PRODUCTION OF IONIUM FROM A PITCHBLENDE RESIDUE

by

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St. Louis, Missouri

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Report Number: MCW 1379
Date of Issue: July 28, 1955
Subject Category: Special
Title: PRODUCTION OF IONIUM FROM A PITCHBLENDE RESIDUE

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ABSTRACT

At the request of the Atomic Energy Commission, Mallinckrodt Chemical Works designed and operated a plant for the recovery and purification of thorium230 (ionium) from a pitchblende residue available at the St. Louis Production Center. This plant was based on the Peppard process consisting of a concentration of the thorium by an extraction with 100% tributyl phosphate followed by a hydrofluoric acid strip. The fluoride product is then purified by a solvent extraction flow sheet in hot laboratory equipment.

An account of the technology utilized and an outline of the chemistry on which it was based is given in this report.
I. Introduction

In December of 1954 it was requested of Mallinckrodt Chemical Works by the Atomic Energy Commission that a plant be designed and built for the recovery of thorium230 (commonly referred to as ionium) from pitchblende residues. Production of multi gram quantities of this material was desired in February of 1955. Accordingly, a plant was designed and installed using the basic process developed by D. F. Peppard and his associates at Argonne National Laboratory.1

Ionium is an alpha emitter with a half life of 83,000 years. Since it is a daughter product of uranium238, it is found in uranium ores at secular equilibrium in a concentration of 18.4 parts per million parts of uranium. Since thorium is considered to be a bone seeker in the body, the alpha active isotope, ionium, is an extremely hazardous radioactive poison resembling plutonium and radium. Also associated with uranium in secular equilibrium with its decay products are protactinium231 (32,000 year alpha emitter) and radium226 (1560 year alpha) present in concentrations of 0.33 and 0.35 parts per million parts of uranium respectively. The biology of protactinium is almost entirely unknown, but in absence of contrary information it must also be assumed to be a bone seeker, e.g., the most hazardous possibility. In addition to these long lived alpha emitters, a large variety of short lived alpha, beta, and gamma emitting isotopes are found with uranium. The most important of these are thorium234 (24.5 day beta), lead210 (22 year beta), polonium210 (140 day alpha), actinium227 (21 year beta), thorium227 (18.9 day alpha), and radium223 (11.2 day alpha). The hazards introduced by these radioactive decay products seriously complicate the extraction of ionium from a uranium ore.

Two alternative ionium sources were considered. A waste liquor resulting from the ether extraction of a nitric acid solution of Belgian Congo pitchblende concentrate was available. This liquor, called "raffinate liquor" in this report, consisted essentially of a nitrate solution of all of the nitric acid soluble constituents of pitchblende with the exception of the uranium, radium, and lead isotopes. Prior to 1951 this "raffinate liquor" was found by Peppard to contain approximately 7 mg/l ionium. In addition to the "raffinate liquor", a "raffinate cake" was available. This cake had been produced by the precipitation of the alkali insoluble metals in the "raffinate liquor" with lime and filtration of the cake. This "raffinate cake" containing all of the important components of the raffinate liquor had been stockpiled over a period of 10 years.

The stored "raffinate cake" was selected as a starting material for the ionium process because: 1) the material had aged long enough to permit the beta and gamma emitters to decay to negligible activities, and 2) analysis of currently produced "raffinate liquor" indicated an ionium level about one tenth of that expected from earlier work. Whether this lower ionium concentration was due to a pitchblende starting material not being in secular equilibrium or to some other cause was not unequivocally determined. At any rate, the absence of beta and gamma radiation greatly simplifies the problem of shielding personnel during the production operation. An analysis of a particular sample of "raffinate cake" is shown in Table I. The composition of this material is extremely variable hence this analysis should be considered indicative of the type of material used only, and in no sense as representative of the gross composition of the "raffinate cake" storage pile.

### Table I

**Composition of a "Raffinate Cake"**

<table>
<thead>
<tr>
<th>Element</th>
<th>Percent</th>
<th>Element</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>1.8</td>
<td>Pb</td>
<td>1.8</td>
</tr>
<tr>
<td>Ca</td>
<td>2.7</td>
<td>RE(^a)</td>
<td>0.22</td>
</tr>
<tr>
<td>Cr</td>
<td>0.02</td>
<td>Sc</td>
<td>0.015</td>
</tr>
<tr>
<td>Co</td>
<td>1.8</td>
<td>Si</td>
<td>0.82</td>
</tr>
<tr>
<td>Cu</td>
<td>0.9</td>
<td>Sr</td>
<td>0.02</td>
</tr>
<tr>
<td>Fe</td>
<td>0.7</td>
<td>Th(^b)</td>
<td>0.0038</td>
</tr>
<tr>
<td>Mn</td>
<td>0.04</td>
<td>Ti</td>
<td>0.007</td>
</tr>
<tr>
<td>Mg</td>
<td>0.04</td>
<td>U</td>
<td>0.14</td>
</tr>
<tr>
<td>Mo</td>
<td>0.03</td>
<td>V</td>
<td>0.3</td>
</tr>
<tr>
<td>Ni</td>
<td>3.1</td>
<td>Y</td>
<td>0.04</td>
</tr>
<tr>
<td>NO(\text{3})</td>
<td>8.3</td>
<td>L.O.I.@500°C</td>
<td>49.7</td>
</tr>
</tbody>
</table>

\(^a\) See Table II for approximate rare earth distribution.

\(^b\) Sample contained 0.00039% ionium.
Table II

Rare Earth Distribution in a "Raffinate" Cake Sample

<table>
<thead>
<tr>
<th>Element</th>
<th>% of Total Rare Earths</th>
<th>Element</th>
<th>% of Total Rare Earths</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>3.5</td>
<td>Tb</td>
<td>7.0</td>
</tr>
<tr>
<td>Ce</td>
<td>6.0</td>
<td>Dy</td>
<td>24.3</td>
</tr>
<tr>
<td>Pr</td>
<td>7.7</td>
<td>Ho</td>
<td>2.4</td>
</tr>
<tr>
<td>Nd</td>
<td>13.5</td>
<td>Er</td>
<td>4.6</td>
</tr>
<tr>
<td>Sm</td>
<td>5.3</td>
<td>Tm</td>
<td>0.7</td>
</tr>
<tr>
<td>Eu</td>
<td>5.0</td>
<td>Yb</td>
<td>2.6</td>
</tr>
<tr>
<td>Gd</td>
<td>16.9</td>
<td>Lu</td>
<td>0.07</td>
</tr>
</tbody>
</table>

The ionium content of the "raffinate cake" was found to vary widely. Individual samples taken from even closely adjacent locations at the storage pile varied over a four fold range. However, analysis of composite samples at Mallinckrodt and at New Brunswick indicated that a considerable section of the storage pile had an approximate overall ionium content of 5 g Io per dry ton of cake with individual spot samples within this area varying from 2.5 to 14 g/ton. This concentration was considered sufficient for processing. Considerable soil had been mixed with this raffinate pile during pile moving operations during the past 5-9 years adding to the heterogeneity of the starting material. During the two month operation of the plant an overall ionium content of 10 g/ton was actually realized. The problem of obtaining precise analytical data of the gross composition of the pile is an extremely difficult one and has not yet been satisfactorily solved.

The extremely short time for the engineering and construction of a production plant imposed several special restrictions on the design and operation of the process.

1. The process flow sheet developed by Peppard had to be adopted in toto without preliminary piloting despite the comparatively very small scale on which his work had been carried out.

2. An existing building had to be utilized to house the process equipment.

3. Equipment had to be selected which was immediately available from the manufacturer or was in surplus at a Commission site.

4. A considerably greater health risk was accepted than would be tolerated over any more extended period of time.

5. Very little time could be devoted to making any recalcitrant process step or piece of equipment work during the plant startup period if an alternative was available even though the alternative might present less promising ultimate possibilities.
It is important to recognize these conditions when reading the description of the process since a more deliberate effort would undoubtedly utilize very different technology for some parts of the flow sheet.

The material in this report is based on the experience of the Mallinckrodt plant, and development work in the laboratory at Mallinckrodt. In addition, a great deal of information has been abstracted from Peppard’s work. It has been impractical to clearly distinguish in all cases between work done at Mallinckrodt laboratory and that done at Argonne because of the great overlap. Essentially no claim to originality is made for any part of the flow sheet. In many cases data of the two sites are combined into a single table or graph.

II. Description of the Chemical Sheet

The chemical flow sheet utilized for the separation and purification is given in Figure 1. A description of the equipment and procedure used to apply this flow sheet will be found in section III of this report.

Raffinate cake is dissolved in 60% nitric acid to give a solution containing an excess acidity of 0.5 lb/gal and the resulting slurry was filtered. About seven percent of the ionium remains in this unwashed cake. The filtrate (contactor liquor) is then extracted with undiluted tributyl phosphate (TBP) at a volume ratio of 1 gal TBP per 20 gal contactor liquor. Ninety-five percent of the ionium and essentially all of the uranium is extracted from the contactor liquor and one quarter of the rare earths present are also extracted as well as a major fraction of the protactinium and polonium. None of the other metals present are extracted in gross amounts.

The pregnant TBP is stripped with a 1 molar hydrofluoric acid solution at a volume ratio of 1 gal HF per 6.5 gal pregnant TBP. A three phase system results, a TBP phase, an aqueous phase, and a solid phase suspended in the aqueous. Ninety-three percent of the uranium and the polonium remains in the organic phase. The aqueous phase contains all of the protactinium, seven percent of the uranium, and variable minor amounts of the rare earths. The solid phase consists of essentially all of the thorium, scandium and half of the extracted rare earths as fluorides.

The solid phase, separated by decantation, is then dissolved in a saturated aluminum nitrate solution by heating. Sodium acetate is added to buffer the acidity of the solution in the range 0.02N-10^-4N. This solution can then be further purified using laboratory scale operations because of the large volume reduction. One gallon of this aluminum nitrate solution is equivalent to about 1.1 tons of starting material. The thorium is contaminated chiefly with rare earths, uranium, and scandium at this point.

2 Ibid.
FIGURE 1

FLOW SHEET

PEPPARD IONIUM PROCESS
Purification from uranium is obtained by extracting the uranium from the aluminum nitrate solution with diethyl ether in the presence of a sodium acetate buffer to reduce the loss of ionium into the ether. The ionium going into the ether may be recovered by recycling a water scrub of the ether extract to a subsequent contactor batch since the amount of uranium, although gross with respect to the amount of ionium present, is a negligible fraction of the total uranium entering the process.

Final purification from scandium and the rare earths is accomplished by extraction of the ionium into an ether solution of dibutoxytetraethylene glycol, n-C₄H₉O(C₂H₄O)n-C₄H₉, (commonly abbreviated penta ether) and scrubbing the extract with a concentrated ammonium nitrate solution. Nitric acid must be added to override the buffering action of the sodium acetate to allow extraction into the penta ether.

The product is stripped from the penta ether with dilute nitric acid, and the ionium precipitated with ammonia. This thorium hydroxide precipitate can then be converted into any form desired for the product.

Uranium can be removed from the stripped TBP by successive scrubs with sodium sulfate and sodium carbonate solutions. This step also removes the monobutyl and dibutyl phosphate hydrolysis products of TBP thereby permitting recycle of the solvent. The combined sulfate-carbonate scrubs may be scavenged for uranium.

The spent raffinate from the TBP extraction is precipitated by addition of lime to pH 10. If the reslurried filter cake from the filtration of the initial raffinate cake digestion is combined with this precipitated raffinate and the entire slurry filtered, the filter cake obtained is essentially unchanged in composition from the original raffinate cake except with respect to uranium, thorium, scandium, protactinium, and the rare earths.

A more detailed discussion of the chemistry of these processing steps is presented in the Appendix.

III. Plant Operations

As indicated earlier, time considerations made use of an existing garage building necessary. This structure later presented considerable difficulties because of limited overhead room. A large portion of the equipment had to be located in the open because of space limitations.

Plant operations are naturally divided into two sections according to relative scale. As is evident from the flow sheet in Figure 1, the process is large scale until the aluminum nitrate dissolution step and beyond that a laboratory operation. These stages will be described separately.
A. Large Scale Operation (See Figures 2 and 3 for equipment flow sheet)

1. Nitric Acid Digestion

The raffinate cake was drummed at the storage site in 30 gallon drums, containing about 270 pounds each and transported by truck to the refinery where the drums were weighed and sampled. Approximately 5400 pounds of the wet cake were charged into a tank containing 300 gallons of 60% nitric acid. The resulting slurry was then pumped to a digest tank, sampled for a nitric acid analysis, and adjusted to an acidity of 0.45-0.65 pounds per gallon by the addition of nitric acid or more raffinate cake as required. The slurry was heated to 200°F and stirred for two hours. After this digestion, the slurry was filtered on a Feinc filter, and the filtrate polished on a Niagara precoat filter. Average filtration rate realized on the Feinc filter was 2 1/2 gal/hr/ft². The filtrate referred to as contactor liquor is ready for TBP extraction. The cake was discharged from the Feinc unwashed to prevent dilution of the filtrate. It was reslurried in water and the slurry subsequently combined with the spend raffinate for return to the storage site. A loss of about 7% of the ionium was experienced in this unwashed cake.

The initial conception of this digestion step called for water reslurry of the raffinate cake in a concrete mixer, and a digestion of the resulting heavy slurry in 60% acid. This slurry was to be extracted without filtration. When this slurry extraction was attempted on a large scale, serious emulsions were encountered that prevented disengagement of the viscous TBP phase even on long standing.

2. TBP Extraction

One thousand five hundred gallons of contactor liquor were pumped into a 2000 gallon sloping bottom contactor tank. The nitric acid concentration was checked and adjusted again if necessary to 0.45-0.65 pounds nitric acid per gallon. Seventy-five gallons of 100% TBP were introduced into the suction of a recycle pump which was recycling the contents of the contactor. After all the TBP had been introduced, the two phases were mixed using both a mixer and the recycle pump for one hour. After the two phases were allowed to separate for 2 hours, the upper TBP layer was decanted using a vacuum line proceeded by a knockout tank. In this operation almost all of the organic phase and emulsion was removed, along with some of the raffinate or "spent contactor liquor". This decanted mixture was pumped to a hold tank preparatory to filtering on a Niagara filter to break the emulsion. The remaining spent raffinate in the contactor tank was then contacted a second time with TBP to remove any remaining ionium. The decantation, filtration procedure was repeated combining the TBP with the TBP from
FIGURE 2
SCHEMATIC DIAGRAM
OF
CONTACTER LIQUOR PREPARATION
the first extraction. The twice extracted spent contactor liquor was pumped to the precipitation tanks. An average of 95% of the ionium present in the contactor liquor was extracted by this two stage procedure. Operation with a single extraction gave recoveries of 90-94%.

Contactor liquor acidities of 2.0-2.2 pounds per gallon were used in the early part of the operation because of the erroneous assumption that these higher acidities were necessary to solubilize the ionium from the digestion cake. Production was increased by adding a greater quantity of raffinate cake to a given volume of 60% acid to reduce the contactor liquor acidity to 0.5 pounds per gallon. Economies in acid and lime were realized without decreasing the process efficiency. Digestion times of two hours were used but the criticality of this factor was not investigated.

3. Filtration of Emulsion

The decanted mixture from the contactor tank was filtered on a Niagara precoat filter. Dicalite was used as a precoat material backed with a fine stainless steel wire cloth. A sample of the rather small quantity of solids that collected on the filter analyzed $5 \times 10^{-5}$% ionium.

4. Final Phase Separation

Filtration of the mixture decanted from the contactor tank through a Niagara broke any emulsion present. The filtrate from the Niagara was introduced into a large cone bottom tank equipped with a six inch diameter glass section fitted to tank bottom. After the filtrate had settled for one hour to allow complete phase separation, the outlet valve on the bottom of the clear glass section was opened and the aqueous phase removed until the interface was seen in the glass section. This aqueous phase was combined with the spent contact liquor and pumped to the precipitation tanks. The organic phase, "pregnant TBP", was removed from the tank through an outlet line at a point about six inches above the glass section. In this manner the interface, which at times contained some emulsion, was never broken. In addition, cross contamination of phases was avoided since each line from the tank is used for only one phase. The quantity of water removed at this point in the process was usually about 30% of the organic volume.

5. HF Strip

One hundred fifty gallons of this pregnant TBP was pumped into a cone bottom tank having a glass section mounted on the bottom. The liquor was heated to 170°F by recycling from the bottom of the tank through a double pipe heat exchanger back into the top of the tank. After the TBP had reached temperature, the stream of
recycling liquor was allowed to by-pass the heater and 23 gallons of one molar hydrofluoric acid introduced. It was found necessary to heat both the TBP and the HF to form a denser better settling precipitate. The rate of HF addition was controlled to one gal/min. After HF addition was complete, the two phases were mixed by passage through a recycle pump for 1 hour, and allowed to settle 30 minutes. The white flocculent fluoride precipitate settled into the glass section of the tank. The settled fluoride slurry was drained from the strip tank into one of two 20 gallon cone bottom decanter tanks. One of these tanks was equipped with a steam coil, the other with a steam jacket. A slight post precipitation was occasionally observed in the strip tank after removal of the slurry. Therefore, the aqueous hydrofluoric acid supernate and the stripped TBP phases were allowed to stand an additional 5 1/2 hours. Any further precipitate was drained to the decanter tanks. The total volume of fluoride slurry transferred to decanter tanks was 2-3 gallons. Thus a reduction in volume from 1500 gallons of contactor liquor to 2-3 gallons had been realized at this point of the process.

The remainder of the aqueous phase in the strip contactor was passed through a solid bowl centrifuge at a rate of about 1 gal/min to recover any precipitate not recovered by the decantation operation. The centrifuged aqueous phase was pumped to the raffinate precipitation tanks.

The TBP phase, "spent TBP", was pumped to the scrub tank for uranium removal.

From 92-99% of the ionium was removed from the pregnant TBP by the hydrofluoric acid strip based on analysis of pregnant and spent TBP. Because of sampling difficulties, the efficiency of the decantation step was not determined, but a known loss occurred because of incomplete settling of the flocculent precipitate and less than perfect performance of the centrifuge. Early runs with 0.5 molar hydrofluoric acid gave a smaller bulk of precipitate which made good ionium recoveries very difficult at this step.

During the start up of the plant a separation of the fluoride precipitate was attempted by passing the entire three phase mixture from the strip contactor tank through the centrifuge. As high as 30% losses of ionium were observed with this technique. Attempts to centrifuge the aqueous phase only (e.g., after prior separation of the TBP layer in a decanter tank) were unsuccessful. It was decided to use the centrifuge therefore only as a polishing step. After sufficient cake had accumulated in the centrifuge, the bowl was plowed and the product removed as a water slurry. This slurry was then treated the same as the usual decanted slurry in the next step.
6. **Al(NO$_3$)$_3$ Dissolution**

The 2-3 gallons of slurry in the decant tanks were allowed to settle for 6 hours and the supernate decanted back into the centrifuge bowl. To this settled slurry 30 pounds of aluminum nitrate (Al(NO$_3$)$_3$·9H$_2$O) and 11 pounds of sodium acetate (NaC$_2$H$_3$O$_2$·3H$_2$O) were added, the mixture heated to 200°F and stirred for 6 hours. The resulting solution was then cooled by admitting cooling water to the jacket or coils of the decanter tank. This essentially saturated Al(NO$_3$)$_3$ solution was the feed solution to the hot laboratory.

7. **TBP Scrub**

The TBP from the HF strip had to be scrubbed to remove the uranium. This scrubbing operation was carried out in a 400 gallon cone bottom tank equipped with a clear glass section on its bottom. One hundred fifty gallons of TBP was contacted with an equal volume of sodium sulfate solution (1.2 lb/gal) for 1 hour using a recycle pump for mixing. After a one half hour separation time, the aqueous phase was separated. The TBP was then contacted with 150 gallons of sodium carbonate solution (0.96 lb/gal Na$_2$CO$_3$). This scrubbing operation was carried out in the same way as the first except for an increased settling time of 1 hour. The carbonate solution was combined with the sulfate solution and processed for uranium recovery. Essentially all uranium and ionium present in the TBP was removed by this scrubbing operation. The scrubbed TBP was then recycled to a new contactor batch.

8. **Precipitation of Spent Raffinate**

The spent contactor liquor from the TBP extraction, the aqueous phase from the hydrofluoric acid strip, the digestion cake slurry, and water from the floor sump were all combined in the precipitation tanks. Lime was added to give a pH of 9-10 and the slurry filtered through a Peterson Leaf Filter. This filter cake was weighed, sampled, and returned to the storage site where it was kept separate from untreated raffinate cake.

B. **Hot Laboratory Operation**

While the large scale part of the process had to be redesigned from that reported by Peppard because of the great scale up, the hot laboratory phase of the operation was carried out in equipment essentially the same as that used at Argonne\(^3\) except that it was twice as large. See Figure 4 for a schematic drawing of the purification apparatus.

\(^3\) Ibid.
CONTACTOR FLASKS, 5L CAPACITY
1A-1G ETHER HOLDING FLASKS, 1L LEVELING BULBS
2A-2H NH₄NO₃ HOLDING FLASKS, 500-mL LEVELING BULBS
FEED STORAGE BOTTLE, 2½ GAL
ETHER STRIP WASTE BOTTLE, 2½ GAL
SOLVENT HOLDING FLASK, 1L
NH₄NO₃ WASTE BOTTLE, 5L
HNO₃ & NH₄OH ADDITION FLASK
DECANTATION BOTTLE, 50 GAL
MEASURING BURETTE, 1L
STIRRERS, ACE "TRUBORE" 5"
VACUUM MANIFOLDS, LINES-16 TYGON TUBING
STOPCOCKS- VACUUM SYSTEM, 3-mm BORE HIGH PRESSURE
STOPCOCKS- LIQUID SYSTEM, 4-mm BORE HIGH PRESSURE
ALKALINE SUPERNATANT WASTE BOTTLE, 2½ GAL
PRODUCT BOTTLE, 1-qt. POLYETHYLENE

"HOT LABORATORY" EQUIPMENT FOR PURIFICATION OF IONIUM

FIGURE 4
A 2 1/2 liter portion of the buffered aluminum nitrate solution was introduced into the ether contactor. This solution was contacted with 1 liter of diethyl ether for 10 minutes and allowed to settle for 10 minutes. The aqueous phase was then transferred by suction to a holding tank. The aqueous phase was returned to the contactor and stirred with a second 1 liter portion of ether, etc. The aluminum nitrate solution was thus contacted successively with six 1 liter portions of acidified ether, each extract exclusive of the first, being transferred to a holding tank for use in the subsequent run. The first ether extract of each run was extracted with water and the water extract combined with a following contactor batch to scavenge any ionium extracted with the uranium.

Following the sixth ether extraction, the aqueous phase was transferred by vacuum to a second contactor and mixed with 30 ml of 70% nitric acid. A 2 1/2 liter portion of this acidified aluminum nitrate solution was contacted with 0.5 liters of penta ether. (Actually a mixture of 2 volumes of dibutoxytetraethylene glycol with one volume of diethyl ether was used to increase rate of phase disengagement.) After a contacting time of 15 minutes and a settling time of 15 minutes, the waste aluminum nitrate solution was drained to waste. This waste solution contained an average of 14% of the total ionium in the aluminum nitrate feed solution.

The 1.6 liters of penta ether extract was scrubbed successively with nine 0.5 liter portions of 6 molar ammonium nitrate solution in a semi countercurrent manner. Contacting and settling times of 10 minutes were used. This gave one 0.5 liter scrub solution per run for disposal. The waste scrub solution contained an average of 4.2% of the ionium in the aluminum nitrate feed solution.

Following the ninth scrub, the extract was transferred to the third contactor where it was contacted with seven 1 liter portions of 0.1 normal nitric acid with contact and settling times of 10 minutes.

After the strip solution from several runs had accumulated in the 5 gallon bottle, an excess of ammonia was added with stirring to precipitate thorium hydroxide. After this precipitate had settled a minimum of 8 hours, the supernate was removed by suction and the precipitate redissolved in a minimum volume of 70% nitric acid to give the final product. A solution containing from 1 to 3 grams ionium per liter was obtained.

The glass apparatus indicated in Figure 4 was designed by Peppard to provide a completely closed system since the concentration of ionium achieved at this stage in the process gave a very high specific alpha activity. Two purification lines were operated in parallel. Each was housed in an aluminum hood 12 feet long and 3 feet deep. Sliding panels 9 inches high were provided along the front of the hoods to...
permit operation of the equipment with minimum opening of the hood. Hinged doors in the top section of the hoods permitted access to the equipment for maintenance. Electric motors for the stirrers were mounted on top of the hood to avoid explosion hazards from ether vapors and were connected to the stirrers with flexible shafts.

Although the hot laboratory equipment was in general satisfactory, several minor difficulties were encountered. The 12 foot hoods were too small for the scale of the apparatus. The use of standard tubing clamps at tygon to glass tubing connections produced many leaks and eventually all clamps had to be replaced with twisted copper wire. Stopcock lubrication was a problem but satisfactory results were obtained by using "Lubrisal" in the ether system and silicone grease elsewhere.

In spite of these difficulties an average of 7.5 liters of aluminum nitrate solution was processed through the two absorption train every eight hours by two men.

The overall efficiency for the "hot laboratory" portion of the process during the two months operation was 63.7% based on the ionium present in the aluminum nitrate starting solution. Distribution of these losses among the various side streams are shown in Table III.

<table>
<thead>
<tr>
<th>Stream</th>
<th>Io Lost, %</th>
<th>Io Lost Ideal Conditions, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ether extract(^a)</td>
<td>14.9</td>
<td>2.3</td>
</tr>
<tr>
<td>Waste Al(NO(_3)_3) solution(^a)</td>
<td>14.0</td>
<td>0.1</td>
</tr>
<tr>
<td>NH(_4)NO(_3) scrub</td>
<td>4.2</td>
<td>2.8</td>
</tr>
<tr>
<td>Unaccounted</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>Total Loss</td>
<td>36.3</td>
<td>5.2</td>
</tr>
</tbody>
</table>

\(^a\) Ionium lost into the ether extract and the waste aluminum nitrate solution was recovered by recycle of these streams to subsequent contactor batches.
The inefficiencies shown in Table III are considerably greater than those predicted for a well controlled process on the basis of the known chemistry (see Appendix). Because of the severe pressure for production augmented by the hazardous nature of the materials involved, poor control of some steps was known to exist. The high losses in the ether extraction were due to inadequate control of the pH of the aluminum nitrate feed solution. In many cases the buffer capacity of the sodium acetate-acetic acid buffer was exceeded and the high acid concentration permitted appreciable loss of thorium into the ether extract.

Incomplete ionium extraction by the penta ether solution was due to insufficient addition of aluminum nitrate to the solution. A saturated solution is required for good thorium extraction, but supersaturation results in plugging of pipe lines. Both of these losses could be eliminated in a more leisurely designed plant, and hot laboratory efficiencies of 90-95% realized.

IV. Product Purity

Since equipment for the spectrographic analysis of highly radioactive samples was not available at Mallinckrodt only a single analysis of the impurities in the thorium nitrate product is available. The upper limits for these impurities set by Peppard for the process are also given for comparison.

<table>
<thead>
<tr>
<th>Impurity Content of Final Thorium Nitrate Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCW Product</td>
</tr>
<tr>
<td>Sc</td>
</tr>
<tr>
<td>Gd</td>
</tr>
<tr>
<td>Sm</td>
</tr>
<tr>
<td>Eu</td>
</tr>
<tr>
<td>U</td>
</tr>
<tr>
<td>Ca</td>
</tr>
<tr>
<td>B</td>
</tr>
<tr>
<td>Al</td>
</tr>
<tr>
<td>Peppard's Limits</td>
</tr>
<tr>
<td>less than 100 ppm</td>
</tr>
<tr>
<td>less than 1000 ppm</td>
</tr>
</tbody>
</table>

4 The spectrographic and alpha pulse height analysis were carried out at Argonne National Laboratory through the cooperation of D. F. Peppard. The instrument used for the alpha pulse analysis is described by Ghiorso, A., Jaffey, A. H., Robinson, H. P., and Weissbourd, B. B., National Nuclear Energy Series, Div. IV, Vol. 14B, Paper 16.8 (1949).
The ratio of thorium230 to total thorium ranged from 9.3 to 12.9% throughout the production period. A check of a single sample of the Mallinckrodt product by differential alpha pulse height analysis indicated that 94.6% of the alpha activity of the sample was due to thorium230 and the remainder due to thorium227. 5

V. Appendix

A. TBP Extraction

The extractability of thorium, rare earths, and yttrium into TBP is dependent upon both the acidity of the system and the concentration of other nitrate salts. In Figures 5, 6, and 7 the variation of distribution coefficients (defined as concentration in organic phase divided by concentration in aqueous phase) of these elements is presented as a function of nitric acid and calcium nitrate concentration. These distribution coefficients were determined in synthetic systems with calcium nitrate used to simulate the mixture of soluble nitrate present in contactor liquor. It is evident from these curves that maximum extraction is obtained for all three of these elements at minimum acidities and maximum salt concentrations. In practice the minimum acid concentration is limited by that required to keep all constituents of the contactor liquor in solution. The concentration of metallic nitrates is limited by the concentration of nitric acid used as digestion acid. In plant operation the contactor liquor was 1.4-0.9M HNO₃ and 3.7-6.3M in total nitrate. If Ca(NO₃)₂ solutions are assumed to be representative of the salting effects in contactor liquor, the recoveries to be expected from two extractions at a ratio of 1 volume of TBP to 20 volumes contactor liquor are shown in Table V.

<table>
<thead>
<tr>
<th>Element</th>
<th>% Extracted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th</td>
<td>99-99.8</td>
</tr>
<tr>
<td>RE</td>
<td>45-74</td>
</tr>
<tr>
<td>Y</td>
<td>10-30</td>
</tr>
<tr>
<td>Ua</td>
<td>&gt;99.8</td>
</tr>
<tr>
<td>Sca</td>
<td>75-90</td>
</tr>
</tbody>
</table>

a Data for uranium and scandium based on Peppard's work. 6

5 Ibid.
FIGURE 5

THORIUM DISTRIBUTION COEFFICIENT AS FUNCTION OF NITRIC ACID CONCENTRATION AND CALCIUM NITRATE CONCENTRATION OF AQUEOUS PHASE (ORGANIC PHASE TBP)
FIGURE 6
EUROPIUM DISTRIBUTION COEFFICIENT AS A FUNCTION OF INITIAL HNO₃ AND CA(NO₃)₂ CONCENTRATION OF THE AQUEOUS PHASE (ORGANIC PHASE TBP)
FIGURE 7
Yttrium Distribution Coefficient
as a Function of Initial HNO₃ and 
Ca(NO₃)₂ Concentration of the
Aqueous Phase.
Organic Phase TBP

Initial Nitric Acid Concentration (moles/liter)
Qualitatively it was observed that the presence of phosphate or sulfate reduced the extractability of thorium from these liquors, but no quantitative data has been accumulated. It is evident that in absence of serious anion interference, good yields of ionium are to be expected under plant extraction conditions.

**B. HF Strip**

Dilute hydrofluoric acid was selected by Peppard\(^7\) as a strip solution for the following reasons: 1) an extremely large reduction in volume was possible, 2) the resulting fluoride precipitate could be readily dissolved in a form suitable for further processing, and 3) considerable purification of the thorium with respect to uranium, rare earths, and protactinium was possible with good control of precipitation conditions.

Peppard, working on an extract scale of 500 ml of TBP extract, found that it was impractical to use a volume of aqueous hydrofluoric acid smaller than one-sixth of the volume of pregnant TBP regardless of the hydrofluoric acid concentration. Use of smaller volumes resulted in a precipitate of undesirable properties which tended to remain dispersed in the organic phase and to adhere to walls of the strip contactor. The quantity of hydrofluoric acid adopted by Peppard (1 volume of 0.5 molar acid per 4 volumes pregnant TBP) was selected to give appreciable separation from rare earths. He observed precipitation of all of the thorium, 90-95% of the scandium and approximately 25% of the yttrium and rare earths in the extract.

During startup of the process at Mallinckrodt as mentioned earlier, serious difficulty was encountered with the separation of this solid phase. The settling characteristics of the precipitate were markedly improved by carrying out the precipitation as hot as possible. Also, 1 molar acid was used to increase the volume of the precipitate despite the increased rare earth contamination of the thorium resulting at this stage.

The efficiency of uranium extraction from the pregnant TBP is also influenced by the concentration of hydrofluoric acid employed as shown in Table VI. Here the fraction of the uranium removed in the aqueous strip solution is given as a function of the fluoride concentration of the strip solution. A pregnant TBP containing 10 g/l U, 7 g/l rare earths, and 1 g/l Th served as starting material for this experiment. One volume of 1 molar hydrofluoric acid was just sufficient to precipitate all the rare earths and thorium present. In all runs a ratio of phase volumes of four organic to one aqueous was used.

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\(^7\) Ibid.
Table VI
Effect of Hydrofluoric Acid Concentration on Uranium and Thorium Stripping from a Synthetic Pregnant TBP

<table>
<thead>
<tr>
<th>HF Concentration, M</th>
<th>% U Extracted (in Solution)</th>
<th>% Th Extracted (in Precipitate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.4</td>
<td>99</td>
</tr>
<tr>
<td>1.0</td>
<td>0.6</td>
<td>98</td>
</tr>
<tr>
<td>1.5</td>
<td>2.7</td>
<td>99</td>
</tr>
<tr>
<td>2.0</td>
<td>3.5</td>
<td>98</td>
</tr>
</tbody>
</table>

C. Ether Extraction

Although only about 0.1% of the uranium originally present in the contactor liquor reports in the aluminum nitrate solution, it is still present in concentrations of the same order as the ionium. Separation of thorium and uranium is possible by extraction with diethyl ether from a solution buffered in the range 0.02–10^{-4}N nitric acid as is shown by the data in Table VII taken from Peppard.\(^8\)

Table VII

<table>
<thead>
<tr>
<th>Composition of Aqueous Phase, N</th>
<th>Distribution Coefficient(_{\text{org}}^{\text{aq}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(NO(_3))(_3), NaOAC, HOAC</td>
<td>U</td>
</tr>
<tr>
<td>6.7, 1.1, 0.5</td>
<td>52</td>
</tr>
<tr>
<td>6.7, 2.2, 0.5</td>
<td>15</td>
</tr>
<tr>
<td>6.7, 2.2, 1.0</td>
<td>35</td>
</tr>
<tr>
<td>6.7, 0.2N HNO(_3)</td>
<td>70</td>
</tr>
<tr>
<td>6.7, 0.5N HNO(_3)</td>
<td>8</td>
</tr>
</tbody>
</table>

\(^8\) Ibid.
If the acidity rises much above 0.02N, important ionium losses will occur into the ether phase in the course of the six extractions.

D. Penta Ether Extraction

Extraction of thorium from the aluminum nitrate solution with penta ether solvent occurs readily providing enough nitric acid is added to overcome the acetate buffer and the aqueous solution has a sufficiently high concentration of aluminum nitrate. This effect of aluminum nitrate concentration is illustrated in Figure 8. It is evident from this curve that aluminum nitrate concentrations as near saturation as possible are desirable.

To reduce the time necessary for phase disengagement a solution of 2 volumes of penta ether in one volume of diethyl ether was used to give a much less viscous organic phase than pure penta ether.

E. Analytical Method for Determination of Ionium

For routine assay purposes the following method was used for the determination of ionium: 20 ml of solution to be analyzed was saturated with aluminum nitrate and contacted with 10 ml penta ether (P.E.) for five minutes. Following phase disengagement the extract was scrubbed with three 20 ml portions of 10M NH₄NO₃ solution. The depleted raffinate and the three scrubs were discarded. The P. E. extract was then contacted with four 20 ml portions of 0.5N HNO₃. The combined reextract was diluted to 100 ml and duplicate ~50 Ï samples were evaporated on steel dishes and flamed for alpha-counting.

9 Ibid.
EXTRACTION OF THORIUM INTO PENTA ETHER FROM ALUMINUM NITRATE SOLUTION

ORGANIC PHASE 66.7% (PENTA ETHER - 33% ETHER)