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THORIUM AND LITHIUM IN BRAZIL

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ABSTRACT

Brazil has one of the largest reserves of thorium in the world, including rare earth minerals. It has developed a great program in the field of nuclear technology for decades, including facilities to produced oxides to microspheres and thorium nitrates. Nowadays, with the current climate change, it is necessary to reduce greenhouse gas emissions, one of this way is exploring the advent of IV Generation reactors, molten salt reactors, that using Thorium and Lithium. Thorium's technology is promising and has been awaiting the return of one nuclear policy that incorporates its relevance to the necessary levels, since countries like the BRICS (without Brazil) have been doing so for years. Brazil has also been developing studies on the purification of lithium, and this one associated to thorium, are the raw material of the molten salt reactors. This paper presents a summary of the thorium and lithium technology that the country already has, and its perspectives to the future.

1. INTRODUCTION

The principles of Brazilian Nuclear Policy are: the use of nuclear technology, for peaceful purposes, as established in the Constitution; respect for conventions, agreements and treaties to which the Federative Republic of Brazil is a signatory; nuclear safety, radioprotection and physical protection; the field of technology relating to the nuclear fuel cycle; and the use of nuclear technology as a tool for national development and the well-being of society. Thorium and Lithium was chemical elements that became material of great interest in the world due to its utility in the actual industrial world.

The Brazilian Nuclear Policy, Decree Nº.9600, Dezember, 5th, 2018, aims to guide the planning, actions and nuclear and radioactive activities in the Country, in compliance with national sovereignty, with a view to the development, protection of human health and the environment.

2. THORIUM PERSPECTIVES

Thorium can be used to fuel nuclear reactors, just like uranium. It is more abundant in nature than uranium, produces waste products that are less radioactive, and generates more energy per ton. Nevertheless, thorium has not fissile isotopes.

However, thorium has an undeniable advantage over uranium. Unlike the latter, there is no need to mine the thorium. Thorium is found associated with rare earths, essential for numerous industries.

Therefore, rare earth exploration produces a by-product in the form of thorium concentrates. In Brazil, from 1948 until the beginning of the 1990s, the company Orquima, later transformed into Nuclemon, and later INB - Nuclear Industries of Brazil, processed monazite sand found in Brazil between the north of the State of Rio de Janeiro and the south of the State of Bahia.

The product of this activity was the rare earth concentrates, in the form of chlorides, which were exported. During the period of monazite processing, various thorium concentrates were obtained.

During the 1980s and 1990s, Instituto de Pesquisas Energéticas e Nucleares -IPEN produced high purity thorium nitrate to serve the Brazilian industry that used in incandescent gas mantle, by purifying the thorium concentrates resulting from monazite processing, Fig. 1. However, during the period of operation of the abovementioned companies, about 15 thousand metric tons of a waste called Torta-II (or Cake-II – the second cake of the monazite processing) were generated, Fig. 2. This residue, rich in rare earths, was stored by INB in Poços de Caldas-MG.

In addition to rare earths, according to chemical analyzes carried out a few years ago at IPEN, there are approximately 3000 t of thorium contained in Torta-II, constituting an important strategic reserve for the country.

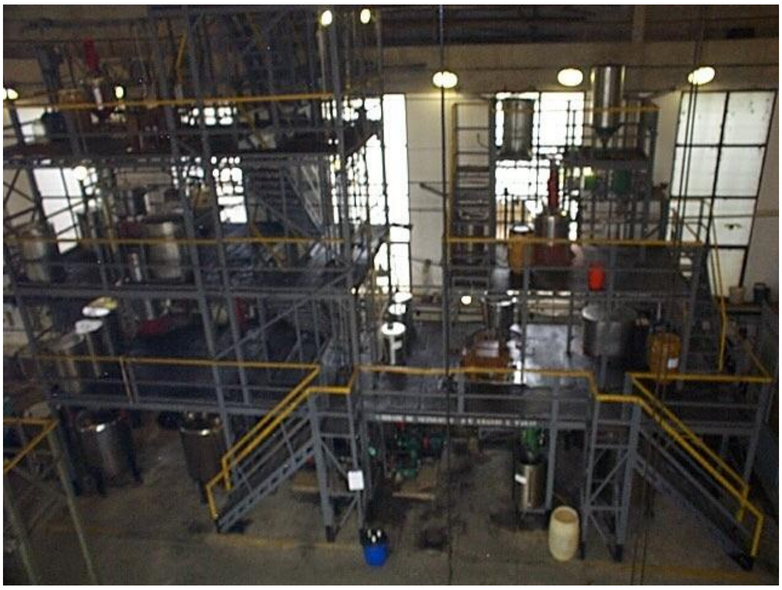

Figure 1: Pilot plant of purification thorium at IPEN.

Figure 2: Torta-II at IPEN.

2.1. Uranium

According to the International Energy Agency, global energy consumption could see an increase of up to 18% by 2030 and 39% by 2050. This will increase the demand for various sources of energy — including nuclear power, and therefore uranium. Even under the IAEA's low case prediction for the future of nuclear power — which would see nuclear energy's share fall from today's 11% of the energy market to just 6% by 2050 — nuclear electrical generating capacity would increase by 24%. There are enough uranium resources accessible with current mining practices for at least 100 years. Nevertheless, with new nuclear power technologies, in some cases less uranium will be required or maybe with the use of stored nuclear waste fuel, increase in nuclear power generation does not necessarily mean a proportional increase in the demand for mined uranium. It is expected an increase in the uranium demand. A way to supply the increased demand consists of extracting uranium from seawater, which contains more than four billion tons of dissolved uranium. Extraction from the sea also promises to be an environmentally friendly and sustainable way to supplement the global uranium supply [1].

2.2. IV Generation Nuclear Reactors

In January 2000 the U.S. Department of Energy's (DOE) Office of Nuclear Energy, Science and Technology convened a group of representatives of nine countries to begin discussions on international collaboration in the development of Generation IV nuclear energy systems. The founding document of the Generation IV International Forum (GIF), a framework for international co-operation in research and development for the next generation of nuclear energy systems was first signed in July 2001 by Argentina, Brazil, Canada, France, Japan, Republic of Korea, South Africa, the United Kingdom and the United States [2].

GIF has conducted an international collaborative project to develop the next generation of nuclear reactors that can help meet the world's future energy needs. Generation IV designs will use fuel more efficiently, reduce waste production, be economically competitive, and meet stringent standards of safety and proliferation resistance.

About 100 experts evaluated 130 reactor concepts proposed by the international community. The work resulted in a selection and a description of the six most promising reactor technologies for further research and development and their associated R&D needs. The selected reactor technologies were: Gas-cooled Fast Reactor (GFR), Lead-cooled Fast Reactor (LFR), Molten Salt Reactor (MSR), Supercritical Water-cooled Reactor (SCWR), Sodium-cooled Fast Reactor (SFR) and Very High Temperature Reactor (VHTR). Some of these reactor designs could be demonstrated within the next decade, with commercial deployment beginning in 2030 [2].

Among the concepts proposed, the Molten Salt Reactor is a concept that could be particularly interesting for Brazil considering the huge thorium resources in the country. Molten Salt Reactor (MSR) technology was partly developed, including two demonstration reactors, in the 1950s and 1960s in the USA (Oak Ridge National Laboratory). In this reactor concept, molten salt fluorides are used as fluid fuel and coolant, presenting low operation pressure and high boiling temperature.

Thorium chemistry is considered difficult, and although not so simple, technological work, in the decades of 70 and 80, was made in the laboratories of the Institutes of the CNEN, aimed at the use of thorium associated with uranium in fuel elements.

These researches have shown that it is possible to leverage new paths in the nuclear area with a focus exclusively on the thorium fuel cycle and not to lose an already established technology, as there is an increasing in articles in the area, enhancing the interest of foreign countries in the area.

3. LITHIUM PERSPECTIVES

Lithium is the lightest of the metals, with extremely low specific mass equal to 0.534 g / cm3 [3]. Its atomic number is 3, atomic weight 6,94 and has two isotopes composition, Li-6 and Li-7 [3,4]. Lithium is the hardest of the alkali metals, hardness 0.6 on the Mohs scale [5], has the highest melting point, 180.54 °C [6] and the highest oxidation potential, 3,045 volts [7]. It is a silver-white metal, good conductor of electricity and heat, quite ductile and with low viscosity. It has the highest ionization and sublimation energies, the highest electronegativity and the lowest ionic radius, which causes the high lithium ion charge density in relation to the other alkali metals.

Lithium is used in several industrial fields such as, chemical, pharmaceutical, ceramic, nuclear and automotive industries. Specifically used in the following products: batteries for electronics devices, specially cell phones, electric cars, nanomaterials, glass ceramics, lubricating greases, pharmaceuticals and nuclear fission and fusion reactors. Its most abundant minerals are: Spodumene, Lepidolite, Amblygonite and Petalite, from which lithium is most frequently obtained and it is the main source of lithium in Brazil, Australia and Canada.

The lithium was discovered in 1817 by Johan August Arfwedson, a Swedish chemist while examining the Petalite ore, whose discovery is due to José Bonifácio de Andrada e Silva (Brazilian naturalist while studying in Sweden in 1800). In 1855, Robert Bunsen and Augustus Mattiesen isolated the metal (Li) from the electrolysis of lithium chloride [8].

Natural lithium is a relatively rare and scarce element because, although it constitutes about 0.002% of the Earth's crust, it is not found in large concentrations but rather dispersed [5]. It is found in natural waters, soils and rocks. The sources of lithium that present economic interest are brines and its four main minerals, spodumene - $LiAlSi_2O_6$ (8.03%), lepidolite - $K(Li,Al,Rb)_2(Al,Si)_4O_{10}(F,OH)_2$ (7.7%), petalite - $LiAlSi_4O_{10}$ (4.5%) and amblygonite $(Li,Na)AlPO_4(F,OH)$ (7.4%) [7].

Among the major lithium compounds, the most important are lithium hydroxide, LiOH and lithium carbonate, Li_2CO_3 which have many industrial applications. The main applications of lithium compounds are, in batteries, lubricating greases, frits, glasses, air conditioning, aluminum, medicines, polymers, ceramics, alloys, and in nuclear reactors [16].

The activities of industrialization, import and export of lithium ores and minerals, organic and inorganic chemicals, lithium metal and lithium alloys in Brazil are supervised by Comissão Nacional de Energia Nuclear (CNEN) Decree nº 2.413, de 04/12/97.

The increasing technological importance of lithium has highlighted the concern with world reserves and the obtaining of the element. Products with a purity of about 85% in Li_2CO_3 are used for applications in synthetic enamels, adhesives, greases and lubricants. However, for uses in nuclear industry, as a nuclear reactor coolant, it is necessary a high level of purity, higher than 99%.

The lithium-7 isotope can be used as a coolant in high temperature reactors due to its low vapor pressure, good thermohydraulic properties and demonstrated compatibility at high temperatures. A nuclear reactor coolant circulates through the reactor core to absorb the heat it generates. The heat is withdrawn from the reactor and is then used to generate steam.

Despite all technological and economic potential, Brazil currently produces only technical-grade lithium compounds, in other words, lithium chemicals (lithium carbonate and lithium hydroxide) with a purity of less than 99%. New technology strategies are needed for the lithium purification, one possible technology is the ion exchange technique.

Ionic exchange is a high efficiency technique that separates the ions through ion exchange chromatography. In ion exchange chromatography, the anions in the sample are charged through an ion exchange resin (stationary phase). Ion exchange resins are polystyrene spheres that have been treated to attach ion exchange sites on the surface of their granules.

Depending on the type of resin, they may be of the acid type (cationic resins) which retain most of the cations by replacing these by H^+ or the base type (anionic resins) which retain most of the anions by replacing these by OH^-.

Since in aqueous solution, the lithium will be in the form of Li^+, cationic resins are frequently used. Several are the cationic resins and the experimental conditions that can be used to obtain such purification. The purity level achieved by this operation varies according to the experimental conditions of this ion exchange operation, the purity of the starting compound, and the impurities present.

The major impurities that may be present and which make it difficult to obtain high purity values in lithium compounds are sodium, calcium and other alkali metals and alkaline earth metals, since all these and even the lithium present very similar chemical characteristics thus making difficult the fractionation between these elements of the two groups.

The main use of lithium (Li-7) in the nuclear fission reactors is as a coolant on primary water cycle of the PWR reactor. The use of Li-6 in the fussion nuclear reactor are main as a fuel component, eq. 1 and 2.

$$\text{Li-6} + n \rightarrow \text{He-4} + \text{H-3} \quad + 4{,}8\ \text{MeV} \qquad (1)$$

$$\text{H-2} + \text{H-3} \rightarrow \text{He-4} + n \quad + 17{,}6\ \text{MeV} \qquad (2)$$

The Li-7 and fluoride salts are important components for the cooling fluid of reactors to molten salts, and with the prospect of the operation of these reactors, currently in development, a much greater demand is expected for this isotope compound, Brazil being with its technology a possible supplier of this salts.

The first commercial production of lithium ores was in the United States in 1901, when Maywood Chemical Works (New Jersey) started production of lithium chemicals in the country. However, the fact that contributed to the growth of the lithium market was the development and application, in 1918, in Germany, of a league called bahnmetal (lithium / lead).

The German company Metallgesellchaft was the first producer of lithium and lithium metal carbonate on an industrial scale, from the year 1923 [9]. In the time of the cold war (1946-1991), in addition to uranium mining, lithium was used as a source of nuclear weapons [10].

Foote Mineral Co. in 1930, from the spodumene contained in alaskitos started the production of lithium carbonate via alkaline process in North Carolina, USA. Lewis and Macdonald in 1936 published the first attempt with good results for separation of lithium. They used exchange between lithium amalgam and lithium solution in organic solvent similar to solvent extraction. Developments subsequent to this method reached a high separation factor of 1.085 [11].

Taylor and Urey in 1937 described amalgam electrolysis as a viable method for enriching the lithium isotope. In addition, by the indication of the isotopic ratio of available lithium compounds that are extracted from aluminosilicate ores, they successfully tested the enrichment in column packed with zeolite [12]. Glueckauf et al. reported the first work on isotopic enrichment of lithium using ion exchange of synthetic organic materials [13].

Lithcoa in 1946 developed the acidic process for the production of lithium carbonate from spodumene. In 1986, Chile (Cyprus Foote) and Argentina (FMC Lithium Division) began production of lithium from brines [12]. With high lithium demand for uses in lithium-ion batteries and in the nuclear area, both lithium ores and brines are exploited.
The main lithium reserves in the world are in Bolivia with 9 million tons of Li_2O lithium oxide, followed by Chile with 7.5 million tons [15].

4. CONCLUSION

Brazil for several decades has gained knowledge in areas such as thorium and lithium purification, fluoride production, fuel element production and reactor projects, as well as related knowledge, allows the development of reactors to molten salts, alone or in partnerships with other countries, and will not necessarily be an initial development. Public policies in this direction can facilitate this development.

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