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RECOVERY OF URANIUM FROM MALAYSIAN NON-CONVENTIONAL SOURCES

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ABSTRACT

The recovery of uranium from non-conventional sources has its importance in the security of nuclear fuel supply as well as producing a more value-added product to the contaminated source. In this paper, uranium is recovered both by developing a hydrothermal process as well as using the removal method. Developing hydrothermal process involves using high uranium concentrated starting material such as xenotime and thorium hydroxide waste produced from the monazite cracking process. Oxalate separation enable to produce a better uranium and thorium separation from the yttrium in xenotime as compared to the hydroxide precipitation. Also, a solvent extraction stage was included to separate the uranium from the thorium in the process using thorium hydroxide waste. The removal method involves using selective leaching for minerals with lower uranium content such as zircon. A better removal for uranium and thorium in zircon is achieved when a heat treatment process was done prior to the leaching stage. White zircon mineral was produced after this treatment and its quality meets the requirement for white ceramic opacifier and glaze.

ABSTRAK

Perolehan semula uranium dari sumber bukan lazim adalah mustahak bagi keselamatan didalam pembekalan bahan api nuklear serta menghasilkan produk sampingan yang bernilai tinggi dari sumber yang berkontaminasi. Kertas kerja ini menunjukkan bagaimana uranium telah diperolehi menggunakan kaedah-kaedah hydrothermal dan pelucutan. Bagi proses hydrothermal bahan permulaan yang mempunyai kandungan uranium yang tinggi seperti xenotime dan sisa thorium hidroksida yang dihasilkan dari kilang pemprosesan monazite. Teknik pemisahan oksalat boleh memisahkan uranium dan thorium dengan lebih baik berbanding dengan menggunakan teknik pemisahan hidroksida. Kaedah pelucutan pula melibatkan teknik nyahlarut pilihan bagi mineral-mineral yang mengandungi kandungan uranium dan thorium yang rendah seperti zircon. Pelucutan uranium dan thorium yang lebih baik bagi zirkon diperolehi apabila kaedah pemanasan dilakukan sebelum nyahlarut. Zirkon yang berwarna putih boleh dihasilkan dari rawatan ini dan kualitinya memenuhi criteria bagi opacifier dan licau.

Keywords*:* uranium, recovery, xenotime, thorium hydroxide, zircon, selective leaching, hydrometallurgy

INTRODUCTION

Due to its strategic importance, uranium has also been recovered from non-conventional sources. Examples of this include the recovery of uranium from sea water by Japan, recovery of uranium from coal ash in China and Hungary, recovery of uranium from phosphate and phosphoric acid in USA, Canada, Spain, Belgium, Israel and Taiwan (IAEA, 2001). The Indian Rare Earth Ltd., a government company in India dealing with radioactive minerals also produced uranium from thorium hydroxide produced from monazite cracking, zircon, phosphate as well as columbite-tantalite mineral (Mukherjee, 2004). Malaysia, being once the main tin producing country in the world, also is a major producer of rare earths and other heavy minerals. These minerals are obtained as by-product from the tin-mining activity. *Amang*, the local term used for the mixed heavy minerals, varies in its mineral content from one tin district to another.

Xenotime (YPO_4), which is also classified as a radioactive mineral like monazite and zircon under the Malaysian Atomic Energy Licensing Act (Act 304), is a highly enriched yttrium phosphate mineral. It had been estimated that the local xenotime mineral consists of about 30-40% yttrium and it is recovered in specific areas such as the Kinta valley in Perak and Gambang in Pahang (Dahan A.R., 1990). Besides containing a higher content of this heavy rare earth elements notably yttrium, xenotime also differs from monazite in the content of their naturally occuring radioactive elements. Analysis of different samples from Malaysian xenotime show that it contain about 0.96 – 1.24% uranium and 0.68 - 0.75% thorium (Meor Yusoff M.S., 1994). It is also the only local mineral that has higher uranium content than thorium. Another rare earth mineral that is predominantly present in amang is monazite. Monazite is a light rare earth phosphate with significant amount of thorium present in it. The mineral was initially recovered for its thorium content for in the application of incandescent lamp but this was subsequently replaced for the recovery of its rare earths. Thorium hydroxide waste was produced by the Asian Rare Earth (ARE) plant in Lahat, Perak. The plant involved cracking of monazite with caustic soda solution to produce rare earths and phosphate products. Rare earths are produce in two different groupings, the light and medium-heavy rare earths, obtained after the solvent extraction process.

The characteristics of Malaysian zircon differ from one source area to another due to the differences in their impurities content, shape and particle size. Iron and titanium impurities in the minerals play an important role in the determination of these grades. As shown in Table 1, the better quality premium grade zircon has lower impurity content than the standard grade.

Table 1: Minimum content of different zircon grades (Skillen A., 1992).

Zircon Grade	$ZrO_2 + HfO_2$	Fe_2O_3	$U_3O_8 + ThO_2$
Premium	66.0%	0.05%	450ppm
Standard	65.0%	0.15%	450ppm

The presence of these elements in zircon may be due to the following sources (Hart K.P., *et al*, 1993):

a. Contamination with radioactive minerals which are also present in *amang* such as monazite and xenotime, as free grains or inclusions,

b. Adsorption of these radioactive elements on the surfaces of lattice defects or crystal and grain boundaries, and

c. Incorporation of thorium and uranium into the concentrated minerals by direct cation substitution at the time of formation in their original host rocks.

EXPERIMENTAL

Two different methods were applied for the recovery of uranium from local xenotime, thorium hydroxide waste and zircon. A hydrometallurgy process was developed separately for the xenotime and thorium hydroxide waste. In the xenotime case, cracking of the mineral was done by the alkaline fusion method where the mineral was first mixed with sodium hydroxide pellets and then fused in a furnace. Several parameters were studied which includes the fusion temperature, time and also particle size of the mineral. Optimum fusion temperature was obtained by varying the temperature used for the fusion process and in the same process the optimum fusion time was determine. Effect of particle size was determined by grinding the mineral to 125 microns using the Fritch pulverisette and its appropriate sieves. After the fusion process, a fused complex is form and this will undergo washing to remove the phosphate component. The yttrium component will then be place in a leaching reactor to be leached by dilute HCl. Yttrium will then be extracted by the precipitation technique where yttrium hydroxide will be precipitate by the addition of ammonia on the yttrium chloride solution. Besides this, anther precipitating method by the oxalate technique was also tried and this was compared with the earlier method. A selective precipitation was also done on the solution to remove uranium and thorium which are present in the leach solution. Yttria was obtained by calcining the yttrium hydroxide or oxalate at 900^{o}C.

The method for recovery of uranium from thorium hydroxide waste involved dissolution of the thorium waste in 4M HCl at elevated temperature. This was then followed by precipitation of rare earths as oxalate and the mixed thorium and uranium in the form of hydroxide. The uranium and thorium concentrate was then dissolved in nitric acid and followed by a single stage solvent extraction using tributyl phosphate diluted in kerosene. Thorium is then recovered in the form of thorium oxalate while the uranium as ammonium diuranate.
For the selective leaching of uranium from zircon mineral, HCl of different molarities were used as the leaching solution. Heat treatment was also used prior to the leaching process and different heating temperatures ranging from 400 – 1000 ^{o}C were tried to determine the optimum uranium removal effect. Other parameters studied include temperature and also particle size.

RESULTS AND DISCUSSION

a. Uranium recovery from xenotime

Alkaline fusion is a well-known mineral processing technique that had been used in other minerals notably in the production of zirconium chemicals from zircon. Sodium hydroxide was chosen as its fusion agent due to its relatively lower fusion temperature requirement and also cheaper than most of the other chemicals. In this process, sodium yttrium phosphate complex will be formed if sufficient temperature and fusion agent are used. It also produces an important by-product, trisodium phosphate which is commonly used as a fertilizer. The effectiveness of this fusion process was measured by the value of degree of reaction (α) and this was calculated from the following equation;

$$\alpha = \frac{\text{Concentration of yttrium in yttria}}{\text{Concentration of yttrium in xenotime}}$$

One of the factors influencing the efficiency of this process is the fusion temperature. In this study fusion temperature are varies from 200°C to 450°C (see Fig. 1). The value of degree of reaction tends to increase linearly as the temperature increases from 200 to 300°C. As the fusion temperature increases further to 350°C only slight increase is registered while further increase does not show any noticeable changes. Comparison on the effect of particle size of the starting material was also done. The original xenotime Kampar sample seems to have mainly a particle size of 150-210 microns and this was then compared to the result obtained by using grinded samples of 125 microns particle size. Results from this study show that there is not much of differences in degree of reaction for the original and grinded samples. The ratio of xenotime to sodium hydroxide also influences the result of this process where the value degree of reaction tends to increase drastically with the initial ratio till a value of 1:2 was used. On further increase in sodium hydroxide does not show much effect on the degree of reaction but analysis of the final product tends to have higher sodium content.

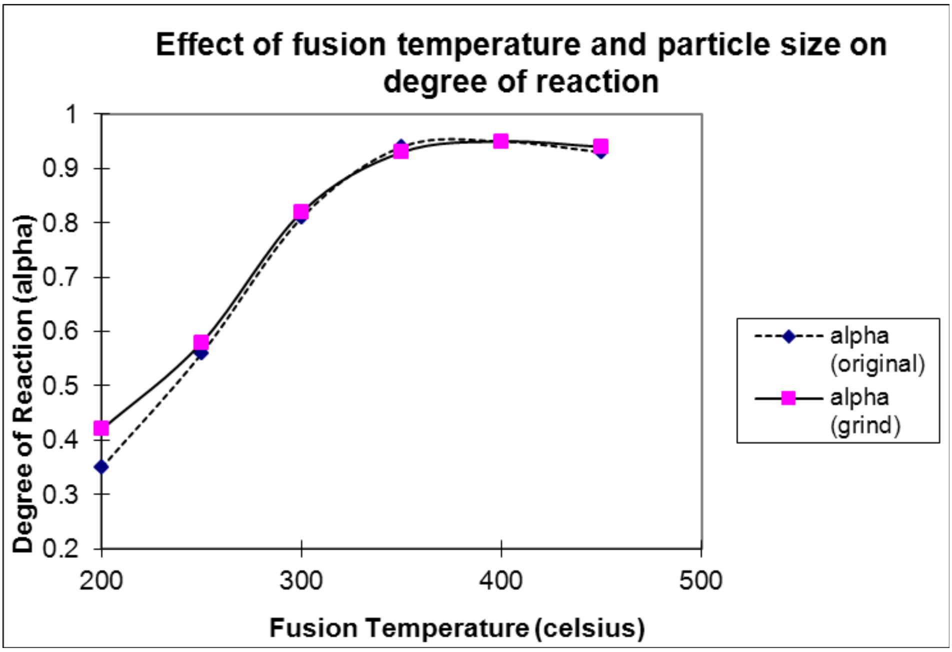

Figure 1: Effect of fusion temperature and particle size on degree of reaction

After the fusion process, the sodium yttrium phosphate complex formed undergoes a washing process to separate the yttrium from the phosphate. This was done by washing the complex with warm water where the soluble phosphate will dissolve in the solution while yttrium which is not soluble will be present as a solid. Trisodium phosphate (50.8% phosphate) is produce by heating and crystallizing the phosphate solution. Analysis of the phosphate product shows that it has a relatively low rare earths, uranium and also thorium. This implies that a good separation process had been achieved between these elements and phosphate during the washing stage.

The next stage of the process is the hydrochloric acid leaching of the yttrium complex and this was carried out in a leaching reactor. Using a 50% HCl solution, leaching efficiency of 98.5% was obtained for yttrium, 98.4% for dysprosium, and 98.6% for erbium, 98.7% for ytterbium, 98.1% for uranium and 98.6 for thorium. These results show a relatively high recovery of the major elements obtained from the alkaline fusion process. If yttria is to be produced directly from this solution, a high concentration of impurity will be present. In making this product marketable, present of significant radioactive elements in the product should be reduced. This is to comply with the regulation imposed by most of the importing countries. Selective precipitation was applied in the next stage of the process to remove uranium and thorium from the final product. As shown in Table 3, yttria with lower radioactive impurity can be produced after this stage. The application of selective precipitation also helps in improving the purity of the yttria product. Another precipitating technique that had been tried was by precipitating the yttrium solution as yttrium oxalate after the selective precipitation stage. As can be seen from product yttria3, the purity of the product tends to improve further by using this precipitation technique. Uranium was then recovered together with thorium as hydroxide and analyisis of this concentrate shows that it has a purity of about 40%. The uranium concentrates needs to further undergo a purification stage using multistage solvent extraction to produce pure uranium for nuclear fuel.

Table 2: Elemental composition of different yttria products

Conditions	Yttria1	Yttria2	Yttria3
	hydroxide and without selective precipitation	hydroxide and with selective precipitation	oxalate with selective precipitation
total rare earths	53.78	58.46	66.27
yttrium	37.22	39.25	42.45
uranium	0.28	0.09	0.07
thorium	0.21	0.04	<0.01

b. <u>Uranium recovery from thorium hydroxide waste</u>

Thorium and uranium that is prominent in the monazite mineral is produce as a waste from the process and the table compares the content of this thorium hydroxide waste to similar waste produced in Brazil and India (see Table 3 below).

Table 3: Thorium hydroxide content from Brazil, India and Malaysia

Content	Brazil	India	Malaysia
Thorium	44.3%	45.0 – 55.0%	32.0 – 33.5%
Uranium	1.2%	1.5 – 1.8 %	1.1 – 1.4%
Rare earths	15.2%	10.0 – 15.0%	27.0 – 28.0%

As can be seen from the above table, thorium hydroxide produced from the Malaysian plant has much lower thorium content than that produced in Brazil and India (Hawkins K.D. and Aral H., 1995). Also another significant different is the higher rare earth content in the thorium hydroxide. The uranium content is almost similar in the three different plants with a slight higher content produced from the India plant. A hydrometallurgy process was developed to produce thorium uranium as well as recovering of the rare earths from the Malaysian thorium hydroxide. The process involves the leaching of rare earths by HCl and precipitated it in the form of rare earth oxalate. Uranium and thorium present in the residue will then be leached in HNO_3 and followed by separation using a single stage solvent extraction. Thorium oxalate of 97.0% ThO_2 purity and 49.0% U_3O_8 purity for the yellow cake were obtained for these two radioactive elements.

c. Uranium recovery from zircon

The project was initiated as a response to the need of using low grade local zircon for the Malaysian zircon plant at Senawang, Negeri Sembilan for white ceramic opacifier and glaze. Analysis was done on different local zircon samples and the result is as that shown in Table 4 below.

Table 4: Impurities content in different Malaysian zircon

Zircon sample	Uranium (%)	Thorium (%)	Iron (%)
Puchong	0.06	0.16	0.11
Dengkil	0.08	0.16	0.09
Lahat	0.06	0.18	0.08
Kampar	0.03	0.13	0.08
Bidor	0.07	0.15	0.08

Malaysian zircon are relatively of the lower grade with most contain a higher uranium and thorium content than maximum permissible value. The iron content in this zircon mineral is also higher that that required for the making of white opacifier and glaze. Initial study shows that uranium and thorium present in zircon may be due to the replacement of zirconium ion (Zr^{4+}) by the U^{4+} and Th^{4+}. This replacement may happen because both of these actinide elements have the same oxidation state with the Zr^{4+}. Furthermore the ionic radius of Zr^{4+} (1.09Å) is quite close to the two radioactive elements, $U4^{+}$ (1.00Å) and Th^{4+} (1.05Å) (Hart K.P., *et al*, 1993). Thus uranium and thorium in the zircon sample may be present on both the mineral surfaces through the absorption process as well as inside the crystal lattice through the cation replacement process. The task of removing these radioactive elements especially those found in the crystal lattice is more difficult and challenging than those present on the surface.

Chemical leaching technique was found to be a cost effective and reliable method for lowering the iron content of zircon. This technique has been applied commercially in Australia by a mining company, named Westralian Sands Ltd (Skillen A., 1992). Previous hydrometallurgical studies also showed that, significant amounts of uranium and thorium can also be removed by using the same technique (Eyal Y. and Olander D.R., 1990). Figures 2 and 3 below show the graphs of uranium and thorium leaching carried out with and without heat treatment.

An important parameter that determines the effectiveness of a leaching process, calculated based on the percentage of element leached can be represented as follows;

$$\text{Percentage (\%) of element leached} = \frac{C_o - C_x}{C_o} \times 100$$

where,

C_o = initial element concentration in zircon

C_x = element concentration in zircon at leaching period

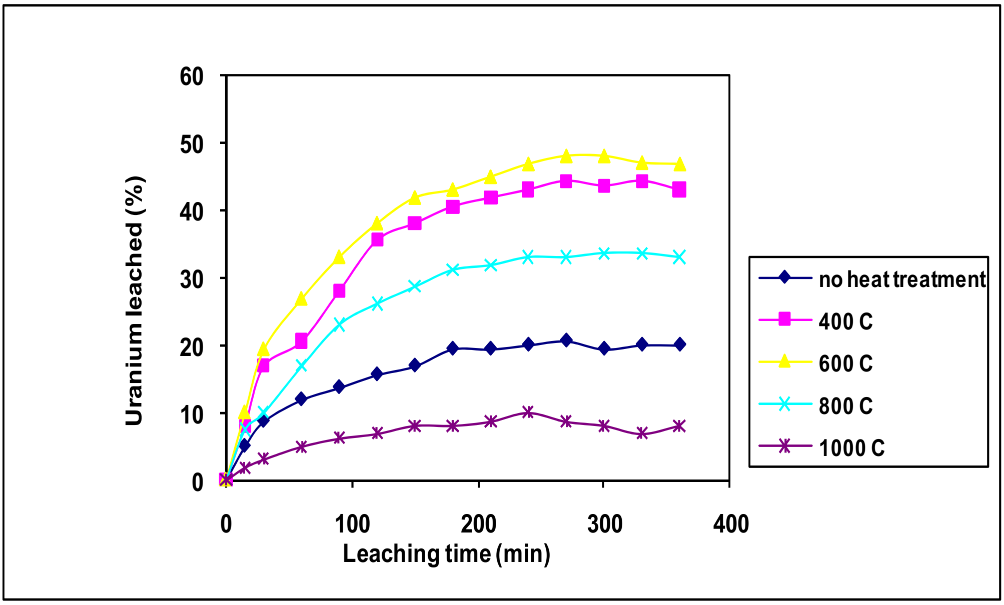

Figure 2: The effect of heat treatment on uranium leaching of zircon sample

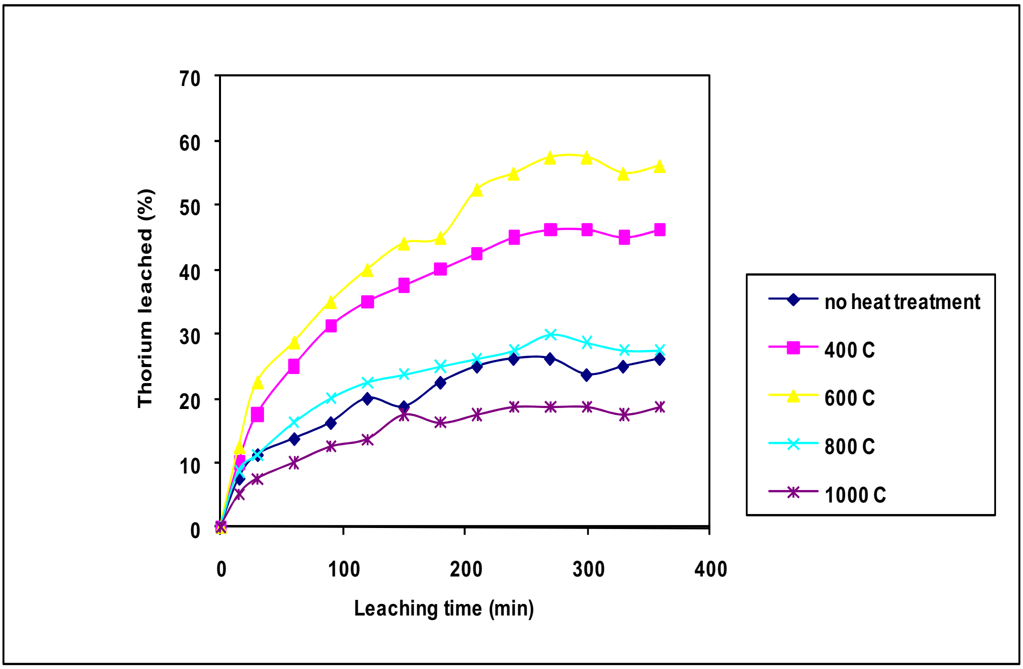

Figure 3: The effect of heat treatment on thorium leaching of zircon sample

In this study, an initial run was conducted using zircon sample that has not undergone any prior heat treatment process. The results as shown in Figures 2 and 3 give maximum percentage elements leached of 20.6% and 26.2% for uranium and thorium, respectively for the zircon sample that is not heat treated. Both results were obtained after a leaching period of 270 min. When heat treatment was applied to the zircon sample, a drastic improvement on value of leaching efficiency was obtained. By using a heat treatment of 400^{o}C, the leaching efficiency of these radioactive elements increases - uranium registers a maximum value of 48.1% and thorium achieves a maximum value of 48.7%. The leaching efficiency for these elements was further improved when a higher heat treatment temperature of 600^{o}C was applied. But further increases in the treatment temperature resulted in drastic decreases in the values as shown by Figure 4.

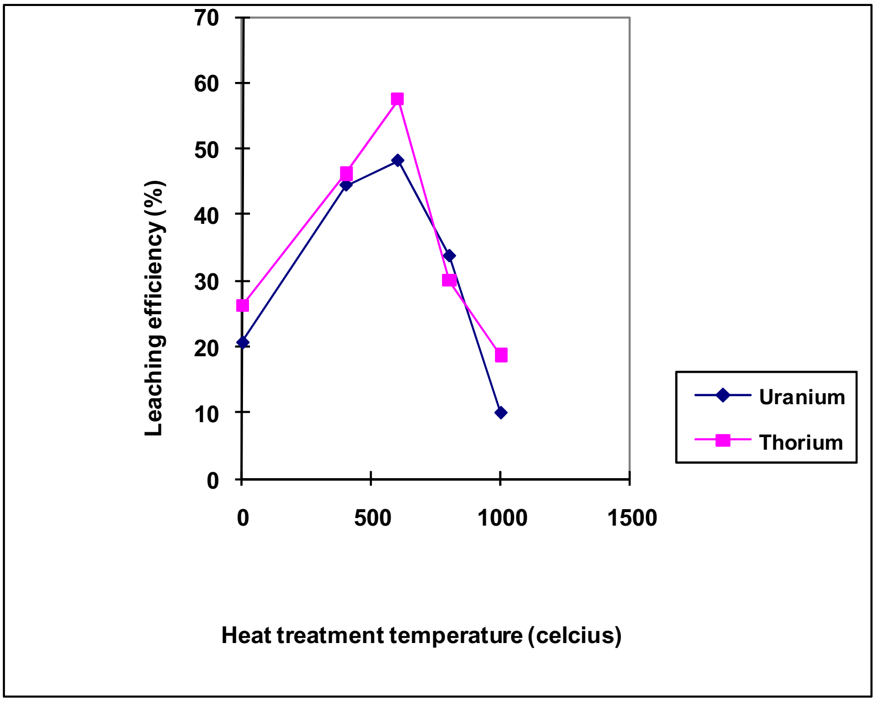

Figure 4: The effect of heat treatment on leaching efficiency of uranium and thorium

Improvement in the leaching efficiency might be due to the changes in oxidation states and crystal properties, occurred in the mineral. Leaching efficiency of radioactive element such as uranium is better if it is in the U^{6+} state compared to the U^{4+} state. The heat treatment process provides the energy required for the conversion to the higher oxidation state of uranium. The leaching capability of untreated zircon might also be related to several mineralogical factors such as textural relationships, fractures or porosity and impurities, present in the solid solution which also improve the rate of leaching. As shown in Figure 5, microfractures were common in the zircon sample. The heat treatment process enabled further formation of these fractures and resulted in its enlargement. This would increase the particle reactivity and also their absorption and diffusion processes. As the rate of a leaching process is dependent on both the absorption of the solvent into the mineral, and its diffusion of the elements into the solution, therefore the creation and enlargement of microfractures would help in enhancing the rate of leaching of these elements.

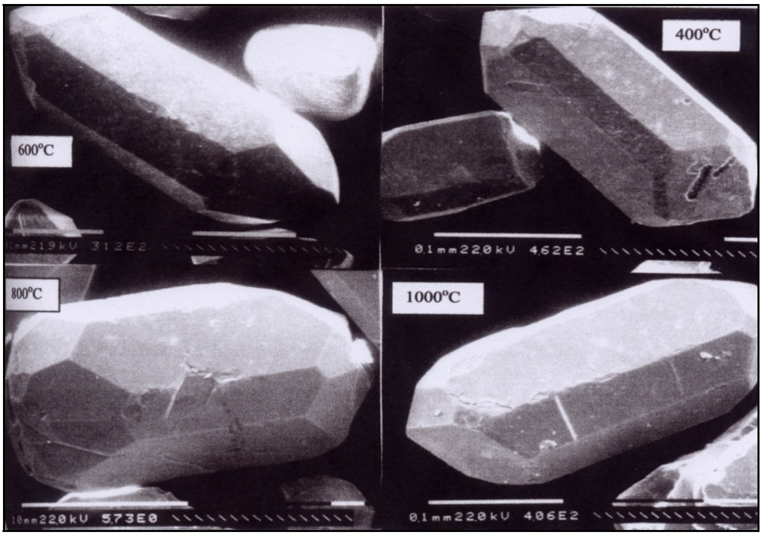

Figure 5: SEM micrographs of zircon taken under various heating temperatures

The SEM micrographs for zircon samples heat-treated at 400° and 600°C show an increase in the number of pores present on their surfaces. But further increase in the treatment temperature, decreased the number of pores. The reason for the reverse results obtained for temperatures higher than 600°C might be attributed to the crystalline effect of the mineral. Uranium and thorium, present in crystal lattice tend to undergo a decay process and this will result in the production of recoil α particles (Ewing R.C., et al, 1988). The recoil α particles could form tracks on the crystal lattice and this would eventually cause the crystal lattice to become less crystalline or metamict.

One of the important chemical properties of metamict zircon is that it is more susceptible to chemical attack than a crystalline zircon (Hart K.P., *et al*, 1993). It was reported that fully metamict zircon has a leaching rate of two orders of magnitude, higher than that of a crystalline zircon. Heating of the metamict zircon was cited as a method of reversing the radiation damage due to the presence of the radioactive elements. But as mentioned by Ewing et al. (1988), crystal changes of the metamict zircon can only happen if the temperature is above 650°C. Thus a lower leaching efficiency was registered for higher heat treatment temperatures. At the treatment temperature of 800°C, the leaching efficiencies of uranium and thorium were lowered to 33.7% and 30.0%, respectively. When zircon was further heated up to 1000°C, a much lower leaching efficiency was obtained. The leaching efficiencies at this temperature were 10.0% and 18.75% for uranium and thorium, respectively. The leaching process does not only removed uranium and thorium but also the iron contaminant in the zircon mineral. At its optimum conditions, the selective leaching process enables to leach 71.5% of iron from zircon and hence the mineral quality that made it possible to be used as white opacifier and glaze. This will help in utilizing the local low quality zircon for the Malaysian zircon plant.

CONCLUSION

Two methods are used to recover uranium from Malaysian non-conventional sources. The first method is by developing a hydrometallurgical process such as that for xenotime and thorium hydroxide waste. A hydrometallurgical process with solvent extraction stage gave higher uranium purity. The second method involved the removal method where uranium is removed by using the selective leaching technique. Effectiveness of uranium being leached is much depended on the heat treatment stage prior to the leaching stage.

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REFERENCES

Dahan A.R., 1990, Recovery and production of ilmenite, xenotime, monazite and zircon from amang of the tin mining industry in Malaysia, Presented at *Seminar on Radiation Protection for Radioactive Mineral Processors,* 22-23 May 1990, Kuala Lumpur

Ewing R.C. Chakoumakos B.B., Lumpkin G.R., Murakami T., Greegor R.B. and Lytle F.W., 1988, Metamict minerals : Natural analogues for radiation damage effects in ceramic nuclear waste forms, *Nuclear Instrument and Methods in Physics Research*, *Section B*.32(1-4): 487-497

Eyal Y. and Olander D.R., 1990, Leaching of uranium and thorium from monazite: I. Initial leaching*, Geochemica et Cosmica Acta*. 54: 1867-1877

Hart K.P., Day R.A., McGlinn P.J., Levins D.M. and Stanojevic R., 1993, Removal of radioactivity from mineral sands products, *Proceedings of the XVIII International Mineral Processing Congress*, Sydney, Australia, 23-24 May 1993, Australasian Insitute of Mining and Metallurgy, Melbourne. 1245-1251

Hawkins K.D. and Aral H., 1995, Metamict zircon: Is its importance understood? Presented at *Zircon 95*, 10-12 May 1995, Munich

IAEA, 2001, Recovery of uranium from non-conventional sources, International Atomic Energy Agency, Vienna

Meor Yusoff M.S., 1994, Analysis of thorium and uranium in Malaysian samples by using EDXRF, disampaikan di Seminar Kebangsaan sinaran Bahan Radioaktif Tabii dalam alam sekitar, K.Lumpur, 17-18 Okt. 1994

Mukherjee, 2004, The role of IREL in the Indian Nuclear Energy Programme, Journal of Nuclear Power, vol. 18 no. 2-3, pp. 81-83

Skillen A., 1992, Zircon: Producers gritting their teeth, *Industrial Minerals*, September 1992: 45-51