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To: Dr. R. A. Staniforth

June 16, 1954

MOUND LABORATORY-MONSANTO
Central File No. 54-6-37

RE: PRELIMINARY SURVEY OF

CURRENT STATUS OF WORK ON THORIUM IN THE A.E.C.

INTRODUCTION

A preliminary survey of the classified literature has been made to determine the status of work on thorium in the AEC. This survey included the areas of raw material, feed material, production, and development. The material presented was derived primarily from Abstracts from Classified Reports for the period January 15, 1953 to May 31, 1954. Since the object was only to develop a picture of the present status and not to compile a complete historical approach, only the most recently published abstracts were reviewed. In some cases, reference was made to actual reports where this seemed advisable and the reports were available.

SUMMARY OF CURRENT WORK ON THORIUM IN THE AEC.

The primary source of thorium is from monazite sand. The naturally occurring mineral found in India, Brazil, North Carolina, Florida, and to a much lesser extent in the Western Plateau of the United States is a rare earth phosphate derived from weathering of granites, gneisses,

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and pegmatites. Typical analyses[(1)] of monazite sands from different sources are as follows:

Constituent	Brazilian	Indian	Domestic (Fla)
ThO_2	6.5	9.8	3.1
U_3O_8	0.17	0.29	0.47
$(RE)_2O_3$	59.2	58.6	40.7 (Inc. Ce_2O_3)
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

Conventional rare earth industry in this country has used monazite sand as a starting material subjecting it to sulfuric acid treatment.[2] Thorium residues from this industry have been a source of thorium for AEC work.

Two basic methods have been developed in the AEC for recovery of thorium from monazite. One of them[3,4] involves dissolving the ore in sulfuric acid followed by fractional precipitation of thorium phosphate. The other method[(1)] is based on caustic digestion of the ore resulting in the hydrated oxides of thorium and rare earths which are then separated. These methods will be described in more detail later in this report.

Following the isolation of thorium it is generally subjected to one or more purifying steps to remove traces of objectionable impurities before being further processed. Impurities which are particularily objectionable are those having high thermal neutron absorption cross sections - such as cadmium, boron, and the rare earths. Precipitation methods,[5] electrodeposition[6,7,8] and solvent extraction[9,10] methods have been investigated. It would appear that solvent extraction is favored for a continuous production facility.[11]

The purified thorium is next converted to the chemical form required for reduction to the metal. These forms are the fluoride, iodide, oxide, or hydride. The actual reduction can be accomplished in several different manners however the process installed at Fernald[12] involves the reduction of ThF_4 with Ca in the presence of anhydrous $ZnCl_2$. A billet of thorium and zinc is produced from which the zinc is distilled before the thorium is melted and cast. Reduction of thorium oxide with calcium metal has been investigated.[13] High purity thorium has been produced by the van Arkel-de Boer process from ThI_4.[14] Electrolysis of fuzed salts has resulted in metallic thorium.[7,8] Some work on the powder metallurgy of thorium has used thorium hydride as a starting material which is reduced in the course of the process to thorium metal.[15]

The thorium metal is usually cast into billets which are then machined, rolled, extruded, or drawn into the desired shapes.[13,16,17,18,19,20] Thorium metal suffers surface oxidation in the air at elevated temperatures so appropriate precautions must be observed.[21] Some work has been done on forming thorium by the techniques of powder metallurgy.[15,22]

The mechanical and physical properties of thorium have been investigated rather widely.[16,23,24,25,26] The influence of minor constituents have been found to modify the properties of the metal.[27,28,29] The effects of radiation on the dimensional stability of thorium has been investigated.[30] Considerable work has been done on studying the alloying properties and phase diagrams of thorium with other metals.[23,28,31,32,33]

Many special problems have arisen in doing what work has already

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been attempted on thorium which may be indicative of the character of future development efforts which might be required. The presence of Ra-228 when large quantities of thorium are being processed may cause a health problem.[34] Some ions catalyze reactions which are important to the process and their influence must be evaluated.[35] Improvements in process techniques may lead to improved product such as the development of heated - mold casting.[36] New metallographic and analytical techniques are required for the different materials as they are encountered in the production process.

THE AMES PROCESS FOR TREATING MONAZITE.

The Ames monazite process consists of the following steps:[9]

1. Digestion of the monzaite sand with H_2SO_4 in a 5-hour cycle during which the temperature goes from 160°C to a maximum of 230° C in the first hour.

2. Dissolution of the digested mass in H_2O to give a monazite-sulfuric acid solution of 0.024 pounds of Th/gal. Separation of the bulk of silica and rutile is effected by decantation.

3. Dilution of the monazite solution and fractional precipitation of thorium phosphate by adjusting the pH to 1.05 with ammonia. Some of the rare earths accompany the thorium as double sulfates.

4. Filtration of the solids.

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5. Dissolution of the thorium filter cake in HNO_3 and removal of the insoluble silica-titanium sludge to prepare feed for the solvent extraction operation.

6. Solvent extraction of the HNO_3 solution to separate the thorium from the rare earths and other impurities.

7. The rare earths and uranium are recovered by further neutralization of the filtrate from step 4. By making a fractional precipitation at pH of 2.3, the bulk of the rare earths can be separated from a uranium concentrate.

THE BATTELLE PROCESS FOR TREATING MONAZITE.

The Battelle process for processing monazite sand consists of the following steps:[1]

1. Reaction of the monazite sand with 73 per cent NaOH solution at 280° F for three hours to produce the hydroxides of the metals.

2. Filtration at 180° F to separate the metal hydroxides from Na_3PO_4 and excess NaOH.

3. Dissolution of the metal hydroxides in HCl.

4. Fractional precipitation of thorium hydroxide by adjusting the pH to 5.8 with waste caustic.

5. Multiple filtration and repulping operations to separate the thorium from the bulk of the rare earths.

6. Dissolution of the thorium filter cake in HNO_3 to prepare feed for the solvent extraction operation.

7. Solvent extraction of the HNO_3 solution to separate the thorium from coprecipitated rare earths and other impurities.

PROCESS CHEMISTRY AND METALLURGY AT FERNALD.

The thorium process to be installed at Fernald involves the following steps:

1. Dissolution of mantle-grade thorium nitrate in water and dilute nitric acid.

2. Precipitation of the $ThF_4 \cdot XH_2O$ with 70% HF.

3. Calcination of the wet fluoride at 550° C under an anhydrous HF atmosphere after preliminary drying to <5% H_2O.

4. Reduction of the dry fluoride with calcium in the presence of anhydrous zinc chloride to make a thorium-zinc biscuit or derby. 150 pounds ThF_4, 54 pounds Ca, 15 pounds of $ZnCl_2$ heated to 1240° F.

5. Biscuit placed in ZrO_2 crucible and heated to 1100° C to distill off the Zn, then thorium melted at 1825° C and poured into heated graphite molds.

SUMMARY OF TOPICS REPORTED FROM DIFFERENT AEC SITES.

Iowa State College (ISC)

Separation of Thorium from Monazite (All phases of acid process).

Reduction of Thorium Salts to Metal (ThF_4, ThO_2).

Melting and Casting of Thorium.

Study of Mechanical and Physical Properties of Thorium Metal.

Effects of Impurities on Properties of Thorium.

Phase Studies of Thorium with other Metals, Preparation of Special Alloys and their Characterization.

Battelle Memorial Institute. (BMI)

Separation of Thorium from Monazite (all phases of caustic process)

Preparation of high Purity Thorium by Iodide Process.

Electrodeposition of Thorium from Fused Salt Baths.

Mechanical and Metallurgical Properties of Thorium and its Alloys.

Corrosion of Thorium and its Alloys.

Fabrication Techniques for Special Shapes.

National Lead of Ohio - Fernald (FMPC)

Installation and Testing of Production Equipment for Thorium Metal.

Process Improvement.

Analytical Control Procedures.

Argonne National Laboratory (ANL)

Electrolytic Refining of Thorium.

Recovery of Thorium from Sea Water by Solvent Extraction.

Testing of Canned Slugs.

Effects of Radiation on Dimensional Stability of Thorium and its Alloys.

Corrosion of Thorium.

Development of Metallographic Techniques for Thorium.

Oak Ridge National Laboratory (ORNL)

Recovery of Thorium from Monazite Sands.

Physical Testing of Thorium.

Effect of Impurities on Thorium.

Radiation Damage to Thorium.

Recrystallization of Thorium.

Horizons, Inc. (NYO)

Production of Thorium Metal by Electrolysis of Fused Double Salts - $NaThCl_5$, $KThF_5$.

Sylvania Electric Products, Inc. (SEP)

Powder Metallurgy of Thorium and Thorium Hydride.

New York Operations Office (NYO)

Design of Equipment for Production Refining and Casting of Thorium (National Research Corp.)

Thorium Fabrication by Powder Metallurgy (Brush Beryllium Co.)

Comparison of Fabrication Methods (NYO).

Hanford Engineering Works (HW)

Examination of Extruded and Rolled Thorium.

Harwell (England).

Preparation, Properties, and Alloying Behavior of Thorium.

Teddington (England).

Determination of Thorium in Phosphate Ores.

Determination of Thorium in Minerals and Ores.

D. L. Timma

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