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MOUND LABORATORY
Operated By
MONSANTO CHEMICAL COMPANY
MIAMISBURG, OHIO

MONTHLY TECHNICAL ACTIVITIES REPORT

THROUGH JANUARY 15, 1956 (DELETED VERSION)

BY

J. F. EICHELBERGER, P. C. MEAD, JR. AND D. L. SCOTT

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MOUND DECLASSIFICATION REVIEW	
1ST REVIEW DATE: <u>2/17/81</u>	DETERMINATION (CIRCLE NUMBER(S))
AUTHORITY: <u>DAOC 5440 1140</u>	1. CLASSIFICATION RETAINED
NAME: <u>J. M. FLANAGAN</u>	2. CLASSIFICATION CHANGED TO
2ND REVIEW DATE: <u>8/25/92</u>	3. CONTAINS NO DOE CLASSIFIED INFO
AUTHORITY: <u>ADP</u>	4. COORDINATE WITH
NAME: <u>ADP</u>	5. CLASSIFICATION CANCELLED
	6. CLASSIFIED INFO BRACKETED
	7. OTHER ACTION

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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.

The first metal vacuum system, used for applying a nickel coat was put into operation. Greater efficiency of operation is contemplated with this type of vacuum system. In addition, an improved type of nickel carbonyl decomposition furnace was incorporated into the vacuum system.

Nine polonium-beryllium neutron sources and two alpha sources were delivered in December, 1955. Six of the neutron sources were for other AEC sites.

The total amount of beta activity discharged to the river was reduced by about 70 per cent. This was accomplished by closer control of the radioactivity from the influent tanks. Data for the Waste Disposal Operations are given in Table I.

TABLE I

DISCHARGE VOLUME	438,700	GALLONS
TOTAL ALPHA ACTIVITY	2.5	MILLICURIES
TOTAL BETA ACTIVITY	16.0	MILLICURIES
ACTIVITY DENSITY		
ALPHA	2	CT/MIN/ML
BETA	11	CT/MIN/ML

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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.

Design of the ionium hot laboratory facility is indicated as about 95 per cent complete with all major items of equipment on procurement. A small sample of a TBP-kerosene extract of airport cake was received from Mallinckrodt Chemical Works. According to the analysis sent with this small sample (about 100 ml), it contained 28 milligrams of ionium per liter. Stripping of this sample was done at Mound by two methods. One portion of 49.5 ml was stripped with 0.1 normal nitric acid in an organic to aqueous ratio of 1:1. The second portion of 49.5 ml was stripped with an aqueous solution of two normal nitric acid one molar in sodium sulfate. An organic to aqueous strip ratio of 10:1 was used for the second portion. An analysis for thorium, uranium and gross rare earth oxides has been made. Ratios indicate a low total thorium concentration and an exceedingly high uranium to thorium concentration. Gross rare earth elements are in about eight parts rare earth oxides per one part of total thorium.

Sufficient information was made available from Mallinckrodt Chemical Works and from the analysis of this small organic feed sample to modify and make up a simulated thorium containing feed material for studies in batch countercurrent and miniature mixer-settler experiments. Data from both the batch countercurrent and miniature mixer-settler studies indicate the feasibility of a purification procedure to be carried out in the hot laboratory by solvent extraction. It has been indicated that the first aqueous feed material will be shipped from Mallinckrodt on March 2. A request has been made for Dr. R. K. Fariss of Mallinckrodt to send Mound a quantity of the organic TBP-kerosene extract of the airport cake. This material will be studied by the Development Group at Mound after stripping into an aqueous feed. There are at present no facilities available at Mallinckrodt for carrying out a scrub, strip and a wash of this organic extract of airport cake.

Satisfactory analyses of samples containing ionium for both thorium and uranium have been made using the X-ray fluorescence method on the XRD equipment. The Tracerlab Frisch Grid Alpha Chamber was leak tested and the vacuum envelope was found to have many leaks due to inferior design and construction. The manufacturer of the chamber was contacted, however, they were either unwilling or unable to affect repairs. A new vacuum envelope is under construction in the machine shop. The Detectolab twenty channel pulse height analyzer has been thoroughly checked and found to be operating in a satisfactory manner. The Jarrell-Ash Company's Ebert spectrograph has been received and is being installed.

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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

Differential thermal analysis of many compositions in the ternary $\text{NaF}-\text{BeF}_2-\text{UF}_4$ system show liquidus transitions which are not easily reproducible nor well defined in shape. As many as one-quarter of the compositions investigated have their liquidus values so affected. The range of values in many cases may be as large as $\pm 15^\circ\text{C}$. Although the locations of the compositions so affected appear to be random and not characteristic of specific primary phase areas, more difficulty has been encountered with samples of high UF_4 and/or BeF_2 content. For these compositions thermal gradient quenches are being made in order to determine the liquidus values precisely and to ascertain the error and difficulties encountered in differential thermal analysis. In addition a steel drybox and a high-rate-of-flow purification system are under construction to enable differential thermal analysis of stirred melts.

DTA has been excellent in showing that no quasibinaries could exist in the ternary except on the $\text{NaBeF}_3-\text{Na}_7\text{U}_6\text{F}_{31}$ join. DTA easily indicated the composition and temperature of the 483°C ternary eutectic, 528°C peritectic, 500°C peritectic, and the slope and general location of boundary lines; but for the area to the right of the $\text{NaBeF}_3-\text{UF}_4$ join, it has been less fruitful. Apparently DTA is not suitable for compositions of greater than 40 mole per cent BeF_2 and 25 mole per cent UF_4 . This is probably due to the slow rate with which compositions in this area attain equilibrium conditions. Moreover, the lack of agitation or stirring aggravates this condition. Some six to eight runs are always necessary to insure attainment of reasonable liquidus values and often these may vary so widely as to be unreasonable.

Some liquidus values based upon heating curves of compositions surrounding the join $\text{NaBeF}_3 - \text{UF}_4$ are shown in Table I. Very little can be deduced from these data until more compositions in this area are examined. Hence, in their present form these figures lend little support to the proposed section of the ternary as shown in an earlier report.

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TABLE I

DIFFERENTIAL THERMAL ANALYSIS

COMPOSITION MOLE PER CENT			LIQUIDUS TEMPERATURE °C
NaF	BeF ₂	UF ₄	
40	40	20	596
48	32	20	590
44	36	20	578
36	44	20	570
32	48	20	550
49	35	16	626
45	39	16	560
39	45	16	575
35	49	16	567
42.5	42.5	15	562
48	40	12	574
42	46	12	548
38	50	12	555
34	54	12	564
45	45	10	530
36	56	8	520
46	52	4	460

FILTRATION STUDIES

Further studies of the ternary phase system resulted in the following data: The valley between Na₂UF₆ and Na₇U₆F₃₁ has been further defined by runs No. 1 and No. 2 of Table II. The filtrate in No. 2 is very close to the point at which this valley meets the phase area for Na₂BeF₄. Consequently, the composition for the peritectic for Na₂UF₆ - Na₇U₆F₃₁ - Na₂BeF₄ can now be fixed at 4.5 mole per cent UF₄ - 35 mole per cent BeF₂ - 60.5 mole per cent NaF.

Runs No. 3 and 4 appear to form a continuation of the valley between Na₂UF₆ and Na₂BeF₄. However, this explanation may not be correct, since samples 3 and 4 should have liquids which originate in the peritectic described in the previous paragraph (this is nearly 500°C) but neither sample No. 3 nor No. 4 appeared to have any liquid below 520°C.

Samples No. 5, 6, 7, 8, and 9 are in the area near the center of the phase diagram. This area is proving to be difficult because of the appearance of the new compound, NaU₂F₉, but as yet no phase area has been found for this compound. At the present time the data are interpreted in the following manner: Runs No. 6 and 7 are in the valley between Na₇U₆F₃₁ and UF₄, while sample No. 5 is in the UF₄ area. The analysis for No. 5 is about 2 per cent high in BeF₂ to fit this explanation, but the BeF₂ determinations are generally slightly high.

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Therefore, this point should be repeated to prove its validity. The starting composition for both samples No. 8 and No. 9 is believed to be in the $\text{Na}_7\text{U}_6\text{F}_{31}$ phase area so that No. 9 is near the point where this phase meets the phase area for NaBeF_3 , and No. 8 is at the ternary eutectic for $\text{Na}_7\text{U}_6\text{F}_{31}$ - NaBeF_3 - BeF_2 .

TABLE II
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	12.5	26.5	61.0	516	6.8	33.6	59.6
2	12.5	27.0	60.5	502	5.5	34.3	60.2
3	6.0	29.0	65.0	527	7.2	28.2	64.6
4	6.5	27.5	66.0	538	7.6	28.2	64.2
5	40	30	30	676	25.9	39.0	35.1
6	20	40	40	570	14.9	46.9	38.4
7	20	40	40	535	7.1	51.0	41.9
8	10	45	45	378	1.8	56.6	41.6
9	10	45	45	408	1.8	53.5	44.6

PETROGRAPH STUDIES

After including the compound NaU_2F_9 in the ternary diagram, attempts were made to extend composition lines from it to other stable compounds to satisfy the conditions found, but none of these possibilities were found to fit. However, a composition line from NaU_2F_9 along the $33\frac{1}{3}$ mole per cent constant NaF line seemed to satisfy the conditions. Above this line UF_4 was always found present in slowly cooled melts, while below the line UF_4 was never found present in slowly cooled melts which presumably had reached equilibrium. To draw this composition line on the ternary diagram was not justifiable since it did not extend to another compound. Instead it intersected the NaF - BeF_2 binary at a point representing $66\frac{2}{3}$ mole per cent BeF_2 . Analysis of this point shows it to be the composition of the theoretical compound NaBe_2F_5 , suggesting that the compound may actually exist. The composition NaF -33.3 mole per cent, BeF_2 -66.7 mole per cent was prepared, and several attempts were made to produce NaBe_2F_5 . If the compound existed, it would occur as a subsolidus compound; therefore, the samples were held for periods of 50 to 120 hours at temperatures in the range of 335°C - 275°C . These temperatures were approached from both directions. X-ray diffraction and petrography failed to show evidence of a new compound.

A thermal gradient quench was made of the ternary composition UF_4 -20 mole per cent, NaF -40 mole per cent, BeF_2 -40 mole per cent. This composition should contain a great deal of Na_2F_6 and no UF_4 when equilibrium has been reached. The primary phase was UF_4 , which was the

liquidus temperature °C and °C where the first crystals appeared.

of NaU_2F_9 occurred. This suggests that NaU_2F_9 may not have an actual primary phase area, occurring instead on the valley separating the UF_4 and $\text{Na}_7\text{U}_6\text{F}_{31}$ primary phase areas.

PHYSICAL PROPERTIES

Fourteen density and twelve viscosity measurements were made on the ternary mixture; sodium fluoride, beryllium fluoride, and uranium fluoride over the temperature range 500° to 900°C . Interpolated values for these properties are given in Table III for 600° and 800°C . In cases where the measurements could not be made at a temperature as low as 600°C values for 700° and 800°C are given in Table IV.

TABLE III

DENSITIES AND VISCOSITIES OF TERNARY MIXTURES - 600° AND 800°C

MOLE PER CENT			600°			800°		
NaF	BeF ₂	UF ₄	η	ρ	η/ρ	η	ρ	η/ρ
			POISE	GM/CM ³	STOKES	POISE	GM/CM ³	STOKES
56	43	1	0.1040	2.132	0.0488	0.0368	2.025	0.0182
46	53	1	0.177	2.115	0.0837	0.0523	2.020	0.0259
52	47	1	0.1074	2.139	0.0502	0.0433	2.034	0.0213
58	41	1	0.0928	2.132	0.0435	0.0378	2.025	0.0187
46	51	3	0.273	2.733	0.0998	0.0716	2.634	0.0272
52	45	3	0.1042	2.294	0.0454	0.0414	2.182	0.0190
58	39	3	0.102	2.399	0.0425	0.0316	2.277	0.0139
40	40	20	0.1458	2.512	0.0580	0.0299	2.403	0.0124
65.9	26	8.1	0.1121	2.787	0.0405	0.0468	2.677	0.0174

TABLE IV

DENSITIES AND VISCOSITIES OF TERNARY MIXTURES - 700° AND 800°C

MOLE PER CENT			700°			800°		
NaF	BeF ₂	UF ₄	η	ρ	η/ρ	η	ρ	η/ρ
			POISE	GM/CM ³	STOKES	POISE	GM/CM ³	STOKES
32.5	32.5	35	0.1672	4.499	0.0371	0.0736	4.381	0.0168
20	20	60		5.578			5.468	
76	0	24	0.1225	3.980	0.0307	0.0724	3.898	0.0186
46	0	54		5.379			5.231	
40	0	60	0.1662	5.569	0.0298	0.1059	5.465	0.0193
58	0	42	0.131	4.946	0.0264	0.0864	4.830	0.0179
30	0	70					5.873	
30	10	60					5.419	
46	7	47		5.075			4.929	
37	16	47		5.091			4.963	
26.5	26.5	47		5.085			4.959	
58	7	35		4.539			4.425	
0	65	35					4.601	

Last month the values for 65.9 NaF, 26.0 BeF₂, 8.1 UF₄ were erroneously reported under the heading 76 NaF, 3 BeF₂, 21 UF₄.

A detailed and relatively comprehensive report on the work which has been completed in the Physical Properties Group during 1955 is in the process of preparation. This report includes a description of the density and viscosity apparatus, a discussion of precision and errors, relevant data on the binary and ternary systems investigated, and a summary of results and conclusions.

ANALYTICAL METHODS

Experiments to improve the analysis of beryllium in the presence of sodium were made. Data obtained from 10 experiments involving double precipitations of beryllium hydroxide indicate that the error produced by the occlusion of sodium ions was almost completely eliminated by double precipitation. The average weight of sodium found per sample is reduced from 1.4 milligrams by a single precipitation to 0.2 milligram present by double precipitation. The overall accuracy of the reprecipitation method is 100.3 per cent with -0.4 milligram per sample maximum deviation.

Some preliminary analyses of uranium and beryllium fluorides have been made in the presence of lithium. Data obtained from six experiments indicate the following points: (1) Quantitative uranium by electrodepositions is good. (2) Lithium interference is slightly greater than that of sodium in the determination of beryllium as the hydroxide (single precipitation). (3) Only minor changes are necessary over those now in use for analyses of beryllium and uranium in the presence of sodium.

X-RAY ANALYSIS

The scintillation detection equipment for X-ray analysis has been tested and is performing satisfactorily. The system consists of a NaI(Tl) crystal covered by a beryllium window and mounted on the face of a No. 6292 photomultiplier. The photomultiplier is supplied a stabilized high voltage by the scaler unit, and the dynode voltages are further stabilized by VR-57 voltage-regulator tubes in place of the usual resistors. The output of the No. 6292 tube is fed into a Detectolab DR-9 preamplifier, DA5 linear amplifier, and DZ15 pulse height analyzer. The output of the pulse height analyzer in turn feeds pulses to an Atomic 1060A scaler and to the General Electric rate meter.

Pulse height curves have been made for La_{Lα2} (4145 e.v.), La_{Lα1} (4674 e.v.), Cu_{Kα} (8679 e.v.), Mo_{Kα} (17561 e.v.), La_{Kα} (33561 e.v.), and Gd_{Kα} (43187 e.v.).

In addition counting rates under optimum conditions were determined and compared with those of the General Electric argon geiger tube. These are given in Table V and represent total readings above background.

We are now reasonably certain that limited rare earth analyses by X-ray fluorescence can be made. By overdriving the X-ray unit, complete coverage of the rare earths may be obtained, though by no means giving optimum excitation conditions which are desirable.

TABLE V
COMPARISON OF SCINTILLATION AND GM COUNTERS

RADIATION	SCINTILLATOR COUNTS PER MIN	G. M. (ARGON) COUNTS PER MIN	*G. M. INHERENT COUNTS PER MIN
Gd _{Kα}	35,733 13 BACKGROUND	2,108	4,891
La _{Kα}	371,418 9 BACKGROUND	31,051	72,038
Mo _{Kα}	672,306 10 BACKGROUND	213,641	495,647
Cu _{Kα}	75,229 29 BACKGROUND	33,574	77,892
La _{Lα1}	216,166 4,825 BACKGROUND	59,884	138,930
La _{Lα2}	2,835 16,760 BACKGROUND	566	1,314

*G. M. INHERENT IS THE ESTIMATED COUNT OF THE TUBE, ASSUMING FULL USE OF THE REFLECTED BEAM.

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

The concentration of the protactinium in the HH-Building is being continued according to the process outlined in previous Technical Activities reports. A total of 41 drums containing 18,260 pounds of raffinate residue received from the Mallinckrodt Chemical Company have been processed. On the basis of seventy per cent recovery of the protactinium and an initial concentration of 0.2 parts per million, 1.16 grams of protactinium have been concentrated in the first treatment.

PROCESS DEVELOPMENT

Work is continuing on a process to recover protactinium from the drums of raw material which cannot be adequately treated by the present protactinium recovery process.

In the last technical activities report, a number of exploratory experiments were described. It has been concluded that the only line of attack with significant promise of early success consisted of depositing all of the protactinium on a residue while dissolving most of the nonradioactive material.

PROTACTINIUM RECOVERY FROM DRUM 51

Drum 51, which contains a raw material representative of the raffinate residue which is not satisfactory for treatment by the present process, was selected for extensive tests. Experiments were carried out to study the effect of a number of variables, including concentration of acid, amount of chloride, contact time, temperature, and rate of cooling.

In order to expedite the experimental work and to reduce the amount of labor required for the analysis of a single run, the raw material was first analyzed for total protactinium by the hydrochloric acid - di-isobutyl carbinol method. The results of this analysis were used as a standard for evaluation of the experimental work. Experimental runs were, in all cases, analyzed in terms of the residues only; i.e., the washed and centrifuged insoluble residue was weighed and then analyzed for protactinium. The results were expressed as weight percentage and protactinium percentage, the latter value being obtained from a comparison of the protactinium recovered from the residue and the total protactinium as previously found by analysis. The results are summarized in Table I and Table II.

Examination of Tables I and II reveals that the best results (i.e., the highest recoveries with the lowest weight residues) were obtained when the raw material was heated with hydrochloric acid to effect solution and was then treated with sufficient chloride to cause precipitation of the protactinium. This was accomplished most simply when concentrated hydrochloric acid was used (24 milliequivalents per gram of raw material, 12^N acid). However, the use of a high concentration of hydrochloric acid is objectionable because of the inadequacy of the equipment available for removing fumes. The use of 6-normal hydrochloric acid proved

effective, but it was necessary to wash the residue several times in order to reduce its weight. It is probable that 6-normal acid would be almost as objectionable as 12-normal acid.

TABLE I
EFFECT OF SEVERAL VARIABLES ON PROTACTINIUM RECOVERY
FROM DRUM 51 RAW MATERIAL. ROOM TEMPERATURE EXPERIMENTS

CHLORIDE (meq/gm)	ACID CONC (N)	CONTACT TIME		RESIDUE	
		STIR (hrs)	STAND (hrs)	WEIGHT %	Pa %
10	2 ^a	2	16	55 ^b 12	51
20	6.7	2	0	58	42
20	6.7	2	16	53	58
20	8.1	6½	16	58	66
20	10	2	0	62	43
20	10	2	16	65	80
30	8.6	6½	16	58	55
40	8.9	6½	16	54	26
40	3.1	6½	16	20	32

a. PRESENT PROCESS

b. WEIGHT BEFORE WASH - 55%. WEIGHT AFTER 6N HCl WASH - 12%

TABLE II
EFFECT OF SEVERAL VARIABLES ON PROTACTINIUM RECOVERY
FROM DRUM 51 RAW MATERIAL. ELEVATED TEMPERATURE EXPERIMENTS

TEMP (°C)	CHLORIDE (meq/gm)	ACID CONC (N)	CONTACT TIME		COOLING RATE	RESIDUE	
			STIR (hrs)	STAND (hrs)		WEIGHT %	Pa %
46	20	4	24 (OCC. STIR)		SLOW	61	33
49	20	4	24 (OCC. STIR)		SLOW	36	54
49	30	6	24 (OCC. STIR)		SLOW	55	38
100	10	2	1	0	FAST	(-) ^a	50
100	20	4	1	0	FAST	(-) ^a	59
100	24	12	1	0	FAST	34	96 ^b
100	24	6	1	0	FAST	65 ^c 31 12	91
100	27	4	1	16	SLOW	46	49
100	34	4	1	16	SLOW	39	38
100	27 ^d	2	1+1	1	SLOW	34	90
100	27 ^e	2	1+1	16	SLOW	31	106

a. POST-PRECIPITATE IN SUPERNATE.

b. ANALYTICAL PROCEDURE

c. RESIDUE AFTER H₂O WASH - 65%. AFTER DIL. HCl WASH - 31%, AFTER SECOND HCl WASH - 12%

d. HEATED 1 HR WITH 2N HCl, COOLED PARTLY, SODIUM CHLORIDE ADDED, HEATED, ALLOWED TO COOL TO ROOM TEMPERATURE BEFORE SEPARATION.

e. HEATED 1 HR WITH 2N HCl LET STAND OVERNIGHT, SODIUM CHLORIDE ADDED, HEATED, ALLOWED TO COOL TO ROOM TEMPERATURE BEFORE SEPARATION.

An attempt to accomplish the objectives by treating the raw material with a mixture of sodium chloride and hydrochloric acid was ineffective. However, it was found when the raw material was first treated with hot, two-normal hydrochloric acid, allowed to cool, and then was treated with sodium chloride, that good results were obtained. A single water wash left the residue with 30-35 per cent of the original weight, but with nearly all of the protactinium. It seems possible that a second wash would improve the concentration still further.

The mechanical problems involved in carrying out a procedure based on the two-normal acid, 27 milliequivalents per gram system are now being studied.

EXTRACTION OF PROTACTINIUM FROM RESIDUES INSOLUBLE IN 2-NORMAL HYDROCHLORIC ACID. Some of the drums of raffinate residue which had been processed yielded unusually high residues, containing a major portion of the protactinium, from the initial step of the process. Various concentrations and amounts of hydrochloric and of sulfuric acids were used to try to put the protactinium into solution from such residues after the initial treatment with two-normal hydrochloric acid. In all cases the acid used was stirred with the residue for two hours.

The results are summarized in Table III. The data for "Residue, Weight %" were obtained by weighing the residue before contacting it with the acid and then weighing the residue remaining after separating the aqueous phase from the residue by centrifuging. The data for "Per Cent Activity in Supernate" were obtained by comparing the activity of the residue at 27 Kev and 300 Kev levels with the activity of the liquid at the same levels.

It appears that any treatment of these residues with hydrochloric acid will not satisfactorily release an acceptable quantity of the protactinium to the solution. However, it is known that the addition of hydrochloric acid or sodium chloride to a system resulting from the contacting of the residue with dilute hydrochloric acid will cause practically all (over 95%) of the protactinium to appear on the residue. The best conditions for this treatment were the use of four normal hydrochloric acid and twenty milliequivalents of acid per gram of residue. The resulting residue, freed of chlorides soluble under these conditions, can be reacted with concentrated sulfuric acid and hydrochloric acid, followed by extraction of the protactinium by di-isobutyl carbinol. The last two experiments reported in Table III indicate the possible treatment with a mixture of hydrochloric and sulfuric acids of the residue which remained after the process treatment of the raffinate residue with two-normal hydrochloric acid. This use of mixed acids to dissolve the protactinium will be investigated more completely.

TABLE III
TREATMENT OF INSOLUBLE RESIDUES FROM
FIRST STEP OF HH-RECOVERY PROCESS

	ACID	ACID CONC	AMOUNT OF ACID (meq/gm)	TEMP (°C)	RESIDUE (wt. %)	PER CENT ACTIVITY IN SUPERNATE	
						27 KEV	300 KEV
1	HCl	2	10	25	-	10.1	8.2
2	HCl	2	10	95	-	10.8	9.2
3	HCl	4	20	25	-	1.8	2.1
4	HCl	4	20	95	-	6.5	3.9
5	HCl	6	12	25	28.5	33.2	17.2
6	HCl	6	24	25	32.4	31.1	15.1
7	HCl	6	24	65	32.8	17.4	10.4
8	HCl	6	24	95	38.5	18.6	11.4
9	HCl	12	12	25	43.8	14.8	6.2
10	HCl	12	24	25	44.0	38.2	22.3
11	H ₂ SO ₄	9	24	25	41.8	60.0	34.8
12	H ₂ SO ₄	9	36	25	40.4	66.4	38.6
13	H ₂ SO ₄	9	48	25	50.5	74.8	47.1
14	H ₂ SO ₄	9	48	65	28.4	53.2	49.0
15	H ₂ SO ₄	9	48	95	33.6	54.9	52.7
16	H ₂ SO ₄	9	60	25	46.3	102.4	55.1
17	H ₂ SO ₄	18	24	25	34.5	46.9	34.7
18	H ₂ SO ₄	18	48	25	49.0	76.6	46.3
19	H ₂ SO ₄	18	60	25	54.1	77.4	50.0
20	H ₂ SO ₄	36	24	25	171.9	11.3	6.4
21	H ₂ SO ₄	36	48	25	180.6	32.0	19.9
22	HCl +	2	10	25	29.7	84.3	47.7
	H ₂ SO ₄	9	48				
23	HCl +	2	13	25	29.5	89.7	52.7
	H ₂ SO ₄	9	60				

EXPERIMENTS ON SOLUTIONS OF SLURRY PRODUCT FROM HH-BUILDING PROCESSING. Development work has continued for the determination of the proper conditions for the solution of the product from the HH-Building Process. The settled slurry, described in the last technical activities report, was used as the starting material. In all the experiments described in this portion of this report, phase separations were effected by centrifuging, and "per cent activity dissolved" refers to the total gamma activity of the liquid (at the designated energy level) expressed as a per cent of the sum of the activity of the liquid and that of the solid residue.

EFFECT OF NORMALITY OF HYDROCHLORIC ACID. To determine the effect of variations in the concentration of the hydrochloric acid solvent on solution efficiency, the normality of the acid was varied from 2-normal to 12-normal. The quantity of acid was fixed at 36 milliequivalents of hydrogen chloride per milliliter of slurry. In each case the slurry sample was pre-washed with four volumes of water for ten minutes prior to solution in the acid; the solution time was one hour. Table IV shows the effect of the acid normality on solution efficiency under these conditions. Minima in the solution efficiency versus normality curves occur at about 6-normal.

TABLE IV

EFFECT OF CONCENTRATION OF HYDROCHLORIC ACID
SOLVENT ON SOLUTION EFFICIENCY

30 MEQ HCl PER ML OF SLURRY FROM INITIAL PROCESSING STEP
SINGLE WATER PRE-WASH; ONE HOUR SOLUTION TIME

HCl NORMALITY	PER CENT GAMMA ACTIVITY DISSOLVED	
	27 KEV	300 KEV
2	69.0	74.0
6	23.0	43.9
9	42.0	51.5
12	84.1	88.3

EFFECT OF AMOUNT OF HYDROCHLORIC ACID. The effect of variations in the amount of hydrochloric acid solvent on solution efficiency was studied while maintaining the concentration of the solvent at 9-normal and again at 12-normal. The 10-minute pre-wash and the 1-hour solution time were again used.

Most of the solutions were unstable, since they formed light colored flocculent precipitates upon standing. The stability of each solution was measured by allowing each solution to stand overnight, removing the precipitate, and counting the solid-free liquid. The reduction in the activity of the liquid, expressed as a per cent of its activity before the precipitation, was taken as a measure of the stability of the solution.

To determine the acidity of the solutions, aliquots were diluted and titrated with standard base, using bromophenol blue as indicator. From the final normality of the solution and its volume, the amount of free acid remaining after solution of the slurry had been

effected was calculated. This amount subtracted from the total amount of acid introduced into the system, gave the amount of acid consumed.

The experimental results are summarized in Table V. As the amount of acid added increased, the solution efficiency decreased approximately linearly. The decrease was much more marked with 9-normal acid than with 12-normal acid. Also, for the same number of milliequivalents of hydrochloric acid, the 12-normal acid was more effective in dissolving the protactinium than the 9-normal acid. There is some indication that increasing the amount of acid decreased the loss by precipitation when 12-normal acid was used. The losses by precipitation, when 9-normal acid was used, were not determined under comparable conditions and are therefore not reported.

TABLE V

EFFECT OF AMOUNT OF HCl SOLVENT ON SOLUTION EFFICIENCY,
STABILITY, AND QUANTITY OF ACID CONSUMED
(SINGLE WATER PRE-WASH; 1 HR STIRRING TIME)

AMOUNT OF HCl ADDED (meq per ml of slurry)	PER CENT ACTIVITY DISSOLVED		PER CENT ACTIVITY LOST IN PRECIPITATE IN ONE DAY		FINAL NORMALITY OF SOLUTION	HCl CONSUMED IN SOLUTION PROCESS (meq per ml of slurry)
	27 KEV	300 KEV	27 KEV	300 KEV		
9-NORMAL HCl						
5.36	95	98			4.30	0.936
10.6	89	96			5.73	1.07
15	76	84			6.20	1.360
25	59	70			7.13	1.692
36	42	52			7.53	2.184
12-NORMAL HCl						
15	91	93	13	19	8.20	2.4
25	88	91	13	20	9.00	25.5
36	84	88	4	12	9.53	45.5

The increase in the final acid normality of the solution with increasing amount of acid solvent used was to be expected. An unexpected result was the increase in hydrogen chloride consumed per milliliter of slurry with increasing amount of acid solvent used. This increase in acid consumption was particularly marked with the 12-normal acid.

The 9-normal hydrochloric acid does not appear attractive as a solvent to prepare solutions for use in ion exchange columns to separate protactinium from other substances. The low

amounts of acid required for high solution efficiency entail excessive reductions in the final acid normality

EFFECT OF SOLUTION TIME. Since the 12-normal hydrochloric acid appeared to be satisfactory as a solvent, a study of variations in solution and washing procedure, using this solvent, was initiated. Table VI shows the effect of increasing the solution time from 1 to 2 hours for various amounts of 12-normal acid used in the solution process.

TABLE VI
EFFECT OF SOLUTION TIME ON SOLUTION EFFICIENCY
AND STABILITY FOR VARYING AMOUNTS OF 12N HCl

(a) PER CENT GAMMA ACTIVITY DISSOLVED

(b) PER CENT GAMMA ACTIVITY PRECIPITATED IN ONE DAY

(SINGLE PRE-WASH)

SOLUTION TIME IN HOURS	27 KEV			SOLUTION TIME IN HOURS	300 KEV		
	1	2	DIFF		1	2	DIFF
AMOUNT OF HCl IN MEQ PER ML OF SLURRY				AMOUNT OF HCl IN MEQ PER ML OF SLURRY			
15	(a) 90.8	87.9	2.9	15	(a) 92.5	89.8	2.7
	(b) 13.8	19.1			(b) 19.2	31.2	
25	(a) 88.0	76.6	11.3	25	(a) 90.6	79.6	11.0
	(b) 13.3	12.6			(b) 19.8	24.2	
36	(a) 84.6	75.1	9.4	36	(a) 86.9	80.3	6.6
	(b) 11.5	2.4*			(b) 3.6	6.1*	

*PER CENT ACTIVITY PRECIPITATED IN TWO DAYS

Increasing the solution time invariably gave reductions in solution efficiency, presumably as a result of post-precipitation during the second hour of solution. There was no consistent effect of solution time on solution stability so far as the 27 kev count was concerned, though the 300 kev count seemed to indicate an increased rate of deterioration as a result of the longer solution time.

SOLVENT EXTRACTION

EFFECT OF HYDROCHLORIC ACID CONCENTRATION ON EXTRACTION OF PROTACTINIUM BY ISOPROPYL ETHER. It had been observed that there was a correlation between the concentration of hydrochloric acid and a tendency of the isopropyl ether, used to extract iron (III) from the aqueous solution of the product of the HH-Building process to extract a part of the

protactinium. Therefore, solutions of protactinium in various concentrations of hydrochloric acid were prepared. The protactinium solutions used had been previously separated from gross impurities by means of the solvent extraction procedure outlined in the last technical activities report. Data were obtained by gamma counting each aqueous solution before contacting it with an equal volume of isopropyl ether (saturated with 7.75 normal hydrochloric acid) and by gamma counting each aqueous phase and each ether phase after vigorously stirring the aqueous phase in contact with the ether phase for five minutes. The results appear in Table VII.

TABLE VII
EFFECT OF HYDROCHLORIC ACID CONCENTRATION ON
EXTRACTION OF PROTACTINIUM

ACID NORMALITY	PER CENT OF ACTIVITY IN ETHER PHASE	
	27 KEV	300 KEV
3.96	0.9	0.4
4.27	0.1	0.0
5.27	1.0	0.7
5.33	0.3	0.4
5.46	0.9	1.1
6.64	2.4	1.3
6.90	6.1	4.3
6.95	9.5	6.1
7.92	36.8	24.6
8.62	68.8	42.7
9.45	71.8	52.1
10.72	67.0	36.9

These data indicate that isopropyl ether extracts a noticeable amount of protactinium at hydrochloric acid concentrations above six-normal. The results reported by R. W. Dodson, G. J. Forney, and E. H. Surft, J. Amer. Chem. Soc. 58 2573, (1936) show that the extraction of iron (III) by isopropyl ether is approaching the region of greatest effectiveness at hydrochloric acid concentrations of six-normal and above. Therefore, it appears likely that isopropyl ether can be used to separate iron and protactinium dissolved in hydrochloric acid. It is not surprising to find that the extractability of protactinium decreases at very high hydrochloric acid concentrations. The extractability of iron (III) by isopropyl ether follows a similar pattern.

Two solutions of protactinium in 3.96 normal hydrochloric acid and 5.46 normal hydrochloric acid respectively were saturated with sodium chloride before being contacted with isopropyl ether. The presence of the sodium chloride had no effect on the extractability of the protactinium by isopropyl ether. Some preliminary studies using magnesium chloride to increase the chloride concentration of the hydrochloric acid indicate that the addition of

magnesium chloride has an effect similar to that obtained by increasing the hydrochloric acid concentration. Additional investigations are being carried out to correlate the effect of the addition of a bivalent metal chloride such as magnesium chloride or a trivalent chloride such as aluminum chloride on the solvent extraction of protactinium from hydrochloric acid solutions.

THERMAL DIFFUSION PROJECT

The Mound Laboratory Thermal Diffusion Project is directed toward the evaluation of the performance of thermal separation columns under a variety of conditions and the study of the mechanics of gases.

The thermal diffusion program has been approved for additional research as of January 1, 1956. Since this program had been suspended for the preceeding six months, most of the work this month has been directed toward the elimination of leaks in the columns and gas handling systems, and the servicing of associated pumps, etc. In addition, work has started on the assembly and testing of the mercury piston gas handling pump which had been designed and fabricated last year.

The mass spectrometer was started up in December in order to have it in good operating condition as soon as separated gas samples are made available.

The immediate program will be centered around the following areas of interest:

- 1 - The activation of the three uranium chemical pumps with hydrogen. These pumps are to be operated in conjunction with the continuous flow operation of the columns in the separation of hydrogen and deuterium gas mixtures.
- 2 - A determination of the temperature range of laminar gas flow in our columns by measuring the column pressure as a function of center wire temperature as suggested by J. W. Corbett and W. W. Watson (to be published).
- 3 - Batch operation and continuous flow measurements with hydrogen-deuterium and hydrogen-helium gas mixtures in order to obtain experimental data which can be compared with calculated values of thermal column performance. (References: CRE-481, KAPL-593, KAPL-642, KAPL-1076, LA-1296 and pertinent unclassified literature.)
- 4 - Thermal diffusion constant and column shape factor determinations with our four twelve-foot long columns which range in diameter from 1.0 inch to 1.61 inches, with various diameter center wires, and with low molecular-weight gas mixtures.