Thorium

Thorium is a chemical element with symbol Th and atomic number 90 . A radioactive actinide metal , thorium is one of only two significantly radioactive elements that still occur naturally in large quantities as a primordial element (the other being uranium) . It was discovered in 1829 by the Norwegian priest and amateur mineralogist Morten Thrane Esmark and identified by the Swedish chemist Jöns Jacob Berzelius , who named it after Thor , the Norse god of thunder .

A thorium atom has 90 protons and therefore 90 electrons , of which four are valence electrons . Thorium metal is silvery and tarnishes black when exposed to air , forming the dioxide . Thorium is weakly radioactive : all its known isotopes are unstable . Thorium @-@ 232 , which has 142 neutrons , is the most stable isotope of thorium and accounts for nearly all natural thorium , with six other natural isotopes occurring only as trace radioisotopes . Thorium has the longest half @-@ life of all the significantly radioactive elements , 14 @.@ 05 billion years ; it decays very slowly through alpha decay to radium @-@ 228 , starting a decay chain named the thorium series that ends at stable lead @-@ 208 . Thorium is estimated to be about three to four times more abundant than uranium in the Earth 's crust , and is chiefly refined from monazite sands as a by @-@ product of extracting rare earth metals .

Thorium was once commonly used as the light source in gas mantles and as an alloying material , but these applications have declined due to concerns about its radioactivity . Thorium is still widely used as an alloying element in TIG welding electrodes (at a rate of 1 % ? 2 % mix with tungsten) . It remains popular as a material in high @-@ end optics and scientific instrumentation ; thorium and uranium are the only significantly radioactive elements with major commercial applications that do not rely on their radioactivity . Thorium is predicted to be able to replace uranium as nuclear fuel in nuclear reactors , but only a few thorium reactors have yet been completed .

Bulk properties

Thorium is a soft , paramagnetic , bright silvery radioactive actinide metal . In the periodic table , it is located to the right of the actinide actinium , to the left of the actinide protactinium , and below the lanthanide cerium . Pure thorium is very ductile and , as normal for metals , can be cold @-@ rolled , swaged , and drawn .

The properties of thorium vary widely depending on the amount of impurities in the sample used : the major impurity is usually thorium dioxide (ThO_2) . The purest thorium specimens usually contain about a tenth of a percent of the dioxide . Experimental measurements of its density give values between 11 @.@ 5 and 11 @.@ 66 g / cm^3 : these are slightly lower than the theoretically expected value of 11 @.@ 724 g / cm^3 calculated from thorium 's lattice parameters , perhaps due to microscopic voids forming in the metal when it is cast. these values lie intermediate between those of its neighbours actinium (10 @.@ 07 g / cm^3) and protactinium (15 @.@ 37 g / cm^3) , showing the continuity of trends across the early actinides .

Thorium 's melting point of 1750 ° C is above both that of actinium (1227 ° C) and that of protactinium (approximately 1560 ° C) . In the beginning of period 7 , from francium to thorium , the melting points of the elements increase (following the trend in the other periods) : this is because the number of delocalised electrons that each atom contributes increases from one in francium to four in thorium , and there is a greater attraction between these electrons and the metal ions as their charge increases from one in francium to four in thorium . After thorium , however , there is a new smooth trend downward in the melting points of the early actinides from thorium to plutonium where the number of f electrons increases from zero to six , due to the increasing hybridisation of the 5f and 6d orbitals and the formation of directional bonds in the metal . Among the actinides , thorium has the highest melting and boiling points and second @-@ lowest density (second only to actinium) .

Thorium has a bulk modulus of 54 GPa , comparable to those of tin and scandium . The hardness of thorium is similar to that of soft steel , so heated pure thorium can be rolled in sheets and pulled into wire . Nevertheless , while thorium is nearly half as dense as uranium and plutonium , it is

harder than either of them . Thorium becomes superconductive below 1 @.@ 4 K.
Thorium can also form alloys with many other metals . With chromium and uranium , it forms eutectic mixtures , and thorium is completely miscible in both solid and liquid states with its lighter congener cerium .

= = Isotopes = =

Although every element up to bismuth (element 83) has an isotope that is practically stable for all purposes (" classically stable ") , with the exceptions of technetium and promethium (elements 43 and 61) , all elements from polonium (element 84) onward are noticeably radioactive . Of these , thorium (element 90) is the most stable , closely followed by uranium (element 92) : the isotope 232Th has a half @-@ life of 14 @.@ 05 billion years , about three times the age of the earth , and even slightly longer than the generally accepted age of the universe (about 13 @.@ 8 billion years) . As such , 232Th still occurs naturally today : four @-@ fifths of the thorium present at Earth 's formation has survived to the present . Thorium and uranium are thus the most well @-@ studied of all the radioactive elements .
The heaviest three confirmed primordial nuclides , 232Th , 235U , and 238U , are the only isotopes beyond bismuth that have half @-@ lives measured in billions of years . Thus , they are the only such heavy isotopes to have survived since their production around ten billion years ago . Hence , thorium and uranium are the only important primordial radioactive elements . Even then , the half @-@ life of 232Th is only a billionth that of 209Bi , the last classically stable nuclide . 232Th is the only isotope of thorium occurring in significant quantities in nature today , and thus thorium is usually considered to be a mononuclidic element . The reason for the existence of this " island of relative stability " at thorium and uranium , where the longest @-@ lived isotopes have half @-@ lives of millions or billions of years , is because the most stable isotopes of these elements have closed nuclear shells ; nevertheless , since thorium and uranium have more protons than lead and bismuth , their nuclei are thus still susceptible to alpha decay because the strong nuclear force is not strong enough to overcome the electromagnetic repulsion between their protons .
232Th is the longest @-@ lived isotope in the 4n decay chain which includes isotopes with a mass number divisible by 4 (hence the name : it is also called the thorium series after its progenitor) . The chain begins with the alpha decay of 232Th to 228Ra , and terminates at stable 208Pb . (232Th very occasionally undergoes spontaneous fission rather than alpha decay , and has left evidence in doing so in its minerals .) Because 232Th is so long @-@ lived , its daughters still exist in nature as radiogenic nuclides despite their much shorter half @-@ lives , the longest among them being the 5 @.@ 7 @-@ year half @-@ life of 228Ra , the immediate alpha daughter of 232Th . Any sample of thorium or its compounds contain traces of these daughters , which are isotopes of thallium , lead , bismuth , polonium , radon , radium , and actinium . As such , natural thorium samples can be chemically purified to extract its useful daughter nuclides , such as 212Pb , which is used in nuclear medicine for cancer therapy .
Thirty radioisotopes have been characterised , which range in mass number from 209 to 238 . The most stable of them (after 232Th) are 230Th with a half @-@ life of 75 @,@ 380 years , 229Th with a half @-@ life of 7 @,@ 340 years , 228Th with a half @-@ life of 1 @.@ 92 years , 234Th with a half @-@ life of 24 @.@ 10 days , and 227Th with a half @-@ life of 18 @.@ 68 days : all of these isotopes occur in nature as trace radioisotopes due to their presence in the decay chains of 232Th , 235U , 238U , and 237Np (produced in minute traces in nuclear reactions in uranium ores) . All of the remaining thorium isotopes have half @-@ lives that are less than thirty days and the majority of these have half @-@ lives that are less than ten minutes .
In deep seawaters the isotope 230Th becomes significant enough that the International Union of Pure and Applied Chemistry (IUPAC) reclassified thorium as a binuclidic element in 2013 , as it can then make up to 0 @.@ 04 % of natural thorium , with 232Th being the remainder . The reason for this is that while its parent 238U is soluble in water , 230Th is insoluble and thus precipitates to form part of the sediment , and may be observed doing so . In fact , uranium ores with low thorium concentrations can be purified to produce gram @-@ sized thorium samples of which over a quarter

is the 230Th isotope , since 230Th is one of the daughters of 238U . Thorium thus has a characteristic terrestrial isotopic composition , and so an atomic mass can be given , which is 232 @.@ 0377 (4) u . Thorium is one of only three significantly radioactive elements (the others being protactinium and uranium) that occur in large enough quantities on Earth for this to be possible .
Thorium also has three known nuclear isomers (or metastable states) , 216m1Th , 216m2Th , and 229mTh . 229mTh has the lowest known excitation energy of any isomer , measured to be (7 @.@ 6 ± 0 @.@ 5) eV . This is so low that when it undergoes isomeric transition , the emitted gamma radiation is in the ultraviolet range .
In the early history of the study of radioactivity , the different natural isotopes of thorium were given different names . In this scheme , 227Th was named radioactinium (RdAc) , 228Th radiothorium (RdTh) , 230Th ionium (Io) , 231Th uranium Y (UY) , 232Th thorium (Th) , and 234Th uranium X1 (UX1) . This reflects that 227Th and 231Th occur in the decay chain of natural 235U (the actinium series) , 228Th occurs in the decay chain of 232Th (the thorium series) , and that 230Th occurs in the decay chain of 238U (the uranium or radium series) . The remaining natural thorium isotope , 229Th , occurs in minute traces as part of the decay chain of 237Np , the neptunium series , which is much less abundant than the other decay chains in nature and was hence discovered much later : therefore it does not have a historical name . When it was realised that all of these are isotopes of thorium , many of these names fell out of use , and " thorium " came to refer to all isotopes , not just 232Th . However , the name ionium is still encountered for 230Th in the context of ionium @-@ thorium dating .
Different isotopes of thorium behave identically chemically , but do have slightly differing physical properties : for example , the densities of isotopically pure 228Th , 229Th , 230Th , and 232Th in g / cm3 are respectively expected to be 11 @.@ 524 , 11 @.@ 575 , 11 @.@ 626 , and 11 @.@ 727 . (The discrepancy between this and the previously mentioned theoretical value of 11 @.@ 724 is because this does not refer to isotopically pure thorium , but rather natural thorium , which as noted above is a mixture of mostly 232Th but also a little 230Th .) The isotope 229Th is expected to be fissionable with a bare critical mass of 2839 kg , although with steel reflectors this value could drop to 994 kg . While 232Th is not fissionable , it is fertile as it can be converted to fissile 233U using neutron capture .

= = Chemistry = =

A thorium atom has 90 electrons , of which four are valence electrons . Three atomic orbitals are theoretically available for the valence electrons to occupy : 5f , 6d , and 7s . Despite thorium 's position in the f @-@ block of the periodic table , it has an anomalous [Rn] 6d27s2 electron configuration in the ground state , as the 5f and 6d subshells in the early actinides are very close in energy , even more so than the 4f and 5d subshells of the lanthanides : in fact , thorium 's 6d subshells are lower in energy than its 5f subshells , because its 5f subshells are not well @-@ shielded by the filled 6s and 6p subshells and are destabilised . Such unusual behaviour is due to relativistic effects , which are increasingly stronger near the bottom of the periodic table , specifically the relativistic spin ? orbit interaction . The closeness in energy levels of the 5f , 6d , and 7s energy levels of thorium result in thorium almost always losing all four of its valence electrons and hence occurring in its highest possible oxidation state of + 4 . Therefore , thorium is much more similar to the transition metals zirconium and hafnium than to its true lanthanide congener cerium in its properties such as ionisation energies and redox potentials , and hence also in its chemistry .
Tetravalent thorium compounds are usually colourless or yellow , like those of silver or lead , as the Th4 + ion has no 5f or 6d electrons . Thorium and uranium are the most investigated of the radioactive elements because their radioactivity is slight enough to not pose major problems of handling and accessibility .

= = = Reactivity = = =

Thorium is a highly reactive and electropositive metal . Finely divided thorium metal presents a fire hazard due to its pyrophoricity and must therefore be handled carefully . When heated in air , thorium turnings ignite and burn brilliantly with a white light to produce the dioxide . In bulk , the reaction of pure thorium with air is slow , although corrosion may eventually occur after several months ; most thorium samples are however contaminated with varying degrees of the dioxide , which greatly accelerates corrosion . Such samples slowly tarnish in air , becoming grey and finally black at the surface .

At standard temperature and pressure , thorium is slowly attacked by water , but does not readily dissolve in most common acids , with the exception of hydrochloric acid , where it dissolves leaving behind a black insoluble residue , probably ThO (OH , Cl) H. It dissolves in concentrated nitric acid containing a small amount of catalytic fluoride or fluorosilicate ions ; if these are not present , passivation can occur , similarly to uranium and plutonium .

= = = Inorganic compounds = = =

Most binary compounds of thorium with nonmetals may simply be prepared by heating the elements together . In air , thorium burns to form the simple dioxide , ThO_2 , also called thoria or thorina . Thoria , a refractory material , has the highest melting point (3390 ° C) of all known oxides . It is somewhat hygroscopic and reacts readily with water and many gases , but dissolves easily in concentrated nitric acid in the presence of fluoride . When heated , it emits intense blue light through incandescence , which becomes white when mixed with its lighter homologue cerium dioxide (CeO_2 , ceria) : this is the basis for its previously common application in gas mantles . Several binary thorium chalcogenides and oxychalcogenides are also known with sulfur , selenium , and tellurium .

All four thorium tetrahalides are known , as are some low @-@ valent bromides and iodides : the tetrahalides are all 8 @-@ coordinated hygroscopic compounds that dissolve easily in polar solvents such as water . Additionally , many related polyhalide ions are also known . Thorium tetrafluoride has a monoclinic crystal structure and is isotypic with zirconium tetrafluoride and hafnium tetrafluoride , where the Th^{4+} ions are coordinated with F ? ions in somewhat distorted square antiprisms . The other tetrahalides instead have dodecahedral geometry . Lower iodides ThI_3 (black) and ThI_2 (gold) can also be prepared by reducing the tetraiodide with thorium metal : These do not contain Th (III) and Th (II) , but instead contain Th^{4+} and could be more clearly formulated as electride compounds . Many polynary halides with the alkali metals , barium , thallium , and ammonium are known for thorium fluorides , chlorides , and bromides . For example , when treated with potassium fluoride and hydrofluoric acid , Th^{4+} forms the complex anion ThF2 ?
6 , which precipitates as an insoluble salt , K_2ThF_6 .

Thorium borides , carbides , silicides , and nitrides are refractory materials , as are those of uranium and plutonium , and have thus received attention as possible nuclear fuels . All four heavier pnictogens (phosphorus , arsenic , antimony , and bismuth) also form binary thorium compounds . Thorium germanides are also known . Thorium reacts with hydrogen to form the thorium hydrides ThH_2 and Th_4H_{15} , the latter of which is superconducting below the transition temperature of 7 @.@ 5 ? 8 K ; at standard temperature and pressure , it conducts electricity like a metal . However , they are thermally unstable and readily decompose upon exposure to air or moisture .

= = = Coordination compounds = = =

In acidic aqueous solution , thorium occurs as the tetrapositive aqua ion $[Th(H_2O)_9]^{4+}$, which has tricapped trigonal prismatic molecular geometry : at pH < 3 , the solutions of thorium salts are dominated by this cation . The Th^{4+} ion is the largest of the tetrapositive actinide ions , and depending on the coordination number can have a radius between 0 @.@ 95 and 1 @.@ 14 Å . It is quite acidic due to its high charge , slightly stronger than sulfurous acid : thus it tends to undergo hydrolysis and polymerisation (though to a lesser extent than Fe^{3+}) , predominantly to $[Th_2(OH)_2]^{6+}$ in solutions with pH 3 or below , but in more alkaline solution polymerisation continues until the gelatinous hydroxide $Th(OH)_4$ is formed and precipitates out (though equilibrium may take weeks to be reached , because the polymerisation usually slows down significantly just before the precipitation) . As a hard Lewis acid , Th^{4+} favours hard ligands with oxygen atoms as donors : complexes with sulfur atoms as donors are less stable and are more prone to hydrolysis .

Large coordination numbers are the rule for thorium due to its large size . Thorium nitrate pentahydrate was the first known example of coordination number 11 , the oxalate tetrahydrate has coordination number 10 , and the borohydride (first prepared in the Manhattan Project) has coordination number 14 . The distinctive ability of thorium salts is their high solubility , not only in water , but also in polar organic solvents .

Many other inorganic thorium compounds with polyatomic anions are known , such as the perchlorates , sulfates , sulfites , nitrates , carbonates , phosphates , vanadates , molybdates , and chromates , and their hydrated forms . They are important in thorium purification and the disposal of nuclear waste , but most of them have not yet been fully characterised , especially regarding their structural properties . For example , thorium nitrate is soluble in water and alcohols and is an important intermediate in the purification of thorium and its compounds . Thorium complexes with organic ligands , such as oxalate , citrate , and EDTA , are much stronger and tend to occur naturally in natural thorium @-@ containing waters in concentrations orders of magnitude higher than the inorganic complexes .

= = = Organothorium compounds = = =

Most of the work on organothorium compounds has focused on the cyclopentadienyls and cyclooctatetraenyls . Like many of the early and middle actinides (up to americium , and also expected for curium) , thorium forms the yellow cyclooctatetraenide complex $Th(C_8H_8)_2$, thorocene . It is isotypic with the better @-@ known analogous uranium compound , uranocene . It can be prepared by reacting $K_2C_8H_8$ with thorium tetrachloride in tetrahydrofuran (THF) at the temperature of dry ice , or by reacting thorium tetrafluoride with MgC_8H_8 . It is an unstable compound in air and outright decomposes in water or at 190 ° C. Half @-@ sandwich compounds are also known , such as (?8 @-@ C_8H_8) $ThCl_2$ (THF) 2 , which has a piano @-@ stool structure and is made by reacting thorocene with thorium tetrachloride in tetrahydrofuran .

The simplest of the cyclopentadienyls are $Th(C_5H_5)_3$ and $Th(C_5H_5)_4$: many derivatives are known . The former (which has two forms , one purple and one green) is a rare example of thorium in the formal + 3 oxidation state ; a formal + 2 oxidation state even occurs in a derivative . The chloride derivative [$Th(C_5H_5)_3Cl$] is prepared by by heating thorium tetrachloride with limiting K (C_5H_5) used (other univalent metal cyclopentadienyls can also be used) . The alkyl and aryl derivatives are prepared from the chloride derivative and have received attention due to the insight they give regarding the nature of the Th ? C sigma bond .

Other organothorium compounds are not well @-@ studied . Tetrabenzylthorium , Th ($CH_2C_6H_5$) , and tetraallylthorium , $Th(C_3H_5)_4$, are known , but their structures have not yet been determined and they decompose slowly at room temperature . Thorium forms the monocapped trigonal prismatic anion [$Th(CH_3)_7$] 3 ? , heptamethylthorate , which forms the salt [Li (tmeda)] 3 [$ThMe_7$] (tmeda = $Me_2NCH_2CH_2NMe_2$) . Although one methyl group is only attached to the thorium atom (Th ? C distance 257 @.@ 1 pm) and the other six connect the lithium and thorium atoms (Th ? C distances 265 @.@ 5 ? 276 @.@ 5 pm) they behave equivalently in solution . Tetramethylthorium , $Th(CH_3)_4$, is not known , but its adducts are stabilised by phosphine ligands .

= = Occurrence = =

= = = Formation = = =

232Th is a primordial nuclide , having existed in its current form for over ten billion years ; it was forged in the cores of dying stars through the r @-@ process and scattered across the galaxy by supernovae . The letter " r " stands for " rapid neutron capture " , and occurs in core @-@ collapse supernovae , where heavy seed nuclei such as 56Fe rapidly capture neutrons , running up against the neutron drip line , as neutrons are captured much faster than the resulting nuclides can beta decay back toward stability . Neutron capture is the only way for stars to synthesise elements beyond iron because of the increased Coulomb barriers that make interactions between charged particles difficult at high atomic numbers and the fact that fusion beyond 56Fe is endothermic . Because of the abrupt loss of stability past bismuth , the r @-@ process is the only process of stellar nucleosynthesis that can create isotopes of thorium and uranium , because all other processes are too slow and the intermediate nuclei alpha decay before they capture enough neutrons to reach these elements .

In the universe , thorium is among the rarest of the primordial elements : it achieves this position because not only because it is one of the two elements that can be produced only in the r @-@ process (with the other one being uranium) , but also because it has slowly been decaying away from the moment it formed . The only primordial elements rarer than thorium are thulium , lutetium , tantalum , and rhenium , the odd @-@ numbered elements just before the third peak of r @-@ process abundances around the heavy platinum group metals . However , on Earth , thorium is much more abundant : with an abundance of 8 @.@ 1 ppm in the Earth 's crust , it is one of the most abundant of the heavy elements , almost as abundant as lead (13 ppm) and significantly more abundant than tin (2 @.@ 1 ppm) . This is because thorium , being a lithophile , is likely to form oxide minerals that do not sink into the core , unlike most of the other heavy elements that are more abundantly produced by the r @-@ process .

= = = On Earth = = =

Natural thorium is essentially isotopically pure 232Th , which is the longest @-@ lived and most stable isotope of thorium , having a half @-@ life comparable to the age of the universe . Its radioactive decay produces a significant amount of the Earth 's internal heat ; the other major contributors are the shorter @-@ lived primordial nuclides , 235U , 238U , and 40K . The other natural thorium isotopes are much shorter @-@ lived ; of them , only 230Th is usually detectable , occurring in secular equilibrium with its parent 238U , and making up at most 0 @.@ 04 % of natural thorium .

On Earth , thorium is not a rare element as was previously thought , having a crustal abundance comparable to that of lead and molybdenum , twice that of arsenic , and thrice that of tin . However , thorium only occurs as a minor constituent of most minerals . Soil normally contains about 6 parts per million (ppm) of thorium .

In nature , thorium occurs in the + 4 oxidation state , together with uranium (IV) , zirconium (IV) , hafnium (IV) , and cerium (IV) , but also with scandium , yttrium , and the trivalent lanthanides which have similar ionic radii . Because of thorium 's radioactivity , minerals containing significant quantities of thorium are often metamict , their crystal structure having been partially or totally destroyed by the alpha radiation produced in the radioactive decay of thorium . An extreme example is ekanite , (Ca , Fe , Pb) 2 (Th , U) Si8O20 , which almost never occurs in nonmetamict form due to thorium being an essential part of its chemical composition .

Monazite is the most important commercial source of thorium because it occurs in large deposits worldwide , principally in India , South Africa , Brazil , Australia , and Malaysia . It contains around 2 @.@ 5 % thorium on average , although some deposits may contain up to 20 % thorium . Monazite is a chemically unreactive phosphate mineral that is found as yellow or brown sand ; its low reactivity makes it difficult to extract thorium from it . Allanite can have 0 @.@ 1 ? 2 % thorium and zircon up to 0 @.@ 4 % thorium .

Thorium dioxide occurs as the rare mineral thorianite , which usually contains up to 12 % ThO2 . However , due to its being isotypic with uranium dioxide , these two common actinide dioxides can form solid @-@ state solutions and the name of the mineral changes according to the ThO2 content . Thorite , or tetragonal thorium silicate (ThSiO4) , also has a high thorium content and is the mineral in which thorium was first discovered . In thorium silicate minerals , the Th4 + and SiO4 ?
4 ions are often replaced with M3 + (M = Sc , Y , Ln) and phosphate (PO3 ?

4) ions respectively . Because of the great insolubility of thorium dioxide , thorium does not usually spread quickly through the environment when released in significant quantities : however , the Th4 + ion is soluble , especially in acidic soils , and in such conditions the thorium concentration can reach 40 ppm .

= = History = =

In 1815 , the Swedish chemist Jöns Jakob Berzelius analysed an unusual sample of gadolinite from a copper mine in Falun , central Sweden . He noted impregnated traces of a white mineral , which he cautiously assumed to be an earth (oxide in modern chemical nomenclature) of an unknown element . (By that time , Berzelius had already discovered two elements , cerium and selenium , but he had made a public mistake once , announcing a new element , gahnium , that turned out to be simply zinc oxide .) Berzelius privately named the supposed tentative element " thorium " in 1817 and its supposed oxide " thorina " after Thor , the Norse god of thunder . However , in 1824 , after more deposits of the same mineral in Vest @-@ Agder , Norway , were discovered , he retracted his findings , as the mineral in question proved to actually be an yttrium mineral , primarily composed of yttrium orthophosphate . As the yttrium in this mineral was initially mistaken as being a new element , the mineral was named kenotime by the French mineralogist François Sulpice Beudant as a rebuke of Berzelius , from the Greek words ????? (vain) and ???? (honour) . However , this became " xenotime " as a misprint from the beginning , blunting the criticism . This misspelt form was later explained as being from ????? (stranger to) and ???? (honour) , supposedly referencing the small , rare and easily overlooked crystals that xenotime occurs as . He determined that thorium was a very electropositive metal , that he placed ahead of cerium and behind zirconium in electropositivity .

In 1828 , Morten Thrane Esmark found a black mineral on Løvøya island , Telemark county , Norway . He was a Norwegian priest and amateur mineralogist who studied the minerals in Telemark , where he served as vicar . He commonly sent the most interesting specimens , such as this one , to his father , Jens Esmark , a noted mineralogist and professor of mineralogy and geology at the University of Oslo . The elder Esmark determined that it was not any known mineral and sent a sample to Berzelius for examination . Berzelius determined that it contained a new element . He published his findings in 1829 , having isolated an impure sample for the first time by reducing KThF5 with potassium metal . Berzelius reused the name of the previous supposed element discovery . Thus , he named the source mineral thorite , which has the chemical composition (Th , U) SiO4 . Berzelius also made some initial characterisation of the new metal and its chemical compounds : he correctly determined that the thorium ? oxygen mass ratio was 7 @.@ 5 (its actual value is close to that , ~ 7 @.@ 3) , but he assumed the new element was divalent rather than tetravalent , and as such assumed that the atomic mass was 7 @.@ 5 times that of oxygen (120 amu) , while it is actually 15 times as large . Berzelius , however , did not isolate the element in its metallic state ; for the first time , thorium was isolated in 1914 by D. Lely Jr. and L. Hamburger . They obtained 99 % pure thorium metal by reducing thorium chloride with sodium metal . A simpler method leading to even higher purity was discovered in 1927 by Marden and Rentschler , involving the reduction of thorium oxide with calcium when calcium chloride was present .

In Dmitri Mendeleev 's 1869 periodic table , thorium and the rare earth elements were placed outside the main body of the table , at the end of each vertical period after the alkaline earth metals . This reflected the belief at that time that thorium and the rare earth metals were divalent . With the later recognition that the rare earths were mostly trivalent and thorium was tetravalent , Mendeleev moved cerium and thorium to group IV in 1871 , which contained the modern carbon group (group 14) , titanium group (group 4) , cerium , and thorium , because their maximum oxidation state was + 4 . Cerium was soon removed from the main body of the table and placed in a separate lanthanide series , while thorium remained with group 4 as it had similar properties to its supposed lighter congeners in that group , such as titanium and zirconium .

Although thorium was discovered in 1828 , it had no applications until 1885 , when Carl Auer von

Welsbach invented the gas mantle , which produces light from the incandescence of very hot thorium oxide , heated to extremely high temperatures by burning gaseous fuels . After 1885 , many applications were found for thorium and its compounds , such as in ceramics , carbon arc lamps , heat @-@ resistant crucibles , and as catalysts for industrial chemical reactions such as the oxidation of ammonia to nitric acid . In the 1990s , however , most of these applications that do not depend on thorium 's radioactivity declined quickly due to safety and environmental concerns . The reason for the great delay between the recognition of the health hazards of radioactivity and the phasing out of thorium was that no serviceable substitutes for thorium for these applications were known until the 1990s .

In the late 19th century onward , the atomic theory underwent significant improvements , which shaped the further history of thorium . Thorium was first observed to be radioactive in 1898 , independently , by the German chemist Gerhard Carl Schmidt and later that year , the Polish @-@ French physicist Marie Curie . It was the second element that was found to be radioactive , after the 1896 discovery of radioactivity in uranium by Henri Becquerel . Between 1900 and 1903 , Ernest Rutherford and Frederick Soddy showed how thorium decayed at a fixed rate over time into a series of other elements . This observation led to the identification of half @-@ life as one of the outcomes of the alpha particle experiments that led to their disintegration theory of radioactivity . The biological effect of radiation was discovered in 1903 ; the danger presented by radioactivity to health and environment was the reason thorium was phased out of use in applications that did not explicitly use the radioactivity .

In 1922 , Niels Bohr published a theoretical model of the atom and its electron orbitals , which soon gathered wide acceptance . The model indicated that the seventh row of the periodic table should also have f @-@ shells filling before the d @-@ shells that were filled in the transition elements , like the sixth row with the lanthanides preceding the 5d transition metals . Such a second extra @-@ long periodic table row , to accommodate known and undiscovered elements with an atomic weight greater than bismuth (thorium , protactinium , and uranium , for example) , had been postulated as far back as 1892 by Henry Bassett , who considered thorium and uranium to be members of a second series of rare earths , and predicted that more elements would be found within this series . Most investigators , however , considered on the basis of their chemical properties that these elements were analogous to the 5d transition elements hafnium , tantalum , and tungsten , and considered the existence of the lanthanides in the sixth row to be a one @-@ off fluke . The existence of a second inner transition series , in the form of the actinides , was not accepted until similarities with the electron structures of the lanthanides had been established . It was only with the discovery of the first transuranic elements , which from plutonium onward have dominant + 3 and + 4 oxidation states (neptunium having + 4 and + 5 as dominant states and + 7 as an unstable state) , that it was realised that the actinides were indeed filling f @-@ orbitals rather than d @-@ orbitals . Thus it was not until 1945 , after Glenn T. Seaborg and his team had discovered the transuranic elements americium and curium , that Seaborg realised that thorium was the second member of the actinide series and was filling an f @-@ block row , instead of being the heavier congener of hafnium and filling a fourth d @-@ block row . Today , thorium 's similarities to hafnium are still sometimes acknowledged by calling it a " pseudo group @-@ 4 element " .

= = Production = =

Thorium is extracted mostly from monazite : thorium diphosphate (Th (PO4) 2) is reacted with nitric acid , and the produced thorium nitrate treated with tributyl phosphate . Rare @-@ earth impurities are separated by increasing the pH in sulfate solution .

In another extraction method , monazite is decomposed with a 45 % aqueous solution of sodium hydroxide at 140 ° C. Mixed metal hydroxides are extracted first , filtered at 80 ° C , washed with water and dissolved with concentrated hydrochloric acid . Next , the acidic solution is neutralised with hydroxides to pH = 5 @.@ 8 that results in precipitation of thorium hydroxide (Th (OH) 4) contaminated with ~ 3 % of rare @-@ earth hydroxides ; the remaining rare @-@ earth hydroxides remain in solution . Thorium hydroxide is dissolved in an inorganic acid and then purified from the rare earth elements . An efficient method is the dissolution of thorium hydroxide in nitric acid , because the resulting solution can be purified by extraction with organic solvents :

$Th (OH)_4 + 4 HNO_3$? $Th (NO_3)_4 + 4 H_2O$

Metallic thorium is separated from the anhydrous oxide or chloride by reacting it with calcium in an inert atmosphere :

$ThO_2 + 2 Ca$? $2 CaO + Th$

Sometimes thorium is extracted by electrolysis of a fluoride in a mixture of sodium and potassium chloride at 700 ? 800 ° C in a graphite crucible . Highly pure thorium can be extracted from its iodide with the crystal bar process .

Since thorium has few applications today , only a few hundred tonnes of it are produced each year , mostly as a by @-@ product of the production of uranium and the lanthanides ; half of this thorium produced is used in gas mantles . Nevertheless , production could easily be increased , and probably would be if thorium became used in large quantities as nuclear fuel .

= = Applications = =

= = = Nuclear = = =

Due to thorium 's radioactivity , the most important possible uses of thorium are in the thorium fuel cycle as a nuclear fuel and in radiometric dating .

= = = = Nuclear energy = = = =

In thermal breeder reactors , the fertile isotope 232Th is bombarded by slow neutrons , undergoing neutron capture to become 233Th , which undergoes two consecutive beta decays to become first 233Pa and then the fissile 233U :

232
90Th + n ? 233
90Th + ? ?- ? 21 @.@ 8 min 233
91Pa ?- ? 27 @.@ 0 days 233
92U ? ? 1 @.@ 59 × 105 y

233U is fissile and hence can be used as a nuclear fuel in much the same way as the more @-@ commonly used 235U or 239Pu . When 233U undergoes nuclear fission , the neutrons emitted can strike further 232Th nuclei , restarting the cycle . This closely parallels the uranium fuel cycle in fast breeder reactors where 238U undergoes neutron capture to become 239U , beta decaying to first 239Np and then fissile 239Pu . The main advantage of the thorium fuel cycle is that thorium is more abundant than uranium and hence can satisfy world energy demands for longer . Furthermore , 232Th absorbs neutrons more readily than 238U , and not only does 233U have a higher probability of fission upon neutron capture than 235U or 239Pu , it also releases more neutrons upon fission on average . An added advantage 233U and 239Pu enjoy over all other fissile nuclei (except the naturally occurring 235U) is that they can be bred from neutron capture by the naturally @-@ occurring quantity isotopes 232Th and 238U . Thorium fuels also result in a safer and better @-@ performing reactor core because thoria has a higher melting point , higher thermal conductivity , and lower coefficient of thermal expansion than the now @-@ common fuel uranium dioxide (UO_2) : thoria is also more chemically stable as , unlike uranium dioxide , it does not further oxidise to triuranium octoxide (U_3O_8) .

However , the main disadvantage is that it is difficult and dangerous to reprocess the used fuel because many of the daughters of 232Th and 233U are strong gamma emitters . Additionally , production of 233U always results in significant impurities of the very dangerous gamma emitter 232U , either from parasitic (n , 2n) reactions on 232Th , 233Pa , or 233U that result in the loss of a neutron , or from double neutron capture of 230Th , an impurity in natural 232Th :

230

90Th + n ? 231
90Th + ? ?- ? 25 @.@ 5 h 231
91Pa ? ? 3 @.@ 28 × 104 y
231
91Pa + n ? 232
91Pa + ? ?- ? 1 @.@ 3 d 232
92U ? ? 69 y

These impurities of 232U make 233U very easy to detect and very dangerous to work on , and the impracticality of their separation limits the possibilities of nuclear proliferation using 233U as the fissile material . Additionally , 233Pa has a relatively long half @-@ life of 27 days and a high cross section for neutron capture . Thus it is a neutron poison : instead of rapidly decaying to the useful 233U , a significant amount of 233Pa converts to 234U and consumes neutrons , degrading the reactor efficiency . To avoid this , 233Pa is extracted from the active zone of thorium molten salt reactors during their operation , so that it only decays to 233U .

A single neutron capture by 238U would produce transuranic waste , along with it fissile 239Pu , whereas five captures are generally necessary to do so from 232Th . 98 ? 99 % of thorium @-@ cycle fuel nuclei would fission at either 233U or 235U , so fewer long @-@ lived transuranics are produced . Because of this , thorium is a potentially attractive alternative to uranium in mixed oxide (MOX) fuels to minimise the generation of transuranics and maximise the destruction of plutonium . A disadvantage of the thorium fuel cycle is the need to neutron @-@ irradiate and process natural 232Th before these advantages become real , and this requires more advanced technology than the presently used fuels based on uranium and plutonium ; nevertheless , advances are being made in this technology . Another common criticism centres around the low commercial viability of the thorium fuel cycle : some entities like the Nuclear Energy Agency go further and predict that the thorium cycle will never be commercially viable while uranium is available in abundance ? a situation which Trevor Findlay predicts will persist " in the coming decades " . Furthermore , though the isotopes produced in the thorium fuel cycle are not transuranic , some of them are still very dangerous , such as 231Pa , which has a long half @-@ life of 32760 years and is a major contributor to the long term radiotoxicity of spent nuclear fuel .

In 1997 , the U.S. Energy Department underwrote research into thorium fuel , and research also was begun in 1996 by the International Atomic Energy Agency (IAEA) , to study the use of thorium reactors . Nuclear scientist Alvin Radkowsky of Tel Aviv University in Israel founded a consortium to develop thorium reactors , which included other companies : Raytheon Nuclear Inc . , Brookhaven National Laboratory and the Kurchatov Institute in Moscow . Radkowsky was chief scientist in the U.S. nuclear submarine program directed by Admiral Hyman Rickover and later headed the design team that built the USA 's first civilian nuclear power plant at Shippingport , Pennsylvania , which was a scaled @-@ up version of the first naval reactor . The third Shippingport core , initiated in 1977 , bred thorium . Even earlier examples of reactors using fuel with thorium exist , including the first core at the Indian Point Energy Center in 1962 . However , in most countries uranium was relatively abundant and hence research into thorium fuel waned for a while . A notable exception was India 's three @-@ stage nuclear power programme . Because India has one of the largest supplies of thorium in the world (accounting for about 30 % of known thorium reserves) , but does not have much uranium , India formulated a nuclear power programme based on the thorium fuel cycle with the goal of achieving energy independence . In the twenty @-@ first century thorium 's potential for improving proliferation resistance and waste characteristics led to renewed interest in the thorium fuel cycle . Currently , some countries such as India are developing technology for thorium nuclear reactors .

= = = = Radiometric dating = = = =

Two radiometric dating methods involve thorium isotopes : uranium @-@ thorium dating , involving the decay of 234U to 230Th (ionium) , and ionium @-@ thorium dating , which measures the ratio of 232Th to 230Th . These rely on the fact that 232Th is a primordial radioisotope , but 230Th only occurs as an intermediate decay product in the decay chain of 238U . Uranium @-@ thorium dating is a relatively short @-@ range process because of the short half @-@ lives of 234U and 230Th relative to the age of the Earth : it is also accompanied by a sister process involving the alpha decay of 235U into 231Th , which very quickly becomes the longer @-@ lived 231Pa , and this process is often used to check the results of uranium @-@ thorium dating . Uranium @-@ thorium dating is commonly used to determine the age of calcium carbonate materials such as speleothem or coral , because while uranium is rather soluble in water , thorium and protactinium are not , and so they are selectively precipitated into ocean @-@ floor sediments , from which their ratios are measured . The scheme has a range of several hundred thousand years . Ionium @-@ thorium dating is a related process , which exploits the insolubility of thorium (both 232Th and 230Th) and thus its presence in ocean sediments to date these sediments by measuring the ratio of 232Th to 230Th . Both of these dating methods assume that the proportion of 230Th to 232Th is a constant during the time period when the sediment layer was formed , that the sediment did not already contain thorium before contributions from the decay of uranium , and that the thorium cannot shift within the sediment layer .

= = = Non @-@ nuclear = = =

Many non @-@ nuclear applications of thorium are becoming obsolete due to environmental concerns largely stemming from the radioactivity of thorium and its decay products ; though these were known for a long time , the phasing out of thorium was greatly delayed because no serviceable substitutes were known until the 1990s . A notable exception is the use of thoria in gas tungsten arc welding (GTAW) to increase the high @-@ temperature strength of tungsten electrodes and improve arc stability . The electrodes labelled EWTH @-@ 1 contain 1 % thoria , while those labelled EWTH @-@ 2 contain 2 % . In electronic equipment , thorium coating of tungsten wire improves the electron emission of heated cathodes .

The melting point of thoria is 3300 ° C ? the highest of all known oxides . Only a few elements (including tungsten and carbon) and a few compounds (including tantalum carbide) have higher melting points . This means that when heated to high temperatures , it does not melt , but merely glows with an intense blue light ; addition of cerium dioxide gives a bright white light . This property of thoria means that thoria and thorium nitrate are used in mantles of portable gas lights , including natural gas lamps , oil lamps and camping lights . A study in 1981 estimated that the dose from using a thorium mantle every weekend for a year would be 0 @.@ 3 ? 0 @.@ 6 millirems (mrem) , tiny in comparison to the normal annual dose of a few hundred millirems : a person actually ingesting a mantle would receive a dose of 200 mrem (2 mSv) . However , the radioactivity is a major concern for people involved with the manufacture of mantles , and an issue with contamination of soil around some former factory sites . Due to these concerns , some manufacturers have switched to other materials , such as yttrium , although these are usually either more expensive or less efficient . Other manufacturers continue to make thorium mantles , but moved their factories to developing countries . As recently as 2007 , some companies continued to manufacture and sell thorium mantles without giving adequate information about their radioactivity , with some even fraudulently claiming them to be non @-@ radioactive while in reality using large quantities of thorium , up to 259 milligrams per mantle .

Thoria is a material for heat @-@ resistant ceramics , as used in high @-@ temperature laboratory crucibles . When added to glass , it helps increase refractive index and decrease dispersion . Such glass finds application in high @-@ quality lenses for cameras and scientific instruments . The radiation from these lenses can darken them and turn them yellow over a period of years and degrade film , but the health risks are minimal . Yellowed lenses may be restored to their original colourless state with lengthy exposure to intense ultraviolet radiation .

Thoria was used to control the grain size of tungsten metal used for spirals of electric lamps . Thoriated tungsten elements are found in the filaments of vacuum tubes , e.g. magnetron found in microwave oven . Thorium is added because it lowers the effective work function with the result that the thoriated tungsten thermocathode emits electrons at considerably lower temperatures . Thoria has been used as a catalyst in the conversion of ammonia to nitric acid , in petroleum cracking and in producing sulfuric acid . It is the active ingredient of Thorotrast , which was used as radiocontrast agent for X @-@ ray diagnostics because of thorium 's high opacity to X @-@ rays . This use has been abandoned due to its carcinogenic nature .

Thorium tetrafluoride is used as an antireflection material in multilayered optical coatings . It has excellent optical transparency in the range of 0 @.@ 35 ? 12 µm , and its radiation is primarily due to alpha particles , which can be easily stopped by a thin cover layer of another material . Thorium tetrafluoride was also used in manufacturing carbon arc lamps , which provided high @-@ intensity illumination for movie projectors and search lights .

= = Precautions = =

As thorium occurs naturally , it exists in very small quantities almost everywhere on Earth : the average human contains about 100 micrograms of thorium and typically consumes three micrograms per day of thorium . This exposure is raised for people who live near uranium , phosphate , or tin processing factories , thorium deposits , radioactive waste disposal sites , and for those who work in uranium , thorium , tin , or phosphate mining or gas mantle production industries . Thorium is especially common in the Tamil Nadu coastal areas of India , where residents may be exposed to a naturally occurring radiation dose ten times higher than the worldwide average . When thorium is ingested , 99 @.@ 98 % does not remain in the body . Out of the thorium that does remain in the body , three quarters of it accumulates in the skeleton . While absorption through the skin is possible , it is not a likely means of thorium exposure . Powdered thorium metal is pyrophoric and often ignites spontaneously in air .

Natural thorium decays very slowly compared to many other radioactive materials , and the alpha radiation emitted cannot penetrate human skin . As a result , owning and handling small amounts of thorium , such as a gas mantle , is considered safe . However , exposure to an aerosol of thorium can lead to increased risk of cancers of the lung , pancreas , and blood , as lungs and other internal organs can be penetrated by alpha radiation . Exposure to thorium internally leads to increased risk of liver diseases .

Because 232Th is only mildly radioactive , but decays to more dangerous radionuclides such as radium and radon , emitting alpha and gamma radiation , a proper assessment of the radiological toxicity of 232Th must include the contribution of its daughters such as 228Ra , which are dangerous gamma emitters . There are concerns about the safety of thorium mantles , as the dangerous daughters of thorium have much lower melting points than thoria (except of course 228Th , which is chemically identical to its parent 232Th) , and they would be volatilised every time the mantle is heated for use . For example , during burning , significant fractions of the thorium daughters 224Ra , 228Ra , 212Pb , and 212Bi are released in the first hour of use alone . Most of the radiation dose by a normal user arises from inhaling the radium , resulting in a radiation dose of up to 0 @.@ 2 millisieverts per use , about a third of the dose sustained during a mammogram . If a mantle is ingested , however , 0 @.@ 4 % of the thorium and 90 % of its dangerous daughters are leached into the body . Some nuclear safety agencies make recommendations about their use , and have raised some safety concerns regarding their manufacture and disposal , because while the radiation dose from one mantle is not a serious problem , that from many mantles gathered together in factories or landfills is .

The chemical toxicity of thorium is low because thorium and its most common compounds (mostly the dioxide) are poorly soluble in water . Nevertheless , some thorium compounds are chemically moderately toxic . People who work with thorium compounds are at a risk of dermatitis . It can take as much as thirty years after the ingestion of thorium for symptoms to manifest themselves .