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January 30, 2002

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Ms. Jill Caverly
Fuel Cycle Licensing Branch
Uranium Recovery Section
U.S. Nuclear Regulatory Commission
11545 Rockville Pike
Two White Flint North, Mail Stop T7 J9
Rockville, MD

Subject: **Classification of Byproduct Material from Iowa State University**
License No.: SUA-1473 Docket No.: 40-8905
Ambrosia Lake Facility

Dear Ms. Caverly:

As a follow-up to our previous discussions regarding the classification of byproduct material to be disposed at Rio Algom's Ambrosia Lake Facility in accordance with license condition 41, additional research has been conducted to determine the history of the material from Iowa State University (ISU). Previously I had presented you with a copy of a report to the United States Department of Energy from Iowa State University entitled, "Fire Service Institute Thorium Remediation Project", dated February, 2000. Additionally, a copy of a letter from Jessie H. Roberson, Assistant Secretary for Environmental Management, Department of Energy, dated October 12, 2001 was also provided. That letter documented that DOE would not object to the disposal of the materials from Iowa State University into the Ambrosia Lake tailings impoundment.

As we discussed previously, there is a question as to how the ISU material should be classified, and there is some uncertainty as to the applicable laws that should be considered for approval of disposal of the material at Ambrosia Lake by NRC. Additional research, by Mr. Ken Kerns of ISU, has identified several documents in the ISU Library archives which indicate clearly that part of the process employed at the Ames Campus for the Manhattan Project involved the extraction of thorium from monazite sands (ore). In our view, the processing of monazite sands for the recovery of thorium establishes the residual materials as Section 11e.(2) under the Atomic Energy Act of 1954, as amended.

Supporting documents attached include excerpts from six (6) documents found in the Iowa Sate University library.

- 1949, Solvent Extraction of Thorium and Rare Earths From Aqueous Solution of Monazite Sand Decomposed with Sulphuric Acid, Max L. Feldman, Iowa State College, discusses a study conducted at Iowa State College to extract either the thorium or all the metallic salts from an aqueous solution of monazite sand decomposed with sulfuric acid. The monazite sand used in the research originated from Travancore, India, and it was supplied by the US Atomic Energy Commission.

NMSS01 Public

- 1949, Effect of a Number of Variables on the Decomposition of Monazite Sand with Sulfuric Acid, Theodore William, Blickwedel, Iowa State College, discusses a study conducted at Iowa State College to extract thorium from monazite sand. The sand came from India through the Maywood Chemical Company, Maywood, New Jersey in conjunction with the US Atomic Energy Commission.
- 1953, A Process for Separating Thorium Compounds From Monazite Sands, Kernal Glenn Shaw, Iowa State College, discusses various methods to digest monazite sands to remove the thorium. The sands studied were from Brazil, Idaho and Travecore, India. The purpose was to test the "Ames Process" versus the "Battelle Process" to remove thorium.
- 1955, Thorium and Uranium From Monazite, Martin Allan Welt, Iowa State College, purpose of study was to attempt to develop a third process to eliminate the shortcomings of the "Ames Process" and the "Battelle Process".
- 1956, The Metal Thorium, Harley A. Wilhelm, American Society for Metals, discusses the process developed at the Ames Laboratory for separating thorium form monazite sands, commonly called the "Ames monazite process".
- Unknown, Thorium Production Technology, F.L. Cuthbert, National Lead Company of Ohio, discusses the development of a sulfuric acid digestion process to recover thorium from monazite sands for application in the atomic energy program at Ames Laboratory.

Both Rio Algom and Iowa State University are most anxious to get moving on the disposal of the roughly 2,500 cubic feet of soil and debris removed during ISU's final clean-up of this site. Rio Algom believes that this material is consistent with the definition of 11e.(2) byproduct material because it was associated with an AEC licensed facility and was the direct result of the extraction of source material from ore. However, before acceptance of this material is initiated under license condition 41, Rio Algom must have NRC concurrence with the classification of this material as 11e.(2) byproduct material. If there are any additional questions or concerns, please call me at (405) 858-4807.

Sincerely,

William Paul

William Paul Goranson, P.E.
Manager, Radiation Safety, Regulatory
Compliance and Licensing

Enclosures

CC: Marvin Freeman, Rio Algom

THE METAL THORIUM

Proceedings of the Conference on Thorium
Held October 11, 1956
at
Cleveland, Ohio
under the joint sponsorship of
U.S. ATOMIC ENERGY COMMISSION
and
AMERICAN SOCIETY FOR METALS

Technical Editor
HARLEY A. WILHELM

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Cleveland, Ohio

oxalate from the double-sulfate filtrate was approximately $0.70 per lb of product containing 50% thoria. The cost was based on an operation producing 200 lb of hydroxides and 25 lb of crude thorium oxalate (33% ThO_2) per week.

In 1952–1953, the Ames Laboratory developed a process for separating thorium from monazite sands, commonly called the Ames monazite process:[7, 8]

1. A pure monazite concentrate is digested with 93% sulfuric acid for 4 hr at about 210° C. The average fineness of the sand was 200-mesh. The weight ratio of acid to digested sand was 1.56.
2. Each pound of the digested mass is dissolved in 10 lb of cold water. The undigested sand is removed from the solution by settling.
3. The monazite sulfate solution is partially neutralized to pH 1.05 to precipitate the thorium as the phosphate. An equal weight of rare earths is occluded with the thorium phosphate precipitate.
4. The solution containing rare earths and uranium is filtered from the thorium phosphate and partially neutralized to pH 2.3. At this pH the rare earths are precipitated as the sulfates; not all of the rare earths are recovered.
5. The rare-earth sulfates are separated from the solution by filtration, and the filtrate is treated to recover the remaining rare earths and the uranium. The filtrate is neutralized to pH 6.0 to precipitate the uranium and the rare earths. The uranium concentrate is removed from the clear solution by filtration.
6. The thorium concentrate is dissolved in strong nitric acid and fed to a multistage extractor in which the thorium is separated from the rare earths.
7. Prior to extraction the rare earth concentrate is digested with caustic to remove the sulfate and phosphate ions. The individual rare earths and any accompanying uranium are then separated by solvent extraction.
8. The uranium concentrate is dissolved in nitric acid. The uranium is extracted from the rare earths in a multistage extractor using tributyl phosphate as the solvent.[9]

The Ames monazite process has a number of disadvantages which are the number of costly filtration steps, the occurrence of the rare earths in all of the concentrates, and the appearance of uranium

1-2 end

THORIUM PRODUCTION TECHNOLOGY

by

F. L. CUTHBERT
*National Lead Company
of Ohio*

PREPARED UNDER CONTRACT WITH THE
UNITED STATES ATOMIC ENERGY COMMISSION

ADDISON-WESLEY PUBLISHING COMPANY, INC.
READING, MASSACHUSETTS, U.S.A.

2-1

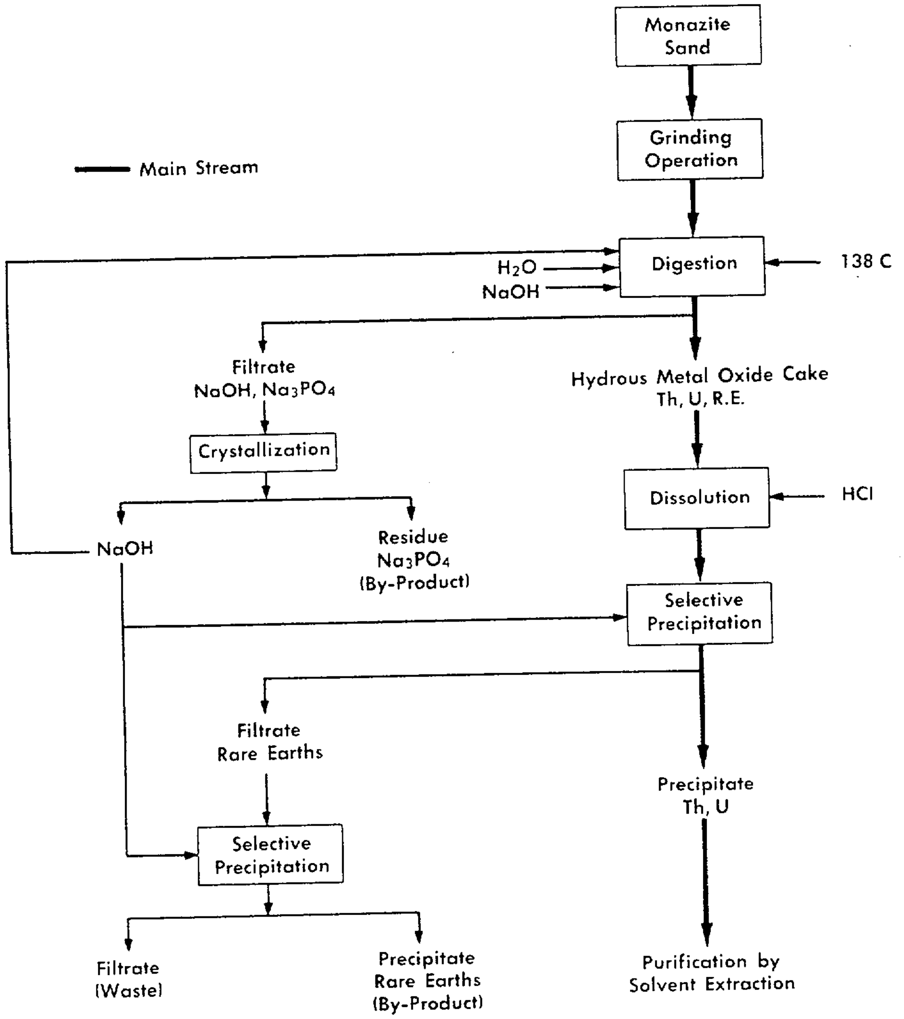

FIG. 4–2. Simplified schematic diagram of caustic soda digestion of monazite sand and recovery of thorium, uranium and the rare earths. (4)

furic acid digestion process and Fig. 4–2 is a schematic process flow diagram for the hot, concentrated caustic soda digestion process.

The sulfuric acid digestion process was developed for application in the atomic energy program at Ames Laboratory, Iowa State College,(2,3) and the caustic soda digestion process was developed by Battelle Memorial Institute.(4,5) Further details on these processes and other methods of digesting monazite sands are discussed by Levy,(6) Andsley, Lind and England,(7) Spencer,(8) Pilkington and Wylie,(9) and Urie.(10)

II. SULFURIC ACID EXTRACTION PROCESS

4–1 Digestion. The reaction between monazite sand and a mineral acid may be regarded as erosion or corrosion proceeding at a rate that depends upon the mineral acid used, the temperature and concentration of

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the acid, and the surface characteristics of the sand particles. When sulfuric acid is used, the fact that the insoluble products of the digestion coat the surface of the monazite sand particles must be considered. The rate of reaction then depends not only on the rate of erosion, but also on the resistance the insoluble coating offers to the acid. This resistance can be reduced by increasing agitation and maintaining the fluidity of the reaction mass.

When monazite sand is first added to the hot sulfuric acid, reaction proceeds rapidly. As the reaction continues, the rate-controlling mechanism gradually changes from one of erosion to one of mass transfer. As the coating thickens, reaction rate decreases; when sufficient solid reaction products have formed, the reaction mixture virtually solidifies. From this point on, reaction proceeds very slowly as the sulfuric acid diffuses through the solid but porous mass. During the first 15 min of digestion, the mixture changes from a pumpable fluid to a kneadable doughlike material and finally, after an additional 15 to 30 min, to a gray solid. The reaction mass contains about 60 percent free acid and occupies a volume about one and one-half times the original volume of acid and sand.

The sands are digested by treatment with an excess amount of concentrated (93 percent) or fuming H_2SO_4 for 5 hr at 155 to 230 C. The objective is to make all constituents (with the exception of silica, zircon, and rutile) water soluble. The gangue, together with any undigested sands, can then be easily removed by dilution and filtration.(3,11,12) The reaction for opening the rare earth (RE) mineral is said to be:

$$\begin{aligned}
2\mathrm{RE(PO_4)} + 3\mathrm{H_2SO_4} &\rightarrow \mathrm{RE_2(SO_4)_3} + 2\mathrm{H_3PO_4}\\
\mathrm{ThSiO_4} + 2\mathrm{H_2SO_4} &\rightarrow \mathrm{Th(SO_4)_2} + \mathrm{SiO_2} + 2\mathrm{H_2O}\\
\mathrm{Th_3(PO_4)_4} + 6\mathrm{H_2SO_4} &\rightarrow 3\mathrm{Th(SO_4)_2} + 4\mathrm{H_3PO_4}\\
\mathrm{SiO_2\cdot xH_2O} + \mathrm{H_2SO_4} &\rightarrow \mathrm{SiO_2} + \mathrm{H_2SO_4\cdot xH_2O}
\end{aligned}$$

Both the speed and completeness of this reaction depend upon the particle size of the monazite sands, the initial temperature at which the ingredients are mixed, the acid-to-sand ratio, the concentration of the acid and the digestion time. The effect of each will be considered.

Particle size. Particles of monazite sands from different sources vary in size, but usually must be reduced if the sand is to be dissolved within a reasonable time. Reducing particle size to as small a value as possible may permit decreases in acid-to-sand ratio and acid concentration, or increases in capacity resulting from shorter reaction time.

Effect of temperature. Conversion of the rare earth and thorium phosphates in monazite sands to the corresponding sulfates is highly exothermic. Figure 4–3 data was obtained from a study of the effect of nominal

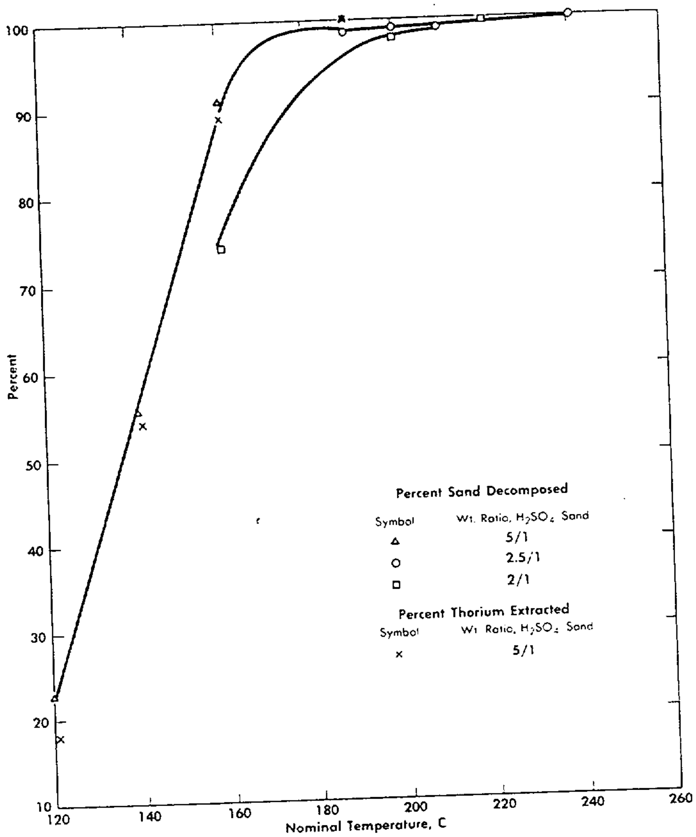

FIG. 4–3. Effect of temperature on decomposition of monazite sand by sulfuric acid; acid concentration, 95 percent; digestion period, 2 hr. The bath temperatures were held within 2 C of the nominal temperatures for the entire digestion period. The temperature of reaction rose considerably higher than the bath temperature in many cases.(2)

temperature upon the amount of sand decomposed within a fixed period.(2) (Nominal temperature is the temperature at which the acid and sand were initially mixed.) In many cases, reaction mixture temperature rose considerably higher than nominal temperature. No data giving a value for this heat of reaction are available, nor are there data on the heat of formation of the products (from which the heat of reaction could be calculated). It is apparent that fairly complete decomposition was obtained at 190 to 240 C for a weight ratio of 2.5 to 1 of 95 percent H_2SO_4 to sand, and at 220 C for a weight ratio of 2 to 1.

After monazite sand is dissolved, an insoluble suspended material is sometimes found in the solution of decomposed sand in addition to undigested monazite residue. Experiments(2) indicate that an insoluble compound of thorium, probably thorium pyrophosphate, is formed when the temperature of the digestion is 300 C or more. Therefore, it is desirable to keep the temperature well below 300 C to obtain complete dissolution of thorium and the other valuable elements. If substantial amounts of

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thorium pyrophosphate are formed, a hot, strong solution of an alkali metal carbonate (such as sodium carbonate) selectively converts the thorium compound to soluble thorium carbonate. Then, when the slurry is filtered, the thorium carbonate and the trisodium phosphate are dissolved in the filtrate. After this, the thorium can be precipitated as the hydroxide, washed and further purified.

Dissolution does not proceed at a satisfactory rate at temperatures substantially lower than 200 C. For example, as-received monazite sand digested for 22 hr at 25 C and 60 C shows only 0.1 percent and 29 percent digestion, respectively. At 100 and 140 C, 75 percent digestion requires 100 and 62 hr, respectively. However, 92 percent dissolution is obtained in 3 hr when the ground sands are added to 93 percent sulfuric acid at 160 C and the reaction is allowed to proceed adiabatically at 230 C. High temperatures not only increase the rate of decomposition of monazite by sulfuric acid but also decrease the acidification needed. Thus, the temperature should be as high as possible without causing thorium pyrophosphate to form. A temperature of 155 to 230 C is recommended.

Acid-to-sand ratio. The minimum ratio of acid-to-digested-sand weight, based on the stoichiometry of the reaction, is about 0.60 to 1 (basis:

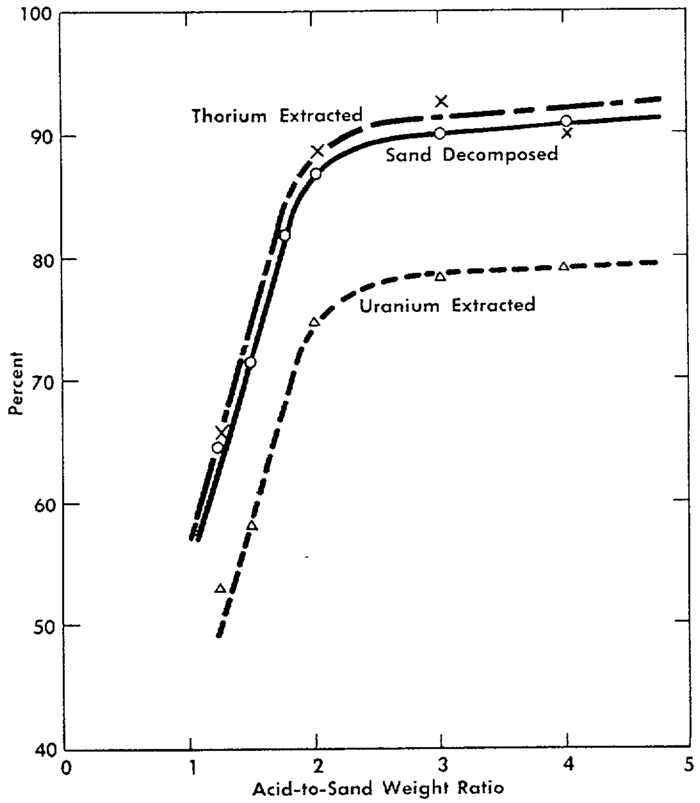

FIG. 4-4. Effect of acid-to-sand weight ratio in digestion of monazite sand by concentrated sulfuric acid; 30-min heating period at 200 C.(14)

2-5

100 percent H_2SO_4). In practice, however, the ratio is limited by the solubility of the thorium phosphate in the resulting monazite sulfate solution. The precipitate when sulfuric acid reacts with the nonsoluble components is voluminous, often causing the solution to gel. Thus, more acid than the stoichiometric amount is necessary. Ames Laboratory(3) has found the optimum ratio of acid to digested sand to be 1.6 to 1. Since not all of the sand is digested, the ratio is actually about two parts of acid (basis: 100 percent H_2SO_4) to one part of monazite sand from Indian and Idaho deposits.(13)

The effect of the acid-to-sand ratio upon the completeness of dissolution was studied at Battelle Memorial Institute.(14) The results of laboratory experiments done at Battelle are presented in Figs. 4–4 and 4–5. Figure 4–4 indicates the percent of the sand dissolved after $\frac{1}{2}$ hr of reaction at various acid-to-sand ratios; Fig. 4–5 indicates the percent dissolved after 3 hr of reaction at various acid-to-sand ratios. Recovery of thorium and uranium from the monazite sulfate solution is also indicated. All curves have the same general form. For a short reaction time, an acid-to-sand ratio of 3 to 1 is desirable, but even at that ratio the total percent recovery is lower than achieved when the reaction is allowed to continue for 3 hr. At the longer time, an acid-to-sand ratio of 2 to 1 is sufficient. It may, therefore, be preferable to let the reaction continue for the longer period of time. The rise in cost caused by reduced capacity because of the longer reaction time may be more than compensated by the lower cost of a lower acid-to-sand ratio. The results obtained when the ratio is varied (Figs. 4–4 and 4–5) agree closely with results obtained in experiments at Ames Laboratory.

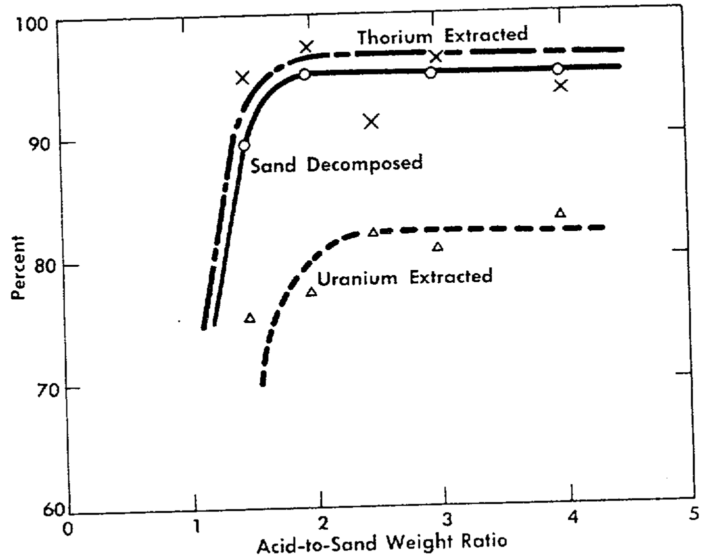

FIG. 4–5. Effect of acid-to-sand weight ratio in the digestion of monazite sand by concentrated sulfuric acid; 3-hr heating period at 200 C.(14)

TABLE 4-1

EFFECT OF ACID CONCENTRATION ON THE DECOMPOSITION OF MONAZITE WITH SULFURIC ACID AND THE EXTRACTION OF THORIUM(2)

Digestion period = 2 hr

Acid concentration, %	Nominal temperature, C	Acid-to-sand weight ratio	Sand decomposed, %	Thorium extracted, %
55	160	5:1	32.2	36.9
65	160	5:1	46.9	44.8
75	160	5:1	55.7	60.3
85	160	5:1	73.6	74.8
90	160	5:1	87.7	90.0
93	160	5:1	95.1	91.8
95	160	5:1	91.9	88.4
98	160	5:1	77.8	77.6
90	200	2.5:1	99.2	
93	200	2.5:1	99.4	
95	200	2.5:1	99.6	
98	200	2.5:1	99.3	

Note that the percentage of thorium extracted nearly equals the percentage of sand dissolved. This may indicate that the thorium is closely bound in the monazite crystal structure and is not present as a separate entity.(15,16) If this is true, selective dissolution of the thorium probably cannot be obtained with any reagent under any conditions.

Monazite sands can be almost completely dissolved, as indicated in Table 4-1. The monazite sand digested in these experiments contained about 5 percent acid-insoluble, thorium-free contaminants, which would not affect the recovery of thorium.

The more the reaction temperature is decreased, the larger the acid-to-sand ratio must be for effective dissolution and the more the solution must be diluted. Selection of a suitable digestion ratio depends, therefore, upon many factors: temperature, degree of dilution at which the solution will be used, particle size, and desired reaction time. Excessive quantities of free acid interfere with fractional precipitation of thorium at a later step, and excess sulfate ion interferes with the later solvent extraction step. Therefore, to keep thorium recovery and purity as high as possible, the monazite sulfate solution should be prepared so that it is stable, containing only enough free sulfuric acid to keep the thorium pyrophosphate from

2-8 end

DECOMPOSITION OF MONAZITE

Effect of a Number of Variables on the Decomposition of Monazite Sand with Sulfuric Acid

by

Theodore William Blickwedel

A Thesis Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
MASTER OF SCIENCE

Major Subject: Chemical Engineering

Approved:

G. L. Bridger
In Charge of Major Work

G. L. Bridger
Head of Major Department

R M Hixon
Dean of Graduate College

Iowa State College

1949

3-1

SUMMARY

The need for a more economical method of producing thorium for use in the program of the Atomic Energy Commission has led to an extensive study of the sources, properties, and chemistry of this element. The only commercial source is the mineral monazite in the form of alluvial sands.

Monazite is widely scattered over the earth. The deposits include sands of other heavy minerals and quartz. Most of these contaminants are removed by beneficiation processes before the monazite is utilized. The better deposits of monazite sand from the standpoint of thorium content are found in Brazil and India. Of the two, the Indian sands excel.

Commercially the monazite sand is "opened" by treatment with concentrated sulfuric acid or oleum. Other methods of decomposition have been proposed such as caustic digestion and nitric acid extraction, chlorination and water extraction, reduction with alkaline earth carbonates, and treatment with perchloric acid. The perchloric acid treatment was of special interest because the time reported for the digestion was about one-fourth that required with sulfuric acid and ceric phosphate precipitated out during the digestion.

Studies were made on Indian monazite sand of the amount of perchloric acid needed for the digestion, and it was found that an acid/sand ratio (basis 100% $HClO_4$) of about 3.5/1 was required. For purposes of getting a soluble thorium product,

3-2

a ratio of sulfuric acid/sand (basis 100% H_2SO_4) of 2/1 had been reported. Since the cost of perchloric acid is much greater than sulfuric acid, it was concluded that the perchloric acid decomposition is not economically feasible at current conditions.

Attention was turned toward the decomposition of monazite with sulfuric acid. Studies were made on the effect of temperature, acid/sand ratio (acidulation), acid concentration, and digestion time on the process. It was found that complete decomposition could be secured with ratios of H_2SO_4/sand as low as 2.5/1, 95% acid, and 200°C. It was also found that an insoluble compound of thorium begins to form at digestion temperatures over 215°C.

✓Of particular interest was the discovery that an acid concentration of 93% gives optimum decomposition under a given set of conditions.

For the purpose of decomposing monazite to secure a solution from which thorium can be extracted, it is recommended that 93% sulfuric acid be used with a weight ratio of H_2SO_4/sand of 2.5/1 at 200°C. If the solution is to be heated or greatly diluted (as may prove necessary in liquid-liquid extraction), a higher ratio with subsequent excess acid will be necessary to prevent formation of a thorium precipitate. Precipitation can be prevented by the addition of sulfuric acid to the solution after the digestion and before dilution or heating.

EXPERIMENTAL

Materials and Apparatus

The monazite sand used in this investigation was secured by the Ames Laboratory of the Atomic Energy Commission from the Maywood Chemical Company, Maywood, New Jersey. The origin of the sand* was Travancore, India. Three samples of the sand were tested on a set of Tyler standard screens, and gave an average screen analysis as follows:

Retained on	65 mesh	4%
Retained on	100 mesh	17%
Retained on	140 mesh	61%
Passed through	140 mesh	18%
		100%

The Analytical Section, Ames Laboratory, Atomic Energy Commission, analyzed the sand and presented the following figures:

Thorium expressed as ThO_2	7.5 ± 2%
Total thoria (ThO_2) and rare earth oxides	68.0 ± 1%
Cerium expressed as CeO_2	28.5 ± 1%
Phosphorus expressed as P_2O_5	25.9 ± 0.5%
Silicon expressed as SiO_2	7.0 ± 2%

The values for the amount of thorium present are useless as far as the present research is concerned; therefore, a separate analysis was made to determine the thorium content of the sand using the analytical procedure of Carney and Campbell (7) as described later. A value of 8.61 ± 0.15% (reported as ThO_2) was

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*In this thesis the monazite sand may frequently be referred to merely as the "sand".

3-4 end

SOLVENT EXTRACTION OF AQUEOUS SOLUTIONS OF RARE EARTHS

138

Solvent Extraction of Thorium and Rare Earths From Aqueous Solution of Monazite Sand Decomposed with Sulphuric Acid

By

Max L. Feldman

A Thesis Submitted to the Graduate Faculty
for the Degree of

MASTER OF SCIENCE

Major Subject: Chemical Engineering

Approved:

G. L. Bridger
In Charge of Major Work

G. L. Bridger
Head of Major Department

R. M. Hixon
Dean of Graduate College

Iowa State College

1949

4-1

SUMMARY

The object of this research was to remove by solvent extraction either the thorium or all the metallic salts from an aqueous solution of monazite sand decomposed with sulphuric acid. Considerable work has been done on the solvent extraction of thorium nitrate from a nitric acid solution, but no attempts to extract the salts resulting from a sulphuric acid decomposition of monazite have been reported in the literature.

A study was made of the stability of solutions of monazite sand decomposed with varying ratios of sulphuric acid to sand in order to determine the effects of temperature, dilution, and heating after dilution on these solutions. A synthetic solution to correspond to a solution of monazite decomposed with a ratio of acid to sand that gives a stable solution was prepared. Cerium was used in this solution to represent all the rare earths. The synthetic solution was then extracted with a series of solvents as part of a solvent search.

Following the solvent search, a set of extractions were made using a solution of decomposed monazite sand and nitromethane. This was followed by another set of extractions wherein the monazite sand solution was extracted with mixtures of n-butyl alcohol and dioxane, n-butyl alcohol and 95% ethyl alcohol, and n-butyl alcohol and ethylene glycol monomethyl ether.

It was concluded that no one of the solvents tried would extract. It was also concluded that the mixtures of n-butyl alcohol with dioxane, 95% ethyl alcohol, and ethylene glycol monomethyl ether would extract the metal salts, but that they were impractical solvents because repeated extractions caused the formation of a precipitate in the raffinate layer. Finally, it was concluded that the thorium could not be extracted selectively with the butyl alcohol mixtures nor could it be selectively stripped with water from the extract layers of the butyl alcohol extractions.

mixed with ethyl alcohol, dioxane, and ethylene glycol monomethyl ether as complexing agents.

Materials

Solvent search

The monazite sand used in this research came from Travancore, India. It was supplied by the United States Atomic Energy Commission. An analysis of the sand made by the Analytical Section, Ames Laboratory, Atomic Energy Commission, shows the following constituents present in the sand in the amounts indicated:

Thorium as ThO_2	7.5% ± 2%
Total Oxides (ThO_2, CeO_2, R_2O_3)	68.0% ± 1%
Cerium as CeO_2	28.5% ± 1%
Phosphorus as P_2O_5	25.9% ±0.5%
Silicon as SiO_2	7.0% ± 2%

Inasmuch as a solution from the decomposition of monazite sand with sulphuric acid was to be extracted, it was felt that the proper conditions for the production of a stable solution should be determined. The effects of temperature, dilution with water, and heating after dilution were studied on a series of solutions obtained by dissolving in water monazite sands decomposed with varying weight ratios of sulphuric acid to sand. Samples of 12.5 grams of monazite sand were digested at a temperature between 180°C and 200°C using weight ratios of sulphuric acid (basis: 100% acid) to sand of 3.5, 4.2, 4.9, 5.6, 7.0, 8.4, and 9.8. The samples were digested for four hours,

4-4 end

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

Approved:

Morton Smutz
G. L. Bridger
In Charge of Major Work

G. L. Bridger
Head of Major Department

R M Hixon
Dean of Graduate College

Iowa State College

1953

SUMMARY

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.

S-3

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

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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.

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THORIUM AND URANIUM FROM MONAZITE

by

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SUMMARY

Monazite sands have been processed for thorium, uranium and rare earths for more than a half century. Two new processes have been developed as a result of work done for the Atomic Energy Commission by the Battelle Memorial Institute and the Ames Laboratory. The purpose of this investigation was to develop another process that would overcome some of the disadvantages of these processes.

A process was developed that appears economically feasible. The first step in the process is a sulfuric acid digestion of the sands. The digested sands are dissolved in water and decanted from undigested sand and insoluble silica. Oxalic acid is added to the resulting solution to precipitate the thorium and rare earths, leaving the uranium in solution. The thorium, uranium and rare earths are then purified by solvent extraction procedures. The advantages of the process are that the thorium and uranium are separated virtually quantitatively in an early step and only one filtration step is necessary. The only disadvantage is the added cost of oxalic acid.

A cost comparison was made between the Ames Laboratory monazite process and the proposed oxalation process for a plant producing five tons of thorium per month. The cost comparison included only those steps in either process that

are required for the production of the thorium, uranium and rare earths in a form that they may easily be purified by solvent extraction. The estimated processing cost for the oxalation process was found to be $11.02 per pound of thorium, as compared with $11.06 for the Ames monazite process. The cost figures quoted do not assume any credit for the large quantities of rare earths produced and assume that Idaho sands serve as the starting material. The production cost for the oxalation process was based solely on laboratory scale investigation. The cost figure obtained does indicate the need for further investigation.

The investigation also included some work on alternative methods of purifying the uranium and thorium obtained after the oxalation step. It was demonstrated that the uranium could be recovered completely from the sulfate-phosphate liquor by using a solution of 10 per cent octyl pyrophosphoric acid in kerosene as the solvent. Additional studies revealed that the uranium could be precipitated from the solvent as the tetrafluoride with 48 per cent hydrofluoric acid.

An alternate process for separating thorium from the thorium-rare earth mixture was developed. The cerium was oxidized to the ceric state and was extracted with the thorium. The thorium purification work was coupled with the extraction of over 90 per cent of the cerium along with the

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thorium into undiluted tributyl phosphate. The high extraction of cerium is obtained by calcining the oxalates prior to preparing the rare earth-thorium feed solution. Upon nitration the cerium present in the calcines is converted to basic ceric nitrate which is readily extracted by tributyl phosphate. The advantage in this is that the largest rare earth component is separated, for the most part, from the remaining rare earths, thereby allowing the other rare earths to be separated from one another more easily. The disadvantage is that the thorium must now be separated from the ceric cerium. It was demonstrated that this disadvantage could be overcome by selectively stripping the ceric cerium away from the thorium with a 0.1 molar aqueous solution of sodium nitrite, or that both components could be stripped from the tributyl phosphate with a sodium nitrite-sulfuric acid stripping system, followed by a mesityl oxide thorium extraction for final purity.

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INTRODUCTION

Since thorium can be transmuted into fissionable U^{233} (29), the Atomic Energy Commission is interested in developing processes for large scale production of high purity thorium. It is essential that the thorium be separated as completely as possible from uranium and from contaminants of high neutron capture cross section, such as some of the rare earths.

Monazite sands are the major commercial source of thorium although the thorium content is usually less than 10 per cent, expressed as the oxide. Domestic sources of monazite rarely exceed four per cent, expressed as thorium oxide (40). Both thorite and orangite have much higher thorium concentration, but no commercial deposits are known (43). The major constituents of monazite are the rare earth orthophosphates. For many years monazite sands were processed to recover the rare earths, and the thorium was recovered as a by-product. Monazite sands also contain a small amount of uranium that can be recovered as a by-product.

Research workers at the Battelle Memorial Institute developed and demonstrated a successful monazite process employing a caustic digestion as the first step in the process (17). Previous workers at the Ames Laboratory developed and demonstrated a successful process starting

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with the more common sulfuric acid digestion (50,52). Cost estimates indicate that the two processes are economically competitive (51).

The purpose of this investigation was to continue the study of monazite processing in the hope that improvements to existing processes or new processing methods could be found which would reduce processing costs. If a promising method were found, sufficient laboratory work was to be carried out to permit a cost estimate to be made to determine whether or not the new method warranted more extensive investigation on a large scale.

PREVIOUS WORK

Monazite sands have been processed industrially for more than a half a century. An extensive review of the existing monazite processes appearing in the U. S. patent literature was prepared by Bearse (10). The sulfuric acid method of "opening" the sand was the usual starting point for the monazite processes. The monazite sands (26,39) were reacted with from two to two and a half times their weight of concentrated or fuming sulfuric acid at about 200°C. The digested mass was dissolved in water for further processing. A number of processes called for a higher digestion temperature in order to form a water insoluble thorium compound that could be recovered with the silica and undigested sands (12,42). Arden (3) substituted strong sulfuric acid for dissolving the digested mass, in order to free the thorium and rare earth sulfates from phosphoric acid. Slowter and Willigman (61) prepared an excellent literature survey on the recovery of thorium from sulfuric acid digested monazite. Other acid digestion processes described in the literature refer to the use of nitric acid (11), perchloric acid (13), and hydrofluoric acid (48), although none of these methods seem to have any commercial significance at this time. Other methods of attacking the sands include chlorination with a reducing agent and

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potassium chloride (1), fusions with coke, lime and feldspar (9), and fusions with sodium peroxide (18).

Prior to the Atomic Energy Commission's interest in monazite, the commercial procedure for preparing pure compounds from monazite involved the use of tedious and costly repeated fractional crystallization steps.

Occurrence and Composition of Monazite

Monazite sand deposits are formed by the action of winds and tides on monazite particles washed down to the sea from placer deposits. Monazite is also found in many pegmatized gneisses where weathering effects have served to concentrate them (39). The sand itself varies from a brown to a honey yellow color, has a specific gravity of from 4.5 to 5.5 and a Mohr hardness of from 5.0 to 5.5. The sands are also slightly paramagnetic.

The principal deposits are found in Travancore, India, and Espirito Santo, Brazil. Lesser deposits of commercial interest are known to exist in Idaho, Florida, Canada, Union of South Africa, Ceylon and Spain (55). A recent survey states that large quantities of monazite sand will be supplied in the near future by Wyoming and South Africa (41). Due to an embargo placed on Indian and Brazilian monazite, the domestic sands have become of increased importance. Table 1 contains a typical analysis of the Indian, Brazilian, and domestic monazite sands.

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Table 1

Composition of Monazite Sands[a]

Constituent	Brazilian %	Indian %	Domestic[b] %
ThO_2	6.5	9.8	3.1
U_3O_8	0.17	0.29	0.47
$(RE)_2O_3$	59.2[c]	58.6[c]	40.7[c]
Ce_2O_3	26.8	27.2	-
P_2O_5	26.0	30.1	19.3
Fe_2O_3	0.51	0.80	4.47
TiO_2	1.75	0.40	-
SiO_2	2.2	1.7	8.3

[a] Table reproduced from Chemical Engineering Progress, 50, May 1954, p. 325.

[b] Florida sand containing about 70 per cent monazite.

[c] Includes Ce_2O_3.

Battelle Monazite Process

Shortly after World War II workers at the Battelle Memorial Institute developed a process for recovering thorium and uranium from monazite. A general description of the Battelle process is given below followed by a brief discussion of the advantages and disadvantages of the process.

1. Ground monazite sand is reacted with 73 per cent sodium hydroxide solution at 300°F for three hours

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to convert the metal phosphates of the sand to hydrous metal oxides and by-product trisodium phosphate.

2. The hydrous metal oxides are filtered at 175°F to effect the separation from the trisodium phosphate and excess sodium hydroxide.
3. The hydrous oxides are dissolved in hydrochloric acid.
4. The filtrate is partially neutralized to a pH of 5.8 with recycle caustic to precipitate the thorium and uranium.
5. The filter cake is repulped and refiltered to remove additional rare earths.
6. The rare earth concentrate is produced by neutralizing the filtrate from step 4.
7. The thorium-uranium concentrate is dissolved in strong nitric acid. The thorium and uranium are extracted from the rare earths in a multistage extraction unit using tributyl phosphate as the solvent.
8. The thorium is selectively stripped from the uranium with 0.05 molar nitric acid. The uranium is then stripped from the solvent with water.

One disadvantage of this process is the difficulty in effecting a clean-cut separation of the thorium from the

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uranium. An advantage of the process is that the caustic digestion removes phosphates from the solutions to be extracted.

Ames Monazite Process

A brief summary of the Ames Monazite Process is shown below. A discussion of the advantages and disadvantages of the process follows the process outline.

1. The monazite sand is digested with 93 per cent sulfuric acid at 400°F for about four hours using an acid-to-digested sand weight ratio of 1.56.
2. The resulting "grey pasty mass" is dissolved in cold water. About 10 pounds of water is added per pound of digested sand.
3. The undigested sand and silica are removed by settling and/or filtration.
4. The resulting monazite sulfate solution is partially neutralized to a pH of 1.05 to precipitate the thorium as the phosphate. About an equal weight of rare earth sulphates are present in the concentrate because of occlusion.
5. The clear solution is separated from the thorium concentrate by filtration and/or decantation.
6. The filtrate from step 5 is partially neutralized to a pH of 2.3 to precipitate the bulk of the rare earths as the sulfates.

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7. The rare earth concentrate is separated from the clear solution by filtration and/or decantation.
8. The filtrate from step 7 is partially neutralized to a pH of about 6.0 to precipitate the uranium and the remaining rare earths. The clear solution is removed from the uranium concentrate by filtration and/or decantation.
9. The thorium concentrate is dissolved in strong nitric acid and fed to a multistage extractor. The thorium is extracted from the rare earths using tributyl phosphate as the solvent.
10. The rare earth concentrate is digested with caustic to remove the sulfate and phosphate ions prior to extraction. The individual rare earths are separated by extraction using tributyl phosphate as the solvent.
11. The uranium concentrate is dissolved in nitric acid. The uranium is extracted from the rare earths in a multistage extractor using tributyl phosphate as the solvent.

There are two serious disadvantages to the Ames monazite process. First, costly filtrations are required due to the gelatinous nature of the concentrates. The second disadvantage is that the uranium is present in both the rare earth and uranium concentrates to the extent of 50 per cent. The primary advantage of the process is that only simple, easily controlled processing steps are required.

Direct Extraction from Monazite Sulfate Solution

Attempts have been made in the past to extract thorium and/or uranium directly from the monazite sulfate solution. Feldman (25) and Whatley (59) tested about 40 different solvents without finding one that appeared suitable for commercial development. Recently, work has been initiated at Oak Ridge National Laboratory (20) to attempt the extraction of thorium or uranium from monazite sulfate solution using long chain primary amines as the solvent. Hamilton (34) has continued this work with amines at the Ames Laboratory.

EXPERIMENTAL WORK

Digestion Studies

Previous workers have studied many methods of digesting monazite sands to produce a water soluble mass that would serve as a starting solution for separating the desired constituents. Both the sulfuric acid digestion method and the caustic digestion method described in the previous section have been studied in considerable detail (17,52).

As an initial step in this research, some of the other possible methods of digesting the sand were studied to determine whether or not some other method would be preferable for industrial processing. Monazite sands were digested in chromic acid solution and in calcium chloride solution. Fusions of the sand were attempted with calcium chloride, sodium chloride, potassium bifluoride and ammonium sulfate. The only experiments that resulted in appreciable digestion of the sands were those which chromic acid and with potassium bifluoride. From an economic standpoint it was decided that neither of these showed sufficient promise to warrant further study.

Because no process for digesting monazite sand was found preferable to the traditional sulfuric acid process, it was decided to base further work on the typical monazite sulfate solution that results from dissolving the digested monazite in water.

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Two batches of monazite sulfate solution were prepared for use throughout this research. One batch was prepared from Brazilian monazite sand and the second batch from Idaho sand. Table 2 contains pertinent data for these digestions and the concentrations of the resulting monazite sulfate solutions.

Table 2

Preparation of Monazite Sulfate Stock Solutions

Monazite Sulfate Solution	Initial Acid Concentration	Acid-to-Digested Sand Weight Ratio	% Sand Digested	Concentration (gms. total oxide per liter)
Idaho	93%	2.41	59.7	36.9
Brazil	93%	1.76	76.9	49.1

The 93 per cent sulfuric acid used was prepared by dilution of 95.5 per cent sulfuric acid obtained from the General Chemical Division of Allied Chemical and Dye Corporation.

Agitation was provided until the digested mass hardened enough to prevent further mechanical stirring. The "gray pasty mass" was allowed to cool to 70°C, then dissolved using 10 parts by weight of ice water per part by weight of charged monazite sand. The resulting solution, commonly called monazite sulfate solution, was stored in carboys for further use.

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