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MOUND LABORATORY

Operated By

MONSANTO CHEMICAL COMPANY

MIAMISBURG, OHIO

**MONTHLY TECHNICAL ACTIVITIES REPORT
THROUGH APRIL 15, 1957**

BY

J. F. Eichelberger and D. L. Scott

~~RESTRICTED DATA~~

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TABLE OF CONTENTS

	Page
PRODUCTION PROGRAM	4
NUCLEAR RESEARCH AND DEVELOPMENT	5
CHEMISTRY AND METALLURGY	5
Ionium Project	5
Protactinium Project	6
Plutonium Urinalysis	11
Plastics Project	12
GENERAL WEAPONS DEVELOPMENT	24
Isotope Separation Project	24
REACTOR DEVELOPMENT PROGRAM	28
CIVILIAN POWER REACTORS	28
HOMOGENEOUS REACTOR	28
Plutonium Solubility	28
AIRCRAFT PROPULSION REACTORS	30
LIQUID CYCLE REACTORS	30
Fused Salts Research	30
DEPARTMENT OF DEFENSE - SIGNAL ENGINEERING LABORATORIES	40
COMPONENTS BRANCH	40
Nuclear Battery - Thermoelectric Type	40

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.

The cathode-holder made from stainless steel which is used to secure the platinum gauzes yielded excellent results. Additional holders of this type will be ordered.

Two polonium alpha sources, eight polonium-beryllium, and twenty plutonium-beryllium neutron sources were shipped during March. Five polonium-beryllium and ten plutonium-beryllium neutron sources were for other AEC sites. One of the polonium-beryllium neutron sources was a replacement for a returned source.

Twenty tanks of influent water were processed during the period. Seven of the tanks required no pretreatment; three tanks required treatment in addition to the standard pretreatment. The painting of clariflocculator "B" was completed. The reactivation of sand filter "B" reduced considerably the alpha activity in the effluent tanks. Effluent discharged to the river was considerably reduced in both alpha and beta activity during the period.

Data for the Waste Disposal Operations are given in Table I.

TABLE I

DISCHARGE VOLUME	497,600 GALLONS
TOTAL ALPHA ACTIVITY	6.7 MILLICURIES
TOTAL BETA ACTIVITY	17.5 MILLICURIES
ACTIVITY DENSITY	
ALPHA	3.9 CTS/MIN/ML
BETA	7.2 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.

Processing - Mallinckrodt Chemical Works is in the process of preparing about 120 gallons of sulfated feed solution for shipment to Mound. This solution is being obtained from their pilot plant runs with two pulse columns. The solution contains between 120 and 150 grams of thorium-230.

The Health Department at Mallinckrodt recommended that they do no further processing under their existing conditions. If any future thorium-230 is received from Mallinckrodt it will be in a dilute solution. Since this would involve the shipment and processing of several thousand gallons of solution, a study of the feasibility of processing this large volume of solution at Mound Laboratory is in progress.

Mixer-Settler Development - This project is awaiting fabrication of several units in the glass shop.

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.

Column Development - It was decided to use the solvent extraction method on the thirty gallons of aqueous product solution obtained from previous pilot plant runs. Fifteen gallons of concentrated sulfuric acid were added to the product solution in the fifty-gallon kettle. This feed was metered out, four gallons at a time, into an intermediate feed vessel where 673 milliliters of 30 per cent hydrogen peroxide were added. This feed stream was blended at the rate of 0.68 gallons per hour with concentrated hydrochloric acid pumped at 0.22 gallons per hour. The organic was pumped at 0.90 gallons per hour into the first column. A stirrer was added to the top of the second and third columns to give additional effective height. The first and third columns were run organic-continuous, and the second column was run aqueous-continuous.

The solution containing protactinium was stripped at the rate of 0.12 gallons per hour with 2M phosphoric acid in the second column, and the organic was stripped in the third column with water at 1.35 gallons per hour. The second and third columns operated very well in spite of emulsion problems. About twenty per cent of the protactinium was discharged with the raffinate from the first column.

Process Development - The aqueous product solutions totaling 30 gallons, from all previous runs in the intermediate pilot plant equipment were consolidated in the 50-gallon glass-lined kettle in SW 1-B. Samples were removed for laboratory experiments on a second cycle.

Several heating experiments led to no precipitation even after boiling down to half the original volume. Therefore, the use of this method was temporarily discontinued. However, since, with the addition of a considerable amount of concentrated HCl and a small amount of $TiCl_3$, a precipitate which carried from 80 to 95 per cent of the protactinium did form on heating, this method will again be considered when a more representative product solution is available from the production runs.

A second-cycle concentration by solvent extraction was investigated. Several concentrations of HCl, H_2SO_4 and H_2O_2 were tried. The most favorable consisted of 15 milliliters of the aqueous product solution, 7.5 milliliters of concentrated H_2SO_4 , 7.5 milliliters of concentrated HCl and one milliliter of 30 per cent H_2O_2 . This solution, which had a total volume of about 30 milliliters, yielded 92 per cent of the protactinium after four four-milliliter extractions with a 50-50 mixture of DIBC-Amsco. This method will also be re-investigated when a more representative sample is available.

Production Facilities - Most of the equipment in HH-Building has been checked and found to be satisfactory. Some mechanical difficulty was encountered with the Sigmamotor pumps, but this difficulty is being worked out. "Hot" processing should start on April 17.

Analytical - Work is in progress on a method for determining the per cent diisobutyl carbinol in a mixture of diisobutyl carbinol and Amsco.

Protactinium Purification - An initial separation of protactinium from niobium was made with the aid of a strip solution containing oxalic and hydrochloric acids. Gamma-counting of niobium-95 tracer added to the strip solution showed that 75.3 per cent of the niobium and 1.5 per cent of the protactinium were stripped from the organic phase.

On overnight standing, the strip solution became very turbid, and the resulting precipitate was separated by centrifugation. The supernate was made ammoniacal, and an additional precipitate appeared, which was separated by centrifugation.

The two precipitates were dried and analyzed spectrographically. In both cases, the principal constituent was niobium. There was no great difference between the two precipitates qualitatively, and the only quantitative differences were in the amounts of phosphorus and iron present. The two analyses are shown in Table I.

The organic phase, which contained about 25 per cent of the original niobium and about 17 milligrams of protactinium-231, was again stripped with a mixture of oxalic and hydrochloric acids, and the phases were separated and counted. The organic phase retained 97.7 per cent of the protactinium and 2.0 per cent of the niobium. The organic phase was then stripped with approximately 3.5-molar phosphoric acid solution, yielding a precipitate, an aqueous phase, and an organic phase. The three phases were separated and counted. The precipitate contained 94 per cent of the protactinium and 1.2 per cent of the niobium. The precipitate was dissolved in sulfuric acid, adjusted with hydrochloric acid, and extracted into diisobutyl carbinol-benzene. The organic phase was separated and set aside. On overnight standing, a white solid plated out on the sides of the glass container in a band around the top of the liquid. A small droplet of turbid aqueous phase settled out on the bottom.

The oxalic acid strip solution containing the niobium was made ammoniacal, and the resulting precipitate was separated by centrifugation. An attempt to wash the precipitate with dilute ammonium hydroxide, however, was unsuccessful; the supernate remained turbid on centrifugation, and failed to clear even after additional ammonium hydroxide was added. The precipitate contained 77 per cent of the protactinium and 41 per cent of the niobium, indicating that some fractionation was occurring. The supernate was made strongly alkaline with sodium hydroxide, and the turbidity cleared almost completely. The supernate and precipitates were recombined, and nearly all of the precipitate dissolved. Centrifugation yielded a small, floating particles which were decanted along with the supernate. The precipitates contained 92 per cent of the protactinium which had been originally precipitated by ammonium hydroxide. The supernate contained about 90 per cent of the niobium.

TABLE I
SPECTROGRAPHIC ANALYSIS OF NIOBIUM
SEPARATED FROM PROTACTINIUM

ELEMENT	AMOUNT ^a	
	FIRST PRECIPITATE ^b	SECOND PRECIPITATE ^c
Si	1.35	4.8
P	267.7	94.6
Au	5.0	2.4
Mg	0.12	0.12
Pb	—	>2.4
Fe	0.11	5.5
Cu	0.02	0.17
Al	—	0.14
Ge	(?) ^d	1.3 (?) ^d
Pt	TRACE (?)	TRACE (?)
Ti	TRACE (?)	TRACE (?)
Ca	—	TRACE

a MICROGRAMS PER MILLIGRAM OF SAMPLE ($\pm 50\%$)

b APPEARED ON OVERNIGHT STANDING

c APPEARED AFTER AMMONIUM HYDROXIDE ADDITION

d POSSIBLE INTERFERENCE FROM NIOBIUM

The above experiment shows that an excellent separation of protactinium from niobium can be made by precipitation of protactinium from a strongly alkaline medium. Niobium is evidently converted to a soluble niobate, while protactinium exhibits little or no amphoteric tendencies. The principal loss of protactinium to the supernate probably occurs in decantation, and could, in that case, be eliminated by filtration.

The separation of iron from protactinium was easier than anticipated. After the niobium was stripped from the organic phase into a hydrochloric-oxalic acid mixture, the protactinium was stripped with a phosphoric acid solution. The aqueous phase was separated by centrifugation from the precipitate, and the precipitate was dissolved and re-extracted. The aqueous phase was made alkaline with sodium hydroxide, and the heavy, orange precipitate was centrifuged off. The supernate, which was colorless and contained virtually no protactinium, was discarded. The precipitate dissolved readily in 6 *N* hydrochloric acid, except for some white crystalline material which settled readily. These crystals were centrifuged out, counted, and found to contain approximately one milligram of protactinium. The supernate was again made alkaline, and the precipitate was washed with water and dried at 100°C. The residue weighed about 23 milligrams and contained about 50 micrograms of protactinium. A sample of the dried residue was analyzed spectrographically and found to contain iron as its principal constituent. The complete analysis is given in Table II.

TABLE II
SPECTROGRAPHIC ANALYSIS OF IRON
SEPARATED FROM PROTACTINIUM

ELEMENT	AMOUNT ^a
Fe	360
Si	34.6
Nb	9.5
Ca	7.5
Al	3.7
Mn	3.5
Mg	1.3
Cu	0.5
P	(?) ^b
Ba	TRACE
Ti	TRACE
Sr	TRACE (?)

a MICROGRAMS PER MILLIGRAM OF SAMPLE ($\pm$ 50 %)

b Fe INTERFERENCE

Further experimentation showed that the separation of iron from protactinium was reproducible. The dried, iron residue was redissolved in hydrochloric acid, and was used thereafter as a scavenger for protactinium in all experiments where non-quantitative fractionations

of protactinium occurred. All waste solutions, prior to being discarded were scavenged by ferric hydroxide precipitation. No losses of protactinium to the alkaline supernate occurred as long as all of the iron was precipitated. Completeness of precipitation was determined by the color of the alkaline supernate; a yellow supernate invariably contained both protactinium and iron, while a colorless supernate was free of both elements. When the supernate was yellow, additional sodium hydroxide was added until, on settling, the ferric hydroxide left a colorless supernate behind.

It was found that the separation of protactinium from iron by hydroxide precipitation, followed by hydrochloric acid dissolution of the ferric hydroxide, depended on the presence of phosphate ion. Repeated precipitation from strongly alkaline solution gradually depleted the iron scavenger of its phosphate, and the protactinium precipitate tended to become soluble in hydrochloric acid.

In one experiment, the protactinium precipitate was washed with approximately 1.5 M sodium hydroxide, and then leached with approximately 2 N hydrochloric acid. Approximately 50 per cent of the protactinium dissolved. The fractions were recombined and dilute phosphoric acid was added. After 30 minutes at room temperature, there was no obvious change in the size of the precipitate. The mixture was heated at 100°C for about one hour, then centrifuged. The precipitate contained 100 per cent of the protactinium. When the precipitate was washed with 2 N hydrochloric acid, only about five per cent of the protactinium dissolved. These results confirmed the belief that the relative solubilities of iron and protactinium in dilute hydrochloric acid were dependent on the presence of phosphate.

A sample of the protactinium precipitate separated from iron by hydrochloric acid was washed with dilute hydrochloric acid and dried for 18 hours at 100°C. By gamma counting, it was determined that the residue contained 56 per cent protactinium by weight. Spectrographic analysis was found to be difficult because of interference from the extremely rich spectrum of protactinium itself. The results, Table III, showed that the compound was probably a phosphate and contained less than one per cent niobium and less than 0.1 per cent iron.

TABLE III

SPECTROGRAPHIC ANALYSIS OF PROTACTINIUM SAMPLE

ELEMENT	AMOUNT ^a
B	0.7
Si	5
P	84
Pt	0.5 ?
Au	0.23 ?
Fe	0.7
Nb	7.3
Th	NOT DETECTED
U	MAY BE PRESENT

a MICROGRAMS PER MILLIGRAM OF SAMPLE ($\pm 50\%$)

The spectrographic analysis and the gamma-counting data are consistent with a molecular formula of $\text{PaO}_2(\text{H}_2\text{PO}_4) \cdot 2\text{H}_2\text{O}$. It should be noted in connection with the thorium and uranium analyses, that no quantitative data are possible from spectrographic analysis because the line-rich spectrum of protactinium would mask any rare earth or actinide lines that might be present in less-than-major amounts. It is questionable whether uranium or thorium could be detected even by X-ray fluorescence unless they were present in amounts of at least 10 per cent.

However, it may be deduced from the previous chemical history of the protactinium that neither uranium nor thorium would be likely to be present in more than trace quantities. Thorium-232, in particular, is assumed to have been separated in the early stages of the protactinium process, along with ionium and thorium-227. There has never been any evidence that uranium was present in the raffinate residue from which the protactinium was recovered. Finally, the specific activity of the protactinium residue precludes the presence of significant quantities of heavy elements.

Attention was next directed towards the separation of protactinium from phosphate ion. The phosphate precipitate was found to be readily soluble in concentrated sulfuric acid, and remained soluble when the solution was diluted to contain about 17 milligrams of protactinium in 20 milliliters of 1.5 *N* sulfuric acid. On the addition of iodic acid to this solution, protactinium iodate precipitated quantitatively and was separated by centrifugation. The iodate was decomposed by 48 per cent hydrobromic acid, but the resulting solution was unstable; protactinium hydrolyzed on standing a short time, and the hydrolysis was quantitative if the solution was heated. The precipitate was, however, soluble in sulfuric acid, and it was found that solutions of protactinium in sulfuric acid were stable even after ten-fold dilution with water.

The purity of the protactinium produced by iodate precipitation is now being checked spectrographically.

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.

Because of the pressure of routine urinalyses for various alpha emitters, it has not been possible to continue the development of an improved method of plutonium urinalysis. There is no further progress to report at this time.

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.

Plastics Formulation - Four large formulations containing two parts of catalyst and of stearate per 100 parts of prepolymer and having a filler plus prepolymer weight of 25 pounds were made in the sigma-blade mixer. Data for these runs and the data for run B33 are given in Table I.

TABLE I

DIALLYL PHTHALATE FORMULATIONS

RUN NO.	PARTS PER 100 PARTS OF DAPON 35			MONOMER	RESIDUAL ACETONE per cent
	FILLER		ACETONE		
B33	CELLULO 200	40	189	2.0	24.3
	HYDRITE-PD-10	60			
B34	CELLULO 200	40	200	3.0	22.5
	HYDRITE-PD-10	60			
B35	CELLULO 200	40	225	3.0	20.6
	HYDRITE-PD-10	60			
B36	CELLULO 200	40	250	5.0	13.5
	HYDRITE-PD-121	60			
B37	CELLULO 200	40	250	5.0	11.3
	HYDRITE-PD-121	60			

The varnish for B34 was filtered in 3.5 hours through a cone of fiberglass filter cloth fitted to a stainless steel funnel on the sigma-blade mixer. A considerable number of foreign particles and small particles of undissolved prepolymer were found on the filter cloth. A stainless steel cartridge-type filter has been ordered from the Cuno Engineering Corporation to make routine filtration practical.

Mixing in the sigma-blade mixer did not appear to be significantly better during run B34 than it had been during Run B33, so the amount of acetone was increased to 225 parts for run B35.

The Esterline-Angus recording wattmeter had been installed and tested during the latter portion of run B34 and was used throughout run B35. The power input to the sigma-blade mixer decreased slowly and this decrease continued after the removal of acetone was started. As more acetone was removed the power input increased slowly and eventually became erratic as the mixture began to ride-up on the blades. It is probable that mixing was somewhat better than in previous runs, but it was still not satisfactory.

The acetone was increased to 250 parts in run B36. This is the maximum amount which can be used without reducing the amount of prepolymer charged. Good kneading action was obtained, but the mixture was still stiff. The power input decreased slowly as mixing was continued for a period of several hours. The power input continued to decrease after acetone removal was started but eventually became constant and then began to increase. Reasonably good kneading action was obtained until the mixture had stiffened considerably, but then mixing became irregular and the power input varied in an erratic manner. It increased to 1.25 KW and then decreased to 0.725 KW at which point the run was stopped. The acetone content was 13.5 per cent, and the cold mixture was difficult to remove from the mixture.

Formulation B37 was the same as B36. The mixture was stirred overnight at atmospheric pressure. It was quite fluid and the input power was lower than it had been the evening before. There was apparently good kneading action in the volume swept out by the sigma blades, but the mixture was so fluid that the stirring of the material on the surface was quite slow. The power input remained constant and then increased as acetone was removed. As the mixture became rather stiff there was a tendency for it to ride-up on the blades, but kneading action was never completely lost. After a short period nearly complete kneading was again effected. During such periods the power input dropped sharply but then increased sharply as more complete kneading started. With such occasional exceptions, the power input increased steadily to a value of 1.58 KW at which the run was stopped. The product appeared more uniform and more plastic than previous runs using Cellulo asbestos. The acetone content was low (11.3 per cent) but the product was removed without undue difficulty while it was still warm.

It would appear that essentially complete defelting of the Cellulo asbestos can be obtained only by prolonged stirring in the presence of large amounts of acetone. Although it may be possible to reduce somewhat the amount of acetone, it does not seem likely that a long period of stirring can be eliminated.

Formulations B33 and B34 were milled in four-pound lots to study the use of the Esterline-Angus recording wattmeter and the maximum surface temperature of the plastic in controlling the milling on the differential rolls. The products were used primarily to study the change in flow-time with age. One four-pound lot of B35 was milled primarily to prepare a sample for calorimetric measurement. B35 milled much better than previous lots containing Cellulo asbestos, indicating that better dispersion of the asbestos had been obtained.

The conditions of milling and approximate values for the flow times of the products are given in Table II.

A general picture of the variation of flow time with average particle size and with age is given in Table III, while more detailed information is given in Tables IV, V, and VI. The variation of flow time between lots milled to the same power input is given in Tables VII, VIII and IX.

In considering the data presented in these tables, the following factors should be kept in mind. Most of the flow times given are for a single measurement since the samples were usually not large enough to permit multiple measurement for any one point. It is believed that a single measurement has a fairly high probability of being within ± 0.5 second of the correct value, but an occasional value may be off by a second or more.

TABLE III

CONDITIONS OF MILLING AND APPROXIMATE FLOW TIME OF PRODUCTS

MILL RUN	MILL TIME MINUTES	MAXIMUM SURFACE TEMP. °C	AVERAGE POWER KW	PEAK POWER KW	WEIGHT AFTER MILLING Kg	FLOW, IN SECONDS, AT 5 TON		
						AT 24 HR.	AT 48 HR.	ESTIMATED ^c ULTIMATE FLOW
B33-1	32.75	75	2.1	2.14	1.85	8.95 ^a	10.25 ^b	22 ± 2
B33-2	28.75	73	2.1	2.15	1.95	9.93	11.18	22 ± 2
B33-3	29.5	73	2.1	2.15	1.95	9.60	10.13	22 ± 2
B33-4	29.5	75	2.05	2.15	1.95	9.43	10.92	22 ± 2
B33-5	26.0	72	1.90	1.98	1.95	8.66	10.24	20 ± 2
B33-6	29.0	71.5	1.90	1.98	1.90	8.88	10.37	20 ± 2
B34-1	27.0	69	1.90	1.98	1.90	9.26	11.42	18.5 ± 2
B34-2	29.0	70	1.90	1.96	1.90	8.56	10.87	18.5 ± 2
B34-3	31.0	70	1.90	1.96	1.95	8.61	10.81	18.5 ± 2
B34-4	30.0	70	1.90	1.95	1.92	9.80	12.02	18.5 ± 2
B34-5	31.0	71	1.90	1.92	1.93	9.15	10.82	18.5 ± 2
B34-6	30.0	70	1.90	1.95	1.92	8.61	10.42	18.5 ± 2
B35-1	24.5	69	1.90	1.96	1.95	d	d	d

a. FLOW TIME AT 22 HRS.

b. FLOW TIME AT 46 HRS.

c. BASED ON AN EXTRAPOLATION OF FLOW TIME VS LOG OF MEAN
EQUIVALENT AVERAGE PARTICLE DIAMETER.

d. DATA NOT AVAILABLE.

TABLE III
VARIATION IN FLOW TIME WITH PARTICLE SIZE AND
WITH AGE AFTER MILLING

FLOW AT 5 TONS		HOURS OFF MILL	FLOW AT 5 TONS			
B33-1 ^a Sec	B33-1L ^b Sec		B33-2/4L ^b <10 MESH Sec	B33-2/4S4 <20 >40 MESH Sec	B33-2/4F ^c <40 MESH Sec	B33-2/4S7 <100 MESH Sec
5.28	6.28	2				
6.31	6.96	3				
6.17	7.04	4				
5.96	7.18	5				
-	-	6		7.30		11.95
7.29	8.95	22		-		-
-	-	24	9.20	9.83	11.84	14.88
8.13	9.35	29	9.87	-	11.71	-
8.28	10.24	46	-	-	-	-
-	-	48	-	10.11	-	-
-	-	49	10.06	-	13.03	-
8.27	10.92	53	-	-	-	-
8.97	10.83	70	-	-	-	-
-	-	72	11.47	-	15.42	-
9.41	11.05	77	-	-	-	-
-	10.37	96	10.95	12.02	15.35	16.55 ^d
9.14	11.90	168	-	-	-	-
-	-	172	13.02	-	16.49	-
-	11.98	191	-	-	-	-
-	-	192	-	14.01	-	-
9.49 ^d	11.56	242	-	-	-	-
-	-	264	13.04	-	16.34	-
-	12.61	336	14.06	13.72	15.57	-
-	-	408	13.60	-	15.70	-
-	-	504	13.61	-	15.73	-
-	12.13	528	-	13.59 ^d	-	-
-	-	600	13.85 ^d	-	16.33 ^d	-
-	13.49 ^d	696	-	-	-	-

a. GROUND IN SLING-SLEDGE MILL AND BLENDED.

b. SLING-SLEDGE BLEND GROUND IN LABORATORY GRINDER USING 10-MESH SCREEN.

c. L-GROUND GROUND IN LABORATORY MILL THROUGH 40-MESH SCREEN.

d. END OF SAMPLE.

TABLE IV
VARIATION IN FLOW TIME WITH PARTICLE SIZE AND WITH AGE AFTER MILLING
BLEND OF B33-2, B33-3, AND B33-4

SAMPLE ^a B33-2/4	MESH RANGE	AVERAGE PARTICLE SIZE <i>Microns</i>	PER CENT BY WEIGHT	FLOW TIME AT 5 TONS				
				AT 6 HR <i>Sec</i>	AT 24 HR <i>Sec</i>	AT 96 HR <i>Sec</i>	AT 264 HR <i>Sec</i>	AT 528 HR <i>Sec</i>
S1	> 4	6,500	1.1	-	-	-	-	-
S2	< 4 > 16	3,425	35.2	4.84	5.90	6.67	9.65	9.52
S3	< 16 > 20	1,015	13.9	6.63	7.71	10.46 ^b	13.34	-
S4	< 20 > 40	630	21.5	7.30	9.83	12.02	13.72 ^c	13.59
S5	< 40 > 60	335	9.3	9.41	12.05	13.86 ^b	-	-
S6	< 60 > 100	200	9.0	11.28	12.81	14.80 ^b	-	-
S7	< 100	110	10.0	11.95	14.88	16.55	-	-

a. GROUND IN SWING-SLEDGE MILL. CLASSIFIED BY USE OF ROTAP.

b. FLOW TIME AT 72 HOURS.

c. FLOW TIME AT 336 HOURS.

TABLE V
VARIATION IN FLOW TIME WITH PARTICLE SIZE AND WITH AGE AFTER GRINDING
BLEND OF B33-5 AND B33-6

SAMPLE ^a B33-5/6	MESH RANGE	AVERAGE PARTICLE SIZE <i>Microns</i>	PER CENT BY WEIGHT	FLOW TIME AT 5 TONS				
				AT 24 HR <i>Sec</i>	AT 144 HR <i>Sec</i>	AT 192 HR <i>Sec</i>	AT 312 HR <i>Sec</i>	AT 480 HR <i>Sec</i>
S 1	> 4	6,500	3.79	3.79	-	-	-	7.35
S 2	< 4 > 16	3,425	50.10	5.39	7.06	7.57	6.88	9.22
S 3	< 16 > 20	1,015	12.20	7.42	10.66	-	10.68	11.93
S 4	< 20 > 40	630	15.52	8.90	-	-	14.19	14.34
S 5	< 40 > 60	335	2.53	11.97	-	-	-	-
S 6	< 60 > 100	200	8.75	11.49	14.72	-	15.03	15.23
S 7	< 100 > 120	137	1.25	-	-	-	-	-
S 8	< 120 > 140	127	1.04	-	-	-	-	-
S 9	< 140 > 160	115	0.59	-	-	-	-	-
S10	< 160 > 180	100	0.23	-	-	-	-	-
S11	< 180 > 200	77.5	0.26	-	-	-	-	-
S12	< 200	55	3.74	16.35	-	16.04 ^b	-	-

a. GROUND IN SLING-SLEDGE MILL. CLASSIFIED BY USE OF ROTAP.

b. FLOW TIME AT 217 HOURS.

TABLE VI

VARIATION IN FLOW TIME WITH PARTICLE SIZE AND WITH AGE AFTER GRINDING
BLEND OF B34-1 THROUGH B34-6

SAMPLE ^a B34-1/6	MESH RANGE	AVERAGE PARTICLE SIZE <i>Microns</i>	PER CENT BY WEIGHT	FLOW TIME AT 5 TONS		
				AT 29 HR <i>Sec</i>	AT 124 HR <i>Sec</i>	AT 292 HR <i>Sec</i>
S 0 ^b	> 4	6,500	2.24	3.48	5.48 ^c	5.22
S 1	< 4 > 16	3,425	50.22	4.51	6.25	7.88
S 2	< 16 > 20	1,015	9.08	6.87	9.61	12.03
S 3	< 20 > 40	630	19.91	8.21	11.03	13.38
S 4	< 40 > 60	335	6.31	10.03	12.45	14.43
S 5	< 60 > 80	213	4.07	11.12	13.34	14.91 ^d
S 6	< 80 > 100	163	1.60	12.52	14.27	-
S 7	< 100 > 120	137	1.30	11.86	14.51 ^d	-
S 8	< 120 > 140	127	0.97	11.98	-	-
S 9	< 140 > 160	115	0.75	13.09 ^d	-	-
S 10	< 160 > 180	100	0.19	-	-	-
S 11	< 180 > 200	77.5	0.10	-	-	-
S 12	< 200	55	3.26	13.80	15.00	15.71

- a. GROUND IN SLING-SLEDGE MILL, CLASSIFIED BY USE OF ROTATAP.
b. FRACTION S 0 SCREENED BY HAND TO MAXIMIZE SAMPLE.
c. FLOW TIME AT 172 HOURS, PREFORMED PRIOR TO DAY TEST WAS RUN.
d. END OF SAMPLE.

TABLE VII

VARIATION OF FLOW TIME BETWEEN THREE LOTS MILLED TO THE SAME POWER INPUT
B33-2, B33-3, AND B33-4

HOURS OFF MILL	FLOW AT 5 TONS				AVERAGE VALUE <i>Sec</i>	MAXIMUM DEVIATION	
	B33-2L ^a <i>Sec</i>	B33-3L ^a <i>Sec</i>	B33-4L ^a <i>Sec</i>	B33-2/4LC ^b <i>Sec</i>		PLUS <i>Sec</i>	MINUS <i>Sec</i>
4	7.30	7.66	8.14	-	7.70	0.44	0.36
24	9.93	9.60	9.43	-	9.65	0.28	0.17
48	11.18	10.13	10.92	-	10.74	0.44	0.61
240	13.31	12.63	12.47	-	12.80	0.51	0.33
360	12.62	13.10	12.58	-	12.77	0.33	0.19
552	-	-	-	13.28	-	-	-

- a. LETTER L INDICATES THAT SAMPLE WAS GROUND IN THE LABORATORY MILL USING 10-MESH SCREEN.
b. BLEND OF RESIDUALS OF B33-2L, B33-3L, AND B33-4L.

TABLE VIII

VARIATION OF FLOW TIME BETWEEN TWO LOTS MILLED TO THE SAME POWER INPUT, AND EFFECT OF GRINDING ON RATE OF CHANGE OF FLOW TIME

HOURS OFF MILL	DEVIATION FROM AVERAGE		AVERAGE				HOURS ^c AFTER GRINDING	HOURS ^c OFF MILL	DEVIATION ^d FROM AVERAGE
			B33-5L	FLOW TIME AT 5 TONS					
	AND	B33-5L ^a <i>Sec</i>	B33-6L <i>Sec</i>	B33-6L2 ^b <i>Sec</i>					
	PLUS								
	MINUS								
<i>Sec</i>	<i>Sec</i>	<i>Sec</i>	<i>Sec</i>	<i>Sec</i>					
6	0.04	0.05	6.44	6.39	6.48	5.93	1	146	-0.51
24	0.11	0.11	8.77	8.66	8.88	8.30	27	172	-0.47
48	0.07	0.06	10.30	10.24	10.37	7.51	48	191	-2.89
144	0.56	0.56	12.23	11.67	12.79	12.94	144	288	+0.71
288	0.59	0.60	13.03	12.43	13.62	13.54	336	480	+0.51
480	0.28	0.28	13.24	12.96	13.52				+0.30

a. LETTER L INDICATES THAT SAMPLE WAS GROUND IN LABORATORY MILL USING 10-MESH SCREEN.

b. STRIP OF B33-6 GROUND 145 HOURS AFTER MILLING.

c. HOURS AFTER GRINDING AND OFF MILL FOR B33-6L2.

d. DEVIATION OF FLOW TIME FOR B33-6L2 FROM AVERAGE FOR MOST CLOSELY CORRESPONDING TIME.

TABLE IX

VARIATION OF FLOW TIME BETWEEN SIX LOTS MILLED TO THE SAME POWER INPUT
B34-1 THROUGH B34-6

HOURS	FLOW TIME AT 5 TONS						AVERAGE	MAXIMUM DEVIATION	
OFF							VALUE	PLUS	MINUS
MILL	B34-1L ^a	B34-2L	B34-3L	B34-4L	B34-5L	B34-6L			
	Sec	Sec	Sec	Sec	Sec	Sec	Sec	Sec	Sec
24	9.26	8.56	8.61	9.80	9.15	8.61	9.03	0.77	0.47
48	11.42	10.87	10.81	12.02	10.82	10.42	11.06	0.96	0.54
120	11.23	11.16	11.97	11.71	11.82	11.16	11.51	0.46	0.35
144	11.75	12.28	11.62	11.96	12.95	11.71	12.05	0.90	0.43
192	12.04	12.59	11.71	11.43	11.91	12.18	11.98	0.61	0.55
312	13.61	13.21	13.87	13.43	12.75	13.34	13.38	0.49	0.63

a. LETTER L INDICATES THAT SAMPLE WAS GROUND IN LABORATORY MILL USING 10-MESH SCREEN.

The data which have been obtained were much too extensive to present in their entirety; only representative portions have been presented in the tables. The following discussion is based on a study of all of the data and of numerous graphical presentations.

There appears to be a definite relationship between the ultimate flow time and the input power to which the material was milled. With the same formulation and the same weight of plastic, it is believed that a high percentage of lots milled to the same power input will have ultimate flows which agree within ± 2 seconds. It may therefore be practicable to prepare blends to a specified flow value within satisfactorily narrow limits.

All material studied to date has been stiffer than 15 seconds at 5 tons and is too stiff for use in production molding. It is believed that material having an ultimate flow of 10 to 12 seconds will reach a stable value more rapidly than the materials studied to date. Hence, the problem of accurately calibrating the input power in terms of ultimate flow may not be as difficult as present data would indicate.

When the flow time data at 24 (or 29) hours in Tables IV, V and VI are plotted, three distinct curves are obtained. These indicate that B33-2/4, which was milled to 2.1 KW, is stiffer than B33-5/6 milled to 1.9 KW, and that B33-5/6, which contained 2 parts of monomer, is stiffer than B34-1/6 which contained 3 parts of monomer, although both were milled to 1.9 KW. When these data are plotted as flow time in seconds against the logarithm of the average equivalent particle diameter in microns, straight lines can be drawn with not unreasonable scatter of the points. This scatter is too great to permit accurate determination of the slope of the line, but it would appear that there is a shift of slope between the stiffest and softest formulations.

When the flow time in seconds is plotted against the logarithm of the time since milling, a straight line can be drawn with some scatter of the points, but again an accurate determination of the slope is not possible. The batches containing large particles definitely increase in flow time at a slower rate, and those containing the finest particles increase at a faster rate than do those containing particles of medium size. There does not appear to be any large difference in the rate of change for formulations containing particles in the range of 20 to 80 mesh.

There is evidence that deviation from the straight line may occur after a sufficient length of time. When plotted on linear coordinates, the curves appear to be approaching a maximum value as a limit. The apparent value of this limit increases as the particle size decreases. Hence, there appears to be a definite tendency to reach an apparent or pseudo-equilibrium at a flow time below the true ultimate value.

Three strips of B29-7, to be used for X-ray studies, were not ground with the bulk of the lot. B29-7 had an initial flow of 6.88 seconds at 5 tons but had reached a flow of 11.29 seconds at 7.5 tons after 28 days. The three strips were ground at 28 days and had a flow, at one hour after grinding, of 8.45 seconds at 5 tons. The flow increased with time, reaching 11.41 seconds at 7.5 tons in eight days.

One strip of B33-6 was ground at 145 hours after milling. This sample was designated B33-6L2 and comparative data are given in Table VIII. The points for B33-6L2 fall quite close to the curve for B33-6 when these data are plotted.

It would therefore appear that the material as sheeted from the mill changes only very slowly with time, and that zero time for studies of the change in flow with time should be the time of grinding rather than the time that the plastic was sheeted off the mill.

Several experiments were made in an attempt to stabilize the flow time by annealing, but all were unsuccessful. It is possible that temperatures high enough to anneal would cause excessive polymerization of the material.

Some preliminary experiments on the rate of hardening of asbestos-filled diallyl phthalate molding powder when heated in an oven have been made. The data obtained to date are summarized in Table X.

TABLE X
OVEN-HEATING OF B6B

CONVECTION OVEN			TIME	FORCED-CIRCULATION OVEN		
OVEN TEMP °C	FLOW TIME seconds ^a	FORCE tons	IN OVEN hr	TEMP °C	FLOW TIME seconds ^a	FORCE tons
ROOM	8.35	5	0	ROOM	7.67	5
68	8.41	5	0.5	78	8.33	5
68	8.45	5	1.0	78	8.56	5
68	8.80	5	1.5	78	8.76	5
68	9.19	5	2.0	78	8.92	5
ROOM	8.41	5	0	—	c	—
ROOM	3.34	10	0	ROOM ^b	7.00	5
80	9.12	10	0.5	80	7.32	5
80	7.41	10	1.0	80	7.37	5
80	NO CLOSE	15	1.5	80	7.26	5
80	NO CLOSE	15	2.0	80	7.53	5
			4.0	80	7.78	5
			6.0	80	7.70	5
			7.0	80	8.01	5
			8.0	80	8.34	5
			16.0	80	8.55	5

a FLOW TIMES ARE AVERAGE OF THREE DETERMINATIONS

b SAMPLE HAD BEEN STORED IN B-BUILDING COLD ROOM; OTHER SAMPLES WERE STORED AT ROOM TEMPERATURE

c FLOW TIMES BELOW ARE AVERAGE OF TWO DETERMINATIONS

B6B was a blend prepared by grinding the broken sheets from all of the B6 mill lots in the sling-sledge grinder with subsequent hand-blending. The plastic was several weeks old before grinding and was stored at room temperature for several weeks before approximately one-half was placed in the B-Building cold room for storage. Formulation B6 was made with 100 parts

were 9.6 per cent, but the rejection due to cracks were only 1.5 per cent, so there may have been some reduction in the number of cracks.

A series of measurements has been started on samples of Mesa 51-01 molding powders, which have been procured by Production Molding, to determine if these materials increase in flow time with age. The samples which were available were of unknown age after grinding, but any rapid changes would have already occurred. The results were inconclusive, but there may have been some increase in flow time with further aging.

A sample of Mesa 51-01 "L" No. 1143 was classified by use of the Rotatap, and the flow time of the various fractions is being determined as a function of time. The data presently available are summarized in Table XI. This sample is much too old to expect any rapid change. An examination of the data indicate that it probably shows the same trend as has been found for material produced at Mound Laboratory, but the changes are not large compared to the probable experimental error.

TABLE XI
VARIATION IN FLOW TIME WITH PARTICLE SIZE AND
WITH AGE AFTER SCREENING
MESA 51-01, NO. 1143 L

SAMPLE M-1143	MESH RANGE	AVERAGE PARTICLE SIZE <i>microns</i>	PER CENT BY WEIGHT	FLOW TIME AT 5 TONS ^a				
				AT X +0 HR <i>sec</i>	AT X +25 HR <i>sec</i>	AT X +169 HR <i>sec</i>	AT X +572 HR <i>sec</i>	AT X +968 HR <i>sec</i>
S-1	>4	6,500	0.24	-	-	-	-	-
S-2	< 4 > 16	3,425	37.70	9.09	9.87	9.96	10.73	11.58
S-3	<16 > 20	1,015	14.55	10.32	9.81	11.31	11.85	-
S-4	<20 > 40	630	19.15	10.78	11.47	11.96	11.60	12.18
S-5	<40 > 60	335	8.15	10.85	12.30	11.83	-	-
S-6	<60 > 100	200	7.85	11.30	12.72	11.37	-	-
S-7	<100	110	12.31	10.75	10.12	11.18	12.10	-

^a THE TIME OF GRINDING IS UNKNOWN, BUT X IS PROBABLY THE EQUIVALENT OF TWO OR MORE WEEKS AT ROOM TEMPERATURE.

One mill-lot having a flow of 12 ± 2 seconds was ordered from Mesa in the form of the sheet as cut-off of the mill. This has been obtained. The material was partially broken and had a flow time near 50 seconds at 5 tons. The density was also about 5 per cent low so that the first flow test cups were made with too heavy a sample. The flow times obtained using the heavy charge were one second or more high. Since the flow time cannot be measured at 5 tons, a direct comparison with previous results cannot be made. The data presently available are not sufficient to permit definite conclusions to be drawn, but it does appear that the Mesa material will follow the general pattern found with material produced at Mound Laboratory.

A complete flow curve was run for a 100-pound lot of Mesa 51-01 molding compound which was ordered by Production Molding to a specification of 14 ± 2 seconds at 5 tons. This material was stiffer than 15 seconds at 5 tons, but it was within specifications.

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 Performance - Work was completed on the accumulation of column performance data with batch-type operation for 50 molecular per cent mixtures of hydrogen and helium with 0.064-inch molybdenum center-wires. A summary of pertinent data is given in Table I. In this table the equilibrium time is that time required for the separation process to attain a value within a very few per cent of the equilibrium value. The equilibrium time was usually determined by examination of the curve for the rate of approach to equilibrium. Although the equilibrium time is not well defined, it is easily selected and is a convenient value for estimating proper column operation. The relaxation time in this table is defined as the time required for the separation factor to reach the fraction 1/e of its equilibrium value.

TABLE I

COLUMN PERFORMANCE WITH 0.064-INCH MOLYBDENUM CENTER-WIRE

COLUMN INSIDE DIAMETER in.	WIRE TEMPERATURE °C	MAXIMUM SEPARATION FACTOR q_e	OPTIMUM INITIAL PRESSURE atm	EQUILIBRIUM TIME Min.	RELAXATION TIME Min.
1.00	300	700	1.41	240	107
	600	4.85×10^5	1.32	150	80
	900	1×10^7 *	1.25*	120*	76*
1.25	300	395	0.987	240	85
	600	4.10×10^4	0.999	150	70
	900	9.33×10^5	0.855	90	54
1.61	300	99.1	0.664	180	56
	600	3,500	0.605	150	51
	900	50,000	0.599	90	44

*PRECISION IS POOR BECAUSE RELATIVE CONCENTRATION OF CONSTITUENTS IN GAS SAMPLES WERE BEYOND THE RANGE OF RELIABLE SENSITIVITY OF THE MASS SPECTROMETER.

Similar data for 0.016-inch diameter center-wires were tabulated in "Mound Laboratory Monthly Technical Activities Report through February 15, 1957", CF 57-2-23.

The curves for the rate of approach to equilibrium and for the optimum pressure were used to compute thermal column shape factors for every combination of 1.00, 1.25, and 1.61-inch columns with molybdenum center-wire of 0.016 and 0.064-inch diameter at 300°, 600° and 900°C.

Values for the thermal diffusion shape factor, h , are determined from the thermal diffusion transport coefficient, H . Since H is proportional to the product of h and the thermal coefficient, α , and since the variation of α is not accurately known for the various conditions, the product, ah , was determined for each of the above conditions. It was observed that ah is not appreciably affected by a large variation in the ratio of the radii of the column and the wire, but is strongly dependent on the ratio of the hot-wire temperature to the cold-wall temperature. Average values of ah are 0.0367 for $T_2/T_1 = 4$, ($T_2 = 1200^\circ\text{K}$); 0.0245 for $T_2/T_1 = 3$, ($T_2 = 900^\circ\text{K}$); and 0.0905 for $T_2/T_1 = 2$, ($T_2 = 600^\circ\text{K}$). These values were used to complete the values for the convection and diffusion remixing shape factors, k_c and k_d listed in Tables II and III.

TABLE II

VALUES FOR CONVECTION REMIXING SHAPE FACTORS, k_c

T_2/T_1	r_1/r_2					
	15.6	19.5	25.5	62.5	78.1	100
4	0.165	0.170	0.159	0.201	0.226	0.233
3	0.122	0.137	0.139	0.185	0.196	0.215
2	0.078	0.071	0.075	0.090	0.099	0.111

TABLE III

VALUES FOR DIFFUSION REMIXING SHAPE FACTORS, k_d

T_2/T_1	r_1/r_2					
	15.6	19.5	25.2	62.5	78.1	100
4	1.80	1.55	1.59	2.02	1.58	1.66
3	1.64	1.45	1.45	1.60	1.37	1.49
2	1.34	1.15	1.13	1.24	0.99	1.21

The numerical values of k_d were observed to be nearly twice as large as those applicable for a Maxwellian gas in the geometry and temperature ranges studied. The values of k_c , however, are of the order of 4, 12, and 24 times as high as the corresponding Maxwellian values for T_2/T_1 , of 2, 3, and 4, respectively. This shows that the effect of non-Maxwellian gases upon theoretical considerations is not insignificant.

Further experiments with the thermal convection pump have indicated that the volume of gas this pump is capable of circulating is not sufficient to be suitable for our use as gas interchanges in thermal column cascades.

Work is in progress on the study of the effect of relative concentration of feed mixtures on the separation factor attainable. For this work, various hydrogen-helium and hydrogen-deuterium mixtures are being used in the 1.61-inch column.

A total of 317 hydrogen-helium samples and 30 hydrogen-deuterium samples were analyzed on the mass spectrometer this month. This work was done in conjunction with the above experimentation.

Gas Purification: - The silver soldering of all copper fittings and connections within the system has been completed. The Plexiglass hood doors also have been hung in place. The second uranium pump was assembled, but is not yet installed. A uranium charge of 1957.72 grams was placed in this pump.

Several leaks in the palladium diffuser were detected with the helium leak detector. The leaks appeared around the Conax fittings and the gasket seal. Therefore, the diffuser will be temporarily by-passed in the process line until these leaks can be stopped.

Liquid Thermal Diffusion: - A 50-50 volume per cent solution of carbon tetrachloride in benzene has been utilized as feed in preliminary tests with the liquid thermal diffusion column. It was found that the method of filling the columns recommended by the supplier (gravity feed through the middle port without evacuation) was unsatisfactory. Gas continued to form at the top of the annulus over a 24-hour period with the power on. This reduced the heat transfer at the top hot-wall couple, causing it to overheat. Since this was the control couple and since the column is poorly insulated, undue temperature cycling resulted throughout the column. Also, the volume of liquid in the top fraction was substantially reduced.

A two-way feed line, with connections at the bottom and middle ports, has now been installed. After evacuation of the annulus, the latter is filled through the bottom port. During the run, the feed-line valve to the bottom port is closed and that to the middle port is left open. This procedure seems considerably more satisfactory although gas problems are still being encountered. A mercury manometer attached to the vacuum line proved to be an inadequate indicator of the degree of evacuation attained in the annulus. However, if low power is supplied to the hot wall heater during evacuation, progress of the latter may be followed by noting the temperatures recorded by the hot-wall couples. As long as gas pressure is decreasing, heat transfer also decreases, causing the hot-wall temperatures to rise.

After gas was displaced from the column and a steady thermal state was achieved, it was found that the top hot-wall couple read 15°C lower than the middle and bottom hot-wall couples when the latter were at a nominal temperature of 50°C. Removal of insulation showed that the top couple was located beyond the last coil of the heater element. A fourth couple has been added to the hot wall at a point 1½ inches below the top end of the heating element. After a steady thermal state was achieved, the new top couple read about 6°C below the middle and bottom hot-wall couples. The original top hot-wall couple is still connected to the controller and will shut off the heater in the event of overheating due to gas accumulation.

Two approximate determinations of the annulus spacing have been made by observing the volume of liquid required to fill the annulus. The values obtained were 0.01222 inches and 0.01229 inches. The determinations will be repeated using the more accurate weight method.

Results of a satisfactory separation of the 50-50 volume per cent benzene-carbon tetrachloride feed are reported in Table IV. This was a 48-hour run. The bottom and middle hot-wall couples registered 48 to 50°C, and the top hot-wall couple registered 43°C. Cooling water temperature was 14°C at the bottom and 17°C at the top. The mean temperature difference between hot and cold walls was thus approximately 30°C. At the end of the run, the fractions were drained into vials and their refractive indices determined.

The table shows that nearly pure components were obtained in the top and bottom fractions, with benzene going to the top and carbon tetrachloride to the bottom. If one defines

"per cent separation" as the difference between the refractive indices of top and bottom fractions, expressed as a per cent of the difference for pure components, then a per cent separation of 95.8 per cent was obtained.

TABLE IV
FRACTIONATION OF A 50-50 VOLUME PER CENT
BENZENE-CARBON TETRACHLORIDE SOLUTION

FRACTION	REFRACTIVE INDEX AT $12.7 \pm 0.2^{\circ}\text{C}$
1 BOTTOM	1.4650
2	1.4653
3	1.4653
4	1.4666
5 MIDDLE	1.4727
6	1.4894
7	1.4982
8	1.5033
9 TOP	1.5048

NOTE: REFRACTIVE INDICES OF PURE COMPONENTS ARE:

CCl_4 - 1.4648; C_6H_6 - 1.5053

Runs are continuing with the benzene-carbon tetrachloride system to determine proper evacuation technique and reproducibility of column performance. Once satisfactory reproducibility is achieved, the degree of separation attainable with a mixture of heavy water and ordinary water will be measured. A shipment of heavy water has been received. Pycnometers for determining the composition of the fractions are on order.

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 Studies

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.

Four series of runs were made on solubility of the system, plutonium (IV) sulfate, sulfuric acid, and water. The results are listed in Table I. The tubes containing the 6.00 *N* sulfuric acid solutions of plutonium were all raised above 342°C without phase change. However, on return to room temperature, it was found that all samples had the blue color characteristic of plutonium (III) rather than the brown color characteristic of plutonium (IV).

Methods of preparation of solutions of plutonium (III) sulfate in sulfuric acid and water are being developed for investigation of solubility, and consideration is being given the preparation of plutonium (III) carbonate.

TABLE I

SOLUBILITY OF PLUTONIUM (IV) SULFATE IN SULFURIC ACID

0.068 N H ₂ SO ₄		0.600 N H ₂ SO ₄		1.00 N H ₂ SO ₄		6.00 N H ₂ SO ₄	
TEMP. OF Pu	CONC.	TEMP. OF Pu	CONC.	TEMP. OF Pu	CONC.	TEMP. OF Pu	CONC.
PHASE CHANGE °C	g/liter	PHASE CHANGE °C	g/liter	PHASE CHANGE °C	g/liter	PHASE CHANGE °C	g/liter
58.3	12.40	138.0	17.65	169.8	17.44	> 343.8	14.04
59.0	7.37	143.2	12.48	172.6	12.51	> 343.8	9.10
59.6	4.76	148.0	7.60	185.2	7.07	> 348.7	5.49
61.6	3.49	157.2	4.83	217.4	4.76	> 343.7	3.86
66.4	1.93	174.6	2.49	257.0	2.53	> 343.0	2.54
77.6	0.89	196.6	1.49	279.0 ± 2 *	1.46	> 342.2	1.12
84.3	0.66	232.8	0.98	285.0 ± 2 **	0.96	> 343.0	1.06

*POSITIVE IDENTIFICATION 281.0°C

**POSITIVE IDENTIFICATION 287.2°C

AIRCRAFT PROPULSION REACTORS

LIQUID CYCLE REACTORS

The Aircraft Propulsion Reactors 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-RbF-BeF₂ Ternary System - Data obtained thus far from differential thermal analysis studies of various mixtures of LiF, RbF, and BeF₂ are summarized in Figure 1. Some of the previously reported liquidus temperatures of compositions in the region adjacent to the 295°C ternary eutectic point have been revised on the basis of cooling curve studies of continuously-stirred mixtures. Such compositions, characterized by high viscosity, supercooling, and slow approach to equilibrium conditions, yielded unreliable liquidus data when examined in the static apparatus. The liquidus transitions of compositions near the eutectic composition were often obscured on the heating curves by the return trace of the eutectic transition. The quantity of heat involved in transitions for these compositions was always considerably less than the heat expected on the basis of data obtained from fusions of LiF, BeF₂, and RbF as separate salts. Thus, it is indicated that samples of these ternary mixtures in the vicinity of the eutectic are not crystalline. Annealing the mixtures at 280°C in the sealed differential thermal analyses sample tubes for seven to ten days usually caused sufficient crystallization to take place so that reliable phase transition temperatures were obtained. The use of the recently developed differential thermal analysis apparatus in which the samples can be stirred has been of great value in the detection of the various phase transitions of this system.

A partial phase and temperature contour diagram showing the interpretation of data obtained to date appears as Figure 2. The temperature contour lines are correct within 10°C. The location of the 295°C ternary eutectic point was fixed on the basis of the liquidus and boundary intersection temperatures in its vicinity. The course of the BeF₂-Li₂BeF₄ eutectic binary was fixed by a series of reproducible boundary intersection values obtained from compositions examined in each respective primary phase area. The course of the BeF₂-RbBe₂F₅ boundary was determined by petrographic examinations of primary phase areas, and boundary intersection and general liquidus values of bordering compositions. Insufficient data have been collected to completely define the course of the boundary connecting the peritectic point on the LiF-BeF₂ binary to the 295°C eutectic point. This boundary appears as a dashed line on Figure 2.

Additional data obtained from petrographic examination of thermal gradient quenches of compositions in the LiF-RbF-BeF₂ system in which BeF₂ was the major constituent appear in Table I. Compositions R-8, R-9, and R-10 were re-examined after being held in the thermal

TOP NUMBER — LIQUIDUS
BOTTOM NUMBER — EUTECTIC

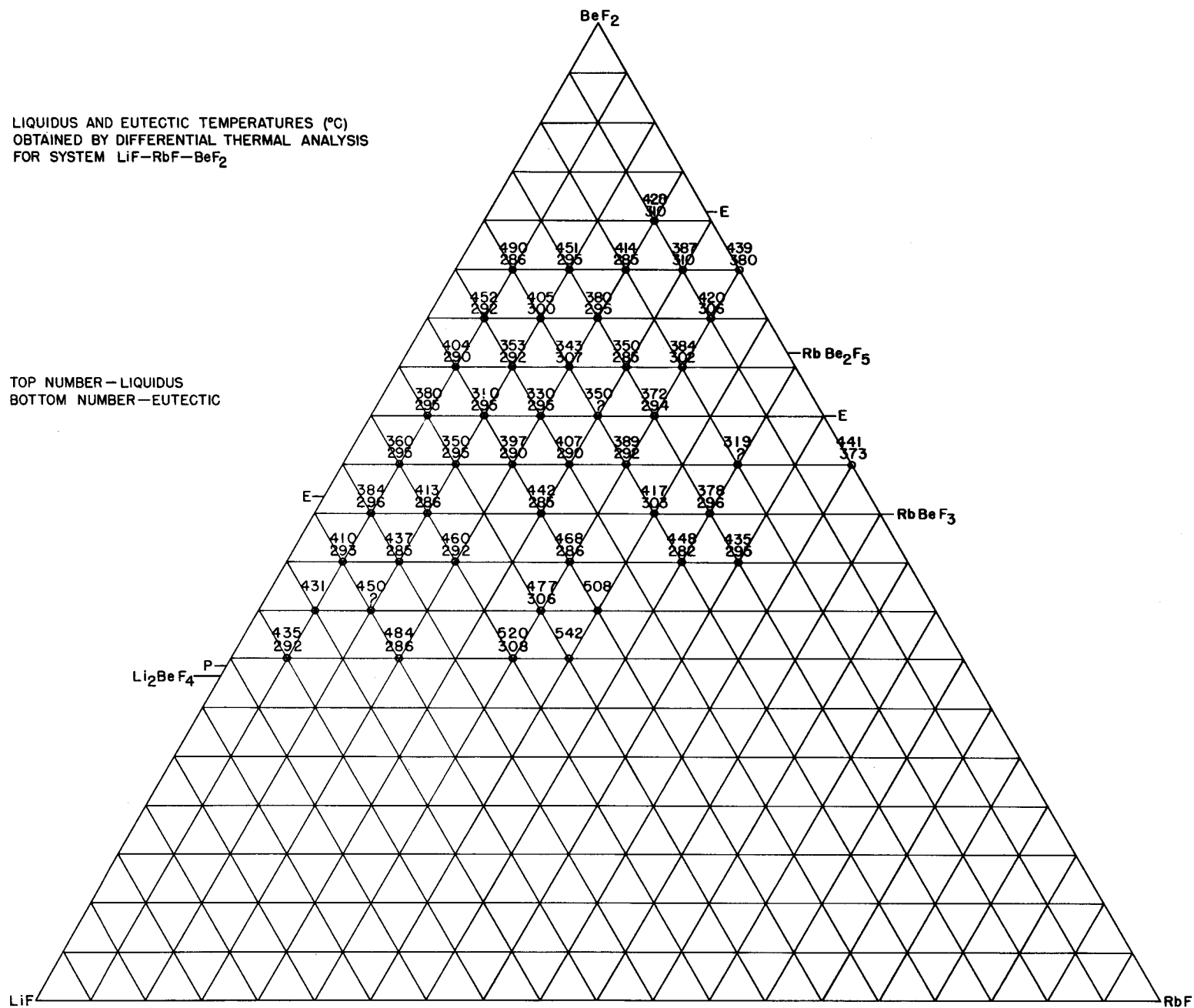


FIGURE 1

PARTIAL PHASE DIAGRAM AND TEMPERATURE
CONTOURS FOR THE SYSTEM LiF-RbF-BeF_2
OBTAINED BY D.T.A.

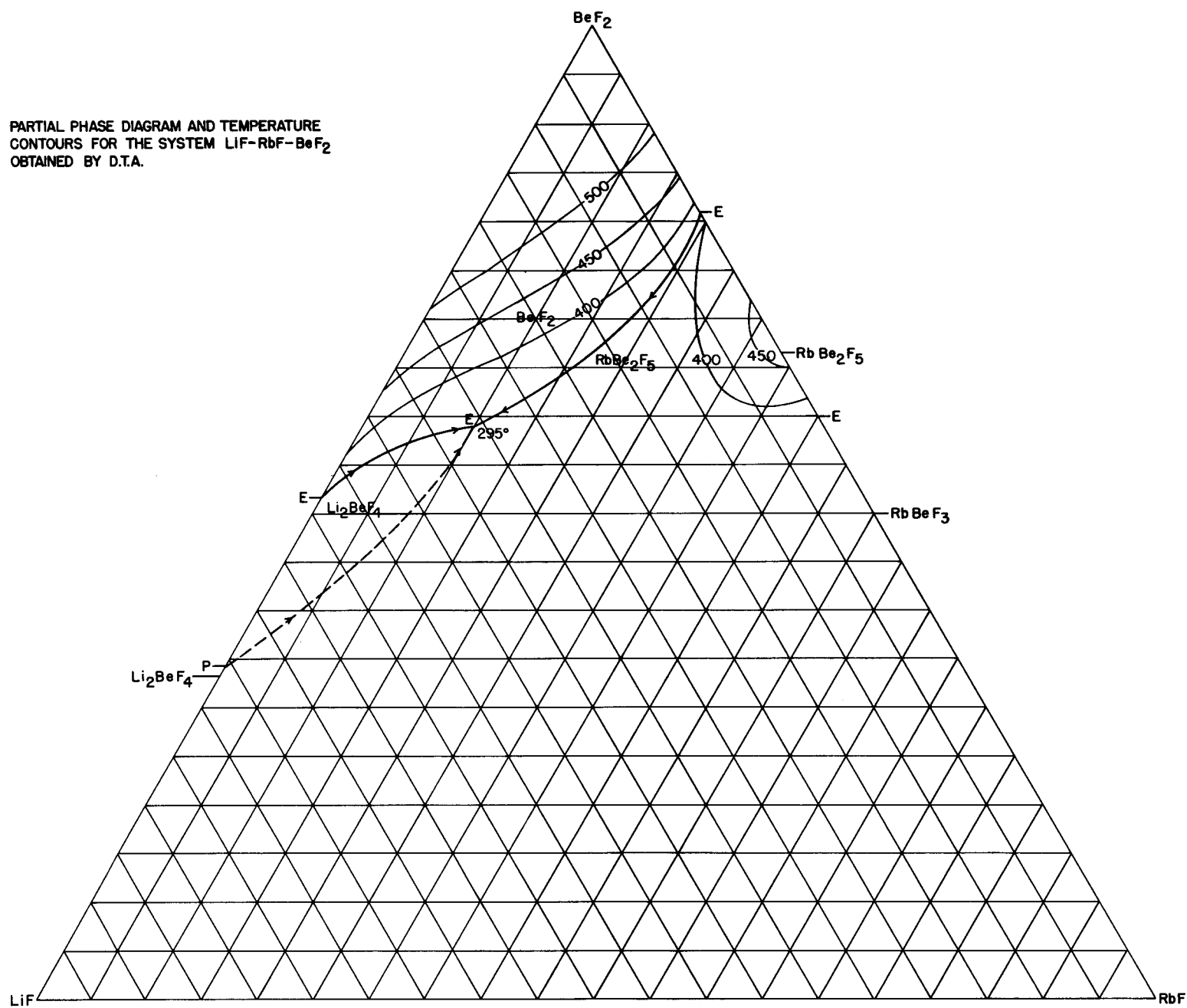


FIGURE 2

gradient furnace for over 100 hours, but equilibrium conditions in these mixtures were not obtained by the extended thermal treatments.

TABLE I
THERMAL-GRADIENT QUENCHING DATA OF THE LiF-RbF-BeF_2 SYSTEM

COMPOSITION NUMBER	COMPOSITION MOLE PER CENT			PHASE CHANGE TEMPERATURE °C	PHASES FOUND JUST ABOVE PHASE CHANGE	PHASES FOUND JUST BELOW PHASE CHANGE	INTERPRETATION
	LiF	RbF	BeF ₂				
R- 15	15	17	68	330	LIQUID	LIQUID, BeF_2	LIQUIDUS AND PRIMARY PHASE
R- 17	35	10	55	340	LIQUID	LIQUID, RbBeF_3^*	LIQUIDUS AND PRIMARY PHASE
R- 18	15	32	53	363	LIQUID	LIQUID, RbBeF_3^*	LIQUIDUS AND PRIMARY PHASE
R- 19	25	12	63	328	LIQUID	LIQUID, RbBeF_3^*	LIQUIDUS AND PRIMARY PHASE
				320	LIQUID, RbBeF_3	LIQUID, RbBeF_3 , BeF_2	BOUNDARY INTERSECTION
R- 20	50	6	44	426	LIQUID	LIQUID, Li_2BeF_4	LIQUIDUS AND PRIMARY PHASE
				373	LIQUID, Li_2BeF_4	LIQUID, Li_2BeF_4 , RbBe_2F_5	BOUNDARY INTERSECTION
R- 8 (REPEAT)	40	5	55	358	LIQUID	LIQUID, Li_2BeF_4	LIQUIDUS AND PRIMARY PHASE
				326	LIQUID, Li_2BeF_4	LIQUID, Li_2BeF_4 , BeF_2	BOUNDARY INTERSECTION
R- 9 (REPEAT)	13	27	60	357	LIQUID	LIQUID, RbBe_2F_5	LIQUIDUS AND PRIMARY PHASE
				334	LIQUID, RbBe_2F_5	LIQUID, RbBe_2F_5 , BeF_2	BOUNDARY INTERSECTION
R- 10 (REPEAT)	20	35	45	439	LIQUID	LIQUID, RbBeF_3^*	LIQUIDUS AND PRIMARY PHASE

*NOT VERIFIED BY X-RAY.

Compositions R-17, R-18, and R-19 are tentatively listed in Table I as being in the RbBeF_3 primary phase area. However, an unknown but identical X-ray pattern continues to be obtained on selected quenched samples of these, and other compositions previously reported, which is not the accepted X-ray pattern for RbBeF_3 . The possibility of one or more ternary compounds being present in this portion of the phase diagram is being investigated.

The X-ray examination of several selected quenched samples of compositions in this same area points to the possibility of the presence of quench-growth in sufficient quantities to produce X-ray patterns. Samples of compositions quenched immediately above and below the liquidus temperatures yielded X-ray patterns of an unknown compound. The fact that an X-ray pattern was obtained for a sample quenched above its liquidus temperature where only glass is

normally present, suggests quench-growth. However, this same unidentified X-ray pattern has also been obtained in some instances from slowly-cooled melts, which suggests that the material may be an equilibrium phase. Inasmuch as the unidentified X-ray pattern is quite persistent in quenched samples, the presence of this unidentified compound may obscure the pattern for the true primary phase as observed microscopically. This effect may explain the inability to confirm the primary phase identification by X-ray.

The data obtained from high-temperature filtration examinations of the liquidus surface of the LiF-RbF-BeF₂ ternary system are reported in Table II. Although these data are related to scattered points generally outside areas that have been investigated by differential thermal analyses and petrographic techniques, they confirm certain data obtained by these other studies. The crystallization paths for compositions FR-6, FR-12a, and FR-12b are away from the LiF corner of the ternary diagram. Apparently this ternary system has a relatively large LiF phase area. The crystallization paths for compositions FR-7, FR-8, and FR-9 are toward an invariant point which has been tentatively assigned as another ternary eutectic point. The starting composition of FR-10 is in a different composition triangle from FR-7 since the crystallization path of FR-10 does not proceed toward the same invariant point as does FR-7. The direction of the crystallization path for composition FR-11 suggests the existence of a ternary compound.

TABLE II
LIQUIDUS VALUES BY FILTRATION

	STARTING COMPOSITION MOLE PER CENT			TEMPERATURE OF FILTRATION °C	FILTRATE COMPOSITION MOLE PER CENT		
	LiF	RbF	BeF ₂		LiF	RbF	BeF ₂
FR-6	40	30	30	550	33.3	33.6	33.1
FR-7	27.5	27.5	45	402	16.9	33.6	49.5
FR-8	10	30	60	360	12.2	31.2	56.6
FR-9	10	40	50	352	13.8	37.0	49.2
FR-10	23	22	55	380	24.4	21.6	54.0
FR-11	50	10	40	412	53.2	6.8	40.0
FR-12a	55	15	30	488	50.3	16.5	33.2
FR-12b	55	15	30	525	51.4	18.0	30.6

LiF-BeF₂ Binary System - The search for various compounds and the identification of these compounds in the LiF-BeF₂ subsolidus system has been reopened for investigation. A possible total of eight subsolidus compounds has been indicated. The only solidus compound which has been positively identified is LiBeF₃. Although it had been stated previously that the low-temperature form of LiBeF₃ (Lo-LiBeF₃) had been identified, this information was in error. Various binary samples containing 20 and 25 mole per cent LiF have been heated at 152° and 172°C for extended periods of time. Examination of these systems by X-ray diffraction techniques after thermal treatment has revealed that the strength of the pattern previously assigned as "Lo-LiBeF₃" increased with increasing BeF₂ content. Additional diffraction lines for this compound have been found, and a re-indexing is being attempted. A tentative indexing in the orthorhombic system gives $a = 5.68\text{\AA}$, $b = 6.07\text{\AA}$, $c = 6.80\text{\AA}$, and $V = 236\text{\AA}^3$. Three compounds could fit into this cell

pattern, namely, $\text{LiBe}_5\text{F}_{11}$, BeF_2 , and LiBeF_3 . The LiBeF_3 is eliminated from consideration on the basis of the experimental information previously presented. The assignment of BeF_2 as the compound is not impossible, but is improbable. The structure would require that three BeF_2 units be arranged asymmetrically about a point. The theoretical density of such a BeF_2 cell is 1.98 whereas the density of BeF_2 glass is 2.01 grams per cubic centimeter.

Samples of BeF_2 glass were devitrified under conditions identical to those outlined for the binary mixtures. The X-ray patterns obtained were totally different from the previously obtained patterns. The devitrified BeF_2 yielded a pattern with one strong line at 4.18A, two or three weak lines, and a strong halo pattern such as that produced by a glassy substance.

Binary mixtures containing 50 mole per cent LiF and 50 mole per cent BeF_2 which had been held at 152°C and 172°C for extended periods of time gave an X-ray pattern entirely different from the patterns obtained from binary systems containing 33.3 mole per cent LiF .

In all systems examined, the binary samples were heated to 800° in thick-walled nickel capsules, shaken violently to maintain homogeneity, quenched to a glass, and then held at the desired temperature for 300 hours.

High Temperature Calorimetry - Two dimensionally different thermal conductivity cells designed for fused salt mixtures have been tested in the high-temperature calorimeter. The thermal conductivity of water from 30° to 50°C was measured. These cells are machined entirely from nickel. The outer shell of each has a wall thickness of 0.030 inch, is 2.835 inches long, and of 0.793-inch outside diameter. The cell fits completely into the sample space of the high-temperature calorimeter. A right cylindrical bob is supported on the same axis as the cell at one end of and inside the shell by a stem 0.25-inch long by 0.120-inch in diameter. A thermocouple well 0.060-inch in diameter was drilled through this stem to the mid-point in the bob. The bob is 1.38 inches long. A space of 1.25 inches at one end of the shell remains as a void for filling with a powdered sample to be melted. The bob must be completely submerged in the liquid. When a measurement is made the sample container is loaded with powdered material through the end opposite the thermocouple well. A cover is welded in place to seal the cell.

The two cells differ only in the outside diameters of the inner bobs, which yield gaps of 0.062-inch and 0.125-inch, respectively. A solid nickel cylinder with a similar thermocouple well is placed in the opposite twin of the calorimeter. A fused, iron-constantan thermojunction of BS No. 30 wire was inserted into each of the walls with the leads each insulated by a two-hole 0.056-inch outside diameter "Alundum" insulator. The two junctions were connected differentially by joining the constantan leads at the midpoint of the outer jacket. The iron leads were brought out and soft-soldered to copper leads and these junctions were inserted into a hole in a massive block of copper. The copper leads connect the differential voltage output of the thermocouples to a Leeds and Northrup DC amplifier which drives a 0-100 millivolt Speedomax recorder.

The theory of operation requires that the outer surfaces of the conductivity cell and the solid nickel cylinder be at the same temperature at all times. This is accomplished by maintaining a constant bridge potential with a controller supply power to one of the calorimeter heaters. The controller is a Leeds and Northrup DC amplifier, chopper, and audio amplifier, which have been described previously. The calorimeter jackets have the normal complement of controllers.

The operational procedure is to maintain a constant jacket temperature until both thermojunctions reach an equilibrium temperature as indicated by a straight line trace on the recorder. This temperature, T_1 , is determined by measuring the calorimeter bridge resistance. The temperature of the calorimeter is then raised to a higher temperature T_2 , and maintained until the recorder trace is again a straight line. The area A, under the transient curve between T_1 and T_2

is measured in arbitrary planimeter units. The planimeter is calibrated by turning off the inner bridge controller and measuring the calorimeter bridge potential under equilibrium conditions. A constant current is then maintained in the sample-side heater until the bridge potential again reaches a steady-state. From the bridge unbalance, the temperature rise of the sample-side can be determined. In the meantime, the differential thermocouple trace has advanced from one straight line to a higher one. The latter trace is maintained for about a one-half hour after equilibrium is obtained, and the area swept out in this time is planimeted. Since this area in °C-seconds is known, the planimeter is now calibrated.

The conductivity of the sample is given by the following equation:

$$K_s = \frac{\frac{C_s (r_1^2 - r_2^2)}{4} + (C_n - C_s) r_2^2 \ln \left[\frac{r_1}{r_2} \right]}{\frac{A}{T_2 - T_1} + \frac{C_n (r_2^2 - r_1^2)}{4K_n}} \quad (\text{cal} - ^\circ\text{C}^{-1} - \text{cm}^{-1} - \text{sec}^{-1})$$

where

C_s = heat capacity of sample in $\text{cal} - ^\circ\text{C}^{-1} - \text{cm}^{-3}$

C_n = heat capacity of nickel in $\text{cal} - ^\circ\text{C}^{-1} - \text{cm}^{-3}$

r_1 = I.D. of shell in cm

r_2 = O.D. of bob in cm

K_n = conductivity of nickel in $\text{cal} - \text{sec}^{-1} - ^\circ\text{C}^{-1} - \text{cm}^{-1}$

A = area of transient unbalance in going from a constant T_1 to T_2 in $^\circ\text{C} - \text{sec}$

$T_2 - T_1$ = change of temperature in $^\circ\text{C}$

The second term in the denominator can be neglected if K_n/K_s is large; thus, for water, it is about one per cent since $K_n/K_s \approx 100$. Note that if the heat capacity of the sample is small, as in the case of a gas, the first term in the numerator would be small and K_s would be no more accurate than C_n . If the sample has about the same heat capacity as nickel, such as is the case with water, the second term would be small and K_s would be determined by C_s .

Several years ago the heat capacity of nickel at 28°C was measured six times by three different methods with Mound Laboratory's room-temperature calorimeter. The mean value obtained was $0.1060 \pm 0.0002 \text{ cal} - ^\circ\text{C}^{-1} - \text{gm}^{-1}$. The density of the nickel used in these cells was measured at room temperature using two solid 1.0610-inch diameter cylinders with an average result of 8.862 g/cm^3 . Therefore, the heat capacity per unit volume is $C_n = 8.862 \times 0.1060 = 0.939 \text{ cal} - ^\circ\text{C}^{-1} - \text{cm}^{-3}$. The heat capacity of water used to test the thermal conductivity cells per unit volume at 42°C is $C_s = 0.9915 \times 0.9981 = 0.9896 \text{ cal} - ^\circ\text{C}^{-1} - \text{cm}^{-3}$. The thermal conductivity of nickel is approximately $0.14 \text{ cal} - ^\circ\text{C}^{-1} - \text{mg}^{-1} - \text{cm}^{-1}$. The two cells have the following dimensions: $r_1 = 0.9601$ and $r_2 = 0.7728$ cm for Cell No. 1, and $r_1 = 0.8857$ and $r_2 = 0.3755$ cm for Cell No. 2. Substitution of these values into Equation 1 for each cell yields for Cell No. 1,

$$K_s = \frac{0.0760}{A (T_2 - T_1) + 0.54} \quad \text{cal} - ^\circ\text{C}^{-1} - \text{cm}^{-1} - \text{sec}^{-1} \quad (1)$$

and for Cell No. 2,

$$K_s = \frac{0.1221}{A (T_2 - T_1) + 0.86} \text{ cal} - ^\circ\text{C}^{-1} - \text{cm}^{-1} - \text{sec}^{-1} \quad (2)$$

The conductivity cells were each filled with a known weight of distilled water so that water to a depth of 1/4-inch covered the inner right cylinder in each cell. The cover of each cell was sealed into place. The thermal conductivity of the distilled water in each cell was measured. The complete experimental results for a total of seven different sets of measurements on cells 1 and 2 appear in Table III.

TABLE III
THERMAL CONDUCTIVITY OF WATER

RUN	CELL	A °C - sec	T ₂ °C	T ₁ °C	K _s Cal - °C ⁻¹ - cm ⁻¹ - sec ⁻¹
1	1	289	53.508	46.913	0.00172
2	1	803	49.737	32.001	0.00166
3	2	795	42.467	33.232	0.00140
4	2	712	51.753	42.467	0.00158
5	2	1473	50.136	31.362	0.00154
6	1	844	51.922	34.798	0.001526
7	1	915	51.252	32.804	0.001516

The average thermal conductivity of water for runs 6 and 7 at their average temperature is considered to be the best value for these measurements, i.e., $K_{\text{H}_2\text{O}} = 0.001521 \text{ cal} - ^\circ\text{C}^{-1} - \text{cm}^{-1} - \text{sec}^{-1}$ at 43°C. During runs 6 and 7, the stability of the various thermocouples appeared to be much improved over previous runs. The agreement between the results obtained from Cell No. 1 and Cell No. 2 suggest that convection within the cells does not contribute to the error in measuring the thermal conductivity of water.

In 1955 with similar cells in a water-bath room-temperature calorimeter the following value for the thermal conductivity of water was obtained.

$$K_{\text{H}_2\text{O}} = 0.001442 \text{ cal} - ^\circ\text{C}^{-1} - \text{cm}^{-1} - \text{sec}^{-1} \text{ at } 26^\circ\text{C}$$

Jakob² has reported the following values for the thermal conductivity of water

Temperature °C	Thermal Conductivity
0	0.00133 cal - °C ⁻¹ - cm ⁻¹ - sec ⁻¹
20	0.00142
40	0.00150
60	0.00156

It appears that the measurements in the high-temperature calorimeter at least at lower temperatures will be entirely adequate.

REFERENCES

1. K. C. Jordan, "A General Method of Determining The Total Time Integrals of Transients in Linear Systems", to be published.
2. Max Jakob, "Heat Transfer", Vol. I, p. 78, John Wiley and Sons, Inc., New York (1949).

Density and Viscosity - The density and viscosity data obtained on quaternary mixtures of NaF, LiF, BeF₂ and UF₄ containing 6 mole per cent UF₄ are tabulated in Table IV.

TABLE IV

DENSITY AND VISCOSITY OF QUATERNARY MIXTURES OF NaF, BeF₂, LiF AND UF₄
AT 6 MOLE PER CENT UF₄

COMPOSITION				MELTING POINT °C	600°C			700°C			800°C		
MOLE PER CENT					ρ G/CM ³	η POISE	η/ρ STOKES	ρ G/CM ³	η POISE	η/ρ STOKES	ρ G/CM ³	η POISE	η/ρ STOKES
NaF	LiF	BeF ₂	UF ₄										
13	34	47	6	345	2.492	-	-	2.441	-	-	2.430	-	-
13	66	11	6	601	-	-	-	2.617	0.0543	0.02075	2.561	0.0324	0.01265
13	81	0	6	700	-	-	-	2.748	0.0586	0.02132	2.681	0.0358	0.01335
25	22	47	6	417	2.556	-	-	2.503	-	-	2.450	-	-
25	33	36	6	338	2.590	0.1060	0.04093	2.532	0.0678	0.02678	2.475	0.0352	0.01422
25	54	15	6	574	2.676	0.1173	0.04383	2.615	0.0632	0.02417	2.555	0.0377	0.01476
25	69	0	6	670	-	-	-	2.724	0.0422	0.01549	2.661	0.0351	0.01319
35	12	47	6	394	2.553	-	-	2.493	-	-	2.480	-	-
46	12	36	6	402	2.626	-	-	2.562	-	-	2.497	-	-
46	33	15	6	509	2.691	0.1010	0.03753	2.620	0.0653	0.02492	2.548	0.0457	0.01794
46	48	0	6	580	2.796	-	-	2.726	-	-	2.655	-	-
70	12	12	6	651	-	-	-	2.657	-	-	2.607	-	-
70	24	0	6	733	-	-	-	-	-	-	2.683	-	-

The density and viscosity of binary mixtures of NaF and ZrF₄ containing from 19 to 65 mole per cent ZrF₄ are listed in Table V. All data reported were obtained from interpretation of the respective measurements over a temperature range from the liquidus temperature to 900°C. The vapor pressure of the ZrF₄ in mixtures containing over 60 mole per cent ZrF₄ became excessive above 800°C so that inert gas exhaust lines from the measuring cells were plugged by the ZrF₄ sublimate.

The following empirical equation was developed for calculating the densities of various mixtures of NaF and ZrF₄ with an average deviation of 0.84 per cent over a range from 25 to 65 mole per cent ZrF₄.

$$\rho = 2.929 + 0.0134 N_{Zr} - 0.00091t$$

where

ρ = density, g/cc

t = temperature, °C, and

N_{Zr} = mole per cent ZrF_4

TABLE V

DENSITY AND VISCOSITY OF BINARY MIXTURES OF NaF AND ZrF_4

COMPOSITION		MELTING POINT °C	600°C			700°C			800°C		
MOLE PER CENT ZrF_4	NaF		ρ G/CM ³	η POISE	η/ρ STOKES	ρ G/CM ³	η POISE	η/ρ STOKES	ρ G/CM ³	η POISE	η/ρ STOKES
19.2	80.8	700	-	-	-	-	-	-	2.553	0.0664	0.02601
21.1	78.9	733	-	-	-	-	-	-	2.585	0.0671	0.02596
22.1	77.9	770	-	-	-	-	-	-	2.582	0.0868	0.03362
22.7	77.3	770	-	-	-	-	-	-	2.569	0.0890	0.03464
24.6	75.4	780	-	-	-	-	-	-	2.580	0.0675	0.02616
25.2	74.8	790	-	-	-	-	-	-	2.578	0.0668	0.02591
26.6	73.4	810	-	-	-	-	-	-	2.556*	0.0423*	0.01655
28.6	71.4	742	-	-	-	-	-	-	2.615	0.0642	0.02455
31.0	69.0	674	-	-	-	2.694	-	-	2.616	0.0513	0.01961
35.2	64.8	514	2.823	0.1120	0.03967	2.725	0.0737	0.02705	2.665	0.0523	0.01962
35.3	64.7	538	2.832	0.0993	0.03506	2.751	0.0688	0.02501	2.668	0.0504	0.01889
40.4	59.6	452	2.904	0.1065	0.03667	2.812	0.0717	0.02550	2.721	0.0513	0.01885
41.4	58.6	435	2.884	0.1043	0.03617	2.815	0.0678	0.02409	2.745	0.0478	0.01741
45.6	54.4	480	3.064	0.0972	0.03172	2.960	0.0678	0.02291	2.855	0.0498	0.01744
48.4	51.6	481	3.064	0.1025	0.03345	2.960	0.0649	0.02193	2.852	0.0443	0.01553
51.5	48.5	480	3.107	0.0897	0.02887	3.004	0.0513	0.01708	2.891	0.0322	0.01114
56.7	43.3	502	3.192	0.1190	0.03728	3.077	0.0619	0.02012	2.961	0.0354	0.01196
60.4	39.6	518	3.227	0.1030	0.03192	3.110	0.0623	0.02003	2.995	0.0407	0.01359
64.5	35.5	613	-	-	-	3.159	0.0750	0.02374	3.047	0.0468	0.01536

* VALUES AT 900°C

DEPARTMENT OF DEFENSE

U. S. ARMY SIGNAL ENGINEERING LABORATORIES

Ft. Monmouth

COMPONENTS BRANCH

(Contract No. R-50-799965-SC-01-91)

Nuclear Battery - Thermoelectric Type

The Army Signal Corps Engineering Laboratory is concerned with the development of sources of electricity with particular application to military use. They are interested in a battery suitable as a power source of moderate output, light weight, small bulk and ability to operate under extreme conditions.

The development of a thermal energy conversion system for the direct conversion of the energy of radioactive decay as heat into electrical energy is under investigation by Mound Laboratory. Radioactive materials will be evaluated as heat sources with consideration given to availability, cost, half life, shielding, health hazard and efficiency. Thermocouples and factors for optimum shape and configuration for maximum efficiency output will be considered and prototype thermal battery will be constructed.

Isotopes which had been selected for consideration on the basis of their nuclear properties were investigated to determine if they were available, or if a feasible production scheme could be determined.

Two expressions were derived (see MLM CF 57-4-34) to allow calculations of the amount of desired isotope formed by irradiation in a nuclear reactor. For a first order reaction $X^y + {}_0n^1 \rightarrow X^{y+1}$, where X is the element of y atomic weight and n is a neutron, the number of molecules of X^{y+1} formed (N_2) is:

$$N_2 = \frac{N_1 {}^0\sigma_1 nv}{\lambda_2 + nv(\sigma_2 - \sigma_1)} \left[e^{-nv\sigma_1 t} - e^{-(\lambda_2 + nv\sigma_2)t} \right]$$

where N_1 is the number of molecules of X^y originally present. If one mole of N_1 is taken, the results will turn out in mole fraction. σ_1 is the neutron cross section of X^y , σ_2 is the neutron cross section of X^{y+1} , λ_2 is the $\log_e 2$ /half life of X^{y+1} , nv is the flux of neutrons in the reactor, and t is the time.

If a second order reaction of type $X^y + {}_0n^1 \rightarrow X^{y+1} + {}_0n^1 \rightarrow X^{y+2}$ is required, the following expression for the amount of isotope X^{y+2} formed (N_3) is applicable:

$$N_3 = \frac{N_1 {}^0(nv)^2 \sigma_1 \sigma_2}{\lambda_2 + nv(\sigma_2 - \sigma_1)} \left[\frac{e^{-nv\sigma_1 t} - e^{-(\lambda_3 + nv\sigma_3)t}}{\lambda_3 + nv(\sigma_3 - \sigma_1)} + \frac{e^{-(\lambda_3 + nv\sigma_3)t} - e^{-(\lambda_2 + nv\sigma_2)t}}{\lambda_3 - \lambda_2 + nv(\sigma_3 - \sigma_2)} \right]$$

where, $\lambda_3 = \log_e 2 / \text{half life of } X^{y+2}$

$\sigma_3 = \text{neutron cross section of } X^{y+2}$

A series of calculations were made to determine the power output of a mole of each isotope. Other calculations were made to show power output for the amount of isotope formed per mole of pure parent isotope irradiated but unseparated from daughter isotope, and for the power output of the amount of isotope formed per mole of naturally-occurring element unseparated from the daughter isotopes. Times chosen for irradiation were 30 days, 90 days, 180 days and 360 days with reactor fluxes of 10^{13} , 10^{14} , and 10^{15} neutrons per square centimeter per second.

An integration was performed to get total energy outputs for pure isotopes obtainable over a one-year period of natural decay. Values are shown in Table I.

TABLE I

POWER/MOLE FOR VARIOUS ISOTOPIC HEAT SOURCES

ISOTOPE	HALF-LIFE	POWER WHEN REMOVED FROM REACTOR (WATTS)			ENERGY PER MOLE OF PURE ISOTOPE PER YEAR <i>watt-hours</i>	REMARKS
		PER MOLE OF PURE ISOTOPE	PER MOLE OF PURE PARENT IRRADIATED	PER MOLE OF NATURAL PARENT IRRADIATED		
SULFUR-35	87.1 d	5.93×10^2	1.57×10^{-1}	6.62×10^{-3}	1.75×10^8	
ARGON-42	3.5 y	-	-	-	-	INSUFFICIENT DATA
CALCIUM-45	164 d	4.79×10^2	5.21	1.08×10^{-1}	2.37×10^8	
NICKEL-63	80 y	6.67×10^{-1}	1.35×10^{-1}	4.94×10^{-3}	2.32×10^5	
KRYPTON-85	10.6 y	4.94×10^1	2.03×10^{-1}	1.16×10^{-1}	5.42×10^8	
STRONTIUM-89	51 d	8.88×10^3	(1.61×10^{-3})	(1.33×10^{-3})	(1.57×10^7)	
STRONTIUM-90	28 y	8.62×10^1	-	-	9.82×10^5	COMBINED WITH YTTRIUM-90
*STRONTIUM-89 + 90 (FP)	-	-	-	-	-	
YTTRIUM-91	58 d	8.26×10^3	-	-	1.65×10^7	
CADMIUM-113m	5.1 y	9.63×10^1	1.37×10^{-4}	3.3×10^{-5}	1.02×10^8	
TIN-121m	5 y	7.09×10^1	4.66×10^{-2}	2.19×10^{-3}	$\left\{ \begin{array}{l} 7.50 \times 10^5 \\ 1.40 \times 10^7 \end{array} \right\}$	AS IRRADIATED PRODUCT 1
TIN-123	131 d	3.35×10^2				
CERIUM-144	290 d	3.40×10^3	-	-	2.43×10^7	INCLUDES PRASEODYMIUM-144
PROMETHIUM-146	2 y	5.93×10^2	-	-	4.53×10^8	
PROMETHIUM-147	2.52 y	7.48	-	-	7.26×10^5	
SAMARIUM-151	100 y	6.35×10^{-3}	-	-	7.33×10^3	
EUROPIUM-152	13 y	1.17×10^1	-	-	1.76×10^8	

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TABLE I (CONT'D.)

POWER/MOLE FOR VARIOUS ISOTOPIC HEAT SOURCES

ISOTOPE	HALF-LIFE		POWER WHEN REMOVED FROM REACTOR (WATTS)			ENERGY PER MOLE OF PURE ISOTOPE PER YEAR <i>watt-hours</i>	REMARKS
			PER MOLE OF PURE ISOTOPE	PER MOLE OF PURE PARENT IRRADIATED	PER MOLE OF NATURAL PARENT IRRADIATED		
EUROPIUM-154	16	y	1.32×10^1	-	-	8.31×10^5	
EUROPIUM-155	1.7	y	8.36×10^1	3.17×10^{-2}	7.14×10^{-3}	7.72×10^5	
GADOLINIUM-148	35	y	4.78×10^3	-	-	1.91×10^7	
THULIUM-170	129	d	2.31×10^3	3.18×10^2	3.18×10^2	9.42×10^8	
THULIUM-171	693	d	4.59×10^1	1.13×10^2	1.68×10^1	5.62×10^5	
LUTETIUM-174	165	d	2.25×10^2	-	-	1.12×10^8	
TUNGSTEN-185	74	d	1.80×10^3	2.93×10^1	8.97	4.56×10^8	
TUNGSTEN-188	165	d	-	-	-	-	INSUFFICIENT DATA
OSMIUM-194	-	-	-	-	-	-	INSUFFICIENT DATA
THALLIUM-204	3	y	2.10×10^2	5.4×10^1	1.59×10^1	2.10×10^8	
LEAD-210	19.4	y	6.30×10^2	-	-	7.13×10^8	INCLUDES Po ²¹⁰ , Bi ²¹⁰
POLONIUM-208	2.93	y	3.69×10^3	-	-	1.40×10^7	
POLONIUM-209	100	y	9.28×10^1	-	-	1.06×10^8	
POLONIUM-210	138	d	2.97×10^4	8.12	8.12	1.29×10^8	
CURIUM-244	162.5	d	2.90×10^4	-	-	1.43×10^8	

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