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**MONTHLY TECHNICAL ACTIVITIES REPORT
THROUGH DECEMBER 15, 1955**

BY

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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.

Ten polonium-beryllium neutron sources and one alpha source were delivered in November. Five neutron sources and the alpha source were for other AEC sites. Two of the neutron sources were of the Mark II type, and each had a neutron emission of 2.1×10^8 neutrons per second.

An attempt to determine small concentrations of hydrogen by counting the gammas emitted in the $H(n,\gamma)D$ reaction was reported in October. By using a four inch diameter sodium iodide crystal and moderating the neutrons from a polonium-beryllium source in a graphite sphere, the sensitivity was greatly increased. However, when a neutron source with an emission of over 10^8 neutrons per second was used, the photomultiplier tube was overloaded.

Data were obtained for two samples of frit containing different concentrations of hydrogen. Curves were obtained which showed differences from each other and from a blank run in the peaks for 2.2 Mev gammas resulting from neutron capture in hydrogen. However, the difficulties in keeping the equipment operating and the uncertainties in the determination are such that much development work will be required to make this method feasible for concentrations of hydrogen in the range of 0.1 per cent.

The work on the hydrogen analysis will be brought to a close and the work on the other elements resumed to establish the relations between source size, sensitivity of equipment, and neutron absorption cross section.

Protactinium wastes continue to be processed and the alpha and beta counts from this material are well within tolerance. Data for the Waste Disposal Operations are given in Table I.

TABLE I

DISCHARGE VOLUME	609.800	GALLONS
TOTAL ALPHA ACTIVITY	3.6	MILLICURIES
TOTAL BETA ACTIVITY	58.9	MILLICURIES
ACTIVITY DENSITY		
ALPHA	2	CT/MIN/ML
BETA	28	CT/MIN/ML

DEVELOPMENT PROGRAM**IONIUM PROJECT**

The ionium project is directed towards the development and operation of a process for the extraction of ionium from partially processed raffinates from the Mallinckrodt uranium refinery. The process must produce ionium suitable for use by Los Alamos as a tracer.

Information received from Mallinckrodt Chemical Works indicates that a small amount of ionium feed solution will be available in the near future. This feed will be very dilute in thorium and ionium and will be in nitric acid solution. As soon as this sample is received an analysis of it will be made so that a simulated feed for cold work can be prepared.

Consideration has been given in the past weeks to preparation of a simulated feed material which will best serve to represent the material which will be ultimately sent to us from Mallinckrodt. This feed material will probably contain considerable scandium along with the yttrium rare earth elements. We have on order a concentrate of the yttrium rare earths containing about 80 per cent yttrium. Separation of the lanthanum rare earth elements, mostly lanthanum and cerium, from Brazilian sludge and from bastnäs site (mixed rare earth fluoride and carbonate) is under way in the laboratory. The simulated feed material will be prepared from a mixture of the rare earths from these sources mentioned with lanthanum taking the place of the scandium, and with the addition of uranium and thorium.

The new XRD-3 for analyzing for total thorium has been put in operating condition and calibration curves have been established for the glass cells with mica windows. New cells made of teflon and with polyethylene windows have been designed and constructed. These are being tested as cells to be used with "hot" solutions with the XRD-3.

The twenty channel pulse height analyzer has been received from the manufacturer and is undergoing complete testing. The Frisch alpha grid-chamber, used in conjunction with the twenty channel analyzer for ionium analysis, is not in good working condition due to leaks and a lack of necessary resolution. The manufacturer of this alpha grid-chamber has given us no satisfaction as to putting it in good working condition. As a consequence, we are handling this ourselves since time is an important factor.

Hood space is being prepared for handling solutions containing ionium. This is necessary for sampling of feed material to be obtained from Mallinckrodt and the ionium product solution which has been received from Los Alamos Scientific Laboratory. The material obtained from Los Alamos will be used as a spike for health physics and solvent extraction work, and as a means of checking our counting equipment.

The mixer settler equipment from Knolls Atomic Power Laboratory has been received. The two ten-stage banks of mixer settlers are to be placed in operating condition and are to be used as part of the process equipment to obtain the ionium Los Alamos needs by next Spring.

RESEARCH PROGRAM

FUSED SALTS RESEARCH PROJECT

The Aircraft Nuclear Propulsion Project 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.

PHASE STUDIES

The identity of a green crystalline compound reported in the September 15, 1955, report has now been established. A pure sample of the compound was obtained by utilizing differences in solubilities as follows: A slowly cooled melt from the ternary composition NaF - 40 MPC, BeF₂ - 40 MPC, and UF₄ - 20 MPC contained NaBeF₃, BeF₂ (?) and the unidentified compound. The material was finely ground, leached with warm distilled water, the precipitate was washed, and the product was dried under an infrared lamp. Microscopic examination indicated the crystalline powder to be pure and apparently free of any water of hydration. The powder was analyzed chemically and contained UF₄ - 92.31, BeF₂ - 0, NaF - 7.69 weight per cent, the last by difference. This confirms the identity of the material as the subsolidus compound NaU₂F₉, the theoretical UF₄ content of which is 93.8 weight per cent representing a purity of 98.5 per cent in the sample. The remainder was undoubtedly water present in the sample due to the method of preparation. A purer form of the compound will be made in order to obtain closer agreement. X-ray diffraction patterns of the Mound samples agree with the patterns reported for NaU₂F₉ reported by ORNL.

The positive identification (see also X-ray data) as NaU₂F₉ dispels the theory that it was a ternary compound. The area of the phase diagram designated previously as the primary phase area for the ternary compound now becomes the NaU₂F₉ primary phase area. The shape of the area must be changed to a slender segment extending across the diagram in the direction of NaU₂F₉ on the binary and separating the phase areas Na₇U₆F₃₁ and UF₄.

In addition to the above required revision, the course of the eutectic valley originating at 56.5 mole per cent UF₄ on the NaF - UF₄ binary has been changed to cross over the NaBeF₄ - UF₄ join. It then intersects the valley along the NaF - BeF₂ base line forming a peritectic near the ternary eutectic.

The composition lines previously drawn from Na₂BeF₄ to the two unstable compounds, Na₃UF₇ and Na₅U₃F₁₇, have been dropped from the diagram.

Investigations are in progress to determine the course of the eutectic valley separating the primary phase areas Na₃UF₇ and Na₂UF₈. Conflicting data for this area have made results inconclusive. However, it is likely that the valley does not intersect the Na₂BeF₄ - Na₂UF₈ join as shown on the last proposed diagram.

FILTRATION STUDIES

Referring to Table I, run No. 1, which was filtered at the temperature where liquid was noted first in the sample, locates the ternary eutectic between NaF - Na₂BeF₄ - Na₃UF₇. The sample contains about one per cent less UF₄ than had been found previously in this eutectic by filtration and agrees now more closely with DTA data.

TABLE I

LIQUIDUS COMPOSITIONS BY FILTRATION

RUN NO.	ORIGINAL COMPOSITION MOLE PER CENT			TEMPERATURE OF FILTRATION °C	COMPOSITION OF FILTRATE MOLE PER CENT		
	UF ₄	BeF ₂	NaF		UF ₄	BeF ₂	NaF
1	13.5	15.0	71.5	488	10.7	16.5	72.8
2	13.5	15.0	71.5	500	12.1	17.4	70.5
3	8.0	25.0	67.0	523	9.2	24.0	66.8
4	12.0	20.0	68.0	520	9.4	22.1	68.5
5	17.0	14.2	68.8	517	9.9	21.2	68.9
6	17.0	14.2	68.8	551	13.0	18.3	68.7
7	18.0	14.5	67.5	569	13.8	18.7	67.5
8	12.5	24.0	63.5	510	4.7	32.0	63.3
9	8.5	27.5	64.0	500	4.5	34.0	61.5
10	8.5	27.5	64.0	515	5.3	30.5	64.2
11	8.5	27.5	64.0	525	6.6	30.0	63.4
12	25.0	13.0	62.0	584	18.2	21.7	60.1
13	15.0	26.0	59.0	559	9.7	31.5	58.8
14	35.0	11.5	53.5	666	29.3	20.2	50.5

Experiments 2, 3, 4, and 5 define the valley which runs from the eutectic described above to the apparent peritectic at the intersection of the primary phase areas Na₃UF₇ - Na₂UF₆ - Na₂BeF₄ and show rather conclusively that this is a peritectic and not a eutectic point. Experiments No. 6 and 7 show how the valley between Na₃UF₇ and Na₂UF₆ leads away from the peritectic in one direction. It is doubtful that this valley can cross the composition line (connecting Na₂BeF₄ and Na₂UF₆) as shown in the diagram of November, 1955. Investigations in this area are being continued.

The valley between Na₂BeF₄ and Na₂UF₆ contains less UF₄ than had been proposed previously as shown by the results of experiments No. 8, 9, and 10. Apparently, experiment No. 11 has left this valley and is located on the Na₂UF₆ phase area. This set of experiments show that one end of this valley starts apparently at the peritectic formed by Na₂UF₆ - Na₇U₆F₃₁ - Na₂BeF₄, while the other terminates in the peritectic described in the previous paragraph. Somewhere along this line there must be a high point where compositions on one side of this high point will flow to one peritectic, and compositions on the other side of this high point will flow to the other peritectic. Investigations are being made to determine this high point.

The valley between Na₂UF₆ and Na₇U₆F₃₁ is apparently being plotted by the points in experiments No. 12 and 13. More work along this line is being done.

Experiment No. 14, which is not in any valley, indicates the temperature does not initially decrease rapidly when moving away from the compound Na₇U₆F₃₁. The location of the initial composition and filtrate composition with respect to the quasibinary indicate that

the analysis of the filtrate is probably in error by several mole per cent. Table III gives data on the errors observed in the analysis of some known samples.

PHYSICAL PROPERTIES

Eleven density and fourteen viscosity measurements were made on mixtures of sodium fluoride, beryllium fluoride, and uranium fluoride over the temperature range 550° to 900°C. Interpolated values for these properties are given in Table II for 600° and 800°C. Also a single rerun was made on the density of an equimolecular mixture of lithium fluoride and beryllium fluoride over the same temperature range.

TABLE II

DENSITIES AND VISCOSITIES OF TERNARY MIXTURES

MOLE PER CENT			600°C			800°C		
NaF	BeF ₂	UF ₄	η (Poise)	ρ (g/cc)	η/ρ (Stokes)	η (Poise)	ρ (g/cc)	η/ρ (Stokes)
52	38	10	0.0941	2.926	0.0321	0.0300	2.794	0.0107
70	20	10	0.1293	3.024	0.0427	0.0494	2.874	0.0172
76	6	18	0.1620	3.602	0.0449	0.0597	3.494	0.0171
70	15	15	0.1425	3.376	0.0422	0.0485	3.215	0.0151
76	9	15	0.1684	3.417	0.0492	0.0623	3.291	0.0189
42.5	42.5	15	0.241	3.311	0.00728	0.0548	3.184	0.0172
76	3	21		2.785			2.667	
32.5	32.5	35		-			4.380	
76	0	24		4.066			3.895	
64	24	12	0.0994	3.122	0.0318	0.0325	2.983	0.0155
46	46	8	0.1586	2.749	0.0576	0.0485	2.632	0.0184
70	24	6	0.1107	2.633	0.0420	0.0416	2.505	0.0166
58	36	6	0.0975	2.601	0.0375	0.0330	2.477	0.0133
70	26	4	0.0631	2.476	0.0255	0.0263	2.350	0.0122
46	51	3		2.733			2.634	
55.6	42.65	1.75	0.1189	2.203	0.0540	0.0424	2.095	0.0202
58	41	1		2.132			2.025	
56	43	1		2.132			2.025	
52	47	1		2.138			2.034	
46	53	1	0.177	2.115	0.0837	0.0523	2.020	0.0259
	LiF	BeF ₂						
	50	50		1.973			1.882	

ANALYTICAL METHODS

The research work in progress is aimed at establishing a definite concept as to the accuracy of the analytical procedure used for the determination of uranium and beryllium fluorides from a ternary system. Sodium fluoride is calculated by difference. Data obtained (see Table II) from a series of samples covering a wide range of ternary compositions indicates the degree of accuracy of the analytical method. Uranium was separated by electrolysis from a hot ammonium acetate solution followed by a single precipitation of beryllium as the hydroxide. The resulting uranium and beryllium salts are both ignited and weighed as the oxides.

TABLE III
ANALYSIS OF U AND Be IN 3 TERNARY COMPOSITIONS
(12-32-56, 4-32-64, AND 12-15-73 MPC UF_4 - BeF_2 - NaF)

12-32-56 Na = 63 mgm				12-32-56 Na = 63 mgm			
UF_4				BeF_2			
ADDED	FOUND	DIFF.	ERROR	ADDED	FOUND	DIFF.	ERROR
mgm	mgm	mgm	%	mgm	mgm	mgm	%
99.1	99.1	0.0	0.00	40.8	42.9	+2.1	+ 5.15
101.3	101.0	-0.3	-0.30	41.5	43.2	+2.3	+ 5.54
102.1	101.6	-0.5	-0.49	42.1	45.1	+3.0	+ 7.12
96.7	97.4	+0.7	+0.72	42.1	42.7	+0.6	+ 1.42
102.9	102.7	-0.2	-0.19	39.7	41.9	+2.2	+ 5.54
104.2	102.7	-1.5	-1.44	40.1	43.2	+3.1	+ 7.73
100.1	100.0	-0.1	-0.10	39.1	38.5	-0.6	- 1.53
101.6	101.2	-0.4	-0.39	39.6	39.9	+0.3	+ 0.78
AVERAGE		-0.3	-0.29			+1.6	+ 3.97
4-32-64 Na = 98 mgm				4-32-64 Na = 98 mgm			
46.9	46.7	-0.2	-0.43	55.9	56.6	+0.7	+ 1.25
45.1	44.8	-0.3	-0.66	57.1	58.1	+1.0	+ 1.75
45.8	45.0	-0.8	-1.74	62.9	63.2	+0.3	+ 0.48
47.5	47.7	+0.2	+0.42	56.2	56.6	+0.4	+ 0.71
49.1	49.1	0.0	0.00	55.8	58.3	+2.5	+ 4.48
48.2	48.4	+0.2	+0.41	53.7	55.5	+1.8	+ 3.35
47.5	47.2	-0.3	-0.63	56.5	58.7	+2.2	+ 3.89
52.4	52.2	-0.2	-0.38	56.7	59.4	+3.3	+ 5.82
46.6	47.5	+0.9	+1.93	55.3	55.6	+0.3	+ 0.54
46.4	46.4	0.0	0.00	54.1	57.9	+3.8	+ 7.02
AVERAGE		-0.2	-0.11			+1.6	+ 2.93
12-15-73 Na = 82 mgm				12-15-73 Na = 82 mgm			
99.1	98.7	-0.4	-0.40	17.5	19.4	+1.9	+10.85
100.5	101.2	+0.7	+0.69	19.6	19.9	+0.3	+ 1.53
100.6	99.7	-0.9	-0.89	17.8	18.2	+0.4	+ 2.25
100.2	99.5	-0.7	-0.70	18.8	21.1	+2.3	+12.23
100.6	100.4	-0.2	-0.20	17.9	18.8	+0.9	+ 5.03
101.5	100.8	-0.7	-0.69	18.7	20.1	+1.4	+ 7.49
97.2	96.8	-0.4	-0.41	17.4	18.6	+0.8	+ 4.60
101.3	100.7	-0.6	-0.59	19.5	19.9	+0.4	+ 2.05
99.3	98.9	-0.4	-0.40	21.7	23.2	+1.5	+ 6.91
99.8	100.8	+1.0	+0.99	21.8	22.4	+0.6	+ 2.75
AVERAGE		-0.3	-0.26			+1.1	+ 5.57

From the results of 28 analyses for U the average error was found to be less than -0.3 mg per sample or -0.2 per cent by weight ratio. To some extent the presence of sodium ion in the precipitating medium affects the analysis of beryllium. Error from this source ranges from -0.6 mg to +3.3 mg per sample or about +1.5 mg average in the determination of beryllium. The error due to sodium is not influenced appreciably by the weight ratio of sodium versus beryllium. The ratio of NaF to BeF₂ by weight for 12-15-73 mole fraction ternary mixture was approximately 4:1, and for 4-32-64 mole fraction mixture it was about 2:1.

Double precipitation of beryllium hydroxide should result in a purer product. Experiments are in progress to determine the extent of the reduction of contamination by sodium hydroxide when the beryllium is reprecipitated.

A total of 96 solutions were analyzed during this period for uranium and beryllium content.

X-RAY ANALYSIS. Modifications of the XRD-3 unit for X-ray diffraction work have been made to decrease sample processing time on the recorder and the spectrometer scanning unit. A new scintillation arrangement has been made. A preliminary test with Cu K_α radiation indicates excellent detectability with low background.

PROTACTINIUM SEPARATION PROJECT

A program has been undertaken to isolate and purify a gram of protactinium-231. This material is important since it will provide a relatively stable isotope to study the physical and chemical properties of the 27-day protactinium-233 which will be created in the Th-232 → Pa-233 → U-233 sequence in thorium-breeder blankets.

PROCESSING

A total of 33 drums of raffinate residue received from The Mallinckrodt Chemical Works has been concentrated at the HH-Building by the preliminary concentration process. The total weight of material processed is 14,600 pounds. On the basis of a protactinium concentration of 0.2 parts per million and seventy per cent recovery of the protactinium by the present process, a total of 0.93 grams of protactinium has been concentrated by the first concentration process.

PROCESS DEVELOPMENT

Simulated process analysis for the distribution of protactinium in the residue from the solution step, the carrier precipitate, and the waste solution from the carrier precipitation has been discontinued. A pattern has been established indicating that, in about one-half of the drums of raw material, i.e. drums numbered from 1 to 36 inclusive, a major portion of the protactinium present will be recoverable by the present process. In the latter half, the recoveries by present process would range downward to as little as ten per cent.

Work has been started on an alternate process for recovering the protactinium from the drums which cannot be efficiently treated by the present process. It is hoped that a new process can be developed before most of the available protactinium in those drums has been committed to residues or waste solutions from which its recovery may be even more difficult.

Because of the limited time available, the following course of investigation has been adopted: Since the hydrochloric acid analytical procedure (which consists of dissolving 65 to 90 per cent of the inert materials while leaving 90 to 100 per cent of the protactinium on the residue) has worked consistently when used with numerous drums of varying composition; since recovery of protactinium from these residues by digestion in sulfuric acid has been consistently good; and, since the extraction of protactinium from this sulfuric acid solution into di-isobutyl carbinol has never failed; this procedure may serve as a basis for an alternate process. Experience has shown that protactinium cannot be extracted from a sulfuric acid solution of the original raffinate residue and has shown that if pretreatment of the raw material leaves a residue which is high in sulfuric acid-soluble salts, the recovery of protactinium from the residue and its subsequent extraction into di-isobutylcarbinol is erratic. Concentrated (11.6 *N*) hydrochloric acid at elevated temperatures is considered objectionable because of inadequate plant facilities for removing fumes. Therefore, a series of experiments was carried out to determine whether other conditions would be suitable. The objective was to reduce the weight to 10 per cent of the weight of the original material while retaining 90 per cent or more of the protactinium on the residue.

Approximately five grams of raffinate residue from Drum 51 was used in all experiments. Drum 51 was selected for investigation since it appears to be typical of the raffinate which does not give satisfactory recovery of the protactinium by the present plant process. Table I gives the results.

TABLE I
PER CENT SOLUBILITY OF RAFFIDUE

CONDITIONS (SOLUTION ADDED TO 5 G SAMPLE)	RES WT/RAFF WT X 100
1. 25 ML 2 N HCl STIRRED 2 HRS. LEFT OVERNIGHT	55.3
2. SAME PLUS 2 ML 85 PER CENT H ₃ PO ₄	45.0
3. RESIDUE PLUS SUPERNATE FROM (1) PLUS 5.0 ML 10 N HCl STIRRED 15 MIN	56.0
4. RESIDUE PLUS SUPERNATE FROM (3) PLUS 2.0 ML 16 N HNO ₃ STIRRED 15 MIN	43.8
5. RESIDUE PLUS SUPERNATE FROM (4) PLUS 3.0 ML 16 N HNO ₃ STIRRED 15 MIN	29.0
6. SAME STIRRED 45 MIN	26.4
7. 20 ML 6 N HCl HEATED 1 HR AT 100°C. COOLED. RESIDUE WASHED WITH 10 ML H ₂ O	64.5
8. RESIDUE FROM (7) WASHED WITH 12 ML 2 N HCl	31.2
9. RESIDUE FROM (8) WASHED WITH 12 ML 2 N HCl	11.9
10. 10 ML 8 N HNO ₃ HEATED 1 HR AT 100°C	99.8
11. RESIDUE FROM (10) WASHED WITH 15 ML H ₂ O	15.3
12. RESIDUE FROM (1) PLUS 20 ML 6 N HCl STIRRED 50 MIN	12.1

The distribution of protactinium in the residue and supernate from each of the more promising methods of treatment was made by the usual method, which consists of digestion of residues in sulfuric acid and scavenging of supernates with titanium carrier followed by solution of the titanium precipitate in sulfuric acid. Both sulfuric acid solutions are adjusted to 6 N hydrochloric acid and extracted with di-isobutyl carbinol.

An analysis of the raffinate residue from drum 51 was first made to determine the total amount of protactinium recoverable. The drum was found to contain 0.60 of the total protactinium in drum 31 (selected arbitrarily as the standard). The residue from the concentrated hydrochloric acid treatment contains 33.5 per cent of the original weight and 95.7 per cent of the protactinium. In the first extraction, 83.1 per cent of the protactinium was recovered.

The residue from treatment with 6 N hydrochloric acid (condition 7) was found to contain 69.2 per cent of the protactinium in the sample, based on the above analysis.

The residue from treatment with 8 N HNO₃ had only 4.5 per cent of the protactinium. The supernate was treated with sodium chloride to bring about the usual carrier precipitation, but the evolution of lower oxides of nitrogen due to the aqua regia reaction constitutes an objectionable feature for a plant process, and this technique was discarded.

In a similar experiment, an attempt was made to precipitate a portion of the dissolved solids from the nitric acid solution in the hope that protactinium would be carried quantitatively. However, only about 27 per cent of the protactinium coprecipitated when the solution was partially neutralized with sodium hydroxide.

An attempt was made to bring about precipitation of protactinium on the residue with the simultaneous dissolution of most of the inert material by a combination of 4 N hydrochloric acid and sufficient sodium chloride to saturate the solution. The residue weight was 42.9 per cent of the original weight, and only 45 per cent of the protactinium was deposited on the residue.

In the light of results obtained by these exploratory experiments, it appears that the most promising attack lies along the lines previously indicated, namely, adaptation of the analytical procedure. There is little doubt that a satisfactory method can be developed which will give good recovery for drum 51 (just as a satisfactory method for drum 19 was developed). However, the severe restrictions imposed by the limitations of equipment and available time make it doubtful that it will be possible to develop a single method which is applicable to all the remaining drums.

A sample of the combined insoluble residues remaining after the digestion with 2-normal hydrochloric acid of the raffines from drums 23, 40, and 30 in the NH-Building was tested to determine the effect of further dilute hydrochloric acid treatment on these residues. The resulting solutions and residues were analyzed as follows: The residues were digested with concentrated sulfuric acid, extracted with di-isobutylcarbinol after adding hydrochloric acid, and the organic phase was counted. The solutions were heated with sodium chloride and titanium tetrachloride to precipitate the protactinium, the precipitate was digested with concentrated sulfuric acid, extracted with di-isobutylcarbinol after adding hydrochloric acid, and the organic phase was counted. The data are summarized in Table II.

TABLE II
PER CENT SOLUBILITY OF RESIDUE FROM 2 N HCl DIGESTION
(2 HOURS STIRRING)

PER CENT OF 27 KEV ACTIVITY	10 MEQ 2 N HCl/GM RES.		20 MEQ 4 N HCl/GM RES.	
	25°C	95°C	25°C	95°C
SOLUTION	10.1	10.8	1.8	6.5
RESIDUE	89.9	89.2	98.2	93.5

No further appreciable solution of protactinium in dilute hydrochloric acid was indicated. As has been indicated in previous reports, it is easily possible to precipitate the protactinium on the residue, but no further solution of bulk constituents was apparent.

ION-EXCHANGE DEVELOPMENT

SEPARATION OF PROTACTINIUM FROM FLUORIDE IN HCl-HF ION EXCHANGE COLUMN EFFLUENT. The effect of adding aluminum chloride to the HCl-HF ion exchange column effluent prior to feeding the latter onto a second column was described in the November Technical Activities Report, Central File No. 55-11-39. This additive was effective in greatly reducing the amount of protactinium breaking through in the effluent, even though the column was washed with 9 normal hydrochloric acid until no test for aluminum could be obtained. Further experiments with the aluminum chloride additive have been temporarily suspended because of the appearance on standing of a precipitate in the treated feed which carried about one-half of the activity.

Because of the known stability of the fluoborate ion, boric acid was also tried as an additive. Here again a precipitate was formed, but since it carried no activity, it was removed and the supernatant liquid was passed onto the column. Two runs with 4-centimeter deep and 1-centimeter diameter columns, in which the HCl-HF effluent was made 0.1 molar and 0.25 molar respectively in boric acid gave essentially identical results so far as the 27 kev

activity was concerned. When the boric acid was added, only 2 per cent of the feed activity appeared in the sorption and the 9-normal hydrochloric acid wash effluents as compared with 40 per cent when no additive was used. When the column was eluted with 2-normal hydrochloric acid, a very sharp elution curve was obtained. The resulting effluent contained all of the protactinium, except the 2-per cent lost in the wash, and was approximately eight times as concentrated in protactinium as the feed. This procedure thus appears attractive both for freeing the protactinium from the influence of the fluoride ion as well as for increasing the volume concentration of the product.

Since the HCl-HF protactinium fraction used in these experiments was not representative of the product which is obtainable from ion exchange columns operated under more nearly optimum conditions, it is hoped that the precipitates resulting from aluminum chloride and boric acid treatments may be avoided in future work.

SCALE-UP OF BREAKTHROUGH EXPERIMENT. The use of a more concentrated protactinium feed, still 9 normal in hydrochloric acid, in connection with a 2-centimeter deep Dowex-1 column, has been described in the November Technical Activities Report, Central File No. 55-11-39. Under these conditions essentially all of the protactinium broke through into the sorption and 9-normal hydrochloric acid wash effluents, leaving the bulk of the iron on the column. This experiment has now been scaled up sixteen-fold. In the scale-up, a 2-centimeter deep bed was again used while the bed diameter was increased from 1 to 4 centimeters. The flow rate was increased in proportion to the increase in cross-sectional area, i.e. from one-half milliliter per minute to eight milliliters per minute. Ten column volumes of feed and 5 column volumes of wash were used in each experiment.

Considering that the feeds used in the two experiments though similar were not identical, the agreement between the results was good. Allowing for the difference in column volumes of hold-up between the small and large columns, the integral breakthrough curves were nearly identical. The curve for the small column leveled off at 97.6 per cent of 27 kev activity charged, that for the large column at 99.1 per cent. The weight concentration factor for the small column was 1.31 while that for the large column was 1.27. The volume concentration factors for small and large columns were 0.66 and 0.77, respectively.

BREAKTHROUGH RECYCLE EXPERIMENT. It was thought that if the protactinium-containing effluent from the breakthrough column were recycled through a second 2-centimeter deep column, the remainder of the iron might be removed with essentially all of the protactinium again passing into the effluent. However, when this was tried with a 1-centimeter diameter column, breakthrough was much slower and less complete. In the first breakthrough operation, 99 per cent of the feed activity was recovered in fourteen column volumes of effluent, whereas in the recycle, this volume contained only 66 per cent. At nineteen column volumes the integral breakthrough curve for the recycle experiment leveled off at only 76 per cent of the charge.

BEHAVIOR OF BREAKTHROUGH COLUMN PRODUCT IN STANDARD ION EXCHANGE COLUMN PROCESS. It was desired to learn how the product of the large breakthrough column would behave when used as feed in the standard ion exchange column operation in which the protactinium is first sorbed on the resin in 9-normal hydrochloric acid and then eluted with HCl-HF solution.

The breakthrough capacity for this new feed was first determined, using a column 4 centimeters deep and 1 centimeter in diameter. The protactinium broke through at about 6 milliliters of effluent. This new feed was 60 per cent more concentrated in protactinium and 40 per cent less concentrated in total solids than the feed (F_2) which had been used in previous experiments and which had not broken through until about 34 milliliters of effluent.

In standard ion exchange process experiments with the new feed, the depth of the 1-centimeter diameter bed was increased to 8 centimeters in order to increase the breakthrough capacity. In addition, the quantity of feed was calculated at 75 per cent of breakthrough capacity which was higher than that used in previous experiments. In calculating the breakthrough capacity, the latter was assumed to be proportional to resin bed depth. After the sorption step the column was washed with five column volumes of 9-normal hydrochloric acid. In the first experiment the standard flow rate of one-half milliliter per minute was used. Only 3 per cent of the 27 kev gamma activity charged appeared in the sorption and wash effluents. In a second experiment, in which the flow rate was doubled, this loss was increased to 20 per cent. Only the latter experiment was carried through the elution stage. Fifteen column volumes of an elutriant which was 7-normal in hydrochloric acid and 0.05-normal in hydrofluoric acid was used. The remainder of the protactinium was recovered in the elution effluent. The weight concentration factor, ignoring the 20 per cent loss, was 145, and the volume concentration factor was 0.45. The overall weight concentration factor for the combined breakthrough and standard columns was 1.27×145 or 184; similarly, the overall volume concentration factor was 0.77×0.45 or 0.35.

EXPERIMENTS ON SOLUTION OF SLURRY PRODUCT FROM HH-BUILDING RUNS. Experiments are in progress to determine the proper conditions for the solution of thirty gallons of pooled slurry product from eight drums processed in the HH-Building. This product corresponds to 3550 pounds of original raffidre. Before pooling, the slurry had been hot-water washed by dilution to five volumes subsequent to the caustic treatment. The solid phase of a sample of the slurry was found to settle to 62 per cent of the total volume in 48 hours and to 55 per cent of this volume in 3 weeks. At the end of the 3-week period the supernatant liquid was syphoned off and the remainder bottled for experimental work.

The settled slurry was found to contain 0.0938 gram of dry solids per milliliter. Assuming 50 per cent moisture in the original raffidre, this corresponds to a weight concentration factor of 137 on the dry basis. The corresponding volume concentration factor was estimated to be 17.

Since the eight plant runs, which produced the slurry product, had given good protactinium yields, it was assumed that the pooled slurry product would behave similarly to the product from the drum 20 run. Samples of the slurry were therefore pre-washed with four volumes of water prior to treatment with hydrochloric acid. The solid phase settled to its original volume after the water wash. The washed slurry was then treated with three times its volume of 12-normal hydrochloric acid and stirred for 1 hour. This gave a solution approximately 9-normal in hydrochloric acid. The amount of hydrochloric acid was 36 milliequivalents per milliliter of settled slurry. Solution efficiencies were found to be unsatisfactorily low and remained so when a hot-water wash was substituted for the cold.

Table III gives the results of a balanced experiment devoted to the influence of amount of hydrochloric acid and concentration of acid on solution efficiency. To render these two factors independently variable the cold water wash had to be completely removed by centrifuging. After stirring with the acid for one hour, the phases were separated by centrifuging and counted. Table III shows the beneficial effect of reducing the amount of acid from 36 to 15 milliequivalents per milliliter of slurry. The best results were obtained when the lower amount of acid was used while keeping the concentration at 6-normal.

The beneficial effect of decreasing the amount of acid with the 9-normal concentration is further delineated in Table IV. It is hoped that with still further reduction in the amount of acid, higher solution efficiencies may be obtained with the 9-normal acid, since this normality is desired for the ion exchange column feed.

TABLE III

EFFECT OF AMOUNT AND NORMALITY OF HCl
ON PER CENT GAMMA ACTIVITY DISSOLVED*

27 KEV			300 KEV		
NORMALITY OF HCl			NORMALITY OF HCl		
MEQ/ML OF HCl	6	9	MEQ/ML OF HCl	6	9
15	89	76	15	92	84
36	23	42	36	44	52

$$*PER\ CENT\ ACTIVITY\ DISSOLVED = \frac{COUNT\ ON\ SOLUTION}{COUNT\ ON\ SOLUTION\ PLUS\ COUNT\ ON\ RESIDUE}$$

TABLE IV

EFFECT OF AMOUNT OF HCl ON PER CENT ACTIVITY DISSOLVED

MILLIEQUIVALENTS OF 9 N HCl PER ML OF SLURRY	PER CENT 27 KEV ACTIVITY DISSOLVED	PER CENT 300 KEV ACTIVITY DISSOLVED
15	76	84
25	59	70
36	42	52

ION EXCHANGE STUDY AT HIGHER ACTIVITY LEVELS. A group of effluents of unknown compositions from previous ion-exchange operations was precipitated with sodium hydroxide and centrifuged. The solids were acidified with 9-normal hydrochloric acid and were evaporated to dryness twice on a steam bath to remove hydrogen fluoride. The residue was dissolved in 9-normal hydrochloric acid for use as column feed. The column used was 1.4 centimeter in diameter. The resin bed depth was 14.5 centimeters, with a 1-centimeter solution "cushion" above the resin. The column volume was 30 milliliters. The flow rate varied from 0.25 to 0.5 millimeter per minute. During the sorption step it was necessary to apply vacuum (aspirator) on the discharge side of the column to maintain flow. After the feed solution and the column volume of wash solution had been passed, vacuum was no longer needed. The protactinium was eluted with a solution 7-normal in hydrochloric acid and 0.1-normal in hydrofluoric acid. The column has not yet been stripped of iron, etc. Data thus far are summarized in Table V

As indicated in Table V, over 95 per cent of the protactinium was recovered in about 30 per cent of the feed solution volume.

TABLE V

DISTRIBUTION OF PROTACTINIUM IN RECYCLED HCl-HF SOLUTIONS

FRACTION	VOLUME IN ml	TOTAL c/m at 27 Kev	% of Feed
FEED SOLUTION	191.5	3,393.000	100
SORPTION PLUS WASH EFFLUENT	222.5	9.300	0.3
95% Pa EFFLUENT	61.0	3,245.600	95.7
BALANCE OF EFFLUENT	130.5	48.700	1.4
NOT ACCOUNTED	-	89.400	2.6

SOLVENT EXTRACTION DEVELOPMENT

Since the concentration of protactinium by solvent extraction techniques appears to be promising, additional experiments with the HH-Building products from various drums have been carried out.

A quantity of slurry obtained by the processing of drum 20 in the HH-Building was centrifuged and washed with a volume of water equal to the volume of liquor removed. After each washing, the solids were precipitated by centrifuging. A total of six washings was carried out. Four samples of 10 grams each of the wet solids were each mixed with 20 milliliters of concentrated hydrochloric acid, and were heated with intermittent stirring for one-half hour in a hot water bath at 95°C. The insoluble material was removed by centrifuging. In each case the volume of the liquid decanted from the solids was 24 milliliters. Each solution was mixed vigorously for fifteen minutes with 10 milliliters of a mixture of equal volumes of di-isobutylcarbinol and Amsco kerosene which had been previously saturated with six molar hydrochloric acid. After mixing, the two phases were separated, the organic layer was removed, and the aqueous solution was mixed again with 10 milliliters of fresh di-isobutylcarbinol - Amsco solution. The aqueous liquor was counted before and after each extraction at 27, 68, 90, and 300 kev levels with the gamma pulse-height counter. Table VI shows that substantially all the protactinium is removed from the HCl solution by two di-isobutylcarbinol extractions.

TABLE VI

DI-ISOBUTYLCARBINOL EXTRACTION OF PROTACTINIUM
(PER CENT ACTIVITY REMAINING IN AQUEOUS PHASE)

KEV	1ST EXTRACTION	2ND EXTRACTION
27	9.1	2.3
68	25.0	20.7
90	13.9	11.3
300	8.6	3.9

The effect of the concentration of hydrochloric acid in the aqueous liquid on the effectiveness of the extraction by di-isobutylcarbinol - Amsco kerosene was investigated. Six systems were prepared as described. Two solutions were extracted directly, the hydrochloric acid solutions were assumed to be six molar after heating the system for one-half hour. Two solutions were mixed with one-half volume of water to reduce the hydrochloric acid concentration to approximately four molar. Two solutions were mixed with one half the volume of concentrated hydrochloric acid to increase the hydrochloric acid concentration to approximately 8 molar. The aqueous liquor was extracted twice with 10 milliliters of the di-isobutylcarbinol - Amsco kerosene solution, and was counted before and after each extraction. The average results for the duplicate runs are given in Table VII. The values for the 27 kev level in excess of 100 per cent may be attributed to the removal of absorptive material by the extracting solvent. The data show that the HCl concentration must exceed four molar for extraction of protactinium to occur.

TABLE VII
EFFECT OF ACID CONCENTRATION OF EXTRACTION ON
PROTACTINIUM WITH DI-ISOBUTYLCARBINOL

KEY	PER CENT PROTACTINIUM REMAINING					
	4 M HCl		6 M HCl		8 M HCl	
	1ST EXTRACTION	2ND EXTRACTION	1ST EXTRACTION	2ND EXTRACTION	1ST EXTRACTION	2ND EXTRACTION
27	123.8	122.1	15.2	3.5	4.0	2.0
68	94.5	94.3	36.8	23.8	22.9	22.0
90	102.4	101.6	31.4	13.2	10.6	7.5
300	94.6	94.1	14.5	4.0	4.3	2.9

The effect of the hydrogen ion concentration of the aqueous hydrogen peroxide used to extract the protactinium from the di-isobutylcarbinol - Amsco kerosene mixture was investigated

All the organic fractions obtained in the previous experiment were combined and divided into four equal fractions of 20 milliliters each. The first fraction was extracted twice with 10 milliliters of 10 per cent hydrogen peroxide. The second fraction was extracted twice with 10 milliliters of 10 per cent hydrogen peroxide which was one-molar in hydrochloric acid. The third fraction was extracted twice with 10 milliliters of 10 per cent hydrogen peroxide which was one-half molar in hydrochloric acid. The fourth fraction was extracted twice with 10 milliliters of 10 per cent hydrogen peroxide which was one-half molar in sodium hydroxide. The acidified peroxide gave slightly poorer results than the neutral hydrogen peroxide whereas the basic hydrogen peroxide gave slightly better results. However, the greatest amount remaining was only one per cent in any case.

Since iron in solution as ferric chloride was readily extracted from the acid solution by the di-isobutylcarbinol - Amsco kerosene mixture and since the effectiveness of isopropyl ether to extract ferric chloride is known, a series of investigations were made to determine whether protactinium would be extracted by isopropyl ether. The slurry from drums 23 and 40

A series of experiments were carried out on unwashed settled slurry from the processing of drums 23 and 40 using the conditions judged best from the results given in Table VIII. One volume of slurry was digested with two volumes of concentrated hydrochloric acid with stirring for fifteen minutes in a hot water bath at 95°C. After cooling to room temperature, the undigested solids were removed by centrifuging and decanting the liquid. The liquid was stirred vigorously for 10 minutes with one-half its volume of isopropyl ether, which had been previously saturated with 7.75 molar hydrochloric acid. After separation of the ether from the aqueous phase eight samples of the aqueous liquor were each stirred vigorously for 15 minutes with one-half of its volume of a mixture of di-isobutylcarbinol and Amsco kerosene which had been previously saturated with six molar hydrochloric acid. The aqueous phases of two of these extractions were extracted a second time with the di-isobutylcarbinol - Amsco mixture. After the organic phases were separated from the aqueous phases, they were combined. Two samples from the organic phase were extracted with an equal volume of 10 per cent hydrogen peroxide. Two samples were extracted with one-half their volume of ten per cent hydrogen peroxide, followed by a second extraction with one-half their volume of ten per cent hydrogen peroxide. Two other samples were extracted with ten per cent hydrogen peroxide which was 0.3 normal in ammonium hydroxide. The solutions were gamma counted in each case before and after extraction. The data are summarized in Table IX.

TABLE IX

PROTACTINIUM LOSSES IN SOLVENT EXTRACTION PROCESS

KEV	PER CENT OF ACTIVITY REMOVED BY ISOPROPYL ETHER EXTRACTION OF FERRIC CHLORIDE	PER CENT OF ACTIVITY REMAINING IN AQUEOUS PHASE AFTER EXTRACTION WITH DI-ISOBUTYL CARBINOL-AMSCO MIXTURE	PER CENT OF ACTIVITY REMAINING IN AQUEOUS PHASE AFTER SECOND EXTRACTION WITH DI-ISOBUTYL CARBINOL MIXTURE
27	2.95	8.8	4.0
68	1.52	66.8	60.5
90	2.60	25.6	20.6
300	3.84	8.2	3.8

	PER CENT OF ACTIVITY REMAINING IN ORGANIC PHASE AFTER EXTRACTION WITH H ₂ O ₂	PER CENT OF ACTIVITY REMAINING IN ORGANIC PHASE AFTER EXTRACTION WITH H ₂ O ₂ -0.3 N NH ₄ OH
27	0.26	0.23
68	0.26	0.30
90	0.28	0.12
300	0.28	0.19

Extraction of the protactinium from the di-isobutylcarbinol mixture with one-half the volume of ten per cent hydrogen peroxide gave results similar to the data in Table IX and were therefore not included in the table.

The final solutions of hydrogen peroxide were evaporated to dryness in weighed crucibles. The weight concentration factor obtained was 312. The volume concentration factor was four. The hydrogen peroxide extractants containing 0.3 molar ammonium hydroxide were also evaporated to dryness in weighed crucibles. The weight concentration factor was 16.2 with the same volume concentration factor of four. The lower weight concentration factor was obtained because the ammonium salts were not expelled by ignition.

It was desired to determine the effect of variations in phase volume ratios on the efficiency of the extraction procedures. For this investigation, the slurry product from drum 36 was employed as starting material. Subsequent to the caustic wash in HH-Building, this slurry had a double hot-water wash (4 volumes of water to one of slurry) instead of the customary single wash. After settling and decantation of the supernate, a portion of the slurry was stirred for one-half hour with twice its volume of concentrated hydrochloric acid. After cooling, samples of the resulting mixture were stirred with isopropyl ether for 15 minutes. After phase separation, the aqueous layer was stirred with di-isobutylcarbinol - Ansco mixture for one-half hour. The phases were again separated and the organic layer stirred for fifteen minutes with ten per cent aqueous hydrogen peroxide. After final phase separation, the aqueous layer was warmed to decompose excess hydrogen peroxide. All liquid phases were counted without removal of any insoluble materials which formed in the various steps. Aliquots of the initial slurry and the final aqueous phases were evaporated and weighed to determine overall weight concentration factors.

Table X shows the effect of the variations in phase volume ratios on the activity losses in each of the three stages and on the overall volume and weight concentration factors. Evidently, no losses occurred in the initial ether extraction since the results of Runs 2 and 7 appear to be spurious for this stage. Activity losses in the di-isobutylcarbinol extraction average about 5 per cent and appear to be independent of the variations in the volume ratios. Losses in the final peroxide extraction were again very small. Neglecting the multiple extraction experiment number 5, a higher ratio of isopropyl ether to slurry yields a higher concentration factor.

TABLE X
EFFECT OF VOLUME RATIOS ON ACTIVITY LOSS
AND ON CONCENTRATION FACTORS

RUN NO.		3	4	1	5	2	6	7
VOLUME RATIO ISOPROPYL ETHER TO SLURRY		0.3	0.3	0.3	0.4*	0.5	0.8	0.8
VOLUME RATIO DI-ISOBUTYL CARBINOL TO SLURRY		0.5	0.5	0.5	0.2	0.5	0.2	0.2
VOLUME RATIO DI-ISOBUTYL CARBINOL TO 10% H ₂ O ₂ SOLUTION		0.2	0.1	0.2	0.5	0.2	0.3	0.3
	KEY							
PER CENT OF ACTIVITY REMOVED BY ISOPROPYL ETHER	27	0.0	0.0	0.0	0.0	5.0	0.0	8.6
	68	0.0	1.5	0.7	0.0	6.3	1.8	8.3
	90	0.0	1.3	2.3	0.0	7.2	1.3	7.5
	300	0.0	0.0	0.0	0.0	8.0	0.0	13.5
PER CENT OF ACTIVITY REMAINING IN AQUEOUS PHASE AFTER DI-ISOBUTYL CARBINOL EXTRACTION	27	6.2	6.2	6.5	5.6	4.7	5.5	5.6
	68	54.5	55.7	45.0	53.5	46.7	51.4	57.3
	90	18.2	18.5	21.4	18.7	20.2	18.8	19.2
	300	5.7	5.4	6.0	4.9	5.0	6.0	6.5
PER CENT OF ACTIVITY REMAINING IN DI-ISOBUTYL CARBINOL AFTER H ₂ O ₂ EXTRACTION	27	0.02	0.12	0.15	0.02	0.09	0.04	0.02
	68	0.02	0.04	0.09	0.0	0.03	0.0	0.00
	90	0.10	0.10	0.23	0.04	0.10	0.01	0.02
	300	0.10	0.09	0.10	0.0	0.01	0.01	0.01
VOLUME CONCENTRATION FACTOR		10	10	5	20	5	17	17
WEIGHT CONCENTRATION FACTOR		76	95	103	417	224	401	395

*1 LITER OF SLURRY WAS EXTRACTED WITH FOUR SUCCESSIVE 100 ML PORTIONS OF ISOPROPYL ETHER