CHAPTER II

EXTRACTION OF THORIUM FROM MONAZITE

The monazite opening process is designed to separate the
entire thorium, rare earths and uranium contents of monazite sand
from its phosphate and silica gangue in a form suitable for fur-
ther separation of valuable elements. This process should use
comparatively inexpensive chemicals, be operable on a large scale
and provide a high rate of recovery for the thorium, rare earths
and uranium contents of monazite sand. Two most common methods
of opening monazite sand are the sulphuric acid and the caustic
soda digestion, both of which destroy the chemical structure of
monazite sand , but selectively digest different components. Since
the sulphuric acid digestion process which was developed by Ames
Laboratory, Iowa State College (3, 4) and the caustic soda diges-
tion process which was developed by Battelle Memorial Institute
(5, 6) seem to suit the requirements, their applicabilities for
the domestic monazites in the aspects of techniques as well as
cost, are investigated and compared.

2.1. Acid Method

In the sulphuric acid digestion process, the sands is digested
by the   treatment with an excess amount of concentrated (93

per cent) or fuming sulphuric acid for 5 hours at 155 to 230°C.
The objective is to make all constituents, with the exception of
silica, zircon and rutile, water soluble. The reaction for opening
the rare earths (RE) is said to be :

$$2 \ RE \ (PO_4) + 3 \ H_2SO_4 \longrightarrow RE_2(SO_4)_3 + 2 \ H_3PO_4$$

$$ThSiO_4 + 2 \ H_2SO_4 \longrightarrow Th(SO_4)_2 + SiO_2 + 2 \ H_2O$$

$$Th_3(PO_4)_4 + 6 \ H_2SO_4 \longrightarrow 3 \ Th(SO_4)_2 + 4 \ H_3PO_4$$

$$SiO_2 . X \ H_2O + H_2SO_4 \longrightarrow SiO_2 + H_2SO_4 . X \ H_2O$$

It has been concluded that in dissolving monazite sand
with concentrated sulphuric acid, the factor of particle size,
temperature of reaction, acid-to-sand ratio and acid concentration
all affect the time required for digestion and the completeness of
digestion. Therefore, the optimum values for variables are **inter-
dependent.** However, since thorium pyro phosphate forms at high
temperature, it is necessary that the temperature of reaction be **below**
210°C; also in order to complete reaction the acid-to-sand ratio
should be between 1.6 to 1 and 2.5 to 1. Optimum digestion
conditions are to dissolve minus 100 mesh monazite sand particles
in 93 per cent sulphuric acid at about 155°C. The mixture is
agitated, and the heat of reaction is allowed to bring the digestion
temperature up to approximately 200°C.

The digestion reaction is allowed to continue until the
resulting mass is a thick, gray paste which should take 2 to 4
hours. The pasty mass is cooled to 70°C and treated with about

6 to 7 parts of water to 1 part by weight of digested sand . The monazite sand ,containing substantially all of the thorium, uranium and rare earths, goes into solution, leaving the silica, rutile, zircon and unreacted monazite as a residue. The resulting monazite sulphate solution (sulphate and phosphate complexes) is stable and is very close to saturation with respect to rare earths and thorium. By raising pH of the monazite sulphate solution to a pH of 1.05, 98 to 99 per cent of the thorium content can be precipitated, whereas most of the rare earths and uranium go into the filtrate. The obtained crude thorium precipitate, is used for further purification by solvent extraction.

2.2. Alkaline method

In the caustic soda digestion process the monazite sand is treated with caustic soda containing 30 to 45 per cent sodium hydroxide. The ratio of caustic soda to monazite sand would be 3 to 1.5 by weight. Moderate agitation would be continued for 3 hours at the boiling point of the solution which varies between $140^{\circ}C$ to $170^{\circ}C$. The reaction may be represented approximately by:

$$2RE(PO_4) + 6NaOH \longrightarrow RE_2O_3 \cdot 3H_2O \text{ (or } 2RE(OH)_3) + 2Na_3PO_4$$

$$Th_3(PO_4)_4 + 12NaOH \longrightarrow 3ThO_2 \cdot 2H_2O \text{ (or } 3Th(OH)_4) + 4Na_3PO_4$$

When the reaction is complete, the reaction mass is diluted with water to a 30 per cent sodium hydroxide content and the slurry

would be heated at 100°C to 110°C for 1 hour prior to filtration to improve the filtering characteristics. This slurry would be filtered at 100°C, washed until all soluble elements were removed and dried. The filtrate contains about two-thirds of the unchanged caustic soda charged and the other one-third of trisodium phosphate whereas the hydrous metal oxide cake contains substantially the entire thorium, uranium and rare earths content of the monazite sand. For a complete recovery of the trisodium phosphate, the filtrate is heated to bring the boiling point of the solution to 137°C, corresponding to a sodium hydroxide concentration of 47 per cent. The concentrated solution is allowed to cool to room temperature, at which temperature and concentration over 95 per cent of the trisodium phosphate crystallizes out of solution and can be removed immediately by filtration.

The dissolution of the hydrous metal oxide cake from the caustic soda monazite reaction can be achieved with hydrochloric, nitric and sulphuric acid. Since quantitative dissolution of the thorium oxide fraction with nitric acid is difficult and the dissolution with sulphuric acid introduces sulphate ion which may interfere with subsequent purification, the dissolution with hydrochloric acid is preferable. The reaction may be represented as:

$$RE(OH)_3 + 3\ HCl \longrightarrow RECl_3 + 3\ H_2O$$

where RE represents the rare earths, thorium and uranium.

After the dissolution of the metal oxide cake, undissolved material in the solution is separated by filtration and thorium can

then be selectively precipitated from the acid solution by adjusting the pH of the solution to 1.05 using sodium hydroxide solution. The crude thorium hydroxide precipitate is subjected to further purification by solvent extraction whereas the filtrate is kept for the separation of rare earths and uranium.

2.3. Purification of thorium concentrates

Thorium used in atomic energy must be of very high purity. Any impurity present which acts as a neutron absorbent will seriously interfere with the formation of U^{233} from Th^{232}. The most significant neutron absorbents are the rare earths gadolinium, samarium and dysprosium, as well as the elements boron and cadmium. It has been calculated that 1 ppm of gadolinium in irradiated thorium results in a loss of U^{233} production of 0.8 per cent and that 1 ppm of samarium results in a 0.2 per cent loss of U^{233} production (7). The crude thorium precipitates from the digestion of monazite may contain up to 50 per cent rare earths and thus must be purified. The process must yield a very pure thorium concentrate and high recovery of rare earths and uranium. Three major methods of purifying thorium concentrate are solvent extraction, fractional crystallization and selective precipitation. Since the solvent extraction process can be performed continuously and can be applied to a large-scale production of very high purity thorium metal, this process is chosen

The purification of thorium by solvent extraction is per-
formed in three steps:

2.3.1. Thorium and uranium are first extracted from the
aqueous feed solution into the organic solvent phase, whereas
most of the impurities remain in the aqueous phase. It has been
found that the extraction of thorium and uranium from a nitric
acid solution using tributyl phosphate (TBP) diluted with xylene
or kerosene (8, 9, 10) as extractant provides the most satisfactory
results. The distribution coefficients for a single-stage extrac-
tion of uranium, thorium and rare earths from a 5 N nitric acid solution
using 50 per cent TBP-kerosene were found to be 5.5, 2.5 and
0.046 (8) respectively.

If the feed to the solvent extraction process is by sulphuric
acid digestion of monazite sand, both sulphate and phosphate ions
are present and adversely affect the thorium distribution co-
efficient (11). The detrimental effect of the sulphate and phos-
phate ions can be counteracted by the use of nitric acid (11),
but the tendency of solvents to be unstable at high acidities
limits the amount of compensable sulphate and phosphate ions. An
alternative method of compensating for the phosphate ion is by the
addition of ferric nitrate. However, the use of ferric nitrate as a
salting agent has so many disadvantages (12, 13) that the method
is not of practical use.

Direct extraction of thorium from the solution obtained by
sulphuric acid digestion of monazite sand using TBP (14), n-butyl

ether (14, 15), mono octyl phosphate (16) and long chain amines (17, 18) as extractants were studied, but further investigations are still required before the methods can be applied to an industrial use. Eliminating the sulphate and phosphate ions purification step before solvent extraction would effect further economic by eliminating chemical and equipment costs. The most common method for the elimination of sulphate and phosphate ions is by caustic digestion, converting thorium, uranium and rare earths into hydroxides.

2.3.2. The rare earths and impurities that remain in the thorium-rich organic phase are removed by scrubbing with fresh aqueous solution.

2.3.3. Thorium is finally stripped from the solvent into an aqueous stream.

The schematic process flow diagrams for the sulphuric acid digestion process and for the hot, concentrated caustic soda digestion process are shown in Figure 2 - 1 and Figure 2 - 2.
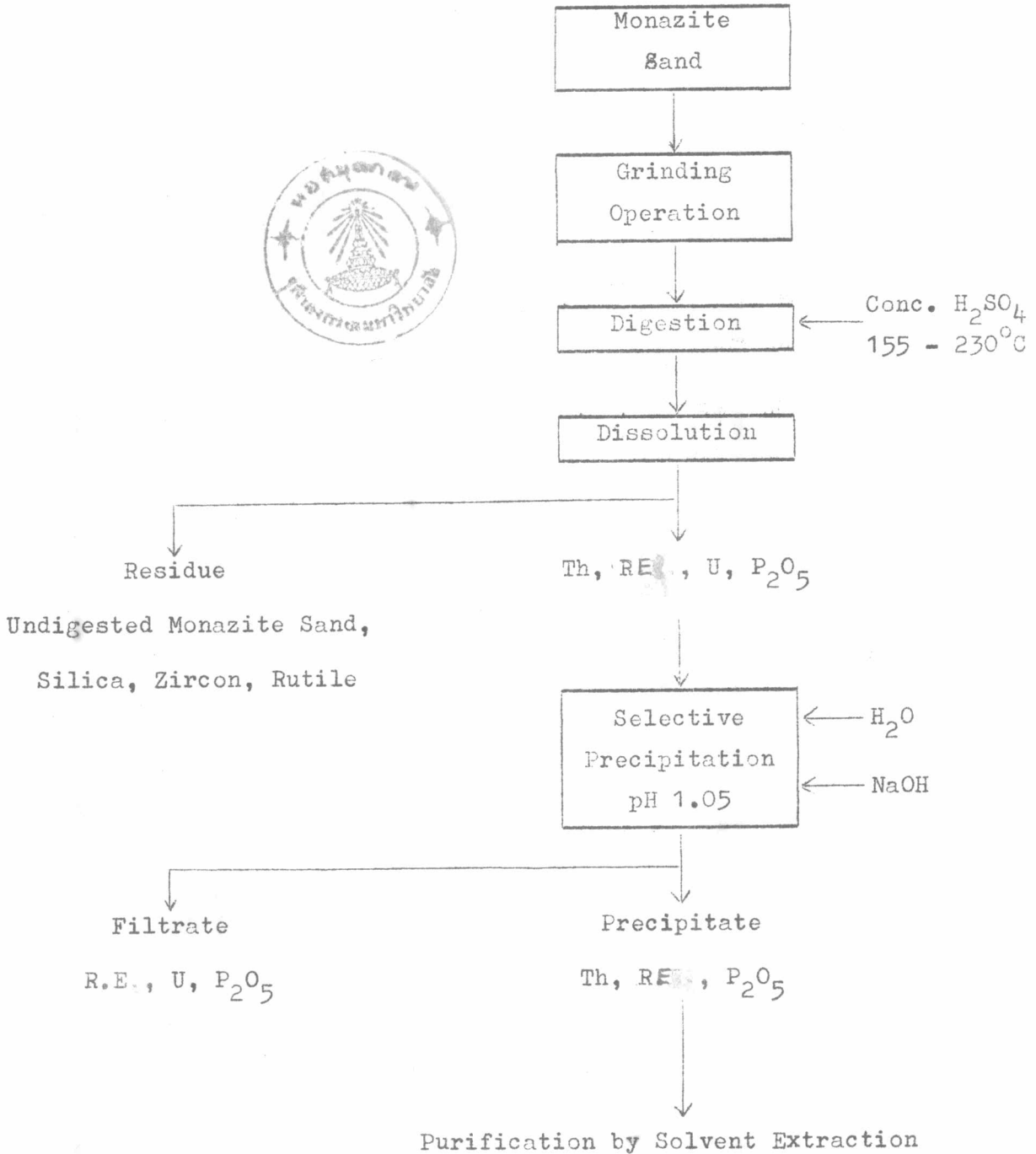
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                                    ┌─────────────────┐
                                    │    Monazite     │
                                    │      Sand       │
                                    └────────┬────────┘
                                             │
                                             ▼
                                    ┌─────────────────┐
                                    │    Grinding     │
                                    │    Operation    │
                                    └────────┬────────┘
                                             │
                                             ▼
                                    ┌─────────────────┐        Conc. H₂SO₄
                                    │    Digestion    │ ◄───── 155 - 230°C
                                    └────────┬────────┘
                                             │
                                             ▼
                                    ┌─────────────────┐
                                    │   Dissolution   │
                                    └────────┬────────┘
                             ┌───────────────┴───────────┐
                             ▼                           ▼
         Residue                              Th, RE., U, P₂O₅

  Undigested Monazite Sand,                            │
                                                       ▼
    Silica, Zircon, Rutile              ┌─────────────────┐
                                        │    Selective    │ ◄───── H₂O
                                        │   Precipitation │
                                        │     pH 1.05     │ ◄───── NaOH
                                        └────────┬────────┘
                             ┌───────────────────┴───────────┐
                             ▼                               ▼
         Filtrate                              Precipitate

      R.E., U, P₂O₅                           Th, RE., P₂O₅

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                                        Purification by Solvent Extraction
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Figure 2 - 1   Simplified schematic diagram of sulphuric acid

digestion of monazite sand and recovery of thorium.
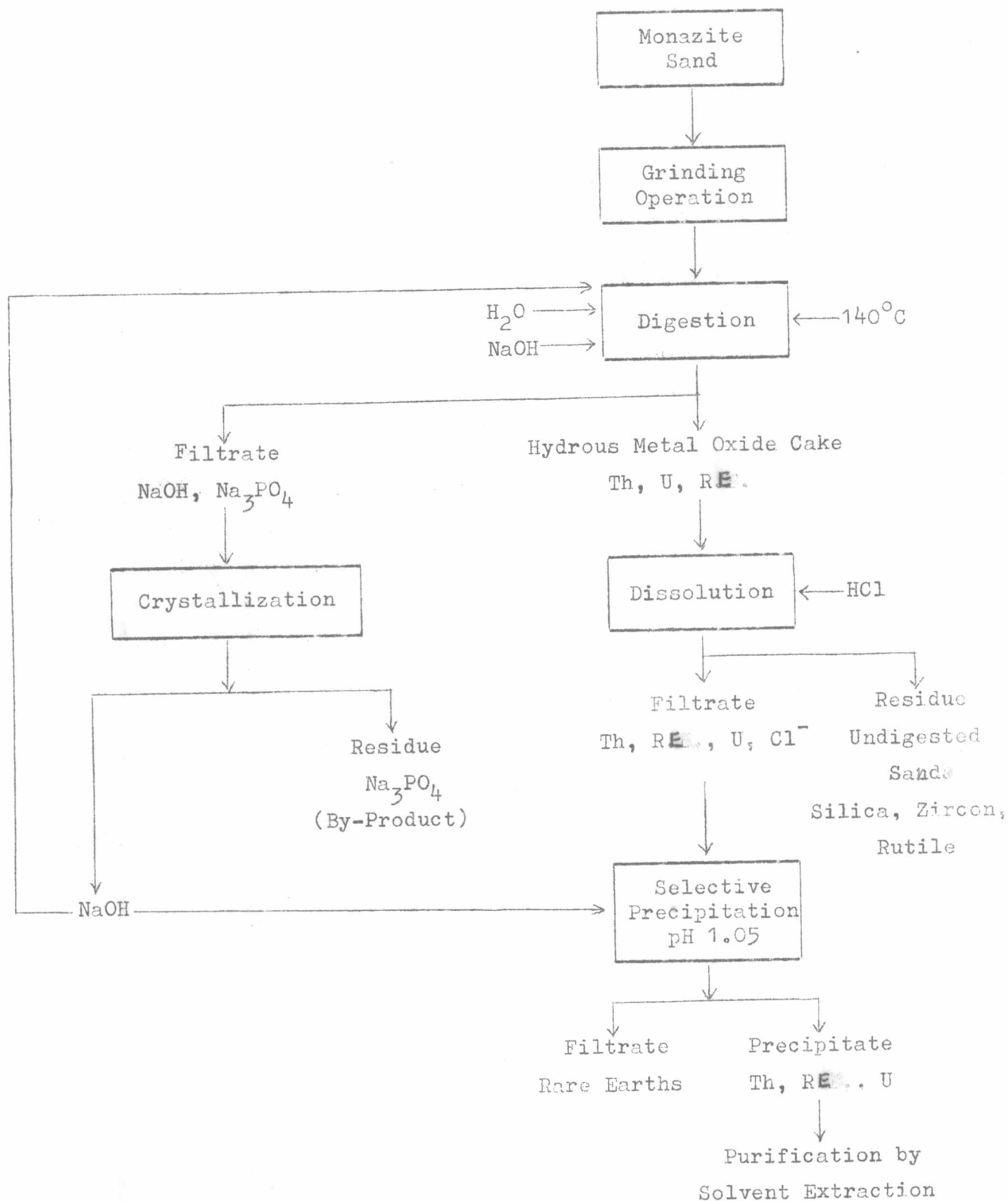
Figure 2 - 2 Simplified schematic diagram of caustic soda digestion of monazite sand and recovery of thorium.