMARKS
B10	HILL BROS. NO. 954	1	1	PIGMENT MILLED IN
B11	FIBER-FRAX	1	1	PRE-POLYMER SOLUTION SQUEEZED OUT DURING MILLING
B12	CELLULO NO. 100	1	3	DRIED AT ROOM TEMPERATURE BEFORE MILLING
B13	CELLULO NO. 100	1	3	PLACED ON ROLLS WITHOUT DRYING
B14	CELLULO NO. 10	0.666	1	ARC RESISTANCE 138 SECONDS
B15	CELLULO NO. 10	0.50	1	STIFF PRODUCT
B16	CELLULO NO. 100	0.50	1	SLIGHTLY SOFT PRODUCT

Batches B10 and B11 were made primarily to demonstrate our processing to Mr. George Price. Batch B11 also served as a preliminary test of the use of Fiber-Frax as a filler. This product was tough, but appeared to be very abrasive. The pre-polymer solution squeezed out when the mix was placed on the rolls and old resin under the roll guards was extracted which resulted in a rather highly-colored product. The spheres were visible in molded pieces made from B11.

Mill runs B12 and B13 were processed with difficulty. The rolls had to be opened wide to get the fibrous material to transfer to the rolls. The material became plastic slowly, and finally gave a very tough sheet. There was little tendency for the material to crack on the edges, and it seemed to retain adhesion to the rolls for a much longer period of time than usual. Although by all previous criteria these two batches should have been soft, they were both very stiff products of low flow.

Mill runs B14 and B15 were made with a lower ratio of asbestos to pre-polymer. They were also difficult to process. Run B15, with the lowest asbestos content, processed more nearly like material made from asbestos floats. It was quite tough and had little tendency to crack on the edges. As a consequence, it was milled too long and had low flow.

Run B16 was made in an attempt to get a product much closer to the desired flow. It was slightly soft but was much closer to the desired value than any of the others of this series.

Product Evaluation - Three preforms each were made of B12 and B16 products. These were molded into heads in production dies. The first preform of B12 gave only one head, but five heads were obtained from each of the other two preforms. These heads were semi-transparent, and the electrodes could be readily seen in strong light. Internal cracks developed on standing in the area diametrically opposite the gate. All three preforms from B16 gave five heads. These were somewhat more transparent. They did not develop stress cracks on standing. Although some asbestos fiber clumps were visible to the eye they could not be seen on the X-ray negative.

Production Materiel Control - Several flow curves have been run on Acme and Mesa plastics as part of the testing for suitability for production molding. The Acme material has tended to be stiff and to be too dirty for production use. The first large shipment of Mesa plastic was fairly dirty, but could be used by production.

A preliminary study has been made on some of the problems involved in the use of the Furane cement. The pot life at room temperature is only about 45 minutes. If kept at 10°C after mixing, the pot life is extended to about 2.5 hours, while if kept at 0°C, the pot life is about 5 hours. A large master batch can, therefore, be blended and stored for several hours, if refrigerated and protected from moisture absorption.

The time required for a drop of cement to harden at an elevated temperature is quite short. The time varies with activator concentration; and for a given activator concentration, the hardening time varies with the length of time following the initial mixing of resin and activator. It seems probable that a rapid, semiquantitative test for the activator concentration can be developed on this basis. It is also possible that a similar test can be developed to periodically check whether a pot of cement is still satisfactory for use. Further work is planned along these lines.

GENERAL WEAPONS DEVELOPMENT

Process development work is being conducted on the use of thermal diffusion for the production of certain gaseous isotopes which are not at this time identified with particular weapons, but which are needed for research and development purposes in the weapons program.

Isotope Separation Project

Column Operation - Work has continued on the accumulation of design data for a thermal diffusion column plant for separation of nobel gas isotopes. Preliminary static runs with xenon on the 1.00-inch column have indicated an optimum initial pressure of 50 mm of Hg, or 0.066 atmosphere. At this pressure, and with the 0.064-inch diameter molybdenum center-wire at 1000°C, the column exhibits a separation factor between xenon-129 and xenon-136 of approximately 2.5 after four hours operation. After this period of time the separation process is apparently within a few per cent of equilibrium. Rapid accumulation of data on xenon is hampered by the fact that the mass spectrometer shows decided memory effects for xenon. Two to three samples per eight-hour day seems to be the practical limit under the present mode of operation.

The 1.25-inch column, rebuilt last month, was leak-tested aligned and reinstalled in the south hood. A molybdenum center-wire 0.064-inch in diameter was installed and appropriate wire aligners were built and fitted. This column is to be used in cascade with the 1.00-inch column to determine additional design data for the xenon separation project.

Work was continued on the continuous-flow separation of 10 per cent hydrogen, 90 per cent helium mixtures in the 1.50 and 1.61-inch columns operating in cascade. The interconnecting system of the two columns was modified so that the light constituent product of the 1.61-inch column was used as a feed gas into the 1.50-inch column. The overall separation characteristics of this product-feed system were determined and compared to the characteristics of the system used previously in which a controlled gas interchange was maintained between the top of one column and the bottom of the other. The performance of the two systems was apparently about the same. However, since the product-feed system introduces a problem of matching two independent feed points, one in each column, and also requires an additional gas draw-off at the raffinate end of the second column, it appears that the intercirculation system would be more desirable for purposes of purifying relatively large quantities of gas.

Work was done with the 1.61-inch column to determine the maximum separation under dynamic conditions at a given throughput rate as a function of column pressure. With an input rate of 4.5 liters per hour at the midpoint of this column, with draw-off rates at each end of the column in the same ratios as the mole fractions of the two components of the input mixture, with a center-wire temperature of 1000°C, and with a raffinate purity maintained at 99.5 per cent or better, this column exhibited a maximum separation at 800 mm of Hg operating pressure, or about 525 mm of Hg initial pressure.

Since it was then observed that the separation factor varies with the raffinate and product purities, it was decided to determine the separation factor only when these purities were equal. Under these conditions, and at 800 mm of Hg operating pressure, the draw-off rates were adjusted to equilize the purities of the product and raffinate. The maximum purities obtained were 98.7 per cent.

In order to complete the study of the effect of pressure on the separation factor of the 1.50 and 1.61-inch columns in cascade under dynamic conditions in a reasonable length of time, and in order to determine the feasibility of long-time continuous operation, the cascade was operated continuously for 104 hours. During this time samples were taken, and flow rates were checked and adjusted at intervals not exceeding six hours. The center wire temperatures and the operating pressure were exceptionally stable throughout the run; both were maintained within ± 1 per cent of their preset values. The flow rates were very constant for the first 75 hours. After this time considerable regular readjustment of the speed of the Sigmamotor pumps was required to offset decided decreases in the flow rates which were attributed to fatique in the Tygon tubing passing through the Sigmamotor pumps. Although the tubes were observed to have fatigued badly, there were no complete failures.

It has been observed that improperly located feed points under dynamic operation are detrimental to the column performance. A manifold was built and installed that permits selection of any of four adjacent feed ports without interrupting the column operation.

A total of 250 hydrogen-helium gas samples and 26 xenon samples were analyzed on the mass spectrometer this month. This work was done in conjunction with the above experimentation.

Gas Purification - A manifold and vacuum system were prepared for testing the effectiveness of a charcoal-liquid air trap in purification of helium. The vacuum system was outgased and pumped down to 4.6 x 10^{-6} mm of Hg.

A glass electrolysis cell was modified so that it worked smoothly without detonation of the hydrogen and oxygen in the re-combiner. The current density was about one ampere at 28 volts, which is the maximum D.C. voltage presently available. Larger capacity will be needed to produce appreciable quantities of re-combined water.

Work is progressing on the uranium chemical pump. The core which houses the heaters is completed. This is the largest machined part.

Material and equipment for the gas purification process in R-106 are beginning to arrive. The work in construction and assembly of the supporting rack will begin immediately upon obtaining the basic materials.

The palladium diffuser unit which had been previously sub-contracted to South Park Tool and Mold, Inc., Dayton, Ohio, was brought to Mound Laboratory. It was leak-tested under helium pressure by personnel of our Research Division, and exterior welds and fittings proved to be leak-proof. A later trip to South Park Tool and Mold, Inc., for a final inspection of the coil windings, showed satisfactory workmanship. After an annealing and cleaning process there, the unit will be returned to Mound Laboratory for final work and installation.

Liquid Thermal Diffusion - Plans are being made for development work on liquid thermal diffusion columns scheduled to arrive shortly. Initial static experiments with simple systems will determine the dependence of separation factor, composition gradient, and equilibrium time on temperature level and temperature gradient. Subsequent dynamic experiments will expand the study to reveal the influence of variations in feed point, feed rate, and relative draw-off rate.

Mass Spectrometric Analysis - Analysis of samples of gas taken from the thermal diffusion columns is routinely done with a Consolidated-Neir Model 21-201 mass spectrometer. Methods have been worked out for determining separate isotopic constituents in a mixture of the light gases hydrogen, deuterium, and tritium. The analysis is complicated not only by the presence in the ionized gas of six species of singly-ionized molecules, H_2^+, HD^+, D_2^+, HT^+, DT^+, and T_2^+ but also by the presence of three monatomic ions, H^+, D^+, and T^+, resulting from the molecular dissociation of the six isotopic compounds at the ionization source. A variety of complex ions consisting of single or multiple charges on polyatomic molecules are also present, but with the possible exception of singly-charged triatomic molecules, these complex ions are considered to have a negligible effect on this particular analysis. The triatomic ions are easily detectable with this instrument, but in general, their beam intensities are very small compared to the beam intensities of the diatomic and monatomic ions. Hence, their presence is thought to have an insignificant effect on the analysis, and for simplification we consider only the normal molecular species and their dissociation products.

Upon scanning the mass spectrum of a gas mixture containing appreciable quantities of the three isotopes of hydrogen, six distinct peaks of ion beam intensity are observed corresponding to masses 1, 2, 3, 4, 5, and 6. The contributions to these peaks is as follows:

mass 1 - H^+
mass 2 - H_2^+ and D^+
mass 3 - HD^+ and T^+
mass 4 - D_2^+ and HT^+
mass 5 - DT^+
mass 6 - T_2^+

It will be noted that these six peaks do not exactly correspond in mass to the six isotopic compounds. Also, since there are contributions to H^+ from the dissociation of H_2, HD and HT contributions to D^+ from HD, D_2, and DT and contributions to T^+ from HT, DT, and T_2, the ion beam intensities of masses 1, 2, and 3 are decidedly affected by the entire molecular constitution of the gas in the source. Hence it is necessary to determine the molecular distribution entering the source before the known mass discrimination effects in the system can be taken into account.

If a situation is considered in which no dissociation occurs, the spectrometer would show a distribution of ion beam intensities thus:

A volts from H_2^+
B volts from HD^+
C volts from D_2^+
D volts from HT^+
E volts from DT^+
F volts from T_2^+

Since the ion beam intensities are, in general, in the same ratios as the partial pressures of the constituents in the source, the relative values of A, B, C, D, E, and F would be the mole fractions of the constituents of the gas reaching the source. Note that C and D both contribute to mass 4. Now, if a molecular dissociation is permitted to occur in the source, there will be a certain fraction of monatomic ions produced for each molecular dissociation, and these ions will be accelerated and detected in the normal manner. Also, it is to be expected that for each of the cross-products, such as HD, the monatomic ions produced from dissociation of any one type of molecule, H^+ and D^+ in this example, would be present in the ion beam in equal quantities. We can now define a value n_i as the fraction of monatomic ion pairs in the total ion beam. From this we designate several values as follows:

$$\begin{aligned} a &= (1 - n_a)\,A \qquad & d &= (1 - n_d)\,D \\ b &= (1 - n_b)\,B \qquad & e &= (1 - n_e)\,E \\ c &= (1 - n_c)\,C \qquad & f &= (1 - n_f)\,F \end{aligned} \qquad (1)$$

These values are then the contributions of the diatomic ions to the ion beam intensities of masses 2, 3, 4, 5, and 6. The amount of H^+, for example, that arises from the dissociation of H_2 will now be $2n_aA$. From equation (1) this amount is $2\frac{n_a}{(1 - n_a)}a$. Let the quantity $\frac{n_a}{(1 - n_a)}$ be called r_a, and b_a be defined as the dissociation coefficient of the molecule H_2. Similar definitions are given for the dissociation coefficients of the other five molecules, the subscript notations being the same as in the equation (1).

The contribution to the mass 1 peak is then two H^+ ions effectively resulting from the dissociation of one H_2 molecule and one H^+ ion each from the dissociations of HD and HT; i.e.:

$$M_1 = 2\ r_a a + r_b b + r_d d$$

where M_1 is the mass 1 peak height. Similarly, it follows that:

$$\begin{aligned} M_2 &= a + r_b b + 2\ r_c c + r_e e \\ M_3 &= b + r_d d + r_e e + 2\ r_f f \\ M_4 &= c + d \\ M_5 &= e \\ M_6 &= f \end{aligned} \tag{2}$$

Thus, in order to interpret the ion intensity values accurately it is necessary to measure r_a, r_b, r_c, r_d, r_e, and r_f directly on the specrometer. This can be done by introducing extremely pure samples of the isotopic molecule in question into the spectrometer and measuring the relative ion beam intensities of the molecule and of its dissociation products. We can obtain very pure samples of H_2, D_2, and T_2 from our thermal diffusion columns for the determination of r_a, r_c, and r_f. The measurement of r_b, r_d, and r_e is complicated by the fact that the pure cross products may be partially equilibrated in the ionizing medium. Also, only samples of HD, HT, and DT of 50 per cent purity could conceivably be obtained from the thermal diffusion columns, since it has been observed that gas samples taken from the columns are completely equilibrated with respect to the isotopic compounds.

Preliminary values for r_a and r_c have been measured using tank samples of hydrogen and deuterium and both were found to be approximately 0.0045. It is not unreasonable to expect that all the dissociation coefficients are of the same order of magnitude. If we assume that $r_a = r_b = r_c = r_d = r_e = r_f = r$, then in equation (1), a, b, c, d, e, and f are in the same ratios as A, B, C, D, E, and F. By solving the six equations in (2) simultaneously, the relative amounts of the six isotopic compounds are obtained in terms of the six observed ion intensities and the dissociation coefficient, r. To a very good approximation:

$$\begin{aligned} a &= M_2 - \frac{r}{R}(2 + r)\ H - \frac{r}{R}(1 - r)\ K + \frac{3r^2}{R}\ L + \frac{(2 + r)}{R}\ M_1 \\ b &= M_3 + \frac{r}{R}\ H - \frac{2r^2}{R}\ K - \frac{r}{R}(1 + 4r)\ L - \frac{M_1}{R} \\ c &= \frac{H}{R} - \frac{2r}{R}\ K - \frac{r}{R}(1 - 2r)\ L - \frac{M_1}{rR} \\ d &= M_4 - c \\ e &= M_5 \\ f &= M_6 \end{aligned} \tag{3}$$

where,

$$\begin{aligned} H &= 2M_2 + M_3 + M_4 \\ K &= M_3 + M_5 \\ L &= M_4 + M_5 + 2M_6 \\ R &= 1 + 3r + 2r^2 \end{aligned} \qquad (4)$$

The more complicated solution of (2) involving unequal dissociation coefficients has not yet been worked out.

Only after the above analysis has defined the molecular constitution of the gas reaching the ionization source can the correction for viscous flow through the leak be applied. It is interesting to note that since this spectrometer does not have the resolution required to distinguish between the two compounds of mass 4, the only method of quantitatively analysing these two molecular species on this instrument is by observing their dissociation products.

No mention is made in the foregoing discussion of the presence of helium-3 from the radioactive decay of tritium. For the analysis to hold true it is necessary either that a gas sample be analysed shortly after the purification of the hydrogen in order that the mass 3 peak not be distorted significantly by the presence of helium-3 or that the mean age of the tritium be known.

Additional work is planned on more accurate determinations of the dissociation coefficients, the effect of unequal coefficients, and the effect of appreciable quantities of helium-3.

Calorimetric Tritium Assay. - It is not feasible to measure the radiation from tritium by electronic methods in instrumentation presently available; the very soft betas emitted will not penetrate anything which would contain the gas. Calorimetry is applicable, however, since the tritium beta particles will be absorbed within the calorimeter, and manifest their energy as heat. From the half-life of tritium and the value of the average beta energy the number of molecules of tritium present can be determined from calorimetric power measurements

The characteristics of Mound Laboratory differential resistance bridge calorimeters are described in Table VI. The equilibrium time for each calorimeter is the time required to reach within 0.01 per cent of the equilibrium temperature rise after application of a constant power input to the heater The sensitivity represents the change in equilibrium bridge potential in microvolts which will take place with five milliamperes of bridge current for each microwatt of power produced in the sample or heater. The detectability indicates the power which has a probable error of 100 per cent per single measurement Since the noise level does not increase appreciably with power, the probable error on a sample having a power 10,000 times the detectability would be 0.01 per cent.

The heat distribution error is the maximum per cent difference between the measured values of a power source placed at various positions in the sample container. The total thermal resistance shows the temperature rise in the calorimeter per watt of power produced in the heater.

The accuracy of the calorimeter has been checked by measuring five radioactive samples of known half-life which were also assayed at the National Bureau of Standards in their ice calorimeter. The individual sample values obtained at Mound checked to within 0.1 per cent or better; the largest deviation between the Mound and the NBS values was -0.09 per cent, and the smallest was +0.05 per cent. The precisions achieved at Mound were equivalent to or considerably better than the National Bureau of Standards results.

TABLE VI

CHARACTERISTICS OF MOUND LABORATORY CALORIMETERS

CALORIMETER NUMBER	SAMPLE SIZE OUTSIDE DIAMETER *in.*	SAMPLE SIZE LENGTH *in.*	EQUILIBRIUM TIME *min.*	SENSITIVITY *v/μw*	DETECTABILITY *μw*	HEAT DISTRIBUTION ERROR *per cent*	TOTAL THERMAL RESISTANCE *°C/watt*
39	1.085	2.875	60	0.0487	3	0.01	4.336
41	0.86	1.25	16	0.0201	–	NONE	–
47	1.12	3	70	0.0531	3	0.35	5.619
49	1.085	2.875	70	0.0525	3	0.03	5.556
51	0.89	3	50	0.1146	3	0.2	8.575
54	1.49	6	45	0.0228	9.5	0.1	1.780
56 WITH SAND	1.44	4.6	23	0.0108	57	0.1	0.575
WITHOUT SAND	1.44	4.6	120	0.1172	2	0.1	6.232
58	1.532	6.0	100	0.0649	4	0.04	2.598
59	1.20	3	37	0.0255	13	0.1	1.883
60	0.3	2	60	1.1965	0.2	NOT MEASURED	73.858
61	1.1	2	30	0.0346	6	0.1	4.043

Two samples of tritium were measured separately in calorimeters 58 and 39, and the two samples together in calorimeter 58. A total of 28 measurements were made over a period of 17 days. Each measurement represented a series of five readings taken on sample and bridge potential zero. Samples were loaded with care to avoid producing stresses in the calorimeter. The sensitivity used for each calorimeter was the average of ten previous sensitivity determinations.

Results of these measurements are given in Table VII. Three values were discarded by Chauvenet's criteria. The results for sample 2 and for the two samples measured together show that the precision of these determinations falls somewhat short of the best obtainable, as indicated by the detectabilities of three and four microwatts given in Table VI for these calorimeters. This can be attributed to the fact that other equipment including a high-temperature calorimeter, had to be operated in the same room while the measurements were being made. Three samples of tritium producing only four, seven, and seven μ w of power were measured in March, 1956 with the expected precision of about ± 3 μw per individual measurement, but room conditions were ideal when these measurements were made.

TABLE VII

POWER MEASUREMENT OF TRITIUM SAMPLES

	SAMPLE 1			SAMPLE 2			SAMPLE 1 & 2		
DATE	CALORIMETER NUMBER	μV	μW	CALORIMETER NUMBER	μV	μW	CALORIMETER NUMBER	μV	μW
AUG. 28	58		207.30						
AUG. 29				58	18.90	291.30*			
AUG. 30	58	13.68	210.84	58	17.78	274.03			
AUG. 31	58	13.91	214.39	58	18.46	284.51			
SEPT. 4	58	13.20	203.45	39	12.81	263.10			
SEPT. 5	39	10.43	214.22	39	13.80	283.44	58	32.41	499.52
SEPT. 6	39	10.11	207.65				58	31.89	491.50
SEPT. 7	39						58	30.89	476.09
SEPT. 10	39	9.61	197.38*				58	30.36	468.92
SEPT. 11	39	9.38	192.66*	39	12.82	263.31	58	30.60	471.62
SEPT. 12	39			39	13.26	272.35	58	31.55	486.26
SEPT. 13	39			39	13.24	271.94	58	31.81	490.27
SEPT. 13	39							31.47	485.03
SEPT. 14	39	10.18	209.09	39	13.61	279.53		31.74	489.19
SEPT. 14	39							31.80	490.12
MEAN			209.56			274.03			484.85
P. E. (SINGLE OBSERVATION)			2.65			5.53			6.53
P. E. (MEAN)			1.00			1.95			2.07

NOTE: CAL. 39 SENSITIVITY = 0.0486879 μV/μW CAL. 58 SENSITIVITY = 0.0648445 μV/μW

*NOT AVERAGED

REACTOR DEVELOPMENT PROGRAM

CIVILIAN POWER REACTORS

HOMOGENEOUS REACTOR

The Civilian Power Reactor Program is concerned with the development of reactors suitable for the production of power or heat for civilian use. Homogeneous reactors are one of the types being investigated. In a homogeneous reactor, the fuel is by definition evenly dispersed in the moderator, so that solutions of uranium-233, uranium-235, or plutonium-239 are acceptable fuels if their chemical and physical properties permit low capital and operating costs.

Plutonium Solubility

A project has been initiated to investigate aqueous systems containing plutonium as a fuel for a homogeneous reactor. Initially the solubility of various plutonium salts in aqueous solution up to 300°C will be measured. The maximum concentration of plutonium will be ten grams per liter. A second solubility study will be carried out on an aqueous system containing up to 300 grams of uranium per liter and five grams of plutonium per liter.

One hundred eighteen milligrams of plutonium were received as plutonium sulfate in dilute sulfuric acid solution from Oak Ridge National Laboratory.

The procedure for the analysis of plutonium process solution given in the Oak Ridge National Laboratory procedure manual was modified for use with the sample size and conditions anticipated in our work. In the modified procedure ten microliters of solution containing up to 10 milligrams per liter of plutonium sulfate is added to 0.5 milliliter of solution containing 0.25 milligram of chromous sulfate recently passed through a Jones Reducer. Air is allowed to oxidize the excess chromous sulfate to an end point > 0.6 v, which is detected with a Fischer titrimeter between gold and platinum electrodes. The unknown is then titrated with standardized ceric sulfate solution in an ultramicro burette to a second end point (> 0.5 v). Results were reproducible to 0.5 per cent.

Equipment for filling and sealing the quartz sample tubes with active solutions has been developed. The card bibliography on plutonium has been extended.

AIRCRAFT PROPULSION REACTORS

LIQUID CYCLE REACTORS

The Aircraft Propulsion Reactor activity is concerned with the development of reactors suitable for the propulsion of aircraft or missiles or suitable for the production of auxiliary power for such vehicles. A liquid-cycle reactor is one of the types under development. In such a reactor, a liquid containing the fuel circulates through the reactor and a heat exchanger. The fluid for operating a turbine or jet is heated at the exchanger. Suitability of liquids for such reactors is based on extensive knowledge of their physical and chemical properties.

Fused Salts Research Project

The Liquid Cycle Reactor is considering the use of a fused-salt fuel system. Mound Laboratory has been assigned the problem of determining the phase relationships and physical properties of the components of some of the proposed fuel systems.

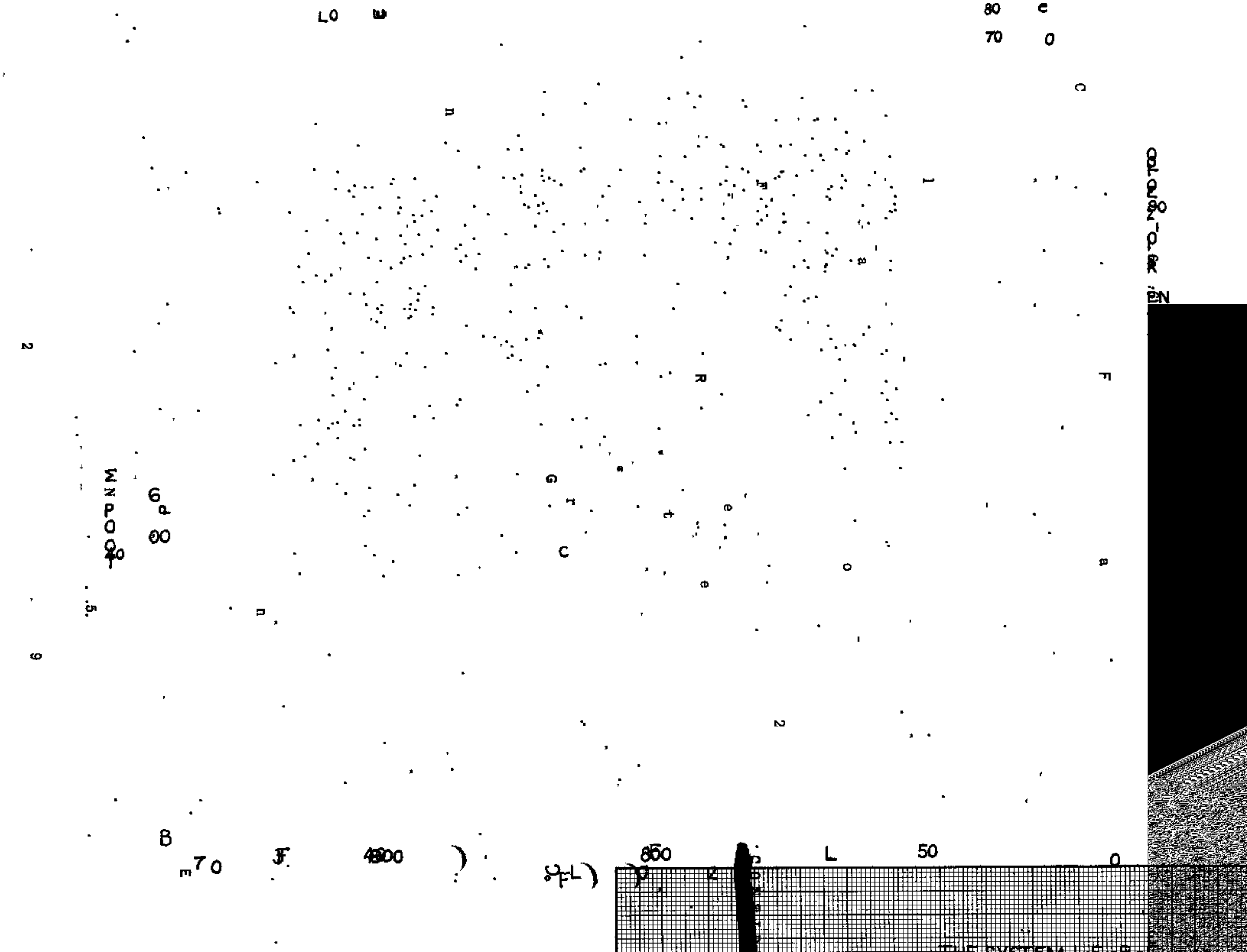
LiF-BeF_2 System - Information in the open literature on the LiF-BeF_2 binary system has not been in complete agreement. The course of the liquidus curve descending from the LiF-side of the diagram, the existence of certain subsolidus compounds, and the congruent or incongruent melting of the compound Li_2BeF_4 are some of the unresolved points.

Thilo and Lehmann [Thilo, E. and Lehmann, H., "Uber das System LiF-BeF_2 und seine Beziehungen zum System MgO-SiO_2"; *Z. anorg. chem.* *258*, 332-355 (1949)] reported the existence in this binary system of an incongruently melting compound, $LiBeF_3$, a compound, Li_2BeF_4, which melts congruently at 475°C with a resulting eutectic at 69 mole per cent LiF, and the possible existence of two other compounds, $Li_3Be_2F_7$ and $LiBe_2F_5$.

Novoselova and coworkers [Novoselova, A. V., Yu. P. Simanov, and E. Yarembash, "Thermal and X-ray Analysis of the Lithium-Beryllium Fluoride System", *Zhur. Fiz. Khim.* *26*, 1244-58 (1952)] reported that the compound Li_2BeF_4 has two polymorphic transitions and melts incongruently at 461°C with a peritectic at 61.5 mole per cent LiF. A subsolidus compound, $LiBe_2F_5$, and the compound $LiBeF_3$ yielding a peritectic at 353°C were also reported.

In a study of this binary system by Roy, Roy, and Osborne [Roy, D. M., R. Roy, and E. F. Osborne, "Fluoride Model System IV: The System LiF-BeF_2 and PpF_2-BeF_2", *J. Amer. Ceramic Soc.*, *37*, 300-305 (1954)] the subsolidus compounds, $LiBeF_3$ and $LiBe_2F_5$, and the compound Li_2BeF_4 which melted congruently at 458°C with an accompanying eutectic at 70 mole per cent LiF were reported.

The phase equilibrium diagram for the LiF-BeF_2 binary system which has been examined thoroughly by personnel at this laboratory appears as Figure 2 of this report. This phase diagram has been constructed from data obtained from differential thermal analysis studies and X-ray diffraction examinations of quenched and slowly-cooled compositions along the entire binary system. The diagram indicates an uninterrupted liquidus curve descending from the LiF-side of the binary system which intersects at 66 mole per cent LiF with the liquidus curve ascending from the BeF_2-Li_2BeF_4 eutectic at 48.5 mole per cent LiF. The temperature of this intersection is 455° ± 5°C. All binary compositions containing more than 66 mole per cent


80
70
50
0
R
G
C
B

LiF showed a phase transition at 455°C. Therefore it is concluded that a binary peritectic point exists at 66 mole per cent LiF and the compound Li_2BeF_4 melts incongruently at 455°C. No data indicated the existence of the postulated compounds Li_2BeF_5 and $Li_3Be_2F_7$. The subsolidus compound, $LiBeF_3$, was found to be unstable above 300°C in agreement with the published data of Roy and coworkers. No polymorphism of the compound Li_2BeF_4 was observed below its melting point. However, a metastable crystalline form of Li_2BeF_4 was obtained when binary compositions containing more than 65 mole per cent LiF were quenched from temperatures above their melting points.

In Mound Laboratory report number CF 56-10-40 it was reported that the subsolidus compound that coexisted with $LiBeF_3$ (low-temperature form) was BeF_2. Recent studies have shown that this conclusion was incorrect. Although the identification has not been completed, it appears that the subsolidus compound is located between $LiBeF_3$ and BeF_2 on the binary system. Two different systems were examined by X-ray diffraction after being subjected to similar heat treatments. A sample of BeF_2 was quenched from 600°C and then held for 20 days at 199°C. X-ray examination showed only the quartz form of BeF_2. Another sample containing a composition equivalent to $LiBe_2F_5$ was quenched from 600°C and held for 20 days at 197°C. X-ray examination of this second sample indicated the presence of the previously observed $LiBeF_3$ (low-temperature form) and the unidentified compound, possibly $LiBe_3F_7$

$LiF-BeF_2-UF_4$ Ternary System - The ternary phase diagram for the $LiF-BeF_2-UF_4$ system has not been revised for this report. Recent studies have indicated that some minor revision of this diagram will be necessary during the next month.

TABLE VIII

PETROGRAPHIC IDENTIFICATION OF PRIMARY PHASES AND LIQUIDUS TEMPERATURES FOR $LiF-BeF_2-UF_4$ SYSTEM

COMPOSITION NUMBER	TERNARY COMPOSITION MOLE PER CENT			PRIMARY PHASE	LIQUIDUS TEMPERATURE °C	PHASE APPEARING AT FIRST BOUNDARY INTERSECTION	TEMPERATURE OF FIRST BOUNDARY INTERSECTION °C
	LiF	BeF_2	UF_4				
1-R	69	23	8	Li_2BeF_4	432		
9-R	70	19	11	$Li_7U_6F_{31}$	438	Li_2BeF_4	
7-R	69	25	6	LiF	450	Li_2BeF_4	
32	71	15	14	LiF	485		
37-R	46.5	21.5	32	LiU_4F_{17}	693		
38-R	72	25	3	LiF	> 540	Li_2BeF_4	
43	56	34	10	LiU_4F_{17}	520	$Li_7U_6F_{31}$	516
44	41	13	46	UF_4	792		

The primary phase appearing at 520°C in Composition 43 listed in Table VIII was found by petrographic analysis to be LiU_4F_{17}. At approximately 516°C the boundary intersection with $Li_7U_6F_{31}$ was reached. These data indicate that this composition lies almost directly on the

[redacted]

the phase boundary separating the LiU_4F_{17} and the $Li_7U_6F_{31}$ primary phase areas. The course of this boundary will be revised to a lower UF_4 content.

Thermal gradient quench analyses of Compositions 1, 7, 9, and 38 in Table VIII were repeated to verify the revisions previously made in the current phase diagram of this ternary system, Figure 3.

The examination of Composition 37 reported in the "Mound Laboratory Monthly Report for October 1956", CF 56-10-40 had given a liquidus temperature of 733°C which appeared to be too high. The examination of this composition was repeated. The liquidus temperature in Table VIII is in agreement with other liquidus data in the same area of the phase diagram. The appearance of well-formed quench-growth crystals of LiU_4F_{17} in the high-temperature segment of the quench tube which persisted through the entire length of the tube, caused the incorrect temperature to be reported.

The position of the boundary between the $Li_7U_6F_{31}$ phase area and the LiU_4F_{17} phase area was examined by high-temperature filtration techniques. Composition N listed in Table IX which is in the LiU_4F_{17} phase area, was selected. The analysis of the filtrate obtained at 638°C indicated that it was practically on a direct crystallization path away from LiU_4F_{17} but still in the LiU_4F_{17} phase area. The analysis of the composition of the filtrate obtained at 601°C placed it on the boundary between the LiU_4F_{17} and the $Li_7U_6F_{31}$ phase areas. These data verify the position of the phase boundary, as drawn on Figure 3, adjacent to the LiF-UF_4 binary peritectic.

TABLE IX

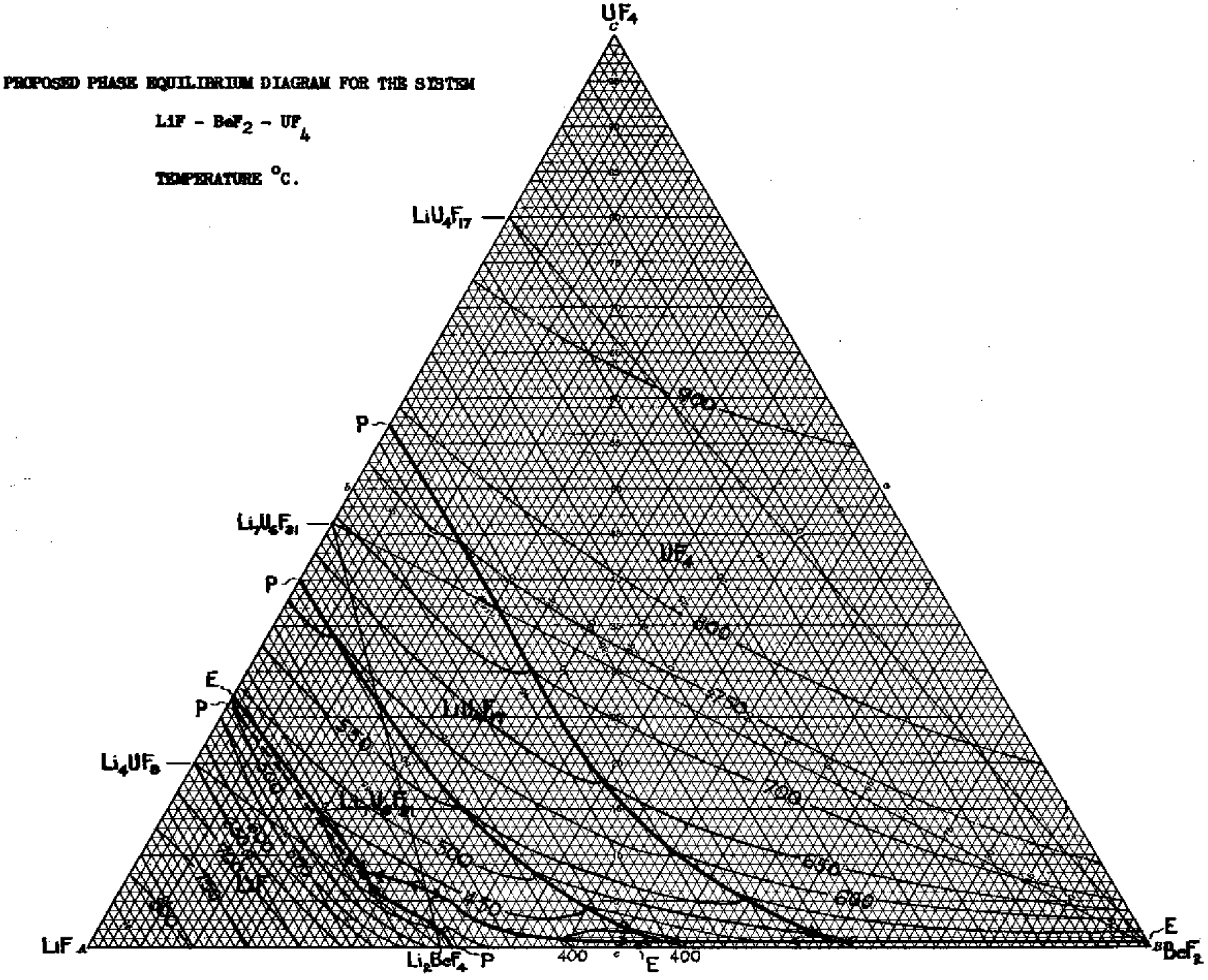
LIQUIDUS VALUES OBTAINED BY HIGH-TEMPERATURE FILTRATION

COMPOSITION NUMBER	STARTING COMPOSITION MOLE PER CENT			FILTRATION TEMPERATURE °C	COMPOSITION OF FILTRATE MOLE PER CENT		
	LiF	BeF_2	UF_4		LiF	BeF_2	UF_4
N	50	5	45	601	59.9	10.2	29.9
				638	58.0	7.7	34.3
12	30	65	5	438	40.7	57.5	1.8
				450	36.0	61.9	2.1
P	38	60	2	442	38.2	60.0	1.8
				404	43.6	55.1	1.3

Both filtrates obtained from Composition 12, which is in the UF_4 phase area, indicate that the crystallization path of this composition had crossed the LiU_4F_{17} phase area to terminate in the valley between the LiU_4F_{17} and the BeF_2 phase areas. Similarly the filtrates from Composition P in Table IX which were in the LiU_4F_{17} phase area were in the same valley. The examination of the crystallization paths of Compositions 12 and P listed in Table IX by high-temperature filtration indicated that the crystallization paths would terminate at the ternary eutectic between the BeF_2-$Li_7U_6F_{31}$-Li_2BeF_4 phase areas.

Differential thermal analysis data obtained from this ternary system are listed in Table X. Compositions 80K and 82K showed liquidus values which do not satisfy the temperature contour diagrams, shown in Figure 3. The liquidus temperature for Composition 80K was observed only

[redacted]



PROPOSED PHASE EQUILIBRIUM DIAGRAM FOR THE SYSTEM

LiF - BeF$_2$ - UF$_4$

TEMPERATURE °C.

FIGURE 3

during the cooling cycle. The heating cycle yielded acceptable temperature values for the boundary intersection and the eutectic but failed to indicate any liquidus temperature. This effect is not peculiar to this composition alone but is characteristic of all ternary compositions with a high lithium fluoride content which on cooling intersect the boundary separating the LiF and the $Li_7U_6F_{31}$ primary phases. Certain other compositions, examined but not reported in Table X, which lie near the LiF-$Li_7U_6F_{31}$ phase boundary, not only failed to give liquidus temperatures on heating but also supercooled extensively. For these compositions, mechanical stirring of open differential thermal analysis tubes will be tried. Apparatus is under construction to be used in an argon-filled drybox for these studies.

TABLE X

DIFFERENTIAL THERMAL ANALYSIS STUDY OF THE LiF-BeF_2-UF_4 TERNARY SYSTEM

COMPOSITION NUMBER	COMPOSITION MOLE PER CENT LiF	BeF_2	UF_4	EUTECTIC TEMPERATURE °C	UNASSIGNED TRANSITION TEMPERATURE °C	BOUNDARY INTERSECTION TEMPERATURE °C	LIQUIDUS TEMPERATURE °C
80K	83	6	11	427	650	473	740*
82K	83	14	3	427	--	--	721
52K	22	75	4	350	--	508	570
53K	22	70	8	350	-	507	647
54K	22	66	12	350	560	506	685
55K	22	62	16	350	590	502	710
83K	15	60	25	--	338	520	780
90K	10	75	15	--	340	523	746
96K	15	75	10	350	--	520	692

*COOLING CURVE ONLY

The results obtained from other compositions listed in Table X demonstrate that satisfactory liquidus and boundary intersection temperatures can be obtained in those areas having a high beryllium fluoride concentration. The inability to detect any peritectics in such areas may result from a slow reaction rate at the lower temperatures involved. The high viscosity of such a system under these same conditions may also hinder the expected reactions.

NaF-BeF_2-UF_4 System - The ternary phase diagram for the NaF-BeF_2-UF_4 ternary system, shown in Figure 4, has not been revised during the past month, but phase studies have indicated that revision will be necessary to reflect current findings.

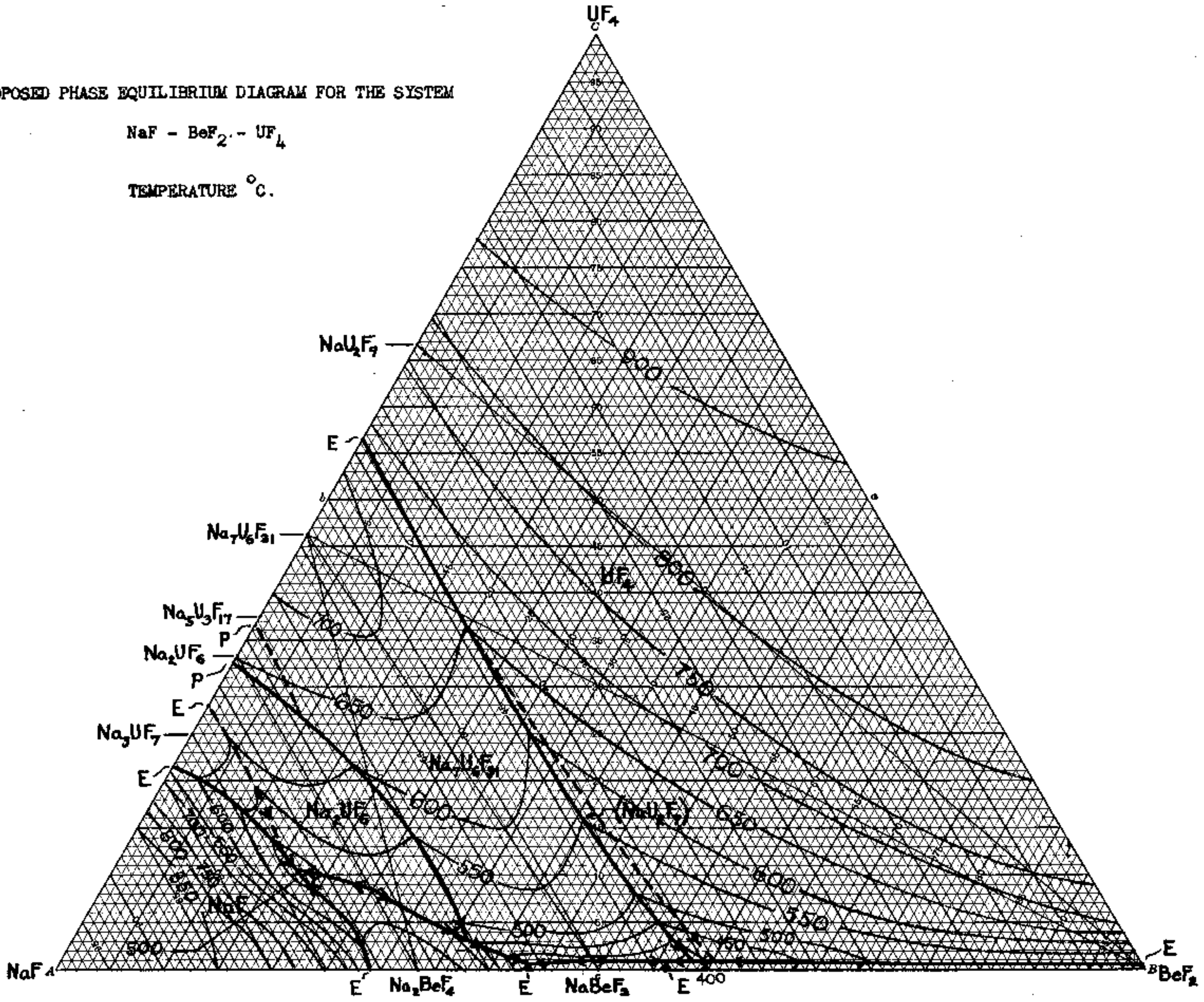
Petrographic analysis of a thermal-gradient-quenched sample of Composition S-3, listed in Table XI, showed a boundary intersection at 460°C with the appearance of Na_2BeF_4. Examination of samples of this composition to 435°C failed to indicate the existence of the Na_2BeF_4-Na_2UF_6-$Na_7U_6F_{31}$ peritectic which had been previously thought to exist at 500°C. Composition S-10 was examined to help define this peritectic. The peritectic was located at 378°C

PROPOSED PHASE EQUILIBRIUM DIAGRAM FOR THE SYSTEM

$NaF - BeF_2 - UF_4$

TEMPERATURE °C.

FIGURE 4



where Na_2BeF_4, Na_2UF_6, and $Na_7U_6F_{31}$ were found together. At a higher temperature $Na_7U_6F_{31}$ was not present, and below this temperature Na_2UF_6 disappeared.

Phase identification of Composition S-7 indicated that this composition does not lie in the Na_3UF_7 phase area as shown in Figure 4.

TABLE XI

PETROGRAPHIC IDENTIFICATION OF PRIMARY PHASES AND LIQUIDUS TEMPERATURES OF $NaF-BeF_2-UF_4$ SYSTEM

COMPOSITION NUMBER	TERNARY COMPOSITION MOLE PER CENT			PRIMARY PHASE	LIQUIDUS TEMPERATURE °C	PHASE APPEARING AT FIRST BOUNDARY INTERSECTION	TEMPERATURE OF FIRST BOUNDARY INTERSECTION °C
	NaF	BeF_2	UF_4				
S-3	62	30	8	Na_2UF_6	539*	Na_2BeF_4	460
S-5	42	49	9	NaU_2F_9	490		
S-7	73	9	18	Na_2UF_6	552	Na_3UF_7	534
S-10	62	35	3	Na_2BeF_4	509	Na_2UF_6	485
S-11	55	42	3	$Na_7U_6F_{31}$	430*	$NaBeF_3$	356
S-15	35.8	57.9	6.3	UNIDENTIFIED PHASE	503	NaU_2F_9	433

*APPROXIMATE VALUE

It appears that the boundary line between the Na_2UF_6 and the Na_3UF_7 phase areas must be revised toward a lower UF_4 content and to decrease the size of the Na_3UF_7 primary phase area. The $NaF-Na_3UF_7-Na_2UF_6$ peritectic was found to be near 500°-505°C in which temperature range NaF appeared and Na_3UF_7 disappeared.

Two high-temperature filtration studies of Compositions N-1 and N-2, listed in Table XII, were made to aid in defining the Na_3UF_6 phase area. Filtrates from N-1 were not on a direct crystallization path from Na_2UF_6 but appeared to be in a valley between the Na_2UF_6 and Na_3UF_7 phase areas. The compositions of these filtrates confirm a new location of this eutectic valley which reduces the area previously assigned to the Na_3UF_7 phase. The filtrates from Composition N-2 are on a direct crystallization path from Na_2UF_6 which indicates that the filtrates were in the Na_2UF_6 phase area. These data substantiate the previous conclusion.

The phase identification by thermal gradient quench studies of Composition S-11, Table XI, verified the $Na_2BeF_4-NaBeF_3-Na_7U_6F_{31}$ compatibility triangle. The final phase appearing in the sample, Na_2BeF_4, was found at 339°C. This is the temperature of the ternary eutectic which is the lowest melting eutectic composition in this ternary system.

The identification of NaU_2F_9 as the primary phase in Composition S-5, Table XI, verified the postulated existence of this primary phase area. Several other compositions are now being studied to establish the phase boundaries for the NaU_2F_9 phase area.

TABLE XII

LIQUIDUS VALUES OBTAINED FROM HIGH-TEMPERATURE FILTRATIONS

COMPOSITION NUMBER	STARTING COMPOSITION MOLE PER CENT NaF	BeF_2	UF_4	FILTRATION TEMPERATURE °C	FILTRATE COMPOSITION MOLE PER CENT NaF	BeF_2	UF_4
N-1	73	7	20	532	73.2	10.6	16.2
				540	73.6	9.5	16.9
N-2	70	5	25	535	72.9	9.6	17.5
				550	72.9	8.9	18.2
				560	71.4	9.0	19.6

The primary phase in Composition S-15 was an unidentified compound which had not been previously observed. The compound is yellowish-green in color and varies in refractive index from 1.596 to 1.611. This material may be a subsolidus compound toward the UF_4-end of the NaF-UF_4 binary system. In the petrographic examination of Composition S-15, the unidentified phase was found to disappear at approximately 410°C - 420°C. At temperatures below 410°C, the only phase present which could be identified by petrography and X-ray diffraction was NaU_2F_9. Since NaU_2F_9 was the only identifiable phase at the eutectic temperature, 357°C, it appears that the present phase diagram will require a revision in this area. In order to show $NaBeF_3$, BeF_2, and NaU_2F_9 as the three phases existing in equilibrium at the 357°C eutectic, the boundary line between $Na_7U_6F_{31}$ and NaU_2F_9 must be revised toward a higher NaF content. This will result in a peritectic appearing between $Na_7U_6F_{31}$, NaU_2F_9, and $NaBeF_3$. If this condition is true the compatibility triangles must also be changed by deleting the composition line between $Na_7U_6F_{31}$ and BeF_2 and substituting a composition line between $NaBeF_3$ and NaU_2F_9.

High-Temperature Calorimetry- Differential thermal analyses were continued with the high-temperature calorimeter on four samples in the system NaF-BeF_2-UF_4. Since variations in thermal effects were observed in the region of the 485°C eutectic temperature, a 7.5 gram sample of approximately eutectic composition from the LiF-BeF_2-UF_4 system having 70 mole per cent LiF, 22 mole per cent BeF_2, and 8 mole per cent UF_4 was run to determine whether these variations were characteristic of eutectic transitions in general. This sample gave reproducible results regardless of whether obtained by continuous, controlled heating or cooling, or in finite temperature steps. Data obtained from the samples in the NaF-BeF_2-UF_4 system will be re-evaluated and will be reported next month.

The sample from the LiF-BeF_2-UF_4 system was found to absorb 325 joules per gram as the temperature was raised from 390°C to 490°C either in steps or at a constant rate of 1.7°C per minute. During super cooling, 146 joules per gram were released almost instantaneously. In runs started at 321°C the bulk of the 325 joules per gram were absorbed between 431° and 458°C. However, when the sample was cooled from 533°C to 373°C, the bulk of the heat was absorbed between 400°C and 412°C. An almost instantaneous release of 22.7 joules per gram observed at 315°C may be pertinent in this apparent lowering of the eutectic temperature. The heat of fusion of this eutectic has been calculated to be approximately 74 calories per gram.

Density and Viscosity - Nine density and twelve viscosity measurements were made this month. Results are reported in Table XIII.

TABLE XIII

DENSITY AND VISCOSITY VALUES FOR MIXTURES OF UF_4, NaF, LiF, AND BeF_2

COMPOSITION MOLE PER CENT				MELTING POINT	600°C			700°C			800°C		
UF_4	NaF	LiF	BeF_2	°C	η Poise	ρ g/cm^3	η/ρ Stokes	η Poise	ρ g/cm^3	η/ρ Stokes	η Poise	ρ g/cm^3	η/ρ Stokes
2	13	85	0	745	–	–	–			–		2.172	
2	35	63	0	592		2.264			2.218	–	–	2.172	–
2	46	52	0	650				0.0520		–	0.0382		
2	58	40	0	667				0.0728	2.292	0.0318	0.0379	2.230	0.0170
2	70	28	0	794							0.0857	2.237	0.0383
2	13	75	10	725							0.0393	2.157	0.0182
2	46	42	10	570	0.0711	2.357	0.0302	0.0513	2.298	0.0223	0.0390	2.238	0.0174
2	13	65	20	650				0.0570	2.204	0.0259	0.0399	2.162	0.0185
2	35	43	20	605	–	–		0.0523	2.253	0.0232	0.0390	2.204	0.0177
2	13	54	31	400	0.1080	2.225	0.0485	0.0680	2.191	0.0310	0.0462	2.155	0.0214
2	24	43	31	410*		2.198*			2.147*			2.097*	
2	35	32	31	340	0.1065	2.238	0.0476	0.0652	2.271	0.0287	0.0432	2.214	0.0195
2	13	41	44	370	0.1900	2.172	0.0875	0.1000	2.121	0.0471	0.0583	2.070	0.0282
2	13	41	44	370*		2.170*			2.124*			2.079*	
2	24	30	44	320	0.1758	2.173	0.0809	0.0943	2.125	0.0444	0.0558	2.077	0.0269
2	35	19	44	360	0.1530	2.240	0.0683	0.0858	2.176	0.0394	0.0526	2.122	0.0248
4	14	82	0	725	–	–		–	–	–	–	2.396	–

*RERUN

Four density measurements were made on mixtures of UF_4, NaF, LiF, and BeF_2. Three of these density measurements were reruns, and these data are marked by an asterisk in Table XIII. Five density measurements were made on mixtures of UF_4, NaF, and LiF. Nine viscosity measurements were made on mixtures of UF_4, NaF, LiF and BeF_2, and three were made on mixtures of UF_4, NaF, and LiF. All measurements were made over the temperature range from the liquidus point to 900°C. Interpolated values are given at 800°C and, when possible, at 700°C and 600°C.

The following compositions were found to be corrosive to both the inconel pots and the platinum sinkers.

MOLE PER CENT		
UF_4	NaF	LiF
2	13	85
2	35	63
2	46	52 **
2	58	40 *
2	70	28 **

Viscosity values for those compositions followed by an asterisk are not completely reliable, and the same is true for the density values of those followed by a double asterisk. Corrosion of the inconel pots did not take place at the surface of the melts entirely but also appeared beneath the surface along the walls of the pots. If time permits these particular compositions may be rerun at a later date.