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MOUND LABORATORY
Operated By
MONSANTO CHEMICAL COMPANY
MIAMISBURG, OHIO

MONTHLY TECHNICAL ACTIVITIES REPORT
THROUGH JULY 17, 1955

BY

D. L. SCOTT, J.F. EICHELBERGER, AND F. C. MEAD, Jr.

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POLONIUM-210 OPERATIONS

This program is concerned with the production of polonium sources and the disposal of radioactive waste. Work is being done to improve the present methods and processes.

Thirteen polonium-beryllium neutron sources, one polonium-carbon neutron source, one polonium-sodium fluoborate neutron source, one americium-beryllium neutron source, and five alpha sources were fabricated and shipped in June 1955. Six of the polonium-beryllium sources, the polonium-sodium fluoborate source, the americium-beryllium source, and the five alpha sources were for other AEC sites.

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

TABLE I

DISCHARGE VOLUME	-	381.400	GALLONS
TOTAL ALPHA ACTIVITY	-	6.0	MILLICURIES
TOTAL BETA ACTIVITY	-	14.1	MILLICURIES
ACTIVITY DENSITY	-		
ALPHA	-	5.0	C/MIN/ML
BETA	-	11.0	C/MIN/ML

THERMAL DIFFUSION PROJECT

Several thermal-diffusion columns are to be designed so as to permit study of the separation factor as a function of the variables in the equations. Experiments are to be made on the separation of various binary mixtures of light-element gases. It is hoped that predictions can be made of and observations extended to the isotopic separation of ternary mixtures by thermal diffusion.

Work was completed on the equilibrium time and optimum pressure determination of 50 per cent molecular mixtures of hydrogen and helium in the 1.00 inch ID column for a center wire temperature of 600°C. The separation process reaches a substantial equilibrium between three and four hours of operation. The optimum initial pressure was not clearly defined but the results indicate that the optimum pressure is in the range of 1.20 to 1.30 atmospheres under these conditions. Optimum pressure and equilibrium time data are now available for the 1.00 inch ID, the 1.25 inch ID, and 1.61 inch ID columns for a center wire temperature of 900°C and also for center wire temperatures of 310°C and 600°C for the 1 inch ID column

Work has been continued on the column mis-alignment effects by using argon isotopes in natural abundance in the 1.25 inch ID column. Center wire eccentricity data are still not conclusive enough for quantitative evaluation, but the effect is definitely detrimental to the separation factor. However, if the center wire is held concentric with the tube, the twelve-foot column may be moved several centimeters out of verticality without apparently degrading the separation factor.

A total of 45 hydrogen - helium gas samples and 67 argon samples were analysed on the mass spectrometer during this period in conjunction with the above experimentation.

All work on the thermal diffusion columns has been curtailed as of July 1, 1955 pending approval of the proposed program for additional research

LIVERMORE PROJECT

The Livermore program is concerned with production of lithium deuteride blocks, pressed and canned to meet specifications of a Livermore Laboratory research project.

INTRODUCTION

The installation of the Lectrodryer into the helium atmosphere drying system reduced the water vapor content to very low levels. The specification which limited the hydroxide content of the canned blocks was waived by the University of California Radiation Laboratory The remainder of the first fifty kilograms of enriched salt (old reprocessed material) was processed and sealed into cans. Shipment number three was sent to Livermore, California, and shipment number four is in the process of being packed. Operations have started on the new enriched material.

OPERATIONS

DRY-BOX ATMOSPHERE. The original piping of the circulating drying system was modified considerably with the installation of the Lectrodryer unit All globe valves were replaced with gate valves so that air stream impedance would be a minimum. The installation of four gate valves permits the sealing dry-box to be isolated from the other three dry-boxes so that optimum conditions of dryness will prevail Helium atmosphere samples for dew point measurements can be selected from five different locations within the drying system, and pressure drops can be measured at these same points The panel which held the control valves was mounted near the blower unit The entire new system was found to be versatile and efficient in its operation.

During the operations when the remainder of the first fifty kilograms was sealed the dew points were found to be at about -80°F. Some readings were -100°F and lower. Difficulties were encountered with the uranium furnace which removes the oxygen from the helium atmosphere. Since the temperature required to react the oxygen with the uranium sometimes exceeds 350°C, the silicone rubber gaskets deteriorated and leakage of helium gas occurred The furnace had to be disassembled, reassembled, and filled with freshly cleaned uranium chips. New gaskets were installed to help keep the oxygen content low.

The capacity of the Lectrodryer, with two-hundred and fifty pounds of activated alumina, was large enough to maintain low dew points during periods of maximum sealing operations, without the use of additional drying agents in the recirculating system. The cost of chemical drying agents has exceeded the cost of a complete Lectrodryer unit

CURING AND SEALING. Nine cured batches containing about 18 7 kilograms of type "A" salt were canned in 18 two inch cans, 93 four inch cans, and 48 six inch cans. All cans were inspected, leak checked, and prepared for shipment. Out of the first 50 kilograms of old type "A" material, about 44 kilograms were processed into blocks, cured, sealed, inspected, and accepted for shipment. The remaining 5.9 kilograms will be accounted for as scrap and will not be processed. Shipment number four is being processed for immediate delivery.

ANALYSIS. The lithium hydroxide analysis of the second 25 kilogram shipment of salt from Oak Ridge National Laboratory (part of the original 50 kilograms) was erratic and inconclusive. The very high percentage of impurities introduced many difficulties into the analytical techniques, and the results were very questionable. The lithium hydroxide content in cured, sealed, cans varied from 500 to over 2,100 parts per million. It is reasonable to assume that, in many instances the actual hydroxide content may have been considerably lower, because of reaction of the impurities with the iron crucible during analysis.

The electronic controller unit to be used in conjunction with the induction heater for the hydroxide analysis has been completed, and the equipment is ready for test runs.

WEIGHING, PRESSING AND CHAMFERING. About 88 kilograms of newly processed type "A" material was received from Oak Ridge for processing the remaining blocks. Theoretically about 59.2 kilograms of this material must still be processed to prepare the total quantity of cans required. The Oak Ridge analytical results report a hydroxide content of about 1.5 per cent, while other impurities are considerably less than for the first 50 kilograms of this material.

Operations were started in weighing, pressing, gaging, and chamfering this salt, and will continue for two to three weeks.

ALUMINUM CAN PREPARATION. The cans and lids required for sealing all of the remainder of the type "A" salt have been prepared. Work is proceeding on those that will be used for canning the remainder of the type "B" material, which will be canned after all of the typical "A" material has been processed.

THORIUM PROJECT

The thorium project is directed toward development and operation of a process suitable for extraction of thorium from Brazilian monazite sludge and AEC waste materials. The process must produce a thorium salt suitable for the preparation of metallic thorium of high purity.

INTRODUCTION

Since the thorium project was cancelled in May, work has continued on the development of a process flow sheet for the extraction of thorium from Brazilian hydroxide sludge. The batch counter-current and the pilot plant solvent extraction work have continued, but the analytical development work and the waste treatment work have been stopped.

SOLVENT EXTRACTION

A summation of batch counter-current data for thorium extraction from Brazilian sludge as presented in the progress report for June 17, 1955, was followed by a study of partitioning, using batch counter-current equipment, during the period ending July 17, 1955. For the first cycle of the designed thorium refinery, sufficient data is available, from batch counter-current studies for the extraction of thorium from digested sludge and for the partitioning of thorium from uranium, to present sufficient data to permit pilot plant study. Although a few runs by batch counter-current equipment have been made on the clean up of the tributylphosphate in Amsco solvent, especially the stripping of uranium from this solvent with sodium carbonate, these data are insufficient to permit any conclusions to be drawn.

Analyses on the partition, batch counter-current runs for comparison purposes were made at the 61st equilibration. The feed was of the same concentration in partition runs 10P to 18P inclusive. This feed was obtained from batch counter-current extraction runs 25A/o. It contained 40.02 grams per liter of thorium, 1.12 grams per liter of uranium, and had a free nitric acid concentration of 0.234 N. The organic solvent in these partition runs was 40 per cent tributylphosphate in Amsco (Special Naphtha No. 1) diluent. Table I summarizes the data from these partition runs, which used a variance in flow ratios as well as a variance in the nitric acid concentration of the aqueous scrub. Distribution ratios, extraction factors, per cent saturation, and the concentration of thorium, uranium and acid, for the five scrub and eight strip stages are available but are not included in this report.

The data in Table I indicates a flow ratio of 1 of feed to 0.9 of 0.15 N nitric acid aqueous scrub to 0.3 of 40 per cent tributylphosphate in Amsco (Special Naphtha No. 1) as the best condition for the partitioning of thorium and uranium.

TABLE I

PARTITION RUN NO.	FLOW RATIO F:S:O	SCRUB N-HNO_3	THORIUM LOSS PER CENT	U-Th SEPARATION FACTOR	Th-U SEPARATION FACTOR
10P	1:0.9:0.3	0.3	5.07	100	24.5
11P	1:0.9:0.3	0.2	4.13	1940	31.0
12P	1:0.9:0.3	0.1	1.46	1401	95.3
13P	1:0.9:0.4	0.1	1.67	1129	83.4
14P	1:0.9:0.2	0.1	2.67	105	46.6
15P	1:1:0.3	0.1	2.21	948	54.6
16P	1:0.8:0.3	0.1	4.54	2221	31.9
17P	1:1.1:0.3	0.1	4.84	376	20.4
18P	1:1.2:0.3	0.1	3.12	125	30.2

The run suggested in last months report using all five pulse columns was attempted. Satisfactory operation of column five was never achieved. Listed below are the operating conditions for Run Number 6.

1. Column I
   - a. 24 feet extraction section (aqueous continuous).
   - b. Slurry feed

     Thorium = 252.16 gm/l
     Uranium = 6.10 gm/l
     HNO_3 = 3.41 N
   - c. 38.4% TBP - 61.6% Amsco
   - d. Pulsed at 60 cycles per minute and one inch amplitude
   - e. Feed rate was 0.50 gal/hr
   - f. Organic rate was 3.02 gal/hr
   - g. Total throughput was 3.77 gal/hr
2. Column II
   - a. 24 feet scrub section (organic continuous)
   - b. Scrub solution was 0.25 M aluminum nitrate
   - c. Pulsed at 60 cycles per minute and one inch amplitude
   - d. Scrub rate was 0.25 gal/hr

   e. Total throughput was 3.27 gal/hr

3. Column III

   a. 12 feet organic scrub section (aqueous continuous)

   b. Organic scrub rate was 0.90 gal/hr

   c. Pulsed at 60 cycles per minute and one inch amplitude

   d. 12 feet stripping section (aqueous continuous)

   e. Total throughput was 6.63 gal/hr

4. Column IV

   a. 24 feet stripping section (aqueous continuous)

   b. Strip solution rate was 2.71 gal/hr and was 0.2 N nitric acid

   c. Pulsed at 60 cycles per minute and one inch amplitude

   d. Total throughput was 6.63 gal/hr

5. Column V

   a. 12 feet sodium carbonate stripping section (organic continuous)

   b. 12 feet aqueous scrub section (organic continuous)

   c. Pulsed at 60 cycles per minute and one inch amplitude

   d. Sodium carbonate rate was 0.10 gal/hr, was 10% Na_2CO_3 and was introduced into 4th section.

   e. Aqueous rate was 0.92 gal/hr and was introduced at top of column

   f. Total throughput was 4.94 gal/hr

The analytical data in Table II represent the nearest approach to equilibrium conditions obtained during the run.

The thorium loss in the raffinate was 3.1 per cent.

No further runs with the fifth column will be attempted until batch counter-current experiments have been made.

A run was made using only the first four columns. This was an extended run; the columns operated 16 hours and were assumed "on stream" for about 11 hours. The analytical results are not yet available; hence, the column conditions and the analytical data will be reported next month.

Future plans call for additional work on the fifth column, including flooding studies with both phases continuous.

TABLE II

ANALYTICAL RESULTS RUN NUMBER 6

STREAM	Th (gm/l)	U (gm/l)	HNO_3 (N)	RATIO Th/U
FEED	252.16	6.10	3.41	
ORGANIC FROM 1ST COL.	36.94	0.60	0.58	
ORGANIC FROM 2ND COL.	25.42	0.55	0.37	46.3
ORGANIC FROM 3RD COL.	0.68	1.36	0.04	0.5
ORGANIC FROM 4TH COL.	0.65	0.62	0.03	1.0
*ORGANIC FROM 5TH COL.	0.69	0.04	0.008	
RAFFINATE FROM 1ST COL.	3.91	0.26	0.09	
TNT PRODUCT FROM 3RD COL	33.22	0.13	0.59	255.6
REFLUX 4TH TO 3RD	1.04	1.77	0.21	0.6
REFLUX 2ND TO 1ST	12.46	0.32	1.43	
*URANIUM PRODUCT FROM 5TH	1.09	0.55	0.03	

*THESE TWO SAMPLES WERE THE ONLY TWO OBTAINED FROM THE 5TH COLUMN AND PROBABLY ARE NOT EQUILIBRIUM SAMPLES.

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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

Differential-thermal-analysis data are nearly complete for compositions of 16 and 20 mole per cent UF_4, 4 to 24 mole per cent BeF_2, and 60 to 80 mole per cent NaF in 4 mole-per-cent steps. Various areas of the ternary which have doubtful data or unreliable interpretation are being checked. In addition, ternary mixtures are being prepared for D.T.A. and petrographic examination from binary compounds to assist in determining the slope and position of ternary eutectics.

X-ray diffraction examinations have been made of the top and bottom sections of six slow-cooled D.T.A. ternary mixtures. Analyses of the middle sections should be completed soon. Preparation of X-ray diffraction standard samples have been completed for all binary compounds of the ternary with the exception of various forms of quenched Na_2UF_6

Results of the X-ray fluorescent analysis of UF_4 content in binary and ternary mixtures indicated low and scattered answers when compared to the uranium electrodeposition analyses. This disagreement may be due to the volatilization of UF_6 while dissolving the sample in perchloric acid at elevated temperatures. At present it is believed that solution of a sample in a highly oxidizing and anhydrous system might be undesirable.

X-ray diffraction patterns of known materials to be used for comparison purposes were made of the following compounds. NaF, $NaBeF_3$, Na_2BeF_4, $NaUF_5$, γ-Na_2UF_6, α-Na_3UF_7, β-Na_3UF_7, $Na_5U_3F_{17}$, and $Na_7U_6F_{31}$. (Standards were available for UF_4, BeF_2, and U_3O_8).

$Na_5U_3F_{17}$ was determined to be face-centered cubic with a = 5.58Å. This information is not listed in standard references, although it may be given in classified references unknown to us.

Three samples of UF_4 from Oak Ridge were analyzed by X-ray fluorescent analysis. Errors from the weighed amounts were 0.1, 0.1 and 0.24 per cent. Further work is in progress to improve X-ray fluorescent analysis for uranium.

To correlate results more easily, to avoid duplication of sample preparation and to reduce the amount of analytical chemistry, it was decided that D.T.A. and petrographic analysis would use separate portions of each sample preparation. This procedure is of added value in that the D.T.A. results for each sample can be used in designating the temperature range to be covered by the thermal-gradient quench. It is proposed to test the practicality of petrography using a portion of D.T.A. sample.

Following the breakdown of the thermal-gradient-quench apparatus during a run, portions of the apparatus were modified in design and replaced. To improve quenching conditions and to reduce error in temperature measurement caused by cooling of the sample while falling from the furnace, a deeper quench bath was made and was positioned as close to the furnace as possible. Also quench oil was substituted for the vacuum-pump oil previously used.

Three thermal-gradient quenches were made for study of the ternary sample of composition 12 mole per cent UF_4, 16 mole per cent BeF_2, and 72 mole per cent NaF.

The temperature range, 515°C to 434°C, was approached from above by heating the entire sample to temperatures above the liquidus, from 624°C on the hot end of the sample to 520°C on the cold end. The sample was then brought to and held at the desired temperature range for three-and-one-half hours prior to quenching. At the highest quench temperature, 515°C, a clear, green, isotropic material (n_d = 1.373) and a crystalline material were observed. The crystals were fibrous, pale green, of low birefringence, with average n_d = 1.383, and exhibited a tendency towards twinning. This material was identified by X-ray diffraction as Na_3UF_7. As the crystals were found in material quenched from temperatures above the liquidus determined by D.T.A. results, and since the crystals had an abnormal index of refraction and appearance, the material was probably a crystalline modification of Na_3UF_7 occurring as a quench product. Consequently, the liquidus temperature could not be determined from these quenched samples.

At 497°C, traces of crystalline β_3-Na_2UF_6 and Na_2BeF_4 were observed and were found in increasing amounts at all lower temperatures. In all cases, β_3-Na_2UF_6 was the major phase observed. The observed eutectic temperature, 497°C, is 14° higher than the corresponding temperature as determined by D.T.A. This discrepancy may be due largely to quench growth. NaF was found in the sample at approximately 493°C and below, although it is likely that the appearance of NaF resulted from nonhomogeneity of the sample. At approximately 471°C, the crystalline modification of Na_3UF_7 and the associated isotropic material completely disappeared, and the normal form of Na_3UF_7, n_d = 1.411 - 1.417, was observed in the sample. At approximately 453°C, the Na_3UF_7 disappeared resulting in an increase in the amounts of β_3-Na_2UF_6 and NaF present. At approximately 476°C and below, the β_3-Na_2UF_6 and Na_2BeF_4 present were observed to be combined together in a structure of fine alternate layers. An X-ray pattern of this material showed only the presence of β_3-Na_2UF_6, although it was estimated that up to fifteen weight-per-cent Na_2BeF_4 could be present without affecting the pattern.

For use in the preparation of standards for X-ray diffraction analyses, all compounds existing in the NaF-UF_4 and NaF-BeF_2 binary systems were prepared. As α-Na_3UF_7, β-Na_3UF_7, and $Na_5U_3F_{17}$ do not exist in slow-cooled samples, these compounds were prepared by single-temperature quenches. All of the compounds were examined petrographically and were found to be in close agreement with their optical properties as listed in ORNL 1712. No information is available as yet differentiating between α-Na_3UF_7 and β-Na_3UF_7. No difference could be detected. No description at all is available for the compound $Na_5U_3F_{17}$. This was found to be isotropic material, n_d = 1.479. An unidentified compound was detected in a quenched recrystallized sample of α-Na_3UF_7. This was possibly one of the crystalline modifications of Na_2UF_6.

The densities of four ternary mixtures were measured this month. The compositions varied from 70 mole per cent NaF, 18 mole per cent BeF_2, 12 mole per cent UF_4 to 52 mole per cent NaF, 36 mole per cent BeF_2, 12 Mole per cent UF_4. The densities of two special mixtures from ORNL were also measured. Densities of each mixture were measured between their liquidus point and approximately 900°C. The density slopes of the two special mixtures from ORNL were:

EE377CS: -4.65×10^{-4} gms/cc-C°

EE378CS: -5.55×10^{-4} gms/cc-C°

while density slopes of the four ternary mixtures made at Mound Laboratory averaged -7.458×10^{-4} gms/cc-C° in the temperature range of 600° to 800°C.

[redacted]

Results of the density measurements are given in Table I

TABLE I

DENSITY OF FUSED SALTS

SAMPLE MOLE PER CENT	TEMP. (°C)	DENSITY (GMS/CC)
70 NaF-18BeF$_2$-12 UF$_4$	800	3.039
	600	3.190
64 NaF-24 BeF$_2$-12 UF$_4$	800	2.962
	600	3.130
58 NaF-30 BeF$_2$-12 UF$_4$	800	3.002
	600	3.165
52 NaF-36 BeF$_2$-12 UF$_4$	800	2.985
	600	3.105
ORNL NO. EE377CS (COMPOSITION 84)	800	1.911
	600	2.002
ORNL NO. EE378CS (COMPOSITION 84)	800	2.205
	600	2.317

A series of viscosity measurements was made on each of three sodium fluoride and beryllium fluoride mixtures containing 12 mole per cent uranium fluoride. The results are given in Table II. Plots of the logarithm of the viscosity as a function of the reciprocal of the absolute temperature gave linear curves with slopes similar to those obtained from previous mixtures of sodium, beryllium and uranium fluorides. Also the viscosity of one of the special salt mixtures from ORNL was measured from 350° to 900°C.

TABLE II

VISCOSITIES OF FUSED SALTS

SAMPLE	600°C RESULTS		800°C RESULTS	
MOLE PER CENT	(CENTIPOISE)	$\frac{\mathrm{CM}^4}{\mathrm{SEC}} \times 100$	(CENTIPOISE)	$\frac{\mathrm{CM}^4}{\mathrm{SEC}} \times 100$
76 NaF-12 BeF$_2$-12 UF$_4$	0.1181	0.0363	0.0434	0.0151
70 NaF-18 BeF$_2$-12 UF$_4$	0.0853	0.0273	0.0341	0.0122
64 NaF-24 BeF$_2$-12 UF$_4$	0.0680	0.0218	0.0291	0.00948
ORNL NO. EE377SC (COMPOSITION 84)	0.0836	0.0390	0.0287	0.0140

A large hood was constructed around the viscosity and density equipment to decrease the hazard of beryllium fumes in the laboratory.

Decreasing the ring orifice above the sample chamber, which controls the flow of helium, reduced the difficulty caused by oxidation of the sample and the sample container at high temperature.

Some measurements of specific heat have been made at room temperature to learn something about the use of our present calorimeters in examining salt samples. The heat capacities (which are numerically equivalent to specific heats) have been measured for several individual compounds and for a ternary-system compound. The results are given for the temperature range 25.5°C - 28.5°C in Table III If calculated from the specific heats of the individual salts, the stoichiometric mixtures of the last three compounds would have heat capacities of 0.2654, 0.1090, and 0.1259, cal-gm^{-1} -°C, respectively. These values differ from the compounds by + 0.8 per cent, - 1.9 per cent, and - 0.3 per cent which differences are within experimental error. The ternary mixture, assuming no compound for formation, should have had a specific heat of 0.1780, which is lower by 9.6 per cent than the measured value. Further runs on ternary systems may determine whether the 9.6 per cent difference is real or is due to experimental causes. The ternary-system sample had been previously used in the viscosimeter and perhaps a nonrepresentative portion was taken from the viscosimeter cup.

TABLE III

SPECIFIC HEATS AT ROOM TEMPERATURE

(25.5° - 28.5°C)

Cal - Gm^{-1} - °C^{-1}

MATERIAL	MEASURED	CALCULATED FOR MIXTURE	PER CENT DIFFERENCE MEAS. W.R.T. CALC.
NaF	0.2700		
BeF_2 (GLASSY)	0.2646		
BeF_2 (CRYSTALLINE)	0.2613		
UF_4	0.0874		
64 NaF-24 BeF_2-12 UF_4 (MOLE PER CENT)	0.1969	0.1780	+ 9.6
$NaBeF_3$	0.2634	0.2654	- 0.8
$NaUF_5$	0.1111	0.1090	+ 1.9
Na_2UF_6	0.1263	0.1259	- 0.3

ANALYTICAL METHODS

Work has continued on the regular analysis of ternary mixtures. UF_4 and BeF_2 are determined quantitatively and the NaF is determined by difference.

Eight experimental runs were made to determine the effect, if any, of the presence of NaF in the mixtures on the plating of uranium. It was found that the mere presence of some sodium ion caused an average deficiency of uranium plate of about 1.4 per cent, but larger amounts of NaF produced little increase in uranium defficiency.

A satisfactory method for analysis of air samples for fluoride content is being sought, since a method is needed for health checks of the amount of fluoride in the laboratory during the working day.

Some preliminary work has been done on the X-ray fluorescent analysis of zirconium and uranium. Determinations of peaks and interference data are being gathered. Standard samples were prepared but as yet have not been run. More pressing work prevented further active participation at this time.

The purification work has been concerned with preparing several 200-gram batches of the following compounds for use in petrographic and X-ray work: Na_3UF_7, Na_2UF_6, $Na_7U_6F_{31}$, $Na_5U_3F_{17}$, and Na_2BeF_4.

During the preparation of these materials, it was noted that the frozen salt cakes had a metallic film across the top. When a layer of the salt was removed to contain as much of this film as possible, analysis showed nearly 0.37 weight per cent nickel to be present, while the center of the cake contained only 0.06 weight per cent nickel. This means that the fluorides do dissolve some of the nickel from the nickel crucibles in which they are melted. Apparently, the long hydrogen "stripping" during the purification run reduces any nickel fluoride to metallic nickel which floats on the surface of the molten salt. If nickel fluoride were present, it would be expected to be soluble in the molten salt and evenly distributed throughout the mixture, but this is not the case. These results are encouraging since insoluble nickel metal would cause no trouble in D.T.A. work while dissolved nickel fluoride would lower all of the liquidus lines.

FILTRATION STUDIES

To resolve the discrepancy between eutectic temperatures as determined by D.T.A. and petrographic methods in the region of 12 NaF-16BeF_2-72UF_4 mole per cent, filtrations are being made at different temperatures. The filtrates are then chemically analyzed which should give the liquidus composition at the temperature of filtration, since only the liquid phase can pass through the filter. A more sensitive temperature measuring method is being used than that of last month, so that temperatures can now be measured to ± 1°C.

The low point for this eutectic appears to be at 12 mole per cent UF_4-15 mole per cent BeF_2-73 mole per cent NaF. Therefore, a sample of this composition was investigated. The D.T.A. work shows this eutectic to be 483°C, while this filtration was made at 492°C. The composition of this liquidus (average of 3 determinations) is given in Table IV. The NaF was not determined but was calculated by difference. To find the absolute minimum point here, another filtration will be made nearer to 483°C.

[redacted]

TABLE IV

LIQUIDUS COMPOSITIONS BY FILTRATION

TEMPERATURE	COMPOSITION MOLE PER CENT UF_4	BeF_2	NaF
492°C	11.9	15.8	72.3
520°C	7.8	20.4	71.9
527°C	7.2	19.5	73.3

To find the valley away from this low point toward the low UF_4 side, a composition of 5 mole per cent UF_4-20 per cent BeF_2-75 per cent NaF was filtered at 520° and 527°C with the results given in Table IV.

volume than the original precipitate. This method of separating the protactinium preparatory to counting with the gamma-pulse-height analyzer is being investigated further to determine if other mineral acids or combinations thereof can be used with equal success.

The coprecipitation of protactinium with titanium from concentrated hydrochloric acid solutions of the raffinate residue was examined by several experiments.

(1) The raffinate residue was mixed with concentrated nitric acid, 0.5 milliliters of acid per gram of raffinate residue. Concentrated phosphoric acid was added. The system was diluted to make the solution 1.7 molar in nitric acid and 0.7 molar in phosphoric acid. The slurry was heated for one hour in a hot water bath, centrifuged, and the insoluble residue washed with 2.0 normal nitric acid. This insoluble residue had a gamma spectrum which showed no protactinium to be present but was characteristic of thorium-227 and radium-223. It was concluded that a hypothesis that the titanium did not precipitate because of lack of sufficient phosphate ion was false. (2) One and one-half grams of ammonium nitrate per gram of raffinate residue was added to the clear solution obtained by centrifuging in the foregoing experiment. The resulting solution was heated in a hot water bath for two hours. No precipitate formed. Thus, if a concentrated ionic solution will coagulate a colloid, it seems that in this case the coagulation of a colloid is not the mechanism of the precipitation of protactinium with its carrier. (3) Concentrated hydrochloric acid was added in small aliquots to the clear solution containing the ammonium nitrate while it was in the hot water bath. No precipitate appeared until the amount of concentrated hydrochloric acid added was equal to one milliliter per gram of raffinate residue. However the precipitate did not coagulate until the total amount of concentrated hydrochloric acid was 1.5 milliliters per gram of raffinate residue. The precipitate carried approximately one half of the protactinium. The remaining protactinium was recovered by the addition of titanium trichloride. This experiment was repeated with no ammonium nitrate present. The same results were obtained. It is suggested that the iron in the raffinate residue forms a strong complex with titanium and protactinium and the addition of the chloride ion in high concentration is necessary to destroy such a complex and release the titanium and protactinium for precipitation as phosphates. (4) One milliliter of 85 per cent phosphoric acid, 14.6 molar, was added to ten milliliters of solution containing ten milligrams of titanium (III) in distilled water. The system was heated in a hot water bath for ten minutes. No precipitate formed. The solution had the characteristic violet color of titanium (III). The addition of one drop of concentrated nitric acid resulted in the immediate formation of a white precipitate. The solution became colorless. One milliliter of concentrated nitric acid was added. To the hot system, 0.6 grams of solid ferric nitrate nonahydrate containing 83 milligrams of iron, 1.5 millimoles, was added. The precipitate disappeared as the ferric nitrate dissolved. The solution remained clear during ten minutes additional heating. One milliliter of 85 per cent phosphoric acid was added. No precipitate formed during ten minutes of heating. Concentrated hydrochloric acid was added in 0.2 milliliter portions. The solution was heated in the hot water bath for ten minutes after each addition. The first addition of hydrochloric acid produced a very faint turbidity and a characteristic yellow color. When the chloride to iron molar ratio reached approximately six to one, with a total of 0.8 milliliters of concentrated hydrochloric acid added, the yellow color was very strong and fairly large aggregates became visible. A total of three milliliters of concentrated hydrochloric acid was required to produce the same amount of precipitate as that obtained when ten milligrams of titanium (III) had been precipitated as titanium (IV) phosphate.

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The study of improvements in conditions for processing the Sperry filter cake received from Mallinckrodt has continued. Since a major consideration in our separation process is the initial contact of the filter cake with hydrochloric acid and the resulting solution of the protactinium in this medium, a balanced experiment was devoted to the influence of hydrochloric acid concentration (2 N and 6 N), solution time (2 hours and 7 hours) and solution temperature (room temperature and 100°C) on the efficiency of the solution step.

The efficiency was determined in each case as the per cent of the gamma activity dissolved, i.e., gamma count on the solution was divided by the sum of the gamma counts on the solution and on the insoluble residue and multiplied by 100 per cent. A complete gamma spectrum was not determined in each case; instead samples were counted at 27, 68 and 300 kev levels.

The results of the experiment suggest the following conclusions: (1) Increasing the hydrochloric acid concentration from 2 N to 6 N produced decreases in the efficiency of solution at room temperature similar to those observed in the previous study in which the effect of changing the hydrochloric acid concentration from 1 N to 8 N on the efficiency of the solution step was studied. However, at 100°C these decreases became phenomenal and resulted in more than half of the activity associating itself with the residue. (2) Increasing the solution time from 2 hours to 7 hours appeared to have little effect at room temperature. At 100°C, an increase in solution efficiency occurred when the time was increased if 2 N hydrochloric acid was used. However if 6 N acid was used at 100°C, a post precipitation apparently occurred, since more activity became associated with the insoluble residue as the time was increased. (3) Increasing the temperature invariably reduced the efficiency of the solution step as judged by the more reliable 27 kev count. Although the reduction was only minor with 2 N HCl it was approximately 10 fold with 6 N acid. (4) In all cases as judged by the 68 kev count, nearly 90 per cent of the ionium became associated with the liquid phase, but the ionium appears to exhibit a very weak tendency to follow the protactinium

A 3-factor experiment to determine carrier efficiency is in progress. The three factors under consideration are hydrochloric acid concentration in the initial solution liquid, amount of auxiliary carrier (titanium trichloride) that may be added, and the hydrochloric acid concentration of the carrier wash liquid