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This is Copy 19 of 22A
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MOUND LABORATORY
Operated By
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MIAMISBURG, OHIO

MONTHLY TECHNICAL ACTIVITIES REPORT
THROUGH JUNE 17, 1955

BY

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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.

Ten polonium-beryllium neutron sources, one polonium-boron neutron source, and one alpha source were shipped in May. Five of the polonium-beryllium sources were for other AEC sites.

The large 260 PKV X-ray machine has been moved from the "B" Building to Room 212 of the "T" Building. All craft work has been completed and health physics personnel are making a radiation survey in the new area. Routine radiographic operations will be resumed as soon as this survey is completed.

As a result of reduced services and consolidation of work, waste disposal effluent samples are to be counted by the Operations Counting Group after June 30. Two beta counting instruments have been moved into the "T" Area for this purpose and the operators are being given instructions in their use.

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

TABLE I

WASTE DISPOSAL OPERATIONS

MAY 16, 1955 THROUGH JUNE 15, 1955

DISCHARGE VOLUME -	397,800	GALLONS
TOTAL ALPHA ACTIVITY -	1.8	MILLICURIES
TOTAL BETA ACTIVITY -	17.0	MILLICURIES
ACTIVITY DENSITY		
ALPHA	1.0	C/MIN/ML
BETA	12.0	C/MIN/ML

It has been proposed that the high neutron absorption cross section of rare earths in thorium raffinate could be used as a basis for process control. The Neutron Source Group undertook an examination. A sample containing about 15 per cent rare earths was placed in a 4-inch diameter stainless steel tube between a B-wall tube and a neutron source emitting 1.22×10^{7} neutrons per second. This sample absorbed 45.6 per cent of the neutrons. The absorption was, therefore, approximately 11 per cent per inch of solution. The sensitivity was such that a change in rare earth concentration of 0.1 per cent could be easily detected. By use of a stronger neutron source a change of 0.05 per cent in rare earth concentration could be determined.

[redacted]

The use of polonium alpha sources as static eliminators in the printing industry is being investigated. Experimental work is underway in cooperation with the Dayton plant of the McCall Corporation.

The static electricity can be removed from the six foot wide paper as it runs through the press, but so far we have been unable to satisfactorily discharge the cut and folded booklets as they come from the press.

Additional work is planned on this problem.

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.

Continued work on the operating parameters of the thermal diffusion columns has led to the determination of equilibrium time and optimum pressure as functions of the center wire temperature for the 12 feet long by 1 inch ID column. For a 50 per cent molecular mixture of hydrogen and helium and a center wire temperature of 310°C the equilibrium time, or time required for the separation process to approach to within a very few per cent of equilibrium, is about four hours. The optimum initial pressure for a center wire temperature of 310°C, was found to be 1.35 atmospheres as compared to a value of 1.25 atmospheres for a center wire temperature of 900°C. For a center wire temperature of 600°C the equilibrium time is more nearly three hours. Work is in progress at present to determine the optimum initial pressure at the center wire temperature of 600°C.

The values for the time for the system to reach one-half the equilibrium time and the optimum initial pressure will be used as a basis of computing shape factors for the 1 inch column as a function of the wire temperature.

More work on the separation of argon isotopes with natural abundance on the 12 feet long by 1.25 inch ID column indicates that the equilibrium time for the mass 36 - 40 separation reported last month was in error, and that for a center wire temperature of 900°C substantial equilibrium is achieved after 2½ hours.

The effect of center wire misalignment is under investigation on this column; argon isotopes are used for separation data. As expected, the separation factor decreases as the wire is moved away from the axis of the tube, but persistent oxidation of the center wire has prevented accumulation of acceptable quantitative data. At present the source of the contaminating oxygen has not been located.

A total of 88 gas samples of hydrogen - helium mixtures and 96 samples of argon were analysed on the mass spectrometer this month in conjunction with the above experimentation. In addition, 12 deuterium gas samples, two dry box gas samples, and two helium tank samples were analysed for the Livermore project.

Another operator is being trained to analyse gas samples on the spectrometer. This is necessary to fill the vacancy created by the resignation of the present operator. Spectrometer Number 1 has been shut down indefinitely. No analyses have been possible on this instrument for the past two months because of large memory effects of the gases analysed. A thorough cleaning of the instrument will be required before it can be placed in operation again.

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

After the first phase of the "B" type material had been shipped the dryboxes were converted for processing the "A" type material. The first major shipment of the type "A" material was processed to two stages of completion. Three-fifths of the material was pressed, canned and sealed while two-fifths was pressed into two inch blocks and stored in sealed jars. Since the moisture content of the dryboxes could not be reduced to a lower point with present drying methods, canning operations were held up temporarily so that a thorough investigation could be made to attempt improving this condition. Facilities were added to improve the analytical sampling techniques and increase the capacity of the equipment.

DEVELOPMENT

DRY-BOX ATMOSPHERE. Before starting sealing operations a daily analysis was made of samples exposed to the dry-box atmosphere. If the active hydroxide content was low, operations were begun to seal the cured blocks into cans. Analysis for hydroxide content of nearly all the canned batches of material "A" showed results which varied from 250 to 550 parts per million. The values were not low enough according to the extimations made by the representatives from Livermore. Three-hundred and eleven cans were sealed during the period from May 17 to May 24 and no swelling of any cans was detected during an inspection made on June 6, 1955. Since the shelf life of the cans is expected to be about a year or longer, less than 100 parts per million of lithium hydroxide can be tolerated to achieve this result. Consequently, after a meeting with the Livermore representatives, calculations showed that the dew point for water vapor content in the sealing dry-box should be less than -77°F. It is quite evident that the drying equipment must be capable of producing a dew point of less than -100°C if adequate conditions of dryness are to be maintained during operations. Work is proceeding to improve the drying system specifically for the sealing dry-box.

Calculations were made to determine the rate of flow of helium gas through the desiccant container and it was found that the blower initially installed produced a flow of only four cubic feet per minute. Since this was deemed inadequate a Roots-Connersville air pump was obtained from Livermore and installed in the system. The pump delivered about 100 cubic feet per minute and this blast of the helium gas blew the powdered lithium hydride drying agent out of the container and into the dry-boxes. Several types of filters were installed to block the powder from escaping from the desiccant container. They filled rapidly and blocked any circulation of gas. Larger mesh size hydride was ordered to be purchased and upon its arrival will be packed in a drying container and tested.

Since the Roots-Connersville pump was designed to operate with air, a light gas such as helium was found to leak through the shaft and housing of the pump. To stop the helium from escaping, the metal box which housed the original blower was modified to fit over the air pump.

Investigations are in progress to obtain a set of Lectrodryer units which it is hoped will greatly aid in reducing the moisture content of the atmosphere in the sealing dry-box. There is a possibility that a desiccator unit may have to be employed in conjunction with the Lectrodyer.

The dry-boxes were examined with a helium leak-detector and some points of leakage were repaired. Some leakage was detected through the welds under the studs in the curing crucibles. They were rewelded and the leaks continued. Finally this condition was solved by applying a thin coat of silver solder under the flanges of the crucibles.

ANALYSIS

It was suggested that more consistent and reproducible analytical results for lithium hydroxide content should be obtained from the canned sample of the "A" type material. To help accomplish this an experimental die was made and tested for obtaining a uniform size (surface to volume ratio) sample for analysis. A vacuum dry-box was obtained from Livermore and installed in the analysis room. Since the condition of the sealing dry-box can be evaluated from a hydroxide analysis, an extra load was cast upon the one analytical system now in use. Another analytical system was constructed and is being installed to help reduce the time required to obtain results. The hydroxide analytical methods and procedures now appear to be developed to a very satisfactory stage.

OPERATIONS

Fourteen curing batches containing 30.5 kgm. of type "A" salt were canned in 311 cans. This included 30 two inch cans for samples, 244 four inch cans and 37 six inch cans. In addition about 9.5 kgm. was canned and leaks were found in the soldered joints. About 8.9 kgm was cured in crucibles and was ready to assemble and seal into cans. Hydroxide analytical results of ten sealed and leak-tested batches showed that seven batches had 550 or less parts per million. Three batches showed results from 1,000 to 1,400 parts per million lithium hydroxide. Five completed batches showed less than 350 parts per million with two batches having the lowest results thus far obtained of 250 parts per million.

Work continued on electroplating and tinning the cans and lids which will be required for the sealing operations.

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

Although the thorium project was cancelled in May, work is continuing on the development of a process flow sheet for the extraction of thorium from Brazilian hydroxide sludge. This work includes the analytical development work necessary to complete this job and both batch countercurrent and pilot plant solvent extraction work. In addition, we expect to present a proposal for handling the wastes from such a process.

ANALYTICAL

The completed working curves for the determination by X-ray fluorescent spectrometry of thorium and uranium in the aqueous feed, raffinates, and organic phase have been reevaluated recently. For all practical purposes the results from raffinate working curves approximated the results of the aqueous feed curves when raffinate samples were treated as feed samples. The organic phase procedure did not require any revision.

The uranium limits were reworked to give values to 0.01 milligram per milliliter for the aqueous solution. During this investigation it was found that the reagent grade strontium nitrate contained an impurity which interfered with the uranium L_{α_1} peak. This resulted in a slightly higher result. Although this impurity could be removed from the strontium nitrate no attempt was made to do so The amount of strontium nitrate was always added to the solutions in a constant and fixed concentration. Correction for the impurity was easily made on the results.

The earlier methods used for determining gamma quantities of uranium in the organic and aqueous samples did not give good results. The thiocyanate spectrophotometric method was especially troublesome. Since our samples contained large amounts of thorium and other interfering elements, it was decided to separate the uranium from these interfering elements by anion exchange resin. The uranium was then analyzed fluorimetrically using the Galvanek-Morrison fluorimeter. Reproducibility of 3 per cent was found for samples analyzed in the 0.1-10 γ/ml range. Details of the method are being written up as a final report.

A spectrographic analytical procedure based upon the work of Scribner and Mullin of the National Bureau of Standards has been successfully applied to the analysis of the common elements. A more rigorous attempt was made in the preparations of the standard solutions needed. Reagents and solvents needed were repurified as far as possible, individual elements or compounds were of the highest purity obtainable, and the final solutions were stored in polyethylene containers.

Due to an abrupt change of the urgency of this problem, and the subsequent shifts in group personnel, no further work is anticipated on the common element analysis.

Working curves have been set up for the determination of dysprosium, europium, gadolinium and samarium by spectrographic analysis. The analysis for europium is still not satisfactory.

The use of TTA for the separation of the rare earths prior to the spectrographic analysis has proven to be excellent. The TTA separation method was obtained from Oak Ridge National Laboratory.

The thorium iodate separation method for gross rare earths has been found subject to error because of considerable and variable supersaturation. A TTA separation was substituted for the thorium iodate method; however, a modification of the TTA procedure is necessary for an evaluation of total rare earth elements. It has been found that the water solubility of the thorium-TTA compound must be considered.

Work was completed on setting up procedures for analyzing samples of thorium for tracer amounts of rare earths by means of neutron-absorption measurements.

The procedure was tested by determining the neutron absorption of a known amount of cadmium oxide in a mixture of cadmium oxide and thorium dioxide. The counting arrangement is described in report Mound memorandum 55-6-18, page 3. The effective cross section of the ThO_2 was measured with high precision. The ThO_2 was then "spiked" with known amounts of CdO (Cross section 3,100 barns). The CdO content in molecules per million molecules of ThO_2 determined by neutron absorption was compared to the CdO content known to be present in each mixture. Results are given in Table II.

TABLE II

DETERMINATION OF CdO CONTENT BY NEUTRON ABSORPTION

SAMPLE	KNOWN CONC. (ppm)	MEASURED CONC. (ppm)	DEVIATION (%)
A	4,682	4,237	− 9.5
B	8,322	8,650	+ 3.9
C	20,708	20,081	− 3.0
D	207,075	168,619	−12.2

This indicates that in our counting arrangement about 4,000 parts of CdO per million parts of ThO_2 can be measured with errors of ± 10 per cent.

The maximum rare earth content allowable in the thorium is about 1.7 parts per million, with 0.5 parts per million cerium, 0.5 parts per million europium, 0.2 parts per million gadolinium, and 0.5 parts per million dysprosium. Calculations using these proportions give an approximate total cross section for the allowable rare earth content of 9,000 barns per 10^6 atoms of Th. Because of the high cross section of many of the rare earths, it is estimated that about 1,000 parts per million of rare earth in thorium could be measured with errors not exceeding ± 10 per cent. This would necessitate a concentration of 1,000 to 1 of the rare earth content of processed material before it is measured.

We used a 4 curie polonium-beryllium source for this work. A 10 curie source with more paraffin between the source and absorber would make possible more precise measurements, and smaller amounts of rare earth could be measured.

[redacted]

Expressions for rare earth content in both oxide and nitrate mixtures are given below:

$$n_1 = \begin{array}{l}\text{molecules of } R_2O_3 \\ \text{per million molecules} \\ \text{of } ThO_2\end{array} = \frac{6.023 \times 10^{27}\, \sigma\, ThO_2 - (A/W)6.0788 \times 10^{6} \log I_0/I}{(A/W)8.1051 \log I_0/I - 54.21}$$

$$n_2 = \begin{array}{l}\text{molecules of } R(NO_3)_3 \\ \text{per million molecules} \\ \text{of } Th(NO_3)_4\end{array} = \frac{6.023 \times 10^{27}\, \sigma\, ThO_2 - (A/W)1.1052 \times 10^{7} \log I_0/I}{(A/W)7.7827 \log I_0/I - 54.21}$$

Where A = Area of sample in square centimeters

W = Weight of sample in grams

R = Symbol for rare earth

I_0 = Neutron flux without absorber

I = Neutron flux with absorber

SOLVENT EXTRACTION

Although preliminary information from batch countercurrent solvent extraction experiments was available for pulse column pilot plant runs and for preliminary design purposes these data were not complete For extraction column data on such variables as the thorium concentration in the feed, acid concentration of the feed, flow ratios of feed to scrub to organic solvent, concentration of aluminum nitrate in the aqueous scrub, use of OK liquor in the aqueous scrub, the use of Amsco, (an aliphatic diluent for tributylphosphate) or the use of an aromatic diluent such as Solvesso, a systematic study is needed. Likewise, a study of these variables as applied to the partitioning of thorium and uranium needs further systematic study. Consideration of a two cycle system and determining the conditions for the extraction of uranium from the organic phase requires more data than is available from preliminary concepts In order to obtain these data further experiments in batch countercurrent equipment are being obtained from an installation of two units of suitable apparatus set up in May

Planning these batch countercurrent experiments to obtain the largest amount of pertinent data in a minimum of time has necessitated limiting these experiments to a nitric acid feed solution of Brazilian hydroxide sludge. A further limitation was the use of a clear filtered feed solution for the starting material. The question of whether to use a slurry feed or a filtered feed in the thorium refinery process can best be determined from a pilot plant study.

Extraction experiments on the Brazilian hydroxide sludge feed material for the first cycle have been run; however, not all of the analytical data has as yet been reported. Data remaining to be reported are on trace amounts of rare earth elements in the organic product which in turn allows calculation of rare earth decontamination factors.

A summary of the data for the extraction runs for the first cycle is presented (Table III). This summary does not include distribution coefficients, extraction factors, per cent saturation at the various stages, profiles or decontamination factors for rare earths. These detailed data with the exception of a portion of the rare earth analytical data have been obtained and are available.

[redacted]

TABLE III

BATCH COUNTERCURRENT EXPERIMENTS, SAMPLED AT 21ST EQUILIBRATION, 5 SCRUB AND 8 EXTRACTION STAGES, FILTERED BRAZILIAN HYDROXIDE SLUDGE FEED

RUN NO.	14	15	16	17	18	19	20	21	22	23
FEED AQUEOUS FILTERED	Th 216 g/l H^+ 3.07 *N*	SAME SAME	SAME SAME	SAME SAME	SAME SAME	SAME SAME	Th 199 g/l H^+ 2 17 *N*	SAME SAME	SAME SAME	SAME SAME
SCRUB AQUEOUS	*Al 0.5 *M*	*Al 0.25 *M*	*Al 0.125 *M*	SAME	SAME	SAME	OK LIQUOR	OK LIQUOR PLUS *Al 0.25 *M*	SAME	SAME
ORGANIC SOLVENT	TBP 40% AMSCO 60%	SAME SAME	SAME SAME	SAME SAME	SAME SAME	SAME SAME	SAME SAME	SAME SAME	SAME SAME	TBP 30% SOLVESSO 70%
FLOW RATIOS F:S:O	1:1:4	SAME	SAME	1:1:5	1:0.5:4	1:0.5:5	SAME	SAME	SAME	1:1:6.5
PER CENT LOSS	1.74	3.85	6.32	2.08	2.42	2.30	2.73	5.71	4.27	4.51
PER CENT EXTRACTION	84.2	73.1	58.0	93.9	92.5	73.8	94.6	94.5	86.7	90.5

*AS ALUMINUM NITRATE MONO-HYDRATE

From these data a run using optimum operating conditions is being made to obtain material for experiments which will determine the best operating conditions for the partition columns. These partitioning batch countercurrent experiments are to be followed by experiments studying the clean—up of uranium from the organic solvent. Upon completion of experiments dealing with the first cycle a series of experiments should be run in order to determine conditions for a second cycle.

Some progress has been made on the pulsing units for the pilot plant. It is now possible to pulse all five 2-inch columns in the pilot plant with a 1-inch amplitude at 60 cycles per minute.

Flooding studies have been carried out on the last column (solvent clean-up column) using 1 inch amplitude. These data are shown in Table IV.

TABLE IV

FLOODING STUDIES

GALLONS/HR/SQ.FT.	FREQUENCY (CPM)
1,000	50
1,280	60
1,000	70
900	80

A pilot plant run was made operating the third and fourth columns (partitioning columns where the uranium is separated from the thorium). The conditions for this run are shown in Table V.

TABLE V

CONDITIONS OF PILOT PLANT

1. 36 FEET STRIPPING COLUMN (ORGANIC CONTINUOUS)
2. 12 FEET ORGANIC SCRUB COLUMN (ORGANIC CONTINUOUS)
3. STRIP SOLUTION WAS 0.2 *N* NITRIC ACID.
4. BOTH COLUMNS PULSED AT 60 CYCLES PER MINUTE WITH A 1-INCH AMPLITUDE.
5. THE PULSE PUMPS WERE OPERATED TO OBTAIN THE MAXIMUM COALESCENCE AFTER THE UPWARD STROKE.
6. THE FRESH ORGANIC SCRUB WAS 38% TBP AND 62% AMSCO.
7. FEED:ORGANIC:STRIP WAS 1:0.3:0.9.
8. TOTAL THROUGHPUT WAS 6.63 GALLONS PER HOUR.

The following analytical data represents the nearest approach to equilibrium conditions obtained during this run.

TABLE VI

ANALYTICAL RESULTS

STREAM	Th*(gr/l)*	U*(gr/l)*	NITRIC ACID *(N)*	RATIO Th/U
ORGANIC FEED	49.46	1.43	0.123	34.6
ORGANIC FROM 3RD COL.	1.92	0.73	0.056	2.6
ORGANIC FROM 4TH COL.	1.09	0.38	0.035	2.9
REFLUX 4TH TO 3RD	2.99	1.68	0.238	1.8
AQUEOUS PRODUCT FROM 3RD (OK LIQUOR)	35.00	0.08	0.263	437.

We expect to make the next run operating all five columns under conditions obtained from batch countercurrent data on columns one through four, while the conditions set up by the Catalytic Construction flow sheet will be used for the fifth column. The conditions are shown in Table VII.

TABLE VII*

COLUMN CONDITIONS

COLUMN	TOTAL THROUGHPUT *(gal/hr)*	AQUEOUS FEED	ORGANIC FEED	0.25 *M* ALUMINUM NITRATE	0.2 *N* NITRIC ACID	10% SODIUM CARBONATE SOLUTION	WATER	FRESH ORGANIC
1	3.77	0.50	3.02	0.25	-	-	-	-
2	3.27	-	3.02	0.25	-	-	-	-
3	6.63	-	3.02	-	2.71	-	-	0.90
4	6.63	-	3.92	-	2.71	-	-	-
5	4.94	-	3.92	-	-	0.10	0.92	-

*ALL FIGURES IN THIS TABLE ARE GALLONS/HOUR.

WASTE TREATMENT AND HANDLING

Work on this phase of the problem has been temporarily suspended due to the higher priority of other work necessitating movement of personnel.

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 of more than twenty compositions in the ternary NaF-BeF_2-UF_4 has been performed during the past month in the area of 4, 8, and 12 mole per cent UF_4 with compositions of 8 to 56 mole per cent BeF_2 and of 80 to 36 mole per cent NaF. Two major changes have been adopted as standard procedure in order to obtain reproducible and reliable data. Each sample tube is homogenized at a temperature well above the liquidus and quenched in water prior to each heating cycle. Cooling and heating rates of 0.8°C per min. and 1.3°C per min. have been employed because of the increased mechanical and electrical stability which has been made available through various changes in the differential-thermal-analysis apparatus. Rupture of sample tubes at the sealing weld has been encountered after repeated homogenizations but does not present too serious a problem except when rupture occurs during a run and the apparatus must subsequently be renovated.

Differential-thermal-analysis tubes which have been slowly cooled are being opened and subjected to petrographic and X-ray diffraction study. Samples of various compounds in the binary NaF-UF_4 and the binary NaF-BeF_2 are being prepared as standards to enable evaluation of diffraction patterns of the above ternary compositions

The optical-thermal-analysis apparatus has been equipped with inside glove-port covers and plans are in progress to equip the dryboxes with a purification train similar in size and capacity to that which is used by the Bureau of Standards and which is reported in the March 1954 issue of Industrial and Engineering Chemistry.

The data in Table VIIIhave been obtained from heating and cooling curves of differential thermal analysis. The values followed by an asterisk are approximate and are associated with insufficient data or poorly defined transitions. Solid-solid transitions (320°C and 342°C) have been reported for only one temperature value for all compositions; since during differential thermal analysis equilibrium does not exist and consequently transitions may occur over a 10°C range.

In the area of interest, 12 mole per cent UF_4, 12 mole per cent BeF_2, and 76 mole per cent NaF, a ternary eutectic at 483°C ± 5°C is apparently present over the greater portion of the sodium fluoride corner of the ternary. Some compositions yield very satisfactory and reproducible transition breaks both from the heating and cooling curves, but other compositions yield only a fairly well defined eutectic and an erratic liquidus.

Electrolytic analysis of the 50 mole per cent UF_4-50 mole per cent BeF_2 preparation showed 48.99 mole per cent UF_4. The 75 mole per cent UF_4-25 mole per cent BeF_2 preparation was found to contain an average of 63.9 mole per cent UF_4 by volumetric analysis and an average of 76.13 mole per cent UF_4 by electrolytic analysis.

[redacted]

TABLE VIII

RESULTS OF DIFFERENTIAL THERMAL ANALYSIS STUDIES

COMPOSITION			TRANSITIONS °C					LIQUIDUS °C
MOLE PER CENT UF_4	MOLE PER CENT BeF_2	MOLE PER CENT NaF	S-S	S-S	E	UNASSIGNED HEATING AND COOLING	UNASSIGNED COOLING	
12	8	80			483	500	450*	541
12	12	76	320		483	501	450*	514
12	16	72	320		483		440*	490
12	20	68	320		483	500*	445*	553
12	24	64	320	342		500*	500*	553*
12	40	48		342	367*			571
8	16	76	320		483		440*	496
8	20	72	320		483		440*	513
8	24	68	320		483		440*	528
8	28	64	320	342			511*	521
8	32	60		342	367*		482*	501
8	36	56		342	367*		441*	518
8	40	52		342	367*			530*
8	44	48		342				527
8	48	44		342	367*			516
8	52	40		342	367*			544*
4	28	68	320		483			561

S = SOLID

E = EUTECTIC

* = APPROXIMATE

[redacted]

[redacted]

Attempts were made, by single temperature quenches, to determine the index of refraction, n_d, of the 75 mole per cent UF_4-25 mole per cent BeF_2 glass and of pure UF_4 as a glass. These values were needed to complete the relationship of mole-per-cent-composition to index-of-refraction of the glass in the binary UF_4-BeF_2 system. The index of refraction for the 75 mole per cent UF_4-25 mole per cent BeF_2 glass was found to be 1.559. The index of refraction for the pure UF_4 glass could not be measured, however, as only one sample did not fail on heating and it was found to be completely crystallized. Table IX was compiled using an average of the analytical results which were believed to be most accurate.

TABLE IX

COMPOSITION VERSUS INDEX REFRACTION

MOLE PER CENT UF_4	WEIGHT PER CENT UF_4	n_d OF GLASS
0	0	1.280
10.2	43.1	1.330
25.5	69.6	1.413
49.0	86.5	1.518
76.1	95.5	1.559
100.0	100.0	NOT DETERMINED

The previously reported value for the index of refraction of BeF_2 glass was 1.284. This figure was an average value taken from the temperature-versus-index-of-refraction curve of BeF_2 glass. This value has been changed to 1.280 which is the measured index of refraction of BeF_2 glass just above the melting point. Changing this value requires relocation of the eutectic which is now calculated to occur at approximately one-half mole per cent UF_4. This value is in closer agreement with D.T.A. work than the value of one mole per cent UF_4 as previously reported.

The study was completed for the ternary thermal-gradient-quench sample of composition 4 mole per cent UF_4, 28 mole per cent BeF_2, and 68 mole per cent NaF. At approximately 475°C and below crystalline Na_2UF_6 was observed. The crystals were green, uniaxial negative, of low birefringence, and n_d was 1.490 to 1.494. A colorless isotropic material of low index (1.322) was found in all portions of the sample. This material was identified as NaF by comparison with a purified sample of NaF. As this NaF was present even in the portion of the sample raised to the highest temperature, the sample apparently did not become homogeneous, and the effective starting composition was of lower NaF content than intended.

PHYSICAL PROPERTIES

The densities of nine ternary systems containing 64 to 76 mole per cent sodium fluoride, 12 to 28 mole per cent beryllium fluoride, and 8 to 12 mole per cent uranium fluoride have been measured between their liquidus and approximately 900°C. Although the density of any system is most dependent upon its uranium content, it is of interest to note that the change in density with temperature is nearly the same for each mixture. The slope of the density curves is approximately -7×10^{-4} grams per cubic centimeter per degree centigrade.

[redacted]

A series of viscosity measurements were made on ternary mixtures containing 100 grams of sodium fluoberyllate (Na_2BeF_4) and 0, 25, 50, 100, and 150 grams respectively of sodium fluouranate (Na_2UF_6). The logarithms of the viscosities as measured when plotted against the reciprocals of the absolute temperature of the measurement gave a family of lines with similar slopes. The viscosities obtained ranged from 2 to 3.5 centipoises at 870°C to 13 to 16 centipoises at 870°C.

A second series of viscosity measurements have been started on a mixture of sodium fluoberyllate ($NaBeF_3$) and sodium fluouranate (Na_2UF_6). It is indicated that viscosities of this system will be in the same range as the first mixture.

Certain parts of the viscometer, which had been originally fabricated from nickel, have been remade of Inconel. The use of the Inconel has reduced the corrosion of the components so that machining of these components between each determination is not required.

ANALYTICAL METHODS

Two multistation electroanalyzers were received and are being used for determination of uranium and the separation of uranium from beryllium in solutions obtained from mixtures of the fused salts being investigated in this program. The electrodeposition method of analysis for uranium has an error of not greater than 0.5 per cent. After the uranium has been removed from the solution, the beryllium is precipitated as the hydroxide and weighed after ignition. The beryllium determination has resulted in an error as high as 1.5 per cent for mixtures having less than ten per cent beryllium. This error is due to the difficulty in obtaining a quantitative precipitate of beryllium hydroxide from very dilute solutions of beryllium. Preliminary investigation indicates that a change in precipitation technique will reduce this error to less than 0.5 per cent in the beryllium determination when it is present in low concentrations.

It has been found that sodium does not interfere with either the uranium or the beryllium determinations. For the present, the sodium content of the ternary mixtures being investigated is determined by difference. Several random analyses of ternary mixtures for sodium content by the conventional zinc uranyl acetate gravimetric method have indicated that such a procedure is satisfactory.

Some preliminary studies have been made using fluorescent X-ray spectrometry for the determination of total uranium in fused-salt samples. Tentative working curves have been set up to cover the range 0-50 mole per cent uranium.

FILTRATION STUDIES

Ternary mixtures of sodium, beryllium, and uranium fluorides having a high sodium fluoride content are difficult to study by petrographic techniques. Filtration of such fused mixtures at various temperatures in the vicinity of the liquidus temperature coupled with analyses of the original materials and the filtrates is being used to determine the liquidus temperatures, i.e., the minimum temperature at which the filtrate has the same composition as the starting material.

A eutectic for this ternary mixture appears to be in the vicinity of 73 mole per cent sodium fluoride, 15 mole per cent beryllium fluoride and 12 mole per cent uranium tetrafluoride. A mixture of approximately this composition was prepared. The minimum temperature observed at which the filtrate had the same composition as the original material was 500°C. At 490°C, a satisfactory filtrate was not obtained. The analyses are given in Table X.

TABLE X

ANALYSIS OF FILTRATION MATERIAL

MATERIAL	SODIUM FLUORIDE	MOLE PER CENT BERYLLIUM FLUORIDE	URANIUM TETRAFLUORIDE
ORIGINAL	73.3	15.1	11.6
FILTRATE AT 500°C	73.5	14.9	11.6

The measurements of differential thermal analysis showed the temperature of this eutectic to be 487°C, whereas by filtration methods, no liquid was obtained at 490°C but was present at 500°C. The temperature measuring equipment is being calibrated to determine whether or not the temperature difference is real.

In the previous monthly report, a method was described for determining protactinium in raffinate residues. The method consisted of heating the raffinate residue with concentrated hydrochloric acid and centrifuging off the insoluble residue. The residue was then treated with tetrasodium ethylene diamine tetraacetate (Versene). The remaining insoluble residue had a gamma spectrum which was characteristic of pure protactinium. The various supernates from the insoluble residue showed no peak at 27 kev gamma energy and were assumed to be free of protactinium.

In order to check the reliability of the gamma counting method, it was desirable to recover the protactinium from the insoluble residue in a form suitable for alpha counting. Inasmuch as the conditions used were arbitrarily chosen, the procedure will not be given in complete detail at this time, as further work is necessary to optimize the various volumes, times, and concentrations which were used.

The Versene treatment is eliminated in this method. The insoluble residue from the treatment with hydrochloric acid is washed with dilute hydrochloric acid. The residue is heated with concentrated sulfuric acid for one or two hours at steam bath temperature. The slurry is diluted with an equal volume of water, and concentrated hydrochloric acid is added to make the mixture six normal in chloride. The slurry is shaken briefly with a mixture of di-isobutylcarbinol and kerosene previously saturated with six normal hydrochloric acid. The organic phase is separated and the aqueous phase is discarded. The organic phase is shaken with an equal volume of distilled water and the organic phase is discarded. Cerium (IV) ion is added to the aqueous phase, followed by a drop or two of phosphoric acid. Ammonium hydroxide is added until the acidity of the solution has been adjusted to pH 0.5 - 1.0. The mixture is stirred for fifteen minutes, then centrifuged. The supernate is discarded. The precipitate is washed with 0.05 normal nitric acid and the wash is discarded. The precipitate is mounted as a slurry in water and alpha-counted. In drum 3, the protactinium content of the raffinate residue was estimated to be 0.17 parts per million. Because of inhomogeneity, however, the estimate must be regarded as tentative only.

Qualitative experiments with titanium have led to the conclusion that the carrier of protactinium is not metatitanic acid, as previously believed, but titanium (IV) phosphate. It is believed that the high chloride concentration required for quantitative precipitation of the protactinium is necessary to complex all of the iron present, thus releasing sufficient phosphate ion to exceed the solubility limit of titanium (IV) phosphate. Further experiments suggest the possibility that titanium is present in the raffinate residue as titanium (III), and that the reaction of chloride with nitric acid is necessary to oxidize all of the titanium and to yield insoluble titanium (IV) phosphate. The reaction may also involve the oxidation of protactinium from some lower oxidation state to protactinium (V).

On the basis of these experiments, it was found possible to scavenge the supernates from the analytical procedure described above. Titantium (III) is added as the chloride to the combined supernate and washings. If the titanium (III) is fresh, only a slight precipitate remains after heating. The addition of a few drops of concentrated nitric acid, however, causes the precipitation of titanium (IV) phosphate. This precipitate may then be treated in the manner described above for the first precipitation. (The titanium precipitate is completely soluble in sulfuric acid.) After adjustment of the sulfate and chloride concentrations, the protactinium which coprecipitates may be extracted with di-isobutylcarbinol and precipitated as previously described. As much as 10 to 15 per cent of the original protactinium was recovered in this manner from solutions previously thought to be free of protactinium.

It is probable that the initial precipitation and the scavenging precipitation may be combined, but work has not yet been done along these lines. The estimate of the protactinium content of drum 3 may now be revised upward to 0.19 parts per million, corresponding to between 85 and 90 per cent of the gamma-ray counting rate at 300 kev. It is expected that similar findings will be reported in the near future with regard to other drums.

It is now possible to analyze all residues and waste solutions obtained in the protactinium recovery process. Residues may be treated with sulfuric acid to recover titanium and protactinium, then extracted with di-isobutylcarbinol to separate thorium isotopes. Waste solutions may be scavenged with titanium carrier and treated as described above. The possibility exists that it may be found expedient or necessary to add titanium carrier in the plant recovery process in order to insure against solubility losses of protactinium.