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MONSANTO CHEMICAL COMPANY
MIAMISBURG, OHIO

MONTHLY TECHNICAL ACTIVITIES REPORT
THROUGH NOVEMBER 15, 1955 DELETED VERSION

BY

J. F. Eichelberger, F. C. Mead, Jr., and D. L. Scott

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PRODUCTION PROGRAM

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

Thirteen polonium-beryllium neutron sources and four alpha sources were shipped in October. Six of the neutron sources were for other AEC sites. One replacement was made for an alpha source shipped in September. It was found that stainless steel windows were not hole-free when less than 0.00008 inch thick. Better methods of examining alpha windows and assembling sources have been developed.

No difficulties were noted in processing the protactinium waste from the HH-Building Data for the Waste Disposal Operations are given in Table I.

TABLE I

DISCHARGE VOLUME	484,000	GALLONS
TOTAL ALPHA ACTIVITY	3.3	MILLICURIES
TOTAL BETA ACTIVITY	36.5	MILLICURIES
ACTIVITY DENSITY		
ALPHA	2	CT/MIN/ML
BETA	22	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.

It was thought that in order to facilitate our part of the program, it would be desirable for Mound to receive the material for next spring in some other form than the fluoride, due to the difficulty involved with the fluoride. It was tentatively decided that Mallinckrodt would furnish the ionium to us in a weak nitric acid solution containing, among other things, some scandium, uranium, and rare earths; and that the material would start coming from them around February 1, 1956.

We plan to carry out the inital in the hoods in which the hot development (pilot plant) work will ultimately be carried out. The actual solvent extraction work will be carried out with two ten-stage mixer-settlers which will be obtained from Knolls Atomic Power Laboratory.

Consideration is being given to the process equipment for the pilot plant and to equipment for instrumental analysis. We have a considerable number of samples from preliminary analysis. We have a considerable number of samples from preliminary simulated feed laboratory scale extraction runs made with the miniature mixer-settler and batch countercurrent equipment. These samples will be run for thorium and uranium by X-ray fluorescence as soon as the XRD-3 is calibrated and placed in reliable working condition. Laboratory test runs have been made to determine the type of centrifuges which will be needed with the pilot plant.

Although it has been tentatively agreed that Mallinckrodt will initial supply us with a weak nitric acid solution, the type of material to be supplied us for the pilot plant has not been settled. This will depend upon further work by both Mallinckrodt and Mound, plus certain decisions from the AEC concerning their interest in other values in the raffinate, such as the scandium and rare earths

REACTOR 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 ternary compound found in samples investigated along the $NaBeF_3$ - UF_4 join is either orthorhombic or monoclinic with a β angle slightly greater than 90° Continued difficulties in attaining equilibrium conditions in this area have hindered efforts to locate the composition point of the ternary compound. However one sample in which near-equilibrium was attained indicated that the composition probably is greater than 30 mole percent UF_4. Samples investigated along the same join at less than 20 mole percent UF_4 have been worthless because of repeated change in effective composition. This nonequilibrium condition is probably the result of UF_4 having a higher affinity for reaction with NaF than does BeF_2.

The location of the ternary peritectic surrounded by the primary phase areas Na_2BeF_4, Na_3UF_7 and Na_2UF_6 was revised slightly to locate it outside the Na_2BeF_4 - Na_2UF_6 - $Na_5U_3F_{17}$ composition triangle. This seemed necessary when a sample on the Na_2BeF_4 - Na_2UF_6 composition line was found, both by DTA and petrographic results, to flow past the peritectic to the ternary eutectic.

Differential Thermal Analysis has obtained two differing temperatures, an accepted value of 483°C and a second value of 476°C, for the ternary eutectic occurring in the primary phase areas NaF, Na_3UF_7 and Na_2BeF_4. The 483°C eutectic temperature had been found for compositions made from low melting compounds and/or mixtures of xNaF - yUF_4 and xNaF - $yBeF_2$ - zUF_4 which had been purified in the molten state. The 476°C eutectic temperature was obtained from compositions made directly from the individually purified salts BeF_2, NaF, and UF_4, the latter two being purified in the solid state because of their high melting points, 1040°C and 995°C respectively. (It is felt that the purification apparatus cannot withstand a temperature above 900°C.) This had indicated that the impurities in the UF_4 and/or NaF were not removed during the purification of the solid salt. Furthermore, when a composition giving a 476°C ternary eutectic temperature is given a purification treatment at a temperature considerably above its liquidus, the eutectic temperature changes to the accepted value of 483°C. It has been noted also that the HF and H_2 purification of UF_4 as a solid at 900°C does not convert the small UO_2 content to UF_4. Hence, complete purification can be achieved only when the individual salts UF_4, BeF_2 and NaF, or their mixtures, are treated in the molten state with HF and H_2. Since the impurity is present in extremely small traces its identity will be difficult to determine. The impurity effect upon earlier liquidus data is being investigated, but indications show that the liquidus was unaffected.

A preliminary summary of the phase studies has been issued in Mound Laboratory Report Central File No. 55-11-14.

FILTRATION STUDIES

The data for the filtration studies for which analyses are complete are summarized in Table I.

Sample No. 1 is important since it locates the ternary eutectic between $Na_7U_6F_{31}$ - $NaBeF_3$ - Na_2BeF_4 which is probably the lowest liquidus temperature on the diagram. The temperature of this eutectic has been found by DTA to be slightly under 350°C, but a filtration could not be made at that temperature since the liquid was very viscous. Consequently, the composition of the eutectic may be slightly different than was found in sample 1, and the eutectic probably contains even less UF_4.

TABLE I

LIQUIDUS COMPOSITIONS BY FILTRATION

NO	STARTING 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	5	40	55	380	1.1	42.9	56.0
2	5	28	67	529	8.4	24.5	67.1
3	12	20	68	541	10.4	22.0	67.6
4	2	32	66	575	2.4	32.0	65.6
5	2	32	66	556	3.8	29.4	66.8

Sample 2 which lies practically on top of some previously reported samples, adds further evidence to the assumption that the eutectic (or peritectic) for Na_3UF_7 - Na_2UF_8 - Na_2BeF_4 occurs in this area. Sample 3 indicates the start of the valley away from the eutectic.

No valley is traced by samples 4 and 5, but they show how rapidly the liquidus temperature is decreased in moving away from the compound Na_2BeF_4.

A preliminary summary of the filtration studies has been issued in Mound Laboratory Report, Central File No. 55-11-14.

PHYSICAL PROPERTIES

DENSITY AND VISCOSITY. The density determinations of the ternary mixture sodium fluoride - beryllium fluoride - uranium fluoride, in the compositions bounded by 0-12 mole percent uranium fluoride, and 76 - 42 mole percent sodium fluoride have been completed from 900° to 500°C at 2 mole percent intervals, of UF_4 and 6 mole percent NaF. The curves have been evaluated and necessary reruns have been made. In addition, two runs have been made on the binary, lithium fluoride - beryllium fluoride, over the same temperature range.

Viscosity determinations of the ternary mixtures have been made over the same area of compositions as for the density. These data are now being evaluated. Density and viscosity values are given at 600° and 800°C in Table II. A preliminary summary of density and viscosity values of the NaF - BeF_2 - UF_4 ternary in the temperature range of 500° to 900°C has been issued in Mound Laboratory Report, Central File No. 55-11-14.

TABLE II

VISCOSITY, DENSITY, AND DYNAMIC VISCOSITY OF NaF-BeF_2-UF_4 TERNARY MIXTURES

MOLE PER CENT			600°C			800°C		
NaF	BeF_2	UF_4	η Poise	ρ gm/cm^3	η/ρ Stokes	η Poise	ρ gm/cm^3	η/ρ Stokes
64	24	12		3.122			2.983	
58	30	12		3.117			2.986	
52	38	10		2.926			2.794	
64	30	6		2.604			2.481	
46	48	6	0.2230	2.579	0.0865	0.0468	2.441	0.0192
58	38	4	0.0972	2.443	0.0398	0.0342	2.313	0.0148
52	44	4	0.1284	2.397	0.0536	0.0431	2.279	0.0189
46	50	4	0.1647	2.381	0.0692	0.0440	2.275	0.0193
76	22	2		SOLID		0.0261	2.152	0.0121
70	28	2	0.0629	2.249	0.0280	0.0226	2.144	0.0105
64	34	2	0.0740	2.254	0.0328	0.0310	2.144	0.0145
58	40	2	0.0970	2.227	0.0436	0.0342	2.118	0.0161
52	46	2	0.1284	2.211	0.0580	0.0431	2.104	0.0201
46	52	2	0.1647	2.181	0.0755	0.0440	2.082	0.0211
55.6	42.65	1.75		2.203			2.095	
LiF	BeF_2							
62.7	37.3		0.0864	1.923	0.0449	0.0341	1.857	0.0184
56.8	43.2		0.1339	1.988	0.0673	0.0456	1.886	0.0242

DESIGN OF A MULTIPURPOSE CALORIMETER TO OPERATE BETWEEN -183° AND $900^\circ C$

It has been the aim of the calorimetry group through the years to design versatile calorimeters, even ~~though the assaying of~~ radioactive materials was the primary objective. As a consequence our existing calorimeters are capable of assaying a wide range of radioactive samples both in power level and physical size and are equally well suited for measuring specific heats of materials and transient calories, such as heats of chemical reactions. The latter applications are essentially limited to room temperature measurements, however. This limitation is primarily imposed by materials of construction, and secondarily by the water baths. The design of a calorimeter to operate at high temperatures is then only a matter of changing the present design in a manner imposed by materials that will be stable at high temperatures and of eliminating the water baths.

So far, the materials of construction chosen are platinum for bridges and heaters, Sauereisen Cement for insulation, and nickel for all other parts. As for the bath, it seems possible that it may be eliminated entirely. Essentially all that a bath does is keep the jackets of the calorimeters at a constant and uniform temperature. With two arms of a temperature bridge and a heater both uniformly wound along the jacket, it seems probable that the jacket can be maintained at a uniform and constant temperature by means of the same temperature controller that is now employed with out water baths. To obtain some idea of how well this might be accomplished, the controller was connected to the bridge and one heater of calorimeter 58. The bridge was maintained $1^\circ C$ above the jackets with the controlled heat to within ± $.001^\circ C$. Control was tenacious as evidenced by removing sample cans from the calorimeter, taking the calorimeter from the bath, and touching the jackets - all without losing control. If the jacket of a high temperature calorimeter can be satisfactorily controlled in this manner it would be equivalent to having, as would appear to calories originating within the calorimeter, an infinite heat sink, with a short time constant in going from one controlled temperature to another. This arrangement would enable one to enclose the calorimeter in any suitable environment such as liquid nitrogen, room air, baths, or furnaces, and operation would be possible so long as these environments were constant to $1^\circ C$ or better. Since a Foxboro controlled Leeds and Northrup furnace is available, it will probably be used as the high temperature environment for the calorimeter. A five-gallon stainless steel dewar could be used with liquid nitrogen for low temperatures, if any low-temperature measurements are needed.

An interesting result of using nickel throughout as the material of construction is that the "air-gap" is readily accessible and can be filled with practically any material. This would permit measuring conductivities of liquids, solids, and gases, in addition to the advantage of being able to control the speed and sensitivity of the calorimeter by the proper choice of gradient medium.

Such a calorimeter would be more versatile than our present calorimeters even at room temperatures, however its accuracy and precision would be somewhat less, but an order of magnitude less would be acceptable.

ANALYTICAL METHODS

Work has been started to determine the accuracy of the analytical procedure in use for the analysis of UF_4 - BeF_2 - NaF ternary fused-salt system.

In the electrolytic determination of uranium from weighed samples of purified UF_4 a total of ten determinations were made. An average yield of 99.8% of uranium as an oxide was recovered from solution with a probable error of ± 0.2%. In all cases, a negative uranium test was obtained by the addition of ammonium hydroxide to the plating solution following electrolysis, indicating complete plating of the uranium from the solution.

Forty-five solutions were analyzed. This includes both analytical research and routine samples.

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 20 drums of raffinate residue received from the Mallinckrodt Chemical Company have been concentrated at the HH-Building by the preliminary concentration process. A schedule of between three and four drums a week is being maintained.

The arrangement originally installed for charging the salt to the heated Pfaudler kettle to effect the precipitation of the carrier proved to be entirely unsatisfactory. Arrangements have been completed to hoist the unopened bags of salt to the platform level with the manhole at the top of the Pfaudler kettle. The salt is now charged directly into the kettle from the original shipping bags.

In some drums, (e.g. drum 35) where the percentage of protactinium left in the residue was low but where a significant percentage of the protactinium could be expected to be lost in the waste solution, the recommendation was made that titanium carrier be added before the precipitation was carried out. Unfortunately, time did not permit development of this innovation on a laboratory scale, but preliminary results obtained on the plant scale indicate that this treatment was effective. The amount of added titanium recommended was about one-half that used in the analytical procedure, or about 0.4 milligram of titanium (as titanium trichloride) per gram of raffinate residue. The titanium is added as titanium trichloride in the initial process step, i.e., along with the hydrochloric acid. The titanium (III) is oxidized to titanium (IV) which forms a carrier precipitate during the second process step in which the solution is heated to boiling temperatures and the total carrier is salted out.

Simulated process analysis of the Mallinckrodt raffinate residue on a drum-by-drum basis is continuing. Of the eighty drums of material received, twenty-three drums have been analyzed by the method described in last month's report. The result are reported in Table I.

EXPLANATION OF TABLE I

RESIDUE WEIGHT PER CENT. The residue weight was not obtained in the first fifteen samples analyzed. Previous experience had not indicated any significant variability in the degree of solution of the raffinate residue from the various drums. However, when it became apparent from visual observation that such variability did exist and that it was connected with relatively large losses of protactinium, this additional step was incorporated in the procedure. The residue is weighed in the wet condition after centrifugation in a 50-milliliter centrifuge cone at 1500 rpm for five minutes.

$$\text{Residue weight per cent} = \frac{\text{wet residue weight}}{\text{weight of sample}} \times 100$$

PER CENT PROTACTINIUM IN RESIDUE, CARRIER, AND WASTE SOLUTION. Each of the fractions obtained is digested with two milliliters of hot concentrated sulfuric acid, cooled and made 9 normal in sulfuric acid and 6 normal in hydrochloric acid. It is extracted with two four-milliliter portions of a one-to-one mixture of di-isobutyl carbinol and Amsco kerosene presaturated with 6 normal hydrochloric acid. The organic phase is counted in each case at 27 and at 300 kev. The sum of the counts at both energies in all fractions of each sample is taken as representing the total protactinium in the sample, and, since the samples are run in duplicate, the average percentage of each fraction is reported Satisfactory agreement has been found between the counts at 27 and 300 kev, and between duplicate samples from the same drum.

RELATIVE TOTAL PROTACTINIUM. The average sum of the counts at 300 kev for each sample is expressed as counts per minute per gram and related to the counting rate per gram in drum 31 (arbitrarily taken as a standard). Correction is made for differences in the counting rate of a standard sample.

Values marked with an asterisk (*) are doubtful, chiefly because the residues were unusually large. In all such cases there is some question as to whether all the protactinium in the residue was recovered in the analysis, despite the fact that the residue, after extraction, is digested a second time with fresh concentrated sulfuric acid and reextracted.

RELATIVE RECOVERABLE PROTACTINIUM. The percentage values given under "Per cent Protactinium in Carrier" are misleading particularly in those cases where the residue weight was high. A more accurate picture of the amount of protactinium recoverable in the present process is obtained if the percentage value is multiplied by the value for "Relative Total Protactinium". This product is reported in the last column.

TABLE I

ANALYSIS OF RAFFINATE RESIDUES

DRUM NO.	RESIDUE WT. %	PER CENT PROTACTINIUM IN:			RELATIVE PROTACTINIUM	
		RESIDUE	CARRIER	WASTE SOLN.	TOTAL	RECOVERABLE
9	9.1	4.0	51.5	45.0	0.32	0.16
13	6.8	3.8	42.4	53.8	0.71	0.30
20	-	3.2	84.2	12.6	0.82	0.69
24	-	7.3	67.2	25.5	0.82	0.55
25	-	9.5	71.2	19.3	0.69	0.49
27	-	15.3	67.7	17.0	1.09	0.74
28	-	32.3	51.9	15.8	0.88	0.46
29	-	38.1	46.0	15.9	0.97	0.45
30	-	24.5	63.3	12.2	1.07	0.68
31	-	8.4	75.4	16.2	1.00	0.75
32	-	3.9	71.4	24.7	0.93	0.66
33	-	3.4	73.7	22.9	1.03	0.76
34	-	2.4	81.5	16.1	1.29	1.05
35	9.3	2.7	65.3	32.0	1.16	0.76
39	57.5	33.2	63.9	2.9	0.75*	0.48
42	28.9	16.7	67.3	16.3	0.74*	0.50
43	10.6	16.9	47.0	36.1	0.85	0.40
49	65.4	67.7	13.6	18.7	0.16*	0.02
51	-	88.3	6.3	5.4	0.26*	0.02
55	-	40.0	56.4	3.6	0.29*	0.16
56	42.8	36.4	59.6	4.1	0.26*	0.15
59	-	78.9	13.4	7.7	0.35*	0.05
75	-	34.4	60.9	4.7	0.31*	0.19

*VALUES ARE DOUBTFUL

[redacted]

ION EXCHANGE DEVELOPMENT

EFFECT OF CONCENTRATION OF HYDROCHLORIC ACID AND HYDROFLUORIC ACID IN ELUTRIANT. Experiments with one-centimeter-diameter columns filled with anion resin, Dowex-1, have continued. Six runs with varying concentrations of hydrochloric acid and hydrofluoric acid in the elutriant were carried out. The resin bed depth was fixed at 4 centimeters and the feed rate at 0.4 milliliter per minute per square centimeter of column. The feed (F_2) was prepared by dissolving one volume of slurry product, from drum 20 run at the HH-Building, in three volumes of 12 normal hydrochloric acid. In the sorption step, 16 milliliters of this feed, corresponding to about 50% of breakthrough capacity, was fed to the column. After the feed solution had been passed through the column, the column was washed with five column volumes (16 milliliters) of 9 normal hydrochloric acid; next it was eluted with 15 column volumes (48 milliliters) of the designated elutriant; and then it was stripped with 10 column volumes (32 milliliters) of 1 normal hydrochloric acid.

The volume of the elution effluent fraction which contained 95% of the 27 kev activity associated with protactinium was noted. This fraction was evaporated to dryness and the resultant residue was weighed. The effect of hydrochloric acid concentration and of hydrofluoric acid concentration in the elutriant on the weight concentration factors and on the volume concentration factors for the 95% fractions is shown in Table II.

TABLE II

EFFECT OF ELUTRIANT COMPOSITION

	CONCENTRATION FACTOR			
	WEIGHT		VOLUME	
HF	0.05 *N*	0.10 *N*	0.05 *N*	0.10 *N*
HCl				
5 *N*	66	39*	2.00	1.33*
7 *N*	62	33	1.52	1.14
9 *N*	30	44	0.62	1.07

*BASED ON 90% FRACTION

In general, both weight and volume concentration factors were increased by decreasing the hydrochloric acid concentration. Decreasing the hydrofluoric concentration was also generally beneficial. The run with 9 normal hydrochloric acid and 0.10 normal hydrofluoric acid gave results which may be anomalous.

The various effluents from the two runs with 7 normal hydrochloric acid were evaporated and weighed to determine how the dry solutes were distributed among the different fractions. The results are shown in Table III. About 70 per cent of the solute impurities were not absorbed on the resin from the sorption plus wash effluents. These impurities are salts of cations which were not sorbed on the column in the presence of the high chloride concentration. These resultant solids may consist largely of sodium introduced into the plant process. About 25 percent of the solutes appeared in the one normal hydrochloric acid strip solution. This residue was reddish brown, indicating mainly iron. Three to five per cent of the

U N C [redacted]

TABLE III

DISTRIBUTION OF DRY SOLUTES IN EFFLUENTS

ELUTRIANT: 7N HCl + 0.05N HF

	Weight of Residue (gm)	Per cent of Total
Sorption plus wash fraction	0.3255	71.2
Fraction containing 95% of protactinium	0.0073	1.6
Remainder of elution effluent fraction	0.0126	2.75
Strip fraction	0.1120	24.5
ELUTRIANT: 7N HCl plus 0.10N HF		
Sorption plus wash fraction	0.3180	67.5
Fraction containing 95% of protactinium	0.0136	2.9
Remainder of elution effluent fraction	0.0216	4.6
Strip fraction	0.1177	25.0

[redacted]

non-protactinium solutes are eluted, after the 95 per cent protactinium fraction, by the hydrochloric acid - hydrofluoric acid elutriant.

EXPERIMENTS WITH PROTACTINIUM BREAKTHROUGH. By decreasing the bed depth or by increasing the feed concentration, greater and greater percentages of protactinium may be caused to appear in the feed and wash effluents without the use of a hydrochloric acid - hydrofluoric acid elutriant. By pre-washing "Drum 20 run" slurry before solution in hydrochloric acid, it was possible to prepare a 9 normal hydrochloric acid feed which was twice as concentrated in protactinium as that which was used in the previous experiments. Sixteen milliliters of this feed was used in runs with bed depths varying from 2 centimeters to 6 centimeters. In each case, the column was washed with five column volumes of 9 normal hydrochloric acid. The results of the runs are shown in Table IV.

TABLE IV

EFFECT OF BED DEPTH ON Pa BREAKTHROUGH

BED DEPTH (cm)	PER CENT 27 KEV ACTIVITY IN FIRST 20 ML OF EFFLUENT	MAXIMUM PER CENT OF 27 KEV ACTIVITY BREAKING THROUGH
2	97.5	97.5
3	87.5	90.0
4	83.0	85.0
6	63.0	69.0

Evaporation of the effluents indicated that about 25 percent of the solutes were left behind on the column in these experiments. Since the effluents were colorless and the column was reddish brown, and since iron has a greater affinity for the resin than protactinium, it seems likely that iron is the principal constitutent removed by the breakthrough procedure. This procedure is being considered as a method of pre-treating the feed prior to its sorption on a second column, followed by elution with the mixed hydrochloric acid - hydrofluoric acid elutriant.

RELEASE OF PROTACTINIUM IN HYDROCHLORIC ACID - HYDROFLUORIC ACID EFFLUENT. The protactinium is presumably present in the hydrochloric acid - hydrofluoric acid elution effluent as a stable fluoride complex The presence of the fluoride would be expected to suppress many of the characteristic reactions of the protactinium and would also render the element unsorbable by Dowex-1 resin in the event that further purification by ion exchange was contemplated.

Experiments are in progress to determine whether or not the addition of aluminum ion to the hydrochloric acid - hydrofluoric acid elution effluent will render the protactinium resorbable by Dowex-1. Thirty-two milliliters of such an effluent being 9 normal in hydrochloric acid and 0.1 normal in hydrofluoric acid was fed through a four centimeter column and was washed with 40 milliliters of 9 normal hydrochloric acid. The experiment was then repeated after first making the feed approximately one-half molar in aluminum chloride. The first forty milliliters of the effluent from the control run contained 37 per cent of the 27 kev activity whereas, for the run utilizing the aluminum-treated feed, the breakthrough was only 4 per cent. The final breakthrough was 40 percent for the control run and five per cent for the aluminum-treated run. Since the results are promising, the experiments are being continued.

BATCH PROCESS INVESTIGATION. Three experiments were conducted to determine the capacity of the anion resin, Dowex-1, when slurried with the feed solution and the possible use of this resin to extract protactinium by a batch process. The feed solution was prepared by dissolving one volume of slurry product in three volumes of concentrated (12 N) hydrochloric acid. In each experiment, 100 milliliters of feed solution was used. This feed solution was stirred with the anion resin for 30 minutes in a Buchner funnel having a fritted glass disk and fitted with a stopcock in the stem. The feed solution was allowed to drain from the resin. The resin was stirred with 50 milliliters of 9 normal hydrochloric acid for five minutes and then allowed to drain off. The resin was next stirred with successive portions of hydrochloric acid - hydrofluoric acid mixtures for 15 minutes to elute the protactinium. The results of these experiments are summarized in Table V.

TABLE V

SORPTION AND ELUTION OF PROTACTINIUM

RUN NO.	VOLUME OF DOWEX-1 (ml)	PROTACTINIUM IN FEED RETAINED ON DOWEX-1 (ml)	ELUTRIANT	ELUTRIANT PER BATCH (ml)	VOLUME OF ELUTRIANT TO REMOVE 95% OF ABSORBED Pa (ml)
I	25	46	9 N HCl - 0.1 N HF	25	175
II	50	83	9 N HCl - 0.2 N HF	25	275
III	50	96	9 N HCl - 0.2 N HF	50	300

NOTE: The resin in numbers I and II was used as received in the chloride form.

The resin in number III was pretreated by stirring it with 9 normal hydrochloric acid for 20 minutes.

On the basis of the concentration of the protactinium obtained in the elutriant, the conditions for the third experiment were the best. Pretreatment of the anion resin with 9 normal hydrochloric acid increased the capacity of the resin 14 per cent. Elution with acid which was 0.2 normal in hydrofluoric acid was 16 per cent more effective in removing the protactinium than was the acid which was 0.1 normal in hydrofluoric acid.

LARGE SCALE EXPERIMENT. One investigation of the use and behavior of an ion exchange column having an anion resin (Dowex-1) volume approximately 275 times that of the small research-size columns which have been previously studied was completed. The column had a diameter of 9 centimeters and a resin bed depth of 13.5 centimeters. Nineteen lengths of 18 millimeter glass tubing, each length 10 centimeters long, were packed vertically in the column before filling the column with resin. The glass tubing minimized movement of the resin particles during the addition of liquids to the column.

The feed liquor was prepared by dissolving one volume of concentrate, produced in the preliminary processing at the HH-Building, in three volumes of concentrated hydrochloric acid. After filtration this feed, which had a volume of 0.9 liters, was passed through the resin. After sorption of the feed, the resin was washed with 3 liters of 9 normal hydrochloric acid. The protactinium was eluted from the resin with a mixture of acids which was

During a recent conversation with Dr. Fletcher Moore of Oak Ridge National Laboratory, the possible addition of oxalic acid to the aqueous phase prior to extraction was discussed. Various concentrations with respect to oxalic acid were extracted with di-isobutyl carbinol. Systems were investigated in which the solutions were heated after the addition of the oxalic acid as well as those which were not so heated. The results of these experiments are summarized in Table VII.

TABLE VII

EFFECT OF OXALIC ACID ON Pa EXTRACTION BY DIBC

CONCENTRATED HCl ADDED TO 5 GM HH.PPT. (ml)	PER CENT PROTACTINIUM LEFT IN AQUEOUS PHASE PER CENT OXALIC ACID 0	2 HEATED	2 UNHEATED	4 HEATED	4 UNHEATED	6 HEATED	6 UNHEATED
15	3.0	7.6	9.7	11.0	9.5	12.0	16.8
20	3.6	6.3	7.5	6.7	9.8	10.1	14.2

In every case the addition of oxalic acid decreased the effectiveness of the organic solvent in extracting the protactinium. The oxalic acid reduced the iron from iron (III) to iron (II) but the results suggested the strong possibility that either the protactinium forms an oxalate complex which is not extractable, or that the protactinium is reduced by oxalic acid to a lower valence level which is not extractable. Previous experience suggests the first possibility as more likely.

Studies to date on the use of 10 percent hydrogen peroxide to strip the protactinium from the di-isobutyl carbinol indicate that this treatment is quantitative.

A four-stage, batch, counter-current extraction of protactinium from hydrochloric acid solution into di-isobutyl carbinol (DIBC) was carried out to evaluate the possible use of solvent extraction as a method of separating protactinium from other substances in the concentrate prepared in the HH-Building process.

The product slurry as received from the HH-Building process was washed four times by centrifuging the solids away from the liquid, discarding the liquor and reslurrying the solids with water. Each batch of feed for the extraction process was prepared by dissolving twenty grams of the centrifuged and washed solids (wet) in 40 milliliters of 12 normal hydrochloric acid and heating the mixture for one-half hour in a hot water bath. After cooling, the insoluble material was removed by centrifuging and discarded. A four milliliter aliquot of the supernate was gamma counted at levels of 27, 68, 90, and 300 kev. The aliquot was returned to the aqueous solution and the total volume of the aqueous solution was measured. Ten batches of feed were prepared in this manner.

The organic extractant was prepared by mixing equal volume of di-isobutyl carbinol and Amsco kerosene and then saturating this solution with 6 normal hydrochloric acid by rapid agitation.

The following procedure was followed to study the extraction. Ten milliliters of the organic extractant (DIBC) was added to the aqueous feed in a 125 milliliter separating funnel. The volume of the aqueous phase was approximately 54 milliliters. The mixture of the organic extractant and the aqueous liquor was shaken vigorously for three minutes and allowed to stand for at least 30 minutes, i.e., until the separation of the organic and aqueous phases appeared to be completed. Four milliliter aliquots of each phase were gamma counted at levels of 27, 68, 90, and 300 kev and the aliquots were then returned to their respective phases.

A four-stage, counter-current cycle was employed. Fresh feed solution was introduced at the first stage and was transferred successively, after undergoing extraction, through the fourth stage. The fresh organic extractant was introduced at the fourth stage and was transferred successively, after contacting the aqueous phase, through the first stage.

Comparison of the effectiveness of the various stages of the extraction was made by comparing the magnitude of the gamma counts in the aqueous phase at the various energy levels. The data are summarized in Table VIII.

TABLE VIII

EFFECTIVENESS OF EXTRACTION FROM AQUEOUS PHASE IN PER CENT

	27 KEV	68 KEV	90 KEV	300 KEV
1ST STAGE				
FRESH AQUEOUS FEED ORGANIC FROM 2ND STAGE	80.9	68.2	78.6	82.6
2ND STAGE				
AQUEOUS FROM 1ST STAGE ORGANIC FROM 3RD STAGE	15.0	8.9	11.5	13.3
3RD STAGE				
AQUEOUS FROM 2ND STAGE ORGANIC FROM 4TH STAGE	2.25	1.5	1.1	1.8
4TH STAGE				
AQUEOUS FROM 3RD STAGE FRESH ORGANIC	0.5	0.2	0.2	0.2

An extraction and concentration of protactinium was accomplished. The only contaminate in the protactinium which was extracted to an appreciable degree was iron. Although both phases were gamma counted at the various energy levels, comparison is made here only of the aqueous phases. Due to the fact that absorption of the gamma rays is not the same in the organic medium as in the aqueous medium, a material balance on the basis of counts per minute was impossible when the gamma counts from both phases were considered.

Examination of the data indicates that the protactinium is extracted by the di-isobutyl carbinol whereas the thorium-230 tends to remain behind in the aqueous phase. This solvent extraction technique offers a process whereby the protactinium may be separated from impurities with the exception of iron and possibly of certain other trivalent ions.