Global and Turkish Perspectives of Thorium Fuel for Nuclear Energy

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Natural Properties of Thorium (Th) 
*(Earth’s Forgotten Treasure)*

- Occurs naturally,
- Identified almost two centuries ago,
- Exists in nature almost entirely as stable Th-232 isotope,
- Th itself cannot sustain a nuclear chain reaction,
- Is a lustrous silvery-white metal,
- Is dense and only slightly radioactive actinides, you can carry a lump of it in your pocket without harm (less radiotoxic),
- Th is fertile material, accept a neutron and transmute into fissile U-233 and decays to stable Pb-208.
- Th is usually a by-product of the REE containg monazite or bastnasite minerals.
THORIUM BASICS
(New Green Nuke Nuclear Renaissance)

• Is plentiful in nature and virtually inexhaustable fuel.
• Is a thermal breeder (i.e. creates enough new fuel as it breaks down to sustain a high-temperature chain reaction indefinitely).
• It is impossible to make nuclear weapons and/or bombs from Th by terrorists (i.e. peaceful)
• Nuclear power without proliferation has obvious political appeal for governments.
• Has a high heat capacity (i.e. smaller reactors)
• Does not require costly mining and mineral processing methods (i.e. less expensive),
• Is extraordinarily efficient nuclear fuel (i.e. allows longer fuel burn-up)
• Produces more neutrons per collision; thus 20-40 times more energy is generated, less fuel consumed and 47 times less radioactive nasties left behind.
• Th fuel is completely used up in the reactor; thus, there is relatively little nuclear waste.
• Th waste needs to be stored for only few hundred years (as long as 300 years) not for a few thousand (10000 years) like U wastes.
• Th reactors has zero risk of melt down as opposed to U reactors.
• Th reactors can use liquid fuel which has significant advantages in operation, control and processing over solid fuels.
• Liquid fuels works at high temperature without pressurization.

“Th should be heart of the nations’ atomic power effort”
WHY Thorium?
(New Era of Safe, Clean and Affordable Energy)

There is a treat of climate change,
There is an urgent demand for carbon-free energy/electricity.

• Th is 3-4 times more abundant than U in nature and distributed evenly in most countries in the world.
• Th can be mined with relatively low-cost and environment friendly mining methods from high grade alluvial deposits.
• Th extraction is relatively straightforward.
• Th has a better radiation stability and longer fuel cycle.
• Th has a higher energy density and fuel economy.
• Th wastes have a less radiotoxic period due to absence of transuranic wastes (i.e. Pu, Np, Ce and Am).
• Th mixed oxide (TMOX (Pu+Th)) fuel can be burned in any reactor that is lisenced to use MOX.
• There is a huge spent toxic material/plutonium that has being piled up from U-fuel. Th fuel can be used to safely incinerate these unwanted stockpiles.

Global energy needs for one year can be supplied by approximately 6600 tons of Th.
Today’s preferred fuel in commercial reactors,
U has been adequate to meet today’s supply needs,
Reserve: 5.5*10^6 tons; Yearly Production: 65*10^3 tons,
Producers: 19; Life Expectancy: 50-60 years
U ores are generally not harmful, but is dangerously toxic to humans if ingested, inhaled or even of prolonged contact.
Reactors requires extremely rare $^{235}$U (0.7%) which must be purified/enriched from natural $^{238}$U.
U mining, enrichment and extraction are expensive and complex,
U-fuel leaves large amount of toxic wastes containing Pu-239 that can be used in making bombs and weapons,
The used/depleted fuel can be reprocessed by expensive Pu-U extraction (Purex) process to remove fissile material and refabricate new fuel elements,

R&D on U will fade away in favour of Th.

<table>
<thead>
<tr>
<th>Country</th>
<th>RAR Th (tonnes)</th>
<th>EAR Th (tonnes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brazil</td>
<td>606,000</td>
<td>700,000</td>
</tr>
<tr>
<td><strong>Turkey</strong></td>
<td><strong>380,000</strong></td>
<td><strong>500,000</strong></td>
</tr>
<tr>
<td>India</td>
<td>319,000</td>
<td>-</td>
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<tr>
<td>United States</td>
<td>137,000</td>
<td>295,000</td>
</tr>
<tr>
<td>Norway</td>
<td>132,000</td>
<td>132,000</td>
</tr>
<tr>
<td>Greenland</td>
<td>54,000</td>
<td>32,000</td>
</tr>
<tr>
<td>Canada</td>
<td>45,000</td>
<td>128,000</td>
</tr>
<tr>
<td>Australia</td>
<td>19,000</td>
<td>-</td>
</tr>
<tr>
<td>South Africa</td>
<td>18,000</td>
<td>-</td>
</tr>
<tr>
<td>Egypt</td>
<td>15,000</td>
<td>309,000</td>
</tr>
<tr>
<td><strong>Other Countries</strong></td>
<td><strong>505,000</strong></td>
<td>-</td>
</tr>
<tr>
<td><strong>World Total</strong></td>
<td><strong>2,230,000</strong></td>
<td><strong>2,130,000</strong></td>
</tr>
</tbody>
</table>
## Th containing Rare Earth Elements (REE)s

### Phosphate Mineral

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Density (g/cm³)</th>
<th>Magnetic Property</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monazite (Ce)</td>
<td>(Ce, La, Nd, Th)PO₄</td>
<td>4.98-5.43</td>
<td>Paramagnetic</td>
<td>35-71</td>
</tr>
<tr>
<td>Monazite (La)</td>
<td>(La, Ce, Nd, Th)PO₄</td>
<td>5.17-5.27</td>
<td>Paramagnetic</td>
<td>35-71</td>
</tr>
<tr>
<td>Monazite (Nd)</td>
<td>(Nd, Ce, La, Th)PO₄</td>
<td>5.17-5.27</td>
<td>Paramagnetic</td>
<td>35-71</td>
</tr>
</tbody>
</table>

### Silicate Mineral

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Density (g/cm³)</th>
<th>Magnetic Property</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thorite</td>
<td>(Th, U) SiO₄</td>
<td>6.63-7.20</td>
<td>Paramagnetic</td>
<td>&lt;3</td>
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</table>

### Carbonate Mineral

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Density (g/cm³)</th>
<th>Magnetic Property</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basnasite (Ce)</td>
<td>(Ce, La, Th)(CO₃)F</td>
<td>4.90-5.20</td>
<td>Paramagnetic</td>
<td>70-74</td>
</tr>
<tr>
<td>Basnasite (La)</td>
<td>(La, Ce, Th)(CO₃)F</td>
<td>4.90-5.20</td>
<td>Paramagnetic</td>
<td>70-74</td>
</tr>
<tr>
<td>Basnasite (Y)</td>
<td>(Y)(CO₃)F</td>
<td>3.90-4.00</td>
<td>Paramagnetic</td>
<td>70-74</td>
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</tbody>
</table>
MONAZITE (REE-Th PO₄)

- A phosphate mineral with Rare Earth Oxide (REO) content of 70% (Ce, La, Pr and Nd).
- Monazite is found in granites, syanites, pegmatites, beach sands etc.
- World monazite resources are estimated to be about 12 million tons.
- Includes 3-14% Th and variable amount of U.
- Found in placer deposits, beach sands and is also a component of the Bayan Obo deposit in China.
- World monazite production is between 5000-6000 tons/y.
- Major Monazite producers are Mt Weld (Australia), (Andhra Pradesh, Tamil Nuda, Odisha) India and Guandong (China), Malaysia and Brazil.
ThO₂ Mining from Monazite

- Th from monazite deposits can be mined with relatively low-cost and environment friendly mining methods, because it exists in high concentrations and in high-grades at the surface or in beach sands.
- The ore/sand can be skimmed off the surface by dredge mining.
- Monazite mining is more economical due to presence of Th as a by-product in the REE ore.
- U mine can be developed in 10-15 years, Th mine can be developed in 2-3 years due to less regulatory scrutiny.
- ThO₂ is liberated from monazite by gravitational, magnetic and electrostatic concentration methods, employing a minimum of dangerous chemicals (i.e. acids). Whereas U is mined by expensive underground mining and in-situ acid leaching methods.
BEACH SAND (Quartz, Garnet, Magnetite, Zircon, Ilmenite, Rutile, Monazite)

Quartz: 2.7 (L)
Garnet: 3.5 (L)
Magnetite: 5.5-6.5 (D, F)
Zircon: 4.6-4.7 (D, NM, P)
Rutile: 4.2 (D, NM, T)
Ilmenite: 4.5-5.0 (D, M, T)
Monazite: 4.9-5.2 (D, M, P)

Typical beach sand treatment flowsheet.

L: light
D: Dense
F: Ferromag.
NM: Nonmag.
M: Mag.
T: Thrown
P: Pinned

REEs + Th
BASTNASITE (REE-$\text{ThFCO}_3^2$)

- A fluorocarbonate mineral with a REO content of approximately 70% (Ce, La, Pr and Nd).
- Basnasite is the primary source of light REOs and accounts for 80% of the overall amount of REO in the world.
- In the last 50 years basnasite replaced monazite as a chief mineral source of REEs.
- Basnasite has been extracted on a large scale only in Mountain Pass, USA and Bayan Obo, China (supply 45% of world demand).
- Expensive underground mining methods are used.
- Processing depends on fine grinding; gravity, magnetic and flotation separations; calcination, HCl leaching and solvent extraction steps.
Uranium and Thorium Deposits of Turkey

Black Sea

Eskisehir

Ankara

Sivrihisar-Eskisehir Light REE+Th Deposit

Mediterranean Sea
Comparison of some REO Deposits according to Reserve Size

Kaynak: Greenfields Research Ltd; (Data: Company websites)
ThO$_2$ contents of some REO Deposits

Kaynak: Greenfields Research Ltd; Data: Company websites
Reserve Development Studies in Eskişehir-Sivrihisar-Kızılcaören Light REEs+Th Field

• First reserve calculations depended on 50-200 m deep drilling studies in 1959.

• In 2011, two 500 m deep drilling bores were opened.

• Analyses showed further reserves at deeps.

• In 2012; 10,000 m drilling were performed at 38 locations.

• Between 2014 and 2017; 116,000 m drilling will be performed at 289 locations.

• 45,000 samples will be taken for geochemical and 1,000 samples will be taken by XRD analyses.
**Eti Mines Eskişehir-Sivrihisar Deposit’s Operation Plan**

### Ore Properties

- **Mineral:** Bastnasite
- **Ore Characteristic:** Complex, finely disseminated,
- **Ores:** Layers, lenses and veins besides impregnation and brecciated zones (Hydrothermal deposit).
- **Area:** 1,758 hectare
- **Reserve:** 30,358,268 ton
- **Mineral Grade Distribution:**
  - 37.44% CaF$_2$
  - 31.04% BaSO$_4$
  - **3.14%** REE (Ce (2.01%)+La (1.5%)+ Nd (0.39))
  - **0.21%** ThO$_2$
  - Along with psilomelan, ilmenite, rutil and some mica minerals.

  - Florite: 11,366,135 tons
  - Barite: 9,424,424 tons
  - REE: 953,587 tons (CeO$_2$+La$_2$O$_3$+Nd$_2$O$_3$)
  - Thorium: 380,000 tons
  - Gangue: 8,612,182 tons.

### Production Plan

- **Eti Mine** prepared a feasibility report for;
  - 10,000 ton/y REO
  - 72,000 ton/y Barite
  - 70,000 ton/y Florite
  - **250 ton/y** Thorium production.

- **Mining:** Open pit mining will be carried out by Eti Mines of Turkey

- **Mineral Processing/Enrichment:** Performed by Domestic and/or Foreign private expert company with service procurement tender for 10 years.

- **Products:** Marketed by Eti Mines. ThO$_2$ will be stored.
Th has been extracted from monazite through a complex multi-stage process (AMEX). Monazite is dissolved in 120-150 °C hot concentrated H₂SO₄ for several hours. Th is extracted as an insoluble residue into an organic phase containing an alkyl amine. Then it is separated/stripped using an ion such as nitrate, chloride, hydroxide or carbonate returning Th to an aqueous phase. Finally Th is precipitated and collected.

Th extraction is a complex process because of similar chemical properties with REOs.
THORIUM CONCENTRATION FLOWSHEET

- ORE
- HNO₃ or H₂SO₄ LEACHING (pH:1.2)
  - Precipitation of some impurities
  - Solvent Extraction (SX) or Ion Exchange (IE)
    - Th(NO₃)₄.nH₂O
- Drying (105 °C, 20h) → Water ↑
- Th(NO₃)₄
- Calcination (575°C)
- ThO₂ concentrate
EFFECTS OF ROASTING and THIOUREA ADDITION on BASTNASITE LEACHING (Yörükoğulları, Obut, Girgin, 2002 and 2003)

1. Pre-concentration

Pre-Concentrate (21.3% REO)

Scrubbing (75% solids, N: 2060 rpm, t: 15 min.)
BaSO₄ Flotation
CaF₂ Flotation

2. Bastnasite Pre-Concentrate Leach

Particle Size: 0.053 mm  S/L: 1/20 g/mL  N: 450 rpm  t: 6 hours
REEs in solution were analysed by ICP spectrometer. Ba and high concentration REE were analysed by gravimetric methods based on sulphate and oxalate precipitation.

2a. Leaching without Roasting using Concentrated Acids
- 8M HNO₃ at 70°C: 100% total REE dissolution
- 15 M H₂SO₄ at 25°C: 89.25%
- 2.5M HCl at 55°C: 82.2%

2b. Roasting+Dilute Acid Leaching
After roasting at 750°C for 1 h, leaching with 1-3M H₂SO₄ at 25°C.
(Roasting decomposes carbonates and oxidize Ce).

Total REE contents for unroasted: 18.59%, roasted: 22.00% and roasted+leached 47.4%.

2c. Roasting+Dilute Acid Leaching and Thiourea Addition (extracting agent for Au, Ag and REE)
Thiourea conc.: 0-2 M and 1-3 M H₂SO₄
Roasted without thiourea: 17.6% REE dissolution  Roasted with thiourea: 89.0% dissolution
(at 3M H₂SO₄ and 1M thiourea)

3. Hydroxide-Oxalate Mixture Precipitation (Mish metal) from Leach Solution+
Heating to 900°C for 2 hours
Total REE 93.6%, REO: 92.6%
EFFECTS OF ROASTING and THIOUREA ADDITION on BASTNASITE LEACHING
(Yörükoğulları, Obut, Girgin, 2002 and 2003)

• Roasting decomposes the fluurocarbonate structure of REEs in the preconcentrate with the formation of fluocerite and cerianite as new phases (XRD results).

• This change in composition increases the selective dissolution of lanthanum and neodymium in $\text{H}_2\text{SO}_4$ solution causing 5.6 times increase in the total REs dissolution.

• Addition of thiourea ($\text{CS(NH}_2)_2$) to the leaching medium increases the dissolution of total REEs in the unroasted and especially in the roasted preconcentrate reaching a dissolution of 89%.

• 92.6% mixed REO precipitation with $\text{H}_2\text{SO}_4$-thiourea medium was achieved.
PILOT SCALE ACID LEACH and SOLVENT EXTRACTION TESTS for REEs and Th from ESKISEHIR ORE by MTA (2004)

Particle size: - 1mm;
Oxidizing Roasting Temperature: 600-900°C; t: 1-6 hours
Leach: 3 M $\text{H}_2\text{SO}_4$ REE dissolution: 86% (Ce, La, Nd ve Th) and 3 M HCl REE dissolution: 92% (Ce, La, Nd ve Th) (89% REO mishmetal)
Oxalate Precipitation: Th Grade: 98.7% , Th Recovery: 98%
The Effects of **Particle Size and Roasting Time** on Thorium Recovery during $H_2SO_4$ and HCl Leaching *(Yorukoglu et.al., 2012)*

- **Sample**: 3 t representative homogenized
- **Particle Sizes Tested**: 0.065, 0.2, 1 and 3 mm
- **Oxidizing Roasting Temp. and Time**: 900 °C and 1, 3 and 6 hours
- **Leaching**: 3 M $H_2SO_4$ and 3 M HCl, 3 h, 25°C, separately
- **Leaching Recovery**: (REEs + Th) %

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**Graphs**

- **3 M $H_2SO_4$**
  - Without Roast:
  - 1 Hour of Roast:
  - 6 Hours of Roast:

- **3 M HCl**
  - Without Roasting
  - 1 Hour of Roasting
  - 3 Hours of Roasting
  - 6 Hours of Roasting

---

$R = 79\%$, 1 mm, 1h

$R = 73\%$, 1 mm, 3 h
The Effects of **Particle Size and Roasting Time** on Thorium Recovery during **H₂SO₄ and HCl Leaching** (Yorukoglu et.al., 2012)

- 3 M H₂SO₄ gives better leaching recovery than HCl.
- H₂SO₄ is cheaper than HCl.
- Oxidizing roasting at 900 °C at 1 hour, before atmospheric leaching is necessary.
- The best particle size for leaching is 1 mm.
- 79% (REEs+Th) dissolution can be achieved.
CONCLUSIONS from TURKEY’S POINT OF VIEW

• Energy is major concern for developing Turkish society. Turkey today exports more than 70% of its energy as fossil fuels. In the last 50 years, Turks are sceptical, anxious and indecisive about having nuclear energy.

• In the last 10 years, we are bringing Th into Turkish government’s attention and national discussion as a new, safe, clean, affordable, CO$_2$-free, alternative, strategic and domestic nuclear energy fuel.

• In Turkey, we are trying to find funds to support education and R&D on Th. We are expecting to establish Thorium Research Center (ThoReC) in Turkey for Th mining+enrichment+extraction+fuel fabrication+prototype reactor testing+nuclear fuel cycle testing.

• Turkey recently contacted four VVER-1200 type Russian Nuclear Power Reactors using U as a fuel in Akkuyu (Rosatom) and another four units will be established in Sinop in the next decade by Japan (Mitsubishi-Westinghouse). We will enforce government to use Th along with U as an alternative fuel in the new reactors.

• If Turkey can process it’s important domestic low grade bastnasite resource in Eskisehir for Th, it can supply its own Th fuel for more than 100 years and become self-sufficient in energy sources.
THANKS FOR YOUR INTEREST
## Comparing Reactors

<table>
<thead>
<tr>
<th></th>
<th>U Fueled Light Water Reactor</th>
<th>U+Th Seed and Blanket Reactor</th>
<th>Th Liquid Fluoride Reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fuel</strong></td>
<td>U fuel rods</td>
<td>Th+U oxide rods</td>
<td>Th+U fluoride solution</td>
</tr>
<tr>
<td><strong>Fuel input per GW output</strong> *</td>
<td>250 tons raw U</td>
<td>2.4 tons raw Th + 177 tons raw U</td>
<td>1 ton raw Th</td>
</tr>
<tr>
<td><strong>Annual fuel cost for 1 GW reactor</strong></td>
<td>$50-60 million</td>
<td>$50-60 million</td>
<td>$10000</td>
</tr>
<tr>
<td><strong>Coolant</strong></td>
<td>Water</td>
<td>Water</td>
<td>Self regulating (FLiNaK) salt/gas</td>
</tr>
<tr>
<td><strong>Proliferation potential</strong></td>
<td>Medium</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td><strong>Footprint</strong></td>
<td>200000-300000 ft² surrounded by a low-density population zone</td>
<td>2000000-300000 ft² surrounded by a low-density population zone</td>
<td>2000-3000 ft² With no need for a buffer zone.</td>
</tr>
</tbody>
</table>

* equivalent energy from 3.5 million tons of coal

Richard Martin (2009)
Dünya enerji ihtiyacı toryum tek başına 6600 ton ile karşılayabilecektir.
<table>
<thead>
<tr>
<th>MINERAL</th>
<th>GRAIN SIZE (micron)</th>
<th>CONTENT (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorite</td>
<td>2-4000</td>
<td>38-45</td>
</tr>
<tr>
<td>Barite</td>
<td>10-1400</td>
<td>19-36</td>
</tr>
<tr>
<td><strong>Bastnasite</strong></td>
<td><strong>7-26</strong></td>
<td><strong>7-26</strong></td>
</tr>
<tr>
<td>Opak Minerals</td>
<td>12-1200</td>
<td>20-22</td>
</tr>
</tbody>
</table>

**REE and Th are in fine size fraction**
HCl Leaching of Sivrihisar Bastnasite Ore (Gülmez et.al., 2012)

- **Sample**: 3 t representative homogenized
- **Particle Sizes Tested**: 0.065, 0.2, 1 and 3 mm
- **Leaching**: 3 M H$_2$SO$_4$ and HCl, 3 h, 25°C, separately
- **Leaching Recovery**: 92.09 % (REE + Th)
- **Mishmetal concentrate**: 73.8% REE/89.4%REO (saleable)

### Chemical Analyses of Composite Sample

<table>
<thead>
<tr>
<th></th>
<th>F</th>
<th>BaO</th>
<th>CeO2</th>
<th>La2O3</th>
<th>Nd2O3</th>
<th>ThO2</th>
<th>SO3</th>
<th>Ca</th>
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<tbody>
<tr>
<td></td>
<td>20.80</td>
<td>20.80</td>
<td>2.01</td>
<td>1.5</td>
<td>0.4</td>
<td>0.1</td>
<td>12.1</td>
<td>20.3</td>
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### HCl Leaching Tailing Chemical Analyses

<table>
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<th>La2O3</th>
<th>Nd2O3</th>
<th>ThO2</th>
<th>SO3</th>
<th>Fe2O3</th>
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<td>25.10</td>
<td>22.30</td>
<td>0.50</td>
<td>0.40</td>
<td>0.10</td>
<td>0.013</td>
<td>13.6</td>
<td>3.60</td>
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</table>
Comparison of some REO Deposits according to REO Grades
Th recovery from monazite usually involves leaching with NaOH at 140°C followed by complex processes to precipitate pure ThO₂.
THORIUM CONCENTRATION STUDIES


SİVRİHİSAR-ESKİŞEHİR ORE
GRAVITY CONCENTRATION
MAGNETIC CONCENTRATION
FLOTATION
ACID LEACHING
Optimum Conditions:
HCl dosage: 200kg/t
Leaching Time: 3 hours
Th Grade: %99

ACID TOREX PROCESS

ThO2 recovery from used (U233/Th) fuel
Hot acid leach
(13M HNO₃, 0.05M HF, 0.1M Al nitrat
at boiling temperature)
Centrifuging → Solid residue
Th(NO₃)₄ + UO₂(NO₃)₂
Solution
SX Columns
Purification

Tributyl phosphate (TBP)