# GLOBAL AND USA THORIUM AND RARE EARTH ELEMENTS RESOURCES

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#### ABSTRACT

An assessment of the available global and USA thorium and rare earth elements resources is presented. The rare earths, a misnomer, are a moderately abundant group of 17 elements consisting of the 15 lanthanides, in addition to scandium and yttrium. What is rare is the occurrence of economically exploitable mineral deposits. These are being sought in a global effort to secure reserves for a nascent green industrial thrust.

Thorium, as an unexploited energy resource, is about four times more abundant than uranium in the Earth's crust and presents a more abundant fuel resource. Its occurrence is associated with the rare earth elements as well as yttrium and scandium, which are acquiring heightened interest in their use in critical new technologies.

Thorium presents itself as the basis of a valuable, either complementary or alternative,  $Th^{232}-U^{233}$  nuclear fuel cycle possessing more attractive characteristics compared with the present  $U^{238}$ -Pu<sup>239</sup> fuel cycle.

The increased availability and decreasing extraction cost of the rare earths is expected to introduce them into new applications and will also make Th readily available as a byproduct. Eventually, primary Th ores such as thorite and monazite could be accessed. Depleting hydrocarbons as well as uranium resource bases mandate the consideration of alternative energy sources, including thorium based cycles; which is otherwise a valuable yet unused energy resource.

#### **1. INTRODUCTION**

With the present-day availability of fissile  $U^{235}$  and  $Pu^{239}$ , as well as fusion and accelerator neutron sources [1-15], a fresh look at the Thorium- $U^{233}$  fuel cycle is warranted. Thorium, as an unexploited energy resource, is about four times more abundant than uranium in the Earth's crust and presents a more abundant fuel resource as shown in Table 1 and Fig. 1.

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Thorium as well as yttrium and scandium ores are characterized by the presence of rare earth elements, also known as the Lanthanides. The rare earth elements formally constitute the group of elements in the periodic Mendeleev table of the elements including: <sub>57</sub>Lanthanum, <sub>58</sub>Cerium, <sub>59</sub>Praseodymium, <sub>60</sub>Neodymium, <sub>61</sub>Promethium, <sub>62</sub>Samarium, <sub>63</sub>Europium, <sub>64</sub>Gadolinium, <sub>65</sub>Terbium, <sub>66</sub>Dysprosium, <sub>67</sub>Holmium, <sub>68</sub>Erbium, <sub>69</sub>Thulium, <sub>70</sub>Ytterbium and <sub>71</sub>Lutetium (Table 2).

Table 1. Relative abundances of some elements	in	the
Earth's crust.		

Element	Coursela e 1	Abundance	
Element	Symbol	[gms / ton]	
Lead	Pb	16	
Gallium	Ga	15	
Thorium	Th	10	
Samarium	Sm	7	
Gadolinium	Gd	6	
Praseodymium	Pr	6	
Boron	В	3	
Bromine	Br	3	
Uranium	U	2.5	
Uranium Beryllium	U Be	<b>2.5</b> 2	
Uranium Beryllium Tin	U Be Sn	<b>2.5</b> 2 1.5	
Uranium Beryllium Tin Tungsten	U Be Sn W	2.5 2 1.5 1	
Uranium Beryllium Tin Tungsten Molybdenum	U Be Sn W Mo	2.5 2 1.5 1 1	
Uranium Beryllium Tin Tungsten Molybdenum Mercury	U Be Sn W Mo Hg	2.5 2 1.5 1 1 0.2	
Uranium Beryllium Tin Tungsten Molybdenum Mercury Silver	U Be Sn W Mo Hg Ag	2.5 2 1.5 1 0.2 0.1	
Uranium Beryllium Tin Tungsten Molybdenum Mercury Silver Uranium <sup>235</sup>	U Be Sn W Mo Hg Ag U <sup>235</sup>	2.5 2 1.5 1 0.2 0.1 0.018	
Uranium Beryllium Tin Tungsten Molybdenum Mercury Silver Uranium <sup>235</sup> Platinum	U           Be           Sn           W           Mo           Hg           Ag           U <sup>235</sup> Pt	2.5 2 1.5 1 0.2 0.1 0.018 0.005	

The joint occurrence of Th and the rare earth elements in some ores such as Monazite and Thorogummite  $(Th(SiO4)_{1-x}(OH)_{4x})$ , a variant of Thorite containing hydroxyl, is shown in Table 3. It occurs as nodules 0.5-1.0 inch in diameter in

residual soil and weathered bedrock and appears associated with hematite; an iron oxide [16].

Lanthanide	Earth Crustal Abundance [ppm]	Solar System Abundance Relative to 10 <sup>7</sup> atoms Si
39Y	33	46
57La	30	4.5
<sub>58</sub> Ce	60	12
<sub>59</sub> Pr	8.2	1.7
<sub>60</sub> Nd	28	8.5
<sub>61</sub> Pm	0	0
<sub>62</sub> Sm	6	2.5
<sub>63</sub> Eu	1.2	1.0
<sub>64</sub> Gd	5.4	3.3
<sub>65</sub> Tb	0.9	0.6
<sub>66</sub> Dy	3.0	3.9
<sub>67</sub> Ho	1.2	0.9
<sub>68</sub> Er	2.8	2.5
<sub>69</sub> Tm	0.5	0.4
<sub>70</sub> Yb	3.0	2.4
<sub>71</sub> Lu	0.5	0.4

Table 2: Crustal Abundances of the lanthanides [29].



Figure 1. Logarithmic abundance of the elements relative to silicon in the Earth's crust. Source: USGS.

The Cerium<sup>142</sup> isotope with a natural abundance of 11.114 percent in Ce is radioactive with a half life of  $> 5 \times 10^{16}$  years. Cerium has a crustal abundance of 60 ppm, comparable with Ni at 75 ppm and Cu at 55 ppm.

The least abundant lanthanides, thulium and lutetium are more abundant than silver and bismuth. Promethium does not occur in nature and has no stable isotopes.

Induced fluorescence using a short wave ultraviolet light or a laser and chemical reaction with a basic reagent containing an alkali metal such as sodium hydroxide (lye) or sodium bicarbonate (baking soda) and with a halide acid such as hydrochloric acid, is used to detect the presence of the rare earths. The presence of radioactive elements in half of their 30 important minerals helps in the detection and location of the rare earths deposits, but poses a health physics operation protection of the workers, as well as an environmental disposal consideration for the tailings (Table 4). Radiation detectors, scintillometers and airborne radiometric surveys are used in identifying placer deposits.



Figure 2. Thorium dioxide with 1 percent cerium oxide impregnated fabric, Welsbach incandescent gas mantles (left) and ThO<sub>2</sub> flakes (right). Yttrium compounds now substitute for Th in mantles.

Table 3. Spectroscopic analysis showing the common occurrence of Th and rare earth elements in Thorogummite [26].

	Thorogummite,
	$(Th(SiO4)_{1-x} (OH)_{4x})$
Element	Syenite complex,
	Wausau, Wisconsin [26]
	[percent]
Th	> 10
Fe	5-10
Si	2-5
Al, Ca, Mg, Y	1-2
Ti	0.5-1.0
Mn, Na, Ce, Dy, Er, Gd, La, Sm	0.2-0.5
Nd, Yb	0.1-0.2
Cu, Nb, Pb, V	0.05-0.1
Ba, Co, Sc	0.01-0.02
Be	0.002-0.005
U	2.5

The rare earth elements are finding new applications in metallurgical alloys, and electrical instruments and tools. Some uses of the rare earth elements are shown in Table 5.

Added to other elements, they help maintain or alter their physical and structural conditions under different conditions. Used alone, they hold unique magnetic, electrical, chemical and luminescence properties.

The rare earths are used in catalytic activities. A lanthanum rich rare earth mixture is used in petroleum refining to increase the yield of gasoline and other aromatics from heavy crude.

Lanthanum and yttrium compounds possess high temperature superconducting properties.

Mischmetal, a product of the electrolysis of anhydrous mixed rare earths chlorides is used in the iron and steel industry to improve the rolling properties. High strength low alloy steels treated with rare earths are used in the automobile industry.

Rare earths metals are used in the manufacture of permanent magnets resulting in lighter, smaller and more efficient electrical motors and generators.

Europium and yttrium oxides are used in the red phosphor component in color television sets. Neodymium is used in the face plates to enhance the picture brightness and contrast.

Lanthanum or gadolinium is used in x-ray intensification screens to reduce patient diagnostic radiation effective dose exposure.

In ceramics and optics they are used as polishing compounds and glass additives.

The rare earth elements are constituent in more than 100 minerals. The most important ones are monazite, bastnäsite, davidite, xenotime, euxenite, samarskite, and allanite (Table 4). Thorium as well as uranium appear as components in many of these minerals. The extraction industry has favored the use of minerals free of Th or U such as bastnäsite, even though it contains  $Ce^{142}$  which is radioactive albeit with a long half life and hence a low activity.

Table 4. Chemical	composition of some rare earth ores with	th
	Th and U occurrence.	

Ore	Chemical composition
Allanite	$(Ca, Ce, Th)_2(Al, Fe, Mg)_3Si_3O_{12}(OH)$
Monazite	$(Ce,La,Pr,Nd,Th,Y)PO_4$
Parisite	$2(Ce,La,Di,Th)OF.CaO.3CO_3$
Polymignite	(Ca,Fe,Y, <b>Th</b> )(Nb,Ti,Ta,Zr)O <sub>4</sub>
Euxenite	$(Y,Ca,Er,La,Ce,U,Th)(Nb,Ta,Ti)_2O_6$
Cheralite	$(Ca, Ce, Th)(P, Si)O_4$
Samarskite	$(Y,Er,Ce,U,Ca,Fe,Pb,Th)(Nb,Ta,Ti,Sn)_2O_6$
Thorogummite	$(\mathbf{Th}(SiO4)_{1-x} (OH)_{4x})$
Davidite	$(La,Ce)(Y,U,Fe^{+2})(Ti,Fe^{+3})_{20}(O,OH)_{38}$
Fergusonite	(Y,Er,Ce,Fe)(Nb,Ta,Ti)O <sub>4</sub>
Loparite	(Ce,Na,Ca)(Ti,Nb)O <sub>3</sub>
Bastnäsite	(Ce,La,Di)F.CO <sub>2</sub>

In the early 1980s, the General Motors (GM) Company developed an alternative method to manufacture magnets. Rather than use solid iron magnets, a magnetic powder which could be mixed with rubber and injected into molds then sintered, was adopted. This powder, like many highperformance magnets, required the use of neodymium, a rare earth. With the powder, less metal was needed, so that vehicle parts could be lighter in weight. GM's magnet division was named Magnequench. It followed a pattern of acquisition and outsourcing in USA manufacturing. Seeking favorable labor conditions, environmental regulations and better access to resources, its manufacturing facilities were moved overseas in 2004 after being acquired in 1995 by the San Huan New Materials Company, partially owned by National Nonferrous Metals Import and Export Company.





Table 5. Some technological uses of the rare earth elements[17].

Rare earth element	Usage
Cerium	Automotive emission control, catalytic converters. Chemical and oil industries, oxidation and cracking catalyst. Manufacture of glass, paint, ceramics Ultra Violet UV cut glass. Polishing powder for glass, lenses and mirrors.
Lanthanum	Fluid cracking catalysts, processing of heavy crude oil and tar sands. Glass and ceramics production.
Samarium	Samarium cobalt (SmCo) ultra-high temperature magnets for space applications, lighting products, neutron absorber.
Europeum	Red phosphor color in display applications, television, digital projectors.
Gadolinium	Electronics, magnetic refrigeration, alloying agent, nuclear medicine.
Yttrium	Cathode Ray Tube (CRT), lasers and semiconductors.
Dysprosium, Terbium	High operating temperature magnets, jet and rocket engines, high performance motor vehicles.
Europium	Liquid Crystal Displays (LCDs).

Yttrium	
Cerium	
Cerium	Diesel Fuel additive.
Lanthanum	
Neodymium	Hybrid electric automobile motor and
Praseodymium	generator.
Dysprosium	Wind turbines generators' magnets.
Terbium	
Neodymium	Neodymium iron boron (NdFeB) high
	strength, light weight permanent
	magnets.
	Electric motors' permanent magnets.
	Wind turbine generators.
	Magnetic bearings, jet engines, wind
	generators, uranium enrichment
	centrifuges.
Cerium/Zirconium	Motor vehicles' catalytic converters.
Lanthanum	
Lanthanum	Nickel metal hydride (NiMH)
Cerium	rechargeable batteries.
	Hybrid automobile batteries.

#### 2. PROPERTIES OF THORIUM

Thorium (Th) is named after Thor, the Scandinavian god of war. It occurs in nature in the form of a single isotope:  $Th^{232}$ . Twelve artificial isotopes are known for Th. It occurs in Thorite, (Th,U)SiO<sub>4</sub> and Thorianite (ThO<sub>2</sub> + UO<sub>2</sub>). It is four times as abundant as uranium and is as abundant as lead and molybdenum.

It can be commercially extracted from the Monazite mineral containing 3-22 percent  $ThO_2$  with other rare earth elements or lanthanides. Its large abundance makes it a valuable resource for electrical energy generation with supplies exceeding both coal and uranium combined. This would depend on breeding of the fissile isotope U<sup>233</sup> from thorium according to the breeding reactions [20]:

$${}_{0}n^{1} + {}_{90}Th^{232} \rightarrow {}_{90}Th^{233} + \gamma$$

$${}_{90}Th^{233} \rightarrow {}_{91}Pa^{233} + {}_{-1}e^{0} + \nu^{*} + \gamma$$

$${}_{91}Pa^{233} \rightarrow {}_{92}U^{233} + {}_{-1}e^{0} + \nu^{*} + \gamma$$

$${}_{0}n^{1} + {}_{90}Th^{232} \rightarrow {}_{92}U^{233} + {}_{-1}e^{0} + 2\nu^{*} + 3\gamma$$

$$(1)$$

Together with uranium, its radioactive decay chain leads to the stable  $Pb^{208}$  lead isotope with a half-life of 1.4 x  $10^{10}$  years for Th<sup>232</sup>. It contributes to the internal heat generation in the Earth, together with other radioactive elements such as U and K<sup>40</sup>.

As Th<sup>232</sup> decays into the stable Pb<sup>208</sup> isotope, radon<sup>220</sup> or thoron forms in the chain. Rn<sup>220</sup> has a low boiling point and exists in gaseous form at room temperature. It poses a radiation hazard through its own daughter nuclei and requires adequate ventilation in underground mining. Radon tests are needed to check for its presence in new homes that are possibly built on rocks like granite or sediments like shale or phosphate rock containing significant amounts of thorium. Adequate ventilation of homes that are over-insulated becomes a design consideration in this case.

Thorium, in the metallic form, can be produced by reduction of  $ThO_2$  using calcium or magnesium. Also by electrolysis of anhydrous thorium chloride in a fused mixture of Na and K chlorides, by calcium reduction of Th tetrachloride mixed with anhydrous zinc chloride, and by reduction with an alkali metal of Th tetrachloride.

Thorium is the second member of the actinides series in the periodic table of the elements. When pure, it is soft and ductile, can be cold-rolled and drawn and it is a silvery white metal retaining its luster in air for several months. If contaminated by the oxide, it tarnishes in air into a gray then black color (Fig. 2).

Thorium oxide has the highest melting temperature of all the oxides at 3,300 degrees C. Just a few other elements and compounds have a higher melting point such as tungsten and tantalum carbide. Water attacks it slowly, and acids do not attack it except for hydrochloric acid.

Thorium in the powder form is pyrophyric and can burn in air with a bright white light. In portable gas lights the Welsbach mantle is prepared with  $ThO_2$  with 1 percent cerium oxide and other ingredients (Fig. 2).

As an alloying element in magnesium, it gives high strength and creep resistance at high temperatures.

Tungsten wire and electrodes used in electrical and electronic equipment such as electron guns in x-ray tubes or video screens are coated with Th due to its low work function and associated high electron emission. Its oxide is used to control the grain size of tungsten used in light bulbs and in high temperature laboratory crucibles.

Glasses for lenses in cameras and scientific instruments are doped with Th to give them a high refractive index and low dispersion of light.

In the petroleum industry, it is used as a catalyst in the conversion of ammonia to nitric acid, in oil cracking, and in the production of sulfuric acid.

### 3. ADVANTAGES OF THE THORIUM FUEL CYCLE

The following advantages of the thorium fuel cycle over the  $U^{235}$ -Pu<sup>239</sup> fuel cycle have been suggested [8-14]: 1. Breeding is possible in both the thermal and fast parts of the neutron spectrum with a regeneration factor of  $\eta > 2$  (Fig. 4).



Figure 4. Regeneration factor as a function of neutron energy for the different fissile isotopes.

2. Expanded nuclear fuel resources due to the higher abundance of the fertile  $Th^{232}$  than  $U^{238}$ . The USA resources in the state of Idaho are estimated to reach 600,000 tons of 30 percent of Th oxides. The probable reserves amount to 1.5 million tons. There exists about 3,000 tons of already milled thorium in a USA strategic stockpile stored in Nevada.

3. Lower nuclear proliferation concerns due to the reduced limited needs for enrichment of the  $U^{235}$  isotope that is needed for starting up the fission cycle and can then be later replaced by the bred  $U^{233}$ . The fusion fission hybrid totally eliminates that need. An attempted  $U^{233}$  weapon test is rumored to have evolved into a fizzle because of the  $U^{232}$  contaminant concentration and its daughter products could not be reduced to a practical level.

4. A superior system of handling fission product wastes than other nuclear technologies and a much lower production of the long lived transuranic elements as waste. One ton of natural  $Th^{232}$ , not requiring enrichment, is needed to power a 1,000 MWe reactor per year compared with about 33 tons of uranium solid fuel to produce the same amount of power. Thorium is simply purified then converted into a fluoride. The same initial fuel loading of one ton per year is discharged primarily as fission products to be disposed of for the fission thorium cycle.

5. Ease of separation of the lower volume and short lived fission products for eventual disposal.

6. Higher fuel burnup and fuel utilization than the  $U^{235}$ -Pu<sup>239</sup> cycle.

7. Enhanced nuclear safety associated with better temperature and void reactivity coefficients and lower excess reactivity in the core. Upon being drained from its reactor vessel, a thorium molten salt would solidify shutting down the chain reaction, 8. With a tailored breeding ratio of unity, a fission thorium fueled reactor can generate its own fuel, after a small amount of fissile fuel is used as an initial loading.

9. The operation at high temperature implies higher thermal efficiency with a Brayton gas turbine cycle (thermal efficiency around 40-50 percent) instead of a Joule or Rankine steam cycle (thermal efficiency around 33 percent), and lower waste heat that can be used for desalination or space heating. An open air cooled cycle can be contemplated eliminating the need for cooling water and the associated heat exchange equipment in arid areas of the world (Fig. 5).



Figure 5. Dry cooling tower in foreground, wet cooling tower in background in the THTR-300 pebble bed Th reactor, Germany.

10. A thorium cycle for base-load electrical operation would provide a perfect match to peak-load cycle wind turbines generation. The produced wind energy can be stored as compressed air which would be used to cool a thorium open cycle reactor, substantially increasing its thermal efficiency, yet not requiring a water supply for cooling.

11. The unit powers are scalable over a wide range for different applications such as process heat or electrical production. Units of 100 MWe capacity can be designed, built and combined for larger power needs.

12. Operation at atmospheric pressure without pressurization implies the use of standard equipment with a lower cost than the equipment operated at a 1,000-2,000 psi high pressure in the LWRs cycle. Depressurization would cause the pressurized water coolant to flash into steam and a loss of coolant.

13. In uranium-fuelled thermal reactors, without breeding, only 0.72 percent or 1/139 of the uranium is burned as  $U^{235}$ . If we assume that about 40 percent of the thorium can be converted into  $U^{233}$  then fissioned, this would lead to an energy efficiency ratio of 139 x 0.40 = 55.6 or 5,560 percent more efficient use of the available resource compared with  $U^{235}$ .

14. Operational experience exists from the Molten Salt reactor experiment (MSRE) at Oak Ridge National Laboratory (ORNL), Tennessee. A thorium fluoride salt was not corrosive to the nickel alloy: Hastelloy-N. Corrosion was caused only from tellurium, a fission product.

Four approaches to a thorium reactor are under consideration:

1. Use of a liquid molten Th fluoride salt,

2. Use of a pebble bed graphite moderated and He gas cooled reactor,

3. The use of a seed and blanket solid fuel with a Light Water Reactor (LWR) cycle,

4. A driven system using fusion or accelerator generated neutrons.

#### 4. THORIUM ABUNDANCE

Thorium is four times as abundant than uranium in the Earth's crust and provides a fertile isotope for breeding of the fissile uranium isotope  $U^{233}$  in a thermal or fast neutron spectrum.

In the Shippingport reactor it was used in the oxide form. In the HTGR it was used in metallic form embedded in graphite. The MSBR used graphite as a moderator and hence was a thermal breeder and a chemically stable fluoride salt, eliminating the need to process or to dispose of fabricated solid fuel elements. The fluid fuel allows the separation of the stable and radioactive fission products for disposal. It also offers the possibility of burning existing actinides elements and does need an enrichment process like the  $U^{235}$ -Pu<sup>239</sup> fuel cycle.

Thorium is abundant in the Earth's crust, estimated at 120 trillion tons. The Monazite black sand deposits are composed of 3-22 percent of thorium. It can be extracted from granite rocks and from phosphate rock deposits, rare earths, tin ores, coal and uranium mines tailings.

It has even been suggested that it can be extracted from the ash of coal power plants. A 1,000 MWe coal power plant generates about 13 tons of thorium per year in its ash. Each ton of thorium can in turn generate 1,000 MWe of power in a well optimized thorium reactor. Thus a coal power plant can conceptually fuel 13 thorium plants of its own power. From a different perspective, 1 pound of Th has the energy equivalent of 5,000 tons of coal. There are 31 pounds of Th in 5,000 tons of coal. If the Th were extracted from the coal, it would thus yield 31 times the energy equivalent of the coal.

The calcium sulfate or phospho-gypsum resulting as a waste from phosphorites or phosphate rocks processing into phosphate fertilizer contains substantial amounts of unextracted thorium and uranium.

Uranium mines with brannerite ores generated millions of tons of surface tailings containing thoria and rare earths.

The United States Geological Survey (USGS), as of 2010, estimated that the USA has reserves of 440,000 tons of

thorium ore. A large part is located on properties held by Thorium Energy Inc. at Lemhi Pass in Montana and Idaho (Fig. 7). This compares to a previously estimated 160,000 tons for the entire USA.

The next highest global thorium ores estimates are for Australia at 300,000 tons and India with 290,000 tons.

#### **5. THORIUM PRIMARY MINERALS**

Ore	Composition
Thorite	(Th,U)SiO <sub>4</sub>
Thorianite	$(ThO_2 + UO_2)$
Thorogummite	$Th(SiO4)_{1-x}(OH)_{4x}$
Monazite	(Ce,La,Y,Th)PO <sub>4</sub>
Brocktite	$(Ca,Th,Ce)(PO_4)H_2O$
Xenotime	(Y,Th)PO <sub>4</sub>
Euxenite	(Y,Ca,Ce,U,Th)(Nb,Ta,Ti) <sub>2</sub> O <sub>6</sub>
Iron ore	Fe + rare earths + Th apatite

Table 6: Major Thorium ores compositions.

Thorium occurs in several minerals [16, 19]:

1. Monazite, (Ce,La,Y,Th)PO<sub>4</sub>, a rare earth-thorium phosphate with 5-5.5 hardness. Its content in Th is 3-22 percent with 14 percent rare earth elements and yttrium. It occurs as a yellowish, reddish-brown to brown, with shades of green, nearly white, yellowish brown and yellow ore. This is the primary source of the world's thorium production. Until World War II, thorium was extracted from Monazite as a primary product for use in products such as camping lamp mantles. After World War II, Monazite has been primarily mined for its rare earth elements content. Thorium was extracted in small amounts and mainly discarded as waste.

2. Thorite, (Th,U)SiO<sub>4</sub> is a thorium-uranium silicate with a 4.5 hardness with yellow, yellow-brown, red-brown, green, and orange to black colors. It shares a 22 percent Th and a 22 percent U content. This ore has been used as a source of uranium, particularly the uranium rich uranothorite, and orangite; an orange colored calcium-rich thorite variety.

3. Brocktite, (Ca,Th,Ce)(PO<sub>4</sub>)H<sub>2</sub>O.

4. Xenotime, (Y,Th)PO<sub>4</sub>.

5. Euxenite, (Y,Ca,Ce,U,Th)(Nb,Ta,Ti)<sub>2</sub>O<sub>6</sub>.

6. Iron ore, (Fe)-rare earth elements-Th-apatite, Freta deposits at Pea Ridge, Missouri, Mineville, New York, and Scrub Oaks, New Jersey.

#### 6. GLOBAL AND USA THORIUM RESOURCES

Estimates of the available Th resources vary widely. The largest known resources of Th occur in the USA followed in order by Australia, India, Canada, South Africa, Brazil, and Malaysia.

Concentrated deposits occur as vein deposits, and disseminated deposits occur as massive carbonatite stocks,

alkaline intrusions, and black sand placer or alluvial stream and beach deposits.

Carbonatites are rare carbonate igneous rocks formed by magmatic or metasomatic processes. Most of these are composed of 50 percent or higher carbonate minerals such as calcite, dolomite and/or ankerite. They occur near alkaline igneous rocks.

Table 7. Estimated Global Thorium Resources [16].

Country	ThO <sub>2</sub> Reserves [metric tonnes] USGS estimate 2010 [16]	ThO <sub>2</sub> Reserves [metric tonnes] NEA estimate [22] <sup>***</sup>	Mined amounts 2007 [metric tonnes]*
USA	440,000	400,000	-**
Australia	300,000	489,000	-
Turkey		344,000	
India	290,000	319,000	5,000
Venezuela		300,000	
Canada	100,000	44,000	-
South	35,000	18,000	-
Africa			
Brazil	16,000	302,000	1,173
Norway		132,000	
Egypt		100,000	
Russia		75,000	
Greenland		54,000	
Canada		44,000	
Malaysia	4,500		800
Other	90,000	33,000	-
countries			
Total	1,300,000	2,610,000	6,970

\* Average Th content of 6-8 percent.

\*\* Last mined in 1994.

\*\*\* Reasonably assured and inferred resources available at up to \$80/kg Th

The alkaline igneous rocks, also referred to as alkali rocks, have formed from magmas and fluids so enriched in alkali elements that Na and K bearing minerals form components of the rocks in larger proportion than usual igneous rocks. They are characterized by feldspathoid minerals and/or alkali pyroxenes and amphiboles [19].

Table 8. Locations of USA major ThO<sub>2</sub> proven reserves [19].

Deposit type	Mining District	Location	ThO <sub>2</sub> reserves [metric tonnes]
Vein	Lehmi Pass	Montana-	64,000
deposits	district	Idaho	
	Wet	Colorado	58,200
	Mountain		
	area		
	Hall	Idaho	4,150
	Mountain		

	Iron Hill	Colorado	1,700
			(thorium
			veins)
			690
			(Carbonatite
			dikes)
	Diamond	Idaho	-
	Creek	100010	
	Bear Lodge	Wyoming	_
	Mountains	wyonning	
	Monroe	Utah	
	Convon	Otali	_
	Mountain	California	
	Nountain Dasa district	Camornia	-
	Pass district	A	
	Quartzite	Arizona	-
	district		
	Cottonwood	Arizona	-
	area		
	Gold Hill	New	-
	district	Mexico	
	Capitan	New	-
	Mountain	Mexico	
	Laughlin	New	-
	Peak	Mexico	
	Wausau,	Wisconsin	-
	Marathon		
	County		
	Bokan	Alaska	-
	Mountain		
Massive	Iron Hill	Colorado	28,200
Carbonatite			,
stocks			
	Mountain	California	8,850
	Pass		- ,
Black Sand	Stream	North.	4.800
Placer.	deposits	South	.,
Alluvial	acposito	Carolina	
Deposits		Curonnu	
Deposits	Stream	Idaho	9 130
	placers	Idallo	),150
	Beach	Florida	14 700
	placara	Goorgia	14,700
A 11-01	Deem Ladar	Wuomin	
Aikaline	Bear Lodge	w yoming	-
intrusions	Iviountains	T11' '	
<b>m</b> . 1 110 t	HICKS Dome	Illinois	-
Total, USA	1		194,420



Figure 6. Th concentrations in ppm and occurrences in the USA. Source: USA Geological Survey Digital Data Series DDS-9, 1993.



Figure 7. Lehmi Pass is a part of Beaverhead Mountains along the continental divide on the Montana-Idaho border, USA. Its Th veins contain rare earth elements, particularly Neodymium.



Figure 8. Mountain Pass, Mojave Desert, Nevada. Source: USGS.



Figure 9. Black sand Monazite layers in beach sand at Chennai, India. Photo: Mark A. Wilson [19].



Figure 10. Thorite (Th, U)SiO<sub>4</sub>, a thorium-uranium silicate.

## 7. RARE EARTH ELEMENTS RESOURCES

Global demand of rare earth oxides is estimated at 100,000-120,000 metric tonnes in 2007. It is forecast to grow at 9 percent per year through 2012 [25].

As a major manufacturer, the largest producer and consumer of rare earth elements is China. Being the lowest cost producer, about 94 percent of the rare earth oxides and almost 97 percent of the rare earth metal consumed in the world originate from China. Domestic consumption could exceed supply within 10 years [25].

Table 9. Rare Earth Elements content and price of typical ores[23].

Lanthanide	Bastnäsite Mountain Pass, California [percent]	Monazite Green Cove Springs, Florida [percent]	Price 2007 [\$/kg]
Cerium	49.30	43.70	50-65
Dysprosium	0.031	0.90	160
Erbium	-	-	165

Europium	0.11	0.16	1,200
Gadolinium	0.18	6.60	150
Holmium	-	0.11	750
Lanthanum	33.20	17.50	40
Lutetium	-	-	3,500
Neodymium	12.00	17.50	60
Praseodymium	4.30	5.00	75
Samarium	0.80	4.90	200-350
Scandium	-	-	-
Terbium	0.016	0.26	850
Thulium	-	-	2,500
Ytterbium	-	0.21	450
Yttrium	0.10	3.20	50

#### 8. GLOBAL AND USA URANIUM RESOURCES

Depleting hydrocarbon fuel resources and the growing volatility in fossil fuel prices, have led to an expansion in nuclear power production. As of 2010, there are 56 nuclear power reactors under construction worldwide, of which 21 are in China. Some are replacing older plants that are being decommissioned, and some are adding new installed capacity. The Chinese nuclear power program is probably the most ambitious in history. It aims at 50 new plants by the year 2025 with an additional 100, if not more, completed by the year 2050. Standardized designs, new technology, a disciplined effort to develop human skills and industrial capacities to produce nuclear power plant components all point to a likely decline in plant construction costs in coming years and growing interest in new nuclear projects with ensuing pressure on nuclear fuels.



Figure 11. Number of power reactors under construction worldwide. Total: 56. Net electrical capacity: 51.9 MWe. Data source: IAEA, 2010.

It should be noted that there are currently 150 international reactor projects in some advanced permitting stage. An additional 300 projects are in some early planning stage. Added to a significant fraction of the currently 439 operating power reactors will likely double global nuclear capacity in the coming couple decades (most countries seem willing to try to extend the operating lives of existing reactors through safety-compliant upgrades and retrofits). Building a nuclear power plant practically requires contracting its fuel supply for 40-60 years. When adding all new projects it is reasonable to conclude that fuel requirements could double in the coming couple decades.

About 30 percent of the known recoverable global uranium oxide resources are found in Australia, followed by Kazakhstan (17 percent), Canada (12 percent), South Africa (8 percent), Namibia (6 percent), and Russia, Brazil and the USA, each with about 4 percent of the world production [21].

The uranium resources are classified into "conventional" and "non-conventional" resources. The conventional resources are further categorized into "Reasonably Assured Resources," RAR and the believed-to-exist "Inferred Resources," IR.

The RAR and IR categories are further subdivided according to the assumed exploitation cost in USA dollars. These cost categories are given as < 40 (kg, < 80)(kg, and < 130)(kg.

The non-conventional resources are split into "Undiscovered Resources," UR, further separated into "Undiscovered Prognosticated Resources," UPR with assumed cost ranges of < 80 \$/kg and < 130 \$/kg, and "Undiscovered Speculative Resources" USR.

The USR numbers are given for an estimated exploitation cost of < 130 \$/kg and also for a category with an unknown cost.

In the twentieth century, the USA was the world leading uranium producer until it was surpassed by Canada and Australia. In 2007, Canada accounted for 23 percent and Australia for 21 percent of global production, with the USA at 4 percent. Africa is becoming a new frontier in uranium production with Namibia 7 percent, Niger 8 percent, and South Africa 1 percent. Exploration and new mine development is ongoing in Botswana, Tanzania. Jordan and Nigeria.

The federal, provincial and local governments in Australia have all unilaterally and forcefully banned the development of any new uranium mines, even though existing mines continue operation. The French company Areva was not successful in receiving approval to build a new uranium mine in Australia. It has mining activities in the Niger Republic and received exploration licenses in other countries such as Jordan.

Canadian producer Cameco rates as the first world producer of uranium oxide, followed by French Areva, and then Energy Resources of Australia (68 percent owned by Rio Tinto), which produces some 6,000 tons per year.

As of 2007, five operating uranium mines existed in the USA, with 3 in Texas, one in Wyoming and one in Northern Nebraska as shown in Table 10. The state of Texas has a positive attitude towards uranium mining, and energy production in general, with an advantageous regulatory framework that streamlines the permit process using in situ leaching of uranium. Texas, being an "Agreement State," implies that the USA Nuclear Regulatory Commission (NRC) has delegated its authority to the state regulatory agencies such as the Texas Commission on Environmental Quality (TCEQ), and companies deal directly with the state agencies in Texas rather than with the federal government's NRC. Most of the uranium mining operations in the USA and Kazakhstan use in situ leach methods, also designated as In Situ Recovery (ISR) methods. Conventional methods are used in 62 percent of U mining, with 28 percent as ISR and 9 percent as byproduct extraction.

By 2008, U production in the USA fell 15 percent to 1,780 tonnes  $U_3O_8$ . The U production in the USA is currently from one mill at White Mesa, Utah, and from 6 ISR operations. In 2007, four operating mines existed in the Colorado Plateau area: Topaz, Pandora, West Sunday and Sunday-St. Jude. Two old mines reopened in 2008: Rim Canyon and Beaver Shaft and the Van 4 mine came into production in 2009.

As of 2010, Cameco Resources operated two ISL operations: Smith Ranch-Highland Mine in Wyoming and Cross Butte Mine in Nebraska, with reserves of 15,000 tonnes  $U_3O_8$ . The Denison Mines Company produced 791,000 tonnes of  $U_3O_8$  in 2008 at its 200 t/day White Mesa mill in Southern Utah from its own and purchased ore, as well as toll milling.

Table 10: World main producing uranium mines, 2008.Source: World Nuclear Association, WNA.

Country	Production [tonnes U]	Share of world production [percent]	Main owner	Extraction method	Mine
Canada	6,383	15	Cameco	Conv	McArthur River
Australia	4,527	10	Rio Tinto	Conv	Ranger
Namibia	3,449	8	Rio Tinto	Conv	Rðssing
Australia	3,344	8	BHP Billiton	Byproduct	Olympic Dam
Russia	3,050	7	ARMZ	Conv	Priargunsky
Niger	1,743	4	Areva	Conv	Somair
Canada	1,368	3	Cameco	Conv	Rabbit Lake
Niger	1,289	3	Areva	Conv	Cominak
Canada	1,249	3	Areva	Conv	McLean
Kazakhs	1,034	2	Uranium	ISR	Akdata
tan	27.126	(2)	One		
Total	27,436	62			

Uranium in the Colorado Plateau in the USA has an average grade of 0.25 percent or 2,500 ppm uranium in

addition to 1.7 percent vanadium within the Uravan Mineral Belt.

Goliad County, Texas has an average grade of 0.076 percent (760 ppm) uranium oxide in sandstone deposits permeated by groundwater suggesting in situ leaching methods where water treated with carbon dioxide is injected into the deposit. The leachate is pumped and passed over ion exchange resins to extract the dissolved uranium.

Table 11.	Uranium concentrates production in the USA,
	2007.

Mine	Location	Company	$\begin{array}{c} \text{Production} \\ 2005 \\ [10^6 \text{ lb} \\ U_3 O_8] \end{array}$	Product ion 2006 $[10^6$ lb $U_3O_8]$
Smith	Wyoming	Cameco	1.3	2.0
Ranch/Highland		(Power		
		resources)		
Crow Butte	Nebraska	Crow	0.8	0.7
		Butte		
		Resources,		
		Cameco		
Vasquez	South	Uranium	0.3	0.2
	Texas	Resources		
Kingsville	South	Uranium	-	0.1
Dome	Texas	Resources		
Alta Mesa	South	Alta Mesa	0.3	1.0
	Texas			
Total USA			2.7	4.0
production				

Phosphate rocks containing just 120 ppm in U have been used as a source of uranium in the USA. The fertilizer industry produces large quantities of wet process phosphoric acid solution containing 0.1-0.2 gram/liter (g/l) of uranium, which represent a significant potential source of uranium.

#### 9. NONPROLIFERATION CHARACTERISTICS

In the Th-U<sup>233</sup> fuel cycle, the hard gamma rays associated with the decay chain of the formed isotope  $U^{232}$  with a half life of 72 years and its spontaneous fission makes the  $U^{233}$  in the thorium cycle with high fuel burnup a higher radiation hazard from the perspective of proliferation than Pu<sup>239</sup>.

The  $U^{232}$  is formed from the fertile Th<sup>232</sup> from two paths involving an (n, 2n) reaction, which incidentally makes Th<sup>232</sup> a good neutron multiplier in a fast neutron spectrum:

$${}_{0}n^{1} + {}_{90}Th^{232} \rightarrow 2_{0}n^{1} + {}_{90}Th^{231}$$

$${}_{90}Th^{231} \xrightarrow{25.52h} {}_{-1}e^{0} + {}_{91}Pa^{231}$$

$${}_{0}n^{1} + {}_{91}Pa^{231} \rightarrow \gamma + {}_{91}Pa^{232}$$

$${}_{91}Pa^{232} \xrightarrow{1.31d} {}_{-1}e^{0} + {}_{92}U^{232}$$

$$(2)$$

and another involving an  $(n, \gamma)$  radiative capture reaction:

$${}_{0}n^{1} + {}_{90}Th^{232} \rightarrow \gamma + {}_{90}Th^{233}$$

$${}_{90}Th^{233} \xrightarrow{22.2m} {}_{-1}e^{0} + {}_{91}Pa^{233}$$

$${}_{91}Pa^{233} \xrightarrow{27d} {}_{-1}e^{0} + {}_{92}U^{233}$$

$${}_{92}U^{233} + {}_{0}n^{1} \rightarrow 2{}_{0}n^{1} + {}_{92}U^{232}$$
(3)

The isotope  $U^{232}$  is also formed from a reversible (n, 2n) and (n,  $\gamma$ ) path acting on the bred  $U^{233}$ :

$${}_{0}n^{1} + {}_{92}U^{233} \rightarrow 2_{0}n^{1} + {}_{92}U^{232}$$

$${}_{0}n^{1} + {}_{92}U^{232} \rightarrow \gamma + {}_{92}U^{233}$$
(4)

The isotope  $Th^{230}$  occurs in trace quantities in thorium ores that are mixtures of uranium and thorium.  $U^{234}$  is a decay product of  $U^{238}$  and it decays into  $Th^{230}$  that becomes mixed with the naturally abundant  $Th^{232}$ . It occurs in secular equilibrium in the decay chain of natural uranium at a concentration of 17 ppm. The isotope  $U^{232}$  can thus also be produced from two successive neutron captures in  $Th^{230}$ :

$${}_{0}n^{1} + {}_{90}Th^{230} \rightarrow \gamma + {}_{90}Th^{231}$$

$${}_{90}Th^{231} \xrightarrow{25.52h} {}_{-1}e^{0} + {}_{91}Pa^{231}$$

$${}_{0}n^{1} + {}_{91}Pa^{231} \rightarrow \gamma + {}_{91}Pa^{232}$$

$${}_{91}Pa^{232} \xrightarrow{1.31d} {}_{-1}e^{0} + {}_{92}U^{232}$$
(5)

The hard 2.6 MeV gamma rays originate from  $Tl^{208}$  isotope in the decay chain of aged  $U^{232}$  which eventually decays into the stable Pb<sup>208</sup> isotope:

$${}_{92}U^{232} \xrightarrow{72a} {}_{90}Th^{228} {}_{2}He^{4}$$

$${}_{90}Th^{228} \xrightarrow{1.913a} {}_{88}Ra^{224} {}_{2}He^{4}$$

$${}_{88}Ra^{224} \xrightarrow{3.66d} {}_{86}Rn^{220} {}_{2}He^{4}$$

$${}_{86}Rn^{220} \xrightarrow{55.6s} {}_{82}Po^{216} {}_{2}He^{4}$$

$${}_{84}Po^{216} \xrightarrow{0.15s} {}_{82}Pb^{212} {}_{2}He^{4}$$

$${}_{82}Pb^{212} \xrightarrow{10.64h} {}_{83}Bi^{212} {}_{-1}e^{0}$$

$${}_{83}Bi^{212} \xrightarrow{60.6m} {}_{64\%} {}_{84}Po^{212} {}_{-1}e^{0}$$

$${}_{83}Bi^{212} \xrightarrow{60.6m} {}_{84}Po^{212} {}_{-1}e^{0}$$

$${}_{83}Bi^{212} \xrightarrow{0.298\mu s} {}_{82}Pb^{208}(stable) {}_{2}He^{4}$$

$${}_{81}Tl^{208} \xrightarrow{3.053m} {}_{82}Pb^{208}(stable) {}_{-1}e^{0} {}_{9}(2.6146MeV)$$

As comparison, the  $U^{233}$  decay chain eventually decays into the stable  $Bi^{209}$  isotope:

$${}_{92}U^{233} \xrightarrow{1.592 \times 10^{5}a} {}_{90}Th^{229} + {}_{2}He^{4}$$

$${}_{90}Th^{229} \xrightarrow{7340a} {}_{88}Ra^{225} + {}_{2}He^{4}$$

$${}_{88}Ra^{225} \xrightarrow{14.8d} {}_{89}Ac^{225} + {}_{-1}e^{0}$$

$${}_{89}Ac^{225} \xrightarrow{10.0d} {}_{87}Fr^{221} + {}_{2}He^{4}$$

$${}_{87}Fr^{221} \xrightarrow{4.8m} {}_{85}At^{217} + {}_{2}He^{4}$$

$${}_{83}Bi^{213} \xrightarrow{45.6m} {}_{84}Po^{213} + {}_{-1}e^{0}$$

$${}_{84}Po^{213} \xrightarrow{4.2\mu s} {}_{82}Pb^{209} + {}_{2}He^{4}$$

$${}_{82}Pb^{209} \xrightarrow{3.28h} {}_{83}Bi^{209}(stable) + {}_{-1}e^{0}$$

A 5-10 proportion of  $U^{232}$  in the  $U^{232}$ - $U^{233}$  mixture has a radiation equivalent dose rate of about 1,000 cSv (rem)/hr at a 1 meter distance for decades making it a highly proliferation resistant cycle if the Pa<sup>233</sup> is not separately extracted and allowed to decay into pure  $U^{233}$ .

The Pa<sup>233</sup> cannot be chemically separated from the  $U^{232}$  if the design forces the fuel to be exposed to the neutron flux without a separate blanket region, making the design fail-safe with respect to proliferation and if a breeding ratio of unity is incorporated in the design.

Such high radiation exposures would lead to incapacitation within 1-2 hours and death within 1-2 days of any potential proliferators.

The International Atomic Energy Agency (IAEA) criterion for fuel self protection is a lower dose equivalent rate of 100 cSv(rem)/hr at a 1 meter distance. Its denaturing requirement for  $U^{235}$  is 20 percent, for  $U^{233}$  with  $U^{238}$  it is 12 percent, and for  $U^{233}$  denaturing with  $U^{232}$  it is 1 percent.

The Indian Department of Atomic Energy (DAE) had plans on cleaning  $U^{233}$  down to a few ppm of  $U^{232}$  using Laser Isotopic Separation (LIS) to reduce the dose to the occupational workers.

The contamination of  $U^{233}$  by the  $U^{232}$  isotope is mirrored by another introduced problem from the generation of  $U^{232}$  in the recycling of Th<sup>232</sup> due to the presence of the highly radioactive Th<sup>228</sup> from the decay chain of  $U^{232}$ .

#### **10. DOSIMETRY**

The International Atomic Energy Agency (IAEA) criterion for occupational protection is an effective dose of 100 cSv (rem)/hr at a 1 meter distance from the radiation source.

It is the decay product  $TI^{208}$  in the decay chain of  $U^{232}$ and not  $U^{232}$  itself that generates the hard gamma rays. The  $TI^{208}$  would appear in aged  $U^{233}$  over time after separation, emitting a hard 2.6416 MeV gamma ray photon. It accounts

for 85 percent of the total effective dose 2 years after separation. This implies that manufacturing of  $U^{233}$  should be undertaken in freshly purified  $U^{233}$ . Aged  $U^{233}$  would require heavy shielding against gamma radiation.

In comparison, in the U-Pu<sup>239</sup> fuel cycle, Pu<sup>239</sup> containing Pu<sup>241</sup> with a half life of 14.4 years, the most important source of gamma ray radiation is from the Am<sup>241</sup> isotope with a 433 years half life that emits low energy gamma rays of less than 0.1 MeV in energy. For weapons grade Pu<sup>239</sup> with about 0.36 percent Pu<sup>241</sup> this does not present a major hazard but the radiological hazard becomes significant for reactor grade Pu<sup>239</sup> containing about 9-10 percent Pu<sup>241</sup>. The generation of Pu<sup>241</sup> as well as Pu<sup>240</sup> and Am<sup>241</sup> from

The generation of  $Pu^{241}$  as well as  $Pu^{240}$  and  $Am^{241}$  from  $U^{238}$  follows the following path:

$${}_{0}n^{1} + {}_{92}U^{238} \rightarrow \gamma + {}_{92}U^{239}$$

$${}_{92}U^{239} \xrightarrow{23.5m} {}_{-1}e^{0} + {}_{93}Np^{239}$$

$${}_{93}Np^{239} \xrightarrow{2.35d} {}_{-1}e^{0} + {}_{94}Pu^{239}$$

$${}_{0}n^{1} + {}_{94}Pu^{239} \rightarrow \gamma + {}_{94}Pu^{240}$$

$${}_{0}n^{1} + {}_{94}Pu^{240} \rightarrow \gamma + {}_{94}Pu^{241}$$

$${}_{94}Pu^{241} \xrightarrow{14.7a} {}_{-1}e^{0} + {}_{95}Am^{241}$$
(8)

Plutonium containing less than 6 percent  $Pu^{240}$  is considered as weapons-grade.

The gamma rays from Am<sup>241</sup> are easily shielded against with Pb shielding. Shielding against the neutrons from the spontaneous fissions in the even numbered Pu<sup>238</sup> and Pu<sup>240</sup> isotopes accumulated in reactor grade plutonium requires the additional use of a thick layer of a neutron moderator containing hydrogen such as paraffin or plastic, followed by a layer of neutron absorbing material and then additional shielding against the gamma rays generated from the neutron captures.

The generation of  $Pu^{238}$  and  $Np^{237}$  by way of (n, 2n) rather than  $(n, \gamma)$  reactions, follows the path:

$${}_{0}n^{1} + {}_{92}U^{238} \rightarrow 2_{0}n^{1} + {}_{92}U^{237}$$

$${}_{92}U^{237} \xrightarrow{6.75d} {}_{-1}e^{0} + {}_{93}Np^{237}$$

$${}_{0}n^{1} + {}_{93}Np^{237} \rightarrow \gamma + {}_{93}Np^{238}$$

$${}_{93}Np^{238} \xrightarrow{2.12d} {}_{-1}e^{0} + {}_{94}Pu^{238}$$
(9)

The production of Pu<sup>238</sup> for radioisotopic heat and electric sources for space applications follows the path of chemically separating Np<sup>237</sup> from spent LightWater Reactors (LWRs) fuel and then neutron irradiating it to produce Pu<sup>238</sup>.

Table 12. Typical compositions of fuels in the uranium and<br/>thorium fuel cycles.

Isotopic composition [percent]	Pu <sup>239</sup> weapons grade	Pu <sup>239</sup> reactors grade	U <sup>233</sup>	$U^{233} + 1$ ppm $U^{232}$
$U^{232}$			0.000	0.00
$U^{233}$			100.00	99.99
Pu <sup>238</sup>	0.0100	1.3000		
Pu <sup>239</sup>	93.800	60.3000		
$Pu^{240}$	5.8000	24.3000		
Pu <sup>241</sup>	0.3500	9.1000		
Pu <sup>242</sup>	0.0200	5.0000		
Density [gm/cm <sup>3</sup> ]	19.86	19.86	19.05	19.0
Radius [cm]	3.92	3.92	3.96	3.9
Weight [kg]	5	5	5	5

Table 13. Glove box operation dose rate required to accumulate a limiting occupational 5 cSv (rem) dose equivalent from a 5 kg metal sphere, one year after separation at a 1/2 meter distance [27].

Fuel	Time to 5 cSv	Effective dose		
1 <sup>232</sup> /1 <sup>233</sup>	effective dose	rate		
0 /0	[hr]	cSv/hr		
0.01	0.039	127.0000		
100 ppm	3.937	1.2700		
5 ppm	84.746	0.0590		
1 ppm	384.615	0.0130		
Reactor grade Pu <sup>239</sup>	609.756	0.0082		
Weapons grade Pu <sup>239</sup>	3846.154	0.0013		

Both reactor-grade plutonium and  $U^{233}$  with  $U^{232}$  would pose a significant radiation dose equivalent hazard for manufacturing personnel as well as military personnel, which precludes their use in weapons manufacture in favor of enriched  $U^{235}$  and weapons-grade Pu<sup>239</sup>.

Table 14. Dose equivalent rates in cSv (rem)/hr from 5 kg metal spheres at a 1/2 meter distance for different times after separation [27].

Material	Type of radiation	Dose equivalent rate at time after separation [cSv(rem)/hr]						
		0 yr 1 yr 5 yr 10 yr 15 yr						
Pure U <sup>233</sup>	γ total	0.32	0.42	0.84	1.35	1.89		
$U^{233}$ +1	γ total	0.32	13.08	35.10	39.57	39.17		
ppm U <sup>232</sup>	γ from Tl <sup>208</sup>	0.00	11.12	29.96	33.48	32.64		
Pu <sup>239</sup> ,	γ	0.49	0.71	1.16	1.57	1.84		
weapons	neutrons	0.56	0.56	0.56	0.56	0.56		
grade	$\gamma$ +	1.05	1.27	1.72	2.13	2.40		

Proceedings of the "2<sup>nd</sup> Thorium Energy Alliance Conference, The Future Thorium Energy Economy," Google Campus, Mountain View, California, USA, March 29-30, 2010

	neutron					
Pu <sup>239</sup> ,	γ total	0.49	5.54	16.72	28.64	37.54
Reactor	γ from	0.00	3.24	14.60	26.00	34.80
grade	Am <sup>241</sup>					
	neutrons	2.66	2.66	2.65	2.64	2.63
	γ+	3.15	8.20	19.37	31.28	40.17
	neutrons					

#### **11. ACTINIDES PRODUCTION**

There has been a new interest in the Th cycle in Europe and the USA since it can be used to increase the achievable fuel burnup in LWRs in a once through fuel cycle while significantly reducing the transuranic elements in the spent fuel. A nonproliferation as well as transuranics waste disposal consideration is that just a single neutron capture reaction in  $U^{238}$  is needed to produce  $Pu^{239}$  from  $U^{238}$ :

$${}_{0}n^{1} + {}_{92}U^{238} \rightarrow {}_{92}U^{239} + \gamma$$

$${}_{92}U^{239} \xrightarrow{23.5m} {}_{93}Np^{239} + {}_{-1}e^{0}$$

$${}_{93}Np^{239} \xrightarrow{2.35d} {}_{94}Pu^{239} + {}_{-1}e^{0}$$
(10)

whereas a more difficult process of fully 5 successive neutron captures are needed to produce the transuranic  $Np^{237}$  from Th<sup>232</sup>:

$${}_{0}n^{1} + {}_{90}Th^{232} \rightarrow {}_{90}Th^{233} + \gamma$$

$${}_{0}n^{1} + {}_{90}Th^{233} \rightarrow {}_{90}Th^{234} + \gamma$$

$${}_{90}Th^{234} \xrightarrow{24.1d} {}_{91}Pa^{234} + {}_{-1}e^{0}$$

$${}_{91}Pa^{234} \xrightarrow{6.70h} {}_{92}U^{234} + {}_{-1}e^{0}$$

$${}_{0}n^{1} + {}_{92}U^{234} \rightarrow {}_{92}U^{235} + \gamma$$

$${}_{0}n^{1} + {}_{92}U^{235} \rightarrow {}_{92}U^{236} + \gamma$$

$${}_{0}n^{1} + {}_{92}U^{236} \rightarrow {}_{92}U^{237} + \gamma$$

$${}_{92}U^{237} \xrightarrow{6.75d} {}_{93}Np^{237} + {}_{-1}e^{0}$$
(11)

This implies a low yield of Np<sup>237</sup> however, as an odd numbered mass number isotope posing a possible proliferation concern; whatever small quantities of it are produced, provisions must be provided in the design to have it promptly recycled back for burning in the fast neutron spectrum of the fusion part of the hybrid.

In fact, it is more prominently produced in thermal fission light water reactors using the uranium cycle and would be produced; and burned, in fast fission reactors through the (n, 2n) reaction channel with  $U^{238}$  according to the much simpler path:

$${}_{0}n^{1} + {}_{92}U^{238} \rightarrow 2_{0}n^{1} + {}_{92}U^{237}$$

$${}_{92}U^{237} \xrightarrow{6.75d} {}_{93}Np^{237} + {}_{-1}e^{0}$$
(12)

The  $Np^{237}$  gets transmuted in the  $Th^{232}$  fuel cycle into  $Pu^{238}$  with a short half-life of 87.74 years:

$${}_{0}n^{1} + {}_{93}Np^{237} \rightarrow {}_{93}Np^{238} + \gamma$$

$${}_{93}Np^{238} \xrightarrow{2.12d} {}_{94}Pu^{238} + {}_{-1}e^{0}$$
(13)

A typical 1,000 MWe Light Water Reactor (LWR) operating at an 80 percent capacity factor produces about 13 kgs of  $Np^{237}$  per year.

This has led to suggested designs where  $Th^{232}$  replaces  $U^{238}$  in LWRs fuel and accelerator driven fast neutron subcritical reactors that would breed  $U^{233}$  from  $Th^{232}$ .

Incidentally, whereas the  $Pu^{238}$  isotope is produced in the Th fuel cycle, it is the  $Pu^{240}$  isotope with a longer 6,537 years half-life, that is produced in the U-Pu fuel cycle:

$${}_{0}n^{1} + {}_{92}U^{238} \rightarrow {}_{92}U^{239} + \gamma$$

$${}_{92}U^{239} \rightarrow {}_{93}Np^{239} + {}_{-1}e^{0} + \nu^{*} + \gamma \qquad (14)$$

$${}_{93}Np^{239} \rightarrow {}_{94}Pu^{239} + {}_{-1}e^{0} + \nu^{*} + \gamma$$

$${}_{0}n^{1} + {}_{94}Pu^{239} \rightarrow {}_{94}Pu^{240} + \gamma$$

#### **12. LEGISLATIVE INITIATIVES**

Interest in Th as a fuel resource, as well as the discontinuation of the Yucca Mountain once-through fuel cycle in the USA, led to an initiative, Senate Bill S.3680, by USA Senators Orrin Hatch (Utah) and Harry Reid (Nevada): The Thorium Energy Independence and Security Act of 2008, which amends the Atomic Energy Act of 1954, would establish offices at the USA Nuclear Regulatory Commission (USNRC) and the Department of Energy (DOE) to regulate domestic thorium nuclear power generation and oversee possible demonstrations of thorium nuclear fuel assemblies. The bill was read twice and referred to the Committee on Energy and Natural Resources, but has not become law.

This was followed by Congressional Bill HR1534 by Congressman Joe Sestak (Pennsylvania): To direct the Secretary of Defense and the Chairman of the Joint Chiefs of Staff to carry out a study on the use of thorium-liquid fueled nuclear reactors for naval power needs and other purposes. This bill has been referred to the Subcommittee on Seapower and Expeditionary Forces. The USA Navy declined the offer and its allocated funds.

Senator Evan Bayh (Indiana) and Representative Mike Coffman (Colorado) included amendments in the Fiscal Year 2010 National Defense Authorization Act requiring a government assessment of the availability of rare earth materials to support industry and the defense market.

Senators Orrin G. Hatch (R-Utah) and Harry Reid (D-Nevada), on March 3<sup>rd</sup>, 2010, reintroduced earlier legislation: the Thorium Energy Security Act of 2010; to accelerate the use of thorium-based nuclear fuel in existing and future USA reactors. Their legislation establishes a regulatory framework and a development program to facilitate the introduction of thorium-based nuclear fuel in nuclear power plants across the USA.

It must be noted that the majority of bills and resolutions are primarily political gestures and never make it out of committee.

#### **13. DISCUSSION**

The "rare" earth elements are in fact "moderately abundant" in the Earth's crust even though their discovered minable concentrations are less common than for other ores.

The USA and global resources are mainly in the form of Monazite and Bastnäsite. The Bastnäsite deposits in the USA and China are the largest economic resources.

On the other hand, Monazite deposits in Australia, Brazil, China, India, Malaysia, South Africa, Sri Lanka, Thailand, and the USA constitute the next largest resource. Other ores exist such as Apatite, Cheralite, Eudialyte, Loparite, Phosphorites, rare-earth-bearing ion-adsorption clays, secondary monazite, spent uranium solutions, xenotime, iron ores, uranium ores and yet undiscovered potential resources[24].

With China becoming a world leader in electric batteries and wind turbines manufacturing, and with increased internal demand, its export of rare earth elements decreased to 30,000 tons in 2009, compared with 45,000 tons in 2008 and 60,000 tons in 2002.

A USA document about dual-use technologies: "U. S. National Security and Military/Commercial Concerns with the People's Republic of China," refers to the "Super 863" research and development program, named after its conception date in March 1986 that reportedly involved 30,000 scientists and engineers including about 1,000 doctorate holders. A visionary 1992 outlook attributed to China's late "paramount leader" Deng Xiaoping is: "There is oil in the Middle East. There are rare earths in China. We must take full advantage of this resource." The program started in 1996 and claims the achievement of 1,500 unspecified technological breakthroughs. After the launch of the Super 863 program in 1997, the Chinese Communist Party adopted the "16-Character Policy" in reference to the 16 Chinese characters that describe a four-sentence blueprint for China's ascendance on the world's stage: "Combine the military with the civil. Combine peace and war. Give priority to military products. Let the civil support the military." This signals a possible future competition for the global rare earths resources as feed materials to a new green technologies industrial thrust.

Global demand for rare earth elements is expected to expand at a 9 percent yearly rate of growth. China's share of the world market is a substantial 95 percent. Caused by a product oversupply, producers complain that prices are controlled by the end users.

Nurturing and protecting its rare earth production industry, China promises rare earth resource availability only if the production facilities are located in China, attracting industry, research, technology, manufacturing plants and jobs.

In 2005, the CNOOC Company made a bid for the Unocal (Union Oil of California) Company. Based on these concerns, a competing bid by the Chevron Company was encouraged. The largest USA rare earth elements mine, is privately held, as of October 1<sup>st</sup> 2008, by Molycorp Minerals LLC, and earlier by Unocal then Chevron Minerals. It opened in the USA in the 1950s at Mountain Pass in the Mojave Desert 50 miles south of Las Vegas, Nevada (Fig. 8). It supplied the rare earth europium that generates the red color in television sets. Molycorp Minerals has a joint venture with Sumitomo Metals to sell lanthanide goods in Japan. The company began operations in 1920 with a molybdenum mine in New Mexico. The Mountain Pass, California rare earth refinery resumed operation in 2007 through 2009 beneficiating and extracting rare earth elements from the Bastnäsite ore.

Table 15. Consumption areas of rare earth elements [23].

	China	USA
Usage area	2007	2008
-	[Percent]	[percent]
Permanent magnets	30.7	5.0
Metallurgical	15.2	29.0
applications and		
alloys		
Petrochemical,	10.4	14.0
chemical catalysts		
Glass polishing	10.2	
powders		
Hydrogen storage	8.5	
alloys for batteries		
Phosphors for	6.2	12.0
fluorescent lighting,		
flat panel displays for		
computer monitors,		
color televisions,		
radar, x-ray		
intensifying film		
Glass and ceramic	4.5	6.0
additives		
Automotive catalysts,	3.7	9.0
catalytic converters		
Electronics		18.0
Petroleum refining		4.0
catalysts		

Miscellaneous	10.6	3.0
applications		

New green developing technologies depend on the availability of the rare earths metals. As petroleum set a record price in 2008, the technology of hybrid cars was widely adopted, achieving a mileage of 48 miles/gallon in city driving. A shortage of such vehicles occurred as a result of a shortage of the rechargeable Ni metal hydride (NiMH) batteries using lanthanum.

Thorium supplies constitute a yet unused energy resource. They occur primarily in the rare earth ore mineral Monazite and the thorium mineral thorite. The size of the global resource is estimated at  $1.3 \times 10^6$  metric tonnes of ThO<sub>2</sub>. The USA and Australia hold the world's largest known reserves with uncertain estimates ranging from  $0.19 \times 10^6 - 0.44 \times 10^6$  metric tonnes of ThO<sub>2</sub>. Many of the USA reserves sizes are not known, as a result of unavailable data for lack of economical extraction attractiveness without an energy use option for thorium.

The main international rare earths processors presently opt to process only thorium-free feed materials to avoid its radioactive content, even though they still have to cope with the radioactive isotope  $Ce^{142}$  which occurs in cerium. This has been negative for the low-cost monazite ores and other thorium bearing ores. This could change in the future if thorium is adopted as a byproduct for energy use. Supplies of rare earth elements are globally available in the international trade pipeline from diverse sources without discerned immediate shortages or bottlenecks.

Thorium occurs associated with uranium in some ores such as Thorite  $(Th,U)SiO_4$  and, if exploited, would help expand the known U resource base.

Other ores are associated with rare earth elements or lanthanides such as monazite (Ce, La,Y,Th)PO<sub>4</sub> which also contain other economically significant metal occurrences such as yttrium. In this case, Th as a fuel resource could be extracted for future energy applications as a byproduct of the other more important rare earth elements extraction process until such time when primary Th ores such as thorite and monazite would be exploited.

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## APPENDIX

Table A1. Short Term Global Energy Resource Base in ZJ (Zetajoules)<sup>1</sup>

Resource	Туре	1998 Yearly Consumpti on [ZJ/yr]	Reserve s	Resource s	Resource Base <sup>2</sup>	Consume d By end of 1998	Additional Occurrence s
Oil	Conventional	0.13	6.00	6.08	12.08	4.85	-
	Unconventional	0.01	5.11	15.24	20.35	0.29	45
	Total Oil	0.14	11.11	21.31	32.42	5.14	45
Natural Gas	Conventional	0.08	5.45	11.11	16.56	2.35	-
	Unconventional	0.00	9.42	23.81	33.23	0.03	930
	Total Gas	0.08	14.87	34.92	49.79	2.38	930
Coal	Total Coal	0.09	20.67	179.00	199.67	5.99	-
Total Fossil		0.31	46.65	235.23	281.88	13.51	975
Uranium	Open Cycle Thermal Reactors <sup>4</sup>	0.04	1.89	3.52	5.41	-	$2,000^3$
	Closed Cycle Fast Reactors	negligible	113.00	211.00	324.00	-	120,000
Thorium		6,970 <sup>6</sup>	-	-	1,300,000 -2,610,000 <sup>6</sup>	-	-

<sup>1</sup> 1 ZJ (ZetaJoule) =  $10^3$  EJ (ExaJoule) =  $10^{21}$  J (Joule)

<sup>2</sup> Resource Base = Reserves + Resources

<sup>3</sup> Includes uranium from sea water

<sup>4</sup> 1 tonne Uranium = 589 TJ

 $^{5}$  1 tonne Uranium = 35,340 TJ, a sixty times increase over the open cycle

<sup>6</sup> metric tonnes, ThO<sub>2</sub>