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This Document Consists of 24 Pages
This is Copy 28 of 28A
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MOUND LABORATORY
Operated By
MONSANTO CHEMICAL COMPANY
MIAMISBURG OHIO

Central File No 56-3-46

MONTHLY TECHNICAL ACTIVITIES REPORT
THROUGH MARCH 15, 1956

BY

J. F EICHELBERGER AND D L SCOTT

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PRODUCTION PROGRAM

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

The results obtained from the first tests of the gas decomposition efficiency of the new baffle type nickel decomposition furnaces appear promising. Further results may justify the installation of these units with all vacuum systems using nickel carbonyl.

Six polonium-beryllium neutron sources and four alpha and two dummy alpha sources were shipped in February, 1956. Three neutron sources and two alpha sources were for other AEC sites.

Total Alpha and Beta activity discharged to the river was less than during the previous report period. Data for the Waste Disposal Operations are given in Table I.

TABLE I

DISCHARGE VOLUME	562,000	GALLONS
TOTAL ALPHA ACTIVITY	2.0	MILLICURIES
TOTAL BETA ACTIVITY	14.5	MILLICURIES
ACTIVITY DENSITY		
ALPHA	1	CT/MIN/ML
BETA	8	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

The ionium hot laboratory facilities are presently about 95 per cent completed and will probably be 99 per cent complete during the first part of the week of March 19, 1956 Difficulty at Mallinckrodt Chemical Works delayed shipment of a representative sample of feed material, but fifteen gallons of a "cold" feed solution were prepared with a composition based upon discussions held at Mallinckrodt. This "cold" feed solution was processed in the new facilities.

The feed used in the "cold" run contained approximately ten grams per liter of thorium-232, ten grams per liter of uranium, ten grams per liter of rare earth nitrates, and was two-normal in nitric acid. Operation of the mixer-settler units in the pilot plant with six stages of extraction, four stages of aqueous scrub, six stages of strip and four stages of organic scrub resulted in a thorium loss in the aqueous raffinate of 1.6 per cent and a thorium loss in the organic raffinate of 1.0 per cent The stream components and flow rates used are shown in Table I

TABLE I

STREAM	COMPOSITION	FLOW *(ml/min)*
"COLD" FEED	**2 *N* NITRIC ACID**	55.0
ORGANIC EXTRACTANT	40% TBP 60% AMSCO	55.0
AQUEOUS SCRUB	0.1 *N* NITRIC ACID	8.5
STRIP	0.1 *N* NITRIC ACID	44.0
ORGANIC SCRUB	40% TBP - 60% AMSCO	5.5

The product from the above run was well within specifications on rare earths and common elements, but was somewhat high in uranium content The feed point into the partitioning bank of mixer-settlers has been changed to give four strip stages and six organic scrub stages This will lower the uranium content of the product

A second "cold" run will be made on March 19th or 20th. The feed will be ten grams per liter in thorium-232, one gram per liter in uranium one gram per liter in rare earth nitrates, and two normal in nitric acid This composition is the best estimate for the material which we will receive Minor flowsheet changes may be required when the hot feed is received and analyzed, but this should present no great problem

The first shipment of nitric acid feed solution should leave the Mallinckrodt Chemical Works on March 22, 1956. This first shipment should contain 90 grams of ionium. This solution will be started through the new facilities on March 26th if it is received between March 23rd to 26th. The first shipment of final product from Mound Laboratory will be about 60 grams and should be in the Dayton Air Express Office on April 6, 1956.

The analytical work on an initial shipment of 3.4 grams of ionium in a sulphate solution has been started. Slide mounts have been prepared and counted, and the development of the method of mounting is nearly completed. The new vacuum envelope for the Frisch, Alpha Grid-Chamber has been completed, installed, leak tested, and is being calibrated with the twenty-channel, pulse-height analyzer. Final alignment of the Ebert Spectrograph and all accessories has been completed, and temporary master plates for the analysis of thorium product have been prepared.

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.

DIFFERENTIAL THERMAL ANALYSIS

The area surrounding the composition of 70 mole per cent NaF, 26 mole per cent BeF_2, 4 mole per cent UF_4 in the NaF - BeF_2 - UF_4 ternary system, where optimum viscosity values have been found, was studied again by differential thermal analysis. All compositions shown in Table I give the three primary phases Na_2BeF_4, NaF and Na_3UF_7, and upon cooling proceed to the 484 °C eutectic, in addition to giving the solid transitions of 220 °C for Na_2BeF_4 and 450 °C for Na_3UF_7. These compositions are being checked also for liquidus values by the use of quenching techniques.

TABLE I

DIFFERENTIAL THERMAL ANALYSIS

NaF - BeF_2 - UF_4 TERNARY

DTA NO.	COMPOSITION MOLE PER CENT NaF	BeF_2	UF_4	BOUNDARY INTERSECTION HEATING °C	COOLING °C	LIQUIDUS HEATING °C	COOLING °C
119B	68	28	4	559	560	567	566
200	70	26	4	-	535	542	544
160B	72	24	4	528	530	544	543
201	70	24	6	515	-	527	527
190	68	26	6	522	-	544	544
202	72	26	2	551	-	560	551
203	70	28	2	-	551	555	556

The LiF - BeF_2 binary phase diagram presented by Roy, Roy, and Osborn, J. Amer. Chem. Soc. *3*, 85-90 (1950), is being checked by differential thermal analysis. Table II shows that the BeF_2 - $LiBeF_4$ eutectic of 355 C which we obtained agrees precisely with the value reported by Osborn. However, the liquidus values which we obtained are as much as 22 degrees higher than the corresponding values reported by Osborn. The higher value is generally the preferred value, since a low value may indicate the presence of impurities. The LiF and BeF_2 used for our studies have been purified in the liquid state by treatment with hydrogen and hydrogen fluoride.

[redacted]

TABLE II

DIFFERENTIAL THERMAL ANALYSIS

$LiF - BeF_2$ BINARY

DTA NO.	COMPOSITION MOLE PER CENT LiF	BeF_2	SOLID TRANSITIONS °C	EUTECTIC °C	LIQUIDUS °C	LIQUID* (LITERATURE) °C
2L	40	60	220, 270	355	435	413
5L	55	45	220, 260	355	414	400
6L	60	40	260	355	445	427
7L	65	35	300	--	462	450

*ROY, ROY AND OSBORNE, "PHASE RELATIONS AND STRUCTURAL PHENOMENA IN THE FLUORIDE MODEL SYSTEMS $LiF-BeF_2$ AND $NaF-BeF_2$", J. AMER. CHEM. SOC. 3, 85-90 (1950)

PETROGRAPHIC ANALYSIS

Slowly cooled compositions were prepared for examination of the reported compounds in the $LiF-BeF_2$ and $LiF-UF_4$ binary systems (3 in each). None of these was found to be homogeneous.

In an attempt to make Li_4UF_8 and $Li_7U_6F_{31}$ by recrystallizing the quenched glasses, the compositions for both compounds were quenched from 745°C. Neither of the compositions quenched to a glass. Further attempts to produce these compounds, and also LiU_4F_{17}, were made by holding the compositions at the peritectic temperature for extended periods. The Li_4UF_8 sample was held at 500°C for 37 hours; the $Li_7U_6F_{31}$ sample was held at 608°C for 68 hours, and the LiU_4F_{17} sample was held at 750°C for 20 hours. Each sample was then cooled slowly, but still none of the compounds was found to be homogeneous.

The optical properties of the compounds observed were determined petrographically. The two compounds LiU_4F_{17} and $Li_7U_6F_{31}$ were found to possess optical properties in agreement with those reported by Oak Ridge National Laboratory.

The optical properties were determined for a green crystalline phase which was presumed to be Li_4UF_8. The properties, except for the refractive index values, were in agreement with the properties reported for Li_4UF_8. Considerably higher values for the refractive indices were observed than the reported values of 1.460 to 1.472.

FILTRATION STUDIES

Filtration investigation data for the $LiF - BeF_2 - UF_4$ system are shown in Table III. Samples 1 and 2 probably locate a ternary eutectic, but petrographic examination will be required to determine what phases are present at this eutectic. Sample 3 (composition appears to be on the phase for $Li_7U_6F_{31}$) seems to be moving to the same eutectic. Samples 4, 5, 6 and 7 must be in the valley between Li_2BeF_4 and some $[LiF-UF_4]$ compounds. Apparently, the starting composition for samples 4 and 5 lies on the LiU_4F_{17} phase area, and the starting composition for samples 6 and 7 is on the UF_4 phase area.

[redacted]

TABLE III

LIQUIDUS VALUES BY FILTRATION

$LiF - BeF_2 - UF_4$ TERNARY

SAMPLE NO.	ORIGINAL COMPOSITION MOLE PER CENT			TEMP. OF FILTRATION °C	FILTRATE COMPOSITION MOLE PER CENT		
	UF_4	BeF_2	LiF		UF_4	BeF_2	LiF
1	10	20	70	440	9.3	23.0	67.7
2	10	20	70	437	8.0	24.8	67.2
3	13.5	21.5	67	445	9.4	24.2	66.4
4	10	30	60	430	3.3	36.8	59.9
5	10	30	60	446	4.7	32.5	62.8
6	10	45	45	405	1.6	51.9	46.5
7	10	45	45	430	2.1	49.2	48.7

PHYSICAL PROPERTIES

A series of eight viscosity runs was made on the ternary mixture of sodium fluoride, beryllium fluoride, and uranium fluoride over the temperature range of 500° to 900°C. Interpolated values for 600° and 800°C are given in Table IV.

An error was reported in the Mound Laboratory Report CF 55-11-14 on page 15 by C. J. Barton. It was found that the two mole per cent UF_4 viscosity values had been repeated under the four mole per cent headings in the preliminary $NaF - BeF_2 - UF_4$ viscosity report. In view of the interest in this concentration, a corrected and more complete listing for this series is included in Table IV.

An attempt was made to measure the density and the viscosity of pure lithium fluoride (OR Compound #10) from 840° to 1000°C. The lithium fluoride did not wet the walls of the viscometer, and the viscosity results when plotted against the recipocal of the absolute temperature showed a somewhat different slope than that usually obtained. The results are summarized in Table V.

Two viscosity and eleven density determinations were made on the ternary mixture of lithium fluoride, beryllium fluoride, and uranium fluoride over the temperature range of 550° to 900°C. Interpolated values for 600° and 800°C are given in Table VI.

TABLE IV

DENSITY AND VISCOSITY OF NaF, BeF_2, UF_4 TERNARY MIXTURES

(SUPERCEDES THE 4 MOLE % DATA GIVEN ON P. 15, CF 55-11-44)

MOLE PER CENT			600 °C			800 °C		
NaF	BeF_2	UF_4	η *Poise*	ρ *gm/cm³*	η/ρ *Stokes*	η *Poise*	ρ *gm/cm³*	η/ρ *Stokes*
76	20	4	—	—	—	0.0372	2.328	0.0160
74	22	4	—	—	—	0.0429	2.340*	0.0183
72	24	4	0.1100	2.468+	0.0446	0.0505	2.343*	0.0216
70	26	4	0.0970	2.476	0.0392	0.0365	2.350	0.0155
68	28	4	0.0890	2.473*	0.0360	0.0359	2.348*	0.0153
66	30	4	0.0895	2.470*	0.0362	0.0378	2.347*	0.0161
64	32	4	0.0871	2.467	0.0353	0.0352	2.345	0.0150
58	38	4	0.0891	2.443	0.0365	0.0299	2.313	0.0129
52	44	4	0.1171	2.397	0.0489	0.0355	2.279	0.0156
46	50	4	0.1898	2.381	0.0789	0.0475	2.275	0.0209
20	45	35	—	—	—	0.191	4.418	0.0432

*INTERPOLATED VALUE

+EXTRAPOLATED VALUE

TABLE V

DENSITY AND VISCOSITY OF LITHIUM FLUORIDE

TEMPERATURE °C	ρ *gm/cm³*	TEMPERATURE °C	η *Poise*
856.0	1.720	841	0.0189
902.3	1.709	865	0.0187
925.8	1.694	888	0.0171
951.8	1.688	914	0.0169
997.0	1.670	939	0.0165
		967	0.137

[redacted]

TABLE VI

DENSITY AND VISCOSITY OF LiF, BeF_2, UF_4 TERNARY MMXTURES

MOLE PER CENT				600°C			800°C	
LiF	BeF_2	UF_4	η Poise	ρ gm/cm^3	η/ρ Stokes	η Poise	ρ gm/cm^3	η/ρ Stokes
90	10	0		--			1.800	
80	20	0		--			1.8181	
85	13	2		2.012			2.089	
75	23	2		2.152			2.069	
70	28	2		2.127			2.040	
65	33	2		2.132			2.044	
60	38	2		2.107			2.023	
45	51	4	0.0611	2.306	0.0265	0.2941	2.232	0.132
40	56	4	0.1730	2.231	0.0775	1.264	2.180	0.580
35	61	4		2.247			2.219	

X-RAY ANALYSIS

A furnace for X-ray diffraction sample preparation has been set up. Attempts to prepare standard composition samples have been made. To date only LiF-UF_4 standards have been tried. All preparations have failed to reach equilibrium.

Several quenched samples, submitted by Mr. P. A. Tucker, were analyzed by X-ray diffraction. The results are incorporated in the section on petrographic analysis.

Estimates for the design and construction of a continuously focussing X-ray spectrometer for high temperature phase studies were unrealistic and amounted to $ 17,200. This cost is in access to our present complete G. E. X-ray spectrometer and generating unit. Therefore, some other means and possibilities are being studied as an alternative method of accomplishing the same goal.

HIGH TEMPERATURE BRIDGE CALORIMETER

The bridge will have four arms of No. 36 platinum wire, two arms per side connected differentially. The wire was first turned, using a lathe, into a helix by close winding on a 0.010 inch diameter by 14 inch long piece of music wire stretched between a ball bearing in the tail stock and the chuck. The helix was removed by forcibly pulling out the music wire while one end of the helix was tightly clamped in a vise between two 4-inch rubber stoppers. The coils thus formed are bifilar wound at three threads per inch on six-departure coil forms, made at Mound Laboratory, which are $3\frac{1}{8}$ inch long by 0.953 inch in diameter with a 0.040 inch wall. The six-departure threads are nearly rectangular, 0.022 inch by 0.022 inch. The additional two departures are for the heater windings which will be made from Tophet-A wire because of its unusually low temperature coefficient of resistivity and high temperature stability.

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 43 drums containing 19,360 pounds of raffinate residue received from the Mallinckrodt Chemical Works has been processed by the protactinium concentration process outlined in previous technical activity reports. Fourteen drums were treated according to the method outlined in the Mound Laboratory Technical Activities Report for February 15, 1956, Central Files Number 56-2-44. This treatment with hydrochloric acid and sodium chloride was followed by a decantation of excess liquors from the residues by means of a filter stick. The residues have been temporarily stored pending further treatment to extract the protactinium.

Samples of the precipitation slurry from twelve of the fourteen drums were taken for analysis of the distribution of protactinium. The results are given in Table I.

TABLE I

DISTRIBUTION OF PROTACTINIUM

DRUM NO.	RESIDUE WEIGHT PER CENT[a, b]	PROTACTINIUM PER CENT	SUPERNATE PROTACTINIUM PER CENT	TOTAL RELATIVE PROTACTINIUM[a, c]
51	35	93	7	0.59
52	23	88	12	0.62
59	31	95	5	0.47
60	35	63	37	0.64
61	36	87	13	0.45
62	--	92	8	0.45
70	40	94	6	0.38
73	--	91	9	0.46
74	37	91	9	0.35
75	27	66	34	0.32
76	36	65	35	0.36
77	44	81	19	0.38

a. RESIDUE WEIGHT PER CENT AND RELATIVE TOTAL PROTACTINIUM ARE BOTH BASED ON ESTIMATED VALUES OF THE ORIGINAL RAFFIDUE WEIGHT. RAFFIDUE WEIGHT = SLURRY WEIGHT ÷ 6

b. RESIDUE WEIGHT PER CENT IS BASED ON THE WEIGHT OF THE WASHED, CENTRIFUGED RESIDUE, COMPARED WITH ESTIMATED RAFFIDUE WEIGHT.

c. RELATIVE TOTAL PROTACTINIUM IS BASED ON AN ARBITRARY SCALE, WITH THE PROTACTINIUM CONTENT OF DRUM 31 TAKEN AS UNITY.

Examination of Table I shows that the distribution of protactinium was satisfactory to good in all but three of the samples analyzed. In Drum 60, 65, and 76, the distribution was marginal; approximately one-third of the protactinium was lost to the supernatant waste solution. Presumably, these losses could have been avoided by the addition of titanium carrier prior to precipitation, but it is impossible to do development work on each drum before processing.

PROCESS DEVELOPMENT

Recovery of protactinium from the insoluble residues by digestion in sulfuric acid has been studied as a function of the ratio of residue weight to volume of sulfuric acid, the concentration of sulfuric acid, the amount of supernate remaining with the residue, the temperature, and the digestion time.

A sample of the washed and decanted residue slurry from the processing of Drum 51 was taken for development studies. After the sample had settled for one day, it was possible to decant additional wash supernate amounting to approximately one-fourth to one-third of the total volume. The slurry was, however, still very wet. A sample of this material was centrifuged, and the centrifuged weight of the residue was found to be approximately one-half the weight of the slurry. In the experiments to be described, the residue slurry referred to is the material remaining after as much of the wash supernate as possible had been removed by decantation through a filter stick.

In all experiments dealing with sulfuric acid solution efficiency, the protactinium was extracted twice into di-isobutyl carbinol from a solution which was made six-normal in hydrochloric acid. The aqueous phase was discarded; the insoluble residue was digested with hot, concentrated sulfuric acid; the solution was made six-normal in hydrochloric acid; and the residual protactinium was extracted twice into di-isobutyl carbinol. Results are expressed as percentage of the total protactinium recovered by extraction from the first sulfuric acid treatment.

Table II shows the effect of variation in the ratio of volume of concentrated sulfuric acid in milliliters to weight of residue slurry in grams, the effect of maintaining the temperature of the digested slurry at 100°C, and the effect of the concentration of sulfuric acid in the digestion at 100°C.

The most significant improvement in solution efficiency, according to the results in Table II, was that due to the increase in sulfuric acid concentration to a nominal 36-normal. Some improvement occurred when the ratio of sulfuric acid to residue slurry was increased, but practical considerations make this approach undesirable on a plant scale; an increase of one part of sulfuric acid requires an increase in total aqueous volume of four parts because of the necessity for making the solution six-normal in hydrochloric acid. (Before the hydrochloric acid can be added, the sulfuric acid concentration must be reduced to about 18-normal; otherwise vigorous evolution of hydrochloric acid gas occurs due to the heat of dilution of the sulfuric acid.)

To determine whether the proper conditions for protactinium recovery could be obtained by evaporation, a sample of residue slurry was evaporated to dryness on a steam bath. Concentrated sulfuric acid (one milliliter per gram of residue slurry) was added to the dried cake. No noticeable heat was generated, but the sample effervesced, and fumes of hydrochloric acid were noted. An equal volume of distilled water was added, and the mixture was stirred until it cooled to room temperature. The usual extraction procedure was followed; only 65.1 per cent of the protactinium was recovered by this treatment.

TABLE II

EFFECT OF SEVERAL FACTORS ON SULFURIC ACID SOLUTION EFFICIENCY

H_2SO_4 RATIO	H_2SO_4 CONCN [a] (*N*)	STIRRING TIME (*min*)	COOLING RATE	DIGESTION TEMPERATURE [b]	RECOVERY % Pa
1.0	24	30	SLOW	RT	78.4
1.2	25	30	SLOW	RT	76.7
2.2	29	30	SLOW	RT	86.5
1.0	24	30	SLOW	100°	78.6
1.0	24	60	FAST	100°	80.9
1.0	36	60	FAST	100°	92.4
1.0	18	60	FAST	100°	79.4
1.5	18	60	FAST	100°	74.0

a. SULFURIC ACID CONCENTRATION IS BASED ON THE ASUMPTION THAT ONE-HALF THE RESIDUE SLURRY WEIGHT WAS LIQUID. LOWER SULFURIC ACID CONCENTRATIONS WERE OBTAINED BY ADDING MEASURED VOLUMES OF WASH SUPERNATANT TO THE SLURRY. THE SINGLE 36 *N* H_2SO_4 CONCENTRATION WAS OBTAINED BY CENTRIFUGING THE RESIDUE SLURRY AND DISCARDING THE SUPERNATE.

b. IN ALL CASES, THE ADDITION OF SULFURIC ACID CAUSED A RISE IN TEMPERATURE, BUT THE RT SAMPLES WERE ALLOWED TO COOL TO ROOM TEMPERATURE WITH CONTINUOUS STIRRING. IN THE 100°C EXPERIMENTS, THE SAMPLES WERE MAINTAINED AT THAT TEMPERATURE WITH OCCASIONAL STIRRING DURING THE INDICATED TIME.

To determine whether the recovery of protactinium could be improved by additional washing, a sample of residue slurry was washed three times with ten times its volume of distilled water. The centrifuged residue had 59 per cent of the weight of the original slurry; no protactinium was found in any of the wash supernates. Sufficient water was added to the residue to make up the weight lost during the washing, and concentrated sulfuric acid (one milliliter per gram of residue slurry) was added. The mixture was heated 30 minutes, cooled, adjusted with hydrochloric acid, and extracted. The organic phases contained 92.6 per cent of the protactinium. This value compares favorably to the 92.4 per cent recovery obtained with 36 normal

TABLE III

EFFECT OF ADDITION OF DILUTED SULFURIC ACID

H_2SO_4 RATIO[a]	H_2O RATIO[b]	DIGESTION TEMPERATURE °C	STIRRING TIME[c] min	RECOVERY % Pa
2.0	0.0	RT	60	22.5
2.0	1.0	RT	60	13.7
2.0	2.0	RT	60	14.1
2.0	2.0	100	60	31.0

a. MILLILITERS OF 1:1 H_2SO_4 PER GRAM OF RESIDUE SLURRY

b. MILLILITERS OF DISTILLED WATER ADDED PER GRAM OF RESIDUE SLURRY

c. ALL SAMPLES ALLOWED TO SETTLE OVERNIGHT BEFORE SEPARATION OF PHASES. 100°C SAMPLE COOLED SLOWLY IN HOT WATER BATH OVERNIGHT

The recommendation had been made that means be found for filtering off as much of the supernatant liquor as possible. This has now been done, and the residue slurries have been brought to a condition comparable to that obtainable by laboratory centrifugation. Experimental work was therefore directed towards determining the optimum conditions for recovery or protactinium from centrifuged residues.

Table IV shows the results obtained from experiments in which the residue slurry from Drum 52 was used as source material. In all cases, the residue slurry was centrifuged and the supernatant liquor was discarded. The centrifuged residue was washed with tap water, and the water wash was discarded. The residue was weighed, and concentrated sulfuric acid was added in the ratio indicated (milliliters of sulfuric acid per gram of washed, centrifuged residue). In one sample, distilled water was added to the residue, and in another sample, two milliliters of two-normal nitric acid was added to the residue, before the addition of sulfuric acid. In all cases, the mixtures were heated for 30 minutes at 100°C with occasional stirring.

TABLE IV

CONDITIONS FOR RECOVERY OF PROTACTINIUM FROM WASHED, CENTRIFUGED RESIDUES

H_2SO_4 RATIO[a]	H_2SO_4 NORMALITY	RECOVERY Pa PER CENT
2.0	36	92.6
1.0	36	92.9
0.75	36	87.8
1.0	18	85.4
1.0	18	78.4[b]

a. MILLILITERS OF CONCENTRATED SULFURIC ACID PER GRAM OF WASHED, CENTRIFUGED RESIDUE

b. SOLUTION WAS ONE NORMAL IN NITRIC ACID

The experiment reported in Table IV in which dilute nitric acid was added to the residue was to have been the first in a series to determine if the troublesome organic material usually found at the di-isobutyl carbinol interface could be eliminated by oxidation with nitric acid. The result obtained in the single experiment is reported at this time. However, because of the apparently deleterious effect of nitric acid, future studies on the mechanism of solution of protactinium precipitates in sulfuric acid should include a study of the effect of nitric acid.

In the course of the analytical work reported in Table I, the applicability of the one-to-one sulfuric acid to residue ratio has been tested. The results are reported in Table V.

TABLE V

SULFURIC ACID SOLUTION EFFICIENCY FOR SEVERAL DRUMS

(H_2SO_4/RESIDUE RATIO - 1 ML/GRAM; TEMP. 100°C.)

DRUM NO.	DIGESTION TIME *min*	RECOVERY % Pa
51	60	92.4
52	30	92.9
59	15	94.5
60[a]	60	96.6
61[a]	60	93.9
70	15	96.6
75	15	97.5
76	15	96.9
77	15	96.5

a. RATIO OF H_2SO_4 TO RESIDUE WAS 1.3 ML PER GRAM

RECOMMENDED PROCESS

The final recommendation made in regard to the processing of the remaining drums of raw material and of the residue slurries from drums already processed is as follows:

> To 500 pounds of raw material, add 240 gallons of water and 60 gallons of 20° Baume muriatic acid. Heat the mixture at about 100°C for one hour. Add 500 pounds of salt (water-softner grade) and heat the mixture for one hour at about 100°C. Allow the slurry to cool and settle overnight. Siphon off and discard the supernatant liquor. Wash the residue with 300 gallons of water and allow the slurry to settle overnight. Siphon off and discard as much as possible of the supernatant liquor. Filter off the remaining liquor until the residue is nearly dry. (The residues from several drums may be combined either before or after the washing step.)
>
> Weigh the residue. Add 1.84 lbs of 66° Baume sulfuric acid for each pound of residue. Mix and maintain the slurry at about 100°C for fifteen minutes. Allow

the mixture to cool to room temperature. Add slowly and with constant stirring 0.124 gallon of water per pound of residue (one gallon of water per gallon of sulfuric acid). Allow the mixture to cool to room temperature. Add 0.3 gallons of 20° Baume muriatic acid per pound of residue and mix. Add 0.1 gallon of a one-to-one mixture of di-isobutyl carbinol and inert diluent (such as Amsco Special Solvent #1). Mix the slurry vigorously for fifteen minutes; allow the phases to separate, and siphon off the organic phase. Repeat the addition of di-isobutyl carbinol and the extraction. Combine the organic phases and transfer this mixture to the stripping operation. Discard the insoluble residue and the aqueous phase.

PURIFICATION OF PROTACTINIUM

Approximately one liter of hydroxide slurry from the HH-Building operation was treated with three liters of concentrated hydrochloric acid and extracted with di-isobutyl carbinol. The organic phase was stripped with water, and the aqueous phase was adjusted to six-normal in hydrochloric acid. This solution was extracted with di-isobutyl carbinol, and again stripped. A small precipitate developed in the aqueous strip, and was centrifuged out.

This precipitate was found to be soluble in hot, concentrated sulfuric acid, and underwent several cycles of extraction, stripping, precipitation, and solution. It was finally extracted into approximately two milliliters of di-isobutyl carbinol, and this solution was transferred to a liquid sample holder for examination by X-ray fluorescence.

A strong peak was found at the point predicted for protactinium from the known positions of the thorium and uranium peaks. On the basis of the intensity of the peak of a thorium solution of known concentration, it was estimated that the di-isobutyl carbinol contained approximately five milligrams of protactinium.

The sample contained an unknown quantity of niobium and possibly zirconium, but no tantalum was found. Because of the limitations of the method, it was not possible to analyze for titanium.

It was found that, whenever the protactinium was stripped out of di-isobutyl carbinol into a water solution, a precipitate developed. The addition of a drop of phosphoric acid to one or two milliliters or more of water strip caused this precipitate to carry protactinium quantitatively.

When the precipitate was treated with a very dilute solution of hydrogen peroxide, solution of the precipitate was nearly complete. However, a very minute precipitate remained which was found by gamma counting to contain over 90 per cent of the protactinium. The counting rate was far too high for gamma, pulse-height analysis without absorbing material; in view of the estimate of five milligrams of protactinium by X-ray fluorescence, it seems certain that Mound Laboratory has now produced visible quantities of a pure protactinium compound, probably a hydrated oxide. The precipitate appears to be readily soluble in hot, concentrated sulfuric acid, but the quantity available is so small that it is difficult to determine at this time whether the solution is colloidal or clear.

EFFECT OF MIXED ACID SOLVENT ON SOLUTION OF SLURRY FROM HH-BUILDING

Examination of the residues remaining after the slurry as received from the HH-Building process had been dissolved in concentrated hydrochloric acid had suggested a possible beneficial result if the original slurry were treated with a mixture of hydrochloric and sulfuric acids. Several systems were examined as listed in Table VI.

TABLE VI

EFFECT OF VARIOUS RATIOS OF HYDROCHLORIC ACID AND SULFURIC ACID IN RECOVERY AND EXTRACTION OF PROTACTINIUM FROM SLURRY

RATIO OF VOLUMES SLURRY : CONC. HCl: 18 N H_2SO_4	PER CENT OF Pa REMAINING IN AQUEOUS AFTER EXTRACTION	PER CENT OF Pa EXTRACTED	PER CENT OF Pa REMAINING IN INSOLUBLE RESIDUE
2 : 3 : 1	19.3	78.0	2.7
2 : 4 : 1	4.8	93.3	1.9
2 : 5 : 1	4.6	93.2	2.2
4 : 11 : 1	3.0	91.8	5.2
1 : 3 : 0	4.1	85.5	10.5

Thus it appears that the addition of a small amount of 18-normal sulfuric acid yields a marked increase in the recovery of the protactinium. These findings will be incorporated into the operation of the mixer-settler apparatus described in another section of this report.

The effect of partial substitution in the acid solvent, of sulfuric acid for hydrochloric acid on solution efficiency and residue settling characteristics was studied. The same settled slurry used in experiments described in the last three activities reports was used as starting material. Ten milliliter slurry samples were washed with 40 milliliters of water, and the slurry was separated by centrifuging. (The washed slurry settles satisfactorily under gravity. Centrifuging was used to save time.) The acid solvent was added, the mixture was stirred for one hour at room temperature, and the residue was then allowed to separate by standing overnight. In the control test, three milliliters of 12-normal hydrochloric acid per milliliter of settled slurry was used as solvent. This corresponds to 30 milliequivalents of hydrogen chloride per milliliter of slurry. In the first mixed solvent test, 2.75 milliliters of 12-normal hydrochloric acid and 0.25 milliliters of 18-normal sulfuric per milliliter of slurry were employed. The last test employed 2.50 milliliters of 12 normal hydrochloric acid and 0.50 milliliters of 18-normal sulfuric acid per milliliter of slurry.

The results of the tests are shown in Table VII. The introduction of sulfuric acid reduced the bulk of the residue and lightened its color. The sulfuric acid reduced the amount of flocculent solid which remained suspended in the solution, but failed to eliminate it entirely. Also, the solutions continued to remain unstable, since flocculent post-precipitates appeared in all three solutions after standing forty-eight hours.

The total solution volume was the same in all three tests so that the counting rate on a four-milliliter sample could be taken as a relative measure of solution efficiency. As judged by the 27 and 300 Kev counting rates, the use of sulfuric acid improved the protactinium solution efficiency by approximately ten per cent. The counting rate at 85 Kev was increased by only about seven per cent. This difference in improvement can be attributed to the slight solubility of a radioactive sulfate, perhaps that of radium. As will be shown, a definite fraction of the 85 Kev activity may be due to extra-protactinium constituents.

TABLE VII

EFFECT OF MIXED ACID SOLVENTS ON SOLUTION OF SLURRY[a]

ML OF ACID PER ML OF SLURRY		RESIDUE CHARACTERISTICS			ACTIVITY IN SOLUTION (COUNTS PER MIN PER 4 ML)		
12 *N* HCl	18 *N* H_2SO_4	VOLUME ML	COLOR	SETTLING RATE	27 KEV	85 KEV	300 KEV
3	0	5	GRAY	POOR	6266	1900	1397
2.75	0.25	2	NEARLY WHITE	IMPROVED	6734	2030	1591
2.50	0.50	2	NEARLY WHITE	IMPROVED	6920	2040	1558

a. SLURRY PRE-WASHED WITH 4 VOLUMES OF WATER. ONE-HOUR SOLUTION PERIOD AT ROOM TEMPERATURE. RESIDUE SEPARATED BY OVERNIGHT SETTLING

ION EXCHANGE PROCESS DEVELOPMENT

EFFECT OF FLOW RATE ON BREAKTHROUGH CURVES. To check the effect of flow rate on breakthrough capacity, one-centimeter diameter ion exchange columns were charged with Dowex-1 resin to a depth of two centimeters and were then pre-treated with three column volumes of 9-normal hydrochloric acid. The feed solution was passed steadily through the column, and the effluent was collected in successive fractions and gamma counted.

The first run (Run 51) utilized a feed which had been prepared by pre-washing the slurry with sodium Versene solution, followed by a water wash. The slurry was then dissolved in 12-normal hydrochloric acid, using 36 milliequivalents of hydrogen chloride per milliliter of settled slurry. The residue was allowed to settle for two days, after which the flocculent material remaining in suspension was centrifuged out. This feed (denoted 56L), which had an acid normality of 9.6, was fed through the column at a flow rate of 0.44 milliliters per minute.

Table VIII gives the counting rates of successive effluent fractions, relative to that of the feed. The 27 Kev count gave a typical S-shaped breakthrough curve. The protactinium breakthrough point, taken as the volume at which the relative concentration reached 0.03, came at about 16 milliliters after holdup correction. The 85 Kev curve rose rapidly during the initial effluent fractions, leveled off at a relative concentration of 0.20 and then resumed its rise at the 27 Kev breakthrough point. The 68 Kev curve was similar to that for 85 Kev except that the temporary flat in the curve came at a relative concentration of 0.42. The 300 Kev curve approximated that for the 27 Kev activity. All four curves became asymptotic to a relative concentration of unity as the volume of effluent continued to increase.

The results of Table VIII show that 20 per cent of the 85 Kev activity and 42 per cent of the 68 Kev activity in the feed are due to radioactive constituents not sorbed by the resin. The constituents might be radium and thorium, respectively, which remained in spite of the pre-wash with Versene.

TABLE VIII

BREAKTHROUGH EXPERIMENT: RELATIVE CONCENTRATIONS OF SUCCESSIVE EFFLUENTS AS MEASURED BY GAMMA COUNTING AT FOUR ENERGY LEVELS

(FEED PREPARED BY DIRECT SOLUTION OF SLURRY - RUN 51)

ACCUMULATED EFFLUENT VOLUME ml	RATIO OF EFFLUENT CONCENTRATION TO FEED CONCENTRATION			
	27 KEV	68 KEV	85 KEV	300 KEV
1.7	0.000	0.000	0.005	0.014
5.0	0.006	0.183	0.110	0.015
8.3	0.012	0.332	0.154	0.039
11.6	0.008	0.420	0.189	0.049
14.9	0.012	0.426	0.214	0.033
18.2	0.042	0.421	0.222	0.073
21.5	0.147	0.510	0.330	0.185
24.8	0.531	0.727	0.569	0.561
28.1	0.816	0.931	0.822	0.761
31.4	0.949	0.954	0.899	0.893

Run 52 was similar to Run 51 except that the flow rate was increased about five fold. Another minor difference was caused by the formation of a small amount of additional precipitate in the feed which had to be removed. The precipitation resulted in a slight reduction in the activity as is evident from Table IX where Run 52 is compared with Run 51. However, the large reduction in protactinium breakthrough capacity, from 16 milliliters to 6 milliliters, is believed to be mainly the result of the increased flow rate. The increased flow rate also caused the flats in the 85 Kev and 68 Kev breakthrough curves to become rather indefinite points of inflection.

TABLE IX

RESULTS OF BREAKTHROUGH TESTS ON ION EXCHANGE COLUMNS WITH VARIOUS FEEDS

RUN NO.	FLOW RATE *ml/min*	FEED CONCN. AT 27 KEV *cts/min/3 ml*	ACID NORMALITY OF FEED	BED DEPTH *cm*	RELATIVE CONCN. AT TEMPORARY FLAT 85 KEV	RELATIVE CONCN. AT TEMPORARY FLAT 68 KEV	Pa BREAKTHROUGH POINT ($C/C_0 = 0.03$) *ml*
		FEED PREPARED BY DIRECT SOLUTION OF SLURRY					
51	0.44	6110	9.6	2	0.20	0.42	16.0
52	2.20	5674	-	2	-*	-*	6.0
		SODIUM SULFATE ADDED TO FEED					
53	0.50	4000	8.6	2	0.12	0.42	20.0
		FEED PREPARED BY SOLVENT EXTRACTION					
54	0.50	32436	9.0	2	-	-	3.5
55	0.41	32436	9.0	4	-	-	6.5

*INFLECTION POINTS ONLY BECAUSE OF HIGH FLOW RATE

EFFECT OF SULFATE ION ON BREAKTHROUGH CURVES. To determine how the presence of sulfate ion might affect the breakthrough capacity, the feed used in run 52 was treated with sufficient sodium sulfate to make it 0.1 normal in sulfate ion. An insoluble solid remained which resulted in a 30 per cent reduction in the 27 Kev activity of feed solution. Also, the acid normality was found to have dropped to 8.6. The feed gave a strong positive test for sulfate ion. This feed was run through the column at a flow rate of 0.5 ml per minute. The results of the run (Run 53) are compared with the previous runs in Table IX. The reduction in the relative concentration of the flat in the 85 Kev breakthrough curve, as compared with Run 51, is consistent with the assumption that radium was removed by the sulfate treatment. The marked increase in protactinium breakthrough capacity, in spite of the lower acidity, may be attributed to the reduction in concentration of macro-constituents by the sulfate addition. The presence of sulfate ion in the feed presumably presents no major obstacle to sorption of protactinium by the resin.

BREAKTHROUGH CURVE FOR FEED PREPARED BY SOLVENT EXTRACTION. It was desired to determine the breakthrough capacity of a feed prepared by solvent extraction. The feed, which was available for this purpose, had been prepared by treating the water-washed slurry with a mixture of hydrochloric and sulfuric acids, using the proportions employed in the second run of Table VII. The mixture of solution and residue was extracted with di-isobutyl carbinol (one volume of organic solvent to one volume of original slurry), and the organic was stripped twice with water, (each strip employing 0.06 volume of water to one volume of di-isobutyl carbinol). The combined strip solutions had an acid normality of 4.45. Sufficient 12-normal hydrochloric acid was added to bring the acidity to 9-normal.

As is evident from Table IX the resulting feed (F-61) was perhaps five times as concentrated in protactinium as the previous feeds prepared by simple solution and settling. The total solid content of the feed, on a dry basis, was found to be 0.0404 gram per milliliter. It appeared to be much more concentrated in iron than feeds prepared by simple solution, but gave only a weak test for sulfate ion. The feed prepared as just described had a volume of about one-half that of the original slurry, whereas preparation by simple solution and settling would give a feed whose volume was four times that of the slurry. Also, the feed prepared by solvent extraction has so far proved to be quite stable and devoid of post precipitates

The last section of Table IX gives the results of two breakthrough tests, using the feed prepared by solvent extraction. Run 54 was made with a bed depth of two-centimeters and a flow rate of 0.5 milliliter per minute. The unexpectedly low breakthrough capacity might be attributed to the higher iron concentration. Comparing Run 54 with Run 51 (Table IX) one notes that the 27 Kev counting rate of the feed is approximately inversely proportional to the breakthrough capacity. Gamma counting rates of successive effluent fractions for Run 54 are given in Table X.

TABLE X

BREAKTHROUGH EXPERIMENT: RELATIVE CONCENTRATION OF SUCCESSIVE EFFLUENTS AS MEASURED BY GAMMA COUNTING AT FOUR ENERGY LEVELS

(FEED PREPARED BY SOLVENT EXTRACTION PROCESS-RUN 54)

ACCUMULATED EFFLUENT VOLUME ml	RATIO OF EFFLUENT CONCENTRATION TO FEED CONCENTRATION 27 KEV	68 KEV	85 KEV	300 KEV
1.45	0.000	0.000	0.000	0.000
4.35	0.031	0.038	0.030	0.006
7.25	0.227	0.199	0.208	0.209
10.15	0.736	0.665	0.688	0.711
13.15	0.932	0.929	0.888	0.940
16.05	0.947	0.921	0.952	0.977
18.95	0.969	1.010	0.971	1.027

As a further check, the breakthrough test was repeated, using a Dowex-1 bed four-centimeters deep. As expected, the breakthrough capacity for this run (Run 55) was approximately double that of Run 54, which employed a two-centimeter bed.

A marked difference between the runs with the feed prepared by solvent extraction and those with the feed prepared by direct solution was the complete absence of temporary flats in the 68 Kev and 85 Kev breakthrough curves in the case of the former runs. The breakthrough curves for 68, 85, and 27 Kev activity were all typically S-shaped and identical when the feed prepared by solvent extraction was used. The extraction procedure thus succeeded in removing the radioactive impurities responsible for the flat portions of the 68 and 85 Kev breakthrough curves.

SOLVENT EXTRACTION

CONCENTRATION OF PROTACTINIUM. The processing of 43 drums in the HH-Building yielded approximately 200 gallons of slurry which was used as the starting material for this phase of the protactinium concentration project.

An experimental gravity-fed mixer-settler unit was set up, using regular laboratory glassware and flexible tubing. The feed solution was prepared by mixing one volume of washed slurry as received from the HH-Building with three volumes of concentrated hydrochloric acid. The system was stirred for one-half hour before feeding the mixer-settler. Undissolved material was not removed from this feed. The organic extractant was prepared by mixing one volume of di-isobutyl carbinol, previously saturated with six molar hydrochloric acid, with one volume of Amsco Mineral Spirits. The ratio of the volume of the organic extractant to that of the feed solution was four. Water was used to strip the organic extractant after it had contacted the feed solution. The ratio of the volume of the water strip to that of the organic extractant was one-tenth. One liter of feed solution was extracted three times. For each pass through the mixer-settler, the aqueous solution was contacted with fresh organic extractant. The first extractant removed 78 per cent of the total protactinium, the second extraction removed 18 per cent of the total protactinium, and the third extraction removed three per cent of the total protactinium. It was indicated that counter-current extraction may be beneficial.

An all glass mixer-settler unit readily adaptable to counter-current operation, and having a capacity of about four gallons per hour was fabricated locally. Tests of this unit indicated that it would be satisfactory, so a total of eight units were made up to be installed in the 1-B area of the GP-Building. The same Sigma pumps as used for the pulse-column extraction work will be used.

While the area in the GP-Building was being readied for use, two extraction units and and two stripping units were set up using gravity feed in R-149. Although the gravity feed yielded erratic operation, constant surveillance obtained satisfactory ratios of liquids. One of the mixer-settlers was operated to process 40 liters of feed without cleaning out the solids at the interphase in the settler. The organic effluent remained clear of solids. The organic system was stripped with water and collected over six normal hydrochloric acid. After washing, the di-isobutyl carbinol solution was recycled through the extractor.

Analyses of the feed solution and the raffinate indicated that 93.5 per cent of the protactinium had been extracted in a single pass through the mixer-settler. It may be that the increased efficiency of the mixer-settler unit as fabricated locally will eliminate the need for a two-stage counter-current extraction of the feed solution.

EFFECT OF DIFFERENT DILUENTS. In the previous development work reported for the solvent extraction of protactinium by di-isobutyl carbinol, a special naphtha (oleum treated) was used as the diluent for the di-isobutyl carbinol. In one series of tests, a mineral spirit equivalent to the special naphtha but not oleum treated was used as the diluent. In a second series of tests, a commercial safety solvent, drummed by Sinclair Oil Company, was used to dilute the di-isobutyl carbinol. For these tests, four volumes of the slurry were reacted with eleven volumes of concentrated hydrochloric acid and one volume of 18-normal sulfuric acid to prepare the feed solution. After the feed solution had been stirred for one-half hour, it was contacted vigorously with one-fourth its volume of organic extractant In all cases, extractions appeared to be equally effective with no dependency upon the diluent. During the stripping of the extractant with water, more insoluble material appeared at the interface in the cases where safety solvent was used as the diluent. However, the quantity of solids was not excessive and the aqueous phase was readily separated from the organic layer

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.

Batch operation with the one inch ID by 12 foot long column has led to the optimum pressure and equilibrium time determination for 50 atomic per cent mixtures of hydrogen and deuterium. For a 0.016 inch diameter center wire at a temperature of 900°C the optimum initial pressure is approximately 1.0 atmosphere. After three hours running time under these conditions, the column exhibits an essentially equilibrium separation factor of approximately 4,000. Under the same conditions with an initial pressure of 1.25 atmospheres the equilibrium separation factor is approximately 1,600.

Equilibrium samples of H_2, HD, and D_2 obtained at one-foot intervals along the one inch ID column have been obtained for mixtures of hydrogen and deuterium containing 50, 65, and 80 atomic per cent deuterium, but analyses of these samples have been completed only for the first mixture. The results showed that the gas samples at each port are completely equilibrated with respect to H_2, HD, and D_2 fractions, with the exception of the bottom one-third of the column. As yet no definitive explanation for this apparent anomaly has been established, but there are two possibilities under consideration at present. The analysis indicated that the hydrogen concentration at the bottom end of the column is higher than would be expected; i.e., the hydrogen and deuterium concentrations are not symmetric along the column. The relatively high hydrogen concentration at the bottom of the column may be due to the dead gas volume in the well; or may be due to moisture which may have been admitted to the column with the gas mixture, thereby permitting an exchange of deuterium for hydrogen in the moisture with an exchange period substantially greater than the equilibrium time of the column. A liquid nitrogen trap is being installed in the feed gas-line to remove the moisture and eliminate its possible effects.

Optimum pressure and equilibrium time have been determined for the 1.25 inch ID by 12 foot long column with 50 molecular per cent mixtures of hydrogen and helium for a 0.016 inch diameter center wire temperature of 600°C. The optimum initial pressure for these conditions is approximately 0.80 atmosphere. After two and one-half hours running time, the column exhibits an equilibrium separation factor of approximately 10,000

A total of 125 hydrogen-deuterium gas samples and 65 hydrogen-helium gas samples were analysed on the mass spectrometer this month. This work was done in conjunction with the above experimentation. The mass spectrometer was out of operation for one week while the instrument was shut down to repair a faulty Phillips gauge. A number of standard gas samples covering the concentration range of hydrogen-deuterium mixtures and hydrogen-helium mixtures are being prepared. These samples will be used to recalibrate the mass spectrometer for analysis of column samples in the corresponding concentration ranges.