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CHEMISTRY—GENERAL

UNITED STATES ATOMIC ENERGY COMMISSION

SOLVENT EXTRACTION OF SOLUTION
CONTAINING RARE EARTHS. PREPARATION OF
THORIUM COMPOUNDS FROM MONAZITE BY
SULFURIC ACID DECOMPOSITION AND SOLVENT
EXTRACTION

By
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SOLVENT EXTRACTION OF SOLUTIONS CONTAINING
RARE EARTHS *

Preparation of Thorium Compounds from Monazite by
Sulfuric Acid Decomposition and
Solvent Extraction

by

M. E. Whatley and G. L. Bridger

ABSTRACT

An investigation was made of the feasibility of producing pure thorium compounds from monazite sand by a process involving the digestion of the sand with sulfuric acid and separating the thorium from the rare earths by solvent extraction.

The extractability of the solution produced by taking up the digested sand with water was studied using several common solvents and several complexing agents. This was a continuation of a previous study made in this laboratory. The results were essentially negative leading to the conclusion that extraction from this solution was not practical.

Possibilities for desirable modification of this solution were then considered. Precipitation of the sulfate from the system with lime and nitric acid was tried and found to be partially successful but impractical because of the large losses of thorium by occlusion in the copious calcium sulfate precipitate.

A successful method for producing an extractable solution was found, consisting of neutralizing the original solution with ammonium hydroxide to precipitate the heavy metals as phosphates, and, after filtering and washing, dissolving this precipitate in nitric acid with the aid of ferric nitrate.

* This report is based on a Master's thesis by Marvin E. Whatley submitted in June 1950.

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Studies were made of extracting this type of solution with tributyl phosphate to determine the composition most conducive to extraction. It was found that the presence of small amounts of sulfate ion tended to decrease the proportion but increase the purity of the thorium extracted. It was found that the presence of the ferric ion tended to markedly increase the degree of extraction to the point where 98% of the thorium was being extracted in a single pass. This increase in extraction was accompanied by a slight decrease in the purity of the thorium extracted. It was found that as the concentration of free nitric acid was increased beyond 4 molar, extraction decreased. Calcium nitrate, in concentrations up to 0.5 molar produced no significant effect upon extraction.

A sequence of batch extractions was carried out so as to simulate continuous countercurrent extraction using tributyl phosphate and a typical solution. All of the thorium and uranium were found to be extracted completely out of the aqueous phase. In one experiment a simulated scrubbing section was included, using a nitric acid solution as a wash. This experiment produced thorium nitrate of 93% purity. It was concluded that, by using a sufficient number of equilibrium steps and the proper wash rate, thorium nitrate could be completely recovered from the solution at a very high purity.

The proposed process is as follows: (1) digesting the sand with sulfuric acid, (2) dissolving the digested mass in water, (3) precipitating from this solution, by neutralization, the heavy metals as phosphates, (4) filtering and dissolving this precipitate in nitric acid, preferably with the aid of ferric nitrate, (5) selectively extracting the thorium and uranium from this solution, using tributyl phosphate as a solvent, and (6) separating the thorium from the uranium by further solvent extraction processes.

INTRODUCTION

The principal commercial source of thorium is monazite sand, which contains as phosphates large proportions of the rare earths, small proportions of thorium, and even smaller proportions of uranium. The present commercial method of producing thorium consists of digesting this sand with sulfuric acid followed by a series of selective precipitations (5,7,11). This process, aside from being expensive, produces a grade of thorium which cannot be used for nuclear purposes without further purification.

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The current interest in thorium centers about the fact that thorium is a source of one of the three known fissionable isotopes, uranium 233. This isotope is obtained by the transmutation of thorium upon neutron capture according to the following reaction:

Thorium to be used in breeder piles in this manner must be of a very high purity, virtually free of contaminants of a high neutron capture cross section.

Thorium nitrate purification

In 1945 the Ames Laboratory was asked to supply various sections of the Manhattan Project with thorium metal of a sufficient grade of purity for use in nuclear experimental work. For this purpose a process was devised, one step of which consisted of applying a liquid-liquid extraction technique to separate the thorium from the boron, cadmium, and the traces of rare earths, all of which were found as impurities in the commercial, or mantle grade, thorium nitrate used as a starting material. Although solvent extraction had been previously used to separate uranium from thorium by extracting the uranium into the solvent phase, this was the first application of extracting thorium into the solvent phase for the purpose of purification. The success of this operation is responsible for the subsequent studies, including the present one, to apply solvent extraction to the commercial production of thorium compounds.

The operations performed consisted of dissolving the mantle grade thorium nitrate and adjusting the solution to 0.44 molar thorium nitrate, 3 molar calcium nitrate, and 3 molar nitric acid (19). This solution was fed into the center of a thirty foot column, the bottom section of which served to extract the thorium into the solvent, and the top section served to wash the solvent with a calcium nitrate-nitric acid solution to remove any extracted impurities. The solvent taken from this column was passed through a second column where the pure thorium was re-extracted into a water phase, and the solvent recycled. The thorium was precipitated with oxalic acid, filtered, and ignited to the oxide for further processing (16). The solvent originally used in this unit was hexone, but, since this was found to be unstable upon extended contact with nitric acid, it was replaced by a mixture of 20% tributyl phosphate and 80% dibutyl ether (18).

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In preparation for the construction and operation of the column, considerable data were accumulated on the distribution of thorium nitrate between an aqueous phase and several organic solvents. Data were taken at various acidities and with the use of several salting out agents (15). The solvent for which the most data were taken was hexone (19). This study was made on systems which contained but traces of rare earths, hence is limited in its application to solutions of monazite sand.

There are studies reported by B. F. Rothchild and C. C. Templeton in which the solubilities of thorium nitrate in common solvents are given (12). Their studies indicate that thorium nitrate is quite soluble in the lower ketones and alcohols, and that as the length of the carbon chain increases, the solubility decreases. It was also shown that the solubility of thorium nitrate decreases sharply with halogenation, and that it was negligible in aromatic solvents. Some of the other solvents which were reported to have a favorable solubility included nitromethane and nitroethane. Data on the distribution coefficient of thorium nitrate between an aqueous phase and the lower alcohols and ketones were also reported in these studies (17).

Work of Battelle Memorial Institute

The Battelle Memorial Institute began research work on the commercial preparation of thorium in November 1947 under contract with the Atomic Energy Commission. During the early stages of the Battelle work, the digestion of monazite sand with sulfuric acid was studied and rejected in favor of a caustic soda digestion. At the present stage of development (4) this process consists of treating the sand for two hours with 45% caustic solution. This converts the phosphates to hydroxides, and produces trisodium phosphate which is filtered and washed from the mass. The filtrate containing the excess sodium hydroxide and trisodium phosphate is concentrated by evaporation, the trisodium phosphate crystallized out, and the sodium hydroxide recycled (3). The hydroxide mass containing rare earths, thorium, and uranium is then dissolved in hydrochloric acid, selectively precipitated with ammonium hydroxide leaving 99% of the rare earths in solution to be removed by filtration. The precipitate is then dissolved in nitric acid to make a solution which can be extracted with a mixture of tributyl phosphate and some light petroleum ether. It was the intention to operate a solvent extraction unit of three columns to be used as follows: The enriched nitric acid solution containing thorium, uranium, and rare earths nitrates was to be fed into the middle of the first column where the thorium and

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uranium were to be extracted into the solvent phase and washed free of rare earths. This solvent containing thorium and uranium nitrates was to be stripped out by a dilute nitric acid solution which was then to be washed with fresh solvent to remove uranium. The solvent from this column was then to be fed into a third column where a carbonate solution was to strip out the uranium.

This unit has been simulated and found workable.

The Battelle Memorial Institute quarterly reports include many data on the distribution coefficient of thorium between an aqueous phase and mixtures of butyl phosphate and petroleum diluents for a considerable range of conditions (1,2,3). Most of their data were taken in the presence of large quantities of rare earths.

Work with sulfuric acid - monazite sand systems

The reasons for considering methods of producing thorium based on sulfuric acid digestion of the sand lie in the economic advantages. The acid is the cheapest mineral acid available, and the conditions for the digestion are not difficult to obtain.

One of the previous investigations by this laboratory which helped to form a background for the work reported in this thesis was that of digesting the sand with sulfuric acid conducted by T. W. Blickwedel. He found (5) that there is an optimum acid concentration for digestion at 93% H_2SO_4 and recommended that an acid to sand ratio (H_2SO_4 /sand) of 2.5/1 at a temperature of 200°C to be used. When the sand is digested in this manner it forms a pasty grey mass which dissolves in water to an extent equivalent to fifty grams of sand per liter, putting everything into solution but the silica, rutile and zircon. This solution is stable, but when diluted will precipitate some of the thorium as the phosphate.

The feasibility of applying solvent extraction directly to the sulfuric acid-monazite solution for the purpose of separating the thorium from the rare earths was investigated to some length in this laboratory. Max Feldman (6) lists 22 solvents, including the most common, which he studied and found to give no extraction from this solution. In addition to these he also studied the effect of adding to the system various complexing agents in an attempt to form a soluble complex which might be extracted. He succeeded in obtaining minute amounts of extraction in this manner, but, in general, found it not worthy of further consideration.

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Objectives

It was the overall objective of this research to investigate the feasibility of producing thorium from monazite sand by a process including a sulfuric acid digestion followed by a liquid-liquid extraction step to separate the thorium from the rare earths.

The specific objectives were:

1. To determine if it were possible to extract either the thorium or the rare earths from a sulfuric acid-monazite solution.
2. To determine the feasibility of converting the sulfate solution to a nitrate solution which would be extractable.
3. To obtain data on extraction from a nitric acid-phosphate solution indicative of the effects produced by variation of concentrations of constituents of the solution.

EXPERIMENTAL PLAN

The experimental work followed a progressive pattern consisting of three phases. Since the techniques applied in these three phases are different, they will subsequently be treated individually.

Extraction of a sulfuric acid - monazite solution

The first approach to the problem was an attempt to extract either thorium or the rare earths selectively from the solution produced by taking up the digested monazite mass with water. If a solvent could have been found which would have done this, a process could have been worked out which would have been simpler and less expensive than any in use today. This possibility was therefore studied completely before more involved methods were considered.

The sulfuric acid-monazite solution in its most stable form is about four normal in acid, and contains thorium, uranium, rare earths, and phosphate in the same proportions in which they exist in the sand. A search of the literature revealed no previous solvent extraction studies with a system such as this, or data on the solubility of thorium sulfate

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or phosphate in organic solvents. The data on thorium nitrate systems were not applicable to this solvent search because of the large difference between its ionic properties and those of thorium sulfate or phosphate. There were, therefore, no indications as to which type of solvent might give the best results. The factors finally used to decide which solvents to try were physical properties such as density, solubility in water, and boiling point. In many cases these were ignored so that different types of solvents, like nitrobenzene and tributyl phosphate might be tried.

The solvent search was then expanded to include the use of complexing agents. This field was better covered in the literature, and there were more fundamental concepts to apply. Amino groups, carboxyl groups, hydroxyl groups, and many others were known to be conducive to the complexing of thorium. It was found unfortunate that most complexes are stable only in neutral or slightly basic media, conditions which could not possibly have been obtained since thorium phosphate starts to precipitate at acidities lower than 2 normal.

Precipitation of calcium sulfate from the
sulfuric acid - monazite solution

Having produced no promising results from any attempt to extract from the sulfuric acid-monazite solution, the next step was to modify the solution. Since it was known that thorium nitrate was soluble in certain organic solvents (17) it was attempted to extract the thorium as the nitrate. The simple addition of nitric acid was tried and found unsuccessful. This was not unexpected since it is reported in the literature that both the sulfate and the phosphate interfere with extraction of thorium nitrate (2). It was then considered necessary to conduct a study of the most feasible method of removing one of these.

It seemed most advisable to separate the sulfate from the solution since lime, which is cheap, could be used to form insoluble calcium sulfate, while nitric acid could be added to maintain the acidity of the system and supply the nitrate ion. By varying the amount of lime and nitric acid used, the proportion of excess calcium ion and the acidity of the solution could be controlled.

It was necessary to determine:

1. If the thorium could be kept in solution.

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2. If sufficient sulfate might be removed to permit extraction.
3. If an excess of calcium as the nitrate produced any desirable effect on the precipitation and extraction.

It was expected that an increase in acidity would increase the solubility of calcium sulfate while an increase in calcium ion would decrease it. The precipitation of thorium phosphate was expected to be higher at lower acidities, but there was no way of knowing what the effect of the calcium ion would be. The precipitation of calcium phosphate was not expected because precipitation was being made in acid media.

Extraction of the nitric acid - phosphate solution

When it was found that the precipitation of calcium sulfate was not a desirable method of ridding the system of sulfate, other methods of achieving the same effect were considered. It was known that by neutralizing the sulfuric acid-monazite solution the heavy metals phosphates could be precipitated. Experimental studies showed that this precipitate could be washed, filtered, and dissolved in nitric acid, producing a solution effectively free of sulfate. Thence it was found that the thorium could be removed from the sulfate more easily than the sulfate from the thorium. There is very little known about aqueous thorium phosphate solutions. Spitzer reports that thorium phosphate is soluble in one normal nitric acid to the extent of 0.012 grams ThO_2 per liter (14). Some investigators explain its apparent greater solubility by strong complex action on the part of the phosphate (11) while others imply that it exist in a colloidal state (8). With regard to the latter, it was found that at high dilutions solutions prepared in this laboratory would form lumps of a thin jelly like substance. The addition of ferric nitrate was found to greatly facilitate the dissolution of the phosphates in nitric acid and produce a more stable solution. The actual preparation of the solutions used for this research consisted of precipitating the phosphates out of a sulfuric acid-monazite solution with ammonium hydroxide and washing the precipitate, by settling, with voluminous quantities of water. The precipitate was filtered and taken up with nitric acid. For the preparation of one solution ferric nitrate was used, while for the other it was not.

After confirming that such a solution could be made, attention was turned to determining its extractability when its constituents were varied. It was expected that extraction from it would not be as favorable as from

phosphate free systems, but it was expected to behave better than the sulfuric acid-monazite solution.

The study of the susceptibility of this solution to extraction was approached from the point of view of evaluating the effect of some of the more important variables in order to guide small pilot plant studies and to supply specifications for the preparation of subsequent solutions. The research included the study of the effect of the residual sulfate concentration, the ferric nitrate concentration, the addition of calcium nitrate (to be compared, as an additive, with ferric nitrate), and the acidity. These were all conducted at constant thorium, rare earth, and phosphate concentrations, and for the study of each variable, the other variables were maintained constant.

The most common method of describing the behavior of a solvent extraction system is to report the distribution coefficient, which is defined to be the ratio of the concentration in the solvent phase to the concentration in the aqueous phase at equilibrium. This term was originally invented because, for single solute systems that obey Henry's law, it is constant at low concentrations. For systems that are used in this research, which contain several components effecting equilibrium, there is no reason to believe that it will remain constant. It was therefore considered less desirable to report the data in terms of distribution coefficients than as percent of substance extracted by a single batch extraction under controlled conditions.

The continuous liquid-liquid solvent extraction operation usually employs a column in which one solvent is passed countercurrently to the other so that as the liquid containing the solute enters the column it is first met by solvent that has already picked up much solute, and as the liquid passed through the column it is constantly met with solvent containing less solute until, in its most depleted state, it is met with fresh solvent containing no solute. Thus, at every point in the column it is necessary that the equilibrium conditions are such to drive the solute from the one liquid to the other. In simple systems there is no reason to believe that anything will occur to prevent this, but the behavior of more complex systems is less dependable. So, in addition to the more fundamental studies, there were experiments to determine whether a solvent extraction column could actually be expected to function effectively. These consisted of series of batch extractions performed by using, consecutively, the solvent and aqueous phases from each extraction for further extractions in such a pattern so as to simulate the action of continuous countercurrent extraction columns.

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EXPERIMENTAL PROCEDURE

This section will be divided into the three parts into which the work was divided:

1. The attempts to purify thorium by extraction from a sulfuric acid-monazite solution.
2. The attempts to make an extractable solution by precipitating the sulfate as calcium sulfate from a sulfuric acid-monazite solution.
3. The investigation of extraction from a nitric acid-phosphate solution.

Materials

The main material was the monazite sand which was from Travancore, India. Its composition, as determined by the analytical group of the Ames Laboratory, was:

ThO ₂	7.5 ±	2%
Total thorium and rare earths oxides	68.0 ±	1%
CeO ₂	28.5 ±	1%
P ₂ O ₅	25.9 ±	0.5%
SiO ₂	7.0 ±	2%

The acids used in this research were of analytical grade. The solvents were of "practical" grade. The lime was of commercial grade, of alkalinity equivalent to 72.3% CaO.

The cerium used for the preparation of synthetic solutions was supplied by G. Fredricks Smith Co., and the thorium was made available through Atomic Energy Commission facilities.

Extraction of a sulfuric acid - monazite solution

Three different stock solutions were used, two of which were synthetic and one of which was prepared from monazite sand.

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The procedure consisted of mixing 50 ml. of the solvent with 25 ml. of one of the stock solutions for one half hour with an air stirrer in a 250 ml. erlenmeyer flask. The liquids were transferred to a separatory funnel for separation. The time required for the phases to completely separate varied with the solvent. Some mixtures formed fine suspensions which settled only after long standing. In the early part of the study the raffinate phase was analyzed for rare earths and thorium, and the extraction computed by difference. In the latter part of the study it becomes convenient to analyze the solvent phase. This was usually done by steam-distillation of the solvent and analysis of the aqueous residue. In cases of solvents of low volatility, multiple re-extraction with water was used.

To analyze the solvent phases when complexing agents were used, they were evaporated to dryness, and the residue ignited. This residue was then taken up with hydrochloric acid and analyzed in the usual manner. This was necessary because of the possibility that the complexing agent would interfere with the analytical precipitation.

The method of determining the combined rare earths and thorium consisted of an oxalate precipitation, using an excess of oxalic acid. It is reported in Scott (13) that the phosphate ion will interfere with the oxalate precipitation, and, according to Seidell (14), thorium oxalate is appreciably soluble in solutions above two molar in H_2SO_4 ; however, by using a large excess of oxalic acid and adding the solution to be analyzed slowly to the oxalic acid solution, stirring constantly with an air stirrer, results were obtained which were consistent and in agreement with controls analyzed by the analytical group using other methods.

The precipitate was allowed to stand at least twelve hours, filtered with Whatman #41 paper, and ignited over a Meker burner in a porcelain crucible. As a matter of convenience, the heavy metals, including thorium and the rare earths, are referred to as "total oxides" in this thesis. (Uranium is present in proportions below the order of accuracy of this analysis.)

Thorium was determined and reported as the dioxide, ThO_2 . This analysis consisted of dissolving the total oxides in concentrated hydrochloric acid with the aid of a few crystals of potassium iodide; this required heating four to eight hours. The solution was then evaporated to near dryness to remove the excess hydrochloric acid, diluted to about 100 ml., and neutralized with ammonium hydroxide using methyl orange as an indicator. This solution was heated to boiling and one gram of

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sebacic acid added, precipitating the thorium as the sebacate. The precipitate was immediately filtered and ignited to the dioxide in a porcelain crucible. If the color of the ignited precipitate was other than white, indicating the presence of impurities, it was dissolved and reprecipitated by the same procedure.

The rare earth oxides were computed by subtracting the thorium dioxide from the total oxides.

Precipitation of sulfate as calcium sulfate

For each sample a measured amount of nitric acid was added to a liter of standard sulfuric acid-monazite solution, and a prepared slurry of a measured amount of lime in a liter of water was added to this while the mass was being vigorously stirred with a mechanical stirrer. The amount of lime and nitric acid present at this stage determined the amount of calcium nitrate formed by the lime in excess of that required to precipitate the sulfate, and the acidity from which the calcium sulfate was precipitated, and hence were the variable factors in the procedure. The precipitated mass was agitated for five hours in a four liter crock to insure the completion of the reaction, and the thick slurry was allowed to stand and cool for about four hours before filtering in a Buchner funnel. The filtered calcium sulfate precipitate formed a large cake which retained some of the solution. This was washed with about 200 cc of water, worked relatively dry in the Buchner funnel, then transferred to a large beaker to be stirred to a fine slurry with a liter of water containing 10 cc nitric acid. This slurry was allowed to settle and was filtered. The resulting composite filtrate, which amounted to more than three liters, was concentrated by boiling to about 500 cc. Upon cooling, further calcium sulfate precipitated which was filtered and washed with about 100 cc of water, bringing the volume to 600 cc. This was once more concentrated to 400 cc, cooled, filtered, and diluted to 500 cc in a volumetric flask. These solutions were analyzed by the analytical section for total oxides, thorium dioxide, phosphate, and sulfate.

Extraction of nitric acid-phosphate solutions

Two stock solutions were prepared for use in extraction experiments. The first preparation entailed a precipitation of the heavy metal phosphates using ammonium hydroxide to neutralize the sulfuric acid-monazite

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solution. The precipitate was washed and settled eight times, with removal of two-thirds of the soluble ammonium sulfate each time. The precipitate was then filtered and taken up with nitric acid and ferric nitrate. This was concentrated slightly by boiling to produce a solution of the following analysis:

Total oxides	4.65 g./100 ml.
ThO ₂	0.62 g./100 ml.
Fe ₂ O ₃	1.57 g./100 ml.
P ₂ O ₅	1.96 g./100 ml.
SO ₄	0.16 g./100 ml.
Acidity	4.57 N. HNO ₃

The second was prepared in the same manner as the first up to the dissolution step. Dissolution was effected by using a large amount of nitric acid and no ferric nitrate. This was boiled down and diluted several times to obtain a minimum final nitric acid concentration. At the point where the solution showed signs of being no longer stable this procedure was stopped and the concentration of the metals adjusted to equal those of the first solution. The analysis of this solution was:

Total oxides	4.65 g./100 ml.
ThO ₂	0.62 g./100 ml.
P ₂ O ₅	1.96 g./100 ml.
SO ₄	0.10 g./100 ml.
Acidity	6.0 N. HNO ₃

The solvent for every extraction was tributyl phosphate which had been brought to equilibrium with 3 normal nitric acid. This was prepared at the beginning of the study by a trial and error method consisting of mixing a half gallon of tributyl phosphate with a nitric acid solution and adjusting the acidity by adding either water or acid so that, after thirty minutes of stirring, the aqueous phase was found to be 3.00 normal HNO₃. The tributyl phosphate phase was then removed and stored for use.

The procedure for the preparation of the aqueous solutions to be extracted was the same throughout the entire study, consisting of using 15 ml. of one of the stock solution previously mentioned, and adding to it the desired amount of a standard solution of the constituent under study. This was made up to 25 ml. in a volumetric flask, so that the concentrations of thorium, rare earths, and phosphate were constant for all of the runs. The acidity was fixed at 3 normal HNO₃ for solutions

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of the series concerned with the effect of sulfate and for the series concerned with the effect of ferric nitrate. The acidity of solutions for determining the effect of the presence of calcium nitrate was 3.6 normal HNO_3 by necessity, since the acidity of the ferric free stock solution was so high.

The extraction step throughout consisted of mixing 50 ml. of solvent with the 25 ml. of prepared aqueous solution for five minutes in a 250 ml. erlenmeyer flask, then transferring the liquids to a 100 ml. graduated cylinder to measure any change in volumes. This latter step was found to be unnecessary because the volumes of the phases were found not to change perceptibly; however, since it became a convenient method of handling, it was continued. A 25 ml. aliquot of the solvent was removed from the graduated cylinder by pipette for analysis. In some cases the solvent phase was removed and centrifuged for fifteen minutes before the aliquot was taken, but in most cases the separation in the graduated cylinder was quite complete and this was not necessary.

The analytical procedure consisted of several steps. To obtain total oxides the following was followed.

1. The above mentioned aliquot was re-extracted twice with 2 M. H_2SO_4 to draw all of the metals into the aqueous phase. This procedure was checked by analyzing subsequent re-extractions of selected aliquots and found to be sufficient.
2. The thorium and rare earths were precipitated using ammonium hydroxide, filtered, and washed free of ammonium sulfate.
3. The precipitate and filter paper were placed in a beaker and treated with 10 ml. hot nitric acid to dissolve the hydroxides.
4. The solution was diluted to 200 ml., heated and a large excess of oxalic acid added to precipitate the thorium and rare earths as oxalates.
5. The precipitate was allowed to stand over night, filtered and ignited to the oxides in a porcelain crucible.
6. These were weighed and reported as total oxides.

A standard iodate procedure recommended by the Ames Laboratory analytical group was used for the thorium analysis which required the following steps:

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1. The total oxides were placed in a beaker and dissolved by boiling in 50 ml. of 50% HNO_3 . It was necessary to add one or two drops of 0.1% H_2SiF_3 solution.
2. The cerium was reduced by the addition of about 1 ml. of hydrogen peroxide.
3. The thorium was precipitated by the addition of 100 ml. of potassium iodate precipitating solution (10% KIO_3 in 35% HNO_3).
4. This precipitate was separated by centrifuging it in a 50 ml. centrifuge tube.
5. The precipitate was washed back into the beaker, dissolved in 20 ml. HNO_3 with 20 ml. water.
6. Steps 3, 4, and 5 were repeated and the thorium was then precipitated as the oxalate.
7. The precipitate was allowed to stand over night, filtered and ignited to the dioxide.
8. The ignited precipitate was weighed and reported as ThO_2 .

Two simulated column studies were performed for verification of the workability of a solvent extraction process applied to the purification of thorium nitrate from a nitric acid-phosphate solution. The first consisted of simply a simulated stripping section in which the exit solvent, which contained the thorium, was not washed to remove the rare earths. It was the purpose of this simulated column to show that all of the thorium and uranium could be stripped from the aqueous phase. The column simulated consisted of three equilibrium steps. Each equilibrium operation, in its turn, was performed in an erlenmeyer flask by stirring the phases together for two minutes and then pouring the liquids into a separatory funnel where the phases were separated. In the sequence of operations, the solvent phases were passed countercurrently to the aqueous phases (9). The diagram in Figure 1 indicates the sequence, the exact number of operations made, and where the series was stopped for analysis.

The second study consisted of the simulation of a column of five equilibrium steps, into which the feed was introduced on the third step. In this set-up a nitric acid wash solution was used, which was introduced at the first equilibrium step (equivalent to the top of the column), and

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letters indicate sequence of
operations

* sample for analysis

FIGURE 1

DIAGRAM OF FLOW IN SIMULATED THREE EQUILIBRIUM
STEP COLUMN OPERATION (NUMBER ONE)

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passed "down" through the sequence to join the feed. The solvent was introduced at the fifth equilibrium step (equivalent to the bottom of the column) and passed "up" through the sequence to be removed after it reached the first equilibrium step. The sequence for this study is depicted in Figure 2.

It is realized that, as with actual columns, an infinite number of operations would have been required to reach steady state conditions; however, the error involved in taking samples at the points indicated was no greater than that inherent in the analytical methods.

The methods of sampling and analysis for the simulated column studies were the same as those described for the batch extraction series.

RESULTS

This section includes individual treatment of the results from the three phases of the research already described.

Extraction of sulfuric acid - monazite solution

The attempts to extract either thorium or the rare earths from the sulfuric acid-monazite solution were unsuccessful.

Through the course of the investigation three different solutions were used. The analysis of these are given below.

Analysis of solution "A" (synthetic)

ThO ₂	0.091 g./100 ml.
CeO ₂	2.49 g./100 ml.
P ₂ O ₅	1.08 g./100 ml.
Acidity	4.6 N. H ₂ SO ₄

Analysis of solution "B" (synthetic)

ThO ₂	0.831 g./100 ml.
CeO ₂	2.471 g./100 ml.
P ₂ O ₅	1.12 g./100 ml.
Acidity	5.0 N. H ₂ SO ₄

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letters indicate sequence of
operations

* sample for analysis

FIGURE 2

DIAGRAM OF FLOW IN SIMULATED FIVE EQUILIBRIUM
STEP COLUMN OPERATION (NUMBER TWO)

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Analysis of solution "C"

ThO ₂	0.347 g./100 ml.
Total oxides	2.61 g./100 ml.
P ₂ O ₅	1.15 g./100 ml.
Total acidity	4.08 N.

The solvents which were studied are tabulated in Table 1. Table 2 gives the results of the attempts to effect extraction by complexing the thorium with some organic compound. These results were all negative except for the work with ethyl phosphate. A more intensive study was therefore made of the ethyl phosphate-butyl alcohol system which showed that the extraction of total oxides increased with the increase of the proportion of ethyl phosphate present, to produce a maximum value of that given in Table 2. Further increases in the proportion of ethyl phosphate present resulted in the formation of a precipitate in the aqueous phase. The study of this combination was abandoned for two reasons: first, ethyl phosphate is soluble in the aqueous phase, which is very undesirable in extraction work, and second, analysis of the extracted total oxides showed that the ratio of thorium to rare earths was the same as in the original solution, indicating no selectivity.

These data are significant in the light that they represent a continuation and a supplement to the work conducted by Max Feldman (6). From the summation of these data, it may be concluded that a process based on the solvent extraction of thorium from a sulfuric acid-monazite solution is infeasible.

Precipitation of sulfate as calcium sulfate

The results of this study showed in general that the precipitation of the sulfate from the sulfuric acid-monazite solution using lime in conjunction with nitric acid was infeasible in the respect that the losses of thorium were too high. The method was inherently lengthy and very involved. Sulfate constituted a very large part of the solid constituents of the solution and the precipitation of it meant the handling of a large precipitate, the ratio of calcium sulfate precipitate to thorium dioxide being 260 to 1. It was essential to the workability of such a method that all of the thorium be washed out of the precipitate.

It was found that when the precipitation of thorium was performed in a considerably acid solution, most of the thorium was recovered,

however, when the acidity of the solution became less, there was an accompanying loss of thorium, so that when the acidity was 0.92 N. there was a loss of 90% of the thorium. It was also noticed that as the

Table 1

Solvents Tried with Sulfuric Acid - Monazite
Solution

n-Amyl alcohol (C) ^a	n-Decyl alcohol (C)
Benzene (B)	Ethylene bromide (B)
Benzene sulfo chloride (B)	Methyl n-amyl ketone (C)
Benzyl acetate (B)	Methylethyl ketone (C)
α Bromo naphthalene (A)	Methyl salicylate (A)
n-Butyl alcohol (C)	Nitrobenzene (B,C)
p-tert-Butyl catechol (C)	Nitropropane (B)
Dibutyl ether (C)	Nitromethane (B)
Tributyl phosphate (C,B)	Oleic acid (A)
Carbon tetrachloride (B)	Xylene (B)

^a letters indicate the solution that was tested.

amount of calcium nitrate in excess increased, there was a greater loss of thorium. The sulfate in the final solution was found to correlate with the acidity so that the amount of sulfate left in the solution increased as the acidity increased, and there appeared to be no way to remove the sulfate and recover, at the same time, all of the thorium.

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Table 2

Complexing Agents Tried
with Sulfuric Acid - Monazite Solution^a

Solvent	Complexing agent	% total oxides extracted
n-Amyl alcohol	Catechol (1 g.)	0.0
n-Amyl alcohol	p-tert-Butyl catechol (1 g.)	0.0
Benzene	Resorcinol (1 g.)	0.0
Benzene	Thymol	0.0
Butyl alcohol	Ethyl phosphate (21 g.)	5.0
Methyl n-amyl ketone	Catechol (1 g.)	0.0
Methylethyl ketone	Pyrogalllic acid (1 g.)	0.0
Nitrobenzene	Pyrogalllic acid (1 g.)	0.0
Nitromethane	Urea (3 g.)	0.0

^a Monazite solution "C" was used in every case.

The correlation of the acidity of the precipitation step to the recovery of thorium is shown in Figure 3, and tabulated in Table 3.

Qualitative tests showed that tributyl phosphate would extract from solutions in this group containing small quantities of residual sulfate.

One point of interest which came out of this study is that the amount of thorium lost correlated with the amount of phosphate lost, seeming to indicate that the thorium was being lost as a phosphate.

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FIG.3. EFFECT OF ACIDITY DURING
PRECIPITATION OF CaSO_4 ON
THE RECOVERY OF THORIUM

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The analysis of the stock solution used for the calcium sulfate precipitations was:

Total oxides	3.57 g./100 ml.
ThO ₂	0.46 g./100 ml.
P ₂ O ₅	1.45 g./100 ml.
SO ₄	5.60 g./100 ml.
Total acidity	3.84 Normal

Table 3

Thorium Recovered after Calcium
Sulfate Precipitation

Acidity during precipitation (normality)	Ca in excess to that needed for precipitation (%)	% Thorium recovered in final solution
1.92	4.5%	92.5%
1.42	4.5	48.0
0.92	4.5	9.8
1.92	56.2	69.5
1.42	56.2	42.4
0.92	56.2	4.4

Extraction from a nitric acid - phosphate solution

The results of the research with the nitric acid-phosphate solutions are favorable. It has been shown that it is possible and feasible to extract the thorium selectively from this type of solution. The data presented here also indicate that it would be possible to operate a solvent extraction column to completely strip the thorium from the aqueous phase with tributyl phosphate, without prohibitive interference from the phosphate ion.

Throughout the study of the effect of some variables upon extraction, there were two types of solutions used, different in that one contained ferric nitrate while the other did not. There was also a difference in

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acidity for reasons already discussed. Below are given the "basic analyses" of the solutions as they came in contact with the solvent. For application to the tables of results, the basic analysis is to be read so that the concentration of the constituent being studied is changed to correspond to the value in the table.

"Basic analysis" of solution "1", used in the sulfate and ferric ion studies:

Total oxides	2.787 g./100 ml.
ThO ₂	0.368 g./100 ml.
P ₂ O ₅	0.997 g./100 ml.
SO ₄	0.1 g./100 ml.
Fe ₂ O ₃	0.938 g./100 ml.
Acidity	3.0 Normal

"Basic analysis" of solution "2", used in the calcium ion and acidity studies:

Total oxides	2.787 g./100 ml.
ThO ₂	0.368 g./100 ml.
P ₂ O ₅	0.997 g./100 ml.
SO ₄	0.06 g./100 ml.
Fe ₂ O ₃	none
Acidity	3.6 Normal

In each case the batch extraction was carried out using 25 ml. of aqueous phase, and 50 ml. of solvent phase, mixing for five minutes. The solvent phase was, in each case, tributyl phosphate which had previously been brought to equilibrium with an aqueous phase of 3.0 normal nitric acid.

The first series of runs was concerned with the effect of sulfate on the system, in an attempt to determine the tolerable proportion of sulfate which might remain from the washing of the phosphate precipitate in the preparation of the nitric acid-phosphate solution. With reference to Table 4 and Figure 4 it is seen that the presence of the sulfate tended to increase the selectivity of the extraction, increasing the purity of the thorium in the extracted metals from 32% to 75%, while decreasing the amount of thorium extracted to one third of its first value. Hence, these data do not ascertain the undesirability of sulfate, but rather indicate the existence of an optimum concentration of sulfate for any process, dependent, of course, upon all of the factors involved.

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FIG. 4. EFFECT OF SULFATE UPON EXTRACTION

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Table 4

Effect of Sulfate Ion upon Extraction^a

Sulfate ion as H_2SO_4		% total oxides extracted	% thorium extracted	%ThO ₂ in total oxides
g./100 ml.	molarity			
0.098	0.01	29.5	71.2	32.2
0.59	0.06	17.5	69.7	53.0
1.08	0.11	14.1	57.0	53.8
2.55	0.26	6.5	28.4	58.7
5.01	0.51	4.3	23.0	71.4
7.46	0.76	4.8	24.3	67.7
9.91	1.01	4.7	24.7	75.0

^a Basic solution "1".

The effect of the ferric ion, as is shown in Table 5 and Figure 5, is to increase the amount of thorium and total oxides extracted. Unfortunately, the extraction of the rare earths is increased more than the extraction of thorium, and the purity of the thorium in the extracted product drops from 32% to 29% as the ferric nitrate concentration increases from .06 molar to .35 molar. At a ferric nitrate concentration about .2 molar, 98% of the thorium is extracted into the solvent in one pass. Whether it is more expedient to extract the thorium into the solvent easily and apply more effort to scrubbing, or to extract less but purer thorium per stage of stripping must be considered.

The mechanism by which the ferric ion aids extraction seems to be the complexing of the phosphate ion rather than a simple salting out action. This assertion is founded on a comparison of the ferric ion study with a study of the effect of the calcium ion. The results of this study are given in Table 6 and Figure 6, and indicate that, over a range of concentrations equivalent to that of the ferric ion study, there is no significant change in extraction. Calcium nitrate was chosen for this study because it has been previously successfully used as a salting out agent under somewhat different conditions(15).

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Table 5

Effect of Ferric Ion upon Extraction^a

Ferric ion as		% total oxides extracted	% thorium extracted	%ThO ₂ in total oxides
g./100 ml.	molarity			
2.378	0.0588	29.5	71.2	32.2
4.75	0.1176	37.2	86.5	31.0
7.13	0.1764	38.6	94.2	32.5
9.50	0.2352	41.7	98.7	31.5
11.89	0.2940	42.0	97.4	30.9
14.28	0.3528	44.6	98.5	29.4

^a Basic solution "1".

Table 6

Effect of Calcium Ion upon Extraction^a

Calcium ion as Ca(NO ₃) ₂ ·4H ₂ O		% total oxides extracted	% thorium extracted	% ThO ₂ in total oxides
g./100 ml.	molarity			
0.00	0.0	26.6	84.6	41.4
2.36	0.1	25.3	84.0	44.1
4.72	0.2	24.3	83.0	45.6
7.08	0.3	25.2	77.3	40.9
11.81	0.5	22.6	82.5	48.6

^a Basic solution "2".

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FIG.5. EFFECT OF FERRIC ION
UPON EXTRACTION

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FIG. 6. EFFECT OF CALCIUM ION
UPON EXTRACTION

It is noted that ferric nitrate, in addition to aiding extraction, also serves the purpose of stabilizing the solution and aiding considerably in the dissolution step of the process.

The results of variation of acidity are given in Table 7 and Figure 7. The most significant aspect of the results was that when the acidity of the system went beyond about 4 normal the extraction suffered a definite decrease. The reason for this is not obvious. It is possible

Table 7

Effect of Increased Nitric Acid Concentration^a
on Extraction

Nitric acid as HNO ₃		% total oxides extracted	% thorium extracted	% ThO ₂ in total oxides
g./100 ml.	molarity			
2.21	3.6	26.6	84.6	42.4
3.53	5.6	26.8	79.6	39.5
4.79	7.6	19.3	78.3	54.0
6.05	9.6	18.3	79.4	56.4

^a Basic solution "2".

that the tributyl phosphate phase has a greater affinity for nitric acid than thorium nitrate, and that the increase in nitrate ion in the solvent phase tends to force the thorium back into the aqueous phase. It is also possible that the characteristics of the thorium-phosphate complex are changed by the higher acidity. In any case, it is apparent that there is no advantage in using nitric acid concentrations higher than 4 normal.

The solvent phases of several selected runs were tested for the extraction of iron or phosphate, and in all cases the tests were negative. It can be expected, therefore, that the iron and phosphate, in a column, will follow the aqueous phase and be discharged with the rare earths.

FIG. 7. EFFECT OF INCREASED NITRIC
'ACID CONCENTRATIONS UPON
EXTRACTION

The data on the extraction from a nitric acid-phosphate solution by solvents other than tributyl phosphate, shown in Table 8, indicate that tributyl phosphate is probably unique in its ability to extract thorium nitrate in the presence of phosphate ion. It is considered noteworthy that butyl alcohol will extract small quantities of the rare earths selectively.

Table 8
Solvents Tried
with Nitric Acid - Monazite Solution

Solvent	% rare earths extracted	% thorium dioxide extracted
Diethyl ether	0.0	0.0
Hexone	0.0	0.0
Nitromethane	0.0	0.0
Butyl alcohol	9.96	0.0

Analysis of nitric acid - monazite solution:

Total oxides	2.79 g./100 ml.
ThO ₂	0.372 g./100 ml.
P ₂ O ₅	1.18 g./100 ml.
Fe ₂ O ₃	0.94 g./100 ml.
SO ₄	0.1 g./100 ml.
Acidity	3 N. HNO ₃
Volume aqueous phase	25 ml.
Volume solvent phase	50 ml.
Time of mixing	15 minutes

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The results of the first simulated column show that its operation is very efficient, stripping all of the thorium out of the aqueous phase in two equilibrium steps. Table 9 gives the amount of metals in the solvent phase on each simulated plate with respect to the amount of thorium introduced in a unit feed. It is indicated in the table that all of the uranium was extracted into the solvent phase. This was concluded from the fact that the exit aqueous gave a negative test to the ferrocyanide qualitative analysis for uranium.

The second simulated column, which included a washing section, was not so completely successful as the first, in that the thorium leaving the column with the solvent was but 93% pure. The data for the steady state distribution of the metals in this setup are tabulated in Table 9. It is seen that, as in the first column, the stripping section is very efficient, removing all of the thorium from the aqueous phase before it reached the last equilibrium step. The washing section was not so efficient. The two possibilities for improving this section are increasing the number of equilibrium stages in the washing section, and increasing the wash solution rate. It is known from former studies that the distribution coefficient of thorium between the two phases is a function of its concentration and the concentration of the rare earths, and increases with greater dilutions (3). It seems advisable, therefore, to use a feed concentration as high as conveniently attainable so that a high wash rate descending the column would serve to dilute the feed to the optimum concentration as well as to render the scrubbing section more efficient. Although thorium nitrate, completely free from the rare earths, was not obtained in the present study, it has been shown that the thorium can be transferred to a solvent phase free of phosphate, producing a system which has been shown by previous investigators to be amenable to separation by solvent extraction (3).

Thus the data presented to this point represents the ground work for a process by which pure thorium compounds may be produced from monazite sand. The proposed process would consist essentially of the following steps:

1. The monazite sand is digested with sulfuric acid at an acid to sand ratio of 2.5 to 1.0, and at a temperature of 200°C.
2. The digested mass is dissolved in water in the proportion of about one liter to every 50 grams of sand. Some physical separation step such as settling or filtering may be employed here to remove insoluble silica, rutile, and other impurities. This

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Table 9

Distribution of Metals in
Simulated Column Number One

	<u>100xThO₂ in sample divided by ThO₂ in feed</u>	<u>100xREO in sample divided by REO in feed</u>	<u>% ThO₂ in total oxides</u>	<u>100xU in sample divided by U in feed</u>
Feed	-	-	13.32	-
Solvent from plate 1	100.0	11.7	56.9	100.0
Solvent from plate 2	0.65	11.7	0.85	-
Solvent from plate 3	0	4.1	0	-
Exit aqueous	0	87.9	0	0

Volume ratio of solvent to feed = 1:1

Analysis of feed solution:

Total oxides	1.394 g./100 ml.	Fe ₂ O ₃	0.470 g./100 ml.
REO	1.208 g./100 ml.	P ₂ O ₅	0.498 g./100 ml.
ThO ₂	0.186 g./100 ml.	SO ₄	0.06 g./100 ml.
U ₃ O ₈	0.012 g./100 ml.	Acidity	3 Normal HNO ₃

Solvent: Tributyl phosphate brought to equilibrium with three normal nitric acid.

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Table 10
Distribution of Metals in
Simulated Column Number Two

	<u>100xThO₂ in sample divided by ThO₂ in feed</u>	<u>100xREO in sample divided by REO in feed</u>	<u>% ThO₂ in total oxides</u>
Solvent from plate 1	100.0	0.9	93.6
Solvent from plate 2	101.0	4.9	73.5
Feed	-	-	11.72
Solvent from plate 3	107.8	8.8	61.90
Solvent from plate 4	9.6	16.8	7.03
Solvent from plate 5	0	16.2	0
Exit aqueous	0	99.2	0

Ratio of wash to feed = 1:1

Ratio of solvent to feed = 2:1

. Feed solution analysis:

Total oxides	3.616 g./100 ml.
REO	3.192 g./100 ml.
ThO ₂	0.424 g./100 ml.
P ₂ O ₅	1.292 g./100 ml.
SO ₄	0.18 g./100 ml.
Acidity	7.4 Normal HNO ₃

Wash solution: 3 normal HNO₃.

Solvent: Tributyl phosphate brought to equilibrium 3 normal HNO₃.

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produces the solution referred to in this thesis as the sulfuric acid-monazite solution.

3. This solution is further diluted by four or five volumes to one and partially neutralized with a base such as ammonia, sodium hydroxide, or soda ash, to precipitate the thorium and heavy metals as phosphates. The feasibility of making a selective precipitation at this point so as to leave the bulk of the rare earths in solution is now being investigated in other studies.
4. This precipitate is washed and filtered to produce a bulky, gelatinous mass of high moisture content, but containing only a small fraction of the sulfate ion originally present. The filtrate is passed through ion exchange resins for uranium recovery and is discarded.
5. This mass is dissolved in concentrated nitric acid, possibly with the aid of ferric nitrate, so as to produce a solution about 4 normal in nitric acid, and containing all of the thorium in a concentration of about 7 grams per liter.
6. This solution is fed to a system of solvent extraction columns in which the thorium nitrate is stripped into a solvent phase and washed free of rare earths and impurities. Subsequent solvent extraction steps follow to separate the thorium from the uranium (which is less easily removed from the solvent than thorium), and to transfer the thorium nitrate back to an aqueous phase.
7. The bulk of the nitric acid in every exit aqueous stream is recovered by evaporation operations. The nitric acid in the solvent is recycled with the solvent.
8. The thorium nitrate is either crystallized from the solution, or precipitated as the hydroxide or oxalate for further processing.

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CONCLUSIONS AND RECOMMENDATIONS

The following conclusions are made from the research described in this thesis:

1. Of the solvents tried, which represent practically all types of solvents available commercially, there was none capable of extracting thorium from a sulfuric acid-monazite solution.
2. It is not practical to increase the extractability of the sulfuric acid-monazite solution by the addition of lime and nitric acid to precipitate the sulfate ion as calcium sulfate, because the losses of thorium to the precipitate are prohibitive at the proper conditions to remove sufficient sulfate.
3. A solution from which thorium can be selectively extracted by tributyl phosphate can be prepared from a sulfuric acid-monazite solution by neutralizing it, filtering the precipitated heavy metal phosphates, and dissolving this precipitate in nitric acid. (This is the solution referred to as a nitric acid-phosphate solution).
4. The addition of ferric nitrate aids the dissolution of the phosphates of the rare earths and thorium in nitric acid, and increases the stability of the nitric acid-phosphate solution produced. Ferric nitrate in concentrations of about 0.4 molar markedly increases the extractability of the solution.
5. Calcium nitrate in concentrations up to 0.5 molar does not improve the extraction of thorium from a nitric acid-phosphate solution.
6. The presence of sulfate in a nitric acid-phosphate solution tends to decrease the amount of thorium extraction, but increases the selectivity. Sulfate in concentrations greater than 0.3 molar decreases the extraction a definitely undesirable degree.
7. The result of increasing the acidity of the nitric acid-phosphate solution of thorium and rare earths is to decrease slightly the extractability and to increase slightly the selectivity of extraction toward thorium.

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8. Solvent extraction techniques can be used to strip all of the thorium and uranium, as the nitrates, from a nitric acid-phosphate solution into a tributyl phosphate phase.
9. A process for the production of pure thorium compounds from monazite sand involving: digesting the sand with sulfuric acid; dissolving the digested mass in water; precipitating, by neutralization, the heavy metals from this solution as phosphates; filtering, washing, and redissolving this precipitate in nitric acid; and separating pure thorium nitrate from this solution by solvent extraction, is fundamentally feasible.

It is recommended that: first, a more thorough study be made on the preparation of the nitric acid-phosphate solution, and second, a continuous liquid-liquid extraction unit be built on a small pilot plant scale for the study of the actual production of pure thorium nitrate.

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