COMPREHENSIVE EXTRACTION OF THORIUM, URANIUM, RARE EARTHS AND PHOSPHATE FROM MALAYSIAN XENOTIME AND MONAZITE

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BANGI, SELANGOR
• The radioactive RE minerals in Malaysia
• Mid-stream RE activities
• Radioactive waste issue and method employed
• Malaysian Thorium and RE programmes
• Project Activities
• Concluding Remarks
Heavy minerals in different Amang samples

<table>
<thead>
<tr>
<th>Minerals</th>
<th>% content in Amang samples from different localities</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kinta, Perak</td>
</tr>
<tr>
<td>Zircon</td>
<td>8.0</td>
</tr>
<tr>
<td>Monazite</td>
<td>1.0</td>
</tr>
<tr>
<td>Xenotime</td>
<td>0.5</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>61.5</td>
</tr>
<tr>
<td>Rutile</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Quartz</td>
<td>20.0</td>
</tr>
</tbody>
</table>
BENEFICIATION OF TIN BY-PRODUCT MINERALS

AMANG

TABLEING – gravitational separation to separate the “light” from the “heavy” minerals

“LIGHT” FRACTION

“HEAVY” FRACTION

DRYING – to get rid of the moisture and loosen the grains

MAGNETIC SEPARATION – to separate the magnetic from the non-magnetic minerals

NON-MAGNETIC FRACTION
- Cassiterite
- Zircon
- Quartz
- Rutile
- Pyrite

MAGNETIC FRACTION
- Ilmenite
- Monazite
- Xenotime
- Tourmaline
- Garnet

HIGH TENSION SEPARATION – to separate the conductive from non-conductive minerals by electrostatic means

CONDUCTIVE FRACTION (Thrown fraction)
- Usually dark/black minerals
  - Ilmenite
  - Tourmaline
  - Garnet

NON-CONDUCTIVE FRACTION (Pin fraction)
- Usually lightcoloured minerals
  - Monazite
  - Xenotime

MAGNETIC SEPARATION – to separate the more magnetic from the less-magnetic minerals

LESS MAGNETIC FRACTION
- Monazite

MORE MAGNETIC FRACTION
- Xenotime
MONAZITE VS XENOTIME MINERALS
<table>
<thead>
<tr>
<th>YR</th>
<th>MONAZITE</th>
<th>XENOTIME</th>
</tr>
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<tr>
<td></td>
<td>HS CODE: 2612.20.100</td>
<td>HS CODE: 2530.90.100</td>
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<td>EXPORT</td>
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<td></td>
<td>IMPORT</td>
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</tr>
<tr>
<td></td>
<td>TONNE S</td>
<td>TONNE S</td>
</tr>
<tr>
<td></td>
<td>RM'00</td>
<td>RM'00</td>
</tr>
<tr>
<td>-----</td>
<td>----------------------------</td>
<td>----------------------------</td>
</tr>
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<td>2011 (p)</td>
<td>2209 8490 39 154</td>
<td>362 5536 124 469</td>
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<td>2010</td>
<td>630 2675 0 0</td>
<td>306 1667 80 163</td>
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<tr>
<td>2009</td>
<td>105 385 0 0</td>
<td>0 0 3 141</td>
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<tr>
<td>2008</td>
<td>69 696 0 0</td>
<td>48 354 453 198</td>
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<tr>
<td>2007</td>
<td>398 1718 0 0</td>
<td>200 1163 3 13</td>
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<td>2006</td>
<td>395 711 0 0</td>
<td>37 145 0 0</td>
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<tr>
<td>2005</td>
<td>33 46 0 0</td>
<td>0 0 0 0</td>
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<tr>
<td>2004</td>
<td>336 416 0 0</td>
<td>2 65 0 0</td>
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<tr>
<td>2003</td>
<td>1075 1122 0 0</td>
<td>20 47 143 317</td>
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<td>2002</td>
<td>840 952 0 0</td>
<td>0 0 13 1396</td>
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<tr>
<td>2001</td>
<td>700 971 0 0</td>
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<tr>
<td>2000</td>
<td>1225 1366 0 0</td>
<td>0 0 0 0</td>
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<tr>
<td>1999</td>
<td>4245 1672 0 0</td>
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<td>1998</td>
<td>564 726 0 0</td>
<td>0 0 11 5</td>
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<td>1997</td>
<td>1170 871 0 0</td>
<td>0 0 10 8</td>
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<td>1996</td>
<td>1033 844 0 0</td>
<td>0 0 0 0</td>
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<td>1995</td>
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<td>0 0 0 0</td>
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<td>1994</td>
<td>178 127 0 0</td>
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<td>1993</td>
<td>30 116 0 0</td>
<td>0 0 0 0</td>
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<td>1992</td>
<td>0 0 119 142</td>
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<td>1991</td>
<td>0 0 824 912</td>
<td>0 0 6 7</td>
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<td>1990</td>
<td>412 794 599 1179</td>
<td>0 0 26 34</td>
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<tr>
<td>1989</td>
<td>560 1074 137 161</td>
<td>100 715 6 27</td>
</tr>
<tr>
<td>1988</td>
<td>139 192 62 241</td>
<td>33 26 2 0</td>
</tr>
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</table>
MALAYSIAN RARE EARTH CORPORATION (MAREC)

- Plant located at same place as ARE in Bukit Merah Industrial Estate, Lahat, Perak.
- Malaysian company with BEH Minerals as major shareholder
- Starts operation in late 70s
- Plant has capacity of producing 200 tons of Yttria
- Stop operation in 1985 to consolidate on ARE operation
ASIAN RARE EARTH (ARE)

- 23 Nov 1979 - ARE was set up to recover mixed rare earth compounds from local monazite
- These mixed RE are exported mainly to Japan
- The plant used the caustic soda route where tricalcium phosphate is produced as a by-product of the process
GRINDED MONAZITE

CAUSTIC SODA DIGESTION

Solid/Liquid separation

ACID DIGESTION

Solid/Liquid separation

Precipitation

Multistage solvent extraction

ASIAN RARE EARTH PROCESS: CAUSTIC SODA CRACKING

TRISODIUM PHOSPHATE

THORIUM WASTE

Radium/Lead WASTE

LIGHT RE CARBONATE

HEAVY RE CARBONATE
14 Jan 1994: ARE announce its closure citing the low price of RE as the main reason

Source: Geoscience Australia 2011
Lynas

• Lynas Malaysia Sdn. Bhd. (Lynas), a wholly owned subsidiary of Lynas Corporation Limited (Australia)

• Lynas Advanced Materials Plant (LAMP) located in an area of 100 ha in the Gebeng Industrial Estate (GIE), Kuantan, Pahang.

• The plant will process up to 80,000 tonnes per annum (tpa) wet weight basis of lanthanide concentrates (basnaesite) imported from Mount Weld, Australia
# Lynas Products

<table>
<thead>
<tr>
<th></th>
<th>PRODUCT</th>
<th>APPLICATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SEG-HRE carbonate</td>
<td>phosphors for colour screens and energy efficient lighting (e.g. compact fluorescent lights)</td>
</tr>
<tr>
<td>2</td>
<td>LCPN Carbonate</td>
<td>downstream processing plants for separation into individual lanthanide products</td>
</tr>
<tr>
<td>3</td>
<td>Lanthanum Chloride, Carbonate or Oxide</td>
<td>Fluid Cracking Catalysis (used in oil refining) and to the manufacturers of battery alloy for nickel metal hydride (NiMH) rechargeable batteries</td>
</tr>
<tr>
<td>4</td>
<td>Lanthanum-Cerium Carbonate</td>
<td>glass polishing powder (plasma TV and LCD TV)</td>
</tr>
<tr>
<td>5</td>
<td>Cerium Chloride, Carbonate or Oxide</td>
<td>automotive catalysts powders for the automotive industry</td>
</tr>
<tr>
<td>6</td>
<td>Didymium Oxide and Neodymium Oxide</td>
<td>magnetic alloys, metal production.</td>
</tr>
</tbody>
</table>
Lynas Plant: Sulphuric acid process
RADIOACTIVE WASTE ISSUE
Radioactivity & Safety

- Processing of radioactive contaminated minerals in particular the thorium waste issue have contributed to public concerned on the radioactivity and safety issues of radioactive waste
- Protests were held on the issue of thorium produced from Asian Rare Earth plant in Lahat and the recent Lynas plant in Gebeng
ARE: Radioactive Waste

- 1985: The government decides to relocate the radioactive storage facility from Papan to Kledang Range, 5Km from the ARE plant
- The storage facility is known as Long-Term Storage Facility (LTSF)
- 1989: Construction of LTSF completed and all thorium waste were stored there

<table>
<thead>
<tr>
<th>content</th>
<th>Brazil (Palabrica et al, 1980)</th>
<th>India (Dar et al, 1972)</th>
<th>ARE (Meor Yusoff, 1992)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thorium</td>
<td>44.3%</td>
<td>45 – 55%</td>
<td>32.0 – 33.5%</td>
</tr>
<tr>
<td>Uranium</td>
<td>1.2%</td>
<td>1.5 – 1.8%</td>
<td>1.1 – 1.4%</td>
</tr>
<tr>
<td>Rare earths</td>
<td>15.2%</td>
<td>10 – 15%</td>
<td>27.0 – 28.0%</td>
</tr>
</tbody>
</table>
Long Term Disposal of ARE Waste
Dilution Method by Lynas

- The Lynas WLP residue are contains thorium, uranium and their decay products at concentrations of about 1650 ppm thorium and 30 ppm uranium or 6 Bq/g.
- Lynas intends to dilute this waste to about the Malaysian permissible level of 1 Bq/g and used this diluted material as aggregate for road construction.
- Beneficiation of the residues will be subjected to AELB Act 1984 and EQ Act 1974. If the thorium and uranium levels can be reduced to natural concentration as in Naturally Occurring Radioactive Materials (NORM) the WLP and NUF residues can be feeders to other industries. Failure to do so, permanent safe and secure repository site must be located to cater for WLP, NUF and FGD.
RARE EARTH TASK FORCE

• Following the issue for safe processing of rare earth mineral, the Malaysian cabinet set up 2 task force namely

1. The Establishment of Rare Earth Industry in Malaysia – Academy Sciences of Malaysia (Lead Agency)
2. Thorium for Nuclear Power Programme – Malaysian Nuclear Agency (Lead Agency)
The Establishment of Rare Earth Industry in Malaysia

1. Blueprint on the RE industry in Malaysia - A STRATEGIC NEW SOURCE FOR ECONOMIC GROWTH

2. If it is found that Malaysia does have “economical and minable reserves of HREEs” (exploration of new HREE resource such as Ion absorption clay), the expected desired outcomes are:
   • to become a regional manufacturing center for RE-based and RE-enabled industries;
   • to become a regional center for the R&D on RE-based technology and products;
   • to become a strategic location in the region for FDI to relocate their high-tech R&D and manufacturing activities; and
   • to contribute to achieving the status of high-income nation through the strong economic multiplying effects created by the RE-related industries.
# MALAYSIAN THORIUM FLAGSHIP PROJECTS

<table>
<thead>
<tr>
<th>Sub project Titles</th>
<th>Activities</th>
<th>Institution Involved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thorium resource and supply</td>
<td>1. Exploration of thorium minerals resource</td>
<td>Malaysian Nuclear Agency and Mineral and Geoscience Department</td>
</tr>
<tr>
<td></td>
<td>2. Determination non-conventional resource eg. Radioactive waste from mineral industry</td>
<td></td>
</tr>
<tr>
<td>Extraction of Th, U and RE</td>
<td>1. R&amp;D on Th, U and RE extraction and purification</td>
<td>Malaysian Nuclear Agency, Mineral Research Centre, National University of Malaysia and JAERI</td>
</tr>
<tr>
<td></td>
<td>2. Radiation grafted absorbance polymer for Th, U, RE absorbance and separation</td>
<td></td>
</tr>
<tr>
<td>Pilot plant development</td>
<td>1. Upscaling of R&amp;D project</td>
<td>Malaysian Nuclear Agency, University Malaysia Pahang and Labzinc</td>
</tr>
<tr>
<td></td>
<td>2. Design of pilot plant</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3. Operation of pilot plant</td>
<td></td>
</tr>
<tr>
<td>Process Safety</td>
<td>1. In-situ area monitoring</td>
<td>Malaysian Nuclear Agency</td>
</tr>
<tr>
<td></td>
<td>2. Process safety software</td>
<td></td>
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</tbody>
</table>

2014
[Budget: RM 626731.19]
- Acquisition of basic equipment
- Initial study on Th Resource Mapping

2015
[Budget: RM RM14,055,085]
- Determination of Th minerals from non-conventional resources
- Design of Th laboratory meeting IAEA 3S
- Preparation and characterization of Th and U adsorbents
- Pilot plant process drawing and design
- Pilot plant technical specification for tender
- HRD on thorium extraction and safety

2016
[Budget: RM 22,336,870.76]
- Data analysis of borehole for Th minerals
- Data digitization and mapping
- Setting up of Th laboratory
- Preparation and characterization of selective adsorbents towards Th and U
- Completion of pilot plant site, building and infrastructure
- HRD on pilot processing processing

2017
[Budget: RM 6,729,286.00]
- Data analysis of borehole for Th minerals
- Weightage, model and data spatial analysis
- R&D on new process for recovery, separation and purification of Th, U and REE
- Adsorption and desorption process of Th and U
- Testing and commissioning of pilot plant

2018
[Budget: RM 908,536.55]
- Determination of Th reserve from conventional resources
- Completion of field trial of adsorption and desorption of Th and U
- Pilot plant routine operation
Project 1: Thorium Mineral Resource in Malaysia
MONAZITE AND XENOTIME DISTRIBUTION

MONAZITE

XENOTIME
## PROJECT 2: EXTRACTION OF Th, U, RE AND P

<table>
<thead>
<tr>
<th>Elements</th>
<th>RE MINERALS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Monazite</td>
</tr>
<tr>
<td>Cerium</td>
<td>21.20</td>
</tr>
<tr>
<td>Lanthanum</td>
<td>10.00</td>
</tr>
<tr>
<td>Neodymium</td>
<td>9.02</td>
</tr>
<tr>
<td>Erbium</td>
<td>trace</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>trace</td>
</tr>
<tr>
<td>Dysprosium</td>
<td>2.13</td>
</tr>
<tr>
<td>Terbium</td>
<td>trace</td>
</tr>
<tr>
<td>Yttrium</td>
<td>3.48</td>
</tr>
<tr>
<td>Thorium</td>
<td>9.00</td>
</tr>
<tr>
<td>Uranium</td>
<td>0.35</td>
</tr>
<tr>
<td>Phosphate</td>
<td>27.67</td>
</tr>
</tbody>
</table>
ALKALINE FUSION PROCESS FOR XENOTIME

1. HEAVY RE
2. LIGHT RE
3. RADIUM
4. URANIUM
5. THORIUM
6. SILICA
7. PHOSPHATE

1. CAUSTIC SODA FUSION
2. WATER WASHING
3. SOLID / LIQUID SEPARATION
4. TRISODIUM PHOSPHATE (LIQ)
5. RE / THORIUM HYDROXIDE (SOLID)
6. DILUTE HCL DIGESTION
7. SOLID / LIQUID SEPARATION
8. SILICA SOLID
9. IONIC SOLUTION
10. LEAD/BARIUM PRECIPITATION
11. SOLID / LIQUID SEPARATION
12. LEAD BARIUM RADIUM SULPHATE

1. URANIUM PRECIPITATION
2. SOLVENT EXTRACTION
3. SOLVENT EXTRACTION
4. RE CARBONATE
5. THORIUM OXIDE
6. CALCINATION
7. SOLID / LIQUID SEPARATION
8. RE PRECIPITATION
9. THORIUM PRECIPITATION
10. SOLVENT EXTRACTION
11. DILUTE HCL DIGESTION
12. THORIUM OXALATE POWDER
13. SOLID / LIQUID SEPARATION
14. OXALIC PRECIPITATION
Residue after Acid digestion

Residue after the digestion can be categorized as coarse and fine

**Xenotime**

- Residue from 100g xenotime sample;
  - Course = 17g
  - Fine = 3g

**Monazite**

- Residue from 100g monazite sample;
  - Course = 7g
  - Fine = 13g
SEM Morphology (Xenotime)

- Coarse
- Fine
Coarse vs Fine Residue (Xenotime)

Coarse
- Majority of residue
- Mainly made up of silica mineral
- Relatively no Xenotime detected

Fine
- Minor in residue
- Xenotime accounted for 30% of the mineral
- >95% recovery for xenotime achieved by the alkaline fusion method
Coarse vs Fine Residue (Monazite)

Coarse

Fine
ALKALINE FUSION PROCESS FOR XENOTIME

HEAVY RE
LIGHT RE
RADII
URANIUM
THORIUM
SILICA
PHOSPHATE

CAUSTIC SODA FUSION
WATER WASHING
SOLID / LIQUID SEPARATION
TRISODIUM PHOSPHATE (LIQ)
RE / THORIUM HYDROXIDE (SOLID)
DILUTE HCL DIGESTION
SOLID / LIQUID SEPARATION
SILICA SOLID
IONIC SOLUTION
LEAD/BARIUM PRECIPITATION
SOLID / LIQUID SEPARATION
LEAD BARIUM RADIUM SULPHATE

URANIUM PRECIPITATION
RE PRECIPITATION
SOLID / LIQUID SEPARATION
AMMONIUM DIURANATE

RE CARBONATE
THORIUM OXIDE
CALCINATION
SOLID / LIQUID SEPARATION
RE PRECIPITATION
THORIUM PRECIPITATION
SOLVENT EXTRACTION
DILUTE HCL DIGESTION

THORIUM OXALATE POWDER
SOLID / LIQUID SEPARATION
OXALIC PRECIPITATION

SOLVENT EXTRACTION
Thorium and Uranium Separation

XRF Analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spectrum</th>
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<tbody>
<tr>
<td>Xenolime Std</td>
<td>Heavy</td>
</tr>
<tr>
<td>C2</td>
<td>Heavy</td>
</tr>
<tr>
<td>H2</td>
<td>Heavy</td>
</tr>
<tr>
<td>F2</td>
<td>Heavy</td>
</tr>
<tr>
<td>N2</td>
<td>Heavy</td>
</tr>
<tr>
<td>O2</td>
<td>Heavy</td>
</tr>
<tr>
<td>O3</td>
<td>Heavy</td>
</tr>
<tr>
<td>P2</td>
<td>Heavy</td>
</tr>
<tr>
<td>P3</td>
<td>Heavy</td>
</tr>
<tr>
<td>X</td>
<td>Heavy</td>
</tr>
</tbody>
</table>

Qualitative Analysis Chart

- hydroxide
- oxalate
Grafting process by Ionizing Radiation

polymer → Electron beam → radicals → Grafting polymerization → Introduction of Functional groups

N(CH₃)₃
Electron Beam

Grafting polymerization

Grafted non woven fiber

Radiation dose
30-150 kGy

Monomer emulsion
Temperature: 25-40°C
MMA-g-NWfiber

Before grafting polymerization

after grafting polymerization
CONCLUDING REMARKS

• The are many opportunities in rare earths, from the upstream exploration and mining of rare earths-based minerals in the country, to cracking and processing in the mid-stream sector and finally to the down-stream sector, comprising of value-added industries using rare earths metals in green technology applications.

• The whole ecosystem of rare earths would eventually contribute to the enhancing the nation’s economic growth as well as providing many high-income jobs to Malaysians.

• The growth of the Malaysian RE industry is much relied on method in overcoming the radioactive waste associated with it and turning Thorium into strategic nuclear fuel could be the answer to this issue.
Thank you for your attention