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REVIEW OF THE BRAZILIAN INTEREST IN THE THORIUM FUEL CYCLE AND THE EXPERIENCE IN THE PURIFICATION OF THORIUM COMPOUNDS OBTAINED FROM MONAZITE SANDS

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- IREL/ India and D. Singh

Federative Republic of Brazil

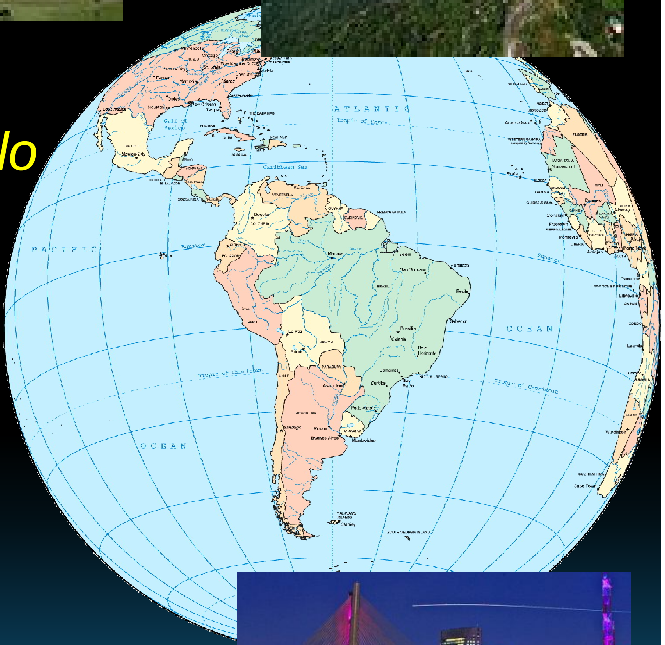
- *26 states and a Federal District*
- Capital: *Brasília*
- Most known and beatiful city: *Rio de Janeiro*
- Biggest city, industrial/economic center: *São Paulo*
- Population: *over 190 million inhabitants (5^{th})*
- Surface Area: *8.514.876 km^2 (5^{th})*
- GDP - Gross Domestic Product (2010)

Source: FMI, World Bank, CIA World Factbook

US\$ 2,090 billion (7^{th} - position in the world)

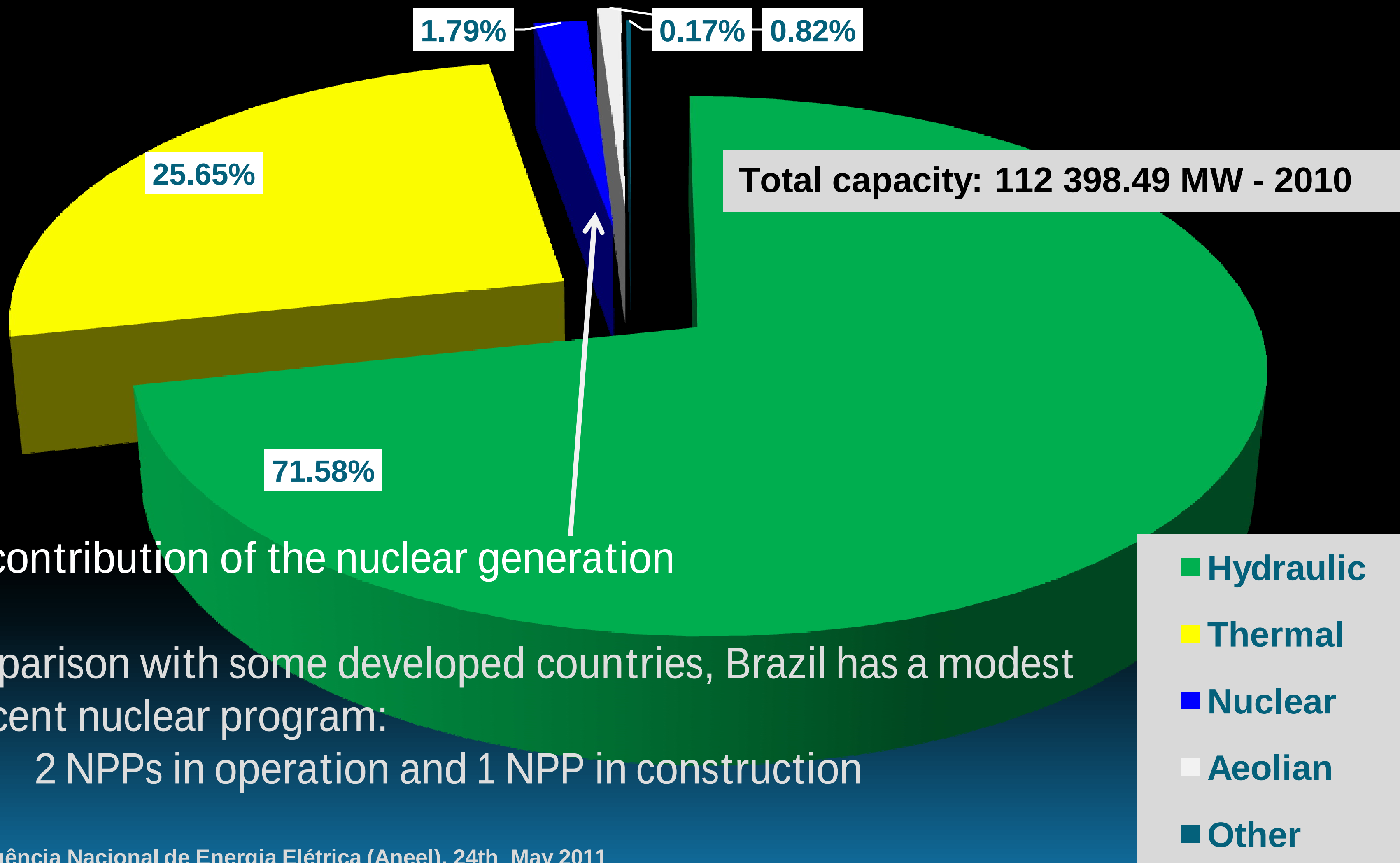
US\$ 10,816 per capita (63^{th} - position in the world)

- *Installed Electricity Generation Capacity: ~**112.4 GW** **(2010)***



Brazilian Installed Electricity Generation Capacity

per source (%)



Small contribution of the nuclear generation

In comparison with some developed countries, Brazil has a modest and recent nuclear program:

2 NPPs in operation and 1 NPP in construction

Source: Agência Nacional de Energia Elétrica (Aneel), 24th May 2011

MAIN BRAZILIAN NUCLEAR FACILITIES

CRCN

CNEN
R & D Centers

CDTN

IEN and IRD

IPEN

CTM
Brz. Navy

Two nuclear power plants:

Angra-I 657 MWe 1985 (com.op.)

Angra-II 1345 MWe 2001(com.op.)

Sixth world uranium reserves

310,000 t U_3O_8 L.C.

Caitite county - Ba

Eletronuclear

NUCLEP

FCN INB

THORIUM IN BRAZIL

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October 2011

Brief History: Thorium Activities in Brazil

1886: beginning of monazite exploitation for gas lighting Prado-Ba

1948: monazite processing - ORQUIMA SA – inside São Paulo city

60's: teoretical studies for a kind of reactor with natural uranium, which would allow subsequently the use of thorium as fertile material : natural U graphite moderated reactor (*Amaral and Nevares* **/CNEN); Heavy water moderated and cooled pressurized reactor (***J. Mello and S. Brito* **- Group of Thorium, IPR / B. Horizonte-MG)**

60's and 70's: experimental studies: purification of Th compunds, obtaining of metallic Th from ThF_4, production of ThO_2 /ThO_2-UO_2 pellets (*Abrão, Costa, Ikuta, Freitas, Haydt, Cintra, Gentile, Capocchi, S. Santos* **– IEA/SP - IPEN)**

80's: utilization of mixed oxides $(Th,U)O_2$ in LWR reactors (79-88) (*Pinheiro, Carneiro, Lameiras, Ferreira, Ferraz, Dias, Soares, Andrade, Mascarenhas, dos Santos, Pinto, Santos, Filgueras, Lopes -* CDTN/Nuclebras in cooperation with Siemens KWU, Nuken, KFA-Jülich)

80's: manufacturing first core IPEN-MB 01*(Riella, Gomes, Urano, Fogaça, Lainetti* IPEN-MB*)*

80's and 90's: separation/purification of thorium and rare earths; production of sol-gel microspheres, microwave denitration;THOREX: separation $^{232}Th/^{233}U$; routine production of thorium nitrate (170 t until 2002); (*Abrão, Freitas, Ikuta, Seneda, Nakamura, Camilo , Carvalho, Figueiredo, Lainetti* - IPEN-CNEN/SP)

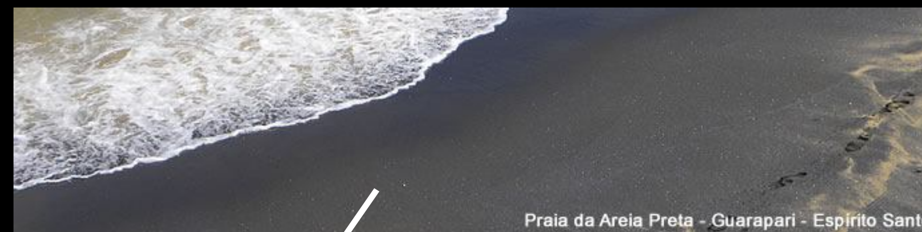
1996 - Proposal for new core $(Th,U)O_2$ for the IPEN-MB 01 reactor (*Moreira, Abe, Figueiredo, Lainetti* - CTM-SP/MB and IPEN-CNEN/SP)

THORIUM IN BRAZIL - History

- In Brazil, the interest in the nuclear utilization of thorium has started in the 50's as a consequence of the abundant occurrence of monazite sands.
- Monazite is the thorium ore with more data availble in Brazil
- The exploitation of the monazite sands in Brazil began in 1886 whith the Englishman John Gordon in the Cumuruxatiba deposit (on the southern coast of Bahia state, municipality of Prado)
- Monazite was processed in Europe to produce salts of thorium and rare earths, used in the manufacture of mantles for incandescent gas lighting
- With the advent of electricity - 20’s , there was a decline in the consumption of monazite, until research on atomic energy
- At the time of World War II, monazite was put again in evidence due to its content of thorium
- In 1951 the Brazilian government prohibited the export of concentrates of monazite
- DNPM estimated that from 1886 to 1950 about 95,000 tons of monazite concentrate were exported from Brazil

Monazite Sands in Brazil

It was the Professor Henry Gorceix, founder of the School of Mines of Ouro Preto, who first investigated the monazite sands in Brazil, as published in the annals of "School" in 1884 and 1885 and reporting to the Academy of Sciences in Paris, France.



Heavy Minerals Unit - UMP, INB Buena, is located in São Francisco de Itabapoana - RJ

Source: INB's website

The heavy minerals are contained in the sands of beaches scattered along the Brazilian coast, mainly in coastlines: northern Rio de Janeiro, Espirito Santo and southern Bahia States

• In Brazil, besides the beaches of Bahia, Espirito Santo and Rio de Janeiro, monazite can be found in the riverbeds of the states of Bahia, Minas Gerais, Goias and Mato Grosso.

• The deposits may contain 25 to 30% monazite (phosphate of rare earths, uranium and thorium).

• The remaining minerals are quartz, zircon (zirconium silicate) , ilmenite (iron titanate), magnetite and rutile (titanium dioxide).

• Thorium can be found in other deposits in Brazil ,as shonw in the table bellow:

Table 1 - Thorium Potential Resources in Brazil [1]

Occurrence	Associated Mineral	Average Content (%)	Measured (t ThO_2)	Estimated (t ThO_2)
Coastal deposits	Monazite	5	2,250	-
Morro do Ferro (MG)	Thorite and others	1 to 2	35,000	-
Barreiro, Araxa (MG)	Pyrochlore	0.09	-	1,200,000
Area Zero, Araxa (MG)	Pyrochlore	0.09	30,000	-
Alluvial and Pegmatite	Monazite	5	3,000	2,500
Total			73,500[a]	1,202,500

[1] Gentile e Figueiredo, Radioactive Minerals - “Diagnosis Project” ,1996.
[a] Including 3,500 t of Monazite sand of INB.
Note: The IAEA gives (1992) 606,000 t as indicated reserves and 700,000 t of inferred reserves.

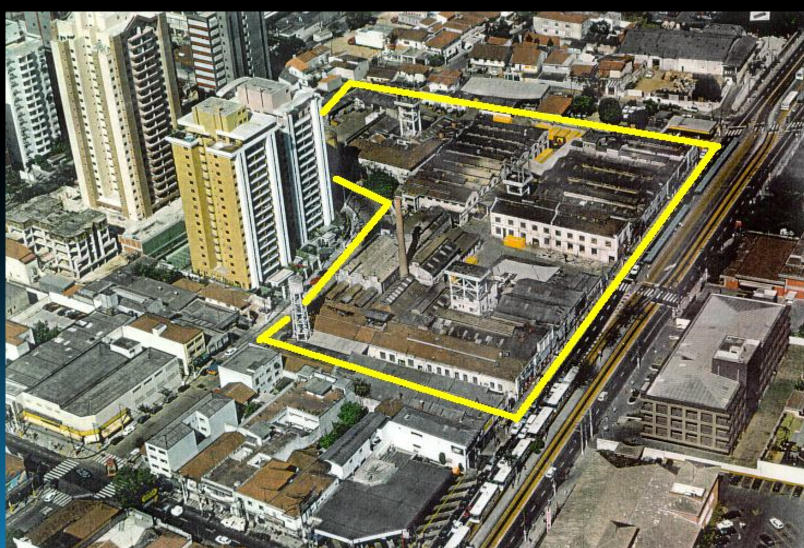
Processing of Monazite Sands in Brazil

Orquima S/A started processing of monazite in the Santo Amaro Plant – USAM – located in São Paulo (the largest Brazilian city), in the end of year's 40.

USAM: physical and chemical treatment of monazites sands and others: ilmenite, zirconite and rutile .

A typical Brazilian monazite contains 39% of cerium oxide, 5% of yttrium, 6% of thorium oxide and 0.3% of U_3O_8 and variable contents of titanium, zirconium, silicon, iron and other elements.

Owing to public pressure, economic and radiological problems, the chemical processing of monazite in USAM was stopped in 1992, plant was decommissioned.



Source : Ferreira, Paulo R. R., IRD-CNEN/RJ "**THE DECOMMISSIONING OF *USAM***"

Monazite Processing at USAM – Santo Amaro Plant

The first phase of the monazite processing consists of the extraction, washing and drying of monazite bearing sands taken from beaches.

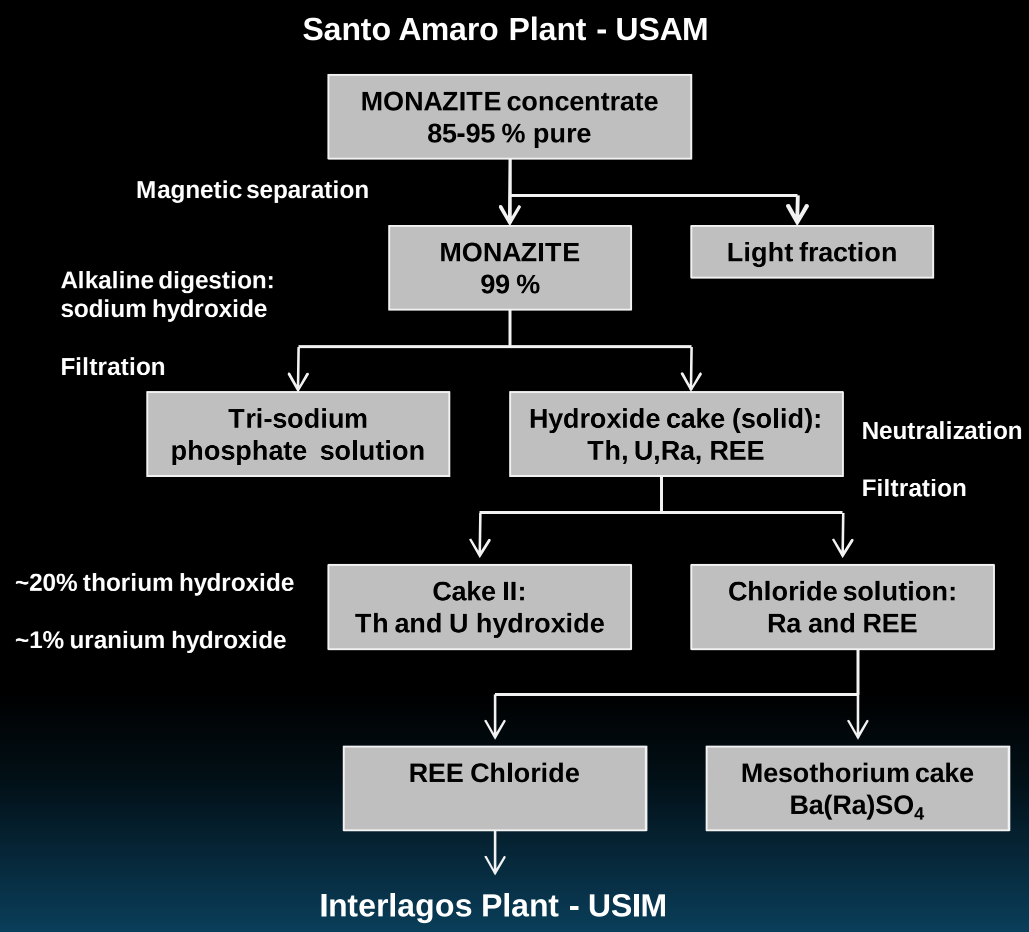
Then, physical separation processes separate the four minerals: ilmenite, rutile, monazite and zircon.

Chemical separation is shown in the figure beside.

The chemical processing of monazite started in 1949, to produce lanthanide chlorides and tri-sodium phosphate .

In 1960 the Brazilian Nuclear Energy Commission – CNEN – acquired the mining rights from the private companies that were exploiting the monazite in the country (SULBA and ORQUIMA).

Nowadays, the monazite mining is performed by the Brazilian Nuclear Industries – INB.



Main steps of the monazite chemical processing in USAM

THORIUM COMPOUNDS PURIFICATION AT IPEN –CNEN/SP

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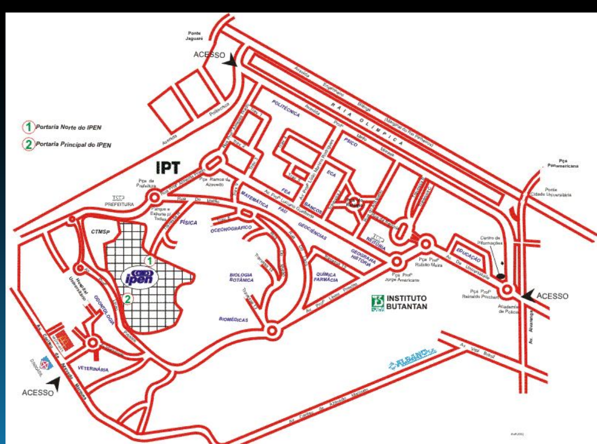
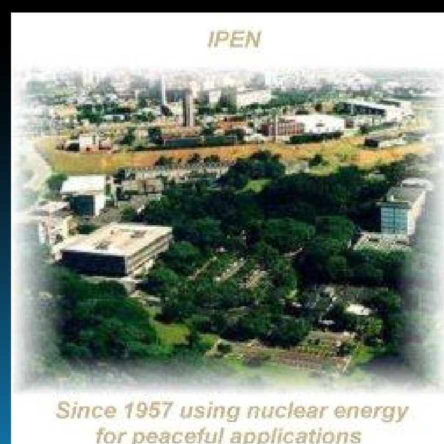
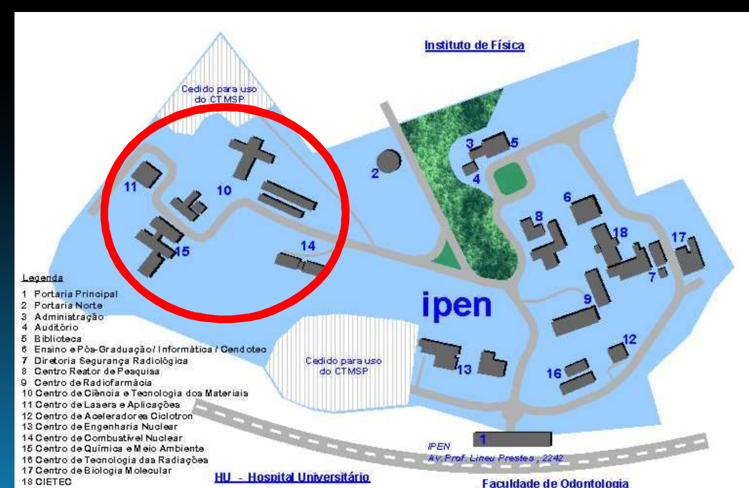
Nuclear and Energetic Research Institute - IPEN

- Is an institution owned by the Government of Sao Paulo State
- Is supported and operated technical and administratively by the Brazilian Nuclear Commission – CNEN (it is the biggest of the CNEN's Institutes)
- Is associated to the University of Sao Paulo for postgraduate courses
- It was created in 1956 with the main purpose of performing research and development of nuclear energy peaceful applications

IPEN is located in Sao Paulo City at the Campus of Sao Paulo University in an area of nearly 500,000 square meters







THORIUM PURIFICATION AT IPEN

In the course of the industrial treatment of monazite in ORQUIMA - São Paulo several concentrates containing thorium and rare earth elements were produced.

IPEN has developed alternative methods for purification of thorium concentrates.

During the period 1985 - 2003, the main product was the thorium nitrate with high purity > 99.5 % supplied to the Brazilian industry and particularly used for gas portable lamps (incandescent Welsbach mantles).

IPEN produced over 170 metric tons of thorium nitrate, purified through solvent extraction from thorium sulfate produced in ORQUIMA.

IPEN's pilot plant for thorium nitrate purification by solvente extraction in pulsed columns

Production of Nuclear Grade Thorium Nitrate

The purification step was accomplished with a compound extraction–scrubbing pulsed column. The thorium concentrate was a crude thorium hydroxide containing uranium and chloride ions.

The thorium pilot plant was equipped to be able to supply crystallized $Th(NO_3)_4.4H_2O$, thorium oxalate and a highly concentrate thorium nitrate solution (about 900 g ThO_2/l).

The thorium nitrate was extracted with TBP-varsol after addition of sodium nitrate (2.2 M) and free nitric acid (0.8 M). The organic phase rich in thorium nitrate was scrubbed with 2.2 M $NaNO_3$–0.8M HNO_3 or with pure $Th(NO_3)_4$ solution. Finally thorium nitrate was stripped from the organic phase with demineralized water.

Table 2. $Th(SO_4)_2.9H_2O$ analysis

Species	(%)
ThO_2	47.0
Rare-earth oxides	0.05
Fe_2O_3	0.1
TiO_2	0.02
P_2O_5	0.045
SiO_2	0.02
UO_3	0.01

For several years IPEN produced highly pure thorium nitrate starting with a second concentrate, the thorium sulfate. Initially the raw material was converted to thorium hydroxide by treatment of the thorium sulfate with sodium hydroxide–sodium carbonate.

The obtained hydroxide was filtered and washed with water until nearly complete elimination of the soluble sodium sulfate. Further operation was the dissolution of the hydroxides (thorium and rare earths) with nitric acid and adjustment for the purification by solvent extraction in the $Th(NO_3)_4$–HNO_3–TBP–Kerosene system by pulsed columns.

Table 3. Typical analysis of ThO_2 produced from the thorium sulfate by XR fluorescence analysis

Oxide	$\mu g\ g^{-1}$
Fe_2O_3	841
SiO_2	489
Na_2O	444
Sc_2O_3	315
PbO	245
Nd_2O_3	179
Eu_2O_3	161
MgO	121
Al_2O_3	66
Er_2O_3	53
CaO	52
Sm_2O_3	50
Tb_4O_7	45
Pr_6O_{11}	20
Tm_2O_3	<20
Y_2O_3	<20
La_2O_3	<20
CeO_2	<20
Gd_2O_3	<20
Yb_2O_3	<20
Lu_2O_3	<20

Main operations - thorium nitrate production

Thorium Sulfate

$H_2O(l)$

Na_2CO_3 and NaOH → Dissolution / precipitation ← Steam heating

Thorium oxocarbonate

Washing ← $H_2O(l)$

Steam heating

Waste water ← Filtering

Th analysis

Discard

Thorium oxocarbonate

Dissolution in nitric acid ← $HNO_3(l)$

Steam heating

Filtering

Thorium nitrate solution

Concentration

Product specifications:

Chemical compound.......$Th(NO_3)_4.4H_2O$
Concentration.................300 to 400 g/L
Density...........................~ 1.65 kg/L
Purity...............................99.0 + 0.5 %

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Decommissioning of Thorium Nitrate Pilot Plant

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Conclusion

- Since the beginning of Nuclear Energy Development in Brazil ,in the fifties and sixties, it was recognized the strategic importance of the thorium utilization for the country.

- Several studies related to different concepts of thorium fueled reactors, different steps of thorium fuel cycle and radiological protection were studied in different instituitons: IPEN-CNEN/SP, IRD-CNEN/RJ, CDTN-CNEN/MG, CTM-SP (Navy Technology Center), IEAv (Institute for Advanced Studies – São Paulo), Federal University of M.Gerais, Federal University of Ouro Preto and São Paulo University.

- Brazil has a long tradition in the thorium technology, from mining of monazite to the obtainment of thorium with purity suitable for nuclear use.

- The processing of monazite sand was started in Brazil in the end of 40's, and IPEN-CNEN/SP produced between 1985 until 2002 more than 170 t of thorium nitrate of high purity, using thorium compounds obtained from the monazite processing.

- Nevertheless, nowadays, 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.

Thank all of you, for your attention!

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