THORIUM RESOURCES IN RARE EARTH ELEMENTS

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INTRODUCTION

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 since they are harder to extract than concentrated deposits of other minerals. The rare earth elements are used in a global effort to secure reserves for a nascent green industrial thrust. Rare earth elements include lanthanum used as a catalyst in oil refineries; neodymium and praseodymium used in magnets for electrical motors; dysprosium used in hybrid vehicles, wind turbines and stealth helicopters; and yttrium used in military jet engines.

Thorium, as an unexploited energy resource, with a longer decay half-life, 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. The Tantalite [(Fe, Mn) Ta_2O_6], Columbite (Niobite) [(Fe, Mn) Nb_2O_6] and Columbite-Tantalite (Coltan) ores, used to manufacture tantalum capacitors in consumer electronics, also contain thorium.

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^{239} fuel cycle. An accelerator-driven subcritical reactor is under development by Norway's Aker Solution, the UK and China; as well as a fast neutron spectrum reactor at Grenoble, France. India operates a Th-based reactor and is considering a Th-based fuel cycle for the long term.

In a molten salt based reactor, any leftover radioactive waste cannot be used to create weaponry. The fuel cost is significantly lower than a solid-fuel reactor. The salts cost roughly $150/kg, and thorium costs about $30/kg. Thorium nuclear waste only stays radioactive for 500 years, instead of 10,000, and there is 1,000 to 10,000 times less of it to start with.

India, with large Th resources, envisions meeting 30 percent of its electricity demand through thorium-based reactors by 2050. India's nuclear regulatory agency issued approval to start construction of a 500 MWe solid-fuel prototype fast breeder reactor. Making solid fuel thorium dioxide is expensive, because as a refractive, its melting point is the highest of all oxides, at 3,300° C. Plans are for six more fast breeder reactors, which "breed" U^{233} and plutonium from thorium and uranium. India's Advanced Heavy Water Reactor (AHWR), would involve a reactor fueled primarily by thorium.

China's Academy of Sciences launched a research and development program on Liquid Fluoride Thorium Reactor (LFTR) technology, which utilizes U^{233} that would be bred in a liquid thorium salt blanket. This molten salt blanket becomes less dense as temperatures rise, slowing the reaction down in a built-in safety catch. China's research is mirrored in programs in Japan, Russia, France, and the U.S.

It is suggested that, based on the observation that the rare earth elements themselves contain isotopes which are naturally radioactive such as La^{138}, Ce^{142}, Nd^{144}, Nd^{145}, Sm^{147}, Sm^{148}, Sm^{149}, Gd^{152}, Dy^{156} and Lu^{176}, there is no point in favoring rare earth ores that contain low percentages of Th and U. The presence of radioactivity in the rare earth ores must be carefully dealt with from the Health Physics perspective, and the extraction of Th and U as byproducts is a judicious alternative.

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. The depleting hydrocarbons as well as the uranium resource bases mandate the consideration of alternative energy sources, including thorium-based cycles; which is otherwise a valuable yet unused energy resource.

THORIUM AND RARE EARTHS ABUNDANCES

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.

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: $_{57}$Lanthanum, $_{58}$Cerium, $_{59}$Praseodymium, $_{60}$Neodymium, $_{61}$Promethium, $_{62}$Samarium, $_{63}$Europium, $_{64}$Gadolinium, $_{65}$Terbium, $_{66}$Dysprosium, $_{67}$Holmium, $_{68}$Erbium, $_{69}$Thulium, $_{70}$Ytterbium and $_{71}$Lutetium (Table 2).

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

Element	Symbol	Abundance [gms / ton]
Lead	Pb	16
Gallium	Ga	15
Thorium	**Th**	**10**
Samarium	Sm	7
Gadolinium	Gd	6
Praseodymium	Pr	6
Boron	B	3
Bromine	Br	3
Uranium	**U**	**2.5**
Beryllium	Be	2
Tin	Sn	1.5
Tungsten	W	1
Molybdenum	Mo	1
Mercury	Hg	0.2
Silver	Ag	0.1
Uranium^{235}	**U^{235}**	**0.018**
Platinum	Pt	0.005
Gold	Au	0.02

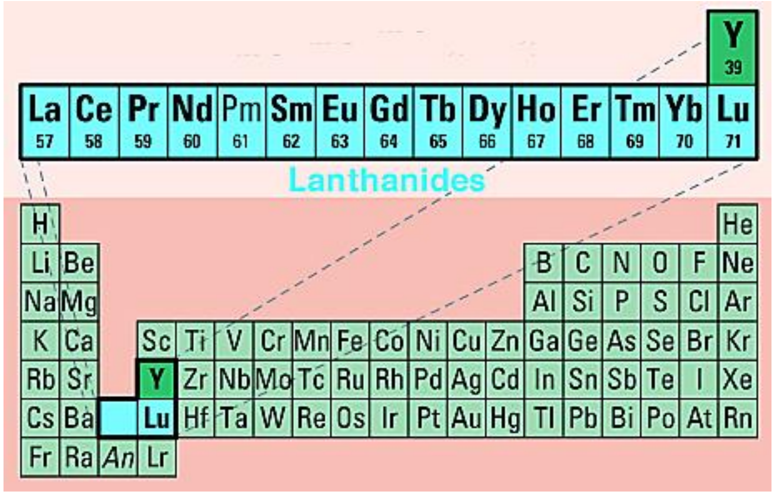


Figure 1. Rare Earth elements position in the periodic table of the elements as the Lanthanides.

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 [17]. In mining circles, Th and U are considered as “contaminants” favoring the mining of ores with low Th and U content.

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

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

$_{71}$Lu	0.5	0.4

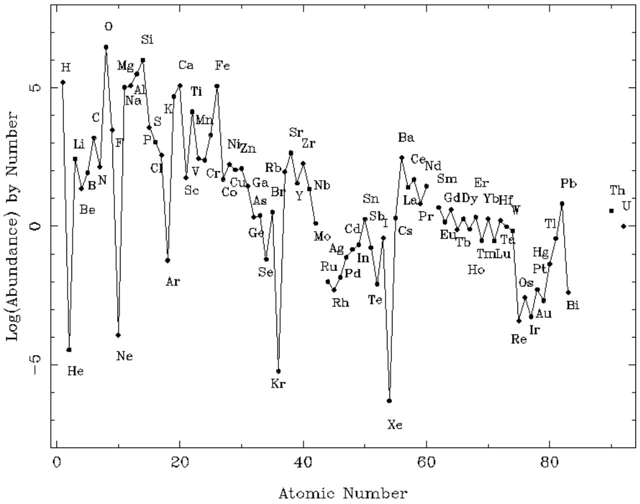


Figure 2. Logarithmic elemental crustal abundance, Log Si = 6.0.

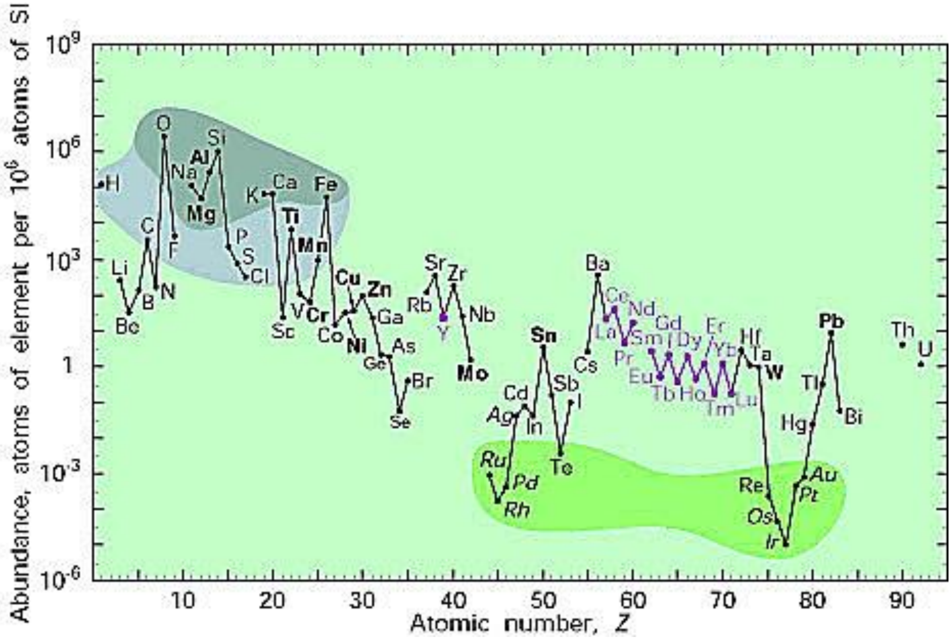


Figure 3. Logarithmic abundance of the elements relative to silicon in the Earth's crust. Source: USGS.

Figure 4. From top center, oxides of praseodymium, cerium, lanthanum, neodymium, samarium and gadolinium. Source: USDA.

The Cerium^{142} isotope with a natural abundance of 11.114 percent in Ce is radioactive with a half-life of > 5x10^{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.

In mining activities, Total Rare Earth Oxides (TREO) refers to the elements lanthanum to lutetium, plus yttrium, expressed as oxides. Heavy Rare Earth Oxides (HREO) refers to the elements Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y, expressed as oxides as a percentage of the TREO. Light Rare Earths (LREO) refers to the elements La, Ce, Pr, Nd, and Sm, expressed as oxides. Neodymium, Dysprosium, Terbium and Europium are in high demand.

Rare earths are also associated with other rare economically useful elements including: Li, Be, Rb, Cs, Y, Zr, Nb, Hf, Ta, Ga, Ge, In, and Sn.

The economics of rare earths extraction involves the balance between the “Heavies” and the “Lights.” The rare earths occur together as a group and must be sequentially separated at additional effort and cost. Most deposits are tilted towards the LREOs which constitute 97-99 percent of the resource base. Deposits having an unusual balance with a high proportion of the HREOs > 20 percent are rare, and consequently more valuable. For instance light cerium can be purchased for about $4 / kg, whereas heavy europium goes for $470 / kg.

The refining process of each element is performed using solvent extraction or ion exchange processes. The balance of chemicals used and the design of the processes depend on the composition of the feedstock concentrates. Solvent extraction is commonly used for the light elements, whereas the ion exchange process is used for the heavy ones.

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 by geological engineers in the field and the laboratories. 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 usually used in identifying placer deposits.

Figure 5. Thorium dioxide with 1 percent cerium oxide impregnated fabric, Welsbach incandescent gas mantles (left) and ThO_2 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].

Element	Thorogummite, $(Th(SiO4)_{1-x} (OH)_{4x})$ 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. Other applications include industrial air conditioners reducing power consumption by about 50 percent, hybrid electric cars, wind turbines and Magnetic Resonance Imaging (MRI) magnets. Dysprosium is used in heat resistant magnets used in automotive applications.

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.

Emerging new technologies include Magnetic refrigeration using alloys of gadolinium and the magneto-caloric effect, electric bicycles using Nd magnets, tidal power and run-of-river hydroelectric power generation.

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 and U occurrence.

Ore	Chemical composition
Allanite	$(Ca,Ce,\mathbf{Th})_2(Al,Fe,Mg)_3Si_3O_{12}(OH)$
Monazite	$(Ce,La,Pr,Nd,\mathbf{Th},Y)PO_4$
Parisite	$2(Ce,La,Di,\mathbf{Th})OF.CaO.3CO_3$
Polymignite	$(Ca,Fe,Y,\mathbf{Th})(Nb,Ti,Ta,Zr)O_4$
Euxenite	$(Y,Ca,Er,La,Ce,\mathbf{U},\mathbf{Th})(Nb,Ta,Ti)_2O_6$
Cheralite	$(Ca,Ce,\mathbf{Th})(P,Si)O_4$
Samarskite	$(Y,Er,Ce,\mathbf{U},Ca,Fe,Pb,\mathbf{Th})(Nb,Ta,Ti,Sn)_2O_6$
Thorogummite	$(\mathbf{Th}(SiO4)_{1-x}\ (OH)_{4x})$
Davidite	$(La,Ce)(Y,\mathbf{U},Fe^{+2})(Ti,Fe^{+3})_{20}(O,OH)_{38}$
Fergusonite	$(Y,Er,Ce,Fe)(Nb,Ta,Ti)O_4$
Loparite	$(Ce,Na,Ca)(Ti,Nb)O_3$
Bastnäsite	$(Ce,La,Di)F.CO_2$

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 high-performance 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.

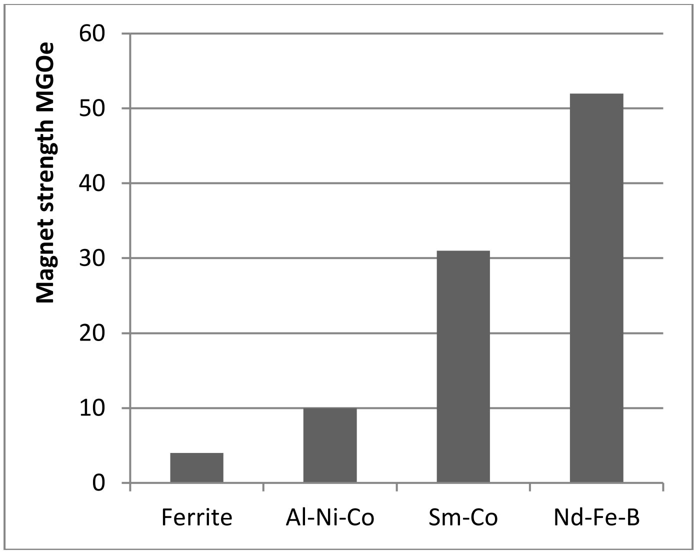


Figure 6. Enhanced field strength in rare earth permanent magnets in Mega Gauss Oersted (MGOe).

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, and ceramics. Ultraviolet UV absorbing cut glass. Polishing powder for glass, lenses and mirrors. Lighter flints
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.
Europium	Red phosphor color in display applications, television, digital projectors.

Gadolinium	Electronics. Magnetic refrigeration. Alloying agent. Nuclear medicine.
Yttrium	Cathode Ray Tube, CRT, TV screens and computer displays. Lasers and semiconductors. Phosphors used in energy efficient lighting.
Dysprosium, Terbium	High operating temperature magnets. Magnets for wind turbines, mobile phones, hybrid cars. Jet and rocket engines. High performance motor vehicles.
Europium Yttrium Cerium	Liquid Crystal Displays, LCDs.
Cerium Lanthanum	Diesel Fuel additive.
Neodymium Praseodymium Dysprosium Terbium	Hybrid electric automobile motor and generator. Wind turbines generators' magnets.
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 Absorbing ultraviolet light. With cerium to decolor glass.
Cerium/Zirconium Lanthanum	Motor vehicles' catalytic converters.
Lanthanum Cerium	Nickel metal hydride (NiMH) rechargeable batteries. Hybrid automobile batteries.
Lanthanum Samarium Gadolinium	Infrared absorption in glass. Improving the refractive index of glass. Microwave oven temperature controls.
Praesodymium	Coloring agent in glass when the index of refraction must remain constant.

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, $(Th, U)SiO_4$ and Thorianite ($ThO_2 + UO_2$). 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^{233} from thorium according to the breeding reactions [20]:

$$\begin{array}{l} {}_0n^1 + {}_{90}Th^{232} \rightarrow {}_{90}Th^{233} + \gamma \\ \qquad {}_{90}Th^{233} \rightarrow {}_{91}Pa^{233} + {}_{-1}e^0 + \nu^* + \gamma \\ \qquad {}_{91}Pa^{233} \rightarrow {}_{92}U^{233} + {}_{-1}e^0 + \nu^* + \gamma \\ \hline {}_0n^1 + {}_{90}Th^{232} \rightarrow {}_{92}U^{233} + 2\,{}_{-1}e^0 + 2\nu^* + 3\gamma \end{array} \tag{1}$$

Together with uranium, its radioactive decay chain leads to the stable Pb^{208} lead isotope with a half-life of 1.4×10^{10} years for Th^{232}. It contributes to the internal heat generation in the Earth, together with other radioactive elements such as the isotopes of U, U^{234}, U^{235}, U^{238} and their decay chain members, and K^{40}.

As Th^{232} decays into the stable Pb^{208} isotope, $radon^{220}$ or thoron forms in the chain. Rn^{220} 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.

Thorium oxide, as a refractory compound, 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.

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.

ADVANTAGES OF THE THORIUM FUEL CYCLE

The following advantages of the thorium fuel cycle over the U^{235}-Pu^{239} 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. 7).

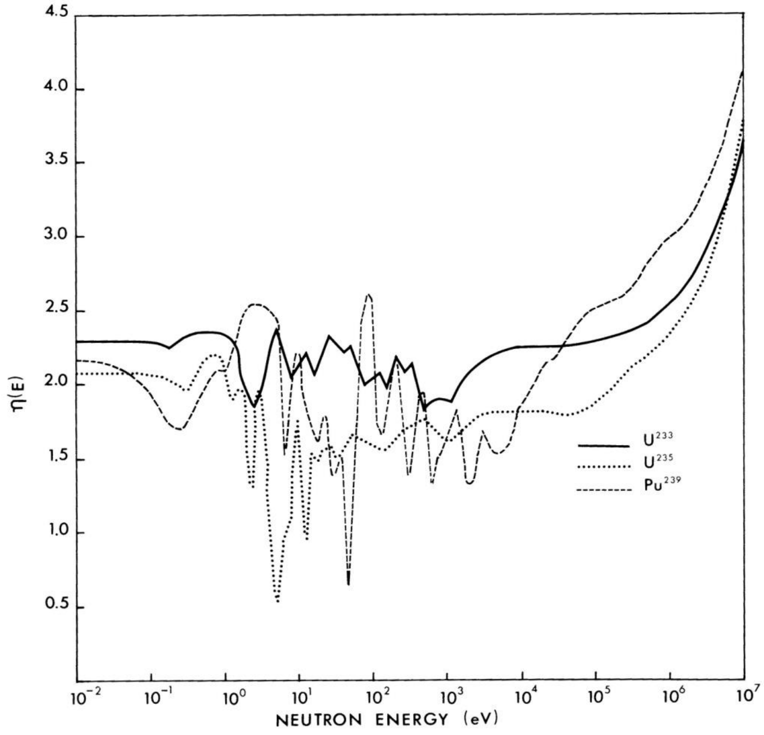


Figure 7. Regeneration factor as a function of neutron energy for the different fissile isotopes.

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^{239} 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.

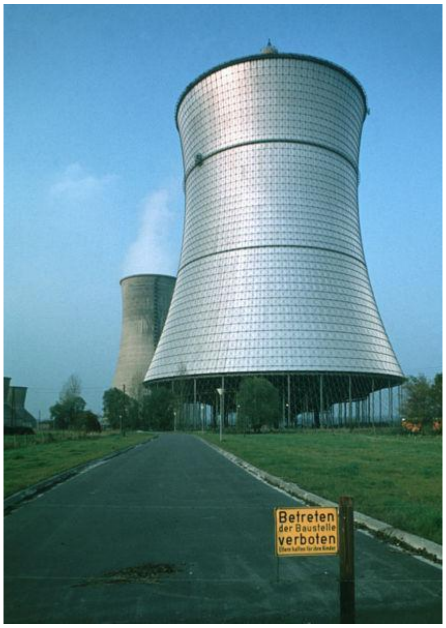


Figure 8. Dry cooling tower in foreground, wet cooling tower in background in the THTR-300 pebble bed Th reactor, Germany.

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 fissionned, 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.

THORIUM ABUNDANCE

Thorium is four times more 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^{239} 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. 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.

THORIUM PRIMARY MINERALS

Table 6: Major Thorium ores compositions.

Ore	Composition
Thorite	$(Th,U)SiO_4$
Thorianite	$(ThO_2 + UO_2)$

Thorogummite	$Th(SiO_4)_{1-x}(OH)_{4x}$
Monazite	$(Ce,La,Y,Th)PO_4$
Brocktite	$(Ca,Th,Ce)(PO_4)H_2O$
Xenotime	$(Y,Th)PO_4$
Euxenite	$(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$
Basnäsite	$(Ce,La,Dy)F.CO_2$
Iron ore	Fe + rare earths + Th apatite

Thorium occurs in several minerals [16, 19]:

1. Monazite, $(Ce,La,Y,Th)PO_4$, 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, $(Th,U)SiO_4$ 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, $(Ca,Th,Ce)(PO_4)H_2O$.
4. Xenotime, $(Y,Th)PO_4$.
5. Euxenite, $(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$.
6. Iron ore, (Fe)-rare earth elements-Th-apatite, Freta deposits at Pea Ridge, Missouri, Mineville, New York, and Scrub Oaks, New Jersey.

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_2 Reserves [metric tonnes] USGS estimate 2010 [16]	ThO_2 Reserves [metric tonnes] NEA estimate [22]***	Mined amounts 2007 [metric tonnes]*	OECD, NEA and IAEA Red Book, 2011 [metric tonnes]*

USA	440,000	400,000	-[**]	434,000
Australia	300,000	489,000	-	521,000
Turkey		344,000		744,000
India	290,000	319,000	5,000	846,000
Venezuela		300,000		300.000
Canada	100,000	44,000	-	172,000
South Africa	35,000	18,000	-	148,000
Brazil	16,000	302,000	1,173	606,000
Norway		132,000		320,000
Egypt		100,000		380,000
Russia		75,000		155,000
Greenland		54,000		86,000
Canada		44,000		172,000
Malaysia	4,500		800	
China				100,000
Finland				60,000
Sweden				50,000
Kazakhstan				50,000
Other countries	90,000	33,000	-	413,000
Total	1,300,000	2,610,000	6,970	5,385,000

[*] 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$_2$ proven reserves [19].

Deposit type	Mining District	Location	ThO$_2$ reserves [metric tonnes]
Vein deposits	Lehmi Pass district	Montana-Idaho	64,000
	Wet Mountain area	Colorado	58,200
	Hall Mountain	Idaho	4,150
	Iron Hill	Colorado	1,700 (thorium veins)

			690 (Carbonatite dikes)
	Diamond Creek	Idaho	-
	Bear Lodge Mountains	Wyoming	-
	Monroe Canyon	Utah	-
	Mountain Pass district	California	-
	Quartzite district	Arizona	-
	Cottonwood area	Arizona	-
	Gold Hill district	New Mexico	-
	Capitan Mountain	New Mexico	-
	Laughlin Peak	New Mexico	-
	Wausau, Marathon County	Wisconsin	-
	Bokan Mountain	Alaska	-
Massive Carbonatite stocks	Iron Hill	Colorado	28,200
	Mountain Pass	California	8,850
Black Sand Placer, Alluvial Deposits	Stream deposits	North, South Carolina	4,800
	Stream placers	Idaho	9,130
	Beach placers	Florida-Georgia	14,700
Alkaline Intrusions	Bear Lodge Mountains	Wyoming	-
	Hicks Dome	Illinois	-
Total, USA			194,420

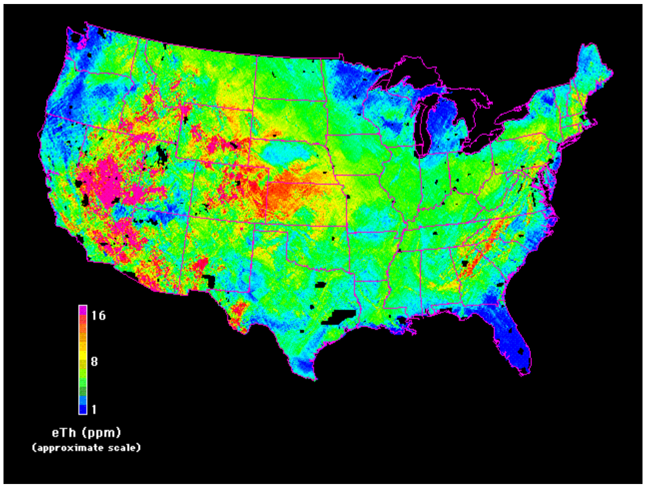


Figure 9. Th concentrations in ppm and occurrences in the USA. Source: USA Geological Survey Digital Data Series DDS-9, 1993.

Figure 10. 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 11. Black sand Monazite layers in beach sand at Chennai, India. Photo: Mark A. Wilson [19].

Figure 12. Black sands Monazite ore on Brazilian beaches are ascribed unsubstantiated medicinal radiation curative properties.

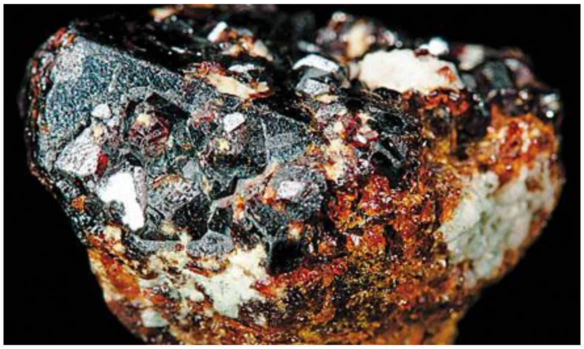


Figure 13. Thorite (Th, U) SiO_4, a thorium-uranium silicate.

Figure 14. Basnäsite, (Ce, La, Dy) F.CO_2 ore, primarily mined by the Molycorp Corporation, USA.

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

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.

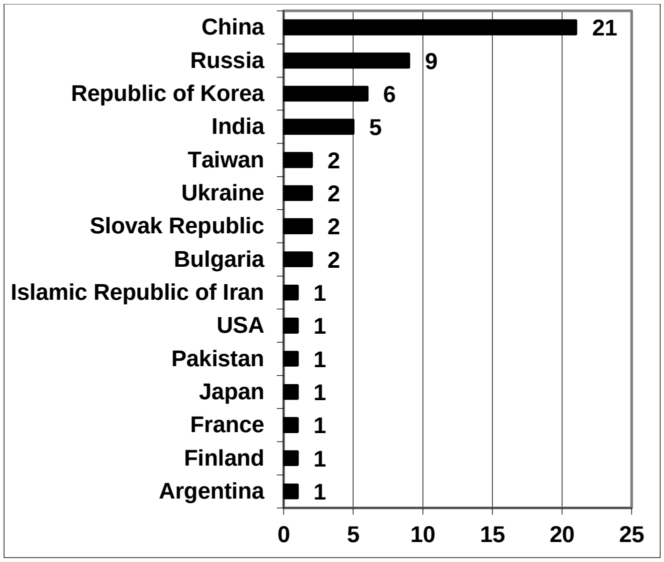


Figure 15. Number of power reactors under construction worldwide. Total: 56. Net electrical capacity: 51.9 MWe. Data source: IAEA, 2010.

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	Conventional	McArthur River
Australia	4,527	10	Rio Tinto	Conventional	Ranger
Namibia	3,449	8	Rio Tinto	Conventional	Rδssing
Australia	3,344	8	BHP Billiton	Byproduct	Olympic Dam
Russia	3,050	7	ARMZ	Conventional	Priargunsky
Niger	1,743	4	Areva	Conventional	Somair
Canada	1,368	3	Cameco	Conventional	Rabbit Lake
Niger	1,289	3	Areva	Conventional	Cominak
Canada	1,249	3	Areva	Conventional	McLean
Kazakhstan	1,034	2	Uranium One	In Situ Retorting, ISR	Akdata
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	Production 2005 [10^6 lb U_3O_8]	Production 2006 [10^6 lb U_3O_8]
Smith Ranch/Highland	Wyoming	Cameco (Power resources)	1.3	2.0
Crow Butte	Nebraska	Crow Butte Resources, Cameco	0.8	0.7
Vasquez	South Texas	Uranium Resources	0.3	0.2
Kingsville Dome	South Texas	Uranium Resources	-	0.1
Alta Mesa	South Texas	Alta Mesa	0.3	1.0
Total USA production			2.7	4.0

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.

NONPROLIFERATION CHARACTERISTICS

The production of U^{233} concurrently yields U^{232} which is a strong gamma-emitter through its decay-chain decay product $Thallium^{208}$ making it extremely difficult to manufacture and to store and also easy to detect.

In the Th-U^{233} 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^{239}.

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

$$\begin{aligned}
&{}_{0}n^{1} + {}_{90}Th^{232} \rightarrow 2\,{}_{0}n^{1} + {}_{90}Th^{231} \\
&{}_{90}Th^{231} \xrightarrow{25.52h} {}_{-1}e^{0} + {}_{91}Pa^{231} \\
&{}_{0}n^{1} + {}_{91}Pa^{231} \rightarrow \gamma + {}_{91}Pa^{232} \\
&{}_{91}Pa^{232} \xrightarrow{1.31d} {}_{-1}e^{0} + {}_{92}U^{232}
\end{aligned} \tag{2}$$

and another involving an (n, γ) radiative capture reaction:

$$\begin{array}{l} {}_0n^1 + {}_{90}Th^{232} \rightarrow \gamma + {}_{90}Th^{233} \\ {}_{90}Th^{233} \xrightarrow{22.2m} {}_{-1}e^0 + {}_{91}Pa^{233} \\ {}_{91}Pa^{233} \xrightarrow{27d} {}_{-1}e^0 + {}_{92}U^{233} \\ {}_{92}U^{233} + {}_0n^1 \rightarrow 2\,{}_0n^1 + {}_{92}U^{232} \end{array} \qquad (3)$$

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

$$\begin{array}{l} {}_0n^1 + {}_{92}U^{233} \rightarrow 2\,{}_0n^1 + {}_{92}U^{232} \\ {}_0n^1 + {}_{92}U^{232} \rightarrow \gamma + {}_{92}U^{233} \end{array} \qquad (4)$$

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}:

$$\begin{array}{l} {}_0n^1 + {}_{90}Th^{230} \rightarrow \gamma + {}_{90}Th^{231} \\ {}_{90}Th^{231} \xrightarrow{25.52h} {}_{-1}e^0 + {}_{91}Pa^{231} \\ {}_0n^1 + {}_{91}Pa^{231} \rightarrow \gamma + {}_{91}Pa^{232} \\ {}_{91}Pa^{232} \xrightarrow{1.31d} {}_{-1}e^0 + {}_{92}U^{232} \end{array} \qquad (5)$$

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

$$\begin{array}{l} {}_{92}U^{232} \xrightarrow{72a} {}_{90}Th^{228} + {}_2He^4 \\ {}_{90}Th^{228} \xrightarrow{1.913a} {}_{88}Ra^{224} + {}_2He^4 \\ {}_{88}Ra^{224} \xrightarrow{3.66d} {}_{86}Rn^{220} + {}_2He^4 \\ {}_{86}Rn^{220} \xrightarrow{55.6s} {}_{82}Po^{216} + {}_2He^4 \\ {}_{84}Po^{216} \xrightarrow{0.15s} {}_{82}Pb^{212} + {}_2He^4 \\ {}_{82}Pb^{212} \xrightarrow{10.64h} {}_{83}Bi^{212} + {}_{-1}e^0 \\ {}_{83}Bi^{212} \xrightarrow[64\%]{60.6m} {}_{84}Po^{212} + {}_{-1}e^0 \\ {}_{83}Bi^{212} \xrightarrow[36\%]{60.6m} {}_{81}Tl^{208} + {}_2He^4 \\ {}_{84}Po^{212} \xrightarrow{0.298\mu s} {}_{82}Pb^{208}(stable) + {}_2He^4 \\ {}_{81}Tl^{208} \xrightarrow{3.053m} {}_{82}Pb^{208}(stable) + {}_{-1}e^0 + \gamma(2.6146MeV) \end{array} \qquad (6)$$

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

$$\begin{aligned}
&{}_{92}U^{233} \xrightarrow{1.592x10^5 a} {}_{90}Th^{229} + {}_{2}He^{4} \\
&{}_{90}Th^{229} \xrightarrow{7340a} {}_{88}Ra^{225} + {}_{2}He^{4} \\
&{}_{88}Ra^{225} \xrightarrow{14.8d} {}_{89}Ac^{225} + {}_{-1}e^{0} \\
&{}_{89}Ac^{225} \xrightarrow{10.0d} {}_{87}Fr^{221} + {}_{2}He^{4} \\
&{}_{87}Fr^{221} \xrightarrow{4.8m} {}_{85}At^{217} + {}_{2}He^{4} \\
&{}_{85}At^{217} \xrightarrow{32.3ms} {}_{83}Bi^{213} + {}_{2}He^{4} \\
&{}_{83}Bi^{213} \xrightarrow{45.6m} {}_{84}Po^{213} + {}_{-1}e^{0} \\
&{}_{84}Po^{213} \xrightarrow{4.2\mu s} {}_{82}Pb^{209} + {}_{2}He^{4} \\
&{}_{82}Pb^{209} \xrightarrow{3.28h} {}_{83}Bi^{209}(stable) + {}_{-1}e^{0}
\end{aligned}$$

(7

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^{233} is not separately extracted and allowed to decay into pure U^{233}.

The Pa^{233} 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. U^{233} is classified by the IAEA in the same category as Highly Enriched Uranium (HEU), with a “Significant Quantity” in terms of Safeguards defined as 8 kgs, compared with 32 kgs for U^{235} and 8 kgs for Pu^{239}.

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^{232} due to the presence of the highly radioactive Th^{228} from the decay chain of U^{232}.

The USA produced about 2 metric tonnes of U^{233} from Th^{232} at various levels of chemical and isotopic compositions in plutonium production reactors. In 1955 the USA tested a device with a dual composite core of Pu^{239}-U^{233} in Operation Teapot. The device “fizzled” with the explosive yield less than anticipated, at 22 kT of TNT equivalent. It is rumored that in 1998 India tested a very small device based on U^{233} designated as Shakti V.

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 Tl^{208} in the decay chain of U^{232} and not U^{232} itself that generates the hard gamma rays. The Tl^{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^{239} fuel cycle, Pu^{239} containing Pu^{241} with a half life of 14.4 years, the most important source of gamma ray radiation is from the Am^{241} 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^{239} with about 0.36 percent Pu^{241} this does not present a major hazard but the radiological hazard becomes significant for reactor grade Pu^{239} containing about 9-10 percent Pu^{241}.

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

$$\begin{aligned}
&{}_0n^1 + {}_{92}U^{238} \rightarrow \gamma + {}_{92}U^{239} \\
&{}_{92}U^{239} \xrightarrow{23.5m} {}_{-1}e^0 + {}_{93}Np^{239} \\
&{}_{93}Np^{239} \xrightarrow{2.35d} {}_{-1}e^0 + {}_{94}Pu^{239} \\
&{}_0n^1 + {}_{94}Pu^{239} \rightarrow \gamma + {}_{94}Pu^{240} \\
&{}_0n^1 + {}_{94}Pu^{240} \rightarrow \gamma + {}_{94}Pu^{241} \\
&{}_{94}Pu^{241} \xrightarrow{14.7a} {}_{-1}e^0 + {}_{95}Am^{241}
\end{aligned} \tag{8}$$

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

The gamma rays from Am^{241} are easily shielded against with Pb shielding. Shielding against the neutrons from the spontaneous fissions in the even numbered Pu^{238} and Pu^{240} 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, γ) reactions, follows the path:

$$\begin{aligned}
&{}_0n^1 + {}_{92}U^{238} \rightarrow 2\,{}_0n^1 + {}_{92}U^{237} \\
&{}_{92}U^{237} \xrightarrow{6.75d} {}_{-1}e^0 + {}_{93}Np^{237} \\
&{}_0n^1 + {}_{93}Np^{237} \rightarrow \gamma + {}_{93}Np^{238} \\
&{}_{93}Np^{238} \xrightarrow{2.12d} {}_{-1}e^0 + {}_{94}Pu^{238}
\end{aligned} \tag{9}$$

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

Table 12. Typical compositions of fuels in the uranium and thorium fuel cycles.

Isotopic composition [percent]	Pu^{239} weapons grade	Pu^{239} reactors grade	U^{233}	U^{233} + 1 ppm U^{232}
U^{232}			0.0000	0.0001
U^{233}			100.0000	99.9999

Pu^{238}	0.0100	1.3000		
Pu^{239}	93.8000	60.3000		
Pu^{240}	5.8000	24.3000		
Pu^{241}	0.3500	9.1000		
Pu^{242}	0.0200	5.0000		
Density [gm/cm^3]	19.86	19.86	19.05	19.05
Radius [cm]	3.92	3.92	3.96	3.96
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, U^{232}/U^{233}	Time to 5 cSv effective dose [hr]	Effective dose rate 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^{239}	609.756	0.0082
Weapons grade Pu^{239}	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^{239}.

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^{233}	γ total	0.32	0.42	0.84	1.35	1.89
U^{233} +1 ppm U^{232}	γ total	0.32	13.08	35.10	39.57	39.17
	γ from Tl^{208}	0.00	11.12	29.96	33.48	32.64
$Pu^{239,}$, weapons grade	γ	0.49	0.71	1.16	1.57	1.84
	neutrons	0.56	0.56	0.56	0.56	0.56

	γ + neutron	1.05	1.27	1.72	2.13	2.40
Pu^{239}, Reactor grade	γ total	0.49	5.54	16.72	28.64	37.54
	γ from Am^{241}	0.00	3.24	14.60	26.00	34.80
	neutrons	2.66	2.66	2.65	2.64	2.63
	γ + neutrons	3.15	8.20	19.37	31.28	40.17

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}:

$$\begin{aligned} {}_0n^1 + {}_{92}U^{238} &\rightarrow {}_{92}U^{239} + \gamma \\ {}_{92}U^{239} &\xrightarrow{23.5m} {}_{93}Np^{239} + {}_{-1}e^0 \\ {}_{93}Np^{239} &\xrightarrow{2.35d} {}_{94}Pu^{239} + {}_{-1}e^0 \end{aligned} \tag{10}$$

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

$$\begin{aligned} {}_0n^1 + {}_{90}Th^{232} &\rightarrow {}_{90}Th^{233} + \gamma \\ {}_0n^1 + {}_{90}Th^{233} &\rightarrow {}_{90}Th^{234} + \gamma \\ {}_{90}Th^{234} &\xrightarrow{24.1d} {}_{91}Pa^{234} + {}_{-1}e^0 \\ {}_{91}Pa^{234} &\xrightarrow{6.70h} {}_{92}U^{234} + {}_{-1}e^0 \\ {}_0n^1 + {}_{92}U^{234} &\rightarrow {}_{92}U^{235} + \gamma \\ {}_0n^1 + {}_{92}U^{235} &\rightarrow {}_{92}U^{236} + \gamma \\ {}_0n^1 + {}_{92}U^{236} &\rightarrow {}_{92}U^{237} + \gamma \\ {}_{92}U^{237} &\xrightarrow{6.75d} {}_{93}Np^{237} + {}_{-1}e^0 \end{aligned} \tag{11}$$

This implies a low yield of Np^{237} 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:

$$\begin{aligned} {}_0n^1 + {}_{92}U^{238} &\rightarrow 2\,{}_0n^1 + {}_{92}U^{237} \\ {}_{92}U^{237} &\xrightarrow{6.75d} {}_{93}Np^{237} + {}_{-1}e^0 \end{aligned} \tag{12}$$

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

$$\begin{aligned} & {}_0n^1 + {}_{93}Np^{237} \to {}_{93}Np^{238} + \gamma \\ & {}_{93}Np^{238} \xrightarrow{2.12d} {}_{94}Pu^{238} + {}_{-1}e^0 \end{aligned} \qquad (13)$$

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:

$$\begin{aligned} {}_0n^1 + {}_{92}U^{238} &\to {}_{92}U^{239} + \gamma \\ {}_{92}U^{239} &\to {}_{93}Np^{239} + {}_{-1}e^0 + \nu^* + \gamma \\ {}_{93}Np^{239} &\to {}_{94}Pu^{239} + {}_{-1}e^0 + \nu^* + \gamma \\ {}_0n^1 + {}_{94}Pu^{239} &\to {}_{94}Pu^{240} + \gamma \end{aligned} \qquad (14)$$

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 3rd, 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.

MOUNTAIN PASS DEPOSIT, USA

The Mountain Pass Mine rare earth carbonatite complex lies at the summit of Mountain Pass near the center of the Ivanpah Mining District. It was discovered when two prospectors using a Geiger-Müller radiation detector staked a series of claims on a radioactive outcrop they thought was a uranium deposit. To their disappointment, the ore was found to be the rare earth fluoro-carbonate Bastnäsite. A larger deposit was located by the USGS on adjoining land. One of the two prospectors was a metallurgist with the Molycorp Company and he urged the company to stake a claim on it.

The new deposit contained less thorium and uranium and hence is thought to contain less radioactivity. What is conveniently ignored is that it contains primarily cerium which itself is radioactive. In fact, the Cerium^{142} isotope with a natural abundance of 11.114 percent in Ce is radioactive with a long half-life of > 5×10^{16} years, hence low activity. It is thought to be a double-beta emitter. Cerium has a crustal abundance of 60 ppm, comparable with Ni at 75 ppm and Cu at 55 ppm.

Figure 16. Mountain Pass, California. Source: USGS.

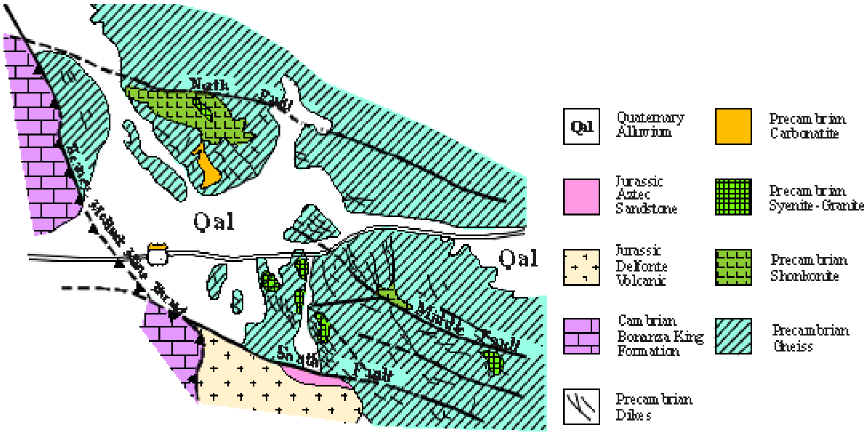


Figure 17. Geological map of the Mountain Pass Deposit.

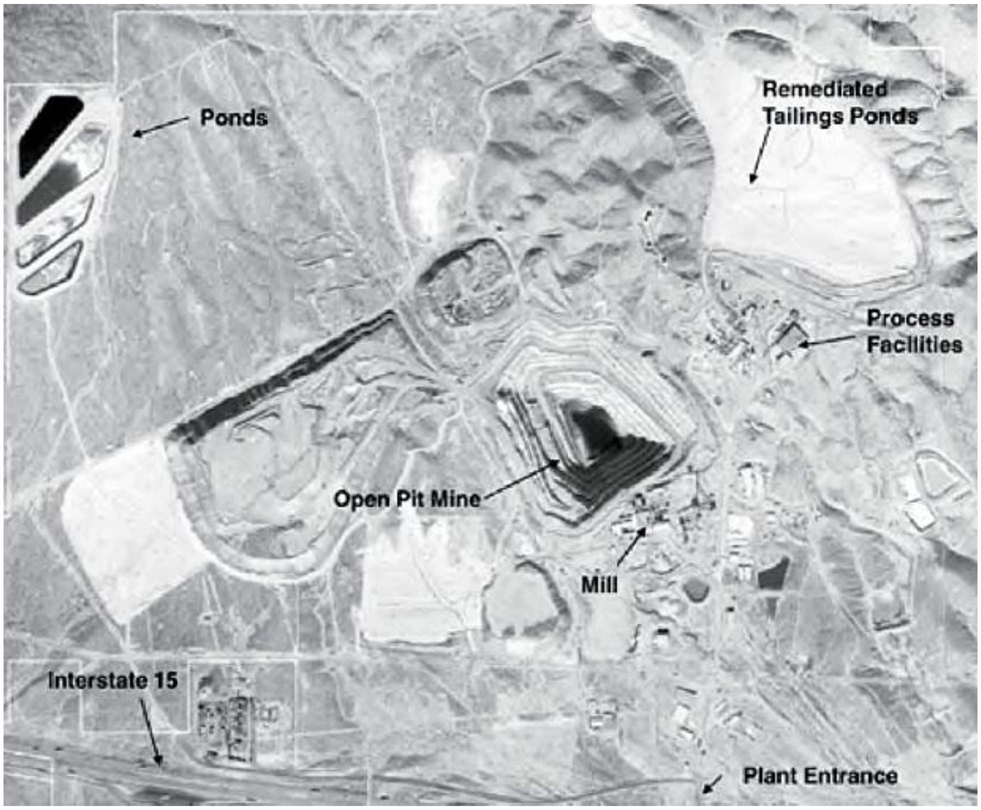


Figure 18. Aerial view of the Mountain Pass deposit, mill and processing plant. Source: Molycorp.

Figure 19. Molycorp plant reprocessed already extracted ore.

This largest USA rare earth elements mine, was privately held, as of October 1st 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.

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.

Molycorp Minerals became a public company in 2010 and 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 that closed in 2002, resumed operation in 2007 through 2009 beneficiating and extracting rare earth elements from the Bastnäsite ore. The mine had suffered environmental problems as toxic wastewater leaks in the 1990s resulting in a $1.6 million fine to settle with state agencies.

Molycorp had plans to double its planned production to 40,000 tons in 2012 to satisfy a world demand, excluding China, of 55,000-60,000 tons per year. It won a San Bernardino County, California permit in 2004 to operate for 30 years and passed an inspection in 2007. It planned to cutting in half the amount of raw ore needed to produce the same amount of rare earths oxides using improved processing, and use water recycling and treatment processes to reduce the mine's fresh water usage by 96 percent.

In 2010 Molycorp became an IPO powerhouse and market capitalization shot up past $7 billion. It supplied the rare earth europium that generates the red color in television sets. Molycorp also sold low value and abundant Lanthanum to the W.R. Grace Company for use in the petroleum industry. It refined its ore in China. The company lasted less than 5 years from IPO to bankruptcy filing. Over that short period it lost through over $3 billion in investors' capital. On July 10, 2017, MP Mine Operations LLC, a Chinese-led consortium including rare earths miner Shenghe Resources, purchased the Mountain Pass mine out of bankruptcy.

Other suppliers are coming online such as Lynas in Australia that is building an A$550 million or $550 million rare earths project at Mount Weld in Western Australia. There are large deposits of rare earths in Greenland, Québec and Colorado.

MOUNT WELD DEPOSIT, AUSTRALIA

Sydney, Australia Lynas company started production from its A$550 million ($541 million) Mount Weld project in Western Australia in the third quarter of 2011 with an initial output of 11,000 metric tons/year, which will double to 22,000 tons by the end of 2012. The ore would be trucked to the port of Fremante and transported to Malaysia by container ship. Lynas was founded by Nicholas Curtis, a previous director of Macquarie Group Ltd., the largest investment bank in Australia.

Lynas is building the world largest rare earths refinery at the Gebeng Industrial zone near the port of Kuantan the capital of the Pahang province on Malaysia's east coast and a resort city, to process its mined Australian ore as well as ore from the Kangankunde deposit in Malawi, Central Africa. Lynas says it had approval to build its refinery in Australia, China and Malaysia but opted for Malaysia as a more suitable site from the business perspectives of water supply availability, wage cost, skilled labor and corporate taxes. The Maylasian government has given the project a supportive "pioneer" status, granting it a 12 years tax exemption. This would turn Malaysia into the next major supplier of rare earth elements after China. It hopes to attract green manufacturing industries that depend on rare earths such as wind turbines and hybrid cars. The refinery would generate $1.7 billion in annual exports; equivalent to 1 percent of Malaysia's GDP and create 350 highly skilled jobs.

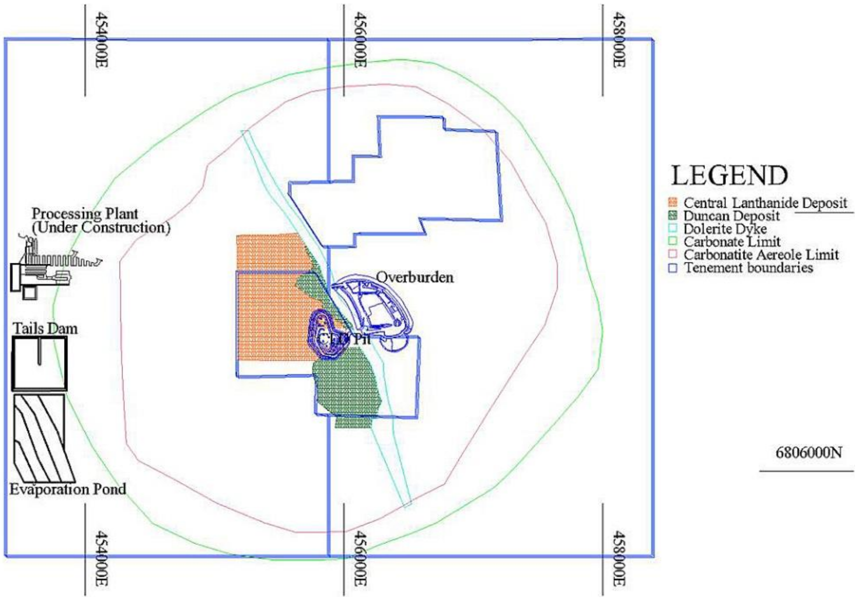


Figure 20. Mount Weld Rare earths deposit, Australia. Source: Lynas Corporation.

However, the Lynas Advanced Materials Plant (LAMP) refinery is drawing environmental protests because of the potential radiological health risks from the presence of thorium in the ore processed for the extraction of the rare earths. The International Atomic Energy Agency (IAEA) appointed an independent panel of 9 health and safety experts to review the project and carry a cost-benefit analysis. Barring any leaks, the IAEA estimates that the yearly occupational dose is equivalent to three chest x-rays for workers at the refinery. Malaysia follows the IAEA's criterion of 10^3 Bq / kg of specific activity for materials to require licensing from a radiation board, whereas this criterion is 4 x 10^6 Bq / kg in Australia. The waste activity from the plant is expected to be 61 x 10^3 Bq /kg, compared with a figure in China of 74 x 10^3 Bq / kg. In the USA, such a refinery would only require licensing under mining and ore regulations. It is suggested that other byproducts can result from an optimized refining process such as phosphate fertilizer and calcium sulfate or gypsum. The IAEA report found the plant, which is about 40 percent completed in east Malaysia, complied with international radiation safety standards but regulation should be improved. Among the 11 recommendations by the IAEA are requirements for long-term waste management and decommissioning of the facility. Lynas is given an operating license as it meets all the conditions.

A joint venture, Asian Rare Earth plant, partly owned by Mitsubishi Chemical Holding Corporation in northern Perak on Malaysia's west coast was shut down in 1992 following protests. The Bukit Merah processing plant used the tailings from tin mining containing a high concentration of Th and U. The plant marketed bags of calcium phosphate as fertilizer and soil pH conditioner on a trial basis to the local farmers as a byproduct of the refinery process. Possible carelessness in separating the radioactive materials may have led to livestock poisoning. The plant closure left a legacy of a radioactive waste cleanup site. Thorium processing by the Maywood Chemical Company in New Jersey, USA also left a waste site.

It is suggested that the main source of Th in Australia is the monazite mineral which contains 8–10 percent of Th. With a target capacity of 22,000 tons / year the Th production from the Gebeng refinery, if extracted separately would amount to 22,000 x 0.08 = 1,760 tons /yr.

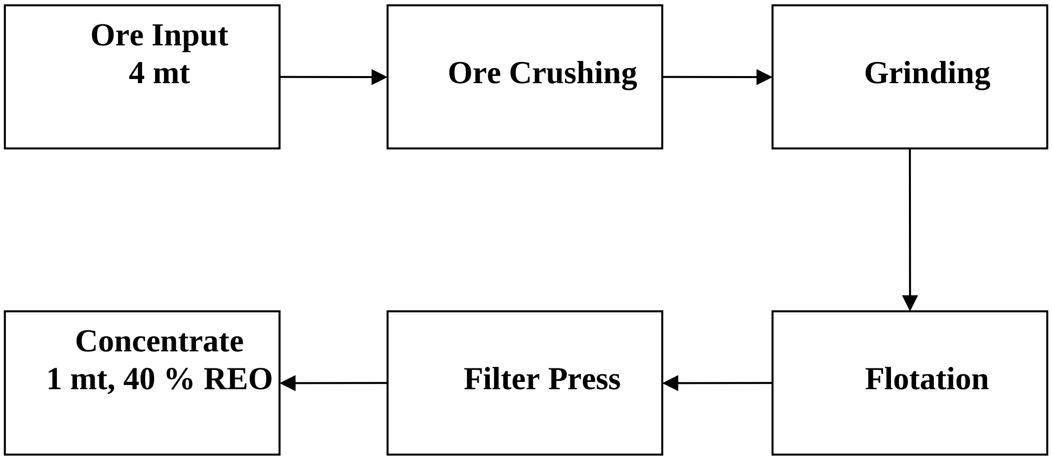


Figure 21. Ore concentration Process of rare earths.

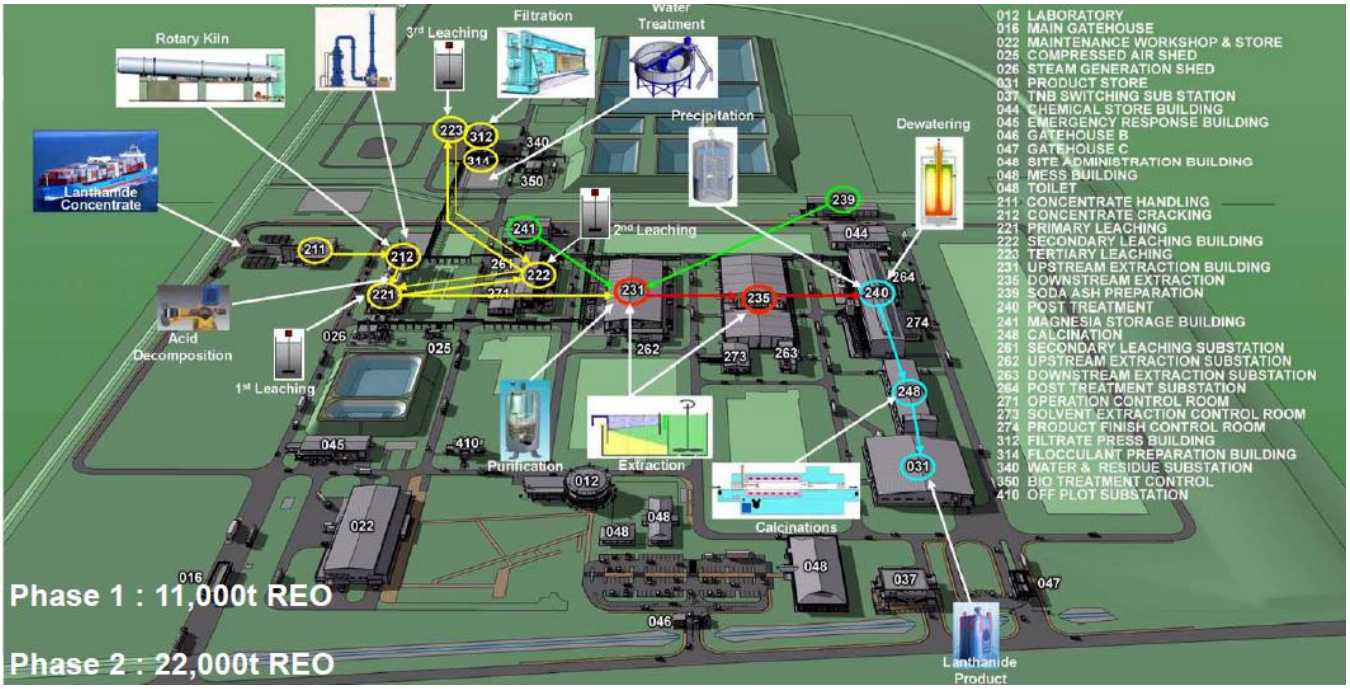


Figure 22. Lynas Advanced Materials Plant, LAMP layout.

Figure 23. Primary leaching process (221). Source: Lynas Corporation.

Figure 24. Primary leaching building.

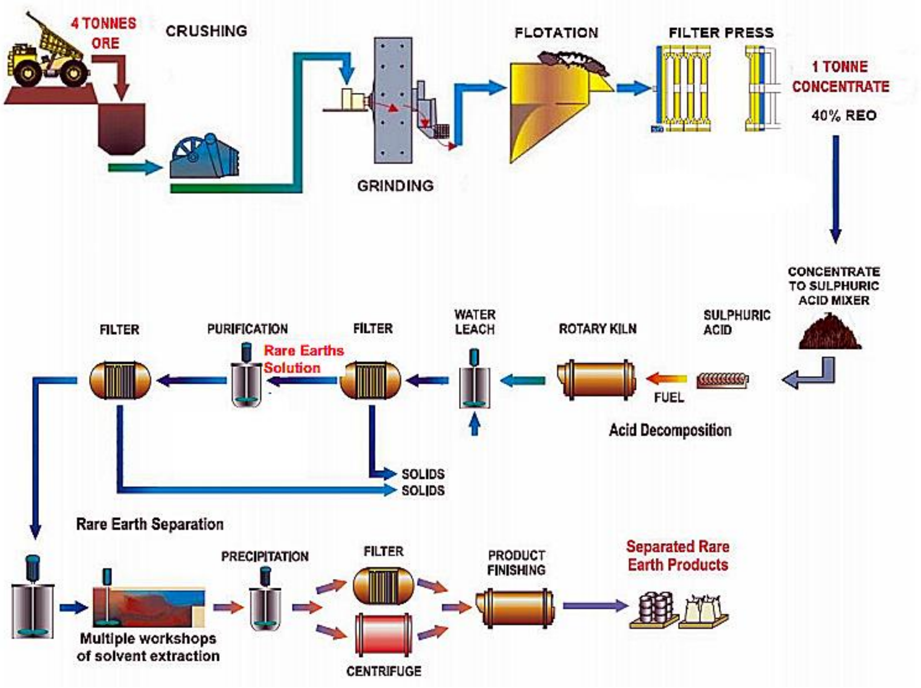


Figure 25. Rare earths ore concentration (top) and production (bottom) flow diagram. Source: Lynas Corporation.

Figure 26. Concentration plant at Mount Weld, Australia. Source: Lynas Corporation.

Figure 27. Concentration plant view. Source: Lynas.

Figure 28. Flotation section at the Concentrationplant at Mount Weld, Australia. Source: Lynas Corporation.

Figure 29. Ball mill and classification circuit at concentration plant. Source: Lynas.

Figure 30. Utilities concentration plant.

Figure 31. Flotation cells at concentration plant.

Figure 32. Flotation cells with initial feed.

Figure 33. Flotation section from Ball Mill concentration plant.

Figure 34. Concentrate cake discharging from filter press.

Figure 35. Secondary leaching.

Figure 36. Thickener concentration plant.

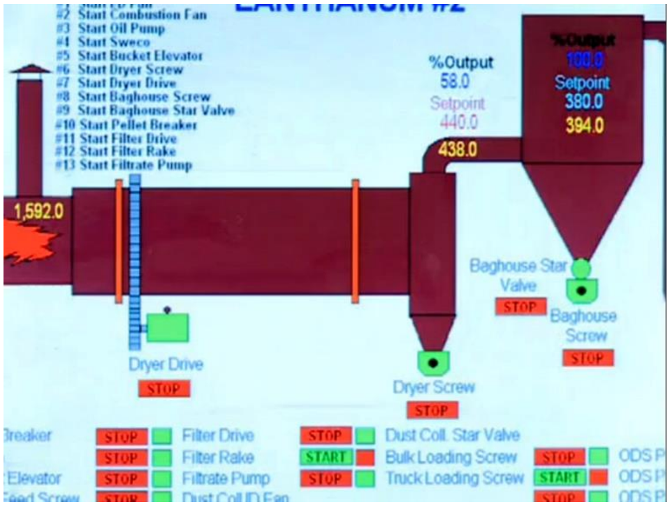
Figure 37. Cracking or Rotary Kiln at Lynas Advanced Materials Plant (LAMP) Rare earths refinery operated by Lynas Corporation at the Gebeng Industrial Zone, Pahang, Malaysia. Source: Lynas Corporation.

Figure 38. Upstream extraction.

Figure 39. Rotary kilns under assembly.

Figure 40. Cracking rotary kiln at processing plant. Source: Lynas.

Figure 41. Tunnel furnaces.



#2 Start Combustion Fan
#3 Start Oil Pump
#4 Start Sweco
#5 Start Bucket Elevator
#6 Start Dryer Screw
#7 Start Dryer Drive
#8 Start Baghouse Screw
#9 Start Baghouse Star Valve
#10 Start Pellet Breaker
#11 Start Filter Drive
#12 Start Filter Rake
#13 Start Filtrate Pump

Figure 42. Dryer control panel display.

Figure 43. Rare earths refinery tanks.

Figure 44. Reagent storage and preparation.

Figure 45. Reagent storage.

Figure 46. Gas treatment plant.

Figure 47. Downstream extraction process.

Figure 48. Post treatment process.

Sulfuric acid would be used to dissolve the rare earths from the concentrated ore. The thorium-containing part of the ore would be mixed with lime to dilute the thorium to less than 0.05 percent, which is the maximum permitted under international standards to allow the disposition of the material with few restrictions. The lime would be turned into tetrapods, which are large control shapes used to build artificial reefs for fish and as sea walls to protect harbors and shore installations from hurricanes and tsunamis, and to reduce beach erosion.

Table 15. Possible byproducts of rare earths refining.

Product	Source	Applications
Synthetic gypsum	Flue gases desulfurization	Plasterboard, Gypsum fiberboard, Cement additive
Magnesium-rich Synthetic Gypsum	Water treatment plant, water neutralization	Magnesium Gypsum fertilizer Booster, MGFB
Iron Phosphogypsum	Leaching stages, non-rare earths remain as solids, including Th and U	Concrete formulations. Road sub-base, Phospho-gypsum. Concrete tetrapods to reduce beach erosin and protection against hurricanes and tsunamis

IRON ORE RARE EARTHS RESOURCES

Geological Engineer Harry Winters [30] describes the rare earths mineralization in the Pea Ridge, Missouri iron ore deposit:

> “The Pea Ridge mine is a very well-known mine. It was originally developed by a joint venture company called Meramec Mining Company. The owners of Meramec were St. Joe Lead Company and Bethlehem Steel Corporation. This was an underground iron ore mine from the outset. Shaft sinking began in late 1957 and the first trainload of iron ore pellets was shipped in March 1964. Meramec operated the mine continuously from 1957 to 1977. The Meramec joint venture was terminated at the end of 1977 and the mine was put on standby. St. Joe Minerals formed the Pea Ridge Iron Ore Company (PRIOC) as a subsidiary in January 1979 and production was restarted. The mine eventually closed in 2001 due to bankruptcy under the then-owners, Woodridge Resources Corporation.
>
> During the underground iron ore mining operations four breccia pipes were discovered that contain substantial amounts of rare earth oxides and gold. The presence of the REO-bearing breccia pipes is well documented in published geological reports. Laurence Nuelle is the author of a 1991 paper on the REO and gold-bearing breccia pipes at Pea Ridge. There is a substantial iron ore resource, estimated at over 150 MM tons, (not necessarily profitably minable reserve) left in the mine. The REO breccia pipes may contain several hundred thousand tons of mineralized rock with a grade of about 12 percent REO. According to the USGS (Castor and Hedrick), bulk samples of REE-rich breccia, which contain monazite and xenotime, average about 12 percent REEs. The Pea Ridge resource is LREE-dominated, but also contains significant HREEs, again according to the USGA and a former geologist who worked at Pea Ridge.
>
> Recent owners of the project have been interested in resurrecting iron ore mining as well as mining the breccia pipes for REOs. The breccia pipe mining project would be a separate mining project from the iron ore mining, although some facilities such as hoisting, ventilation and other support systems might be used by both.
>
> It is my understanding that the monazite contains thorium and that some consideration was given to mining the REOs in the 1990s, but was not followed through because of problems processing the monazite ore as well as potential radioactive waste disposal problems.
>
> I do not know the current status of the property, but there is definitely a significant REO resource there and it contains thorium.
>
> …Table 20 on page 60 of USGS Scientific Investigations Report 2010-5220 shows rare earth elements and thorium concentrations in the four breccia pipes (thorium shown for only three). Thorium content for pipe X-11 is 0.63 percent, for pipe X-13 is 0.23 percent , and for pipe V-14 is 0.41 percent.”

UNDERSEA RARE EARTHS RESOURCES

Deposits of rare earths and other elements such as Fe, Cu and Mn exist on the ocean floor 3,500-6,000 meters (11,500-20,000 ft) below sea level. The undersea deposits may contain 80-100 billion tons of rare earths. This is larger than the surface deposits. A sludge containing the elements would be pumped to the surface and treated with acids for the extraction of the rare earths. The technology to be developed would have to operate in high pressure and highly corrosive environments and is likely to be more expensive than that for above-surface deposits.

RADIOACTIVITY IN RARE EARTHS

Most rare earths ores contain Th and U and their daughter products which must be disposed of responsibly. Rare earths require more chemicals for their extraction than the base metals such as copper, zinc and lead.

Pollution from the rare earths production is significant. China's rare earths industry produced 13 billion m^3 of gas and 25 million tons of waste water containing heavy metals such as Cd. The gases are more than five times waste gases as fluorine and sulfur dioxide than the total released by all miners and oil refiners in the USA.

China uses an ancient process called chloronization using chlorine to refine the rare earth metals. It is a very efficient and inexpensive process. A problem is that chloronization is ecologically disastrous. It destroys streams, lakes and water supplies. In Western countries the use of the chloronization process is banned.

This led China to shut down unregulated rare earth mines to protect its environment. It reduced its export quotas by 72 percent in the second half of 2010 and again by 35 percent in the first half of 2011 to prevent the depletion of its resources, after it supplied the world with 95 percent of the global shipments of rare earth metals. Rising demand and export restrictions led to the price of neodymium used in magnets manufacture to rise from $19.12 / kg in 2009 to $80 / kg in 2010.

Heavy rare earths deposits are more desired than light rare earths deposits. Most common heavy rare earth deposits are in the form of silicates. There are no known economic metallurgical processes to separate them. China has heavy rare earth deposits as Ionic Clays where nature did the metallurgy over billions of years and these deposits are mined with solution mining and then solvent extraction very cheaply.

The only other heavy rare earth mine placed into production was the Kutessay II mine in Kyrgyzstan due to its unique mineralogy. This mine is too small and the grades too low to ever be put back into production. North Korea has reportedly found one of the world's biggest deposits 150 km from Pyongyang. Afghanistan is also a repository for rare earth elements.

Table 16. Composition of Mountain Pass Mine ore.

Component	Percentage
Cerium	50.0
Lanthanum	34.0
Neodymium	11.0
Praesodimium	4.0
Samarium	0.5
Gadolinium	0.2
Europeum	0.1
Others	0.2

Table 17. Some naturally occurring rare earths radioactive isotopes in comparison with Th^{232}.

Component	Radioactive isotopes	Natural Abundance [a/o]	Mode of radioactive decay	Half life [a]
$_{39}Y$				
$_{57}La$	La^{138}	0.0902	$\varepsilon, \beta^-, \gamma$	1.05×10^{11}

$_{58}$Ce	Ce^{142}	11.08	$2\beta^-$, γ, α?	>5x10^{16}
$_{59}$Pr				
$_{60}$Nd	Nd^{144}	23.8	α, no γ	2.29x10^{15}
	Nd^{145}	8.3	α	>10^{17}
$_{61}$Pm				
$_{62}$Sm	Sm^{147}	15.0	α, no γ	1.06x10^{11}
	Sm^{148}	11.3	α, no γ	8.0x10^{15}
	Sm^{149}	13.8	α	2.0x10^{15}
$_{63}$Eu				
$_{64}$Gd	Gd^{152}	0.20	α, no γ	1.08x10^{14}
$_{65}$Tb				
$_{66}$Dy	Dy^{156}	0.06	?	>10^{18}
$_{67}$Ho				
$_{68}$Er				
$_{69}$Tm				
$_{70}$Yb				
$_{71}$Lu	Lu^{176}	2.59	β^-, ε, γ	4.0x10^{10}
$_{90}$Th	Th^{232}	100.0	α, γ	1.405x10^{10}

Cerium is a main component of some rare earths ores, even those with a low content in Th and U. The $_{58}$Cerium^{142} isotope with a natural abundance of 11.114 percent in Ce is radioactive with a long half-life of > 5x10^{16} years, hence low activity. Cerium has a crustal abundance of 60 ppm, comparable with Ni at 75 ppm and Cu at 55 ppm.

Its single beta decay energy can be calculated from:

$$\begin{aligned} E_{\beta} &= M(A,Z) - M(A,Z+1) \times 931.48 \\ &= M({}_{58}Ce^{142}) - M({}_{59}\mathrm{Pr}^{142}) \times 931.48 \\ &= [141.909243673 - 141.910044328] \times 931.48 \\ &= [-0.000800655] \times 931.48 \\ &= -0.745794\, MeV \end{aligned} \qquad (15)$$

As it decays through beta emission into $_{59}$Pr^{142} which is itself a beta emitter with a short half-life of 19.12 hours, it has been reported as a double beta emitter. In this case its beta decay energy would be calculated from:

$$\begin{aligned} E_{2\beta} &= M(A,Z) - M(A,Z+2) \times 931.48 \\ &= M({}_{58}Ce^{142}) - M({}_{60}Nd^{142}) \times 931.48 \\ &= [141.909243673 - 141.907722750] \times 931.48 \\ &= [+0.001520893] \times 931.48 \\ &= +1.416681\, MeV \end{aligned} \qquad (16)$$

The intermediate step $_{59}Pr^{142}$ emits gamma rays and beta particles and decays into the stable $_{60}Nd^{142}$ isotope which has a natural abundance of 27.2 in Neodymium with a branching ratio of 99.98 percent.

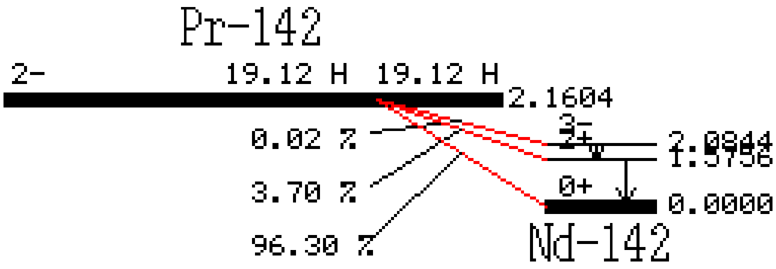


Figure 49. Decay scheme of the $_{59}Pr^{142}$ radioactive daughter of the $_{58}Cerium^{142}$ isotope. Gamma photons of 1.5756 MeV and 0.5088 MeV are emitted.

With a branching ratio of 0.02 percent, it decays through electron capture back into Ce^{142} with a decay energy of 0.745 MeV.

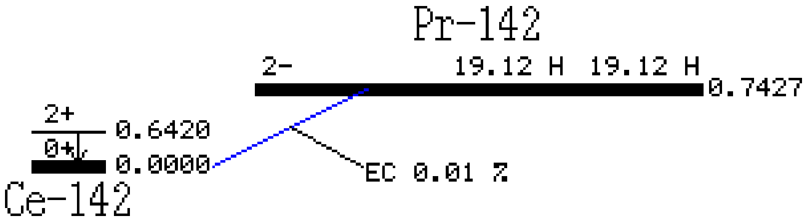


Figure 50. Electron capture in Pr^{142} into Ce^{142}. A gamma photon of 0.642 MeV is emitted.

It is possible that Ce^{142} is also an alpha particle emitter.

The $_{57}Lanthanum^{138}$ with a natural abundance of 0.0902 percent is also radioactive with a half life of 1.05 x 10^{11} years. It decays through beta emission with a 33.6 percent branching ratio and a decay energy of 1.044 MeV, and through electron capture with a branching ratio of 66.4 percent and a decay energy of 1.737 MeV.

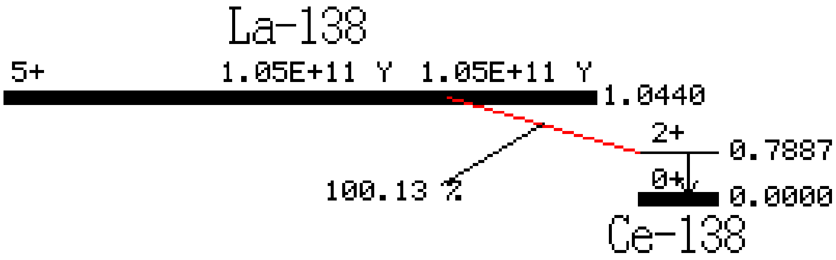


Figure 51. Beta decay of the La^{138} isotope to the stable Ce^{138} isotope. It emits a 0.7887 MeV gamma ray photon.

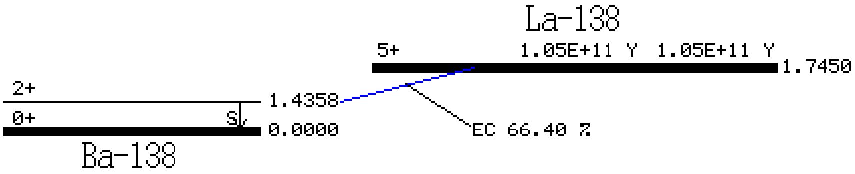


Figure 52. Electron capture of the La^{138} isotope to the stable Ba^{138} isotope. It emits a 1.4358 gamma ray photon.

Table 18. Consumption areas of rare earth elements [23].

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

Miscellaneous applications	10.6	3.0

THORIUM AS AN UNUSED RESOURCE

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 $1.3x10^6$ metric tonnes of ThO_2. The USA and Australia hold the world's largest known reserves with uncertain estimates ranging from $0.19x10^6 – 0.44x10^6$ metric tonnes of ThO_2. 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. Cerium is used in batteries and to cut auto emissions. 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 $(Ce, La,Y,Th)PO_4$ 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.

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. The Baotou region in Inner Mongolia produces half of the annual output of 120,000 tons. The largest producer is Inner Mongolia Baotou Steel Rare-Earth Hi-Tech Company. A tailings dam four stories high at a distance of 7 miles or 12 kms from Baotou has been a source of pollution for the local rivers. Baotou Steel Group that operates the Baiyun

Ebo mine spent $75 million or 500 million yuan with the local government in relocating five villages after seepage from the dam polluted drinking water and agricultural land.

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.

Figure 53. South China ion adsorption clays rare earths ores. Source: Google Earth.

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. Yet, in the case of Neodymium, used to make the Prius electric car’s motors, its price increased from $15 a kilogram in 2009 to $500 in 2011. Dysprosium oxide used in lasers and halide lamps went from $114 a kilogram in 2010 to $2,830 in 2011.

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.

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APPENDIX

Table A1. Short Term Global Energy Resource Base in ZJ (Zetajoules)[1]

Resource	Type	1998 Yearly Consumption [ZJ/yr]	Reserves	Resources	Resource Base[2]	Consumed By end of 1998	Additional Occurrences
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[4]	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[6]	-	-	1,300,000 -2,610,000[6]	-	-

[1] 1 ZJ (ZetaJoule) = 10^3 EJ (ExaJoule) = 10^{21} J (Joule)
[2] Resource Base = Reserves + Resources
[3] Includes uranium from sea water
[4] 1 tonne Uranium = 589 TJ
[5] 1 tonne Uranium = 35,340 TJ, a sixty times increase over the open cycle
[6] metric tonnes, ThO_2