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A process for separating thorium compounds from monazite sands

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UMI
A PROCESS FOR SEPARATING THORIUM COMPOUNDS FROM MONAZITE SANDS

BY

Kernal Glenn Shaw

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of The Requirements for the Degree of DOCTOR OF PHILOSOPHY

Major Subject: Chemical Engineering

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1953
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The purpose of this investigation was to study the sulfuric acid digestion of monazite sand, and to prepare a thorium-containing material from the resulting solution which would be suitable for further purification by liquid-liquid extraction. It was also desired that the by-product rare earths and uranium be recovered in a form convenient for further processing.

Studies were made in the laboratory and in a pilot plant to determine the optimum conditions for the digestion of monazite sand and for the separation of thorium, rare earths, and uranium by fractional neutralization of the monazite sulfate solution. The most effective separation was obtained when the monazite solution was dilute and when ammonium hydroxide was used as a neutralizing agent. The resulting process consisted of the following steps:

1. Digestion of ground monazite sand in 93 per cent sulfuric acid for five hours at 155° -230°C. The acid-to-sand weight ratio was 1.56.

2. Dissolution of the solid reaction products in water and clarification of the solution by allowing the acid-insoluble sludge to settle.

3. Fractional precipitation of thorium phosphate by dilution of the monazite sulfate solution with six parts of water and neutralization to a pH of 1.05 with ammonium hydroxide.
4. Fractional precipitation of the rare earth phosphates by neutralization of the filtrate from the thorium separation to a pH of 2.3 with ammonium hydroxide.

5. Fractional precipitation of uranium phosphate and the remainder of the rare earths by neutralization of the filtrate from the rare earth separation to a pH of 6.0 with ammonium hydroxide.

The precipitates from each fraction were thickened and filtered. The over-all recovery of thorium was 96-97 per cent, of rare earths 98-99 per cent, and of uranium 53-54 per cent. The remainder of the thorium and uranium can be recovered by further processing.

A cost comparison was made between the Ames Laboratory process and a process developed by the Battelle Memorial Institute for a plant which would produce five tons of thorium per month from Idaho monazite sand. The estimated processing cost for the Ames Laboratory process was $9.11 per pound of thorium as compared with $11.48 per pound for the Battelle process. Both of these costs included $4.67 for the cost of the monazite sand. The Battelle caustic digestion process produced two hydroxide concentrates. One contained thorium and uranium. The other contained rare earths. Hydroxide concentrates could also be produced by the Ames Laboratory process by a caustic digestion of the three phosphate concentrates at an additional cost of about $1.25.
INTRODUCTION

By undergoing neutron capture, followed by beta decay, thorium may be used to produce fissionable $^{233}$U (26). The reactions are:

$$\text{Th}^{232}(n, \beta) \rightarrow \text{Th}^{233} \rightarrow \text{Pa}^{233} \rightarrow \text{U}^{233}$$

23.5 min. 27.4 days

The importance of this fact was realized by the Atomic Energy Commission and an intensive research program was begun to study the methods of production and the properties of thorium metal and thorium compounds (36).

The only commercial source of thorium is monazite sands, in which the thorium content seldom exceeds ten per cent. The major constituents are the orthophosphates of the light rare earths. Monazite sands are used commercially as a source of thorium and rare earth chemicals (29). India and Brazil have the richest and most extensive deposits of these sands and have produced most of the world's supply since 1915. Recently, however, both countries have placed an embargo on the export of monazite sands, forcing the Atomic Energy Commission to develop other foreign and domestic sources. Most of the domestic needs are now supplied from Idaho. However, considerable quantities of sands may be obtained from South Africa and Wyoming in the near future (27).
In 1943, projects were initiated at Ames Laboratory and the Battelle Memorial Institute for studying the production and purification of thorium compounds from monazite sands. The Atomic Energy Commission desired that a high percentage of the thorium be recovered and that the final product have an extremely high purity (28). The presence of even a few parts per million of rare earths or any other elements having a high neutron capture cross section would seriously reduce the efficiency of $^{233}U$ production. It was also desired that the rare earths and the small amount of uranium present in the monazite sands be recovered in a useable form. Battelle developed a process which involved digesting the monazite sands with caustic and purifying the thorium by liquid-liquid extraction (13). Ames Laboratory based its process on the more commonly used sulfuric acid method of digestion and purified the thorium by a similar liquid-liquid extraction (47).

The project at Ames Laboratory was divided into the following phases:

1. Studies for decomposing the monazite sands with sulfuric acid and recovering the thorium, the rare earths, and the uranium.

2. Studies for purifying the thorium to meet Atomic Energy Commission specifications.

3. Studies for separating and purifying the individual rare earths.
4. Studies for purifying the uranium.

The research described in this thesis was concerned with only the first phase of the over-all project. The other phases are being studied by other members of the Chemical Engineering Division of Ames Laboratory. The specific objectives of the research were:

1. To make the following studies on a laboratory and pilot plant scale.
   a. The sulfuric acid digestion of the monazite sands.
   b. The preparation of a thorium-containing material suitable for purification by liquid-liquid extraction.
   c. The preparation of concentrates of the rare earths and the uranium.

2. To prepare an economic evaluation of the resulting process and compare with other proposed processing methods.
REVIEW OF THE LITERATURE

The review of the literature was divided into six major categories.

1. Monazite sands.
2. Digestion of the sands.
4. Recovery of the rare earths.
5. Recovery and purification of uranium.
6. Preliminary Ames Laboratory studies.

The rare earth producers were very reluctant to reveal any of their process technology. Therefore, most of the information available in the literature was only of a qualitative nature.

Monazite Sands

Monazite sands are the principal commercial source of thorium and rare earth compounds. Thorium is also found in thorite (55 per cent ThO₂) and in orangite (70 per cent ThO₂) (31). These minerals, however, are not of commercial importance because of their limited supply. The major constituents of monazite sands are the orthophosphates of the rare earths, comprising about 0 to 90 per cent of the total weight (29). Thorium is only a minor constituent and is present in concentrations from 1 to 18 per cent. The
remaining constituents are small amounts of silica, zircon, iron, aluminum, titanium, and uranium. The compositions of monazite sands from various sources are listed by Mellor (29), Taggart (43), and George (21). Palache (31) describes the monazite sands as yellow to reddish-brown in color, and as being very hard and brittle. The specific gravity is 5.0-5.2, and the sands are moderately paramagnetic. The crystalline form is monoclinic.

Monazite sands are widely distributed. Workable deposits are found in India, Brazil, South Africa, Malay States, Australia, Russia, Florida, South Carolina, North Carolina, Idaho, and Wyoming. Monazite is usually found in alluvial sands, and is associated with other minerals, such as ilmenite, zircon, rutile, garnet, and quartz. Very few deposits contain over 20 per cent monazite and most of the domestic sources contain only 0.1 to one per cent monazite. At the present time it is too expensive to mine the monazite sands for themselves alone. Most producers rely on the by-product ilmenite, zircon, gold, and silver to defray part of the mining costs (27).

Separation from the accompanying minerals is accomplished first by tabling to remove the lighter minerals, and then by magnetic concentration. The ilmenite, magnetite, and garnet are removed on the lower intensity poles, and the monazite and small amounts of zircon and rutile are
removed on the higher intensity poles. The tailings consist mostly of gold, residual quartz, feldspar, etc. Flotation, electrostatic separation, and heavy media separation may also be used to concentrate the monazite sands (43).

**Digestion of the Sands**

Several different processes have been developed for chemically decomposing the monazite sands. A review of the processes listed in the U. S. patent literature was prepared by Bearse (6). The most widely used method involved digestion with sulfuric acid. The monazite sands (20, 29, 33, 36) were reacted at 200°C with 2.0-2.5 times their weight of concentrated sulfuric acid until the resulting mass was a thick paste and all the solids had been completely reacted. This reaction usually took from two to four hours. The pasty mass was then cooled and treated with water until the solids were completely dissolved. There was usually a small amount of acid-insoluble residue left containing silica, zircon, and rutile. The resulting solution contained the thorium, the rare earths, and the uranium as sulfates (20), or as phosphate complexes (36). A modification of the usual digestion procedure was described by Wade (45), Berndt (8), and McCoy (30). The mixture of sands and sulfuric acid was first heated to 200°C for about one hour, and then was heated to 300°C for another four to twenty
hours. While the digestion conditions were more severe, this procedure had the advantage that the thorium compounds were water insoluble, and could be recovered in the silica residue. If it were desired to recover the radium in the silica residue, a barium salt was added to the solution or to the original digestion mixture (22). It is believed that none of these methods are in common use today.

Arden and Burstall (3) modified the dissolution procedure by washing the pasty digestion mass with strong sulfuric acid and then removing the solids by filtration. While the acid requirements were high, this procedure had the advantage that the sulfates of the rare earths and thorium were freed from the phosphoric acid liberated during the digestion. In a German patent (18) a process was described in which both the free sulfuric and phosphoric acids were separated from the insoluble sulfate salts. The reaction mass was pulped in an aliphatic alcohol and then filtered. The filtrate was neutralized and the alcohol was recovered by distillation.

Other basically different methods have been developed for digesting the monazite sands. These methods have the advantage of removing the phosphate during the digestion procedure. In the past, however, they have not been able to compete economically with the sulfuric acid digestion method. Shultze (37) described a process in which the
monazite sands were heated with coke and an alkaline earth oxide to 1500°C. The phosphate was reduced to elemental phosphorous and was removed by sublimation. The solids were then treated with hydrochloric acid and dissolved. Attempts were made to fuse the monazite sands with sodium peroxide or sodium hydroxide (13). The reaction was incomplete and the mass was difficult to handle. The Battelle Memorial Institute (13) overcame this difficulty by digesting the sands in 45 per cent aqueous sodium hydroxide. The digestion was carried out on monazite sand ground to minus 300 mesh. The reaction was carried out at 138°C for three hours, followed by dilution with water and heating at 104°C for another hour. This latter step was to facilitate filtration of the hydroxide cake. Complete digestion of the monazite sands was reported. This digestion procedure, followed by removal of the sodium phosphate by filtration, served as a starting point for the subsequent separation and purification of the thorium, the rare earths, and the uranium. This separation procedure is described in more detail in the section covering the recovery and purification of thorium.

Other methods of attacking the monazite sands involved digestion with nitric acid (7), perchloric acid (9, 48), and chlorination with a reducing agent and potassium chloride (1). The treatment with nitric acid gave only partial
dissolution. It is believed that none of these procedures is in commercial use today.

The conversion of the rare earth and thorium phosphates present in monazite sands to the corresponding sulfates is a highly exothermic reaction. However, there were no data in the literature giving a value for this heat of reaction, nor were there data for the heats of formation of the products and reactants from which the heat of reaction could be calculated.

Recovery and Purification of Thorium

A review of a few of the processes used for separating and recovering thorium from monazite sands was made by Willigman and Slowter (49). Only those processes using the sulfuric acid digestion method were covered. It was stated that thorium may be recovered from the monazite sulfate solution by gradually reducing the acidity until the insoluble thorium phosphate precipitated. The rare earth phosphates were more soluble and remained in solution. Davis (15) used sodium carbonate or sodium hydroxide to partially neutralize the solution. About 90 per cent of the thorium was precipitated and the precipitate contained 50 per cent thorium phosphate. Ammonium hydroxide (36) or magnesia (42) could also be used to partially neutralize the monazite sulfate solution. Fernelius (20) reported
that dilution with water alone could be used to reduce the acidity and precipitate the thorium phosphate. The values of pH at which the thorium and the rare earth phosphates precipitated were not given in these references. Battelle (13) reported that at a pH of 1.6, 99 per cent of the thorium had precipitated together with only a few per cent of the rare earths. However, this work was done with a nitrate solution of thorium and rare earths containing only enough phosphate to precipitate the thorium. Arakawa (2) reported that at a pH of 1.0 the thorium phosphate was still partially soluble. Soddy (39) fractionally precipitated the thorium by adding a mixture of sulfuric and phosphoric acids directly to the monazite sulfate solution. The slurry was then filtered, and part of the recovered acid was used to digest another batch of monazite sand. The thorium precipitate contained a considerable amount of excess phosphate.

Dietshoe (16) and Wade (46) developed a separation method using fluoride to fractionally precipitate the thorium. Clark (14) selectively precipitated thorium as an oxide or peroxide by adding potassium permanganate or hydrogen peroxide to the monazite sulfate solution and heating. Other chemicals which have been used to selectively precipitate thorium were sodium metaphosphate, sodium hypophosphate, and sodium pyrophosphate (36).
Final purification of the precipitated thorium compounds from the accompanying rare earths has been accomplished by each of the following procedures:

1. Fractional crystallization of the sulfates, of which the thorium sulfate was the least soluble (49).

2. Sodium carbonate leaching to dissolve the thorium, followed by the addition of sodium hydroxide to reprecipitate the thorium (15,23).

3. Ammonium oxalate leaching of the mixed thorium-rare earth oxalates. The thorium was soluble and the rare earths were left behind (36).

All of these procedures were tedious and many repeated treatments were required to obtain pure thorium compounds to meet Atomic Energy Commission specifications. A much simpler purification procedure used liquid-liquid extraction. Ames Laboratory (40) developed a process for separating small amounts of rare earths from thorium nitrate by liquid-liquid extraction with tributyl phosphate. The final product containing less than one part per million of rare earths was obtained. The New Brunswick Laboratory (35) reported that phosphate and sulfate interfered to a great extent with this extraction. However, Whatley (47) found that the addition of ferric nitrate or nitric acid would reduce the detrimental effect of these ions and thorium could be successfully extracted from the rare earths.
In the research project carried out at the Battelle Memorial Institute a process was developed for purifying thorium and uranium which involved the following steps:

1. Digestion of the monazite sand in 45 per cent solution of sodium hydroxide.
2. Filtration of the resulting hydroxide cake and evaporation of the filtrate to recover the sodium phosphate and the excess sodium hydroxide.
3. Dissolution of the hydroxides of thorium, rare earths, and uranium in hydrochloric acid.
4. Fractional neutralization of this solution to precipitate thorium and uranium hydroxides at a pH of 5.0.
5. Neutralization of the filtrate to precipitate the rare earth hydroxides.
6. Dissolution of the thorium-uranium hydroxide cake in nitric acid.
7. Liquid-liquid extraction of this solution with a tributyl phosphate-naphtha mixture.
8. Recovery of the thorium by selectively stripping the solvent with nitric acid, and then precipitating the thorium as the oxalate.
9. Recovery of the uranium by stripping the solvent with water and precipitating the uranium as the hydroxide.
The over-all thorium recovery was 90 per cent and the over-all uranium recovery was 70 per cent. The thorium produced contained two parts per million of uranium and less than 44 parts per million of rare earths. The lack of a suitable analytical method prevented better estimates of rare earth contamination. The estimated cost of the thorium was reported to be $5.19 per pound for a plant producing five tons per month of thorium from Brazilian monazite sands, and $3.17 per pound for a plant producing 25 tons per month (13). This cost estimate included some credit for the by-product sodium phosphate, and the rare earth and uranium hydroxides.

Recovery of the Rare Earths

The process most commonly used by industry was described by Pilkerton and Wylie (33). It involved the crystallization of the rare earths as sodium double sulfates by the addition of sodium sulfate to a monazite sulfate solution. Only the light rare earths were removed in this manner and the heavy rare earths remained in solution with the thorium. The recovery of thorium was reported to be 60 to 80 per cent. Arakawa (2) indicated that ammonium sulfate could be used to crystallize the ammonium double sulfate from the monazite sulfate solution. If the thorium had been previously separated from the rare earths by
fractional precipitation as the phosphate, the rare earths were precipitated by neutralizing the filtrate (36).

Final purification and separation of the rare earths was accomplished by digesting in caustic to convert the phosphates or double sulfates to the hydroxides and then fractionally precipitating the hydroxides of the individual rare earths. Fractional crystallization of the sulfates or double sulfates has also been used to separate the individual rare earths. At best these separation methods were tedious and the yields of purified material were low. Recently ion exchange (41) and solvent extraction techniques (10,32) have made this separation less tedious and more efficient.

Uranium Recovery and Purification

There were few references found in the literature concerning the separation of uranium from monazite sands. Arden and Burstall (3) described a process which involved the following steps:

1. Digesting monazite sands in sulfuric acid.
2. Washing the digestion mass with sulfuric acid to remove the phosphoric acid.
3. Dissolving the sulfates in water and then precipitating them as hydroxides.
4. Dissolving the hydroxides in nitric acid.
5. Contacting the resulting solution with diethyl ether and tetrahydrosylvane to selectively extract the uranium.

6. Stripping the solvent with water to recover the uranium.

The uranium still contained some thorium, rare earths, and phosphate, and further purification steps were necessary. The recovery and purification of uranium using the Battelle process was described in the section covering the recovery and purification of thorium.

The purification of uranium nitrate solutions has been extensively studied by the Atomic Energy Commission (12,35). Phosphate and sulfate reduced the extractability of the uranium, but not to the same degree as for the thorium. High recovery of uranium was still obtained in spite of these interfering ions (5).

Previous Ames Laboratory Studies

Preliminary studies on the separation and purification of thorium and uranium compounds from monazite sands were initiated at Ames Laboratory in April, 1948. At that time the known methods for digesting monazite sands were surveyed and it was decided that the most economical process would be one using a sulfuric acid digestion of the sands, followed by liquid-liquid extraction of the resulting solution to
separate and purify the thorium and the uranium compounds. Rare earth compounds would be obtained as a by-product.

Blickwedel (9) studied the digestion of the monazite sands with perchloric and sulfuric acids. He found that the perchloric acid digested the sand at a faster rate than did the sulfuric acid. However, due to the high cost of perchloric acid it would not be economical to use for this purpose. No selective dissolution of the thorium or the rare earths was observed. A composite plot of Blickwedel's data for the sulfuric acid digestion, showing the effect of acid-to-sand ratio, acid concentration, and temperature for a two hour digestion, is presented in Figure 1. The data showed that in order to obtain almost complete digestion of the sands, the reaction temperature should be above 180-200°C, the acid concentration above 90 per cent, and the acid-to-sand ratio above 2.0. At conditions less severe than these, the completeness of digestion dropped off very rapidly.

By the use of various organic solvents Feldman (19) attempted to extract the thorium or the rare earths from the monazite sulfate-phosphate solution obtained from the digestion of the monazite sands. Some success was found with nitromethane and with mixtures of butanol with one of the following solvents: dioxane, ethanol, and ethylene glycol monoethyl ether. However, none of these solvents
Figure 1: Digestion of Monazite Sands with Sulfuric Acid

- **Percentage Decomposition of Monazite Sands**
- **Acid Temperature (°C)**
- **95% Sulfuric Acid**
- **Concentrations Other Than 95% Sulfuric Acid**
- **Acid to Sand Ratio**: 1/1, 2/1, 3/1, 5/1

Two hours digestion time on Indian Monazite Sands.

- **95% Sulfuric Acid**
- **Concentrations Other Than 95% Sulfuric Acid**
exhibited any selectivity. Whatley (47) continued these studies and was also unable to find a suitable solvent for extracting the thorium or the rare earths from the monazite sulfate-phosphate solution. He found, however, that a solution suitable for solvent extraction of the thorium could be prepared by the following method. The monazite solution was diluted and neutralized in order to precipitate the thorium, the rare earths, and the uranium as phosphates. The resulting precipitate was washed with water to remove most of the sulfate ion, and then was dissolved in nitric acid. The thorium and uranium could be selectively extracted from this solution with tributyl phosphate. The rare earths were recovered from the raffinate as phosphates. It was also found that the addition of ferric nitrate increased the extractability of the thorium and the uranium by complexing the interfering phosphate ion.
LABORATORY INVESTIGATIONS

The main objectives of the laboratory investigations were: first, to study the digestion of the monazite sands in order to lower the acid requirements and to determine the conditions necessary to make a pilot plant digestion; secondly, to develop a more direct method of preparing a thorium-containing material suitable for purification by solvent extraction with tributyl phosphate. Fractional precipitation of the thorium and rare earth phosphates from the monazite sulfate solution appeared to provide both a direct and an economical method for concentrating the thorium and preparing the feed material. The rare earths, and possibly the uranium, would be recovered from the filtrate.

Raw Materials

The monazite sands used in this study were obtained through the Atomic Energy Commission from Brazil, Idaho, and Travacore, India. The material had been shipped in burlap bags and cement sacks, and when it arrived at this laboratory it contained varying amounts of foreign material such as gravel, coal, and paper. In Idaho monazite sand, pieces of wood and mill scale were also found. The foreign material accounted for less than 1 per cent of the total
weight in the Indian and Brazilian sands; however, there was 2.0-2.5 per cent foreign material present in the Idaho sand. The monazite sands received were hard, brittle, tan in color, and individually rounded like beach sand. The material was radioactive, emitting mostly beta and gamma rays. The radiation level was almost independent of the weight, indicating a considerable amount of self adsorption. One foot from the storage barrels the radiation intensity was six milliroentgens per hour, the maximum daily tolerance level, and it decreased to one milliroentgen per hour at four feet. No radiation shields were required in the sand storage area.

About 4,000 pounds of Idaho monazite sand and 1,080 pounds of Brazilian monazite sand were received in bags, each containing approximately 120 pounds of sand. Samples were taken from the bottom and top of each bag with a small aluminum scoop and put into a five gallon bucket for composite sample storage. The bulk of the sands was transferred to 55 gallon steel drums. When full each drum contained about 600 pounds of sand. The composite samples were then split by means of a 10 inch by 5 inch Jones riffle to obtain four 40 gram samples for chemical analysis and two 200 gram samples for screen analyses. The 40 gram samples were ground to minus 65 mesh before removing material for analysis.
The chemical composition of the Indian, Brazilian and Idaho monazite sands and the thorium content of the screening fractions are shown in Table 1. The methods of analysis may be found in the Appendix A. When these analyses were first attempted in 1946 by the Analytical Group of the Ames Laboratory, the methods were difficult and the results were not reproducible. Recently, with more refined methods, the results have been more consistent and in good agreement with values reported in the literature for the three monazite sands (12, 21, 43). The analyses of the Brazilian sands checked almost identically with the results obtained by the Battelle Memorial Institute on what is believed to be the same shipment of ore. The only difference was the value for total oxides, which Battelle reported as 65.7 per cent. The Ames Laboratory determination was 60.9 per cent. The latter figure is more in line with the values reported in the literature.

The most important physical properties of the as-received monazite sands were measured and are reported in Table 2. The particle size distribution is an important variable in the digestion of the monazite sands. The bulk density is required to estimate storage capacities. The specific gravity is used in estimating the settling rates and the thorium content of the monazite sands.

Particle size distribution was determined by a screen analysis of each of the two samples using eight inch Tyler
Table 1
Chemical Analyses of Monazite Sands, As-Received Basis

<table>
<thead>
<tr>
<th></th>
<th>Indian Monazite Sand</th>
<th>Brazilian Monazite Sand</th>
<th>Idaho Monazite Sand</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Average Chemical Analyses</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Oxides(^a)</td>
<td>69.2</td>
<td>68.1</td>
<td>68.9</td>
</tr>
<tr>
<td>Th(_2)O(_2)</td>
<td>9.4</td>
<td>6.5</td>
<td>3.95</td>
</tr>
<tr>
<td>CeO(_2)</td>
<td>26.5</td>
<td>--</td>
<td>29.2</td>
</tr>
<tr>
<td>U(_3)O(_8)</td>
<td>0.37</td>
<td>0.18</td>
<td>0.15</td>
</tr>
<tr>
<td>P(_2)O(_5)</td>
<td>25.9</td>
<td>26.0</td>
<td>28.5</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>--</td>
<td>2.2</td>
<td>3.14</td>
</tr>
<tr>
<td>Pb</td>
<td>--</td>
<td>--</td>
<td>0.01</td>
</tr>
</tbody>
</table>

| **Thorium Content of Screen Fractions** |                     |                          |                     |
| **Mesh Size**             |                      |                          |                     |
| +10                      | --                   | --                       | 0.68                |
| - 10+20                  | --                   | --                       | 0.25                |
| - 20+28                  | --                   | --                       | 3.64                |
| - 28+35                  | --                   | 6.21                     | 3.57                |
| - 35+48                  | 9.37                 | 6.52                     | 3.86                |
| - 48+65                  | 10.22                | 6.22                     | 4.02                |
| - 65+100                 | 8.46                 | 6.62                     | 4.05                |
| -100+150                 | 8.58                 | 6.14                     | 3.53                |
| -150+200                 | 8.56                 | 5.09                     | 1.12                |
| pan                     | 6.57                 | 4.05                     | --                  |

\(^a\)The total oxides includes the combined oxides of the thorium and the rare earths.
### Table 2

**Physical Properties of Monazite Sands**

<table>
<thead>
<tr>
<th>Screen Analysis</th>
<th>Weight Per Cent Retained</th>
<th>Indian Monazite Sand</th>
<th>Brazilian Monazite Sand</th>
<th>Idaho Monazite Sand</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesh Size</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+10</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>Trace</td>
</tr>
<tr>
<td>- 10+14</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>Trace</td>
</tr>
<tr>
<td>- 14+20</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.04</td>
</tr>
<tr>
<td>- 20+28</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.06</td>
</tr>
<tr>
<td>- 28+35</td>
<td>--</td>
<td>--</td>
<td>2.5</td>
<td>2.3</td>
</tr>
<tr>
<td>- 35+48</td>
<td>0.07</td>
<td>11.9</td>
<td>18.4</td>
<td></td>
</tr>
<tr>
<td>- 48+65</td>
<td>2.9</td>
<td>42.9</td>
<td>47.7</td>
<td></td>
</tr>
<tr>
<td>- 65+100</td>
<td>30.4</td>
<td>38.8</td>
<td>28.3</td>
<td></td>
</tr>
<tr>
<td>-100+150</td>
<td>54.0</td>
<td>3.5</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>-150+200</td>
<td>12.3</td>
<td>0.3</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>pan</td>
<td>0.3</td>
<td>0.1</td>
<td>0.2</td>
<td></td>
</tr>
</tbody>
</table>

**Bulk Density**

<table>
<thead>
<tr>
<th>As-Received Sands</th>
<th>Pounds Per Cubic Foot</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>210</td>
</tr>
<tr>
<td></td>
<td>206</td>
</tr>
<tr>
<td></td>
<td>196</td>
</tr>
</tbody>
</table>

**Specific Gravity**

| As-Received Sands | 5.25 | 5.17 | 5.11 |
standard screens ranging from 10 mesh to 200 mesh. The weight per cents, reported in Table 2, are the averages of the two determinations. In all tests the results had only a 0.5 to 5.0 per cent deviation; the smaller weight fractions showing the larger percentage error. In the case of Idaho sand the plus 10 to plus 20 mesh fractions contained large amounts of foreign material and, as can be seen from the chemical analyses of these fractions, do not contain very much monazite sand. There was also a considerable amount of gangue in the minus 200 mesh fraction.

The bulk density was determined by measuring the volume occupied by a known weight of monazite sand. A 100 milliliter graduated cylinder was filled with a weighed amount of as-received monazite sands. The cylinder was then vibrated by rubbing the bottom on a roughened surface until no more volume decrease was observed. The tests usually took from five to seven minutes and the results were reproducible. The results are reported in Table 2.

The specific gravity of the monazite sands was determined by measuring the displacement of alcohol by a known weight of sand and then referring the volume of liquid displaced to the density of water at 25°C. All determinations were made with as-received monazite sands. Ethyl alcohol was more suitable for these determinations than
water because not all of the entrapped air could be removed when water was used. The results are shown in Table 2.

The specific gravity may be used to estimate the thorium content of the monazite sands. Thorium has a molecular weight of 232 and the rare earths have an average molecular weight of about 140. The addition of thorium should increase the average molecular weight of the heavy metal phosphates, and, thereby, increase the specific gravity of the sand. If the thorium originally entered the sand by randomly replacing the rare earths in the rare earth phosphate structure, the weight per cent thorium should vary linearly with the specific gravity. This replacement reaction would be:

\[
\frac{3}{4} \text{Th} + \text{RPO}_4 \rightleftharpoons \text{Th}_{\frac{3}{4}}\text{PO}_4 + \text{R}
\]

where R symbolizes the rare earths. Assuming that the average molecular weight of the sand is proportional to the specific gravity, the average molecular weight of the monazite sands may be represented by the following equation:

\[
\text{Average Molecular Weight} = \text{PO}_4 + \text{R} (1-X) + \frac{3}{4} \text{Th} X
\]

\[
= (\text{PO}_4 + \text{R}) + X (\frac{3}{4} \text{Th} - \text{R})
\]

If the molecular weights are expressed as constants, then

\[
\text{Average Molecular Weight} = A + B X
\]
where:  
\[ A = PO_4 + R \]
\[ B = 3/4 Th - R \]
\[ X = \frac{M_{Th}}{M_R + M_{Th}} \]

\[ M_{Th} = \text{Rare earth equivalents of thorium per unit weight of monazite sand.} \]
\[ M_R = \text{Equivalents of rare earths per unit weight of monazite sand.} \]

In almost all monazite sands the number of rare earth equivalents per unit weight of sand is constant. The rare earth equivalent of thorium is 3/4 Th. Therefore,

\[ M_{Th} + M_R = \text{Constant} = C \]

and the final equation of average molecular weight, as a function of the weight per cent thorium, is

\[ \text{Average Molecular Weight} = A + B X \frac{M_{Th}}{C} = A + K X \frac{W_{Th}}{C} \]

where:

\[ W_{Th} = \text{Weight of thorium per unit weight of monazite sand.} \]
\[ K = \frac{B}{C \times 3/4 Th} \]

When the data for the weight per cent ThO₂ and the specific gravity were plotted, a straight line resulted passing through the 95 per cent confidence limits for the
three determinations. By means of Figure 2, one should be able to determine the thorium content of monazite sands for field analyses, for accountability estimates, and for other purposes where a rapid estimate is desired. However, this correlation is reliable for only pure monazite sand. As the percentage of gangue material increases low and even negative results may be obtained.

Digestion of Monazite Sands

Before describing the digestion studies conducted during this research, a brief discussion of the digestion mechanism is necessary in order to obtain an insight into the processes taking place during the reaction between the sulfuric acid and the monazite sands. This digestion mechanism was hypothesized from the following observations made from Blickwedel’s digestion studies (9):

1. The rate of digestion may be increased by increasing the acid-to-sand ratio.¹
2. The rate of digestion may be increased by increasing the temperature of the reaction.
3. The optimum acid concentration for the digestion was 93 per cent.
4. During the course of the reaction the digestion mass became pasty and would occasionally solidify.

¹All ratios of acid-to-sand refer to the weight of 100 per cent sulfuric acid to the weight of monazite sands.
FIGURE 2 CORRELATION OF SPECIFIC GRAVITY OF MONAZITE SANDS WITH ThO$_2$ CONTENT.
5. Perchloric acid digested the sands faster than did sulfuric acid.

The reaction between monazite sand and a mineral acid may be regarded as an erosion or corrosion process, proceeding at a rate which is dependent upon the mineral acid used, the temperature and concentration of the acid, and the surface characteristics of the sand particles. When sulfuric acid is used one must also take into account the fact that the products of the digestion are insoluble and form a coating over the surface of the monazite sand particles. The rate of reaction is then dependent not only on the rate of erosion, but also on the resistance of the insoluble coating to the transfer of acid to the surface of the particles. The resistance of this coating can be decreased by increasing the agitation and by maintaining the fluidity of the reaction mass.

When the sand is added to the hot sulfuric acid, the reaction proceeds rapidly. As the reaction continues there is a gradual change of the rate controlling mechanism from one of erosion to one of mass transfer. As the coating becomes thicker the reaction rate decreases and when sufficient solid reaction products have formed, the reaction mixture virtually solidifies. From this point on the reaction proceeds very slowly as the sulfuric acid diffuses through the solid but porous mass. This may be illustrated by the
fact that during the first fifteen minutes of the digestion, the consistency of the reaction mixture changed from a pumpable fluid to a kneadable dough-like material and finally, after an additional fifteen to thirty minutes, to a gray solid. The reaction mass contained about 60 per cent free acid and occupied a volume about one and a half times the original volume of acid and sand.

A faster rate of digestion would be expected with perchloric acid because the products of the reaction are soluble in the acid. The reaction is thus one of erosion and mass transfer of the acid need not be considered.

If 100 per cent sulfuric acid is diluted with water, the reactivity of the acid is decreased and the fluidity of the reaction mixture is increased, thereby, obtaining better agitation. The first effect decreases the over-all rate of reaction and the second effect increases the over-all rate of reaction. Therefore, an optimum concentration of sulfuric acid was expected. Blickwedel found this optimum acid concentration to be 93 per cent. He also found that the rate of reaction decreased more rapidly when the concentration of the acid was less than 93 per cent, than it did when the acid concentration was between 93 and 100 per cent.

The acid requirements for the digestion of the monazite sand could be decreased by lowering the initial acid-to-sand
ratio. The lowest acid-to-sand ratio studied thoroughly by Blickwedel was 2.0. He also had isolated points at ratios of 1.5 and 1.0. While complete digestion was not obtained at these latter two points, the acid-to-digested sands ratios were 1.57 and 1.52, respectively. This would mean that 25 per cent less acid could be used to accomplish the digestion of the sand. Operation at these conditions would necessitate recycle of the undigested sand.

When digesting only a few hundred grams of monazite sand, the reaction was carried out in laboratory glassware. However, in order for a pilot plant digester to withstand the corrosive action of the hot acid, it must be constructed of Duriron, Hastelloy C, ceramic ware, or glass-lined steel. All other materials of construction are unsuitable for operation at 180-220°C with 93 per cent sulfuric acid. By carrying out the digestion at 100-120°C it would be possible to use a steam-heated reactor constructed of cast iron or Carpenter 20 stainless steel. Before such a reactor could be designed, however, it would be necessary to know the rates of digestion of the monazite sand at 100-140°C and at acid-to-sand ratios of 1.2-1.5.

Before considering pilot plant operation it was necessary to make the following studies:

1. Determination of the minimum acid-to-digested sand ratio.
2. Determination of the effect of time and temperature on the digestion of the monazite sand at temperatures below 140°C.

3. Determination of the effect of recycle of the monazite sand on the build-up of acid insoluble materials.

Minimum acid-to-sand ratio

According to Fernelius (20) the reaction between sulfuric acid and monazite sand may be represented by the following equations:

\[ 2RPO_4 + 3H_2SO_4 \rightarrow R_2(SO_4)_3 + 2H_3PO_4 \]
\[ Th_3(PO_4)_4 + 6H_2SO_4 \rightarrow 3Th(SO_4)_2 + 4H_3PO_4 \]
\[ SiO_2 \cdot xH_2O + H_2SO_4 \rightarrow SiO_2 + H_2SO_4 \cdot xH_2O \]

where \( R \) symbolizes the rare earths. The theoretical minimum acid-to-digested sand ratio may be calculated from the above equations and from the chemical analyses of the monazite sands. These values were 0.616 for the Indian monazite sand, 0.610 for the Brazilian monazite sand, and 0.606 for the Idaho monazite sand. This would mean, for example, it would require a minimum of 0.616 pounds of 100 per cent sulfuric acid to completely digest one pound of Indian monazite sand.
There was a lower limit, however, to the amount of acid to be used for the digestion. This limit was governed not by the stoichiometry of the reaction, but by the solubility of the thorium phosphate in the resulting monazite sulfate solution. This precipitate was very voluminous, often causing the solution to gel. Therefore, it was necessary to provide enough free acid in order to avoid difficulties in the operation of the pilot plant, especially with the recovery of the undigested sands.

As-received Indian and Idaho monazite sands were used in this study. The sulfuric acid was reagent grade obtained from the General Chemical Division of Allied Chemical and Dye Corporation. This acid was assayed at 95.5 per cent and was diluted to 93 per cent before the digestions were made. The digestion procedure involved heating the acid to 200°C on an electric hot plate and then adding fifty grams of monazite sands. The mixture was constantly stirred by means of a glass stirring rod, and the temperature was held at 200 ± 3°C. As the reaction proceeded the mixture became more and more difficult to stir. At first it had a dough-like consistency, and finally it solidified. When the desired time had passed (one hour for the Indian sands and one and a half hours for the Idaho sands) the digestion mass was removed from the hot plate and cooled to room temperature. Dissolution of the reaction mass was effected
by adding ten grams of water per gram of sands digested. The undigested sand was separated from the solution, dried, and weighed. The quantity of sand digested was determined by difference. The stability of the solution was determined by allowing it to stand for thirty-six hours. If no precipitate of thorium phosphate formed, the solution was considered stable. If the solution was unstable, the thorium phosphate usually precipitated within an hour. If no precipitation occurred in the first thirty-six hours, it remained stable indefinitely.

The initial acid-to-sand ratio was varied from 2.0 to 1.0 and the final acid-to-digested sand ratio was calculated from the quantity of acid used and the weight of the sands digested. The results are shown in Figure 3. For both the Indian and Idaho sands the resulting monazite sulfate solution was unstable if the acid-to-digested sands ratio was less than $1.61 \pm 0.02$. Above this value the thorium phosphate did not precipitate and the solution was stable indefinitely. Since the minimum acid-to-digested sands ratio was constant for these two sands of widely different thorium contents, similar results are expected for Brazilian or any other type of monazite sands used. Due to the smaller average particle size more complete digestion was obtained with the Indian sand than with the Idaho sand.
FIG. 3  EFFECT OF SULFURIC ACID-TO-SAND RATIO ON THE DIGESTION OF MONAZITE SAND AND ON SOLUTION STABILITY
Low temperature digestions

Both as-received and ground Idaho monazite sands were used in this study. The sulfuric acid concentration was 93 per cent and the initial acid-to-sand ratio was 1.2. Seventy per cent digestion was required to obtain the minimum acid-to-digested sands ratio of 1.61. The reaction temperatures studied were 25°, 60°, 100°, and 140°C.

It was estimated that at these low temperatures ten hours to several days would be required to accomplish about 75 per cent digestion. To insure proper temperature control for this prolonged period of time, a constant temperature bath capable of temperature control of ± 1°C up to 150°C was employed. Mineral oil was used for the heat transfer medium. The reaction between the acid and the sand was carried out in a 250 milliliter filter flask fitted with a one hole rubber stopper. Agitation was accomplished by a motor-driven glass stirrer which passed through the rubber stopper by means of a mercury seal.

The reaction between the sulfuric acid and the sand was initiated by heating the acid to the desired temperature in the reaction flask and then adding the monazite sands. Agitation was continued until the reaction mass was near solidification. After the desired reaction time had elapsed, the flask was removed from the constant temperature bath and the reaction was quenched by the addition of water.
to dissolve the reacted material. The unreacted monazite sand was separated from the solution by decantation, and then was dried and weighed. The percent digestion was calculated by difference.

The data from these digestions are shown in Figure 4. The first two digestions were run at 25°C and 60°C using as-received Idaho sand. The results were very disappointing, showing only 0.1 percent and 3.3 percent digestion, respectively, after 22.5 hours of reaction. Another run at 60°C using ground monazite sand showed 28.5 percent digestion after 22.5 hours. The reaction temperature was then increased to 100°C and 140°C. Three digestions at 100°C using ground sand indicated that over 100 hours (five days) would be required to achieve the desired 75 percent digestion. The results at 140°C showed that the desired percentage digestion could be achieved in 44 hours using ground monazite sand and in 62 hours using the as-received sand. While the digestion rates obtained at 140°C showed considerable improvement over those obtained at lower temperatures, they still did not compare with the rapid digestion rates obtained at temperatures above 200°C.

Recycle of undigested monazite sand

In pilot plant digestions, in order to maintain high thorium recovery, it would be necessary to recycle the
FIGURE 4 LOW TEMPERATURE DIGESTION OF MONAZITE Sands.

- AS-RECEIVED MONAZITE
- GROUND MONAZITE
  2.3% + 100 MESH
  35.6% + 270 MESH
the undigested sand. No difficulty was expected from this operation since this sand was believed to be the residue from the larger particles of monazite sand that were more slowly attacked by the acid. Repeated contacts with the hot acid should completely digest these particles.

The study was made using as-received Indian monazite sand and 93 per cent sulfuric acid. The initial acid temperature was 125°C. The acid-to-sand ratio was adjusted so that the final acid-to-digested sand ratio would be 1.61. The residual sand from one digestion was added to the fresh sand used in the next digestion. Eight digestions were made in a three-neck three liter flask, which was heated by an insulated electric heating mantle.

The reaction between the acid and the sand was initiated by adding as-received Indian monazite sand to the hot 93 per cent sulfuric acid. During the first few minutes the acid temperature dropped as the sand cooled the acid. Then the heat of reaction caused the temperature to rise very rapidly, reaching 240-245°C in about twenty minutes. During this time the consistency of the reaction mass changed from a fluid to a plastic mass and finally to a solid. After about two hours the reaction temperature had cooled to about 200°C, and after four hours the temperature was 150°C. Water was then added, and the undigested sand was recovered by allowing it to settle, and decanting.
the monazite sulfate solution. The sand was dried and weighed, and the quantity of sand digested was obtained by difference. This residual sand was then used in the next digestion.

The results of this study are shown in Table 3. The sixth and seventh digestions showed a lower percentage digestion than expected. This was due to the inadvertent use of 90 per cent acid for the digestion instead of the customary 93 per cent. When the proper concentration of acid was used in the eighth digestion, the expected acid-to-digested sand ratio of 1.62 was again obtained. The over-all thorium recovery for the eight digestions was 98.6 per cent, based on the ratio of the grams of undigested sand remaining after eight digestions to the total weight of sand used. It is known from the silica analysis of the sand that acid-insoluble materials were present. Therefore, if the recycle study was carried on indefinitely, a build-up may be expected.

**Dissolution of the digestion mass**

Dissolution of the sulfate salts produced by the digestion was accomplished by treating the solidified mass with ten grams of water per gram of monazite sand digested. The resulting solution had a concentration very close to saturation with respect to the rare earth and thorium sulfates.
<table>
<thead>
<tr>
<th>Total Weight of Sand</th>
<th>Weight of Recycled Sand</th>
<th>Acid-to-Sand Ratio</th>
<th>Sulfuric Acid Conc. Weight</th>
<th>Max. Reaction Temp.</th>
<th>Per Cent Digested</th>
<th>Acid-to-Digested Sand Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams</td>
<td>Grams</td>
<td>1.35</td>
<td>93</td>
<td>246</td>
<td>87.0</td>
<td>1.56(^a)</td>
</tr>
<tr>
<td>1200</td>
<td>---</td>
<td>1.40</td>
<td>93</td>
<td>247</td>
<td>89.8</td>
<td>1.56(^a)</td>
</tr>
<tr>
<td>1500</td>
<td>169</td>
<td>1.44</td>
<td>93</td>
<td>244</td>
<td>89.1</td>
<td>1.62</td>
</tr>
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<td>1500</td>
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<td>1.44</td>
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<td>242</td>
<td>86.7</td>
<td>1.66</td>
</tr>
<tr>
<td>1500</td>
<td>164</td>
<td>1.42</td>
<td>92.3</td>
<td>240</td>
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<td>1.63</td>
</tr>
<tr>
<td>1500</td>
<td>200</td>
<td>1.42</td>
<td>90</td>
<td>233</td>
<td>83.2</td>
<td>1.71</td>
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<tr>
<td>1500</td>
<td>196</td>
<td>1.42</td>
<td>90</td>
<td>235</td>
<td>83.8</td>
<td>1.70</td>
</tr>
<tr>
<td>1500</td>
<td>252</td>
<td>1.42</td>
<td>93</td>
<td>245</td>
<td>87.6</td>
<td>1.62</td>
</tr>
</tbody>
</table>

\(^a\)Solution unstable.
A typical solution prepared from Indian monazite sands had the following composition:

- Total oxides: 57.2 grams/liter
- $\text{ThO}_2$: 8.01 grams/liter
- $\text{P}_2\text{O}_5$: 22.6 grams/liter
- $\text{U}_3\text{O}_8$: 0.22 grams/liter
- Total acidity: 3.01 N

The reddish-brown color of the solution was attributed to the presence of the red salts of neodymium and the green salts of praseodymium.

A small quantity of very finely divided solids was also present in the solution. These solids settled very slowly, requiring a few hours to settle the largest, and several weeks to settle the smallest. Spectrographic analysis indicated that the major constituent of these solids was silica. A radiation survey showed that they contained a very large fraction of the radioactive daughter products of thorium and uranium, and that care should be taken in handling the solid. Hereafter, these solids will be referred to as the silica sludge.

Fractional Precipitation Studies

The literature indicated that fractional precipitation of the thorium and rare earth phosphates had been used to
separate and recover thorium from the monazite sulfate solution. However, these reports also indicated that only a partial separation was made and that high recovery of the thorium was not obtained. In line with the Atomic Energy Commission specifications that the proposed process have a high recovery of thorium, the objectives of this study were to determine the pH at which complete recovery of the thorium would be obtained, and to determine the values of pH at which the rare earths and the uranium phosphates would precipitate. In order to complete this study it was necessary to determine the effect of the following variables upon the precipitation of the thorium, the rare earths, and the uranium:

1. Neutralizing agent.
2. Time of agitation.
3. Acid-to-digested sands ratio.

Experimental methods

In this study of the fractional neutralization of the monazite sulfate solution the same basic experimental procedure was used for each test. A pipetted aliquot of the monazite sulfate solution, usually 50 or 100 milliliters, was diluted with water and partially neutralized with a
dilute solution of ammonium hydroxide or sodium carbonate. These precipitations were carried out in a 600 or 1000 milliliter beaker. Agitation was provided by a motor-driven stirrer. The pH electrodes were immersed in the solution and were removed occasionally for standardization against a buffer solution. The base was added to the solution as a thin stream from a 50 milliliter burette.

The precipitated solution was agitated at the desired pH for a predetermined length of time. It was then filtered by gravity or suction. This procedure was repeated using the filtrate from each preceding precipitation until a pH of 7.0 had been reached. Filtrations were made at intervals of 0.1-0.5 pH units between pH 0.8 and 3.0 and at intervals of 1.0 pH units between pH 3.0 and 7.0. After a pH of 7.0 there was no longer any thorium, rare earths, or uranium left in solution. The precipitates from each fraction were not washed, but sucked as dry as possible on a vacuum filter. The solids were then dissolved in acid and chemical analyses were made on each sample for thorium, total oxides, phosphate, and uranium. However, due to the lack of a suitable analytical method, the data for the fractional precipitation of the uranium were not available until this research was almost completed.

At the beginning of this study the pH of the solutions was measured by means of a Beckman Model M battery-operated
pH meter. However, the readings, especially between a pH of 0.5 and 2.0, were erratic and affected by motors operating in the general area. Usually after a few weeks of operation the electrodes had to be replaced. Satisfactory measurement of pH's was obtained from a potentiometer or null reading type of pH meter. All values reported in this study were obtained using a Leeds and Northrup Model Number 7663-Al potentiometer type pH meter. Buffer solutions for pH 1.2 and 2.0 were purchased from the LaMott Chemical Products Company. The buffer solutions for pH's 3.0, 4.0, and 7.0 were prepared from "phydrion" buffer tablets made by Micro Essential Laboratory. The pH of these buffers was verified by checking them against standard potassium chloride-hydrochloric acid (25) buffer solutions of pH 1.0 and pH 2.0.

The concentration of the monazite sulfate solution usually varied each time a new solution was prepared. Therefore, in order to have a common basis to which to refer the data, it was necessary to define the concentration of a standard monazite sulfate solution. A concentration was chosen which was nearly saturated with the rare earth and thorium sulfates, and which was approximately the concentration obtained when preparing a liter of solution from 100 grams of monazite sand. The standard monazite sulfate solution was defined as one containing 70 grams per
liter of total rare earth and thorium oxides. It was not necessary to specify the thorium concentration in this standard solution. A concentration basis was chosen for the standard rather than the weight of sands required to make up a volume of liquid because the fractional precipitation data would then be independent of the total oxide content of the monazite sands.

All dilution ratios mentioned in this research were referred to this standard monazite sulfate solution. For example, a dilution ratio of 5.0 means that one part of the monazite solution was diluted to 5.0 times its original volume by the addition of 4.0 parts of water.

Experimental results

The effect of neutralizing agent. Two fractional precipitation tests were made on diluted monazite sulfate solutions in order to determine the pH values at which the thorium and the rare earth phosphates would precipitate. In the first test the solution was neutralized with 1.9 normal sodium carbonate and in the second with 1.9 normal ammonium hydroxide. The dilution ratio was 5.2, i.e., one part of a standard monazite sulfate solution was diluted with water to 5.2 parts of total solution. The acid-to-digested sands ratio was 1.72 and the time of agitation before filtration was five minutes.
The results of this study are shown in Figure 5. Complete precipitation of the thorium phosphate was obtained at a pH of 1.30, and 99.7 per cent recovery was obtained at a pH of 1.18. The initial precipitation of the rare earths occurred between a pH of 1.10 and a pH of 1.18 when both the ammonium hydroxide and the sodium carbonate were used. In the latter test additional rare earths continued to precipitate for a half hour to an hour in the filtrate from the pH 1.18 and the pH 1.30 fractions. These rare earths are included with the others precipitated at a pH of 1.30 and a pH of 1.50, respectively. At a pH of 1.30, 100 per cent recovery of the thorium was obtained and 38.3 per cent of the total rare earths had precipitated. No such post-precipitation was observed when ammonium hydroxide was used. One hundred per cent recovery of the thorium was obtained at a pH of 1.30 and only 18.6 per cent of the total rare earths was precipitated.

These two tests were repeated with one hour of agitation before filtration instead of five minutes. Sixty per cent of the rare earths were precipitated at a pH of 1.30 when sodium carbonate was used. Only 21 per cent of the rare earths precipitated at this pH when ammonium hydroxide was used. The difference in the results was attributed to a lower solubility for the rare earth sodium double sulfate salt than for either the rare earth phosphate
FIGURE 5  EFFECT OF NEUTRALIZING AGENT ON PRECIPITATION OF THORIUM AND RARE EARTH.
AGITATION TIME - FIVE MINUTES
DILUTION RATIO - 5.2 TO 1
100 PER CENT ACID / DIGESTED SANDS RATIO - 1.72
or the corresponding ammonium double sulfate salt (50,51). The effect of time was important because the mechanism was one of crystallization instead of instantaneous precipitation. Chemical analyses of the rare earth fractions revealed that the rare earth precipitates obtained in the pH range of 1.3 to 1.8 did not contain sufficient phosphate to stoichiometrically account for all the rare earths. In the initial rare earth precipitate, when sodium carbonate was used, it was estimated that only 5 to 15 per cent of the total rare earths were present as phosphates. However, when ammonium hydroxide was used, it was estimated that 65 to 80 per cent of the rare earths were present as phosphates. The remainder was ammonium or sodium sulfate and the rare earth sulfates. It was not possible to estimate the nature of any compounds formed.

In the first thorium-rich fraction the rare earths present did not precipitate as a phosphate or a double sulfate, but were dissolved in the solution occluded by the gelatinous thorium phosphate. When a correction was made for the phosphate contained in this occluded solution, \( \text{ThO}_2/\text{P}_2\text{O}_5 \) ratios of 1.85 to 2.10 were obtained. This indicated that the thorium was precipitating principally as \( \text{Th} (\text{HPO}_4)_2 \) and that small amounts of \( \text{Th}_3(\text{PO}_4)_4 \) were present.

Since fractional neutralization of the monazite solution with ammonium hydroxide precipitated less of the rare
earths with the thorium, it was decided to discontinue the studies using sodium carbonate. Ammonium hydroxide was used for all the subsequent fractional precipitation studies.

**Effect of time of agitation.** When sodium carbonate was used as the neutralizing agent, the time of agitation before filtering the precipitate had a marked effect on the quantity of rare earths precipitating with the thorium. Therefore, it was necessary to determine if the agitation time had the same effect when ammonium hydroxide was used. Two tests were made. In one the pH was held constant for 30 minutes before filtering, and in the other the pH was held constant for 60 minutes before filtering. The dilution ratio was 5.2, the acid-to-digested sand ratio was 1.72, and 1.9 normal ammonium hydroxide was used as the neutralizing agent.

The data obtained for agitation times of 30 minutes and 60 minutes are shown in Table 4 along with the data for five minutes agitation obtained from the previous study. Time appeared to have little or no effect on the precipitation of the thorium except at a pH of 0.80. At this pH, 60 minutes of agitation precipitated an additional 3.3 per cent of the thorium over that obtained at 30 minutes of agitation. In the pH range 0.80 to 1.17 the precipitation
Table 4

Effect of Time on Fractional Precipitation of Thorium and Rare Earths

Dilution Ratio - 5.2  Acid-to-Digested Sand Ratio - 1.72
Indian Monazite Sand  Neutralizing Agent - 1.9N NH₄OH

<table>
<thead>
<tr>
<th>pH</th>
<th>Thorium Cumulative Per Cent Precipitated</th>
<th>Rare Earths Cumulative Per Cent Precipitated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 min. 30 min. 60 min.</td>
<td>5 min. 30 min. 60 min.</td>
</tr>
<tr>
<td>0.80</td>
<td>--- 31.5 94.8 ---</td>
<td>4.2 4.0</td>
</tr>
<tr>
<td>0.95</td>
<td>96.0 95.4 98.5 4.2 5.2 4.7</td>
<td></td>
</tr>
<tr>
<td>1.05</td>
<td>99.0 99.0 99.2 5.5 5.6 4.7</td>
<td></td>
</tr>
<tr>
<td>1.17</td>
<td>99.9 99.9 99.9 7.5 6.0 6.4</td>
<td></td>
</tr>
<tr>
<td>1.28</td>
<td>100.0 100.0 100.0 18.6 13.4 9.3</td>
<td></td>
</tr>
<tr>
<td>1.51</td>
<td></td>
<td>59.1 47.3 ---</td>
</tr>
<tr>
<td>1.81</td>
<td></td>
<td>79.5 79.0 78.7</td>
</tr>
<tr>
<td>2.00</td>
<td></td>
<td>88.5 84.8 85.0</td>
</tr>
<tr>
<td>2.20</td>
<td></td>
<td>91.0 --- 89.5</td>
</tr>
<tr>
<td>3.00</td>
<td></td>
<td>98.0 --- 98.6</td>
</tr>
</tbody>
</table>
of the rare earths was also not appreciably affected by time. At values of pH from 1.28 to 1.81 the precipitation curve for the rare earths was very steep (see Figure 4), and an error of only a few hundredths of a pH unit can cause a 10 to 15 per cent difference in the proportion of rare earths precipitated. It was, therefore, difficult to tell if time had an important effect on the precipitation of the rare earths in this pH range. Above a pH of 1.81 time again showed little or no effect on the precipitation of the rare earths.

**Effect of acid-to-digested sands ratio.** Since studies were made to investigate the effect of the quantity of excess sulfuric acid on the digestion of the monazite sands, it was necessary to determine the effect of the excess acid on the precipitation of the thorium and the rare earths. The conditions for these tests were the same as those used in the previous studies. The dilution ratio was 5.2, the time before filtration was one hour, and the neutralizing agent was 1.9 normal ammonium hydroxide. Monazite sulfate solutions having acid-to-digested sands ratios of 1.72, 2.0, and 2.5 were used in this study.

The results are shown in Table 5. The fractional precipitation data for the acid-to-digested sands ratio of 1.72 were obtained from the previous study on the effect
Table 5

Effect of Acid-to-Digested Sand Ratio on the Fractional Precipitation of Thorium and the Rare Earths

<table>
<thead>
<tr>
<th>Dilution Ratio - 5.2 Agitation Time - One Hour</th>
<th>Indian Monazite Sand Neutralizing Agent - 1.9N NH₄OH</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>pH</th>
<th>Cumulative Per Cent Precipitated</th>
<th>Thorium Acid-to-Digested Sand</th>
<th>Rare Earths Acid-to-Digested Sand</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1.72</td>
<td>2.0</td>
</tr>
<tr>
<td>0.71</td>
<td>---</td>
<td>---</td>
<td>71.5</td>
</tr>
<tr>
<td>0.81</td>
<td>93.4</td>
<td>95.9</td>
<td>76.5</td>
</tr>
<tr>
<td>0.95</td>
<td>98.5</td>
<td>96.5</td>
<td>89.0</td>
</tr>
<tr>
<td>1.05</td>
<td>99.2</td>
<td>97.5</td>
<td>94.2</td>
</tr>
<tr>
<td>1.15</td>
<td>99.9</td>
<td>99.0</td>
<td>97.5</td>
</tr>
<tr>
<td>1.25</td>
<td>100.0</td>
<td>99.8</td>
<td>98.6</td>
</tr>
<tr>
<td>1.35</td>
<td>100.0</td>
<td>99.5</td>
<td>14.</td>
</tr>
<tr>
<td>1.50</td>
<td>100.0</td>
<td>---</td>
<td>48.3</td>
</tr>
<tr>
<td>1.80</td>
<td></td>
<td>78.7</td>
<td>78.0</td>
</tr>
<tr>
<td>2.20</td>
<td></td>
<td>89.5</td>
<td>89.5</td>
</tr>
<tr>
<td>2.50</td>
<td></td>
<td>93.0</td>
<td>93.0</td>
</tr>
<tr>
<td>2.80</td>
<td></td>
<td>96.2</td>
<td>96.5</td>
</tr>
<tr>
<td>3.00</td>
<td></td>
<td>98.6</td>
<td>---</td>
</tr>
</tbody>
</table>
of agitation time. The quantity of the rare earths precipitated at a pH of 1.35 was estimated from a plot of the data.

As the amount of free sulfuric acid in the solution was increased, the precipitation of the thorium was suppressed. This made it necessary to neutralize the solution to a higher pH in order to obtain 100 per cent recovery of the thorium. As the acid-to-digested sand ratio was increased, the precipitation of the rare earths was also suppressed, but not to the same extent as the thorium. The over-all effect was that a slightly greater quantity of the rare earths precipitated with the thorium at the higher acid-to-digested sand ratios. Therefore, in order to keep the thorium recovery and purity as high as possible, the monazite sulfate solution should be prepared with only enough free sulfuric acid to keep the thorium phosphate from precipitating. This would be equivalent to using an acid-to-digested sand ratio of 1.61.

Separation of thorium and rare earths by dilution. Fernelius (20) reported that thorium phosphate can be precipitated from the monazite sulfate solution by dilution with water and without the addition of any neutralizing base. It was reported that complete thorium recovery was obtained. If enough dilution water was added to the monazite sulfate solution to lower the pH to 1.1-1.2, it was
thought that 95 to 99 per cent of the thorium could be recovered without the accompanying precipitation of the rare earth phosphates.

To determine the feasibility of such a separation procedure, a monazite sulfate solution was diluted with water and filtrations of the precipitated thorium phosphate were made at dilution ratios of 3, 9, 18, 36, and 290. The composition of the total oxides in the precipitates

Table 6

Separation of Thorium Phosphate from the Rare Earths by Dilution of Monazite Sulfate Solution

<table>
<thead>
<tr>
<th>Acid-to-Digested Sands Ratio</th>
<th>Indian Monazite Sand</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thorium Recovered</td>
</tr>
<tr>
<td></td>
<td>in Precipitate</td>
</tr>
<tr>
<td></td>
<td>ThO₂</td>
</tr>
<tr>
<td>0.12</td>
<td>3.0</td>
</tr>
<tr>
<td>0.61</td>
<td>9.0</td>
</tr>
<tr>
<td>0.80</td>
<td>18.0</td>
</tr>
<tr>
<td>1.00</td>
<td>36</td>
</tr>
<tr>
<td>1.65</td>
<td>290</td>
</tr>
</tbody>
</table>

and the cumulative per cent recovery of the thorium is shown in Table 6. Complete thorium recovery was not obtained until the dilution ratio was 290. This value of recovery was only approximate, since detection of thorium in this dilute solution was very difficult. The addition of
phosphoric acid precipitated more of the thorium at the lower dilution ratios. However, at ratios of 18 and above, the recovery was the same as without the addition of phosphoric acid.

While 92 per cent recovery of the thorium, at a purity of 66 per cent ThO₂ in the total oxides, could be obtained by diluting the monazite sulfate solution to 36 times its original volume, it would not be economical to use this separation procedure commercially due to the handling of such large volumes of water. Fractional neutralization with ammonium hydroxide gave almost 100 per cent thorium recovery with only a slight decrease in the purity.

Effect of source of monazite sands. Since the supply of Indian monazite sand was cut off by an embargo, it was necessary to use domestic monazite sand from Idaho for use in the pilot plant studies. However, before any pilot plant runs could be made using this sand it was necessary to investigate any differences in the fractional precipitation of the thorium, the rare earths, and the uranium from that obtained with the Indian sand. A monazite sulfate solution was prepared from a sample of Idaho monazite sand and a fractional precipitation study was made using conditions similar to those described in the previous sections. The dilution ratio was 5.0, the acid-to-digested sands ratio
was 1.65, the time of agitation was five minutes, and the neutralizing agent was 1.9 normal ammonium hydroxide.

The results of this study are shown in Figure 6. Except in the pH range of 0.90 to 1.1, there were no differences in the fractional precipitation of the thorium and the rare earths from that obtained using Indian sand. More of the rare earths accompanied the thorium when the Indian monazite sulfate solution was used than when the Idaho monazite solution was used. In this pH range the rare earths appear with the thorium by occlusion rather than by precipitation. Therefore, since the Indian sand contained 2.4 times as much thorium, it was expected that a higher percentage of the rare earths would be carried down in this fraction.

The data for the fractional precipitation of the uranium showed that when the Idaho monazite sulfate solution was used, more of the uranium appeared with the thorium and the rare earths. On the other hand, a study made with a synthetic uranium sulfate-phosphate solution\(^1\) that contained no thorium or rare earths revealed that the uranium did not precipitate until a pH of 2.5-2.7 was reached. Therefore, the precipitation of the uranium with the rare earths and the thorium was not due to a limited solubility.

\(^1\)The synthetic solution contained uranium nitrate, sulfuric acid, and phosphoric acid in the same proportions as was present in a standard monazite sulfate solution.
INDIAN MONAZITE SAND
THORIUM
RARE EARTHS
URANIUM

IDAHO MONAZITE SAND
THORIUM
RARE EARTHS
URANIUM

ACID-TO-DIGESTED SAND RATIO - 1.62 - 1.72
DILUTION RATIO - 5.0
AGITATION TIME - FIVE MINUTES
NEUTRALIZING AGENT - 1.9 N. NH_4OH

FIGURE 6 FRACTIONAL PRECIPITATION OF MONAZITE SULFATE SOLUTION FROM IDAHO AND INDIAN MONAZITE SANDS
in the pH range 1.0 to 2.0. Due to the large rare earth to uranium ratio for the Indian sand, 165, and the even larger ratio for the Idaho sand, 445, it was believed that a considerable fraction of the uranium was being coprecipitated with the rare earths. Since there was less uranium present in the Idaho sands, a larger percentage of the total uranium was lost in the rare earth fractions.

The study showed that 60 to 70 per cent uranium recovery could be obtained when using an Idaho monazite sulfate solution by separating the rare earth and uranium fractions at a pH of 2.3.

**Bench-scale processing**

While the pilot plant was being constructed, a bench-scale fractional precipitation run was made in order to simulate the larger scale production of concentrates of thorium, the rare earths, and the uranium. The dilution ratio was 5.0, the acid-to-digested sand ratio was 1.65, the time of agitation before filtration was one hour, and 1.9 normal ammonium hydroxide was used for neutralization. The separation of the thorium and the rare earths was made by neutralizing the solution to a pH of 1.2. The separation of the rare earths and the uranium was made by neutralizing to a pH of 2.3, and the final recovery of the uranium was made by neutralizing to a pH of 6.0.
One hundred milliliters of the monazite sulfate solution were diluted to 500 milliliters with tap water and neutralized to a pH of 1.2. After agitating for one hour, the slurry was filtered and the thorium phosphate precipitate was washed in very dilute sulfuric acid. The wash solution was not added to the filtrate, but kept separate. The filtrate was further neutralized to a pH of 2.3. After one hour of agitation, the rare earths that precipitated were filtered. This filtrate was further neutralized to a pH of 6.0 in order to precipitate the uranium. After one hour of agitation, this slurry was also filtered. The three filtered precipitates were dissolved in acid and analysed for thorium, rare earths, and uranium.

The results of this test are shown in Table 7. Good material balances were obtained for the thorium and the rare earths. The uranium analyses were unreliable because the material balance did not check within 20 per cent. The thorium recovery was 99.1 per cent, and the total oxides contained 47.5 per cent ThO₂. Washing with dilute sulfuric acid (pH of 1.2) increased the purity of the thorium phosphate to 68.5 per cent. Seventy-eight per cent of the rare earths were in the second fraction and 3.5 per cent were in the third or uranium-rich fraction. However, recovery of the uranium in this latter fraction was only 16.0 per cent as compared to the 60-70 per cent
Table 7

Results of Bench-Scale Fractional Precipitation Test

Dilution Ratio - 5.0
Indian Monazite Sand
Acid-to-Digested Sand Ratio - 1.65
Agitation Time - One Hour

<table>
<thead>
<tr>
<th>pH</th>
<th>Composition of Oxides Per Cent</th>
<th>Per Cent of Total in Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ThO₂</td>
<td>R₂O₃</td>
</tr>
<tr>
<td>----</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>47.5%</td>
<td>51.9%</td>
</tr>
<tr>
<td>1.2</td>
<td>68.2%</td>
<td>31.0%</td>
</tr>
<tr>
<td>1.2</td>
<td>---</td>
<td>100%</td>
</tr>
<tr>
<td>2.3</td>
<td>0.2%</td>
<td>99.3%</td>
</tr>
<tr>
<td>6.0</td>
<td>---</td>
<td>96.7%</td>
</tr>
<tr>
<td>6.0</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

Thorium-Rich Precipitate

a. Unwashed precipitate
b. Washed precipitate
c. Wash solution

Rare Earth Precipitate

Uranium-Rich Precipitate

Filtrate

³R symbolizes rare earths.
expected from the previous data. Both the thorium and the rare earth fractions contained more of the uranium than expected. These differences may be partially explained by coprecipitation of the uranium and the rare earths, and partially by the poor uranium material balance.

If an Idaho monazite sulfate solution had been used in the bench-scale fractional precipitation test, the same quantity of rare earths would have precipitated with a smaller quantity of thorium. The purity of the thorium phosphate cake would have been considerably less.

Discussion of Results

In the preceding laboratory investigations it was not possible to study all the variables that might have an effect on the proposed process. However, it was believed that the variables that were studied were the ones most important for the success of the process. It is doubtful if the thorium-rare earth separation and the rare earth-uranium separation would be more efficient if another neutralizing agent such as sodium hydroxide or lime were used. The sodium hydroxide, similar to sodium carbonate, would form the insoluble rare earth sodium double sulfate salt and precipitate the rare earths with the thorium. Lime would form insoluble calcium sulfate which would interfere with the recovery of the thorium.
All the precipitation tests were carried out at a dilution ratio of 5.0. Preliminary studies showed that a large fraction of the rare earths would precipitate with the thorium if lower dilution ratios were used. Studies at higher dilution ratios were not made at this time, but were made later in conjunction with the pilot plant investigations. More precise control of the pH was obtained when dilute ammonium hydroxide was used for neutralization. When the ammonium hydroxide concentration was increased to 6 and 12 normal, slightly more of the rare earths precipitated with the thorium phosphate.

These studies showed that a process for producing concentrates of thorium, the rare earths, and uranium was feasible. The proposed process would consist of the following steps:

1. Digesting the monazite sands in 93 per cent sulfuric acid at 200°C for one to two hours.
2. Dissolving the resulting solid reaction products in water and clarifying by settling.
3. Diluting the monazite sulfate solution with water and neutralizing to a pH of 1.2 to precipitate thorium phosphate.
4. Neutralizing the filtrate from the thorium precipitation to a pH of 2.3 to recover the rare earths.
5. Neutralizing the filtrate from the rare earth precipitation to a pH of 6.0 to recover the uranium. The three concentrates would then be suitable intermediates for further purification steps.

While the process for producing the three concentrates was shown to be feasible on a laboratory scale, there were steps which needed to be studied further in order to properly design the process for commercial use, and to prepare a reliable cost estimate. These studies were concerned with the scale-up of the digestion of the monazite sands and the fractional precipitation and filtration of the three concentrates. It was decided that these investigations would be carried out more satisfactorily on a pilot plant scale.
A pilot plant for digesting monazite sand and preparing concentrates of thorium, rare earths, and uranium was designed and assembled in the pilot plant area in the basement of the Research Building. A large pilot plant was not required, but only one of sufficient size that the process variables and the operation of small scale production equipment could be properly investigated. Batch operation was planned because of the convenience of operation. Not all the steps in the process were operated at the same production rate. In the precipitation and filtration steps the production rate was three pounds of thorium per eight hour day or 60 pounds per month. The digestion vessel was capable of handling 250 pounds of monazite sand per batch. This was equivalent to nine pounds of thorium per eight hour day from Idaho monazite sand. The pilot plant was well suited for studying the process variables and obtaining the necessary design information.

The principal purposes of the pilot plant investigation were to study the steps of the process which would be the most critical toward its commercial success and to obtain information necessary for preparing a reliable cost estimate. In order to carry out these purposes, the objectives were:
1. Determine the operating conditions and the equipment required for digesting the monazite sand at temperatures above 200°C.

2. Determine the optimum pH and dilution ratio for the fractional precipitation of the thorium, the rare earths, and the uranium.

3. Determine the filter characteristics of the three precipitates.

4. Make any other studies necessary in order to prepare a reliable cost estimate of a plant scale production unit.

Digestion of Monazite Sand

The digestion of the monazite sand was carried out on a pilot plant scale by adding Idaho monazite sand to 93 per cent sulfuric acid at 145-160°C, and then allowing the heat of reaction to bring the digestion temperature to 200°C or above. The low temperature digestion studies showed that the rate of digestion of as-received Idaho sand at 140°C was not rapid enough to use this digestion procedure. Therefore, only ground monazite sand was used in this study.

Equipment and materials.

The digestor used in this study was a fifty gallon glass-lined, steam-heated Pfaudler reactor, Series P,
Model 805. A drawing of the reactor and the accompanying piping for fume removal and dissolution is shown in Figure 7. The agitator and an adjustable baffle (not shown in drawing) were also glass-lined. The agitator drive was equipped with a micarta gear as a safety device to prevent damage to the agitator. An ammeter was put in the motor power line to indicate over-load current. The maximum steam pressure in the steam jacket was regulated at 75 pounds per square inch, gauge, by a pop-off valve. The maximum internal reactor pressure was 25 pounds per square inch, gauge. The top or lid of the reactor was removable, but during the digestion it was held firmly in place by adjustable clamps. Three open ports permitted access to the reactor when the top was clamped down. To one of these ports was connected a pipe for removing the acid fumes to a blower-type laboratory hood. The other two ports were used for adding the acid and the sand, and were normally kept closed during the digestion. Later, when the reactor was modified for more convenient dissolution, the pipes carrying the water passed down through these openings. The temperature of the reaction mass was measured by a thermocouple which was placed in the hollow shaft of the baffle. The temperature was continuously recorded on an eight point Brown indicating and recording potentiometer. All eight points were shunted together, so that a reading
FIGURE 7 PILOT PLANT REACTOR FOR DIGESTION OF MONAZITE SANDS
was obtained every time the inking device struck the paper. During three of the digestions, temperatures were measured at a point near the top of the digestion mass by putting a thermocouple inside a stainless steel pipe which entered the reactor through a flange on one of the ports. This pipe was coated with Sauereisen number 31 cement to prevent it from being corroded away before the digestion was completed. The temperatures, due to cooling through the top of the reactor, usually read 5°C to 10°C less than those recorded by the thermocouple located in the baffle. A photograph of the reactor and the temperature recorder in operation is shown in Figure 8.

The sulfuric acid used for the pilot plant digestions was technical grade acid purchased from the General Chemical Division of Allied Chemical and Dye Corporation. The label on the bottle specified the acid concentration as 66° Bé (93 per cent sulfuric acid). However, specific gravity measurements showed that the acid concentration was the same as the 95.5 per cent sulfuric acid used in the laboratory studies. It was, therefore, necessary to dilute to 93 per cent before using. Idaho monazite sand was used in this study. For all digestions except the first, the plus 28 mesh screen fraction was removed and the undersize was ground in an eight inch disc mill to 94-97 per cent minus 65 mesh. The screen analysis of a typical ground
FIGURE 8 PILOT PLANT REACTOR AND TEMPERATURE RECORDER IN OPERATION
sand is shown in Table 8.

**Pilot plant digestion and dissolution procedure**

The digestion procedure was the same for all the pilot plant runs except the first. The procedure used for this run will be described in the section covering the pilot plant digestion runs. For all the other digestions the 93 per cent sulfuric acid, prepared by adding the 95.5 per cent technical grade acid to water, was heated by steam in the Pfaudler reactor to the desired temperature (150-160°C). Then the ground monazite sand was added, and almost instantly the reaction temperature began to rise. Usually the maximum temperature was attained in one hour and then the reaction began to cool slowly. Readings of temperature were taken every 20 seconds during the runs.

Four to five hours after adding the sand, the steam supply was shut off and cooling air was run into the steam jacket until the reaction temperature was 150°C. During the first four digestions the dissolution of the solid reaction products was accomplished by alternately adding water to the reactor, and then removing the solution until the mass was completely dissolved. The procedure required the services of two men and took about two hours. Usually 1.0 to 1.1 gallons of water per pound of sand were required to dissolve completely the reaction products.

In the fifth digestion the procedure was modified,
Table 8
Screen Analysis of Ground Idaho Monazite Sand

<table>
<thead>
<tr>
<th>Screen Mesh Size</th>
<th>Weight Per Cent Retained</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ 35</td>
<td>0.02</td>
</tr>
<tr>
<td>- 35+ 48</td>
<td>0.05</td>
</tr>
<tr>
<td>- 48+ 65</td>
<td>2.0</td>
</tr>
<tr>
<td>- 65+100</td>
<td>22.7</td>
</tr>
<tr>
<td>-100+150</td>
<td>18.5</td>
</tr>
<tr>
<td>-150+200</td>
<td>14.3</td>
</tr>
<tr>
<td>-200+270</td>
<td>8.0</td>
</tr>
<tr>
<td>-270 (wet screened)</td>
<td>34.4</td>
</tr>
</tbody>
</table>
making the dissolution step faster and less tedious. The reactor and the accompanying piping is shown in Figure 7. Two sections of stainless steel pipe were inserted inside the reactor so that one would spray water on the top of the reaction mass and the other would introduce the water near the bottom of the reaction mass. The water was added while agitation was still possible and the water pressure was used to transfer the resulting monazite sulfate solution to a storage tank through an overhead stainless steel pipe.

The dissolution procedure was begun by replacing the fume removal pipe with a stainless steel pipe leading to a 500 gallon storage tank. Valve 1 was opened first (see Figure 7) and then valves 4 and 5 were opened to permit cold water to enter the reactor. For almost 60 seconds steam and sulfur dioxide fumes escaped into the room. This fuming stopped, however, when the reactor was filled with solution. When sufficient water had been added to dissolve the solids (1.0 to 1.1 gallons per pound of sand digested), the water was shut off. Then, low pressure air was admitted through valve 2 until the overhead transfer line was cleared of solution. Valve 1 was then closed, and valve 3 opened to remove 40 of the 50 gallons of solution remaining in the reactor. The air was shut off and valve 6 was opened to remove the remaining ten gallons of solution. This liquid contained a large fraction of
the undigested sand which had settled to the bottom of the reactor. This modified dissolution procedure took only a half hour, and required the services of only one man.

Pilot plant digestion runs

In the pilot plant runs the initial acid temperature and acid-to-sand ratio was varied to make each subsequent digestion an improvement on the previous one. The screen analyses of all the feed sands was very similar to the typical screen analysis presented in Table 8. The sulfuric acid concentration was 93 per cent for all the digestions. Five digestions were made in the study. A summary of the results and the operating conditions is shown in Table 9.

Laboratory digestion. A laboratory digestion was made in order to estimate the conditions required for the pilot plant digestions. The reaction was carried out in a three-neck three liter flask which was heated by an electric heating mantle. The 93 per cent sulfuric acid was heated to 145°C and then ground Idaho monazite sand was added. The temperature rose from 146°C to 230°C in 17 minutes, and then held this temperature for about ten minutes before beginning to cool. Two and a half hours after adding the sand, the temperature was 199°C. The digestion mass was allowed to cool to room temperature, and then was dissolved by allowing water to circulate
Seventy nine per cent digestion was obtained. The initial acid-to-sand ratio was 1.2 and the final acid-to-digested sands ratio was 1.52. Thorium phosphate precipitated in the resulting monazite sulfate solution. The results of this digestion indicated that a digestion carried out in the pilot plant reactor would be capable of reaching temperatures of 230°C, and that 80 per cent digestion or better would be obtained. In order to prevent the precipitation of thorium phosphate in the resulting solution a higher acid-to-sand ratio should be used.

Digestion number one. This run was designed to test the glass-lined Pfaudler reactor under mild operating conditions. As-received Idaho monazite sand was added to 93 per cent sulfuric acid at 25°C, and then steam heat was applied. After a few hours of heating, the maximum reaction temperature of 160°C was reached. The agitator was started, and then stopped to make minor repairs. However, it would not start again due to packing of sand around the blade. The fume removal unit used during this run was a 15 foot length of iron pipe which acted as an air-cooled reflux condenser. It was ineffective in preventing the fumes from coming out into the room. Dissolution was accomplished by alternately adding water to the reactor and then removing the resulting monazite solution. Some
of the solids would not dissolve and they had to be removed by removing the top of the reactor and chipping them out by hand.

Digestion number two. The digestion and dissolution procedure which has been previously described was used during this run. The initial acid temperature was 154°C and the acid-to-sand ratio was 1.36. Agitation of the reaction mass was possible throughout the entire run. However, during the last two to three hours, the agitator was not moving the mass, but just revolving in a self-created hole.

Digestion number three. In order to increase the percentage digestion over that obtained in the first two digestions the initial acid temperature was increased to 166°C. This was accomplished by heating the acid to 155°C with steam, and then to 166°C by means of an electric Glo-Rod heater immersed in the acid. The Glo-Rod heater burned out after a half hour of use due to local over heating. Agitation was possible throughout the entire run. However, during the last two or three hours the agitation was ineffective.

Digestion number four. An initial acid temperature of 150°C was used in order to determine the effect on the digestion of the sand. Agitation was possible throughout the entire run, but as in the other runs, was ineffective.
during the last two to three hours. During the run some Sauereisen number 31 cement was removed from the tip of the stainless steel thermocouple well, and before the digestion was completed, the hot acid dissolved a quarter of an inch of metal from the pipe.

**Digestion number five.** The digestion procedure used during this run was the same as in digestions number two, three, and four. The dissolution procedure was modified as previously described. The initial acid temperature was $160^\circ C$ and the acid-to-sand ratio was 1.43. The time-temperature relationship for this digestion is shown in Figure 9, and, except for the dissolution step, the data are typical of those obtained during the previous runs. When the cold dissolution water was added to the reaction mass, the temperature dropped rapidly. However, this drop in temperature had no apparent detrimental effect on the glass lining of the reactor or on the glass to steel bond. The rise in temperature observed at the end of the dissolution was caused by a ring of acid and solid reaction products falling from the side of the reactor into the water.

A summary of the operating conditions and the results of the pilot plant digestions is shown in Table 9. The per cent digestion was not calculated from the quantity of undigested sands, but from the quantity of the total
FIGURE 9 TIME-TEMPERATURE RELATIONSHIP FOR PILOT PLANT DIGESTION NUMBER FIVE.
oxides and thorium in the resulting monazite sulfate solution. Not all of the undigested sand was recovered from the runs. The unrecovered sand was in the silica sludge. The acid-to-digested sand ratio obtained in the fifth digestion was 1.58. Thorium phosphate did not precipitate, however, because the water added was not sufficient to completely dissolve the solids. This monazite sulfate solution was blended with the solution from the fourth digestion and the combined solutions had sufficient water and free acid to completely dissolve the solids and to prevent the precipitation of the thorium phosphate.

The time-temperature relationship, shown in Figure 9, indicated that most of the digestion took place during the first two hours. After that the partial solidification of the reaction mass and the lowering of the temperature prevented the reaction from going to completion. If the reaction had been stopped at the end of 3 1/2 or 4 hours, the percentage digestion would have been almost as high. Better agitation was obtained in these runs than in the laboratory digestions. However, during the last few hours the agitation was still not sufficiently effective to remove the insoluble coating from the sand particles and permit complete digestion.

A higher conversion of the monazite sand was obtained when both the initial acid temperature and the acid-to-sand
**Table 9**

**Summary of Operating Conditions and Results of Pilot Plant Digestions**

<table>
<thead>
<tr>
<th>Digestion Number</th>
<th>Wt. of Sand</th>
<th>Wt. of 93% H₂SO₄</th>
<th>Acid-to-Sand Ratio</th>
<th>Initial Acid Temp.</th>
<th>Maximum Acid Temp.</th>
<th>Time Hours</th>
<th>Per Cent Digested</th>
<th>Acid-to-Digested Sand Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>177</td>
<td>230</td>
<td>1.21</td>
<td>25</td>
<td>160</td>
<td>80</td>
<td>50</td>
<td>2.4</td>
</tr>
<tr>
<td>2</td>
<td>192</td>
<td>280</td>
<td>1.36</td>
<td>154</td>
<td>220</td>
<td>7</td>
<td>85</td>
<td>1.60</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>314</td>
<td>1.46</td>
<td>166</td>
<td>227</td>
<td>5</td>
<td>92</td>
<td>1.60</td>
</tr>
<tr>
<td>4</td>
<td>250</td>
<td>395</td>
<td>1.47</td>
<td>150</td>
<td>214</td>
<td>6</td>
<td>88</td>
<td>1.67</td>
</tr>
<tr>
<td>5</td>
<td>250</td>
<td>385</td>
<td>1.43</td>
<td>158</td>
<td>227</td>
<td>6</td>
<td>92</td>
<td>1.58&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>Solution stable, but supersaturated with rare earth sulfate.
ratio was increased. From the data it was not possible to tell which had the greater effect. If initial acid temperatures higher than 166°C could have been obtained with this pilot plant digestor, it is believed that the sand would have been almost completely digested.

The digestion procedure and equipment used during the fifth digestion should be directly applicable to plant scale production. Only a minimum of modifications would be necessary. The self-seating flush valve on the bottom of the reactor frequently filled up with solids, making difficult the removal of solution from the reactor. A ceramic plug valve would eliminate this problem. The fume removal unit and solution transfer line could be combined as shown in Figure 7. The dissolution cycle would be started by opening the valve to the solution transfer line and closing the valve on the fume removal line. Almost complete digestion would probably be obtained if the steam jacket was constructed for higher steam pressures (100 psig) and if an additional blade was put on the agitator shaft near the middle of the reactor.

Removal of silica sludge and recovery of undigested sand. The monazite sulfate solution prepared by dissolving
the reaction mass in water contained fine particles of undigested monazite sand and dehydrated silica. The specific gravity of the monazite sand was greater than that of the silica. Therefore, a separation of the two could be made by taking advantage of the differential settling rates. Most of the solids were separated from the monazite solution by overnight settling and then decanting the clarified supernatant solution. The bottoms, usually totaling about two to four per cent of the total solution, contained 90 to 95 per cent of the silica sludge and undigested sand. This thickened slurry was removed from the tank, repulped in a few gallons of monazite solution, and then allowed to settle for ten minutes before decanting again. Later, it was found that one hour of settling was more effective because a greater percentage of the undigested sand was recovered. The residue contained most of the undigested sands and some of the sludge. This material was filtered, dried, and stored. The decanted solution contained most of the silica sludge and the finer particles of monazite sand. No attempt was made to recover this sand. While its radioactivity was not dangerous, this material was never dried, and was handled as little as possible. The slurry was stored in a 12 gallon glass carboy which was protected from breakage
by a wooden box. Extensive filtration tests were not made, but a few laboratory filtrations on a Buchner funnel showed that the addition of filter aid greatly increased the filter rate.

Only 30 per cent of the undigested sand was recovered from the second and third digestions. Part of these losses were due to handling, but most of the unaccounted for sand ended up in the silica sludge. In the fourth and fifth digestions a settling time of one hour instead of ten minutes was used to separate the sand and the sludge. While more of the latter was present in the residue, the recovery of undigested sand increased to 80 to 90 per cent. It was originally proposed to filter the silica sludge in a bag filter. However, the quantity of sludge obtained from the digestions was not sufficient to operate the unit.

Fractional Precipitation Studies

The monazite sulfate solutions prepared from the five pilot plant digestions were used in these fractional precipitation studies. Preliminary pilot plant runs were planned in order to examine the performance of the process in pilot plant scale equipment, and to produce concentrates for other research projects covering thorium purification, rare earth separation and purification, and uranium purification. When these preliminary runs were completed and
evaluated, a series of more comprehensive pilot plant runs were planned. During these runs information useful for design purposes was obtained concerning the following:

1. Filterability of the concentrates.
2. Settling rates of the concentrates.
3. Composition of the filter cakes of the concentrates.
4. Distribution of thorium, rare earths, and uranium in the pilot plant streams.
5. Control of the pH.
6. Performance of the pilot plant scale equipment.

**Equipment**

In the fractional precipitation pilot plant it was necessary that all the equipment be constructed of stainless steel, except the storage tank for the monazite sulfate solution. The equipment used in this study is listed in Table 10 and the pilot plant layout in the basement of the Research Building is shown in Figure 11 (page 95).

The monazite sulfate solution was stored in a 500 gallon stainless steel tank which had previously been sand blasted and given five coats of acid-resistant "Prufcoat" paint. These measures were necessary in order to prevent corrosion of the tank by the sulfuric and phosphoric acids. The diluted monazite sulfate solution used during the fractional precipitation steps was not corrosive toward stainless steel. The Eimco filter was equipped with wash
and filtrate receiving tanks. A gear pump removed the filtrate and a Nash hytor pump provided the vacuum for the system. The 150 and 500 gallon tanks were used for precipitating the thorium-rich, the rare earth, and the uranium-rich fractions, and for storing their respective

Table 10
Pilot Plant Equipment

Fractional Precipitation Studies

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Equipment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Tanks, 500 gallon, stainless steel.</td>
</tr>
<tr>
<td>2</td>
<td>Tanks, 500 gallon, stainless steel, side agitated.</td>
</tr>
<tr>
<td>4</td>
<td>Tanks, 150 gallon, stainless steel.</td>
</tr>
<tr>
<td>4</td>
<td>Drums, 55 gallon, stainless steel, with clamp-on lids.</td>
</tr>
<tr>
<td>5</td>
<td>Drums, 30 gallon, stainless steel, with clamp-on lids.</td>
</tr>
<tr>
<td>1</td>
<td>Filter, Eimco vacuum rotary, 9.45 square feet filter area, stainless steel, complete with drive motors, filtrate and wash receiving chambers, filtrate pump, and vacuum pump. Submerged filter area, 2.81 square feet.</td>
</tr>
<tr>
<td>1</td>
<td>Filter press, plate and frame, 40 square feet filter area, stainless steel.</td>
</tr>
<tr>
<td>2</td>
<td>Pumps, centrifugal, duriron.</td>
</tr>
<tr>
<td>1</td>
<td>Pump, centrifugal, stainless steel.</td>
</tr>
</tbody>
</table>

filtrates. During the preliminary runs the filtration of all concentrates was carried out using the filter press.
During the pilot plant runs the Simco rotary filter was used for filtering the thorium-rich and the rare earth concentrates.

In order to make the pilot plant as flexible as possible, the piping was kept to a minimum. The transfer of solutions and slurries from one piece of equipment to another was accomplished by pumping the liquids through one-inch acid-resistant flexible rubber hose. This hose was cut in eight foot sections, and was fitted with a male union coupling on one end and a female union coupling on the other end. The tanks, pumps, filters, and other equipment were also fitted with union couplings, so that the female union was placed on the discharge side and the male union was placed on the inlet side. The use of flexible rubber hose for piping enabled the entire flow pattern of the pilot plant to be changed in only a few minutes. Also, less pilot plant equipment was necessary, since the same tanks, filters, pumps, and barrels could be used in several different steps in the process.

**Preliminary pilot plant runs**

The monazite sulfate solutions from the first three digestions were used in these preliminary runs. The conditions for precipitating the three fractions were the same as those used in the bench-scale test previously described. The dilution ratio was 5.0 and the neutralizing
agent was 2.0 normal ammonium hydroxide. The acid-to-digested sand ratios were 2.4 for the solution from the first digestion, and 1.60 for the solutions from the second and third digestions. The thorium-rich fraction was precipitated at a pH of 1.2, the rare earth fraction at a pH of 2.3, and the uranium-rich fraction at a pH of 6.0. The time of agitation before beginning the filtration of the thorium-rich fraction was five minutes. However, usually one to four hours passed before the filtration of the thorium-rich fraction was five minutes. However, usually one to four hours passed before the filtration was completed. Both the rare earth and uranium precipitates were settled overnight. The clear supernatant solutions were decanted, and only the bottoms were filtered in the filter press. The filter cakes were stored in five gallon buckets, which had been coated with an acid-resistant paint.

As is usual when pilot plant operation is started, many difficulties were encountered. These problems were a direct consequence of the scale-up from laboratory to pilot plant operation. The following is a summary of the principal difficulties encountered:

1. Precise control of the pH was difficult to obtain during the precipitation of the thorium-rich fraction. The precipitations were carried out in a 500 gallon tank and the agitation was only mild. This resulted in some areas having a higher
pH than others, and, as a consequence, additional rare earths precipitated with the thorium. On several occasions the desired pH of 1.2 was overrun by a few hundredths of a pH unit and this precipitated additional quantities of rare earths with the thorium.

2. The thorium-rich fraction when free of precipitated rare earths filtered rapidly. As the amount of precipitated rare earths increased, the filterability decreased very rapidly and usually about four to six times the length of time was required to filter the same volume of solution.

3. Recovery of the uranium was still lower than desired. A poor uranium material balance was obtained, but the indications were that only 25 to 35 per cent of the uranium was recovered in the uranium-rich fraction. The remainder was in the rare earth fraction.

It was believed that the solution to these difficulties lay in the direction of higher dilution of the monazite sulfate solution, and using a lower pH to precipitate the thorium. Under these conditions the recovery of the thorium would be slightly decreased, but less precise control of the pH could be tolerated. Fewer rare earths would precipitate with the thorium, thereby, increasing
its filter ability. It was also believed that if more dilute solutions were used, the recovery of the uranium in the uranium-rich fraction would be higher.

**Dilution ratio studies**

A study was made in the laboratory to determine the effect of dilution ratio and pH on the recovery of the thorium and the precipitation of the rare earths. An Idaho monazite sulfate solution was used in this study. The acid-to-digested sand ratio was 1.60 and two normal ammonium hydroxide was used as the neutralizing agent. The time of agitation before filtration was five minutes. Tests were made at dilution ratios of 4.25, 5.0, 6.0, and 7.0, and at pH values of 1.0, 1.1, and 1.2. The results of this study are shown in Table 11.

The data showed that the thorium recovery was a function of pH and was but little affected by the amount of dilution water. However, the precipitation of the rare earths was affected by the pH and the amount of dilution water. Precipitation of the thorium at a pH of 1.0 and at a dilution ratio of 4.25 or 5.0 would not be satisfactory for pilot plant operation because filtration of the resulting precipitate was slow and the concentration of thorium in the total oxides was low. At a pH of 1.0 and a dilution ratio of 6.0, only 7.2 per cent of the rare earths appeared with the thorium. However, between a
Table 11

Effect of Dilution Ratio and pH on the Fractional Precipitation of Thorium and Rare Earths

Idaho Monazite Sulfate Solution
Neutralizing Agent - 2.0 N NH₄OH
Acid-to-Digested Sand Ratio - 1.60
Time of Agitation - Five Minutes

<table>
<thead>
<tr>
<th>Dilution Ratio</th>
<th>pH</th>
<th>Per Cent Precipitated</th>
<th>P₂O₅</th>
<th>R₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ThO₂</td>
<td>R₂O₃</td>
<td>ThO₂</td>
</tr>
<tr>
<td>4.25</td>
<td>1.0</td>
<td>98.7</td>
<td>18.5</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>1.22</td>
<td>99.9</td>
<td>54.0</td>
<td>3.8</td>
</tr>
<tr>
<td>5.0</td>
<td>1.0</td>
<td>98.6</td>
<td>7.5</td>
<td>0.82</td>
</tr>
<tr>
<td>6.0</td>
<td>1.0</td>
<td>98.7</td>
<td>3.6</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>99.6</td>
<td>22.1</td>
<td>1.7</td>
</tr>
<tr>
<td>7.0</td>
<td>1.0</td>
<td>98.9</td>
<td>2.5</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>1.05</td>
<td>99.2</td>
<td>3.3</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>99.6</td>
<td>8.0</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>99.8</td>
<td>22.1</td>
<td>1.7</td>
</tr>
</tbody>
</table>
pH 1.0 and 1.1 another 15 per cent of the rare earths precipitated. Under these conditions precise control of the pH to ±0.01 pH units would be required to keep the precipitation of the rare earths to a minimum and to obtain a fast filtering precipitate. When the dilution ratio was increased to 7.0 and a pH of 1.0 to 1.05 was used, only 2.5 to 3.3 per cent of the total rare earths were found in the thorium-rich fraction. This would extend the tolerance in the pH control to ±0.03 to 0.04 pH units. This tolerance in control of the pH was desirable, since the measurement of the pH in the pilot plant would show some variation. Another important reason for using a dilution ratio of 7.0 was that less phosphate was included in the thorium-rich filter cake. Whatley (47) found that phosphate and sulfate had a very detrimental effect of the liquid-liquid extraction of the thorium from a nitrate solution of the thorium phosphate filter cake. The presence of some phosphate was unavoidable, since the thorium was chemically combined with the phosphate. However, it was desirable to keep the phosphate associated with the rare earths to a minimum.

In view of these findings, it was planned to use a dilution ratio of 7.0 in the pilot plant operation. The thorium-rich fraction would be precipitated at a pH of
1.05, the rare earth fraction at a pH of 2.3, and the uranium-rich fraction at a pH of 6.0.

**Pilot plant studies**

A series of eight pilot plant fractional precipitation runs were made in order to study the process on a pilot plant scale and to prepare concentrates of thorium, the rare earths, and uranium for use in the other pilot plant investigations. The operating conditions for these runs were those recommended by previous laboratory studies. The dilution ratio was 7.0, the acid-to-digested sand ratio was 1.62, and 2.0 normal ammonium hydroxide was used for neutralization. The thorium-rich fraction was precipitated at a pH of 1.05, the rare earth fraction at a pH of 2.3, and the uranium-rich fraction at a pH of 6.0. These operating conditions were not varied during the runs, since it was desired to produce concentrates of consistent composition.

During the first series of four runs (PP45A, B, C, and D) the thorium-rich precipitate was filtered without thickening and in the second series of four runs (PP45E, F, G, and H) the thorium phosphate precipitate was thickened before filtering. The flow-sheet illustrating the pilot plant operation during the second series of runs is shown in Figure 10. The same flow-sheet was used during the first four runs, except the thorium concentrate was filtered without thickening.
FIGURE 10 FLOW DIAGRAM FOR PRECIPITATION OF THORIUM, URANIUM CONCENTRATES
TO FUME REMOVAL

IN WATER

MONAZITE SAND DIGESTER

TO FUME REMOVAL

DECAT

SLUDGE FILTRATE

DECANT

BAG FILTER

MONAZITE SAND AND SLUDGE REMOVAL

SAND AND SLUDGE REMOVAL

MONAZITE SULFURIC ACID SOLUTION STORAGE

UNDIGESTED SANDS TO RECYCLE

SILICA SLUDGE

28% NH₃

28% NH₃

pH 2.3

pH 6.0

ROTARY FILTER

ROTARY FILTER

URANIUM CONCENTRATE

RARE EARTH CONCENTRATE

RARE EARTH CONCENTRATE

ENTRATE

FOR PRECIPITATION OF THORIUM, RARE EARTH AND URANIUM CONCENTRATES
The equipment used and the pilot plant layout are shown in Figure 11. The fractional precipitation of the thorium-rich fraction was carried out in two 150 gallon tanks equipped with clamp-on agitators. For each precipitation 17 gallons of the monazite sulfate solution were diluted to 125 gallons with tap water. The 2.0 normal ammonium hydroxide solution was slowly added from an overhead pipe line until a pH of 1.05 was reached. The determinations of pH were made by continually taking samples of the solution and measuring the pH with a potentiometer pH meter. The two tanks were used alternately to provide a continuous supply of slurry to the Eimco filter. During the first four runs the precipitate was pumped directly to the rotary filter when the neutralization was completed. During the last four runs the precipitate was allowed to settle for one hour before decanting. Only the bottoms were pumped to the filter.

The fractional neutralization of the thorium filtrate to a pH of 2.3 was carried out in a 500 gallon side-agitated tank. The neutralizing agent was 28 per cent aqueous ammonia. The resulting rare earth precipitate was allowed to settle overnight and then the clear supernatant solution was decanted into the other 500 gallon tank. This rare earth decant was neutralized to a pH of 6.0 with 28 per cent aqueous ammonia. The thickened
FIGURE II PILOT PLANT EQUIPMENT LAYOUT

A PORTABLE CENTRIFUGAL PUMP
B VACUUM PUMP
C FILTRATE PUMP
D WASH RECEIVER
E FILTRATE RECEIVER
F MIST TRAP
slurries from both the rare earth and uranium concentrates were not filtered at this time. Instead, all the rare earth slurries and all the uranium slurries were combined and stored in separate tanks until the thorium production had been completed. The combined rare earth slurries were filtered on the rotary filter and in the filter press. Following this, the uranium slurries were filtered in the filter press. Samples were taken from all streams during the eight pilot plant runs.

These pilot plant runs were made on consecutive days, except for a two day lay off between the fourth and fifth runs. The normal operating day was between 8 A.M. and 5 P.M. Three days were required for a solution to pass through the pilot plant. During the first day the thorium-rich fraction was precipitated and filtered, and the rare earth fraction was precipitated. The following morning, the supernatant solution was decanted from the rare earth precipitate, and then neutralized to precipitate the uranium-rich fraction. Finally on the third day, the supernatant solution was decanted from the uranium-rich slurry and discarded. From the third day of operation on, precipitation of all three fractions was carried out every day.

The monazite sulfate solutions from the fourth and fifth digestions were combined and labeled Monazite
Sulfate Solution PP45. The analysis of the resulting solution was:

Total oxides - 70.5 grams/liter
ThO₂ - 4.0 grams/liter
U₃O₈ - 0.15 grams/liter
P₂O₅ - 28.5 grams/liter
SO₄ - 161 grams/liter

The products and samples from the first four runs were labeled, respectively, PP45A, B, C, and D. The products for the second four runs were labeled, respectively, PP45E, D, F, and G.

The 2.0 normal ammonium hydroxide used for the precipitation of the thorium-rich fraction was prepared by adding 28 per cent aqueous ammonia to tap water in the proportion of one pound of 28 per cent ammonia to one gallon of water. This neutralizing solution was made fresh every day.

Fractional precipitation runs PP45A, B, C, and D. During the first four pilot plant runs four 17 gallon batches of monazite sulfate solution were processed per eight hour day. When diluted, this was equivalent to 500 gallons of thorium phosphate slurry. The production rate was limited to this figure by the capacity of the rotary filter and the capacity of the thorium filtrate storage tanks. Control of the pH during the precipitation
of the thorium phosphate was good. In only two of the 12 precipitations was the final pH greater than 1.05 ± 0.02. These errors were due to technique rather than the result of poor mixing or unreliable pH meters. Good control would be obtained during plant operation by the use of automatic indicating and controlling equipment.

After the fractional precipitation of the thorium-rich fraction was completed, filtration of the slurry was begun immediately. Usually about two hours were required to filter the 133 gallons of slurry in each batch. The operation of the rotary filter was satisfactory. There was a leakage of air through the take-off manifold, such that the vacuum seldom went above seven inches of mercury. However, this did not impair the efficiency of the filtration, for, as will be shown later, the filterability of the thorium phosphate was almost independent of pressure. Operation of the filter at various drum speeds did not change the filter rate appreciably. Operation at the fastest drum speed (0.49 revolutions per minute) produced a very wet, sloppy cake. On the other hand, operation at the slowest drum speed (0.15 revolutions per minute) produced a cake which was considerably drier. In order to produce as dry a cake as possible and keep the quantity of rare earths and phosphate with the thorium to a minimum, the filter was set at the slowest drum speed for the
remainder of the pilot plant runs. Under these conditions the thorium concentrate filter cake was about 1/8 inch thick and usually cracked during the drying cycle. No trouble was experienced in removing the cake from the cloth during the blowing cycle. The rotary filter is shown in operation in Figure 12.

The average filter rate for the thorium concentrate during these runs was 0.15 gallons per minute per square foot of drum area. However, on occasions when the pH of the solution was above 1.1, the filter rate dropped to 0.050 gallons per minute per square foot of drum area. This drop in the filter rate was due to the presence of appreciable quantities of rare earths with the thorium. Usually when this happened, it was not until near the end of the day's run that enough of the original slurry had been removed to bring the filter rate back to the normal rate. It was noticed that during the runs the filter rate dropped from 0.30 gallons per minute per square foot of drum area, obtained during the first few hours of operation, to 0.13 gallons per minute per square foot of drum area, obtained at the end of the fourth run. This drop in the filter rate was caused by a gradual blinding of the filter cloth by thorium phosphate precipitate and, particularly, by the fine particles of rare earths precipitate which would occasionally accompany the thorium. While the cloth was
FIGURE 12  PILOT PLANT FILTRATION OF THORIUM-RICH CONCENTRATE
scrubbed at the end of each run, there were still enough solids left so that, when the cloth became dry during the night, the solids would harden and plug the open pores. Calculation of filter cloth "admittance" made during the pilot plant runs showed that the "admittance" had dropped to 0.24 gallons per minute per square foot of drum area. This would mean that the blinded filter cloth, which was free of filter cake, would be able to pass only 0.24 gallons of water per minute based on a drum area of one square foot. New cotton duct cloth under the same vacuum would pass over 10 gallons per minute per square foot of filter area, or 3.0 gallons per minute per square foot of drum area.

The rare earth fraction was precipitated at a pH of 2.3 ± 0.05, and the uranium-rich fraction at a pH of 6.0 ± 0.2. More precise control of the pH was not necessary for these precipitations. The rare earth precipitate required about eight hours of settling to approach its maximum thickened concentration. Only one hour of settling was required by the uranium-rich precipitate. Samples were taken of all streams in the pilot plant, and prepared for analyses. The distribution of the thorium, the rare earths, and the uranium in the three concentrates and the final filtrate is
shown in Table 12. The data were averaged from runs PP45A and PP45D. The thorium recovery was 98.6 per cent and the total oxides in the concentrate contained 55 per cent ThO₂.

Table 12

<table>
<thead>
<tr>
<th>Fraction</th>
<th>pH</th>
<th>Per Cent of Total In Fraction</th>
<th>Th</th>
<th>R</th>
<th>U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monazite Sulfate Solution</td>
<td>---</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Thorium-Rich Cake</td>
<td>1.05</td>
<td>98.6</td>
<td>4.9</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>Rare Earth-Rich Cake</td>
<td>2.3</td>
<td>1.4</td>
<td>92.6</td>
<td>46.5</td>
<td></td>
</tr>
<tr>
<td>Uranium-Rich Cake</td>
<td>6.0</td>
<td>---</td>
<td>2.5</td>
<td>49.0</td>
<td></td>
</tr>
<tr>
<td>Filtrate</td>
<td>6.0</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
</tbody>
</table>

By using a dilution ratio of 7.0 the uranium recovery in the uranium-rich fraction was increased from 25 - 35 per cent to 49 per cent.

Fraction precipitation runs PP45E, F, G, and H. In these four pilot plant runs the thorium phosphate was thickened before filtering. All other operating conditions were the same as previously described. Each 17 gallon batch of monazite sulfate solution was diluted to 125 gallons, and then neutralized to a pH of 1.05. At this point, instead of pumping the slurry to the rotary filter, it was allowed to settle for one hour.
The precipitate usually settled to the 25 gallon mark, but decantation was possible only to the 40 gallon mark without disturbing the solids. Another 500 gallon tank was obtained in order to increase the storage capacity for thorium filtrate. Production was then increased to six batches per eight hour day. If additional storage capacity had been available, it would have been possible to precipitate and filter 12 to 16 batches of the thorium-rich fraction in an eight hour day.

Control of the pH during the thorium precipitation was excellent. In only one precipitation out of eighteen was the final pH run over 1.05. On the other hand, however, the operation of the rotary filter was troublesome. The vacuum would not go above ten inches of mercury and in addition the air would not blow the cake from three of the sixteen filter sections located around the drum. The filter rate for the thickened thorium phosphate was 0.11 to 0.12 gallons per minute per square foot of drum area. This rate was only slightly less than that obtained when filtering the unthickened slurry. This indicated that the cloth was blinded, and that most of the resistance to filtration was across the filter media rather than the cake. Occasionally a small hole was found in the filter cloth and it was sealed by applying some Duco cement. However, during the last hour of the last run the cotton duct cloth completely disintegrated. This was undoubtedly
a consequence of filtering an acid solution and allowing the cloth to dry out over night.

As in the previous runs, the precipitation of the thorium filtrates and the rare earth decant solutions was carried out at pH's of 2.3 and 6.0, respectively. The resulting thickened precipitates of the rare earth and uranium-rich fractions were combined with those obtained from the previous runs. At the end of the eight pilot plant runs the volume of the combined rare earth slurries was 600 gallons and the volume of the combined uranium slurries was 180 gallons.

After the thorium production had been completed, the cotton duct cloth was replaced by a monofilament orlon cloth. This cloth was of medium weight, and was resistant to the action of most mineral acids and alkalies. The rare earth slurry was filtered on the rotary filter and in the filter press. At the fastest drum speed (0.49 revolutions per minute) the cake was so thin that it was difficult to remove from the cloth, and at the slowest drum speed (0.15 revolutions per minute) a cake of 1/16 to 1/8 inch was obtained. The average filter rate at a drum speed of 0.15 revolutions per minute was 0.022 gallons per minute per square foot of drum area. The vacuum was ten inches of mercury. During the blowing cycle, a clean removal of the cake from the cloth was
not obtained. The rare earth filter cake from both the rotary filter and the filter press were combined, and stored in 55 gallon stainless steel drums until needed for further processing. The uranium slurry was filtered in the filter press and the resulting cake was stored in a 30 gallon stainless steel drum until needed for further processing.

Because of the difficulties encountered with the rotary filter it was decided to obtain the filter rate data for the thorium, rare earth, and uranium concentrates in the laboratory. It would then be possible to study the filterability over a range of pressures and slurry concentrations.

Complete chemical analyses were made of all samples taken from the pilot plant streams during the four runs. Good material balances were obtained for all the components, even the uranium. The balances usually agreed within 0 to 4 per cent, however, occasionally deviations up to 13 per cent were obtained for one component. The good uranium material balance was made possible by the development of a reliable analytical method in which rapid and reproducible results could be obtained (see Appendix A). The compositions of the streams and the distribution of the components obtained in the four pilot plant runs were averaged. The results are shown in Table 13. During the
### Material Balance for Pilot Plant

<table>
<thead>
<tr>
<th>Stream</th>
<th>pH</th>
<th>Quantity</th>
<th>Composition of</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Th</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Gallons</td>
</tr>
<tr>
<td>Monazite Sulfate Solution</td>
<td>---</td>
<td>61</td>
<td>600</td>
</tr>
<tr>
<td>Thorium-Rich Cake</td>
<td>1.05</td>
<td>--</td>
<td>61.3</td>
</tr>
<tr>
<td>Thorium Filtrate</td>
<td>---</td>
<td>496</td>
<td>4250</td>
</tr>
<tr>
<td>Rare Earth Cake</td>
<td>2.3</td>
<td>--</td>
<td>153^a</td>
</tr>
<tr>
<td>Rare Earth Filtrate</td>
<td>---</td>
<td>495</td>
<td>4210</td>
</tr>
<tr>
<td>Uranium-Rich Cake</td>
<td>6.0</td>
<td>--</td>
<td>41.5^a</td>
</tr>
<tr>
<td>Uranium Filtrate</td>
<td>---</td>
<td>493</td>
<td>4200</td>
</tr>
</tbody>
</table>

^a Weight of cakes estimated from total oxides content.
Table 13

Analysis of Streams Weight Per Cent

<table>
<thead>
<tr>
<th>R</th>
<th>U</th>
<th>SO₄⁻</th>
<th>PO₄³⁻</th>
<th>NH₄⁺</th>
<th>H₂O</th>
<th>Per Cent of Total in Stream</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.90</td>
<td>0.011</td>
<td>13.5</td>
<td>3.35</td>
<td>---</td>
<td>77.9</td>
<td>100</td>
</tr>
<tr>
<td>2.22</td>
<td>0.0041</td>
<td>1.83</td>
<td>2.49</td>
<td>2.80</td>
<td>87.8</td>
<td>98.2</td>
</tr>
<tr>
<td>0.64</td>
<td>0.0015</td>
<td>1.86</td>
<td>0.44</td>
<td>0.21</td>
<td>96.8</td>
<td>4.5</td>
</tr>
<tr>
<td>7.9</td>
<td>0.018</td>
<td>5.49</td>
<td>10.5</td>
<td>0.42</td>
<td>67.</td>
<td>1.8</td>
</tr>
<tr>
<td>0.015</td>
<td>0.008</td>
<td>1.70</td>
<td>0.059</td>
<td>0.60</td>
<td>97.6</td>
<td>93.3</td>
</tr>
<tr>
<td>1.55</td>
<td>0.085</td>
<td>0.58</td>
<td>2.68</td>
<td>0.77</td>
<td>90.5</td>
<td>2.2</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>1.70</td>
<td>0.035</td>
<td>0.62</td>
<td>97.6</td>
<td>87.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Th</th>
<th>R</th>
<th>U</th>
<th>SO₄⁻</th>
<th>PO₄³⁻</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>98.2</td>
<td>4.5</td>
<td>3.8</td>
<td>1.4</td>
<td>7.6</td>
<td></td>
</tr>
<tr>
<td>93.3</td>
<td>42.0</td>
<td>10.4</td>
<td>80.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td>54.2</td>
<td>0.3</td>
<td>5.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>87.9</td>
<td>6.9</td>
<td></td>
</tr>
</tbody>
</table>
runs, the rare earth and uranium-rich fractions were produced as thickened slurries. However, in order to present the data in a more usable form, the volume of slurry has been replaced by the quantity of filter cake which would have been obtained if the slurry had been filtered. The composition of these streams represents the composition of the cake and not the thickened slurry.

The thorium recovery, in spite of a small amount of solids carry-over during the decanting operation, was 98.2 per cent. If a thickener with bottom discharge and a weir overflow were used in plant production, the carry-over of the solids would be almost nil. Under these conditions 98.6 to 99.0 per cent recovery could be expected. A drier filter cake was obtained in these runs and, as a result, less rare earths and uranium were present with the thorium. Uranium recovery was increased from 49 per cent to 54 per cent. The rare earth recovery in the second fraction was 93.3 per cent and the uranium and thorium impurities comprised only 0.27 per cent of the total weight.

Filter characteristics of concentrates

During the operation of the pilot plant the filtration data were obtained at only one dilution ratio and only one pressure, and the filter rates were a combined function of the resistances of the cloth and the filter cake. Therefore,
in order to determine the most economical conditions under which to operate a production plant, it was necessary to determine the filterability of the precipitates at other pressures and independent of the resistance of the filter cloth. The filter characteristics for the thorium phosphate precipitate were measured at a pH of 1.05 and at dilution ratios of 4.0, 5.0, 6.0, and 7.0, and at pressures of 2.0, 3.4, 4.9, and 7.5 pounds per square inch for a dilution ratio of 7.0 and a pH of 1.05. Determinations were made for both thickened and unthickened precipitates. The filter characteristics of the rare earth and uranium-rich precipitates were determined on only the thickened slurries.

By use of the general filtration equation the filterability of the cake and the resistance of the filter cloth may be measured independent of one another. The general filtration equation is (4):

\[ (V + V_c)^2 = \frac{2AP(1-ms)}{\nu \Delta \rho \times s} (\theta + \theta_c) \]

\[ \frac{KAP(1-ms)(\theta + \theta_c)}{s} \]

where

- \( V = \) volume of filtrate
- \( V_c = \) resistance of the cloth, expressed as equivalent volume of filtrate
- \( \theta = \) time required to pass filtrate volume, \( V \)
- \( \theta_c = \) time required to pass equivalent volume, \( V_c \)
A = filter area
P = pressure
s = weight of dry solids 
\( \frac{\text{weight of slurry}}{\text{weight of slurry}} \)
m = weight of wet filter cake 
\( \frac{\text{weight of dry solids}}{\text{weight of dry solids}} \)
\( P = \text{density of filtrate} \)
\( \mu = \text{viscosity of filtrate} \)
\( \alpha = \text{specific resistance of filter cake} \)
\( K' = \frac{2}{\mu \rho \alpha} \)

The most useful term expressing the filterability of the slurries is \( K' \). This term includes the specific resistance of the filter cake and the density and viscosity of the filtrate. The cloth resistance is a function of \( V_c \) and \( Q_c \) and is represented by the symbol \( (\frac{dQ}{dV})_o \). If the general filtration equation is differentiated, the following equations are obtained:

\[ 2(V + V_c) \frac{dV}{dQ} = K' \frac{A^2}{8} (1 - ms) \frac{dQ}{dV} \]

and

\[ \frac{dQ}{dV} = \frac{2V}{K} + \frac{2V_c}{K} \]

where \( K = \frac{K'AP}{8} (1 - ms) \)

A plot of \( \frac{dQ}{dV} \) and \( V \) gives a straight line, the slope of which is \( \frac{2}{K} \) and the intercept at \( V = 0 \) is \( \frac{2V_c}{K} \) or \( (\frac{dQ}{dV})_o \). Therefore, by measuring the volume of filtrate collected as a function of time and plotting \( (\frac{dQ}{dV}) \) and \( V \), values
of $K$, $K'$, and $(dQ/dV)_o$ may be calculated.

A test filter leaf having an area of 0.10 square feet and a monofilament orlon filter cloth were used in this study. An aspirator was used to obtain the necessary vacuum. The filtrate was collected in a glass column, 53 millimeters in diameter, and the height of liquid measured as a function of time.

The effect of dilution ratio on the filterability of the thorium phosphate is shown in Figure 13. The values of $K'$ and $K'P$ obtained from this plot are listed in Table 14, together with the values obtained from tests at other pressures, and from tests using unthickened thorium phosphate. As expected the filterability of the thorium phosphate decreased as the dilution ratio decreased. This was due to the combined effect of the additional solids in the precipitate and the higher specific resistance to filtration of the rare earth precipitate. The effect of pressure on the cake was shown in the terms $K'$ and $K'P$. The filterability coefficient, $K'$, of the thorium phosphate decreased very rapidly as the pressure was increased. This indicated a considerable degree of compression in the cake. However, the term $K'P$ was constant for the four pressures studied. The filter rate of the precipitate was almost independent of pressure in the range studied.
**FIGURE 13** EFFECT OF DILUTION RATIO ON FILTERABILITY OF THORIUM PHOSPHATE.

THICKENED THORIUM PHOSPHATE
PRESSURE - 3.4 PSI
HOLD-UP - 6 HOURS
pH - 1.05

\[ \text{SLOPE} = 0.0145 \text{ sec/ml}^2 \]
\[ \text{SLOPE} = 0.00252 \text{ sec/ml}^2 \]
\[ \text{SLOPE} = 0.00075 \text{ sec/ml}^2 \]
\[ \text{SLOPE} = 0.00048 \text{ sec/ml}^2 \]

FILTRATE VOLUME - MILLILITERS

VOLUME - MILLILITERS
### Table 14

**Filter Characteristics of Thorium Phosphate Precipitate**

*Filter Area - 0.10 square feet*

<table>
<thead>
<tr>
<th>Dilution Pressure Ratio</th>
<th>Ks (l/min)</th>
<th>K'P (gal/lb)</th>
<th>K' (gal/min x ft.² x lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>3.4</td>
<td>0.0563</td>
<td>0.0465</td>
</tr>
<tr>
<td>5.0</td>
<td>3.4</td>
<td>0.332</td>
<td>0.0149</td>
</tr>
<tr>
<td>6.0</td>
<td>3.4</td>
<td>1.12</td>
<td>0.00805</td>
</tr>
<tr>
<td>7.0</td>
<td>3.4</td>
<td>1.74</td>
<td>0.00543</td>
</tr>
<tr>
<td>7.0</td>
<td>2.0</td>
<td>1.92</td>
<td>0.00521</td>
</tr>
<tr>
<td>7.0</td>
<td>4.9</td>
<td>1.80</td>
<td>0.00525</td>
</tr>
</tbody>
</table>

**Thickened Thorium Phosphate**

- Ks: lbs./in.² (gal/ft.²)² min.
- K'P: lbs. solids lbs.filt. (gal/ft.²)² min.
- K': lbs. slurry lbs.slurry min. x ft.² x lb.

**Unthickened Thorium Phosphate**

- A: 3.4 6.15 0.0017 0.98 0.0108 40 x 10⁻⁶
- B: 3.4 3.44 0.0018 0.97 0.0064 24 x 10⁻⁶
In filter test A, using unthickened thorium phosphate, the value for $K'$ agreed with the value obtained for the thickened thorium phosphate under the same conditions. However, in test B a lower value of $K'$ was obtained. This lower value of the filterability coefficient resulted as a consequence of adding the ammonium hydroxide too fast and precipitating some of the rare earths. The data from other tests indicated that $24 \times 10^{-6}$ gallons/minute pound x square foot was a more typical value for the filterability coefficient of the thorium phosphate precipitate.

In order to obtain the maximum filtration rate the value of $K'P$ should be at a maximum. In this study the value of $K'P$ reached its maximum and was constant for dilution ratios above 6.0 and for the pressure range of 2.0 to 7.5 pounds per square inch of pressure. The value of filter cloth admittance, ($dV/dQ$)$_c$, for the orlon cloth used in these tests was found to be 1.76 gallons per minute per square foot of filter area at 3.5 pounds per square inch of pressure. At other pressures the admittance was directly proportional to the pressure. There was no evidence of blinding; however, the tests were of too short duration to be conclusive.

Similar tests were made to determine the effect of pressure on the filterability of the rare earth and uranium-rich slurries produced in pilot plant runs PP45.
The results are shown in Table 15. The filter test for the rare earth precipitate at 25 pounds per square inch of pressure was performed in the pilot plant filter press and the data obtained were converted to the same basis as the laboratory tests. The filterability of the rare earth and uranium-rich slurries was considerably less than that of the thorium phosphate. However, the filter cake was not as compressible and an increase in pressure increased $K'P$. The only limit to the filter rate would be the pressure drop which could be maintained by the vacuum pump on a plant size rotary filter.

The filterability of the uranium-rich slurry was only slightly less than that for the rare earth slurry. However, since the values of $K'P$ were almost constant for the pressures used, the cake appeared to be quite compressible. When filtering the rare earth slurry, the admittance of the filter cloth, $(dV/d\theta)_o$, was found to be 0.43 gallons per minute per square foot of filter area at 9.8 pounds per square inch of pressure. The removal of the cake was not clean, and there were indications that under continuous operation the cloth might become blinded. When filtering the uranium-rich slurry, the filter cloth admittance at 9.8 pounds per square inch of pressure was found to be 0.70 gallons per minute per square foot of filter area. Clean separation of the cloth and cake was
### Table 15
Filterability of Rare Earth and Uranium-Rich Slurries

Filter Area - 0.10 square feet

<table>
<thead>
<tr>
<th>Pressure (lbs./in.$^2$)</th>
<th>$K$ ($\text{gal./ft.}^2$ min.$^{-1}$)</th>
<th>$s$ (lbs./lbf.)</th>
<th>$(1-\text{ms})$ (lbs./lbf.)</th>
<th>$K'P$ ($\text{gal./ft.}^2$ min.$^{-1}$)</th>
<th>$K'$ ($\text{gal./min. x ft.}^2 x \text{lbs.}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rare Earth Slurry</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.9</td>
<td>0.0108</td>
<td>0.0685</td>
<td>0.786</td>
<td>0.00094</td>
<td>1.1 x $10^{-6}$</td>
</tr>
<tr>
<td>9.8</td>
<td>0.0151</td>
<td>0.0685</td>
<td>0.797</td>
<td>0.0013</td>
<td>0.92 x $10^{-6}$</td>
</tr>
<tr>
<td>25</td>
<td>0.0220</td>
<td>0.060</td>
<td>0.622</td>
<td>0.00212</td>
<td>0.59 x $10^{-6}$</td>
</tr>
<tr>
<td>Uranium-Rich Slurry</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.9</td>
<td>0.0483</td>
<td>0.029</td>
<td>0.822</td>
<td>0.0017</td>
<td>2.4 x $10^{-6}$</td>
</tr>
<tr>
<td>9.8</td>
<td>0.0571</td>
<td>0.029</td>
<td>0.860</td>
<td>0.0019</td>
<td>1.3 x $10^{-6}$</td>
</tr>
</tbody>
</table>
obtained and there was no evidence of blinding. These tests, also, were of too short duration to be conclusive.

The filtration data may be used to estimate the filter rates at various drum speeds obtainable with a continuous rotary vacuum filter. The values of $K$, $V_c$, and $\Theta_c$ may be calculated from $K'$ and $(d\Theta/dV)_o$ and then substituted into the general filtration equation:

$$(V + V_c)^2 = K(\Theta + \Theta_c)$$

For this purpose $\Theta$ would be the submergence time for a square foot area of filter cloth and $V$ would be the filter rate in gallons per minute per square foot of filter area. The filter rate in terms of the total drum area could be obtained by multiplying $V$ by the fraction of the drum area submerged in the slurry chamber.

**Sedimentation of concentrates**

The rates of sedimentation were measured for the unthickened precipitates of the thorium-rich, rare earth, and uranium-rich precipitates obtained during the pilot plant runs. The measurements were made in 1000 milliliter graduated cylinders by observing the height of the thickened slurry interface as a function of time. The readings were taken in milliliters, but were converted to inches of height for presentation in Table 16. The sedimentation rates of the thorium-rich and uranium-rich precipitates
was very rapid, settling to within 89 to 90 per cent of their final thickened volumes in about one hour. On the other hand, the sedimentation rate of the rare earth precipitate was slow, requiring 5.5 hours to settle to 90 per cent of its final thickened volume. The sedimentation rate of the rare earth precipitate was substantially increased by flocculating the precipitate by adding 18 milligrams of "Knox" gelatin to one liter of the original slurry. The gelatin was added during the sedimentation tests, but was not added to the slurries produced in the pilot plant.

The sedimentation data may be used for estimating the size of a pilot plant or plant thickeners for thickening the thorium-rich, rare earth, and uranium-rich precipitates. Flocculation of the thorium-rich and uranium-rich precipitates would not be necessary during plant operation. However, in order to increase the thickener capacity, the rare earth precipitate should be flocculated with gelatin or another similar flocculating agent.
Table 16
Sedimentation of Concentrates
Dilution Ratio - 7.0

<table>
<thead>
<tr>
<th>Time Minutes</th>
<th>Height of Interface</th>
<th>Thorium</th>
<th>Rare Earths&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Rare Earths&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Uranium</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>13.5</td>
<td>13.9</td>
<td>13.8</td>
<td>13.5</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>12.3</td>
<td>---</td>
<td>---</td>
<td>10.9</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>11.3</td>
<td>13.8</td>
<td>11.6</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>9.1</td>
<td>13.7</td>
<td>10.0</td>
<td>8.4</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>7.2</td>
<td>13.4</td>
<td>8.5</td>
<td>7.4</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>6.1</td>
<td>13.3</td>
<td>7.7</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>4.0</td>
<td>12.9</td>
<td>5.4</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>2.8</td>
<td>11.5</td>
<td>3.8</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>190</td>
<td>2.4</td>
<td>8.2</td>
<td>3.4</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>226</td>
<td>2.3</td>
<td>5.0</td>
<td>---</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>332</td>
<td>2.2</td>
<td>3.0</td>
<td>3.0</td>
<td>1.90</td>
<td></td>
</tr>
<tr>
<td>526</td>
<td>---</td>
<td>---</td>
<td>2.3</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.60</td>
<td>1.94</td>
<td>1.93</td>
<td>1.60</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>No flocculating agent.

<sup>b</sup>Eighteen milligrams of "Knox" gelatin added per liter of slurry.
Caustic Digestion of Thorium-Rich Concentrate

The purpose of producing a concentrate of thorium was to prepare a feed material suitable for the purification of thorium by liquid-liquid extraction. However, the studies made on extracting the thorium from a nitric acid solution of the filter cake showed that the sulfate and phosphate were detrimental to the extraction process (11). This study was initiated to determine the conditions which would be required to remove the sulfate and phosphate from the concentrate by a caustic digestion. The thorium and rare earths would be converted to their respective hydroxides and the sodium phosphate and sulfate would be removed in the filtrate and the wash.

The thorium-rich filter cake used in this study was produced in pilot plant run PP45A. The analysis of the cake was:

<table>
<thead>
<tr>
<th>Component</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Oxides</td>
<td>5.23 - 5.40%</td>
</tr>
<tr>
<td>ThO₂</td>
<td>3.0 - 3.1%</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>2.58 - 2.74%</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>2.30 - 2.45%</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.20%</td>
</tr>
<tr>
<td>H₂O</td>
<td>88%</td>
</tr>
</tbody>
</table>

The variations in analyses were due to differences in sampling of the cake. In order to get complete conversion sufficient caustic had to be added to neutralize the acid.
in the cake, and to convert the ammonia, the rare earths, and the thorium to their respective hydroxides. Digestions were made at 85, 92, 138, 185, and 370 per cent of the theoretical amount of caustic required for the conversion.

The digestions were carried out in a 600 milliliter stainless steel beaker. Heating was accomplished by an electric hot plate. A motor-driven stainless steel stirrer provided the agitation. The required amount of solid sodium hydroxide was added directly to the 285 grams of filter cake and then the mixture was heated to almost boiling (99 to 104°C). In the first three tests the reaction time was one hour. The water was allowed to evaporate until the mass became pasty and difficult to stir. However, in fourth, fifth, and sixth tests the time of reaction was increased to two hours and water was added continuously to keep the liquid level constant. This change in operating conditions was made in an attempt to increase the phosphate removal over that obtained during the first three tests. When the reaction was stopped, the slurry was diluted with water to the original volume and then filtered immediately. The filtered precipitate was washed with 300 milliliters of water. In the sixth test the cake was washed twice with water. The filtrate, wash, and cake were analysed for
total oxides, sulfate, and phosphate. The results of this study are listed in Table 17.

Table 17

Removal of Sulfate and Phosphate from Thorium-Rich Filter Cake by a Caustic Digestion

<table>
<thead>
<tr>
<th>Per Cent of Theoretical Caustic</th>
<th>Distribution of $SO_4^-$</th>
<th>Distribution of $PO_4^{3-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cake Filt. Wash</td>
<td>Cake Filt. Wash</td>
</tr>
<tr>
<td>85</td>
<td>5.3% 82.2% 12.5%</td>
<td>72.0% 23.0% 5.0%</td>
</tr>
<tr>
<td>92</td>
<td>4.8 83.8 11.5</td>
<td>61.3 30.0 8.7</td>
</tr>
<tr>
<td>92</td>
<td>10.0 68.8 21.2</td>
<td>72.3 20.8 6.7</td>
</tr>
<tr>
<td>138</td>
<td>5.8 65.3 29.2</td>
<td>50.0 33.0 17.0</td>
</tr>
<tr>
<td>185</td>
<td>5.7 53.5 40.7</td>
<td>33.4 36.0 30.3</td>
</tr>
<tr>
<td>370</td>
<td>trace 86.0 14.0</td>
<td>trace 37.8 62.2</td>
</tr>
</tbody>
</table>

The removal of sulfate from the thorium phosphate filter cake was readily accomplished, even when less than the theoretical amount of caustic was added. However, phosphate removal was much more difficult. Complete removal was not obtained until 370 per cent of the theoretical amount of caustic was used in the digestion. Analysis for caustic in the filtrate and wash indicated that the excess over the theoretical amount was recovered in these two solutions. One hundred per cent recovery of the thorium and rare earths in the filter cake was obtained. Figure 14 shows the effect of the amount of caustic added upon the phosphate and sulfate removal from
FIGURE 14 REMOVAL OF SULFATE AND PHOSPHATE FROM THORIUM-RICH FILTER CAKE BY CAUSTIC DIGESTION
filter cake. A straight line correlation resulted for the phosphate removal. The reasons for this behavior are unknown at the present time, but they probably would become apparent if additional studies were made.

The data obtained from these tests was sufficient for design purposes. In order to effect complete removal of the sulfate and phosphate from the thorium-rich filter cake, the requirements were 0.21 pounds of caustic per pound of wet cake, or 7.90 pounds of caustic per pound of thorium. Of this amount 1.96 pounds were required for the conversion, and the other 5.94 pounds were recovered in the filtrate. The equipment needed for this digestion would be a steam-heated reactor, a filter press capable of efficient washing, a centrifugal slurry pump, and a high pressure turbine pump.

This investigation does not represent an exhaustive study of the caustic digestion of a thorium concentrate and undoubtedly improvements will result if further studies are made. If a caustic digestion step were included in the process, it is proposed that the excess caustic present in the filtrate and the wash be used to neutralize the rare earth filtrate to precipitate the uranium-rich fraction. Credit would, thereby, be obtained for this recovered caustic and only the actual amount required for the digestion would be charged toward the chemical costs.
Through the information and experience gained from the laboratory and pilot plant investigations a commercial scale plant was designed for producing concentrates of thorium, rare earths, and uranium from monazite sand. For the purpose of this design Fernald, Ohio, was chosen as the plant site so that it would be near where thorium metal will be produced. The proposed production rate was five tons of thorium per month from Idaho monazite sand. This is approximately equivalent to present commercial production. The digestion of the monazite sand would be a batch operation, but the precipitation, thickening, and filtration of the concentrates would be carried out continuously. Except for carrying out the precipitation and thickening in separate units, the flowsheet for this plant would be the same as is shown in Figure 10 (page 95).

The design was based on operation for an average of 300 days per year. While in operation the plant would run for 24 hours per day and seven days per week. The operating conditions for the production of concentrates would be the same as those recommended from the pilot plant investigations. The digestion would be carried out at 160 to 230°C using 93 per cent sulfuric acid and an acid-to-sand weight ratio of 1.56. The dilution ratio of the monazite sulfate solution prior to the
fractional neutralization would be 7.0. The precipitation of the thorium-rich, rare earth, and uranium-rich fractions would be made at pH's of 1.05, 2.3, and 6.0, respectively. All the precipitates would be thickened before filtering.

The daily production for the plant would be 400 pounds of thorium, 6400 pounds of rare earths, and eight pounds of uranium. The quantities of material handled in the streams in the plant are listed as follows:

- Monazite sand: 525 pounds/hour
- Sulfuric acid, 93%: 61 gallons/hour
- Ammonium hydroxide, 29%: 100 gallons/hour
- Monazite sulfate solution: 438 gallons/hour
- Diluted monazite sulfate solution: 4,230 gallons/hour
- Thickened thorium-rich slurry: 870 gallons/hour
- Thickened rare earth slurry: 850 gallons/hour
- Thickened uranium-rich slurry: 350 gallons/hour

**Equipment Costs**

The equipment required for the proposed production plant is itemized in Table 18. Whenever possible, the equipment costs were obtained from manufacturer's quotations. However, in a few instances it was necessary to obtain the cost from the literature. A factor of 1.43 (24) was used to estimate the installed cost from the cost, F. O. B. the factory. The six-tenths factor (24)
was used to estimate the cost of equipment at sizes other than those quoted. The reactor was designed to digest 4,200 pounds of monazite sand per batch. One batch was planned per eight hour shift. The rotary filters were designed using the filterability data obtained in the pilot plant studies. For the filtration of the thorium-rich precipitate, the filter area was estimated for the slowest drum speed and for a vacuum of 4.9 pounds per square inch. For the filtration of the rare earth and uranium-rich fractions, the filter rates were estimated for the slowest drum speed and for a vacuum of 9.8 pounds per square inch. Complete information was not available for the design of the silica sludge filter, the pulverizer, and the thickeners and these costs were only approximate.

In calculating the capital investment the installed process equipment cost was used as the basis, and the investment for instrumentation, piping, and building were calculated as a fraction of this cost. The accounting method outlined by Zimmerman and Lavine (52) was used. No provision was made for service facilities, such as steam and power generating equipment. It is anticipated that these services will be purchased from a commercial producer or be provided by another plant in the vicinity. The distribution of capital investment is shown in Table 19.
Table 18
Installed Process Equipment Costs
Ames Laboratory Process
Five tons/month Thorium

<table>
<thead>
<tr>
<th>Number</th>
<th>Equipment</th>
<th>Total Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Storage bins, concrete, 100 ft.3</td>
<td>$ 2,000</td>
</tr>
<tr>
<td>1</td>
<td>Tank, 13,000 gallon, steel, sulfuric acid storage</td>
<td>10,900</td>
</tr>
<tr>
<td>1</td>
<td>Tank, 10,000 gallon, steel, ammonium hydroxide storage</td>
<td>6,500</td>
</tr>
<tr>
<td>1</td>
<td>Reactor, 1000 gal., glass-lined, agitated, 90 p.s.i. steam jacket</td>
<td>11,000</td>
</tr>
<tr>
<td>1</td>
<td>Tank, 15,000 gal., lead-lined steel</td>
<td>8,000</td>
</tr>
<tr>
<td>2</td>
<td>Tanks, 5000 gal. lead-lined steel</td>
<td>8,600</td>
</tr>
<tr>
<td>3</td>
<td>Tanks, 250 gal., stainless steel, agitated</td>
<td>3,000</td>
</tr>
<tr>
<td>1</td>
<td>Thickener, steel with asphalt coating, diameter = 28 ft.</td>
<td>11,000</td>
</tr>
<tr>
<td>2</td>
<td>Thickener, steel with asphalt coating, diameter = 16 ft.</td>
<td>14,000</td>
</tr>
<tr>
<td>1</td>
<td>Filter, vacuum rotary, 110 ft.², stainless steel, with auxiliary equipment</td>
<td>32,000</td>
</tr>
<tr>
<td>2</td>
<td>Filter, vacuum rotary, 376 ft.², stainless steel, with auxiliary equipment</td>
<td>141,000</td>
</tr>
<tr>
<td>1</td>
<td>Filter, vacuum rotary, 120 ft.², stainless steel, with auxiliary equipment</td>
<td>34,000</td>
</tr>
<tr>
<td>12</td>
<td>Pumps, centrifugal, duriron, 80 gpm</td>
<td>5,750</td>
</tr>
<tr>
<td>12</td>
<td>Motors, 1 to 3 horsepower</td>
<td>7,000</td>
</tr>
</tbody>
</table>
### Table 18 (continued)

<table>
<thead>
<tr>
<th>Number</th>
<th>Equipment</th>
<th>Total Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Pumps, centrifugal, slurry, 20 gpm</td>
<td>$4,000</td>
</tr>
<tr>
<td>1</td>
<td>Filter, silica sludge</td>
<td>$5,000</td>
</tr>
<tr>
<td>1</td>
<td>Pulverizer, roller with cyclone separator</td>
<td>$12,900</td>
</tr>
<tr>
<td></td>
<td>Miscellaneous</td>
<td>$20,000</td>
</tr>
<tr>
<td></td>
<td><strong>Total installed equipment cost</strong></td>
<td><strong>$336,650</strong></td>
</tr>
</tbody>
</table>
Processing Costs

The processing costs are those directly associated with the daily production of the concentrates and include raw materials, chemicals, labor, supervision, maintenance, etc. These requirements were estimated from the pilot plant data.

At the present, commercial producers are paying $300/ton for Idaho monazite sands and another $22/ton for freight from Idaho to Chicago (27). However, there is a possibility that the price may drop to $200/ton with the development of the deposits in Wyoming. Technical grade sulfuric acid and 29 per cent aqueous ammonia would be the only chemicals required in the process. Their costs were estimated from the listings in the Oil, Paint, Drug, Reporter. Freight rates were estimated for shipping the chemicals from Cincinnati to Fernald.

Seven operators and one foreman would be required per eight hour shift. Three additional men would be required to permit rotation of the shifts and a 40 hour work week. The labor requirements are listed as follows:

Handling and grinding monazite sand 1 operator
Digestion of monazite sand 1 operator
Filtration of silica sludge and recovery of undigested sand 1 operator
Fractional precipitation, thickening, and filtration of concentrates

Supervision

The requirements for maintenance personnel, analysts, and office help were not specifically estimated. Their contribution to the processing cost was calculated as a function of the installed equipment or labor costs. The total fixed capital investment was depreciated over a five year period. Table 20 shows the distribution of processing costs in the preliminary cost estimate. The cost accounting procedure of Dybdal (17) was used in preparing this table.

The total conversion cost of $9.11 per pound of thorium represents the cost of producing concentrates of thorium, rare earths, and uranium as filter cakes. It was assumed that the market for the rare earths would be large enough to consume the total production. During actual production the rare earths would probably assume the bulk of the raw material and conversion costs. However, no credit was allowed for the rare earths in this cost estimate, since reliable cost data were not available. No credit was taken for the uranium produced. It was assumed that the cost for purifying the uranium from the filter cake would equal any credit which might be allowed.
Table 19
Capital Investment for Proposed Thorium Plant
Ames Laboratory Process
Five Tons/Month Thorium from Idaho Monazite Sand

<table>
<thead>
<tr>
<th>Description</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Installed Process Equipment (I. P. E.)</td>
<td>$336,650</td>
</tr>
<tr>
<td>Piping - 25% of I. P. E.</td>
<td>84,000</td>
</tr>
<tr>
<td>Instrumentation - 10% of I. P. E.</td>
<td>33,700</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>$454,350</strong></td>
</tr>
<tr>
<td>Building - 20% of I. P. E.</td>
<td>67,000</td>
</tr>
<tr>
<td><strong>Total Plant Cost (T. P. C.)</strong></td>
<td><strong>$521,350</strong></td>
</tr>
<tr>
<td>Engineering and Construction - 25% of T. P. C.</td>
<td>130,000</td>
</tr>
<tr>
<td>Contingencies - 15% of T. P. C.</td>
<td>78,000</td>
</tr>
<tr>
<td><strong>Total Capital Investment</strong></td>
<td><strong>$729,500</strong></td>
</tr>
</tbody>
</table>
Table 20

Preliminary Process Cost Estimate
for Proposed Thorium Plant

Ames Laboratory Process
Five Tons/Month Thorium from Idaho Monazite Sand
Basis: One Pound of Thorium

<table>
<thead>
<tr>
<th>Materials</th>
<th>Units/lb. Th</th>
<th>Unit Cost</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Raw Materials</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monazite sand</td>
<td>29.0 lbs.</td>
<td>$322/ton</td>
<td>$4.67</td>
</tr>
<tr>
<td>Sulfuric acid, 93%</td>
<td>50.0 lbs.</td>
<td>$ 0.01/lb.</td>
<td>0.50</td>
</tr>
<tr>
<td>Ammonia, 25% aqueous</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thorium precipitation</td>
<td>5.25 lbs.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rare Earth precipitation</td>
<td>8.55 lbs.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uranium precipitation</td>
<td>1.65 lbs.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Freight</td>
<td></td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>Total Raw Materials Cost</td>
<td></td>
<td>$5.93</td>
<td></td>
</tr>
<tr>
<td>B. Direct Conversion Cost</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Labor</td>
<td>0.42 man hrs</td>
<td>$1.75/hr</td>
<td>$0.74</td>
</tr>
<tr>
<td>Supervision</td>
<td>0.06 man hrs</td>
<td>3.00</td>
<td>0.18</td>
</tr>
<tr>
<td>Steam, 1000 lbs.</td>
<td>0.029 man hrs</td>
<td>0.50</td>
<td>0.015</td>
</tr>
<tr>
<td>Power</td>
<td>9.0 KWH</td>
<td>0.01</td>
<td>0.09</td>
</tr>
<tr>
<td>Water, 1000 gals.</td>
<td>0.260</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>Maintenance (5% of installed equipment cost)</td>
<td>0.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Supplies (0.5% of installed equipment cost)</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Laboratory</td>
<td></td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Payroll charges (15% of labor and supervision)</td>
<td>0.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Overhead (40% of labor, supervision and maintenance)</td>
<td>0.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Direct Conversion Cost</td>
<td></td>
<td>$1.84</td>
<td></td>
</tr>
<tr>
<td>C. Indirect Conversion Cost</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Depreciation (20% per year of capital investment)</td>
<td>$1.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Taxes (2% per year of capital investment)</td>
<td>0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Insurance (0.2% per year of capital investment)</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Indirect Conversion Cost</td>
<td></td>
<td>$1.34</td>
<td></td>
</tr>
<tr>
<td>Bulk Manufacturing Cost</td>
<td></td>
<td>$9.11</td>
<td></td>
</tr>
</tbody>
</table>
Cost Comparison

In order to evaluate the process properly, a cost comparison was made with the process developed by the Battelle Memorial Institute (13). Information was not available for making a comparison with the present commercial processes using the sulfuric acid method of digestion. The production of five tons of thorium per month was used as the basis for the comparison. It included only the production of concentrates of thorium, rare earths, and uranium.

Battelle (12) published a processing and equipment cost estimate for plants producing five and twenty five tons of thorium per month from Brazilian monazite sand. This estimate included the cost for the solvent extraction purification of thorium and uranium. Before a fair comparison could be made the Battelle cost estimate had to be increased in order to account for the increased chemical consumption and plant capacity due to the lower thorium content of Idaho monazite sand. The factor used in making this increase was the ratio of the thorium contents of the Brazilian and the Idaho monazite sands. This ratio was taken as 1.65. The following is a list of the steps taken in converting the data presented in the Battelle report to the processing cost estimate shown in Table 21:
1. The chemical and equipment costs associated with the solvent extraction steps were subtracted from the over-all chemical and equipment costs.

2. The chemical costs were increased by the factor 1.65. The steam, power, and water costs were increased by 1.33. This lower factor was used to account for the facilities used in the solvent extraction purification steps.

3. The labor was assumed to be the same as that required in the plant using Brazilian sand. This assumption accounted for any increase in labor due to the increased plant capacity, and the decrease in labor due to the elimination of the solvent extraction steps.

4. The resulting equipment costs (\$405,000) were multiplied by the increase in the engineering construction cost index from June 1950 to January, 1953.

5. The ratio of the increased plant capacity (1.65) to the six-tenths power was used to estimate the equipment cost for the plant handling Idaho monazite sand.

6. The total capital investment was estimated to be \$1,280,000. The accounting method outlined in
Table 19 was used in preparing this estimate. Credit was given for the by-product sodium phosphate at half the market price. This was the same credit allowed by Battelle in their cost estimate. All other processing costs, such as overhead, depreciation, etc., were represented as factors of the estimated labor or equipment costs.

It was difficult to make an accurate estimate of the equipment required for the solvent extraction step. In the Battelle report (12) the equipment was listed in categories, such as tanks, filters, settlers, etc., and was not specifically listed according to size and purpose. The equipment sizes required in the extraction step were only a small fraction of those required for the sections of the plant processing the monazite sand and the rare earths. By calculating this fraction for each type of equipment, it was possible to obtain a reasonable estimate of the equipment costs for the extraction step.

The revised estimate of the manufacturing cost for the production of a combined thorium-uranium concentrate and a rare earth concentrate using the Battelle process was $11.48 per pound of thorium. This cost includes $0.40 per pound credit for the by-product sodium phosphate. This cost estimate may be subject to some revisions, if
better estimates of equipment and labor costs are obtained. This estimate of chemical costs is believed to be accurate.

On the basis of this cost analysis, the process developed in this research would appear to be superior to the Battelle process. However, it must be kept in mind that the Battelle process produces the concentrates in the form of hydroxide filter cakes. These hydroxides are in a form more suitable for the further purification and separation processes than the phosphate concentrates produced in this process. This disadvantage can be overcome by digesting the three concentrates in caustic and converting the phosphates to the hydroxides. The chemical cost for such a conversion is estimated to be $0.40 per pound of thorium. By assuming that this step would require four additional operators and an additional capital investment of $100,000, the processing cost for the conversion would then be $1.25 per pound of thorium. The total conversion cost for producing hydroxide concentrates of thorium, rare earths, and uranium from monazite sand would be $10.36 per pound of thorium. This modified process represents an advantage of $1.12 per pound of thorium over the processing method proposed by Battelle.
Table 21
Revised Preliminary Cost Estimate of Battelle Process
Five Tons/Month Thorium from Idaho Monazite Sand
Basis: One pound of Thorium

<table>
<thead>
<tr>
<th>Units/lb. Th</th>
<th>Unit Cost</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Raw Materials</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monazite sand</td>
<td>29.0 lbs.</td>
<td>$322/ton</td>
</tr>
<tr>
<td>Sodium hydroxide (as 73% liq.)</td>
<td>32.5 lbs.</td>
<td>0.0265/lb.</td>
</tr>
<tr>
<td>Hydrochloric acid, 37%</td>
<td>43.5 lbs.</td>
<td>0.0180/lb.</td>
</tr>
<tr>
<td>Freight</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Raw Materials Cost</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium phosphate credit</td>
<td>20.2 lbs.</td>
<td>0.02/lb.</td>
</tr>
<tr>
<td>Net Raw Materials Cost</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B. Direct Conversion Cost</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Labor</td>
<td>0.60 man hrs.</td>
<td>$1.75/hr.</td>
</tr>
<tr>
<td>Supervision</td>
<td>0.06 man hrs.</td>
<td>3.00/hr</td>
</tr>
<tr>
<td>Steam, 1000 pounds</td>
<td>0.620 man hrs.</td>
<td>0.50</td>
</tr>
<tr>
<td>Power</td>
<td>24 KWH</td>
<td>0.01</td>
</tr>
<tr>
<td>Water, 1000 gals.</td>
<td>0.085</td>
<td>0.05</td>
</tr>
<tr>
<td>Maintenance (5% per year installed equipment)</td>
<td></td>
<td>0.25</td>
</tr>
<tr>
<td>Supplies (0.5% per year installed equipment)</td>
<td></td>
<td>0.03</td>
</tr>
<tr>
<td>Laboratory</td>
<td></td>
<td>0.10</td>
</tr>
<tr>
<td>Payroll charges (15% of labor and supervision)</td>
<td></td>
<td>0.18</td>
</tr>
<tr>
<td>Overhead (40% of labor, supervision, and maintenance)</td>
<td></td>
<td>0.64</td>
</tr>
<tr>
<td>Total Direct Conversion Cost</td>
<td></td>
<td>$2.98</td>
</tr>
<tr>
<td>C. Indirect Conversion Cost</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Depreciation (20% per year, capital investment)</td>
<td></td>
<td>$2.14</td>
</tr>
<tr>
<td>Taxes (2% per year, capital investment)</td>
<td></td>
<td>0.22</td>
</tr>
<tr>
<td>Insurance (0.2% per year, capital investment)</td>
<td></td>
<td>0.02</td>
</tr>
<tr>
<td>Total Indirect Conversion Cost</td>
<td></td>
<td>$2.38</td>
</tr>
<tr>
<td>Bulk Manufacturing Cost</td>
<td></td>
<td>$11.48</td>
</tr>
</tbody>
</table>

aHalf the present market price
Cost of Caustic Digestion of Thorium-Rich Concentrate

The cost estimate for the caustic digestion of the thorium phosphate filter cake is not as precise as the previous processing costs. No design data other than that presented in Table 16 were available. However, in order to evaluate the study in terms of thorium production costs, it is desirable that a cost estimate be made at this time.

The installed equipment cost for this digestion was estimated to be:

1 Reactor, 300 gal., stainless steel, steam-heated, agitated. $4,800
1 Filter press, 246 sq. ft., stainless steel. 17,000
Pumps, motors, control equipment, piping, etc. 8,000

Total installed equipment and piping cost $30,000

The processing cost for the caustic digestion are listed in Table 22. The services of two men would be needed intermittently to empty the filter press. The cost for this labor was charged as though one man was required continuously. The overhead and payroll charges
Table 22
Processing Costs for the Caustic Digestion of Thorium-Rich Concentrate

<table>
<thead>
<tr>
<th>Units/lb. Th</th>
<th>Unit Cost</th>
<th>Cost/lb. Th</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Raw Materials</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium hydroxide, 50%</td>
<td>7.90 lbs.</td>
<td>$0.025/lb.</td>
</tr>
<tr>
<td>Excess sodium Hydroxide Credit</td>
<td>5.94 lbs.</td>
<td>$0.017/lb.</td>
</tr>
<tr>
<td>Total Chemical Costs</td>
<td></td>
<td>$0.10</td>
</tr>
<tr>
<td>B. Direct Conversion Cost</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Labor</td>
<td>0.06 man hrs.</td>
<td>$1.74/hr.</td>
</tr>
<tr>
<td>Repairs (5% per year of installed equipment)</td>
<td></td>
<td>0.01</td>
</tr>
<tr>
<td>Payroll charges and overhead (55% of labor)</td>
<td></td>
<td>0.06</td>
</tr>
<tr>
<td>Total Direction Conversion Costs</td>
<td></td>
<td>$0.18</td>
</tr>
<tr>
<td>C. Indirect Conversion Cost</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Depreciation (20%/yr. on equipment)</td>
<td></td>
<td>$0.05</td>
</tr>
<tr>
<td>Taxes and insurance</td>
<td></td>
<td>0.01</td>
</tr>
<tr>
<td>Total Indirect Conversion Costs</td>
<td></td>
<td>$0.06</td>
</tr>
<tr>
<td>Bulk Conversion Cost</td>
<td></td>
<td>$0.34</td>
</tr>
</tbody>
</table>
were estimated at 55 per cent of the labor cost. Maintenance was estimated at five per cent per year of the installed equipment and piping cost. Credit was given for the excess caustic at the same cost as for an equivalent amount of ammonia.
DISCUSSION

This investigation represents an extensive study of the conditions critical toward the commercial success of the process. These conditions are concerned with the temperature and amount of acid for digesting the monazite sand, and the dilution ratio and pH for separating concentrates of thorium, rare earths, and uranium from the monazite sulfate solution. The information obtained in the laboratory and the pilot plant was sufficient for designing a plant for producing these concentrates. However, before beginning operation of such a plant some additional information would be required.

It was proposed that the fractional precipitation, the thickening, and the filtration steps in the plant be carried out continuously. Continuous operation would have the advantages of lower manpower requirements and a substantial reduction in equipment sizes. Batch operation was used in the pilot plant runs. No trouble would be expected during the continuous mixing of the diluted monazite solution and the ammonium hydroxide. However, the data for designing the thickeners and for specifying the filter cloths were not complete. The sedimentation rates should be observed at different pulp densities and at different pulp heights. It is anticipated that the thorium-rich and uranium-rich precipitates would not
seriously blind the filter cloths, but there are indications that the rare earth precipitate may seriously blind the filter cloth under continuous operation.

The continuous digestion of the monazite sand was not investigated. It is believed that for the size plant proposed in the design, there would be no advantage over the batch digestion method used in the pilot plant investigations. The problems of a suitable material of construction and the semi-solidification of the reaction mass places a considerable obstacle in the path of designing and operating a continuous unit.

Complete studies were not made on the filtration and final disposal of the silica sludge. This operation would not be tedious or expensive, but would require careful consideration in order to eliminate the possibility of it becoming a health hazard. Complete digestion of the monazite sand would be desirable, but would not be essential for economical operation of the proposed plant. If the sand in each batch were completely digested, the recovery of the undigested sand could be eliminated, and there would be no problem of a build-up of an acid-insoluble residue.

The final purification of the thorium and uranium concentrates would be carried out at the same plant site as used for the production of the concentrates. The
purification of the thorium and the uranium would be accomplished by liquid-liquid extraction. The rare earths included in these two concentrates would be recovered from the raffinates and combined with the rare earth concentrate produced by fractional precipitation. The rare earth recovery would, thereby, be 98 to 99 per cent. The only losses would be in the unrecovered monazite sand. If the rare earths are separated and purified by ion exchange or solvent extraction at this plant site, the thorium and the uranium present in this concentrate would be recovered. The thorium recovery would then be 98 to 99 per cent, and the uranium recovery would be increased to 90 to 95 per cent.

A study of the liquid extraction of the thorium from a nitric acid solution of the thorium phosphate concentrate was made at Ames Laboratory by M. E. Whatley (11). He found that if high nitric acid concentrations (13 molar) and dilute feed solutions (30 grams per liter of thorium) were used, the thorium could be successfully separated from the rare earths and purified by countercurrent liquid-liquid extraction. This separation procedure was demonstrated on a pilot plant scale. Ninety nine per cent recovery of the thorium was obtained and the product contained less than 50 parts per million rare earths. The lack of a suitable analytical method
prevented a better estimate of rare earth contamination. No cost data were available for the separation process.

No studies were made in the present investigation to recover and purify the uranium from the uranium-rich filter cake. It is expected that studies will be started in the near future. It is anticipated that the uranium could be purified and recovered by dissolving the uranium concentrate in nitric acid, and extracting under the same conditions as used for the purification of the thorium.

The caustic digestion of the rare earth filter cake to remove the sulfate and phosphate was demonstrated at Ames Laboratory by J. H. Bochinski. He also showed that a nitric acid solution of the resulting hydroxide cake could be used for separating and recovering the individual rare earths by a liquid-liquid extraction process (10). Cost data were not available for either the caustic digestion step or the separation process.

Digesting the monazite sand with sulfuric acid and producing the concentrates by fractional precipitation of the phosphates has several advantages over digesting the monazite sand in caustic, and finally producing the concentrates in the form of hydroxides. These advantages are:

1. The capital investment is lower due to fewer steps in the process and cheaper materials of construction.
2. Less expensive chemicals are required for the digestion and separation steps.

3. The conversion costs are less expensive due to lower power, steam, and maintenance costs.

4. The thorium is recovered early in the process, thereby, insuring a high yield.

The only disadvantage is that the concentrates are produced as phosphates rather than the more conveniently used hydroxides. This disadvantage may be overcome by digesting the concentrates with caustic. The final production cost would still be less than that for the Battelle process.
CONCLUSIONS

1. A process has been developed for recovering concentrates of thorium, rare earths, and uranium from monazite sands. The process was successfully demonstrated on both a laboratory and pilot plant scale.

2. The most economical conditions for the sulfuric acid digestion were an acid concentration of 93 percent, reaction temperatures of 200 to 230°C, and an initial acid-to-sand weight ratio of 1.56.

3. Thorium, rare earths, and uranium were separated as phosphates by fractional neutralization of the resulting monazite sulfate solution.

4. Ammonium hydroxide was superior to sodium carbonate for this neutralization.

5. The optimum precipitation conditions for the separation of the thorium and rare earths were a dilution ratio of 7.0 and a pH of 1.05.

6. The optimum precipitation conditions for the separation of the rare earths and the uranium were a dilution ratio of 7.0 and a pH of 2.3.

7. The uranium, together with a small fraction of the rare earths were recovered by neutralization to a pH of 6.0.

8. The concentrates were suitable feed material for
processes involving the purification and recovery of thorium, and the separation and recovery of the individual rare earths.

9. A comparison of estimated manufacturing costs was made between the Ames Laboratory and the Battelle processes. The basis of this comparison was for a plant producing concentrates of thorium, rare earths, and uranium on a scale of five tons of thorium per month from Idaho monazite sand. The estimated Battelle process manufacturing cost was $11.48 per pound of thorium, and the estimated Ames Laboratory process manufacturing cost was $9.11 per pound of thorium. These costs include $4.67 for the monazite sand. No credit was allowed for the by-product uranium and rare earths.
LITERATURE CITED


42. Spencer, J. F. The metals of the rare earths. London; Longmans, Green, and Co. 1919.


ACKNOWLEDGEMENT

The author wishes to express his appreciation to Dr. G. L. Bridger who suggested the problem and directed the research during the laboratory investigation, and to Dr. M. Smutz who directed the research during pilot plant investigation. The author also wishes to express his appreciation to the members of Chemical Engineering Group IV who assisted in the construction and operation of the pilot plant, and to the Analytical Section of Ames Laboratory who performed the analyses on samples during the latter phases of this research.

The equipment and facilities used in this investigation were provided by the Institute for Atomic Research of Iowa State College under contract W-7405-ENG-82 with the Atomic Energy Commission.
Total oxides. The total oxides, as referred to in this research, included the combined rare earth and thorium oxides.

One gram of ground monazite sand was fused with KHF$_2$ in a platinum crucible until a clear melt was obtained. The melt was cooled to room temperature and then dissolved in water with the aid of a few drops of HF. The water-insoluble fluorides of thorium and rare earths were separated from the solution by centrifuging, and then were dissolved in nitric acid with the addition of boric acid to complex the fluoride. The acidity was adjusted to about 0.5 molar. The solution was brought to a boil and then the thorium and the rare earths were precipitated by the addition of solid oxalic acid. The solution was allowed to stand overnight. Then, the oxalates of thorium and the rare earths were filtered, washed, and ignited at 800°C. The residue was weighed as mixed rare earth and thorium oxides (11).

When total oxides were to be determined in solutions, the procedure was started by adjusting the acidity to 0.5 molar and bring the solution to a boil. From this point on the procedure was the same as previously described.
Thorium. Thorium was determined in monazite sands and in solutions using the method of Byrd and Banks (4b). This method involved extraction with mesityl oxide to separate the thorium from the interfering sulfate, phosphate, and rare earths. Final determination was made colorimetrically using "Thoron".

Uranium. Uranium was determined colorimetrically after removing the interfering sulfate, phosphate, and fluoride ions.

Two to three grams of ground monazite sand were fused with KHP2 in a platinum crucible until a clear melt was obtained. The melt was then cooled to room temperature and dissolved in saturated Al(NO3)3. This solution was extracted with an equal volume of 50 per cent tributyl phosphate-50 per cent heptane. The solvent phase was scrubbed twice with 1:1 HNO3 and then stripped with three equal volumes of water. The uranium was determined colorimetrically in the water strip using either l-ascorbic acid or ammonium thiocyanate (37c).

Uranium was determined in solutions by starting the above procedure by saturating the solution with Al(NO3)3 and then extracting with the tributyl phosphate-heptane solvent. The procedure from this point on was the same as previously described.

Silica. Silica was gravimetrically determined in monazite sands by the perchloric acid dehydration method (37b).
Sulfate. Sulfate in solutions was determined gravimetrically as barium sulfate by precipitation with barium chloride (37b). If large amounts of thorium phosphate were present in the solution, it was necessary to increase the acidity of the solution to 1.0 - 1.5 molar and add a 100 per cent excess of barium chloride.

Phosphate. Phosphate was determined volumetrically in solutions using the ammonium phosphate molybdate method (37b).
During the laboratory phase of this research it was found that thorium could be extracted from a monazite sulfate solution with tributyl phosphate if sufficient nitric acid was added. A study was made to determine the conditions required for this extraction and the feasibility of using this procedure to separate and purify the thorium from the rare earths. The distribution coefficients between the solvent and aqueous phases for the thorium and the rare earths were determined as a function of the equilibrium nitric acid concentration and the dilution ratio of a standard monazite sulfate solution (70 grams per liter of total oxides). When the solution was diluted it represented a decrease in the sulfuric and phosphoric acid concentrations of the original monazite sulfate solution. An Indian monazite solution was used and the analysis of the solution was:

Total oxides - 70.0 grams/liter
ThO₂ - 9.4 grams/liter
P₂O₅ - 26.0 grams/liter
H₂SO₄ - 200 grams/liter

The acid-to-digested sand ratio was 2.0.
The results of this extraction study are shown in Figure 15. By diluting the monazite sulfate solution with nitric acid and by increasing the equilibrium nitric concentration from 3.88 normal to 7.8 normal, the distribution coefficient for the thorium was increased from 0.017 to 20. This represented a 1200 fold increase. At the same time the distribution coefficient for the combined rare earths decreased slightly with an increase in the nitric acid concentration, and increased slightly with an increase in the dilution ratio. All distribution coefficients for the rare earths were between 0.074 and 0.165. This represented a slightly greater than a two fold variation.

Another study was made to determine the effect of acid-to-digested sand ratio upon the extraction of the thorium and the rare earths. This study was made with a monazite sulfate solution having an acid-to-digested sand ratio of 1.1. A comparison of the results of the two acid-to-digested sand ratios studied is shown in Figure 16. The data are shown as a function of the equilibrium nitric acid concentration. At any one nitric acid concentration the concentration of thorium, rare earths, and phosphate is the same, but the concentration of the sulfate decreases proportionately as the acid-to-digested sand ratio is decreased. The extractibility of the thorium was increased
FIGURE 15 EXTRACTABILITY OF THORIUM AND RARE EARTHS FROM MONAZITE SULFATE SOLUTION
FIG 16 EFFECT OF ACID-TO-SAND RATIO ON EXTRACTABILITY OF THORIUM AND RARE EARTHS.
by a factor of four when the acid-to-digested sand ratio was decreased from 2.0 to 1.1. The extractibility of the rare earths was slightly decreased by the decreasing the acid-to-digested sand ratio.

The effectiveness of the direct extraction of thorium from the monazite sulfate solution was tested by continuous countercurrent extraction in a two inch Schiebel column. This unit had seven extraction stages and seven scrub stages. The feed had the following concentration:

- Total oxides - 31.5 grams/liter
- $\text{ThO}_2$ - 4.5 grams/liter
- $\text{P}_2\text{O}_5$ - 12.0 grams/liter
- $\text{SO}_4$ - 108 grams/liter
- $\text{HNO}_3$ - 7.7 normal

The acid-to-digested sand ratio was 1.75. The scrub solution was 7.7 normal nitric acid and the incoming solvent had been previously brought into equilibrium with 7.7 normal nitric acid. The ratio of feed to solvent to scrub in the column was 1.00/0.753/1.32. The dilution ratio of the aqueous solution in the extraction section of the column was 5.0. The results of this column run showed that 96 per cent of the thorium had been extracted and that the product thorium contained 1.5 per cent rare earths. Batch shake up data indicated that if 100 per cent stage efficiency was obtained during the run 99.5
per cent of the thorium would have been extracted and the final product would have contained eight parts per million of rare earths. This indicated that the stage efficiency of the Scheibel column was 10 to 20 per cent. Similar low stage efficiencies were obtained when the column was used with other extraction systems.

In spite of the less-than-desired results which were obtained during this run the process appeared to be feasible. The process would involve digesting monazite sand in as small amount of sulfuric acid as possible. The digestion mass would then be dissolved in seven normal nitric acid and the resulting solution would be fed to an extraction unit to remove the thorium and the uranium. The rare earths and the nitric acid would be recovered from the raffinate by evaporating to volatilize the nitric acid and to precipitate the rare earths as sulfates. The thorium and uranium would then be separated and purified by a selective stripping of the solvent with nitric acid.

While this process is very simple and direct, it has the disadvantage that tremendous amounts of nitric acid are required to effect the extraction of the thorium. If the digestion of the monazite sand could be carried
out at a very low acid-to-sand ratio (0.50 to 0.70), and if a high nitric acid recovery could be obtained, the process could become competitive with the other suggested processing methods.
As a final decay product of radioactive thorium, there should be present in monazite sands a rich concentrate of the lead isotope Pb$^{208}$. Some Pb$^{206}$ should also be present as a final decay product of U$^{238}$. A study was made to determine the feasibility of recovering the lead during the process operations. Calculations, based on the thorium and uranium analyses and assuming the age of monazite sands as $2.5 \times 10^9$ years, revealed that the Idaho monazite sand should contain 0.57 per cent lead and that the Pb$^{208}$ to Pb$^{206}$ ratio should be approximately 7.5. Actual analyses by spectrographic means showed that the Idaho monazite contained less than 0.01 per cent lead. No estimate of the Pb$^{208}$ to Pb$^{206}$ ratio could be made.

Because lead sulfate is insoluble in dilute sulfuric acid solutions, the lead should concentrate in the acid-insoluble silica sludge. One portion of this residue, equivalent to about 30 pounds of monazite sand, was treated with 20 per cent caustic to dissolve the silica and the lead. After removing the silica, 28 milligrams of lead sulfate were recovered. From another portion of the residue treated with hot ammonium acetate, no lead was recovered.
Although the results of the caustic treatment indicated that some lead could be recovered, it did not appear feasible to do on a commercial scale.