

Thorium fuel for nuclear energy

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ABSTRACT

Energy is the major concern for society. It is expected that developing country economies and populations will grow and consume more energy. Interest in nuclear power is rising, while the world looks for non-depletable energy source that will not contribute to global warming. However, it still has concerns of nuclear proliferation, radioactive waste and safety. It is necessary to overcome these concerns if nuclear energy is expanded to developing countries. Thorium (Th) utilization as nuclear fuel will be an opening key of these difficulties because Th produces less Plutonium (Pu) and less radioactive waste with enhanced safety. Research into the use of Th as a nuclear fuel has been taking place over forty years, through with much less intensity than that for uranium (U) or U-Pu fuels. Nuclear industry is currently using only 0.7% of the available energy from mined U.

With huge resources of Th and relatively little U, Turkey has made utilization of Th for large-scale energy production a major goal in its nuclear power programme. Thorium fuel is plentiful and inexpensive. 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 skeptical, anxious and indecisive about having nuclear energy for electricity production. In the last 10 years, Thorium is brought into Turkish government's attention and national discussion as a new, safe, clean, affordable, CO₂-free, alternative, strategic and domestic nuclear energy fuel. 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). Turkish nuclear programme must envisage use of domestic Th as a fertile material.

This paper briefly reviews the developments of Th-fuel cycle for nuclear energy from global and Turkish perspectives. Previous Th reserve development and recovery studies from Turkish bastnasite ore are summarized in this paper.

EARTH'S FORGOTTEN TREASURE: THORIUM

Natural properties

Thorium is naturally-occurring slightly radioactive and dense actinide metal (i.e. less radiotoxic). It is named for the Norse god of thunder and discovered by J.J. Berzelius in 1828. Thorium exists in nature almost entirely as stable ^{232}Th isotope and itself cannot sustain a nuclear chain reaction. Thorium is a lustrous silvery-white metal. It is fertile material, accept a neutron and transmute into fissile ^{233}U and decays until to stable ^{208}Pb . Thorium is usually a by-product of the Rear Earth Elements (REEs) containing monazite or bastnasite minerals.

Thorium basics as a nuclear fuel

Thorium is plentiful in nature, generally well distributed throughout the earth crust and virtually inexhaustible nuclear fuel. Th is one of only a few substances that act as a thermal breeder. It is impossible to make nuclear weapons/bombs from Th by terrorists (i.e. peaceful). Therefore, nuclear power without proliferation has obvious political appeal for many governments in the World. Th can be also used as a “fertile matrix” for fuels containing Pu and Am. Th has a high heat capacity (i.e. smaller reactors). It does not require costly mineral processing methods (i.e. less expensive). Th is extraordinarily efficient nuclear fuel (i.e. allows longer fuel burn-ups in the reactors). Th produces more neutrons per collision; thus, twenty-fourty times more energy is generated, less fuel is consumed and forty seven times less radioactive wastes are left behind to take care. Th fuel is completely used up in the reactor. Th reactor wastes need to be stored for only few hundred years not for a few thousand like U reactors. Th reactors have zero risk of melt down as opposed to conventional U reactors. Th reactors can also use liquid fuel which has significant advantages in operation, control and processing over solid fuels used in U reactors. Liquid fuels work at high temperature without pressurization (Kaya, 2013). Due to above advantages of Th, it should be heart of the most nations’ atomic power effort.

Thorium energy can help check CO_2 and global warming, cut deadly air pollution, provide inexhaustible energy, and increase human prosperity. Our world is beset by global warming, pollution, resource conflicts, and energy poverty. Th can be utilized as a nuclear fuel in parallel with U, not instead of U. The Th fuel cycle offers enormous energy security benefits in the long-term due to its potential for being a self-sustaining fuel without the need for fast neutron reactors. It is therefore an important and potentially viable technology that seems able to contribute to build credible, long-term nuclear energy scenarios. Next generation and revolutionary nuclear reactors will produce clean energy with no green house gas emission. Self sustained, capable of running for decades without refueling, site flexible for electricity generation, smaller, modular and portable plants require no water, located anywhere and fully grid capable reactors will be the fourth generation nuclear reactors. Th fuel is closer to these aims. Conventional U reactors create massive hazardous waste because of their inefficient use of nuclear

materials. Revolutionary new reactors should use vast supply of used nuclear fuel, depleted U and Th. Th-based fuel will steadily gain interest in nuclear industry due to advantageous thermal and chemical properties and low actinide production.

Today's problematic nuclear fuel - Uranium (U)

Uranium is today's preferred conventional nuclear fuel in commercial reactors. Uranium has been adequate to meet today's energy supply needs. World's uranium reserve is about 5.5×10^6 tons; Uranium production is about 65×10^3 tpa. There are nineteen big uranium producers in the World. Life expectancy of uranium ore is about 50-60 years. Uranium ores are generally not harmful, but is dangerously toxic to humans if ingested, inhaled or even of prolonged contact. Conventional uranium reactors requires extremely rare ^{235}U (abundance: 0.7%) which must be purified/enriched from natural ^{238}U isotope. Uranium mining, enrichment and extraction are expensive and complex as compared to Th. Uranium fuel leaves large amount of toxic wastes containing ^{239}Pu 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. In the near future, R&D on uranium will fade away in favor of thorium. According to IAEA-NEA red book in 2007, there were 4.4 million tons of total world known and estimated Th resources, but this excludes data from much of the world. Data for reasonably assured and inferred resources recoverable at a cost of \$80/kg Th or less are given in Table 1 (OECD, NEA & IAEA, 2011). Total World Th reserve is about 5.39 million tons. India has 16%, Turkey has 14% and Brazil has 11% of total reserve of the World.

Table 1 World thorium reserves according to OECD, NEA & IAEA

Country	RAR Th (tones)	% of total
India	846.000	16
Turkey	744.000	14
Brazil	606.000	11
Australia	521.000	10
United States	434.000	8
Egypt	380.000	7
Norway	320.000	6
Venezuela	300.000	6
Other Countries	1234.000	22
World Total	5.385.000	



Thorium containing Rare Earth Elements (REE)s

Radioactive Th and U containing REEs may be phosphate, silicate and carbonate containing minerals. Their formulas, densities, magnetic properties and chemical contents are given in Table 2. Monazite contains up to 20% ThO₂ and 16% UO₂ while bastnasite contains 0.3% ThO₂. Monazite [(REE-Th) PO₄] is 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. It includes 3-14% ThO₂ and variable amount of UO₂. Th is found in placer deposits, beach sands and is also a component of the World's biggest REE Bayan Obo deposit in China. World's yearly monazite production is between 5000-6500 tons. Thorium from monazite deposits can be mined with low-cost and environment friendly mining methods; because, it exists in high concentrations and 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. Uranium mine can be developed in ten to fifteen years while thorium mine can be developed in two to three years due to less regulatory scrutiny (Kaya, 2013).

Table 2 Properties of Th and U containing rare earth minerals (Kaya, 2013)

				REO ThO ₂ UO ₂		
Phosphate Mineral	Formula	Density (g/cm ³)	Magnetic Property	Weight (%)		
Monazite (Ce)	(Ce, La, Nd, Th)PO ₄	4.98-5.43	Paramagnetic	35-71	0-20	0-16
Monazite (La)	(La, Ce, Nd, Th)PO ₄	5.17-5.27	Paramagnetic	35-71	0-20	0-16
Monazite (Nd)	(Nd, Ce, La, Th)PO ₄	5.17-5.27	Paramagnetic	35-71	0-20	0-16

Silicate	Mineral	Formula	Density (g/cm ³)	Magnetic Property	Weight (%)	
	Thorite	(Th, U) SiO ₄	6.63-7.20	Paramagnetic	<3	- 10-16

Carbonate Mineral	Formula	Density (g/cm ³)	Magnetic Property	Weight (%)		
Basnasite (Ce)	(Ce, La,Th)(CO ₃)F	4.90-5.20	Paramagnetic	70-74	0-0.3	0.09
Basnasite (La)	(La, Ce, Th)(CO ₃)F		Paramagnetic	70-74	0-0.3	0.09
Basnasite (Y)	(Y)(CO ₃)F	3.90-4.00	Paramagnetic	70-74	0-0.3	0.09

ThO₂ is liberated from monazite by gravitational, magnetic and electro-static concentration methods, employing a minimum of dangerous chemicals (i.e. concentrated acids). Whereas uranium is mined by expensive underground mining, or open pit mining and in-situ acid leaching methods. Major World's monazite producers are in Australia (Mt Weld), India (Andhra Pradesh, Tamil Nuda, Odisha), China (Guandong), Malaysia and Brazil. Figure 1 shows a typical conventional beach sand treatment flow sheet to recover quartz, garnet, magnetite, zircon, ilmenite, rutile and monazite which contains both Th and REOs. In this flow sheet, gravity, low and high intensity magnetic separation and electrostatic separation methods are used (Kaya, 2013).

Bastnasite $[(\text{REE-Th})\text{FCO}_3^2]$ is a fluorocarbonate mineral with a REO content of approximately 70% (Ce, La, Pr and Nd). Bastnasite 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, bastnasite replaced monazite as a chief mineral source of REEs. Bastnasite has been extracted on a large scale only in Mountain Pass, USA and Bayan Obo, China, which supplies 45% of World demand alone. In the production, expensive underground mining methods are used. Mineral processing of bastnasite ores depend on fine grinding; gravity, magnetic and flotation separations; calcinations; HCl leaching and solvent extraction (SE) steps.

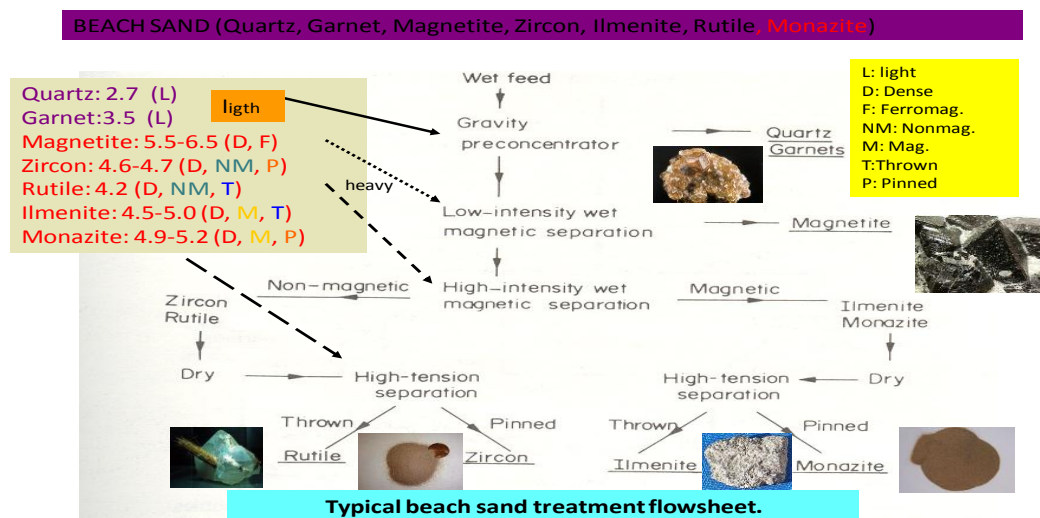


Figure 1 Typical beach sand treatment flow sheet

Reserve development studies, operation and production plans of Eskisehir - Sivrihisar-Kızılcaören (Turkey) light REE+Th field by Eti Mines

Figure 2 shows the Th and Ur deposits in Turkey. There are five U and one Th deposits. Figure 3a shows the comparison of some REO deposits according to reserve size. Eskişehir Th deposit is the 11th biggest Th reserve in the World. According to ThO₂ contents of some REO deposits, Eskişehir Th deposit is the 3rd biggest deposit in the World (Figure 3b).

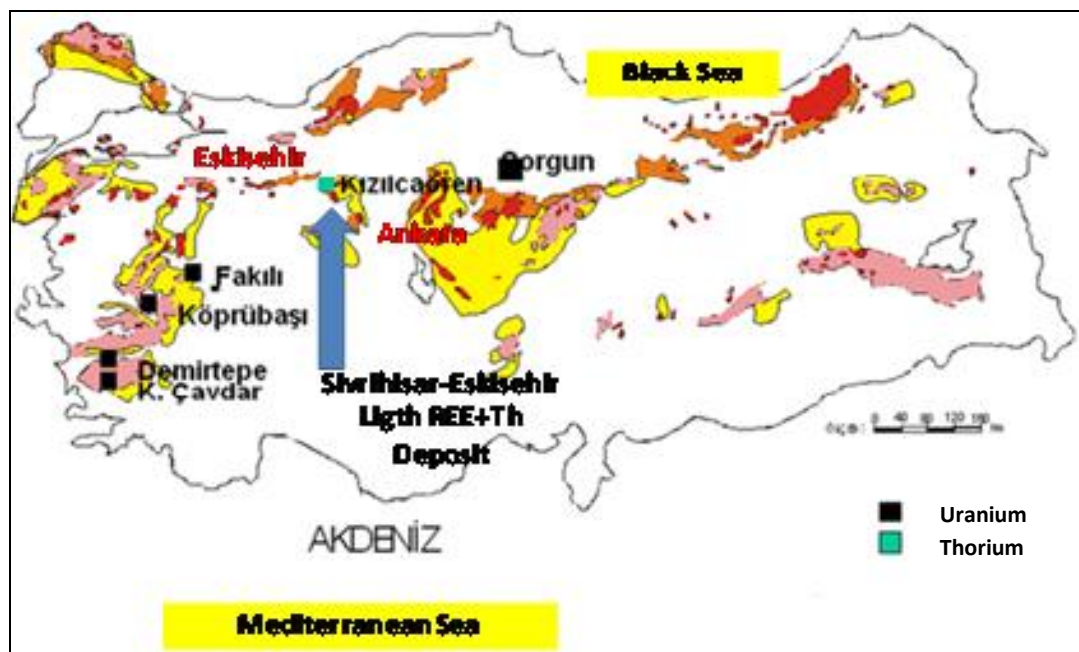


Figure 2 Thorium and uranium deposits of Turkey

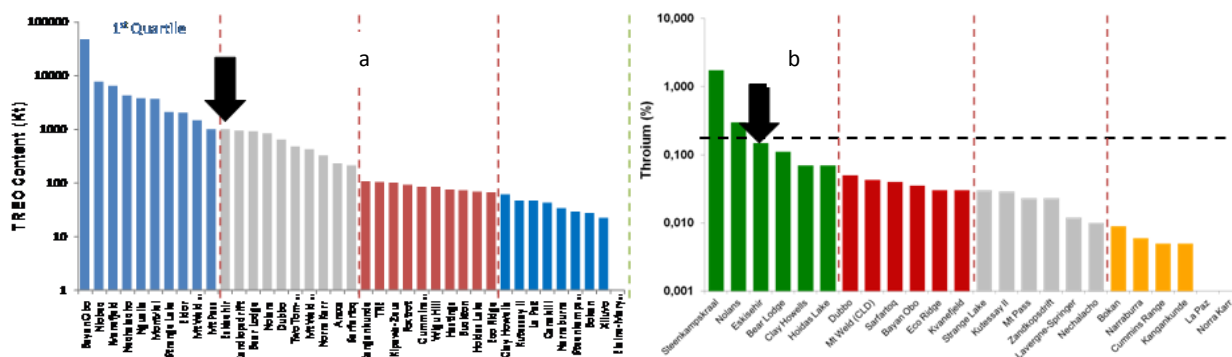


Figure 3a and b Comparison of some REO deposits according to reserve size

Eskişehir Th deposit discovered using air prospecting survey by General Directorate of Mineral Research and Exploration of Turkey (MTA) in 1959. First reserve calculations depended on 50-200 m deep drilling studies in that date. Ore is complex and finely disseminated bastnasite mineral which is found as layers, lenses and veins besides impregnation and brecciate zones. Ore reserve is more than 30 million tones. Bastnasite ore contains 37.44% fluorite, 31.04% barite, 3.14% REE (2.01% Ce + 1.5% La + 0.39% Nd).

Average ThO₂ content is 0.21%. Ore also contains psilomelan, ilmenite, rutile and some mica minerals. Proved and probable ThO₂ reserve is about 380000 tones. In 2011, two 500 m deep drilling bores were opened. Analyses showed further reserves at deeps. In 2012; totally 10000 m drilling were performed at 38 locations. Between 2014 and 2017; 116000 m drilling will be performed at 289 locations. 45000 samples will be taken for geochemical and 1000 samples will be taken by XRD analyses. Operating license of Th deposit is owned by Turkish Government Mining Company of Eti Mines for 10 years. Eti Mines prepared a feasibility report for 10000t/y REO, 72000 t/y barite, 70000 t/y fluorite, 250 t/y Th productions. Open pit mining method will be carried out by Eti Mines. Mineral processing will be performed by domestic/foreign private expert company with service procurement tender for 10 years. Products will be marketed by Eti Mines. Recovered ThO₂ will be stored by the Atomic Energy of Turkey until a Th reactor is established in Turkey.

Mineral processing studies on Turkish light REE+Th ores

Bastnasite is one of the main sources of rare earths and Th as a by-product. Marketable bastnasite concentrate contains about 60% REOs and easily produced by gravity and magnetic separation or by flotation (Pradip and Fuerstenau, 1991). Concentrate is upgraded to 85% REO by acid leaching and roasting can also be used before and after acid leaching for removing carbonates and/or oxidizing cerium to a higher valiancy state for selective separation from other REEs (Koch, 1987). Sulphuric, nitric and hydrochloric acids can be used as leaching reagents and the choice depends on the selectivity in separation of rare-earth elements, type of gangue minerals in the ore and the types of reagents to be used in the further extraction procedures. Although leaching with H₂SO₄ or HNO₃ requires high acid concentrations, HCl leaching can be done at dilute concentrations (Yorukogulları et al. (2003)).

Gravity separation, magnetic concentration, flotation and acid leaching tests were carried out for Eskişehir Th ore by Ipekoğlu (1983). Optimum leaching conditions were found as 200 kg/t HCl dosage and 3 hours leaching time. The highest Th grade achieved was 99%.

MTA (2004) applied both H₂SO₄ and HCl leaches to Eskişehir-Kızılcaören bastnasite ore in pilot scale to recover REEs (Ce, La and Nd) and Th together. 85.7% and 92.1% of REEs and Th dissolved with H₂SO₄ and HCl respectively. After oxalate precipitation, REO concentrate grade was about 85%, which is saleable. Then, leach cake was subjected to the flotation in order to recover barite and fluorite present in the ore. After barite flotation using S-72 collector at a dosage of 300 g/t, a concentrate of 92.7% grade and 92.9 % recovery were obtained. After fluorite flotation, a concentrate of 84% grade and 90% recovery were obtained.

In one of the other previous study, firstly scrubbing followed by barite and fluorite flotation to obtain pre-concentrate containing 21.3% REO were carried out. Leaching characteristics of Eskişehir-Kızılcaören

bastnasite were determined on this pre-concentrate. Leaching with 8M HNO₃ at 70°C achieved 100%; 15M H₂SO₄ at 25°C achieved 89.25% and 2.5 M HCl at 55°C achieved 82.2% REO dissolution by Girgin and Gündüz (1997).

Yorukogulları et al. (2003) studied the effect of roasting and thiourea (CS(NH₂)₂) addition on Turkish bastnasite ore leaching. Bastnasite pre-concentrate dilute acid leaching was performed at particle size of 0.053 mm, H₂SO₄ dosage of 1-3M, solid/liquid ratio of 1/20 g/mL, leach temperature of 25°C for 6 h. Leaching with 3M H₂SO₄ before and after roasting at 750°C for 1 hour achieved 8.5% - 47.4% REE contents, respectively. Roasting decomposes fluocarbonates and oxidizes Ce in the pre-concentrate with the formation of fluorcerite and cerianite as new phases (verified by XRD results). However, addition of 0 - 2M thiourea into the leaching medium after roasting improved the dissolution from 17.6% to 89.0% (at 3M H₂SO₄ and 1M thiourea dosages). The filtrate obtained from the leaching experiment of roasted pre-concentrate was precipitated as hydroxide-oxalate mixture (mish metal) and ignited to oxides at 900°C for 2 hours and total REE of 93.6% and REO of 92.6% were obtained.

The effects of particle size (0.065, 0.2, 1 and 3 mm) and oxidizing roasting temperature (900°C) and time (from 1 to 6 h) on Th recovery during 3M H₂SO₄/HCl leaching for 3 h at 25°C were also investigated by Yorukoglu et al. (2012). Figure 4a and 4b show the effect of roasting time and particle size on leaching recovery with H₂SO₄ and HCl, respectively. The highest Th recovery was 78.74% when 3M H₂SO₄ and 1 mm particle size sample used and 1 h roasting applied and 73.38% when 3M HCl and 1 mm particle size sample used and 3h roasting applied. 3M H₂SO₄, which is cheaper than HCl, achieved better leaching recovery than HCl. Oxidizing roasting at 900°C at 1 hour, before atmospheric leaching, is necessary for Eskisehir Th ore. The best particle size for leaching is 1 mm. Under the optimum conditions 79% REEs+Th dissolution can be achieved.

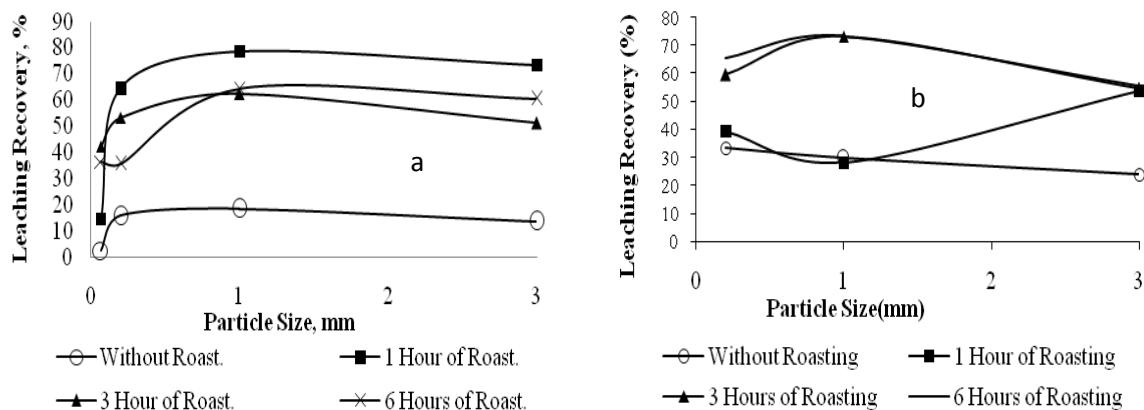


Figure 4a-b Effect of particle size and roasting time on leaching recovery at 3M H₂SO₄ (a) and HCl (b) concentrations

CONCLUSIONS

It is possible to leach bastnasite pre-concentrate in dilute sulphuric/hydrochloric acids at room temperature. Structure decomposing roasting at 750°C increased REEs dissolution nearly 5.6 times increase in the total REEs dissolution reaching a value of about 47%. The addition of H₂SO₄ + thiourea solution in roasted pre-concentrate increased the total REEs dissolution up to 89%. The filtrate obtained from the leaching experiment of roasted pre-concentrate was precipitated as hydroxide-oxalate mixture (mish metal) and ignited to oxides at 900°C for 2 hours and total REE of 93.6% and REO of 92.6% were obtained.

Maximum 79% Th recovery was achieved with 3M H₂SO₄ concentration at 1 mm particle size and 1 h roasting at 900°C. 74% Th recovery was obtained with 3M HCl concentration at 1 mm particle size and 3h roasting at 900°C. H₂SO₄, which is cheaper than HCl, achieved better leaching recovery than HCl. Oxidizing roasting duration at 900°C is shorter with H₂SO₄ than HCl leaching. The best particle size for both acid leaching is 1 mm.

In Turkey, necessary funds to support education and R&D on Th should be provided. Thorium Research Center/ThoReC) for Th mining + enrichment + extraction + fuel fabrication + prototype reactor testing + nuclear fuel cycle testing should be established immediately in Turkey. Turkish government should be enforced to use huge domestic Th resources along with imported U as an alternative fuel in some of the newly constructed nuclear reactors. If Turkey can process its important domestic low grade complex Th containing bastnasite resource in Eskisehir-Kızılcaören, it can supply its own Th fuel for more than 100 years and become self-sufficient in energy sources.

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