THE DIGESTION OF THORIUM CAKE IN NITRIC ACID

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ABSTRACT

Radioactive thorium cake is produced as a waste from the monazite processing plant in Malaysia. Strategic nuclear fuel elements such as thorium and uranium can be extracted from this waste. It was found that the waste contains up to 33% and 1.4% of ThO_2 and U_3O_8, respectively.

Digestion is the first step in this extractive metallurgy process. Laboratory studies have been conducted to obtain optimum conditions for extracting thorium and uranium from the waste. Experiments were carried out by using nitric acid because of its good recovery for these elements and it also acts as the salting agent for tri-butyl-phosphate in the subsequent liquid-liquid extraction stage.

The extraction was found to be sensitive to the concentration of nitric acid. The major dissolution of both elements was obtained at an acid concentration range of 60-80%, percentage of pulp density of 40% and at temperature of 70^oC.

INTRODUCTION

Besides cassiterite, tin-tailing (or locally known as amang) is also produced from most of the Malaysian alluvial tin mines. The amang consists of various accessory minerals, some of which are of economic importance. Among these, monozite, xenotime and zircon are found to contain considerable amount of naturally occuring radioactive elements namely thorium and uranium.

Analysis of these minerals from Malaysian tin mines show that monazite, (Ce, La, Th)PO_4, contains by far a higher concentration of thorium than either xenotime (YPO_4), or Zircon ($ZrSiO_4$) (Table 1). The uranium concentration in these minerals show a different trend, xenotime is the highest among them. Monazite and zircon are the more common and abundant mineral, it is found in most of the tin districts in Malaysia.

A monazite processing plant has been established in Malaysia since 1979. The company which is a joint-venture between Malaysia and Japan operated mainly for the production of rare earth compounds. As a by-product from this process, tricalcium phosphate fertilizer is also being produced. Two types of wastes are also produced from this process, thorium and lead cakes. The production of radioactive thorium cake has led to much controversies on the plant's operation.

The thorium cake is a thick, tan-coloured slurry with a moisture content of 54%. Comparing this thorium cake with that of similar waste from Brazil and India shows that its thorium content is lower than these two countries, while the rare earths content in this sample is much higher than the others (Table 2). Little difference in thorium and rare earths may be because of the lower rare earths recovery that is registered from the Malaysian plant and these differences will minimised once a better recovery is achieved in the future runs.

Meor (1988) discussed the stages involved in the recovery of uranium and thorium. Digestion is the first step in this extractive metallurgy process. Experiments were carried out to determine the effect of temperature, digestion time, stirring speed, acid concentration and pulp density on the recovery rate of uranium and thorium from the thorium cake. The experiments were planned so that the results could be grouped to show the effect of changing a single variable while holding all the other variables constant. The results will be discussed in this paper in the same manner, insofar as the interaction among the variables permits.

Since particle size reduction has been initially carried out at the monazite plant, no further physical pretreatment is done. Nitric acid was chosen far besides its good recovery for these elements, it also acted as the salting agent for tributyl-phosphate in the subsequent solvent extraction stage.

EXPERIMENTAL

A sample of selected quantity of thorium cake was put in a 2000 ml reaction vessel. Then, solution of acid nitric at predetermined percent was added to make a slurry volume of 1000 ml. An agitator was used to mix the slurry homogeneously during the digestion. Diferent stirring speeds were employed. The digestion temperature was set at selected constant temperature by using a heating mantle.

Samples were taken from the leached slurry by using a peristaltic pump at fixed time intervals; usually 30, 60, 90 and 120 minutes. Each sample was filtered; then the filtrate and the solid were analyzed for elemental uranium and thorium compositions by using Neutron Activation Analyzer.

RESULTS AND DISCUSSIONS

The recovery percentage of the radioactive elements was determined by the following equation:

$$\% \text{ recovery} = \frac{\text{Element in solution}}{\text{Element in solution} + \text{Element in solid}} \times 100\%$$

Variation of digestion time

The dissolution of uranium and thorium from the waste was determined as a function of digestion time. As shown on Figure 1, the recovery percentage increased as the digestion time was increased. The uranium and thorium dissolutions started to level off at digestion time of 90 and 60 minutes, respectively. 90 minutes was taken as the optimum digestion period for the maximum percent recovery of uranium and thorium.

Effect of Nitric Acid Concentration

A series of tests was carried out to determine the percent of recovery as a function of nitric acid concentrations. Each test was done at 90 ^{o}C and 300 rpm for 90 minutes. Figure 2 shows the test results for 40 and 50 percent pulp densities. The major dissolution took place in the vicinity of nitric acid concentration at 60%.

Effect of Pulp Density

Pulp density was calculated by taking the ratio of thorium cake (gram) to the total volume of the slurry (ml). At constant nitric acid concentration of 60%, the effect of pulp density was determined from

Table 1: Uranium and Thorium Content in Malaysian Tin Tailing Minerals (2)

Mineral	Uranium %	Thorium %
Monazite	0.1 - 0.3	2.0 - 9.0
Xenotime	0.3 - 0.7	1.0 - 5.0
Zircon	0.2 - 0.4	1.0 - 1.4

Table 2: Comparison of Content of Thorium Cake Produced

	Country (% content)		
Content	Brazil(6)	India(1)	Malaysia
ThO_2	44.3	45 - 55	32 - 33.5
U_3O_8	1.2	1.5 - 1.8	1.1 - 1.4
$(RE)_2O_3$	15.2	10 - 15	27 - 28
$U^{-}Cl^{-}$	2.6	4 - 5	2.5
Moisture	51	5 - 10	54

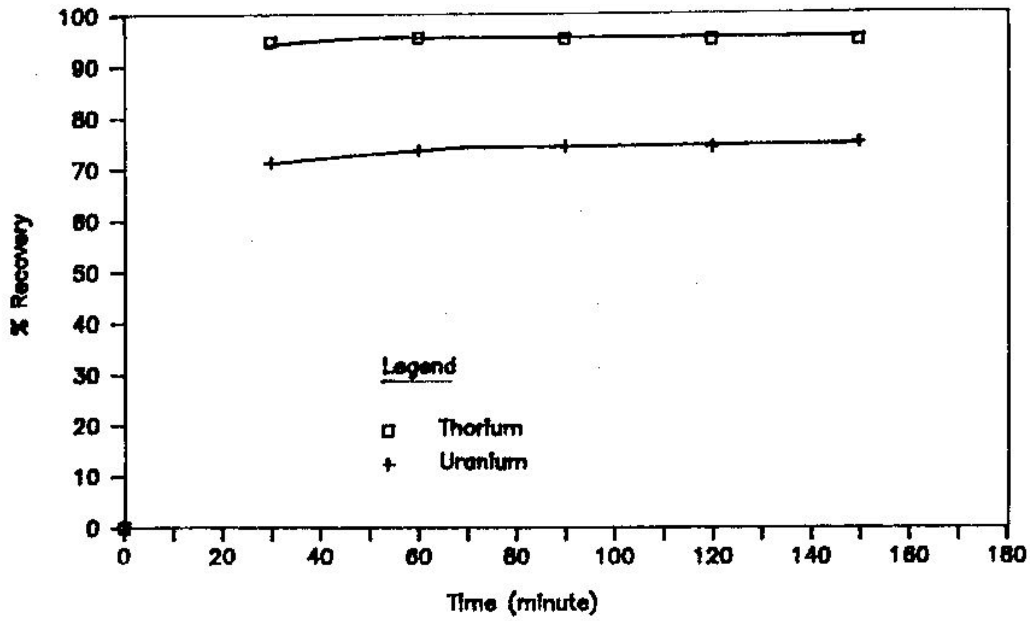

Figure 1 : Digestion Time vs Recovery at 60% HNO_3,
50% Pulp Density, RPM = 300.

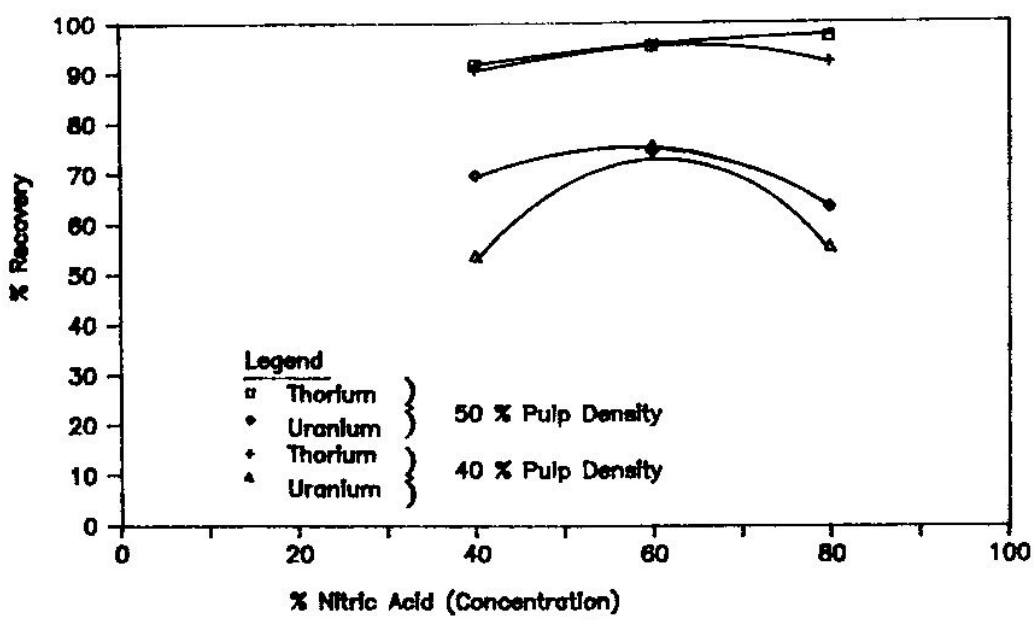

Figure 2 : Effect of Nitric Acid Concentration on Extraction
at T = 90 °C, RPM = 300 and t = 90 min.

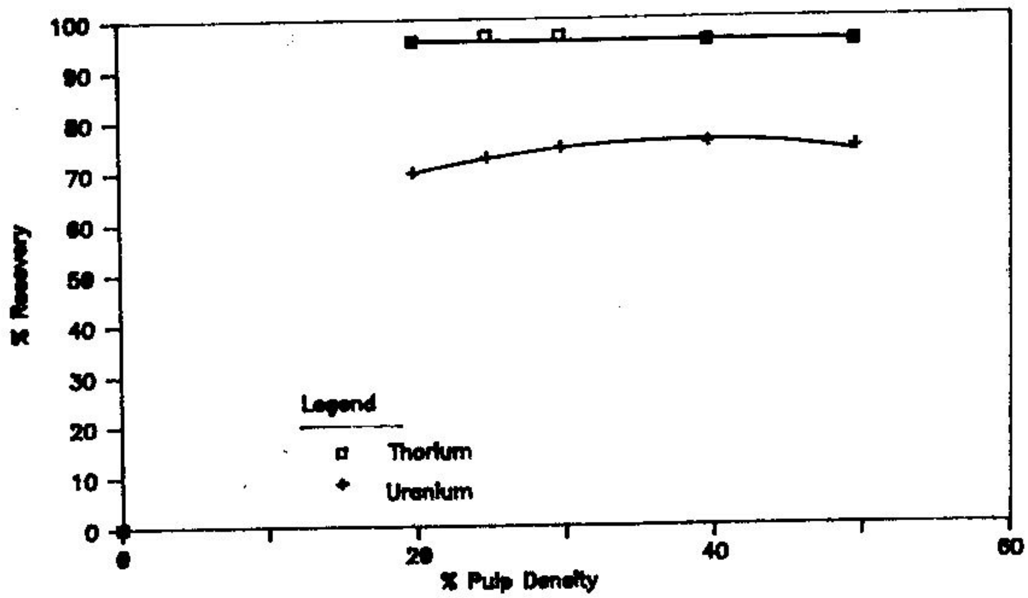

Figure 3: Effect Pulp Density on Extraction at 60% HNO_3
t = 90 min, RPM = 300, T = 90 °C

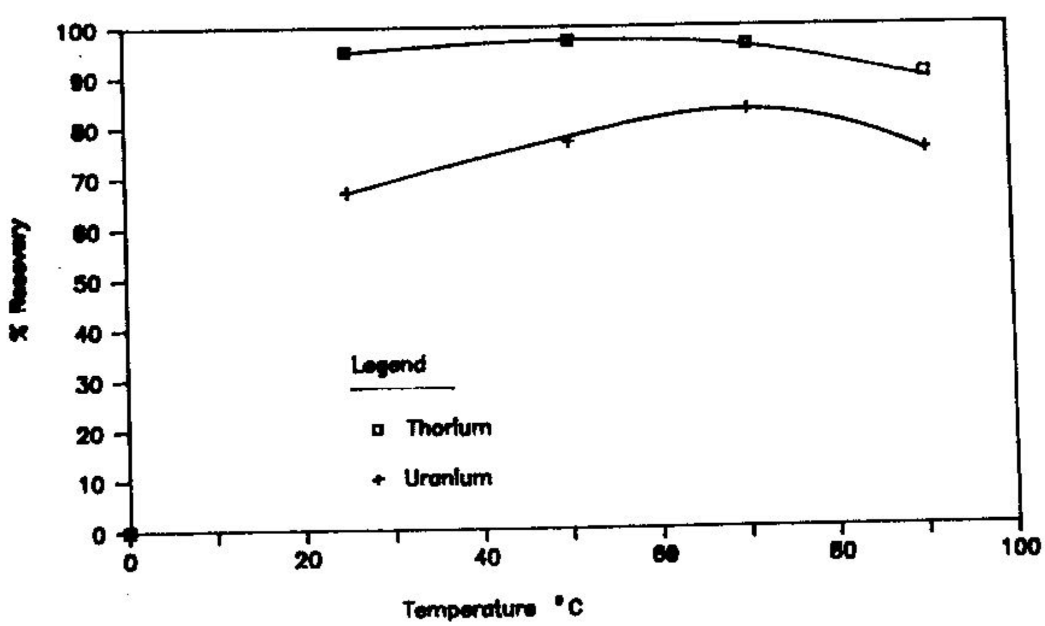

Figure 4 : Effect of Temperature on Extraction at 60% HNO_3,
RPM = 300, 30% pulp density, t = 90 min.

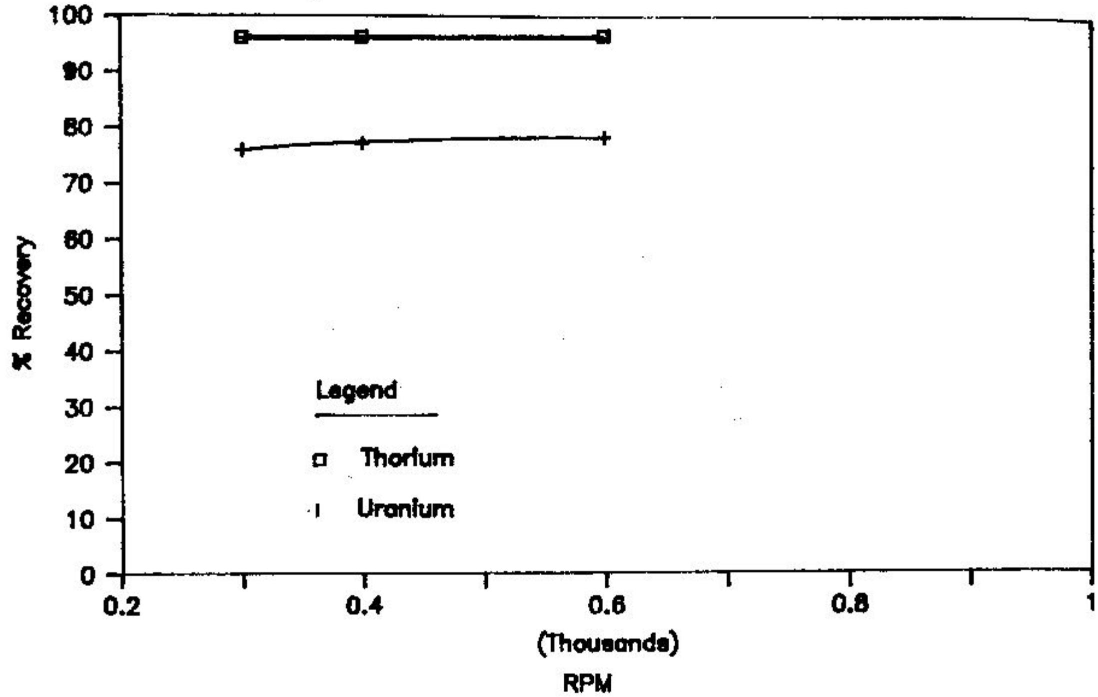

Figure 5: Effect of RPM on Extraction at 60 % HNO_3 , t = 90 min,
T = 70 ^{0} C, and 40% pulp density.

20 to 50 % pulp density. These tests were conducted at 90 °C and 300 rpm for 90 minutes. The results are illustrated in Figure 3. The percent recovery of thorium was not that sensitive to the pulp density. However the uranium dissolution was found to be optimum at 40% pulp density.

Variation of digestion temperature

Four tests were performed at different temperature of 25 °C, 50 °C, 70 °C and 90 °C. As shown in Figure 4 the effect of temperature on the thorium dissolution was very little. However the percent recovery of uranium was effected by the temperature. From Figure 4, the optimum temperature is about 70 °C.

Effect of Stirring Speed

Three tests were done at stirring speed of 300, 400 and 600 rpm under the optimum conditions: digestion time = 90 minutes; percent of nitric acid = 60% ; temperature = 70 °C; and pulp density = 40%. The effect of stirring speed on the percent recoveries of both uranium and thorium were insignificant as shown in Figure 5. Nevertheless strirring speed of 600 rpm is taken as the optimum condition.

CONCLUSIONS

A method of treating thorium cake with nitric acid to recover the uranium and thorium content was developed. Optimum conditions for carrying out the treatment were determined. Results from Figures 1-5 show that uranium and thorium can be recovered up to 78 and 96 per cent, respectively, at the optimum conditions.

The method developed can be used to reduce the content of the radioactive elements in the thorium cake, thus permitting safe disposal of the waste. In addition, the recovered uranium and thorium can be utilised for various purposes deems necessary by the higher authority.

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