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MOUND LABORATORY
Operated By
MONSANTO CHEMICAL COMPANY
MIAMISBURG, OHIO

MONTHLY TECHNICAL ACTIVITIES REPORT
THROUGH MAY 17, 1955

BY

D. L. SCOTT, J. F. EICHELBERGER, D. S. ANTHONY, AND J. R. WIESLER

[redacted]

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POLONIUM-210 AND ACTINIUM-227 RESEARCH PROJECT

Work being performed on this project consists of finishing calculations and writing reports on specific phases started long ago. Such work covers the polonium-208, 209, and 210 isotopes, radium-226 and daughters, actinium-227 and daughters, and thorium-228 and daughters.

HALF-LIFE DETERMINATIONS

Counting was completed on the last two of a series of 8 samples of protactinium-233 prepared in September, 1954, for a half-life determination by beta counting. Results from one sample were discarded because part of the sample deposit flaked from the mount. A least-squares analysis of the data from the remaining samples gave a half-life value of 26.926 ± 0.078 days. Combining the results from the 7 samples, a grand-mean value of 26.998 days was obtained. The probable error of the grand mean was ± 0.005 days for internal consistency and ± 0.011 days for external consistency.

Additional calorimetric runs were made on three half-life samples, polonium-208, polonium-210, and thorium-228.

NEUTRON ABSORPTION MEASUREMENTS

A method is being developed for determining the rare-earth content of thorium oxide by means of neutron absorption measurements. Because of the high cross-section of the rare-earth elements compared to that of thorium, it is expected that 1 part rare earths in 1,000 parts of thorium oxide can be detected with reasonable accuracy.

A polonium-beryllium neutron source is used for the work. A nearly optimum counting rate for thermal neutrons is obtained by placing the source at a depth of 11 centimeters in a paraffin moderator. The best counting arrangement was a boron trifluoride detector with paraffin and cadmium lining around the sides of the tube, so that most of the counts are received through the end of the tube, thus approaching a point detector. The sample of absorbing material is placed on the end of the tube. This arrangement gives an optimum signal-to-noise ratio. The boron trifluoride tube also has a longer voltage plateau than a boron-wall tube and consequently gives more reproducible results.

The system was tested by measuring the cross-section of gold with a number of different thicknesses of gold foil which was found by spectrographic measurements to contain about one per cent copper. A cross-section of 93.3 ± 1.1 barns was found for the foil compared to the value of 95 barns for pure gold. The system is now being tested with samples of thorium oxide spiked with high cross-section contaminants.

A total of 44 samples was analyzed for beryllium by spectrographic methods.

R-BUILDING

25 AIR SAMPLES - RANGE 0.01 TO 1.2 MICROGRAMS OF BERYLLIUM, AVERAGE 0.27 MICROGRAMS OF BERYLLIUM

4 WIPE SAMPLES - RANGE 0.72 TO 3.4 MICROGRAMS OF BERYLLIUM, AVERAGE 2.33 MICROGRAMS OF BERYLLIUM.

T-BUILDING

7 AIR SAMPLES - RANGE 0.14 TO 7.0 MICROGRAMS OF BERYLLIUM, AVERAGE 1.68 MICROGRAMS OF BERYLLIUM.

6 WIPE SAMPLES - RANGE 0.13 TO 0.90 MICROGRAM OF BERYLLIUM, AVERAGE 0.39 MICROGRAM OF BERYLLIUM.

RADIATION CHEMISTRY

The study of effects of alpha radiation on various gases, including nitrous oxide, nitrogen oxide, helium, oxygen, nitrogen, and several stoichiometric mixtures of oxygen and nitrogen was continued. Data have been obtained which should give good values for the heats of reaction leading to the formation of several of the oxides of nitrogen. These data have not been analyzed.

Six neutron sources and one alpha source were calorimetered for the Neutron Source Group.

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 has continued on the determination of operating parameters of the thermal diffusion columns. An investigation of the relationship of separation factor, equilibrium time, and optimum pressure to center-wire temperature for a 50 per cent molecular mixture of hydrogen and helium is in progress on the column 12 feet in length by 1 inch inside diameter. The equilibrium separation factor for this mixture in this column for a center-wire temperature of 900°C at an initial pressure of 1.25 atmospheres is about 2×10^6. Under the same conditions with a center-wire temperature of 600°C, the separation factor is about 50,000; and for a center-wire temperature of 310°C, the separation factor is approximately 350. There is some evidence that the optimum operating pressure is slightly less for the lower temperatures, but data are insufficient to make a quantitative determination of this effect. There is a definite effect on the equilibrium time. With the center wire at 900°C, the column is essentially at equilibrium after 1½ to 2 hours of operation. With the center wire at 310°C, the equilibrium time is nearly 4 hours.

Work was started on the separation of argon isotopes of mass 36, 38, and 40 in natural abundance on the column 1.25 inches inside diameter. With a center-wire temperature of 900°C, the optimum initial pressure was found to be 0.11 atmoshpere. This value agrees very well with a theoretical value which was computed from the neon separation data taken earlier on the column 1 inch inside diameter. The argon gas separation process under these conditions was found to be within one or two per cent of equilibrium after two hours of operation. The mass 36 - 40 separation factor for these conditions is approximately 5.2. For a center-wire temperature of 600°C, preliminary data indicate an equilibrium time of nearly three hours with a mass 36 - 40 separation factor of approximately 3.6.

Earlier data on the separation of neon isotopes and separation of hydrogen-helium mixtures were used as a preliminary basis for calculations of shape factors for the columns. The shape factors that were used were based on theoretical values given by Jones and Furry (Jones, R. C. and Furry, W. H., Rev. Mod. Phys., *18*, 151-224 (1946)). The thermal diffusion transport shape factor, h, for the column 1-inch inside diameter with a center-wire temperature of 900°C was found to be approximately 0.197 for hydrogen-helium mixtures, and 0.174 for neon, mass 20 - 22 separation. These values differ significantly from the theoretical value of 0.116 for these conditions given by Jones and Furry. The convection and normal-diffusion shape factors, k_c and k_d, cannot be calculated until parasitic flow effects in the column have been evaluated.

A total of 165 hydrogen-helium gas samples and 86 argon gas samples was analysed on the mass spectrometer this month. This work was done in conjunction with the experiments described above. In addition, 10 standard samples and 17 gas samples of hydrogen-deuterium mixtures were analysed for the Livermore project.

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

Operations consisted of fabrication of two-inch and four-inch cans containing type "B" lithium deuteride. Two shipments of type "A" lithium deuteride were processed into two-inch pressed blocks for curing and sealing operations. The quantity of hydroxide in the blocks after curing caused six batches, or about 180 four-inch cans, to be reworked. Two batches were cured and canned. Information was learned from the characteristic curves of hydroxide analysis. Preparation of the aluminum cans for sealing operations exceeded preparation of parts. Approximately one week was required to change the dry boxes from type "B" to type "A".

DEVELOPMENT

CURING OPERATIONS. Because the quantity of lithium hydroxide in the type "A" lithium deuteride was excessive, the curing time for several succeeding batches was increased from 4 to 10 hours, and analyses were made to determine the most desirable curing time. A minimum curing time of six hours was indicated. However, since the handling procedure of the batches of salt is variable, a curing time of eight hours was selected.

DRY-BOX ATMOSPHERE. The quantity of water vapor in the helium gas in the boxes and the exposure time of cured blocks were important factors in maintaining the minimum quantity of lithium hydroxide in the blocks. During earlier sealing operations the quantity of water vapor measured in terms of the dew point was maintained at about -50°F as required by specifications. A lower dew-point value must be maintained if sealing operations are to be done with a minimum increase of hydroxide. Additional drying agents were placed in the helium atmosphere. These drying agents were barium oxide and magnesium perchlorate. Dew points in the range of -65° to -75°F were obtained which are equivalent to 40 and 25 parts per million of moisture, respectively. Better methods of covering hands of operators while working in the dry-boxes were used.

LITHIUM HYDROXIDE DETERMINATION. Further work improved the interpretation of results obtained with the Frazer method of analysis. Oak Ridge National Laboratory reported that the first 25-kilogram shipment of type "A" material contained 6½ per cent hydroxide. The result was determined by using the double titration of the Karl Fischer method. Mound Laboratory analyses using the Frazer method indicated that this material contained over 2 per cent hydroxide and 4 to 6 per cent oxide. Generally, the type "A" material contained many impurities. Analysis of this material for hydroxide after curing yielded very high results even under the most carefully controlled conditions Results varied from 1,500 to several thousand parts per million of lithium hydroxide.

OPERATIONS

During the two-week period in May, 1955, approximately 2,160 two-inch blocks were pressed from type "A" lithium deuteride, gauged, chamfered and weighed. About 260 were cured and were sealed into four-inch aluminum cans after the dew-point of the dry boxes was reduced to -70°F. Installation of the second curing furnace was completed and the furnace was placed in operation. An oil-diffusion pump was added to the curing vacuum system so that a comparison of the outgassing and curing operations could be made with these operations in the mechanical pumping system.

Since a different type of material was to be processed in the dry boxes, a complete conversion of these boxes was required The boxes were cleaned of dust and scraps of type "B" material. All machinery, jigs, and fixtures were cleaned, repaired, and adjusted. All used containers, jars, etc., were removed from the boxes. After resealing, the boxes were dried and the helium atmosphere was adjusted to the same operating conditions which existed before any type "A" material was introduced. The leak detector was completely overhauled, and the dew-point potentiometer was replaced so as to obtain more reliable and accurate readings.

One difficulty encountered during this period was the very rapid build-up of gas pressure within some of the sealed four-inch cans after about one week. Results of lithium hydroxide analysis was 3,712 parts per million for the first batch in which this condition was observed. Results of subsequent batches were 3,847; 1,876; 3,357; and 2,514 parts per million of lithium hydroxide. All of this material will be recured and sealed under the best processing conditions available

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 cancellation of the thorium project early in May, 1955, the objective in the thorium work is to develop a flow sheet of a process for extraction of thorium from Brazilian hydroxide sludge. This work will include such analytical development work as is necessary to complete this job, and solvent extraction work, both batch and countercurrent, in the pilot plant. In addition, a proposal for handling the waste from such a process will be presented.

ANALYTICAL

The final phase of the development of analytical methods for thorium and uranium in the organic fractions from batch countercurrent work and from pulse-columns was completed, using X-ray fluorescent spectrometry. Bromobenzene in 60 per cent Amsco-40 per cent tributyl phosphate was used as an internal standard. The thorium and uranium curves indicated a linear relationship in the concentration ranges selected, 0.40 to 50 milligrams per milliliter of thorium and 0.04 to 4.70 milligrams per milliliter of uranium. No difficulties were found when the method was applied to large-scale analysis.

A batch of strontium nitrate aqueous internal standard solutions was prepared and checked. The results were in agreement with the standard solution previously prepared.

A fluorimetric method for analysis of very small quantities of uranium in the presence of large quantities of thorium has been investigated. Initially, it appeared that thorium could be separated from uranium by precipitation of the thorium with sodium hydroxide, followed by leaching the uranium with sodium carbonate. However, during the process sufficient thorium is carried through to affect the results by quenching of the fluorescent light.

An anion exchange column has been set up, although early experiments were not successful in using ion exchange to separate uranium from thorium. Perhaps in earlier attempts to use an anion exchange column, the thorium was incompletely washed from the column. Dowex A-1 resin, 200 to 400 mesh, was used. Known samples, consisting of 10-milliliter portions, were mixed with 10 milliliters of 12.1-normal hydrochloric acid and passed through the column. The thorium is leached through the column with 250 milliliters of 6.5-normal hydrochloric acid. Uranium is eluted from the column with 100 milliliters of 0.1-normal hydrochloric acid and the solution is analyzed fluorimetrically by means of a Galvanek-Morrison fluorimeter. Average results are shown in Table I.

Experiments have been made to prepare very pure thorium matrix material for the common elements which are to be used as primary standards for spectrographic analysis. Some experiments have been successful. Five samples were analyzed for the common elements without difficulty except for the uncertainty caused by the difference in preparation of the present standards and the samples. Two gross analyses of rare earths were made. Also seven spectrographic analyses of the elemental constituents, dysprosium, europium, gadolinium, and samarium, in rare earths were made. Because of various difficulties incurred with the iodate method for separation of thorium in the rare earth analyses, a method to effect the separation which uses theonyltrifluoroacetone is being studied.

TABLE I

RESULTS OF ANALYSES FOR URANIUM

	THORIUM ($\mu g/ml$)	URANIUM ($\mu g/ml$)	URANIUM FOUND ($\mu g/ml$)
SAMPLES 1-3	10,000	1.00	1.01
SAMPLES 4-6	10,000	0.109	0.105
SAMPLES 7-9	10,000	10.0	10.3

SOLVENT EXTRACTION

Various feed materials to be processed in the thorium refinery have been investigated. Data from batch countercurrent experiments were obtained, and conditions for the initial operation of the pilot plant were established. A sample of OK liquor obtained from the batch countercurrent work after concentration contained 217 grams per liter of thorium, 11.7 micrograms per milliliter of uranium, 0.04 part per million of gadolinium, 0.16 part per million of samarium, and 0.08 part per million of dysprosium.

Some difficulty has been experienced in operating the pilot plant satisfactorily, particularly in the adjustment of amplitude and frequency of the pulsing units.

Two extraction-scrub runs in the pilot plant have been completed after an initial shakedown and the results are promising. The conditions of the first run are shown in Table II

TABLE II

CONDITIONS OF PILOT PLANT RUN

1. SLURRY FEED
2. 24 FEET EXTRACTION (AQUEOUS CONTINUOUS)
3. 24 FEET SCRUB (ORGANIC CONTINUOUS)
4. SCRUB WAS 0.25 MOLAR ALUMINUM NITRATE
5. PULSED AT 60 CYCLES PER MINUTE AND 1 INCH AMPLITUDE
6. FEED ANALYZED
   252 G/L THORIUM
   6.1 G/L URANIUM
   3.4 NORMAL NITRIC ACID
7. 43% TBP - 57% AMSCO
8. FEED.ORGANIC:SCRUB RATIO 1:6:1

Calculations from the flow-sheet from batch countercurrent work showed 105 per cent of saturation at the flow ratio used, so the ratio for the feed analysis of the first-run feed was calculated, holding at 105 per cent of saturation. This ratio was 1:5 for feed:organic. Two phases continued to come off the first column, and after it was determined that they were two organic phases, the ratio was changed to 1:6. The analyses of the streams which were the nearest to equilibrium are shown in Table III.

TABLE III

RESULTS OF ANALYSES OF STREAMS

STREAM	THORIUM	NITRIC ACID	RARE EARTHS		
			Dy	Sm	Gd
	(g/l)	*(N)*	*(ppm)*	*(ppm)*	*(ppm)*
RAFFINATE	1.2	0.17			
ORGANIC FROM 1ST COLUMN	49.5	0.45			
ORGANIC FROM 2ND COLUMN	61.5	0.20	0.6	2.4	0.7
REFLUX 2ND TO 1ST	123.3	3.03			

From the above data it appeared that with 24 feet of scrub column, the scrub flow rate could be lowered. This scrub change was incorporated in the second run. All other conditions were unchanged with the exception of the solvent which was only 38 per cent tributyl phosphate. The ratios used were feed:organic:scrub equal to 1:6:0.5. A ratio feed:organic equal to 1:5 was used and the two organic phases reappeared.

The analyses of the streams which were the nearest to equilibrium are shown in Table IV.

TABLE IV

RESULTS OF ANALYSES OF STREAMS

STREAM	THORIUM	NITRIC ACID	URANIUM			
				Dy	Sm	Gd
	(g/l)	*(N)*	*(g/l)*	*(ppm)*	*(ppm)*	*(ppm)*
RAFFINATE	1.0	0.23	0.96			
ORGANIC FROM 1ST COLUMN	58.1	0.66	1.14			
ORGANIC FROM 2ND COLUMN	50.0	0.24	1.10	0.5	1.1	0.5
REFLUX 2ND TO 1ST	140.0	3.70	NO ANAL.			

Data from these two initial and incomplete experiments with insufficient analyses indicate that the quantity of thorium lost in the raffinate is low, but that the amount of uranium is excessive; that reducing the scrub rate by one-half seemed to have no effect on the quantity of rare earths in the final organic product; and that a solution containing thorium in the organic product in a concentration of 50 grams per liter is possible.

Another run in which the organic product from the two extraction and scrub runs was processed through the partitioning and solvent clean-up cycle indicated a need for flooding data and a re-examination of the pulsing units before further pilot-plant runs.

Before establishing a reliable flow-sheet for the thorium refinery, more experimental data from batch countercurrent experiments should be available for use in pilot-plant runs. Experimental work with batch countercurrent equipment is being continued on the hydroxide sludge feed material. The data for flow rates and for economical use of reagents are being studied. For extraction studies, it is necessary to determine the optimum concentration of the aluminum nitrate in the aqueous scrub; the per cent saturation at the several stages; the amount of aqueous scrub necessary; the flow rate of feed to organic solvent; the effective acid concentration in the feed; the effect of thorium nitrate instead of aluminum nitrate in the scrub; the effect of an aromatic diluent such as Solvesso instead of an aliphatic diluent such as Amsco; and any other factors which may be indicated by the pilot-plant studies. For partitioning studies, batch countercurrent data should be directed toward obtaining information for a concentrated OK liquor with a minimum loss of thorium. Data are needed to substantiate information on the stripping of uranium from the organic solvent in the last column. It is hoped the data which can be obtained will give information on whether it is possible to produce an OK liquor with low impurity content in one cycle or whether it would be necessary or be more economical to use two cycles.

WASTE HANDLING AND TREATMENT

Work has continued on handling and treatment of waste from the solvent extraction of Brazilian hydroxide sludge. The present tentative proposal is to precipitate the rare earths and aluminum from the raffinate, filter, and dry the precipitate for burial, and treat the filtrate with a barium salt to remove the last traces of radium-228. Work along these lines will continue.

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 work is being concentrated in the region of 76 mole per cent sodium fluoride - 12 mole per cent beryllium fluoride - 12 mole per cent uranium tetrafluoride. New master samples across the binary sodium fluoride - uranium fluoride at 4, 8, 12, 16 and 20 mole per cent uranium fluoride at 32 mole per cent beryllium fluoride have been prepared, mixed, and ground. A new grinding and mixing procedure has been adopted which involved hand-grinding of the purified samples so as to pass a No. 40 mesh screen, followed by ball-mill grinding for 3 or 4 hours to pass a No. 60 mesh screen. This grinding assures a more homogeneous fluoride sample and permits easier and more exact preparation of petrographic samples.

Differential thermal analysis runs of 8 mole per cent uranium tetrafluoride mixtures are in progress and will be followed by 12 and 16 mole per cent mixtures. A breakdown of the crimped sealing welds has been experienced when measuring samples with compositions in the central area and in the higher sodium fluoride end of the ternary. This failure of the welds is probably due to small amounts of fluoride salts which cling to the inside walls of the differential thermal analysis tubes during loading and which cause bubbles and voids to form in the weld during sealing. Hence, the weld fails when the molten fluoride salts come in contact with the weld during the homogenizing treatment of the sealed sample at 1,000°C. Filling the differential thermal analysis tube by means of a long-stemmed glass funnel appears to eliminate this difficulty. In order to detect the liquidus in the ternary, depending upon the area involved, it has been necessary to homogenize the differential thermal analysis samples at 1,000°C and quench in a very wet cloth prior to each heating-cycle run. Quenching in water is too severe as ruptures often occur in the tube wall. Without this treatment, the liquidus fades completely or rises greatly upon the second or third heating cycle and only the eutectic can be detected.

The differential thermal analysis liquidus and eutectic points listed in Table V can be reported as being reliable.

Further data were obtained on the thermal-gradient quench of sample U_{25} covering liquidus points from 15.5 to 9 mole per cent uranium tetrafluoride.

The ternary composition 4 mole per cent uranium tetrafluoride - 28 mole per cent beryllium fluoride - 68 mole per cent sodium fluoride was studied in a thermal-gradient quench over the temperature range of 458° to 627°C. No crystals were observed above 562°C, although the glass in all quenches above this temperature showed some crystalline character which was attributed to quench growth. At 562°C and below, crystalline sodium fluoroberyllate (Na_2BeF_4) in increasing amounts was observed. The crystals were lath-like in appearance with parallel striations

and extinction, biaxially negative, of low birefringence, and average index $n = 1.304$. In the sample quenched from 518°C and in some others below this temperature, a colorless isotropic material $n = 1.322$ was observed which may be sodium fluoride.

TABLE V

LIQUIDUS AND EUTECTIC POINTS

COMPOSITION SODIUM FLUORIDE (Mole %)	BERYLLIUM FLUORIDE (Mole %)	URANIUM FLUORIDE (Mole %)	LIQUIDUS (C°)	EUTECTIC (C°)
48	40	12	571 ± 5	367 ± 5
68	28	4	545 ± 5	372 ± 5
40	52	8	562 ± 5	483 ± 5

TABLE VI

INDEX OF REFRACTION

TEMPERATURE (C°)	PHASES PRESENT	INDEX OF REFRACTION OF THE GLASS PHASE (n)
773.5	UF_4 CRYST. + GLASS	1.359
770.5	UF_4 CRYST. + GLASS	1.352
767	UF_4 CRYST. + GLASS	1.350
764	UF_4 CRYST. + GLASS	1.345
761	UF_4 CRYST. + GLASS	1.340
758	UF_4 CRYST. + GLASS	1.332
751	UF_4 CRYST. + GLASS	1.326

PHYSICAL PROPERTIES

The densities of three ternary mixtures of fused fluorides were measured between their melting points and approximately 900°C. These mixtures all contained 12 mole per cent uranium tetrafluoride together with either 76 mole per cent, 70 mole per cent, or 64 mole per cent sodium fluoride respectively. The other constituent was beryllium fluoride. The slope of the density *versus* temperature curve is the same for each system, *i.e.*, 7.8×10^{-4} gram per cubic centimeter per degree C.

The viscosity of a binary mixture of fused fluorides containing 30.2 mole per cent beryllium fluoride and 69.8 mole per cent sodium fluoride, 32.6 weight per cent beryllium fluoride and 67.4 weight per cent sodium fluoride, was measured from 580°C, slightly above the melting point of the system, to 832°C at approximately 50°C intervals. At 600°C the viscosity of the system was 4.5 centipoises and at 830°C it was 2.7 centipoises.

Measurement of the viscosities of ternary mixtures of sodium fluoride, beryllium fluoride, and uranium fluoride has been started. The first system being studied contains 66.7 mole per cent sodium fluoride, 25.1 mole per cent beryllium fluoride, and 8.25 mole per cent uranium tetrafluoride. Two tentative values obtained were 4.1 centipoises at 822°C and 3.8 centipoises at 880°C. However, since these ternary systems have a strong tendency to creep up the sides of the container, these values lack the degree of precision which has been obtained for the binary mixtures. Changes have been made in the dimensions of the rotating cup and the torsion cylinder to reduce the effect of the "creep" of the fused salts.

URANIUM TRIFLUORIDE

Additional measurements were made to determine the solubility of uranium trifluoride in a fused-salt mixture containing 75 mole per cent sodium fluoride and 25 mole per cent beryllium fluoride. The uranium trifluoride used in these investigations contained 11 per cent uranium tetrafluoride. The amount of uranium trifluoride dissolved in this system at 800°C was small. The quantity of uranium trifluoride varied from 1.3 to 2.4 weight per cent, whereas the total uranium, uranium trifluoride and uranium tetrafluoride, was 14.7 to 16.7 weight per cent respectively. The uranium tetrafluoride, which was added as an impurity in the uranium trifluoride, was equivalent to only 3.5 weight per cent. However, nearly four times this quantity of uranium tetrafluoride was found. Uranium tetrafluoride appears to be formed by some reaction which occurs during the solubility measurements.

Examinations of the interior of the nickel vessels used to condition the mixture of fused salts for these measurements revealed that a scale had formed on the walls of the vessels which were in contact with the melts. Recent investigations at Oak Ridge National Laboratory have indicated that this scale is an alloy of uranium and nickel or an intermetallic compound. It has been postulated that the uranium trifluoride at the temperatures of the fused salts disproportionates to uranium tetrafluoride and uranium metal which in turn reacts with the nickel metal of the containers. Therefore, the measurements of the solubility of uranium trifluoride in fused mixtures of fluoride salts will be discontinued until further investigations determine methods to improve the stability of uranium trifluoride under these conditions.

ANALYTICAL METHODS

The determination of the uranium content of fused mixtures of sodium fluoride, beryllium fluoride, and uranium fluoride by potentiometric titration with potassium dichromate has continued to yield satisfactory results. The presence of beryllium and sodium ions does not interfere with this procedure. However, since the uranium must be removed from a solution of this binary mixture before the beryllium can be determined by precipitation methods, the uranium content is also being determined by electrolytic separation techniques. The beryllium content is then determined by precipitation of the beryllium hydroxide, which is ignited to beryllium oxide, and weighed. The use of a platinum dish as one of the electrodes during the

electrodeposition of the uranium has caused a small loss of beryllium from the solution which introduces a small error for systems having a high beryllium content. Since this loss of beryllium appeared to be due to "salting-out" effect in the area where the liquid level contacted the platinum dish electrode, a platinum gauze cylinder was substituted as the electrode. The change has produced satisfactory results.

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.

The experiment on three solution factors, concentration of hydrochloric acid, amount of hydrochloric acid, and method of separation of phases, has been expanded to include a third level for amount of hydrochloric acid, 15 milliequivalents of hydrochloric acid per gram of cake. A consistent improvement in recovery of protactinium was observed as a result of this larger amount of hydrochloric acid.

The experiment was further expanded by introduction of a new factor, *i.e.*, solution time. This was accomplished by repeating previous tests, using a 2-hour solution period instead of a 1-hour period. Improvement in recovery of protactinium resulted. Supplementary tests showed that recovery increased with solution time to 4 hours

The beneficial effect of increasing either solution time, concentration of acid or amount of acid tends to decrease as either of the other two factors increases, suggesting that a rate phenomenon is involved However, beneficial effects of decanting cannot be attributed entirely to longer contact times prior to separation of phases.

By carrying the above tests through the carrier precipitation step, the concentration of hydrochloric acid, the amount of hydrochloric acid, and method of separation used in the solution step are found to have no influence on the efficiency of carrier precipitation.

After considerable delay, eight of the precipitated carriers were treated with caustic and redissolved to provide samples suitable for iron analysis by means of colorimetric procedures. No consistent relation has been found between amount of iron carried and values assigned to solution-step factors.

One radiochemical separation indicated that about 60 per cent of the 300-kev count in raw material from drum No. 19 could be attributed to protactinium The 300-kev counts on supernatant solutions from the solution step have ranged to as high as 80 per cent of that in the original cake The discrepancy may be due to differences between counting machines or operators.

No definite 27-kev peak is detected in the raw material for these tests, *i.e.*, cake from drum No. 19. Four of the residues from the solution step was scanned by gamma pulse analysis. No 27-kev peak was found and the 300-kev peak was shifted to 280 kev, probably from radium interference. In fact, it was shown that if radium is separated from the residue, the remaining protactinium fraction not complexed by versene had a 27-kev peak. This is significant when applied to previous claims for the protactinium process efficiency, since these claims were often based on absence of 27-kev peaks in discarded waste material. This absence is evidently no assurance that all of the protactinium has been removed.

A new procedure for use of gamma pulse analysis has been adopted. Cesium and mercury have been abandoned as base-line standards. A fresh protactinium standard is now used, its 27-kev and 300-kev peaks being used to standardize both the kev and "counts per minute" axes.

The procedure in its present form is only partly satisfactory, because it provides a relative estimation of the quantity of protactinium. The tendancy of the counting instrument to drift electronically, the difficulty of obtaining an accurate count on the original sample because the desired count is not at the peak, and the lack of accurate information as to counting efficiency of the gamma counting method combine to make it highly desirable that the procedure be extended so as to provide for recovery of the protactinium from the insoluble residue in a form which will permit the preparation of a sample mount for alpha-counting.

Such work is in progress. Preliminary results show that approximately 30 to 50 per cent of the protactinium is rapidly and easily recoverable by treatment in the cold with oxalic acid solution. Repeated treatment with oxalic acid does not recover appreciable additional amounts of protactinium, indicating that the mechanism of the protactinium precipitation is, in part, true coprecipitation rather than adsorption.

The protactinium is readily recoverable almost quantitatively by treatment, either hot or cold, with approximately five per cent hydrofluoric acid. On the addition of phosphate ion to the hydrofluoric acid solution and neutralization to pH 4, a precipitate was recovered, which, by spectrographic analysis, contained iron, aluminum, and titanium. The detection of titanium in moderate amounts is very suggestive, as titanium is easily hydrolyzed. It is possible that the mechanism of the reaction involved is the coprecipitation of a protactinic acid with metatitanic acid. Investigation is continuing.

Samples from drum No. 3 and drum No. 19 have been analyzed by the method described and it is found that about 80 and 60 per cent of their respective counts at 300 kev are due to protactinium. However, it is found that drum No. 19 is richer in protactinium than drum No. 3, containing 143 counts per minute per gram as compared with 128 counts per minute per gram as compared with 128 counts per minute per gram in drum No. 3. The difficulty of obtaining representative samples, however, may account for this difference. In a series of four samples from drum No. 3, the counting rate of the original material at 300 kev increased progressively with each sample taken, from 157 to 169 counts per minute per gram.

BIOLOGY PROGRAM

This is the last monthly report of the biology program at Mound Laboratory because the program will cease to exist in approximately one month. Virtually all of the staff have obtained other employment or are in advanced stages of negotiation. An approximate breakdown of the probable final placement of the 22-man scientific staff is shown in Table VII.

TABLE VII

PLACEMENT OF STAFF MEMBERS

1.	TO INDUSTRY		7
	MONSANTO CHEMICAL COMPANY	(9% OF THE TOTAL)	2
	DOW CHEMICAL COMPANY		1
	OTHERS		4
2.	GOVERNMENT LABORATORIES OR CONTRACTORS		6
	U.S. PUBLIC HEALTH SERVICE		2
	ARGONNE NATIONAL LABORATORY		1
	CHEMICAL CORPORATIONS		1
	CONTRACTOR AT WRIGHT FIELD		2
3.	UNIVERSITIES		5
	WASHINGTON STATE COLLEGE		1
	UNIVERSITY OF UTAH		1
	UNIVERSITY OF FLORIDA		1
	UNIVERSITY OF DAYTON		1
	ANTIOCH COLLEGE		1
4.	OTHER		4
	HOSPITALS		2
	PRIVATE LABORATORIES		2

Final reports and scientific publications are appearing at a rapid rate. Three were completed this month, and substantial progress was made on several others.