2015 International Nuclear Atlantic Conference - INAC 2015
São Paulo, SP, Brazil, October 4-9, 2015
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: 978-85-99141-06-9

THORIUM AND ITS FUTURE IMPORTANCE FOR NUCLEAR ENERGY GENERATION

Paulo E. O. Lainetti[1]
[1] Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
lainetti@ipen.br

ABSTRACT

Thorium was discovered in 1828 by the Swedish chemist Jons J. Berzelius. Despite some advantages over uranium for use in nuclear reactors, its main use, in the almost two centuries since its discovery, the use of thorium was restricted to use for gas mantles, especially in the early twentieth century. In the beginning of the Nuclear Era, many countries had interested on thorium, particularly during the 1950-1970 period. There are about 435 nuclear reactors in the world nowadays. They need more than 65.000 tons of uranium yearly. The future world energy needs will increase and, even if we assumed a conservative contribution of nuclear generation, it will be occur a significant increasing in the uranium prices, taking into account that uranium, as used in the present thermal reactors, is a finite resource. Thorium is nearly three times more abundant than uranium in the Earth's crust. Despite thorium is not a fissile material, ^{232}Th can be converted to ^{233}U (fissile) more efficiently than ^{238}U to ^{239}Pu. Besides this, since it is possible to convert thorium waste into non-radioactive elements, thorium is an environment-friendly alternative energy source. Thorium fuel cycle is also inherently resistant to proliferation. Some papers evaluate the thorium resources in Brazil over 1.200.000 metric t. Then, the thorium alternative must be seriously considered in Brazil for strategic reasons. In this paper a brief history of thorium is presented, besides a review of the world thorium utilization and a discussion about advantages and restrictions of thorium use.

1. INTRODUCTION

In the 1960s and 1970s, the development of thorium fuel for nuclear energy was of great interest worldwide. Since the beginning of Nuclear Energy Development, Thorium was considered as a potential fuel, mainly due to the potential to produce fissile ^{233}U. It was demonstrated that thorium could be used practically in any type of reactors. Besides this, Thorium-232, used as fertile material for breeding uranium-233, has the main advantage, over uranium-238, that virtually no plutonium or other transuranic elements are produced, and the waste products are therefore free of long-lived α-emitters.

Production of thorium has been limited due to a lack of demand (it is used mainly in Welsbach mantles, special glasses and alloys). It is a by-product of the separation of rare earth elements. Thorium nitrate is used in the manufacture of the mantles for incandescent lamps. The production of thorium is presently some hundred tons per year.

Despite some advantages over uranium for use in nuclear reactors, its main use, in the almost two centuries since its discovery, the use of thorium was restricted to use for gas mantles, especially in the early twentieth century. In the beginning of the Nuclear Era, many countries had interested on thorium, particularly during the 1950-1970 period. Nevertheless, the nuclear industry is quite conservative, and the biggest problem with Thorium is that we are lacking in operational experience with it.

2. HISTORY OF THORIUM AND ITS MAIN PROPERTIES

2.1. Brief history of thorium

Thorium is a natural heavy element. Thorium, represented by Th and with atomic number 90, is a radioactive actinide and metallic element. In 1829, the Swedish chemist Baron Jons Jacob Berzelius discovered a new mineral: thorite. He named it Thor, the god of thunder in the Nordic mythology. Berzelius extracted thorium from a rock specimen sent to him by an amateur mineralogist who had discovered it near Brevig and realized that it had not previously been reported. The mineral turned out to be thorium silicate, and it is now known as thorite. Berzelius even produced a sample of metallic thorium by heating thorium fluoride with potassium, and confirmed it as a new metal [1].

The abundance of Th in the earth is 0.0006% (6,000 ppb), three times that of uranium - 0.00018%, and it is found naturally in its isotope ^{232}Th (practically 100%), since almost all thorium found in nature is the isotope thorium-232 (several other isotopes exist in trace amounts or can be produced synthetically). Thorium is radioactive with half-life of 14 billion of years (T1/2= $1.4x10^{10}$ years).

According to the theories developed, the Earth's uranium was produced in one or more supernovae. The main process concerned was the rapid capture of neutrons on seed nuclei at rates greater than disintegration through radioactivity. The neutron fluxes required are believed to occur during the catastrophically explosive stellar events called supernovae. [2] Further nucleosynthesis processes can occur, in particular the r-process (rapid process) and first calculated by Seeger, Fowler and Clayton, in which the most neutron-rich isotopes of elements heavier than nickel are produced by rapid absorption of free neutrons. The creation of free neutrons by electron capture during the rapid compression of the supernova core along with assembly of some neutron-rich seed nuclei makes the r-process a primary process. The r-process is responsible for our natural cohort of radioactive elements, such as uranium and thorium, as well as the most neutron-rich isotopes of each heavy element. [3]

The process by which Earth makes heat comes from radioactive decay. It involves the disintegration of natural radioactive elements inside Earth – like uranium, for example. Much of the internal heat of the earth has been attributed to thorium and uranium natural decay.

The most common source of thorium is the rare earth phosphate mineral, monazite. In 1885, Carl von Welsbach, an Austrian Baron, discovered the brilliant light emitting properties of rare earths oxides containing thoria. This discovered gave origin to the gas mantle industry. Then, Thorium has been very used as the light source in gas mantles, mainly in the beginning of the 20^{th} Century, before the advent of the electricity. Besides this, the application in lightning has declined due to concerns about its radioactivity.

Thorium is a dense (11.7 grams per cubic centimeter) silvery metal. It has a high melting temperature of approximately 1,750 °C. Below about 1,360 °C, the metal exists in the face-centered cubic (fcc) crystalline form; at higher temperatures up to its melting point, it takes on the body-centered cubic (bcc) form. Thorium is also used as an alloying element in non-consumable TIG welding electrodes, incandescent lamp filaments, electron tubes, besides some applications in the chemical and pharmaceutical industry. Thorium dioxide, or thoria, is used in laboratory crucibles and in molds for casting metals and alloys that have a high melting point.

2.2. Thorium - nuclear properties and benefits

Differently from uranium, its properties do not allow it to be used directly to fuel a nuclear power plant and make electricity. Thorium itself will not split and release energy. Rather, when it is exposed to neutrons, it will undergo a series of nuclear reactions until it eventually emerges as an isotope of uranium called U-233, which will readily split and release energy next time it absorbs a neutron. Thorium is therefore called fertile, whereas U-233 is called fissile.

Fertile thorium can be converted in to fissile uranium by the following nuclear reactions:

$$^{232}_{90}Th + n \rightarrow \gamma \rightarrow {}^{233}_{90}Th \rightarrow \beta \rightarrow {}^{233}_{91}Pa \rightarrow \beta \rightarrow {}^{233}_{92}U$$

In its natural chain decay produces isotopes like ^{228}Ra; ^{228}Ac; ^{228}Th, ^{224}Ra, ^{220}Rn, ^{216}Po, ^{212}Pb, ^{212}Bi, ^{208}Tl to a stable ^{208}Pb. With the primary reactions for ^{233}U production, side reactions lead to the formation of ^{232}U. The Th-U cycle invariably produces some U-232, which decays to Tl-208, which has a 2.6 MeV gamma ray decay mode. Bi-212 also causes problems. These gamma rays are very hard to shield, requiring more expensive spent fuel handling and/or reprocessing.

When bombarded by thermalized neutrons (usually released by the fission of uranium-235 in a nuclear reactor), thorium-232 is converted to thorium-233. This isotope decays to protactinium-233, which in turn decays to uranium-233. The fissile properties of uranium-233 can be utilized immediately or after recovery from the irradiated reactor fuel.

Uranium-233 can be recovered and purified from neutron-irradiated thorium reactor fuels through the thorium extraction, or Thorex [4] process, which employs tributyl phosphate extraction chemistry. Irradiated fuel, containing either thorium metal or oxide, is dissolved in nitric acid containing a small amount of fluoride ion. Uranium-233 and thorium are coextracted into a tributyl phosphate solution, which is then contacted with an aluminum nitrate solution to remove traces of accompanying fission products. Dilute nitric acid is used to preferentially remove thorium from the scrubbed organic phase. Uranium-233 remaining in the tributyl phosphate solvent is stripped into acidified water; the resulting strip solution is passed through an ion-exchange resin bed in order to concentrate and purify the uranium-233.

3. THORIUM PROCESSING AND MAIN COMPOUNDS

As mentioned before, the most important ore of thorium is monazite, a mineral composed of thorium dioxide and a variety of rare-earth elements. The biggest deposits of monazite are found in Australia, India, Malaysia, Brazil, and South Africa. Thorium also occurs combined with uranium in the minerals thorite (a silicate mineral - $ThSiO_4$) and thorianite (ThO_2).

Monazite sands are found with a variety of other minerals, including silica, magnetite, ilmenite, zircon and garnet. Concentration of monazite is accomplished by using washing and electromagnetic separation, which separate monazite from other minerals by their different magnetic permeabilities.

Differently of uranium, and maybe one of its main advantages, Th is mainly obtained from monazite sands as a by-product of extracting rare earth metals. One important point to be considered when thorium or uranium are compared for using in nuclear reactors is that, differently from the need of uranium mining, thorium is associated to rare earths. In other words, to obtain uranium, it is necessary to mine it, generating a considerable amount of wastes, since the U content is in the range of approximately 0.2-0.5% in mass. Nevertheless, in the case of thorium, the rare earths will be mined anyway and the tails containing thorium can be used without the generation of additional wastes. Then, in different words, it is not necessary mining thorium, since it will be available anyway as a side product of the rare earth industry. This avoids big problems related to the mining industry, mainly from the environmental point of view.

Brazil has a long tradition of thorium technology, from mining of monazite to obtaining thorium with purity suitable for nuclear use. The first reports on the exploitation of monazite in Brazil date back to 1886, when Englishman John Gordon began exporting to the ore mined in the municipality of Prado, Bahia State in Europe, for use in lighting (incandescent gas lamps), before the advent electricity from the 1920s, when there was a decline in the consumption of monazite [5]. A typical Brazilian monazite contains 39% of cerium oxide, 5% of yttrium, 6% of thorium oxide and 0.3% of U_3O_8. In Brazil, monazite occurs mainly on the beaches of the States of Bahia, Espirito Santo and Rio de Janeiro [6]. In the late of 19th and early of 20th century, the interest in monazite increased owing to the use of thorium nitrate by gas mantle industries. Later, the use of lanthanide elements turned monazite into a much more important commodity than it was in pre-war years [7].

In 1949, the chemical processing of monazite, to produce lanthanide chlorides and tri-sodium phosphate, was started at the Santo Amaro mill (Usina Santo Amaro - USAM that belonged to the company Orquima S/A), located in Sao Paulo city. The first phase of the monazite processing consists of the extraction, washing and drying of monazite bearing sands taken from beaches. Then, physical separation processes separate the four minerals: ilmenite, rutile, monazite and zircon. Owing to public pressure, economic and radiological problems, the chemical processing of monazite stopped in 1992 [8].

There are two classical methods for chemically process the monazite: it can be attacked by both strong mineral acids, such as sulfuric acid - H_2SO_4 or alkalis, such as sodium hydroxide - NaOH. In the acid treatment, finely ground monazite sand is digested at 150 to 230 °C highly concentrated (93 percent) H_2SO_4. This converts both the phosphate and the metal content of the monazite to water-soluble species. The resulting solution is contacted with aqueous ammonia, first precipitating hydrated thorium phosphate as a gelatinous mass and then transforming the thorium phosphate to thorium hydroxide. Finally, the crude thorium hydroxide is dissolved in nitric acid to produce a thorium nitrate-containing feed solution suitable for final purification by solvent extraction.

In alkaline digestion, finely ground monazite sand is treated with a concentrated NaOH solution at approximately 130-140°C to produce a solid hydroxide product. The following treatment with hydrochloric acid yields a solution of thorium and rare earth chlorides. Then, thorium is partially separated from the rare earths by addition of NaOH to the acidic chloride solution. The crude thorium hydroxide precipitate is then dissolved in nitric acid for final purification by solvent extraction.

The production and purification of thorium compounds was carried out at IPEN for about 18 years. The raw materials used were some thorium concentrates obtained from the industrialization of monazite sands, a process carried out in Sao Paulo between 1948 and 1994 on an industrial scale by the company ORQUIMA, later NUCLEMON (acronym for Nuclebrás Monazita). The main raw material employed during the thorium nitrate production period was the thorium sulfate produced in ORQUIMA. The crystallized thorium sulfate was first transformed in thorium carbonate by addition of water, sodium carbonate and sodium hydroxide. Further, the carbonate was transformed in thorium nitrate by dissolution with nitric acid. To obtain high purity thorium nitrate, the most satisfactory process is purification by solvent extraction. The main product sold was the thorium nitrate with high purity (mantle grade), having been produced over 170 metric tons of this material in the period, obtained through solvent extraction. During the period of production, it was employed the solvent extraction in pulsed columns [9]. Aqueous solutions of highly purified thorium nitrate, $Th(NO_3)_4$, are used in the production of gas mantles. Welsbach mantles are made by impregnating cotton or synthetic fibers with a 25 to 50 percent solution of $Th(NO_3)_4$ containing 0.5 to 1 percent each of thorium sulfate and cerium nitrate. The added cerium nitrate improves spectral emission properties. Eventually, the impregnated fibers are treated with aqueous ammonia, producing thorium hydroxide, $Th(OH)_4$, and this compound is calcined to produce ThO_2 that, when heated, emits brilliant white light.

3. CONCLUSION

Since the fifties, the progress of nuclear energy has oscillated in accordance to the public acceptation, from enthusiasm to anti-nuclear sentiment. The quick development observed from the middle of 50s years until 1980 was interrupted with the nuclear catastrophes of Three Mile Island (1979) and Chernobyl (1986). Nevertheless, in the 90's and especially in the first years of the new century, occurred an increasing global awareness about environmental questions, such as global warming due emission of greenhouse gases from burning fossil fuels. These concerns lead to a resurgence of the interest in nuclear generation of electricity. Again, the renewed interest was interrupted due the Fukushima accident.

But, how will the humankind solve the future needs of energy? Mainly considering some serious constraints and concerns such as limited reserves of fossil fuels and their progressive depletion, global warming due the use of fossil fuels, increasing of global population, aspiration for better life conditions implicating in increasing of the power consumption, besides the high cost and inconstancy of some power generation alternatives, like Aeolic and Solar. Even in a pessimist scenario, a significant part of the electricity generation will be supplied by nuclear energy. There are about 435 nuclear reactors operating in the world nowadays and the electricity generation capacity is about 370 Gw(e). The power reactor fleet needs more than 65.000 metric tons of uranium yearly. The nuclear energy generation capacity will reach in the next 30 or 40 years, in a pessimist scenario, 600 Gw(e). In an optimistic scenario, 1400 Gw(e). In an intermediate scenario, there will be 1000 Gw(e) from nuclear in the world. Each Gigawatt added means approximately 200 tU/year. Then, in an intermediate scenario, by 2050 the consumption of uranium will reach 190.000 tU/year. Therefore, it will be necessary the production of 125.000 tU/year in addition to the present production. So advanced fuel cycles, which increase the reserves of nuclear materials, are interesting, particularly the use of thorium to produce the fissile isotope ^{233}U.

The future world energy needs will increase and, even if we assumed a conservative contribution of nuclear generation, it will be occur a significant increasing in the uranium prices, mainly taking into account that uranium, as used in the present thermal reactors, is a finite resource. Therefore, the interest about thorium stems mainly from an expected substantial increase in uranium prices.

The thorium fuel cycle presents some advantages, such as: good characteristics of the U-233, from a neutronic point of view; the thermal stability of ThO_2 (melting point around 3,200-3,300^{o}C) that permits high burn-ups and high temperatures; the ecological argument of much lower quantity of long-lived actinides generated from fission with the thorium cycle, resulting much less long-lived wastes; the average abundance of thorium in the earth's crust that has been estimated three times as great as uranium. However, owing to its chemical toxicity and radiotoxicity, adequate precautions are required in the mining and processing of thorium. Some shielding is required for processing large amounts. As a consequence, preparation of thorium fuel is more complex and more expensive than for uranium.

Since the beginning of nuclear energy development in Brazil in the 1950s, it was recognized the strategic importance of the thorium utilization for the country. Brazil has a long tradition in the thorium technology, from mining of monazite to the obtainment of thorium with purity suitable for nuclear use. Nevertheless, the lack of a Brazilian Thorium Program and the quick aging/retirements of the personnel involved are important factors determining the loss of the acquired knowledge.

REFERENCES

1. http://www.rsc.org/periodic-table/element/90/thorium, accessed in June, (2015).
2. http://www.world-nuclear.org/info/Nuclear-Fuel-Cycle/Uranium-Resources/The-Cosmic-Origins-of-Uranium/, accessed in June, (2015).
3. http://en.wikipedia.org/wiki/Nucleosynthesis, accessed in June, (2015).
4. Camilo, R. L., "*Dados de Equilíbrio no Sistema* $Th(NO_3)_4$-$UO_2(NO_3)_2$ *TBP/Varsol-*HNO_3-H_2O*. Optimização das Variáveis para a Separação de Th-232-U-233*" M.Sc. thesis, 82 p. Instit. de Pesq. Energéticas e Nucleares. São Paulo-SP in Portuguese (1982).
5. Gentile, E. and Filho, P. M. F., *Minerais Radioativos - Projeto Diagnóstico*. **Brazilian Association of Metallurgy and Materials Report**. São Paulo, SP. In Portuguese (1996).
6. Ikuta, A.. "Tecnologia de Purificação de Concentrados de Tório e sua Transformação em Produtos de Pureza Nuclear. Estudo do Sistema $TH(NO_3)_4$-HNO_3-TBP-Varsol." M.Sc. thesis, 111 p. Universidade de São Paulo. In Portuguese (1976).
7. Maciel, A. C., and Cruz, P. R., *Perfil Analítico do Tório e Terras-Raras*. **DNPM - National Department of Mineral Production report. 72 DNPM/BOLETIM/28**. R. de Janeiro, RJ in Portuguese (1973).
8. Paschoa, A. S.. "*Potential Environmental and Regulatory Implications of NORM (Naturally Occurring Radioactive Materials)*" **Applied Radiation Isotopes 49 (3): 189-96** (1998).
9. Lainetti, P. E. O., Abrão, A., Freitas, A. A., Carvalho, F. M., Bergamaschi, V., Cunha, E. F., and Ayoub, M. S. J. 2000. "*Histórico e Perspectivas da Produção e Purificação de Compostos de Tório no IPEN*" In Proceedings of the 12th ENFIR Encontro Nacional de Física de Reatores e Termohidráulica , October 15-20, 5 p. Available in http://www.ipen.br/bilioteca/2000/cgen/07195 In Portuguese (2000).