Annex A: Thorium recovery

A.1 Introduction

This section is primarily concerned with the steps needed to recover thorium, beginning at its major mineral forms and proceeding to nuclear-grade purity suitable for fuel fabrication.

If recovered, thorium will most likely initially be a by-product (or co-product, depending on cost sharing analysis) of ilmenite (titanium ore) mining, uranium mining, iron ore mining, and/or rare earth ore mining. Beach sand mining requires less waste rock removal, ore crushing and sizing energy than the other options, but the chemical processes used to isolate thorium are relatively similar between cases. Since bastnasite and monazite are both actively recovered minerals, even with thorium’s currently small market, they will be the primary focus of this assessment.

Both bastnasite and monazite are almost always obtained in conjunction with other minerals and must be isolated before being processed further. The steps used to achieve this isolation are similar for both minerals. The initial step involves crushing the raw ore. Then, gravitational, flotation, electromagnetic, and/or electrostatic methods or, more often, a combination of these techniques, are used to achieve mineral purities greater than 90%. The exact sequence depends on the mix of minerals encountered in the ore deposit, the primary products desired and any co-products or by-products desired. Once bastnasite or monazite is isolated from the other minerals, the particle size must be further reduced for the subsequent acidic or caustic attack (known as digestion) to be effective. The impacts of these steps are attributable to producing the primary product (e.g. REEs, titanium) and not to thorium production.

To obtain a reactor-grade thorium product, thorium-bearing ores that may contain multiple valuable elements are subjected to multiple processing steps (see Figure A.1). First, the thorium-bearing minerals must be isolated from other ore constituents, a step which is typically accomplished by mechanical, electrostatic, and magnetic processes. Second, these minerals are attacked by aggressive chemicals to dissolve the valuable elements and other constituents. The valuable elements are separated from the other constituents and each other using chemical processes such as solvent extraction or ion exchange. Finally, the separated thorium stream is purified to yield high-purity reactor-grade thorium suitable for use in nuclear fuel. Each of these steps is described in more detail in the following sections.

**Figure A.1. Overview of thorium recovery process**

![Diagram of thorium recovery process]

INTRODUCTION OF THORIUM IN THE NUCLEAR FUEL CYCLE, NEA No. 7224, © OECD 2015
A.2 Pre-separation beneficiation

**Figure A.2. Pre-separation beneficiation processes to concentrate minerals of interest**

A.2.1 Initial grinding

The minerals are ground to facilitate the subsequent separation of different minerals. The particle size must be sufficiently small to be compatible with typical heavy metal concentrators, which separate the desired heavy minerals (e.g. ilmenite, zircon, rutile, monazite, bastnasite) from lighter undesired minerals, like quartz.

A.2.2 Beneficiation of bastnasite or monazite from other minerals

Bastnasite beneficiation schemes have been developed as a primary product (e.g. Mountain Pass, Nevada, United States) and as a secondary product of iron ore production (e.g. Bayan Obo, Mongolia). Even with its rare earth content, monazite is rarely the primarily sought mineral where it is produced. In the case of beach sand mining, ilmenite is often the primary product, followed by zircon and rutile. At least some monazite is generally present at all major bastnasite deposits; however, the reverse is not necessarily true.

A.2.2.1 Bastnasite beneficiation

- A.2.2.1.1 Magnetic separation

At Bayan Obo, the presence of highly magnetic iron ores, like magnetite and hematite, make electromagnetic separations a logical first step to remove them after particle sizing. Bastnasite’s low magnetic attraction makes this step a very clean and effective separation.

- A.2.2.1.2 Flotation

The number of flotation steps that attract unwanted content into a surface layer that can be skimmed depends on the content of the raw ore, but unwanted gangue minerals like calcite and quartz are generally removed by exploiting bastnasite’s hydrophilicity (attraction to water). Surfactants such as fatty acids or dicarboxylic acids are added to enhance the attraction of unwanted minerals to the surface layer.

- A.2.2.1.3 Gravitational separation

Bastnasite is mostly isolated after flotation, but monazite has very similar hydrophilic characteristics to bastnasite and must be separated from the bastnasite. Due to monazite’s exceptionally high specific gravity, density-based separations are effective. Fairly high-purity streams of both minerals are produced as a result of this process. In principle, subsequent processing of monazite could be viable if the REE content in the ore
is sufficiently high. However, monazite’s considerably higher specific radioactivity relative to bastnasite is often a deterrent to subsequent monazite processing.

A.2.2.2 Monazite beneficiation
- A.2.2.2.1 Gravitational separation

With a specific gravity often in excess of five, monazite is usually among the densest, if not the most dense, mineral obtained during monazite mining operations. As a result, gravity-based separations are effective in isolating the mineral.

- A.2.2.2.2 Magnetic separation

Ilmenite (frequently the primary ore of interest where monazite is found) is highly magnetic and can be readily removed from the monazite. Monazite has a rather moderate susceptibility to magnetism and remains with the less magnetic minerals.

- A.2.2.2.3 Electrostatic separation

Unlike most of its accompanying minerals, monazite has a low electrostatic attraction. Thus, most remaining minerals are removed by this means, and very pure monazite can be obtained. The order of the monazite separation steps may vary by facility, based on the predominance of the various materials; for instance, electrostatic separations may precede the magnetic separations.

A.2.3 Further size reduction of particles

For subsequent chemical processing to be effective, the particle size must be reduced to the order of a hundred microns, by grinding and/or crushing. In some cases, the initial crushing may have been sufficient, and this step would be unnecessary.

A.3 Digestion and valuable element extraction processes

Once the purified thorium mineral has been sized to an appropriate range, it must be solubilised to achieve REE and thorium recovery. Both bastnasite and monazite have very refractory crystal structures, which require a highly concentrated, potent chemical agent to open the lattice and extract the valuable content. Either a strong acid or a base can be used for this, and variations exist within both routes. In the case of bastnasite, the prospect of readily removing fluoride and carbonate anions make the acidic process preferable. Both variants have been used extensively for monazite. Neither the acid nor the alkali digestion process is selective for thorium extraction, so further separation is necessary.

This section of the report addresses bastnasite and monazite processing up to the point where solids containing significant concentrations of thorium are recovered by filtration. These solids can undergo subsequent refining to recover a nuclear-grade thorium product. In bastnasite processing, the REEs remain with the thorium until the refining stages. In monazite processing, most of the rare earths are separated from the thorium prior to refining. This is because thorium is a much more notable impurity in monazite (>5%) than in bastnasite (<0.5%), and more care is taken to keep this thorium out of the REE refining systems.

The following sections describe acidic processes for recovering thorium from bastnasite and monazite and a process using strong bases for recovering thorium from monazite.
A.3.1 Acidic bastnasite digestion processes

Figure A.3. Sulphuric acid digestion process for extraction of thorium from bastnasite

A.3.1.1 Ore digestion

The initial strong acid attack accomplishes two main objectives. The first is to break down bastnasite’s tightly bound mineral structure and release its content to an aqueous state for subsequent processing. The second is that bastnasite is a carbonate mineral with substantial fluoride content. The addition of a strong acid converts these into carbon dioxide and hydrogen fluoride gas, respectively, which is liberated from the system. While the efficiency of this separation makes the acidic process convenient, potential corrosion and safety concerns arise from the release of hydrogen fluoride. Sulphuric acid is frequently identified as the acid of choice, though hydrochloric acid has also been used.

A.3.1.2 Filtration of non-extracted components

Any ore components which remain undissolved after the digestion process must be removed from the system. Since thorium and the REEs are in the aqueous phase of the slurry resulting from digestion at this point, a solid-liquid separation is required. The solids resulting from the separation (assumed to be filtration here) are disposed of as waste. The thorium/REE solution is then sent to thorium refining.
A.3.2 Monazite acid digestion processes

Figure A.4. Sulphuric acid digestion process for extraction of thorium from monazite

2. Pre-Separation Stages

2.2.1 Ore Digestion
Reagent: 16 M H₂SO₄
95% thorium dissolved
Product: Slurry of monazite components

2.2.2 Filtration of Undissolved Components
Product: Monazite sulfate/phosphate solution
Waste: Filter cake waste to disposal

2.2.3 Dilution with Water

2.2.4 Alkaline Precipitation of Thorium
Product: Slurry of Monazite Components
98-99% efficient recovery of Th as ppt
Rare earths and uranium in solution

2.2.5 Filtration/Drying
ThO₂/rare earth oxides in solid concentrate to refining
Filtrate to rare earth and uranium recovery

4. Refining

A.3.2.1 Ore digestion

In this step, a strong acid is used to break monazite's sturdy mineral structure and dissolve the desired components into the aqueous phase. Monazite particles are added to a solution of concentrated strong acid. A solution consisting of 93% sulphuric acid can, with sufficient digestion time, achieve 95% recovery of monazite particles up to 150 μm. This puts most of the contents of the monazite in a soluble sulphate form. Nitric acid or hydrochloric acid could also be used, resulting in nitrates and chlorides, respectively. At this degree of acidification, virtually all of the phosphate ions present in monazite become phosphoric acid.

A.3.2.2 Filtration of non-extracted components

The purpose of this step is to remove undissolved monazite constituents and other solid ore components such as silica and zircon. This is a physical, rather than a chemical, stage. The digested solution is typically diluted and allowed sufficient time to permit the solids from the aqueous monazite to settle. Some sources indicate that a flocculating agent may be added in this step to speed settling of the solids.
A.3.2.3 Dilution
The thorium-bearing sulphate-phosphate solution is diluted with water by a factor of 6-7 in preparation for subsequent steps.

A.3.2.4 Precipitation of thorium concentrate
Depending on the process, more than one precipitation reaction could be used. The goal here is to add an agent that results in the formation of a thorium-rich precipitate. Ammonium hydroxide can be used to lower the pH and shift the phosphoric acid solution back to phosphate ions, resulting in a thorium phosphate precipitate. Another option is adding sodium hydroxide in sufficiently large amounts, which shifts the thorium, REEs, and uranium to a solid hydroxide form.

A.3.2.5 Filtration of thorium concentrates
Once the thorium has been precipitated, physical processes can again be applied to separate the aqueous product containing most of the REEs from the solid phase which contains the thorium. This is a not a perfect separation and rare earths can constitute up to 30% of the concentrate. However, subsequent refining to nuclear grade removes these impurities.

A.3.3 Caustic monazite digestion processes

Figure A.5. Caustic (alkali) digestion process for extraction of thorium from monazite
A.3.3.1 Ore digestion

Much like the acidic version, a strong caustic chemical is used to break monazite's mineral structure and dissolve components to an aqueous phase. Monazite particles are dissolved in a solution of concentrated strong base, usually sodium (assumed here) or potassium hydroxide; monazite particles at 44 μm have been extracted with 45% sodium hydroxide, and with sufficient digestion time can extract 95% of monazite's thorium content, i.e. roughly the same as the acidic process. In contrast to the acidic process, this version results in the thorium, uranium, and REEs being present in the solid phase as hydroxides and oxides, while the phosphates from the monazite end up in the aqueous phase as sodium or potassium phosphate. Separating the phosphates at this early stage is one of the major advantages of the caustic process, since it simplifies subsequent precipitation schemes. It also enables the phosphate content to be recovered as a by-product such as tri-sodium phosphate.

A.3.3.2 Slurry dilution/conditioning

The hydroxide slurry is diluted with water to reduce the sodium hydroxide concentration to about 30%. Sufficient time (about 1 hour) at 110 degrees Celsius allows the hydroxides to form a precipitate that is suitable for subsequent solid-liquid separation.

A.3.3.3 Solid-liquid separation

Physical processes such as filtration are used to separate the aqueous phosphate solution from the solid thorium/uranium/REE hydroxide concentrate. The phosphate solution may be subsequently refined as a by-product.

A.3.3.4 Dissolution of the concentrate

The hydroxide concentrate is dissolved in a strong acid. Some processes involve the addition of concentrated hydrochloric acid, while others use sulphuric acid. Sufficient time is allowed to dissolve at least 99% of the hydroxides.

A.3.3.5 Filtration of undesired solids

Physical processes such as filtration are used to separate the thorium/uranium/REE solution from undesired solids which are managed as waste. This step is analogous to step A.2.2.2 for the acid process.

A.3.3.6 Precipitation of thorium/uranium

This step is analogous to A.2.2.4 of the acid separation process. Generally, dilute sodium hydroxide is added to precipitate thorium and uranium as hydroxides. This method has the limitation that extra measures must be taken to remove the uranium later in the refining process. However, washing the precipitate with a mixture of sodium carbonate, sodium hydroxide and hydrogen peroxide can remove as much as 80% of this uranium.

A.3.3.7 Filtration and drying

Filtration separates the thorium-rich solid phase from the REE-rich aqueous phase. The solid phase, which still contains residual uranium and REE hydroxides, is dried and prepared for the refining process.

A.4 Refining thorium concentrates to nuclear-grade material

Depending on the mining scenario, all processes described up to this point may already occur in efforts to recover REEs. Even when obtained as a by-product of iron ore, bastnasite’s REE content is almost always recovered, meaning that beneficiation and extraction impacts would not be attributable to nuclear applications. The same is not necessarily the case for monazite, which is generally a by-product of ilmenite. Though the impacts of physical beneficiation would still be covered, many ilmenite operations simply discard monazite-bearing material as waste.
The impacts of the steps described in this section would generally be attributable to the nuclear fuel cycle, since their primary purpose is to produce a purified thorium product for nuclear applications from a material that would otherwise be managed as a waste. Since schemes to produce a thorium product from bastnasite have not been formally considered, the processes discussed are based on experiences with bastnasite that remove thorium as a waste. In contrast, thorium has been refined from monazite by a number of entities around the world and on a commercial scale in India.

A.4.1 Solvent extraction following bastnasite processing

The concentration of thorium in bastnasite is low enough that it is often neglected in mass flow diagrams altogether, as subsequent separation of individual REEs is generally sufficient to remove most thorium impurities. However, a few Chinese laboratories have developed processes for removing the impurities in REEs simultaneously via solvent extraction. Not all of the documentation concerning these processes has been translated, but those that are translated provide a basis for the thorium by-product recovery methods discussed below.

The incoming stream to this solvent extraction system would likely be a REE/thorium sulphate solution (see Section A.3.1). Generally, the uranium content of bastnasite is negligible and would not impact the requirements of the solvent extraction system. A primary amine, N-1923, can be used to recover well over 99% of the thorium from bastnasite feed, although it is also accompanied by a nontrivial amount of cerium. Other designs using different amines or esters have been developed, employing a sequence of solvent extraction steps to recover bastnasite’s cerium, fluorine, and thorium content. In these latter cases, the objective was to remove undesired impurities, and the resultant purity of the thorium streams is not clear.

A.4.2 Solvent extraction following monazite processing

Figure A.6. Refining monazite thorium to nuclear grade

- 3. Thorium Concentrate from Beneficiation and Separation
- 3.2.1 Dissolution of Thorium Concentrates
  - Dissolve thorium cake in strong acid
  - Chemically reduce cerium (IV) to cerium (III)
- 3.2.2 Uranium Removal
  - Extract uranium nitrate from HNO₃ solution with TBP and scrub
  - Strip uranium nitrate from TBP phase for recovery or disposal
  - Aqueous thorium-bearing rafinate goes to next step
- 3.2.3 Thorium Cleanup
  - Extract thorium nitrate from HNO₃ raffinate with TBP and scrub
  - Strip pure thorium nitrate from TBP phase and evaporate or precipitate to yield thorium product
- Fuel Fabrication
A.4.2.1 Dissolution of thorium concentrates and cerium reduction

This step achieves two objectives simultaneously. The first is to dissolve the thorium concentrate with a strong acid. As thorium nitrate has historically been the preferred compound for storage and use and TBP-nitrato systems are well-known, nitric acid is the most likely candidate. Furthermore, cerium, a rare earth present in significant quantities in monazite, has much of the same chemical behaviour as thorium in the tetravalent state. Since the only other available valence states for cerium are less than four, a reducing agent must be used. Hydrogen peroxide is the typical choice.

A.4.2.2 Uranium removal

Uranium mostly follows thorium up to this point in processing and must be separated from the final thorium product. The extent and nature of this step depends on two factors. First, the separation method used (see Section A.2) directly impacts how much uranium is present in the refining steps. The acidic digestion process removes considerably more uranium than the caustic process, so feed from the caustic process might require a greater number of uranium extraction stages. Second, the solvent choice could potentially eliminate the need for this step entirely. The solvent with the most nuclear-related experience is TBP. Its familiarity and availability are strong advantages, but it is more selective for uranium than thorium, thus necessitating a series of stages that keeps most of the thorium in the raffinate.

Research with other solvent choices like esters and amines is ongoing and should a viable solvent be found that is selective for thorium, the need for these stages could be eliminated. Recent experiments suggest that some amines can be configured to be slightly selective for thorium. However, a dual extraction scheme in which uranium is first separated and then thorium is purified is still generally used.

A.4.2.3 Thorium clean-up

Once the uranium has been removed, a series of solvent extraction and scrubbing stages is used to obtain a thorium-rich product stream containing only trace amounts of other elements. The choice of solvent should be selective for thorium versus rare earths and other elements. TBP is generally used for this purpose, since U levels are negligible after the first solvent extraction system. The extraction steps are used in conjunction with scrubbers that return rare earth impurities to the aqueous phase.

A number of solvent/extractant systems have been proposed as alternatives. One study explored the use of aliquat 336, a long-chain amine, in kerosene. This species achieved 96% extraction for thorium, 99% for cerium (this experiment did not pre-reduce the cerium), 53% for uranium, and much less for rare earths in a single stage. Other promising amines include primene JM-T and primene 34R, which have been shown to achieve over 90% extraction for thorium while less than 10% for uranium.

Once purified, the thorium in the product stream must be removed from the organic phase. A strong acid is usually used for this purpose. If thorium nitrate is the desired product, nitric acid is the ideal choice. However, in recent times, thorium oxalate may be a more desirable product since it is safer to store and transport. Subsequent treatment would depend on the fuel type. For instance, for oxide fuels, calcination of thorium nitrate/oxalate to thorium oxide would be required prior to fuel fabrication.

A.5 Summary of predicted health impacts

A.5.1 Introduction

The following section intends to briefly identify the categories of health impacts that might result from the various stages of a thorium refining facility. This list is not intended to be comprehensive but rather a starting point for considerations in future efforts to evaluate health impacts.
A.5.2 Projected health impacts for pre-separation beneficiation

These impacts are expected to be absorbed by extant mining industries unless a new mine were opened for the primary purpose of obtaining thorium, which is unlikely. The grinding and crushing of ores would release $^{220}\text{Rn}$, the analogue of the U-decay-chain's $^{222}\text{Rn}$. $^{220}\text{Rn}$ has a much shorter half-life than $^{222}\text{Rn}$ (56 seconds vs. 3.8 days), so it would only pose a hazard to those in the immediate vicinity. The radon hazard could be heightened as bastnasite or monazite is concentrated from other, less radioactive ores. This is more of a concern in the case of monazite, since its thorium content is much higher than that of bastnasite.

A.5.3 Projected health impacts for digestion and separation processes

The use of concentrated strong acids and strong bases represents a significant chemical hazard regardless of processing scheme. The digestion process also produces radioactive waste streams. In any scheme, undigested solids with a moderate specific activity must be disposed of. The bulk of the radioactivity is carried by $^{228}\text{Ra}$, which chemically tends to follow the REEs. This results in a waste stream with a high specific activity during REE processing, but this would not be attributable to the nuclear fuel cycle. In the case of the caustic monazite process, another low-activity waste stream would result from refining phosphate into a usable by-product. As in previous stages, radon inhalation would continue to be a hazard. As discussed at the outset of Section A.4, some of these impacts would likely be attributable to primary product (Ti, REE, iron, etc.) production while the incremental impacts would be attributable to thorium production with the allocation depending on the specific flowsheet being used.

Another waste from recovery of thorium or uranium is the undigested solid tailings that contain around 5% of the thorium or uranium that was in the feed material, plus some of the decay products from the thorium or uranium. In the case of uranium, the activity and toxicity of the tailings decline slowly because the rate-controlling radionuclide is $^{238}\text{Ra}$ which has a 1,000-year half-life. Beyond 10,000 years, the activity and radiotoxicity of uranium tailings have dropped by about 20-fold (for 5% residual uranium) and then remain constant for a time controlled by the 4.5-billion-year half-life of $^{238}\text{U}$ (Li et al., 2004). However, in the case of thorium tailings, the rate-controlling radionuclide is $^{238}\text{Ra}$, with a half-life of only 5.6 years. As a result, the activity and radiotoxicity drop by 20-fold within a century and then remain constant for a time controlled by the 14-billion-year half-life of $^{232}\text{Th}$. The long-term activity and toxicity of thorium tailings per tonne of thorium recovered is about 25% of that for uranium tailings from each tonne of uranium recovered.

A.5.4 Projected health impacts for refining

In addition to the presence of strong acids and bases, extractants for solvent extraction systems are typically toxic and exposure would need to be limited. Any raffinate streams leaving the system would represent radioactive waste, albeit of a low specific activity. As in previous stages, radon inhalation would continue to be a hazard.

References