LECTURE 4

Alkaline Fusion Process of Monazite and Xenotime (thorium and yttrium)

Monazite and xenotime are rare-earth phosphate (REP) minerals that contain considerable amounts of thorium and yttrium sequentially. The recovery (extraction) of mixed rare earth elements and removal of thorium and yttrium from their minerals are accomplished (achieved) by **chemically leaching with concentrated sulphuric acid**, which is hazardous (toxic) to the environment. At present, **sodium hydroxide (**an environmentally friendly method of REP processing that can replace the sulphuric method) is used as an alternative, which helps to improve the leachability of **yttrium, thorium** and other **valuable rare earth oxide elements** (such as uranium).

Monazite (Ce,La,Th,PO_4) and xenotime (YPO_4) are **lanthanide** phosphate minerals, which are the major raw materials for rare earth oxide (REO) elements known as Lanthanides. Lanthanide is a family of 15 chemical elements whose atomic numbers vary from lanthanum La (Z= 57) to lutetium Lu (Z= 71) in the periodic table. **Monazite contains some thorium** (4–12 % ThO_2), cerium (20–30 % Ce_2O_3), small amounts of uranium and variety of light rare- earth elements REEs (La to Sm), approximately (10–40 % as oxides). However, **xenotime** is a rich source of **yttrium**-group oxides (54 to 67 %) and cerium-group oxides (1 to 11 %) together with silica (sand), zirconia, thoria (thorium oxide) etc. The rare earth elements (REEs) of xenotime belong mainly to the heavy elements (Eu to Lu).

The increasing demand for rare earth metals has motivated research into developing an effective method of extracting these elements from their REP minerals such as monazite and xenotime. The higher demand for these valuable elements is due to their importance in nuclear fuels to generate electricity in addition to their applications in green technology such as wind turbine and electric motors. **An environmentally friendly, alternative process of alkaline fusion** has been developed to replace the hazardous (toxic) concentrated sulfuric acid currently in use. The direct leaching of monazite with acids has faced a serious problem (strong acid attack).

On the other hand, there are some **benefits of using the alkaline method compared to the sulfuric route (methode).**

- First, overcoming the environmental pollution relating to the release of atmospheric SO_X gases during sulphate acide decomposition.
- Another advantage is the **very little quantity** of radioactive waste (emitting radiation) generated from the alkaline operation due to the volume of undissolved solid in the post-leaching stage.
- In addition, **highly pure products** of thorium, yttrium and REEs have been obtained using this method.

1. ALKALINE FUSION PROCESS OF MONAZITE

The removal of thorium from monazite and recovery process of mixed rare- earth metals by alkaline method consist of the following steps:

1. Fine grinding of monazite sand in a ball mill to less than 10 μm particle size, which is important for efficient decomposition.
2. The fine- grounded monazite sand is dissolved in 70% sodium hydroxide solution (caustic soda) for 2 h at approximately 150^0C to produce individual solid hydroxides of thorium, uranium and rare earth elements. For effective decomposition, very fine- grounded monazite sand is leached with 40-50 wt. % sodium hydroxide solution for 3 h at approximately 160 ^{0}C.

Thus, insoluble hydroxides of lanthanides (rare earth RE), thorium, and uranium are formed according to the equations listed below (1-3):

$$REPO_4 + 3NaOH \rightarrow RE\ (OH)_3 + Na_3PO_4 \quad (1)$$

$$Th_3(PO4)_4 + 12NaOH \rightarrow 3Th(OH)_4 + 4Na_3PO_4 \quad (2)$$

$$UO_2HPO_4 + 2NaOH \rightarrow UO_2\ (OH)_2 + Na_2HPO_4 \quad (3)$$

This method has attracted attention due to the economic recovery of trisodium phosphate (Na_3PO_4) at the initial stage as a solution and thorium hydroxide ($Th\ (OH)_4$) as a solid.

3. Subsequently, separation of the insoluble mixed hydroxides of thorium, uranium and rare earth elements REES by leaching with hydrochloric, nitric or sulfuric acid. Fig.1

clarifies the flowchart process of monazite digestion by alkaline fusion.

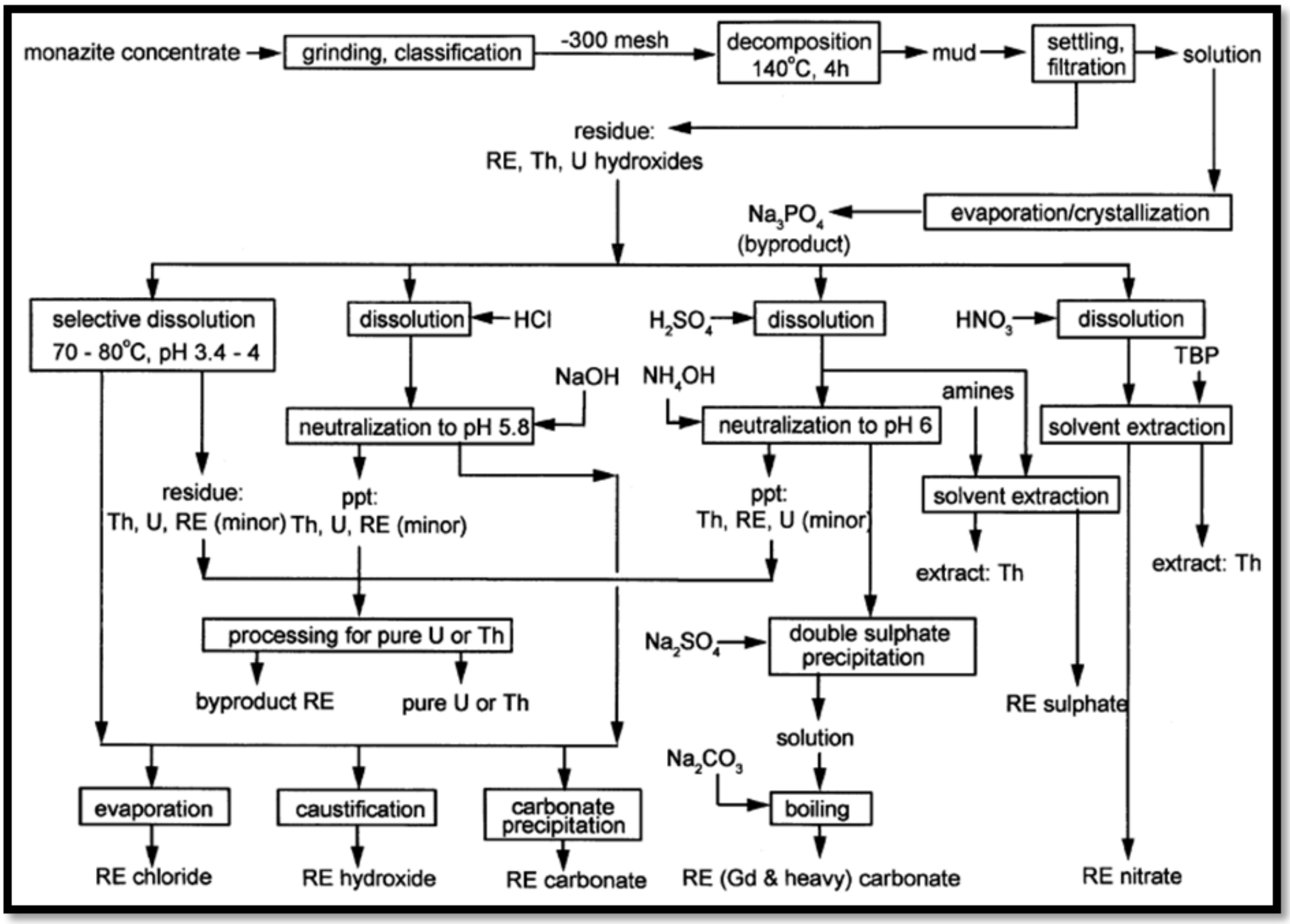

Figure 1. The alkaline fusion process of Monazite. As shown by the flowchart, there are many leaching pathways after the pre- treatment of monazite.

The effective process for removing thorium ions completely and in a high state of purity can be achieved through solvent extraction method involving higher amines. These amines complex group function well with a sulphate solution such as sulfuric acid (H_2SO_4).

The dissolution of the hydroxides in nitric acid and extraction of thorium with tri-butyl phosphate (TBP) were effectively used. However, the use of TBP solvent faced difficulties due to the partial oxidation of cerium which reduces the degree of thorium extraction.

Some researchers used a leaching medium of hydrochloric acid (HCL) with NaOH. The solid phase of hydroxide residue produced from the alkaline digestion is leached in 10 mole HCl at 80 ^{0}C for 30 min and subsequently diluted with water to yield a soluble phase of thorium and rare earth chlorides.

2. ALKALINE FUSION PROCESS OF XENOTIME

The alkaline cracking or breakdown processes of xenotime are as follows:

1. The finely grounded xenotime concentrates of a particle size (125 µm or less) is mixed with NaOH and fused in a furnace at 400 °C. A number of parameters must be considered, such as the fusion time, temperature, particles size and xenotime concentrate/alkali molar ratio.

2. A fused compound of sodium phosphate is formed similar to Eq. (1). In order to separate the soluble phosphate component from the REES, the leached product will be washed with warm water. The loose phosphate will dissolve in the solution while the insoluble REEs will be retained as a solid.

3. After leaching out the phosphates, the deposited hydroxide is dissolved in a small amount of hydrochloric acid and filtered from impurities such as silica. Finally, a precipitation process to recover the rare earth metals. Fig.2 presents the alkaline breakdown process of xenotime.

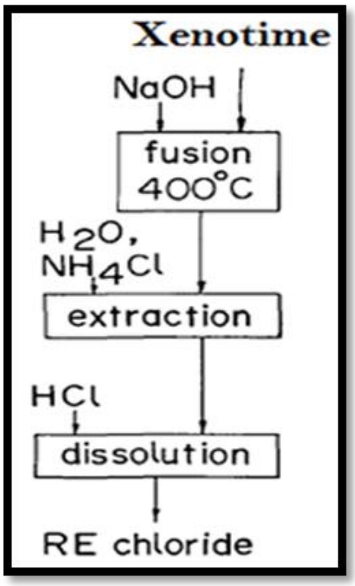

Figure. 2 The alkaline fusion method of xenotime