

IAEA-TECDOC-1450

# *Thorium fuel cycle — Potential benefits and challenges*



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## FOREWORD

Thorium is three times more abundant in nature compared to uranium and occurs mainly as 'fertile'  $^{232}\text{Th}$  isotope. From the inception of nuclear power programme, the immense potential of  $^{232}\text{Th}$  for breeding human-made 'fissile' isotope  $^{233}\text{U}$  efficiently in a thermal neutron reactor has been recognized. Several experimental and prototype power reactors were successfully operated during the mid 1950s to the mid 1970s using (Th, U) $\text{O}_2$  and (Th, U) $\text{C}_2$  fuels in high temperature gas cooled reactors (HTGR), (Th, U) $\text{O}_2$  fuel in light water reactors (LWR) and  $\text{Li}^7\text{F}/\text{BeF}_2/\text{ThF}_4/\text{UF}_4$  fuel in molten salt breeder reactor (MSBR).  $^{232}\text{Th}$  and  $^{233}\text{U}$  are the best 'fertile' and 'fissile' materials respectively for thermal neutron reactors and 'thermal breeding' has been demonstrated for (Th, U) $\text{O}_2$  fuel in the Shippingport light water breeder reactor (LWBR).  $\text{ThO}_2$  has also been successfully used as blanket material in liquid metal cooled fast breeder reactor (LMFBR) and for neutron flux flattening of the initial core of pressurized heavy water reactor (PHWR) during startup. So far, thorium fuels have not been introduced commercially because the estimated uranium resources turned out to be sufficient. In recent years, there has been renewed and additional interest in thorium because of: (i) the intrinsic proliferation resistance of thorium fuel cycle due to the presence of  $^{232}\text{U}$  and its strong gamma emitting daughter products, (ii) better thermo-physical properties and chemical stability of  $\text{ThO}_2$ , as compared to  $\text{UO}_2$ , which ensures better in-pile performance and a more stable waste form, (iii) lesser long lived minor actinides than the traditional uranium fuel cycle, (iv) superior plutonium incineration in (Th, Pu) $\text{O}_2$  fuel as compared to (U, Pu) $\text{O}_2$  and (v) attractive features of thorium related to accelerated driven system (ADS) and energy amplifier (EA). However, there are several challenges in the front and back end of the thorium fuel cycles. Irradiated  $\text{ThO}_2$  and spent  $\text{ThO}_2$ -based fuels are difficult to dissolve in  $\text{HNO}_3$  because of the inertness of  $\text{ThO}_2$ . The high gamma radiation associated with the short lived daughter products of  $^{232}\text{U}$ , which is always associated with  $^{233}\text{U}$ , necessitates remote reprocessing and refabrication of fuel. The protactinium formed in thorium fuel cycle also cause some problems, which need to be suitably resolved.

The information on thorium and thorium fuel cycles has been well covered in the IAEA-TECDOC-1155 (May 2000) and IAEA-TECDOC-1319 (November 2002). The objective of the present TECDOC is to make a critical review of recent knowledge on thorium fuel cycle and its potential benefits and challenges, in particular, front end, applying thorium fuel cycle options and back end of thorium fuel cycles. The review has been prepared based on three consultancy meetings held at IAEA, Vienna 1–3 July 2002, 14–16 April 2003 and 15–16 September 2003, where experts from Canada, France, India, Israel, Japan, the Russian Federation, USA and IAEA had participated and supported by information and published papers from specialists on thorium fuels and fuel cycles.

The IAEA wishes to express its gratitude to C. Ganguly (India) for chairing this working group and shaping this publication.

The IAEA officers responsible for this publication were F. Sokolov, K. Fukuda and H.P. Nawada of the Division of Nuclear Fuel Cycle and Waste Technology.

### *EDITORIAL NOTE*

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## 1. SUMMARY

The outlook for nuclear power around the world has generally brightened with progressive improvement in the operating performance of existing reactors, ensuring economic competitiveness of nuclear electricity in liberalized electricity markets. At the end of 2002, some 441 nuclear power plants, with total installed capacity of 358 GW(e), were in operation worldwide, generating some 16% of global electricity. In the reference scenario, the annual average rate of growth of world nuclear capacity is expected to be in the range of 0.9% up to the year 2025 by which time the total installed nuclear power would be some 438 GW(e).

Thorium is 3 to 4 times more abundant than uranium and is widely distributed in nature as an easily exploitable resource in many countries. Unlike natural uranium, which contains ~0.7% 'fissile'  $^{235}\text{U}$  isotope, natural thorium does not contain any 'fissile' material and is made up of the 'fertile'  $^{232}\text{Th}$  isotope only. Hence, thorium and thorium-based fuel as metal, oxide or carbide, has been utilized in combination with 'fissile'  $^{235}\text{U}$  or  $^{239}\text{Pu}$  in nuclear research and power reactors for conversion to 'fissile'  $^{233}\text{U}$ , thereby enlarging the 'fissile' material resources. During the pioneering years of nuclear energy, from the mid 1950s to mid 1970s, there was considerable interest worldwide to develop thorium fuels and fuel cycles in order to supplement uranium reserves. Thorium fuels and fuel cycles are particularly relevant to countries having large thorium deposits but very limited uranium reserves for their long term nuclear power programme. The feasibility of thorium utilization in high temperature gas cooled reactors (HTGR), light water reactors (LWR), pressurized heavy water reactors (PHWRs), liquid metal cooled fast breeder reactors (LMFBR) and molten salt breeder reactors (MSBR) were demonstrated. These activities have been well documented in several extensive reviews and conference proceedings published by US Atomic Energy Commission [1], US Department of Energy [2], [3], KfA, Germany [4] and IAEA [5]. More recently, the proceedings of IAEA meetings on Thorium Fuel Utilization: Options and Trends has summarized the activities and coordinated research projects (CRP) of IAEA and the status of thorium fuel cycle option, including ADS, in Member States [9]. The initial enthusiasm on thorium fuels and fuel cycles was not sustained among the developing countries later, due to new discovery of uranium deposits and their improved availability. However, in recent times, the need for proliferation-resistance, longer fuel cycles, higher burnup, improved waste form characteristics, reduction of plutonium inventories and in situ use of bred-in fissile material has led to renewed interest in thorium-based fuels and fuel cycles in several developed countries. The two main international projects, namely Innovative Nuclear Reactors and Fuel Cycles Programme (INPRO) initiated by the IAEA and the US-led Generation IV International Forum (GIF), are also considering thorium fuels and fuel cycles. Thorium fuels and fuel cycles have the following benefits and challenges:

### Benefits

- Thorium is 3 to 4 times more abundant than uranium, widely distributed in nature as an easily exploitable resource in many countries and has not been exploited commercially so far. Thorium fuels, therefore, complement uranium fuels and ensure long term sustainability of nuclear power.
- Thorium fuel cycle is an attractive way to produce long term nuclear energy with low radiotoxicity waste. In addition, the transition to thorium could be done through the incineration of weapons grade plutonium (WPu) or civilian plutonium.



- The absorption cross-section for thermal neutrons of  $^{232}\text{Th}$  (7.4 barns) is nearly three times that of  $^{238}\text{U}$  (2.7 barns). Hence, a higher conversion (to  $^{233}\text{U}$ ) is possible with  $^{232}\text{Th}$  than with  $^{238}\text{U}$  (to  $^{239}\text{Pu}$ ). Thus, thorium is a better 'fertile' material than  $^{238}\text{U}$  in thermal reactors but thorium is inferior to depleted uranium as a 'fertile' material in fast reactor.
- For the 'fissile'  $^{233}\text{U}$  nuclei, the number of neutrons liberated per neutron absorbed (represented as  $\eta$ ) is greater than 2.0 over a wide range of thermal neutron spectrum, unlike  $^{235}\text{U}$  and  $^{239}\text{Pu}$ . Thus, contrary to  $^{238}\text{U}$ – $^{239}\text{Pu}$  cycle in which breeding can be obtained only with fast neutron spectra, the  $^{232}\text{Th}$ – $^{233}\text{U}$  fuel cycle can operate with fast, epithermal or thermal spectra.
- Thorium dioxide is chemically more stable and has higher radiation resistance than uranium dioxide. The fission product release rate for  $\text{ThO}_2$ –based fuels are one order of magnitude lower than that of  $\text{UO}_2$ .  $\text{ThO}_2$  has favourable thermophysical properties because of the higher thermal conductivity and lower co-efficient of thermal expansion compared to  $\text{UO}_2$ . Thus,  $\text{ThO}_2$ –based fuels are expected to have better in-pile performance than that of  $\text{UO}_2$  and  $\text{UO}_2$ –based mixed oxide.
- $\text{ThO}_2$  is relatively inert and does not oxidize unlike  $\text{UO}_2$ , which oxidizes easily to  $\text{U}_3\text{O}_8$  and  $\text{UO}_3$ . Hence, long term interim storage and permanent disposal in repository of spent  $\text{ThO}_2$ –based fuel are simpler without the problem of oxidation.
- Th–based fuels and fuel cycles have intrinsic proliferation-resistance due to the formation of  $^{232}\text{U}$  via (n,2n) reactions with  $^{232}\text{Th}$ ,  $^{233}\text{Pa}$  and  $^{233}\text{U}$ . The half-life of  $^{232}\text{U}$  is only 73.6 years and the daughter products have very short half-life and some like  $^{212}\text{Bi}$  and  $^{208}\text{Tl}$  emit strong gamma radiations. From the same consideration,  $^{232}\text{U}$  could be utilized as an attractive carrier of highly enriched uranium (HEU) and weapons grade plutonium (WPU) to avoid their proliferation for non-peaceful purpose.
- For incineration of WPU or civilian Pu in 'once-through' cycle, (Th, Pu) $\text{O}_2$  fuel is more attractive, as compared to (U, Pu) $\text{O}_2$ , since plutonium is not bred in the former and the  $^{232}\text{U}$  formed after the 'once-through' cycle in the spent fuel ensures proliferation-resistance.
- In  $^{232}\text{Th}$ – $^{233}\text{U}$  fuel cycle, much lesser quantity of plutonium and long-lived Minor Actinides (MA: Np, Am and Cm) are formed as compared to the  $^{238}\text{U}$ – $^{239}\text{Pu}$  fuel cycle, thereby minimizing the radiotoxicity associated in spent fuel. However, in the back end of  $^{232}\text{Th}$ – $^{233}\text{U}$  fuel cycle, there are other radionuclides such as  $^{231}\text{Pa}$ ,  $^{229}\text{Th}$  and  $^{230}\text{U}$ , which may have long term radiological impact.

## Challenges

- The melting point of  $\text{ThO}_2$  (3 350 $^{\circ}\text{C}$ ) is much higher compared to that of  $\text{UO}_2$  (2 800 $^{\circ}\text{C}$ ). Hence, a much higher sintering temperature (>2 000 $^{\circ}\text{C}$ ) is required to produce high density  $\text{ThO}_2$  and  $\text{ThO}_2$ –based mixed oxide fuels. Admixing of 'sintering aid' (CaO, MgO, Nb $_2\text{O}_5$ , etc) is required for achieving the desired pellet density at lower temperature.
- $\text{ThO}_2$  and  $\text{ThO}_2$ –based mixed oxide fuels are relatively inert and, unlike  $\text{UO}_2$  and (U, Pu) $\text{O}_2$  fuels, do not dissolve easily in concentrated nitric acid. Addition of small quantities of HF in concentrated  $\text{HNO}_3$  is essential which cause corrosion of stainless

steel equipment and pipings in reprocessing plants. The corrosion problem is mitigated with addition of aluminium nitrate. Boiling THOREX solution [13 M HNO<sub>3</sub>+0.05 M HF+0.1 M Al(NO<sub>3</sub>)<sub>3</sub>] at ~393 K and long dissolution period are required for ThO<sub>2</sub>-based fuels.

- The irradiated Th or Th-based fuels contain significant amount of <sup>232</sup>U, which has a half-life of only 73.6 years and is associated with strong gamma emitting daughter products, <sup>212</sup>Bi and <sup>208</sup>Tl with very short half-life. As a result, there is significant build-up of radiation dose with storage of spent Th-based fuel or separated <sup>233</sup>U, necessitating remote and automated reprocessing and refabrication in heavily shielded hot cells and increase in the cost of fuel cycle activities.
- In the conversion chain of <sup>232</sup>Th to <sup>233</sup>U, <sup>233</sup>Pa is formed as an intermediate, which has a relatively longer half-life (~27 days) as compared to <sup>239</sup>Np (2.35 days) in the uranium fuel cycle thereby requiring longer cooling time of at least one year for completing the decay of <sup>233</sup>Pa to <sup>233</sup>U. Normally, Pa is passed into the fission product waste in the THOREX process, which could have long term radiological impact. It is essential to separate Pa from the spent fuel solution prior to solvent extraction process for separation of <sup>233</sup>U and thorium.
- The three **stream** process of separation of uranium, plutonium and thorium from spent (Th, Pu)O<sub>2</sub> fuel, though viable, is yet to be developed.
- The database and experience of thorium fuels and thorium fuel cycles are very limited, as compared to UO<sub>2</sub> and (U, Pu)O<sub>2</sub> fuels, and need to be augmented before large investments are made for commercial utilization of thorium fuels and fuel cycles.

Table 1 summarizes the experimental reactors and power reactors where thorium based ceramic nuclear fuels have been used in the form of ‘coated fuel particles’ (‘microspheres’) in graphite matrix in HTGRs or as Zircaloy/stainless steel clad fuel pin assemblies containing high density ‘fuel pellets’ or ‘vibratory compacted’ fuel particles or microspheres. In the past, in the two helium cooled Pebble Bed HTGRs of Germany, namely AVR 15 MW(e) and THTR 300 MW(e), ‘coated fuel particles’ of highly enriched uranium (HEU)-thorium, mixed oxide and mixed di-carbide, embedded in graphite matrix and consolidated in the form of spherical fuel elements of diameter ~60 mm were successfully utilized. Later, in the wake of international non-proliferation requirements, the HEU was replaced with low enriched uranium (LEU: <20% <sup>235</sup>U). Coated fuel particles of mixed uranium thorium oxide and di-carbide, embedded in graphite, were also employed in the form of prismatic blocks in the helium-cooled HTGRs of USA, namely Peach Bottom (40 MW(e)) and Fort St. Vrain (330 MW(e)). The HTGR in UK, namely the Dragon reactor, has also used ‘coated fuel particles’ of mixed thorium uranium oxide and di-carbide in graphite matrix.

Table 1. Thorium utilization in different experimental and power reactors

Name and Country	Type	Power	Fuel	Operation period
AVR, Germany	HTGR Experimental (Pebble bed reactor)	15 MW(e)	Th+ <sup>235</sup> U Driver Fuel, Coated fuel particles Oxide & dicarbides	1967 – 1988
THTR, Germany	HTGR Power (Pebble Type)	300 MW(e)	Th+ <sup>235</sup> U, Driver Fuel, Coated fuel particles Oxide & dicarbides	1985 - 1989
Lingen, Germany	BWR Irradiation-testing	60 MW(e)	Test Fuel (Th,Pu)O <sub>2</sub> pellets	Terminated in 1973
Dragon, UK OECD-Euratom also Sweden, Norway & Switzerland	HTGR Experimental (Pin-in-Block Design)	20 MWt	Th+ <sup>235</sup> U Driver Fuel, Coated fuel particles Dicarbides	1966 - 1973
Peach Bottom, USA	HTGR Experimental (Prismatic Block)	40 MW(e)	Th+ <sup>235</sup> U Driver Fuel, Coated fuel particles Oxide & Dicarbides	1966 – 1972
Fort St Vrain, USA	HTGR Power (Prismatic Block)	330 MW(e)	Th+ <sup>235</sup> U Driver Fuel, Coated fuel particles Dicarbide	1976 - 1989
MSRE ORNL, USA	MSBR	7.5 MWt	<sup>233</sup> U Molten Fluorides	1964 - 1969
Borax IV & Elk River Reactors, USA	BWRs (Pin Assemblies)	2.4 MW(e) 24 MW(e)	Th+ <sup>235</sup> U Driver Fuel Oxide Pellets	1963 - 1968
Shippingport & Indian Point, USA	LWBR PWR (Pin Assemblies)	100 MW(e) 285 MW(e)	Th+ <sup>233</sup> U Driver Fuel, Oxide Pellets	1977 – 1982 1962 - 1980
SUSPOP/KSTR KEMA, Netherlands	Aqueous Homogenous Suspension (Pin Assemblies)	1 MWt	Th+ HEU Oxide Pellets	1974 - 1977
NRU & NRX, Canada	MTR (Pin Assemblies)		Th+ <sup>235</sup> U Test Fuel	Irradiation– testing of few fuel elements
KAMINI, CIRUS, & DHRUVA, India	MTR Thermal	30 kWt 40 MWt 100 MWt	Al- <sup>233</sup> U Driver Fuel 'J' rod of Th & ThO <sub>2</sub> 'J' rod of ThO <sub>2</sub>	All three research reactors in operation
KAPS 1&2, KGS 1&2, RAPS 2,3&4, India	PHWR (Pin Assemblies)	220 MW(e)	ThO <sub>2</sub> Pellets For neutron flux flattening of initial core after start-up	Continuing in all new PHWRs
FBTR, India	LMFBR (Pin Assemblies)	40 MWt	ThO <sub>2</sub> blanket	In operation

In water cooled nuclear power reactors also, thorium has been used in the past in the form of Zircaloy clad high density sintered 'fuel pellets' of  $\text{ThO}_2$  and  $(\text{Th}, \text{U})\text{O}_2$  and to a very limited extent as  $(\text{Th}, \text{Pu})\text{O}_2$ . The BORAX IV (20 MWt/2.4MW(e)) and Elk River reactor (64 MWt/22 MW(e)), the two boiling light water reactors (BWR) of USA, were in operation in the 1960s using high density  $(\text{Th}, \text{U})\text{O}_2$  fuel pellets containing 4–7%  $\text{UO}_2$ . In the first core of the 270 MW(e) Indian point pressurised water reactor (PWR) of USA, high density  $(\text{Th}, \text{U})\text{O}_2$  pellets containing nearly 9.1%  $\text{UO}_2$  (HEU: 93%) was used. The 60 MW(e) Shipping Port 'light water breeder reactor' (LWBR) of USA has been the major thorium-based reactor in the world to demonstrate thermal breeding (breeding ratio:  $>1$ ). This reactor utilized seed blanket modules containing Zircaloy 4 clad high density  $(\text{Th}, {}^{233}\text{U})\text{O}_2$  and  $\text{ThO}_2$  pellet-pin assemblies respectively. The reactor operated for nearly 5 years till 1982 and the fuel achieved a maximum burnup of 60 000 MWd/t without any fuel failure.

In India, there has always been a strong incentive for development of thorium fuels and fuel cycles because of large thorium deposits compared to the very modest uranium reserves. Aluminium clad thorium oxide 'pellets' are being regularly irradiated in CIRUS and DHRUVA research reactors in BARC. Subsequently, the irradiated thoria were reprocessed by THOREX process and the recovered  ${}^{233}\text{U}$  has been utilized in the 30kWt research reactor KAMINI in the form of Al-clad Al-20%  ${}^{233}\text{U}$  plate fuel element assemblies. Large quantities of high density sintered  $\text{ThO}_2$  pellets have been manufactured at Nuclear Fuel Complex (NFC) and are being used in: (i) fast breeder test reactor (FBTR) as stainless steel clad blanket pin assemblies and (ii) PHWRs as Zircaloy clad pin assemblies for neutron flux flattening of initial core during start-up. Several R&D activities are underway on  $(\text{Th}, \text{U})\text{O}_2$  and  $(\text{Th}, \text{Pu})\text{O}_2$  fuels containing  $<5\%$  uranium or plutonium oxide for use in water cooled reactors and  $(\text{Th}, \text{Pu})\text{O}_2$  containing 20–30%  $\text{PuO}_2$  and 70–80%  $\text{PuO}_2$  for use in LMFBR with large and small cores respectively. Apart from the classical 'Powder-Pellet' route, advanced process flowsheets, based on Sol-Gel Microsphere Pelletization (SGMP) and Impregnation techniques, amenable to automation and remotisation, have been developed for fabrication of  $\text{ThO}_2$ -based mixed oxide pellets of controlled density and microstructure. Essential thermophysical properties of these fuels, including thermal conductivity, co-efficient of thermal expansion and hot hardness (in turn indentation- creep) have been evaluated. Several Zircaloy clad  $(\text{Th}, \text{Pu})\text{O}_2$  fuel pins have been successfully irradiated to burnups in the range of 15 000–18 000 MWd/t in the pressurised water loop (PWL) of CIRUS reactor. Design and developmental activities are underway for construction of an advanced heavy water reactor of 300 MW(e) (AHWR 300) with  $(\text{Th}, \text{Pu})\text{O}_2$  and  $(\text{Th}, {}^{233}\text{U})\text{O}_2$  driver fuel. A case study of AHWR 300 is in progress at the IAEA, to validate the methodology finalized in Phase IA of INPRO [10].

The GIF has identified 'very high temperature reactor' (VHTR), deployable by 2020, as one of the candidates for high temperature process heat applications, primarily for thermochemical hydrogen production, coal gasification, etc. in addition to electricity generation and desalination [11]. For this, the reference reactor concept has been a 600 MWt, helium cooled prismatic block fuel of the gas turbine-modular helium reactor (GT-MHR) or the pebble fuel of pebble bed modular reactor (PBMR). Th-based, ZrC coated fuel particles 'TRISO' of oxide, mixed oxide, di-carbide or mixed di-carbides in graphite matrix are strong candidate fuels for this type of reactor.

Thorium cycles are feasible in all existing thermal and fast reactors, e.g. LWRs (including WWERs especially WWER-T), PHWRs, HTGRs, MSBRs and LMFBRs and in ADS. In the short term, it should be possible to incorporate the thorium fuel cycle in some of the above existing reactors without major modifications in the engineered systems, reactor control and

the reactivity devices. However, for the innovative reactors and fuel cycles, a lot of reactor physics studies and other technological developments would be required before these could be implemented. The proceedings of the Annual Conference of Indian Nuclear Society on “Power from Thorium: Status, Strategies and Directions” held in Mumbai in June 2000 [12] and the EURATOM report on Thorium as a Waste Management Option” [13] give a comprehensive review of all aspects of thorium fuels and fuel cycles.

All aspects of thorium fuel cycle, including global resources, reactor experience, fuel properties & performance, fuel cycle options, conventional & advanced methods of fuel fabrication, spent fuel handling & intermediate storage, reprocessing & waste management and proliferation-resistance were discussed in these meetings. The experts from the Member-States presented their views and summarized the work of the specialists from their countries. The present TECDOC mostly includes the statements and the presentation materials of these experts and specialists. The objective of the document is to update information and make a critical review on “Thorium Fuel Cycle: Potential Benefits and Challenges”, mainly based on the developments since the year 2000, with focus on the upcoming thorium based reactors, current information base, front and back end issues, including manufacturing and reprocessing of thorium fuels, proliferation-resistance and economic issues. The concluding chapter summarizes future prospects and recommendations pertaining to thorium fuels and fuel cycles.

## **2. RATIONALE FOR THORIUM-BASED FUEL CYCLES**

The first three prototype nuclear power plants in the world were commissioned in the Russian Federation, UK and the USA in the mid 1950s and by the mid 1980s, nuclear power had blossomed as a matured industrial technology in North America, Europe and a few countries in Asia with a track record of success and good prospect for the future. Unfortunately, the growth of nuclear power dramatically slowed down, particularly in the USA and Europe, after the Chernobyl catastrophe in 1986, which heightened anti-nuclear sentiments. The competitive ability of nuclear power was subsequently weakened by a steep rise in the cost of ensuring and persuasively demonstrating the safety of nuclear plants. However, interest in nuclear power started improving ever since 1990 and the most significant current trend has been steady increase in the availability factor of nuclear power plants. Recent concerns about global warming, and the Kyoto accords limiting CO<sub>2</sub> suggest that future energy demands cannot be met solely through the burning of fossil fuels, and a return to some reliance on the nuclear option may be required. Two major international projects, namely the IAEA initiated INPRO, and the US-led GIF, are presently underway for innovations in nuclear reactors and fuel cycles in order to meet the global energy needs in the 21<sup>st</sup> century and beyond. In addition, the European Union has also initiated the MICANET programme with similar objectives. Some of the common objectives of INPRO and GIF are long term sustainability and favourable economics of nuclear power and addressing associated public concerns in the areas of safety, nuclear waste storage, disposal and environmental protection and actinide management and proliferation-resistance in nuclear fuel cycles. The INPRO and GIF mission also aim at developing nuclear energy systems to deliver a combination of electricity and process heat. Depending on the type of reactor, the process heat could be supplied either at sufficiently high temperatures (>700<sup>0</sup>C) to support steam-reforming or thermochemical production of hydrogen or at relatively lower temperature for applications like desalination for potable water, district heating, etc. The hydrogen-based energy system can then progressively replace the carbon-based fuel in the transportation sector and minimize CO<sub>2</sub>

and other greenhouse gas emission. At the end of 2002, some 441 nuclear power plants, with total installed capacity of 358 GW(e), were in operation worldwide, generating some 16% of global electricity. In the reference scenario, the annual average rate of growth of world nuclear capacity is expected to be in the range of 0.9% up to the year 2025 by which time the total installed nuclear power would be some 438 GW(e).

Uranium and thorium, the two heaviest elements occurring in nature, are the basic materials for nuclear fission energy. Unlike natural uranium, which contains ~0.7% 'fissile'  $^{235}\text{U}$  isotope (the balance 99.3% is mostly the 'fertile'  $^{238}\text{U}$  isotope), natural thorium does not contain any 'fissile' material and is made up of the 'fertile'  $^{232}\text{Th}$  isotope only. The annual world requirements of uranium is expected to grow from the present level of some 66 000 tonnes 'U' to nearly 82 000 tonnes 'U' by the year 2025. At the end of 2002, world uranium production (36 042 tonnes) provided about 54% of world reactor requirements (66 815 tonnes), with the remainder being met by secondary sources, including civilian and military stockpiles, uranium reprocessing and re-enrichment of depleted uranium. However, by 2025, secondary sources will decline in importance and provide only about 4–6% of requirements, depending upon the demand projections used. At that juncture, introduction of thorium fuel cycle will play a complementary role and ensure easy availability of basic materials for nuclear fission energy. For utilization of thorium in nuclear power programme, an additional step of first converting 'fertile'  $^{232}\text{Th}$  into 'fissile'  $^{233}\text{U}$  is needed.  $^{233}\text{U}$  is by far the best 'fissile' isotope for thermal neutron spectrum and can be used for breeding in both thermal and fast reactors. Hence, during the pioneering years of nuclear energy, from the mid 1950s to mid 1970s, there was considerable interest worldwide to develop thorium fuels and fuel cycles in order to supplement 'fissile'  $^{235}\text{U}$  reserves with  $^{233}\text{U}$ . The initial enthusiasm was not sustained among the developing countries later, due to new discoveries of uranium deposits and their improved availability. However, lately, a renewed interest in thorium-based fuels has arisen in several developed countries based on the need for proliferation resistance, longer fuel cycles, higher burnup and improved waste characteristics. The rationale for thorium fuel cycles differ from country to country and are based on the following facts:

### **Abundance of thorium in nature and easy mining operations**

Thorium is widely distributed with an average concentration of 10 ppm in earth's crust in many phosphates, silicates, carbonates and oxide minerals and is 3 to 4 times more abundant in nature than uranium and has not been exploited commercially so far. In general, thorium occurs in association with uranium and rare earth elements (REE) in diverse rock types: as veins of thorite, thorianite, uranothorite and as monazite in granites, syenites, pegmatites and other acidic intrusions. Monazite is also present in quartz-pebble conglomerates sand stones and in fluvial and beach placers. Monazite, a mixed thorium rare earth uranium phosphate, is the most popular source of thorium and is available in many countries in beach or river sands along with heavy minerals—ilmenite, rutile, monazite, zircon, sillimanite and garnet. The present production of thorium is almost entirely as a by-product of rare earth extraction from monazite sand. The mining and extraction of thorium from monazite is relatively easy and significantly different from that of uranium from its ores. The overburden during mining is much smaller than in the case of uranium and the total radioactive waste production in mining operation is about 2 orders of magnitude lower than that of uranium. The so-called Radon impact is also much smaller than in the uranium case due to the short lifetime of thoron as compared to that of radon, and needs therefore, much simpler tailings management than in the case of uranium, to prevent long term public doses. As far as occupational doses are concerned, there is no need to control ventilation with respect to Rn-220 inhalation because monazite extraction is done in open pit.

In India, there has been sustained interest in thorium fuels and fuel cycles because of large deposits of thorium (518 000 tonnes) in the form of monazite in beach sands as compared to very modest reserves of low-grade uranium (92 000 tonnes). The long term sustainability of indigenous nuclear power programme in India depends to a great extent on large-scale utilization of the vast thorium resources for breeding  $^{233}\text{U}$  and recycling the same in self-sustaining  $^{232}\text{Th}$ – $^{233}\text{U}$  ‘closed’ fuel cycle in thermal breeder reactors.

### **Better nuclear characteristics of $^{232}\text{Th}$ and $^{233}\text{U}$**

$^{232}\text{Th}$  is a better ‘fertile’ material than  $^{238}\text{U}$  in thermal reactors because of the three times higher thermal neutron absorption cross-section of  $^{232}\text{Th}$  (7.4 barns) as compared to  $^{238}\text{U}$  (2.7 barns). Thus, conversion of  $^{232}\text{Th}$  to  $^{233}\text{U}$  is more efficient than that of  $^{238}\text{U}$  to  $^{239}\text{Pu}$  in thermal neutron spectrum though the resonance integral of  $^{232}\text{Th}$  is one-third of that of  $^{238}\text{U}$ .

For the ‘fissile’  $^{233}\text{U}$  nuclei, the number of neutrons liberated per neutron absorbed (represented as  $\eta$ ) is greater than 2.0 over a wide range of thermal neutron spectrum, unlike  $^{235}\text{U}$  and  $^{239}\text{Pu}$ . Thus, the  $^{232}\text{Th}$ – $^{233}\text{U}$  fuel cycle is less sensitive to the type of reactor, thermal or fast. The capture cross-section of  $^{233}\text{U}$  is much smaller (46 barns) than the  $^{235}\text{U}$  (101 barns) and  $^{239}\text{Pu}$  (271 barns) for thermal neutrons, while the fission cross-section of all the three fissile isotopes is of the same order (525, 577 and 742 barns for  $^{233}\text{U}$ ,  $^{235}\text{U}$  and  $^{239}\text{Pu}$  respectively). Thus, non-fissile absorption leading to higher isotopes ( $^{234}\text{U}$ ,  $^{236}\text{U}$  and  $^{240}\text{Pu}$  respectively) with higher absorption cross-sections is much less probable. This makes recycling of  $^{233}\text{U}$  less of a problem from reactivity point of view compared to plutonium burned in thorium systems.

### **Higher chemical and radiation stability of $\text{ThO}_2$**

Thorium dioxide is chemically more stable and has higher radiation resistance than uranium dioxide. The fission product release rate for  $\text{ThO}_2$ –based fuels are one order of magnitude lower than that of  $\text{UO}_2$ .  $\text{ThO}_2$  has favourable thermophysical properties because of the higher thermal conductivity and lower co-efficient of thermal expansion compared to  $\text{UO}_2$ . Thus,  $\text{ThO}_2$ –based fuels are expected to have better in-pile performance than that of  $\text{UO}_2$  and  $\text{UO}_2$ –based mixed oxide.  $\text{ThO}_2$  is relatively inert and does not oxidize unlike  $\text{UO}_2$ , which oxidizes easily to  $\text{U}_3\text{O}_8$  and  $\text{UO}_3$ . Hence, long term interim storage and permanent disposal in repository of spent  $\text{ThO}_2$ –based fuel are simpler without the problem of oxidation.

### **Excellent past performance of $\text{ThO}_2$ , $(\text{Th,U})\text{O}_2$ , $\text{ThC}_2$ and $(\text{Th,U})\text{C}_2$ fuels in HTGRs**

The coated fuel particles of thoria, mixed thoria urania, thorium di-carbide and mixed thorium uranium di-carbide have demonstrated excellent performance in the past in the high temperature gas cooled reactors (HTGR) in Germany, USA and UK [14]. On this basis, there is enough incentive and rationale to consider thorium-based mixed oxide and mixed di-carbide as candidate fuels for the helium cooled very high temperature reactors (VHTR) of 600 MWt, with coolant outlet temperature in the range of 1 000<sup>0</sup>C, identified by GIF as the nearest-term hydrogen production system, estimated to be deployable by 2020. The thorium-based coated fuel particles is attractive for VHTR 600 MWt based on either the prismatic block fuel of the Gas Turbine – Modular Helium Reactor (GT–MHR) or the pebble fuel of the Pebble Bed Modular Reactor (PBMR).

## **Intrinsic proliferation–Resistance of $^{232}\text{Th}$ – $^{233}\text{U}$ and burning plutonium in fast neutron reactor in ‘once–through cycle’**

The potential proliferation of nuclear weapon material produced as a by–product of the nuclear fuel cycle is responsible for much of the public’s concerns, and may be one of the major obstacles to worldwide expansion of nuclear power. Public concerns related to the proliferation potential of the civilian nuclear energy industry have led to abandonment of the reprocessing option for spent fuel in the USA, regardless of its potential to improve the resource utilization of the current nuclear fuel cycle. Therefore, among other considerations, in order for nuclear power to be accepted as a significant contributor of primary energy in the next century, it should be based on a fuel cycle, which is highly proliferation-resistant. The non-proliferative nature of the fuel cycle material flow should be supported not only by a combination of administrative controls and safeguards measures, but also by avoiding production of any material of sufficient quantity and quality as to be of possible military use. Therefore, in order to completely divorce from the development and expansion of nuclear power from the potential danger of nuclear weapons proliferation, international safeguards are necessary but not sufficient. A decisive barrier to proliferation should be based on inherent properties of the fuel cycle itself. Th–based fuels and fuel cycles have intrinsic proliferation-resistance due to the formation of  $^{232}\text{U}$  via (n,2n) reactions with  $^{232}\text{Th}$ ,  $^{233}\text{Pa}$  and  $^{233}\text{U}$ . The half-life of  $^{232}\text{U}$  is only 73.6 years and the daughter products have very short half-life and some like  $^{212}\text{Bi}$  and  $^{208}\text{Tl}$  emit strong gamma radiations: 0.7–1.8 MeV and 2.6 MeV respectively. Hence,  $^{232}\text{U}$  could be utilized as an intrinsic proliferation-resistant barrier for diversion of highly enriched uranium (HEU) and weapons grade plutonium (W–Pu) for non-peaceful purposes. For incineration of WPu or civilian Pu in fast reactors utilizing ‘once-through’ cycle, (Th, Pu) $\text{O}_2$  fuel is a better option, as compared to (U, Pu) $\text{O}_2$  [15]. In thoria matrix fuel, plutonium is not bred, instead  $^{232}\text{U}$  is formed in the spent fuel which ensures proliferation-resistance because of the high gamma radiation associated with the daughter products. In addition, these fuels could be directly disposed in permanent repositories taking advantage of the high chemical stability of and inertness  $\text{ThO}_2$ .

### **Excellent possibility in CANDU–PHWR, ACR and AHWR**

In Canada, ‘Once-Through Thorium’ (OTT) cycles in mixed channel and mixed bundle scheme is being studied in the existing CANDU and in the advanced CANDU reactors (ACR) mainly with the purpose of reducing plutonium production and taking advantage of better thermophysical properties and chemical stability of  $\text{ThO}_2$  for improved burnup and stability of the waste form [16]. In the 43–element CANFLEX bundles, the 8 inner elements are being proposed to be of pure  $\text{ThO}_2$ , whereas the remaining 35 elements would consist of slightly enriched uranium (SEU) oxide containing 2.2–3%  $^{235}\text{U}$ .

In India, a ‘closed’ self-sustaining  $^{232}\text{Th}$ – $^{233}\text{U}$  fuel cycle is being pursued for judicious utilization of the vast thorium resources. An Advanced Heavy Water moderated light boiling water cooled Reactor of 300 MW(e) (AHWR 300), a vertical pressure tube type of reactor, with passive safety and on-power fuelling features has been designed with (Th,Pu) $\text{O}_2$  and (Th,  $^{233}\text{U}$ ) $\text{O}_2$  as driver fuel [17].

### **Advantages of thorium–fuelled ADS**

Accelerated Driven sub critical assembly System (ADS), with family of Energy Amplifiers (EA), and thorium as the breeding fuel offers potentially significant advantages in thorium fuel cycle (‘once-through’ or ‘closed’) in terms of minimizing radiotoxicity of nuclear waste



and ensuring proliferation-resistance at the same time. The  $^{233}\text{U}$  could be denatured by addition of  $^{238}\text{U}$  and recycling the same. In ADS, 1 GeV protons are made to collide with a heavy target (usually Pb or Pb–Bi alloy) to produce spallation neutrons of energy in the range of 20 MeV. The amplifier consists of sub-critical assembly of  $^{232}\text{Th}/^{233}\text{U}$ , with  $k_{\text{eff}} = \sim 0.95$  such that a further neutron multiplication of  $1/(1-k_{\text{eff}}) = 20$  can be expected. Depending on moderator/coolant used, these neutrons in an Energy Amplifier (EA) can be completely Thermalized (T–EA) with graphite moderator, partially thermalised with Pressurised Water (PW–EA) or remain Fast (F–EA) [18]. The waste from such thorium-fuelled EA are approximately 30 times less toxic than that of uranium fuel for the first, 30 000 years cooling time.

### **Lesser problems in handling transuranium (TRU) waste**

The public concerns about nuclear waste from commercial nuclear power plants are related primarily to the long term toxicity of the spent nuclear fuels; in the current ‘once-through’ fuel cycle, this is dominated by plutonium and other minor actinides. The actinides play a dominant role both in terms of total radioactivity and potential dose to the public. In  $^{232}\text{Th}$ – $^{233}\text{U}$  fuel cycle, much lesser quantity of plutonium and long-lived Minor Actinides (MA: Np, Am and Cm) are formed as compared to the  $^{238}\text{U}$ – $^{239}\text{Pu}$  fuel cycle, thereby minimizing toxicity and decay heat problems. Also, the stability of  $\text{ThO}_2$  may help retard the migration of actinides in the repository.

## **3. IMPLEMENTATION SCENARIOS AND OPTIONS**

### **3.1. Open and closed thorium fuel cycles**

Large scale utilization of thorium for nuclear power is possible only with the introduction of an additional step of first converting the ‘fertile’  $^{232}\text{Th}$  into the ‘fissile’  $^{233}\text{U}$ . The subsequent use of  $^{233}\text{U}$  is conceivable in the following ways:

- ‘Open’ fuel cycle based on irradiation of  $^{232}\text{Th}$  and in situ fission of  $^{233}\text{U}$ , without involving chemical separation of  $^{233}\text{U}$ .
- ‘Closed’ fuel cycle based on chemical reprocessing of irradiated thorium or thorium based fuels for recovery of  $^{233}\text{U}$  and refabrication and recycling of  $^{233}\text{U}$  bearing fuels.

#### **3.1.1. Open fuel cycle**

The open fuel cycle avoids the engineering processes and other complications associated with reprocessing and refabrication of highly radiotoxic  $^{233}\text{U}$ –based fuels. An example of thorium utilization in the once-through mode is the Radkowsky concept [19] of light water reactor (LWR), which is also applicable to fit the Russian WWER–T (thorium) reactor concept [20], [21]. The essence of the core layout of such a concept is that each fuel assembly (FA) is made up of a central seed with fissile material (medium enriched uranium, plutonium) and thorium blanket. The seed components are more frequently replaced as compared to the FAs during refueling. Separation of seed and blanket, optimization of moderator (water) to fuel ratio and the very long fuel campaign (900 and 2620 effective full power days for seed and blanket respectively) offer possibility of such a system up to  $\sim 40\%$  of power to be defined by fission of  $^{233}\text{U}$ . Such ‘open’ fuel cycle concept for introducing thorium in nuclear power reactor is

very attractive from the point of view of 'in situ' utilization of  $^{233}\text{U}$  and avoiding handling of 'dirty'  $^{233}\text{U}$  outside the core.

Another incentive to use thorium in once-through fuel cycle is the possibility of incineration of weapons-grade plutonium (WPu) in combination with thorium in light-water reactors of WWER-1000 type to burn and not breed  $^{239}\text{Pu}$ . For this, mixed thorium plutonium oxide, containing ~5%  $\text{PuO}_2$ , could be used as driver fuel. The exclusion of uranium from fuel composition results in an essential increase in the rate of plutonium incineration compared to the use of standard mixed uranium plutonium oxide (MOX) fuel [22], [23]. The spent mixed thorium plutonium oxide on achieving the standard burnup (~40 MWdays/kg HM) of LWR fuel is not only degraded in terms of WPu content but also becomes 'proliferation-resistance' with the formation of  $^{232}\text{U}$  [by (n,2n) reaction with  $^{232}\text{Th}$ ], which has very strong gamma emitting daughter products.

Likewise, the stock of civil plutonium could be significantly decreased by using the same in combination with thorium in WWER-1000 type reactors. A direct replacement of low enriched uranium oxide fuel is possible by mixed thorium plutonium oxide fuel without any major modifications of core and reactor operation. In such a reactor, there is no need to use burnable absorber in the form of gadolinium, integrated into the fuel. The  $^{240}\text{Pu}$  isotope, present in significant quantities in civilian grade plutonium, is a good burnable absorber. Two layouts of WWER-1000 reactor core with full load of mixed thorium plutonium fuel are considered. In the standard core, all fresh fuel assemblies are located at the periphery and in the modified core only 12 fuel assemblies out of 54 are located in the periphery row. A typical WWER-1000 reactor core with full load of thorium plutonium oxide would consume around 1 694 kilogram of civilian grade plutonium. The plutonium unloaded from these reactors will have isotopic composition containing 28%  $^{239}\text{Pu}$ , which could be utilized only in fast reactors or disposed. Some 300 kg of  $^{233}\text{U}$  will be produced in the spent fuel, which would contain ~3 500 ppm  $^{232}\text{U}$ . One of the main advantages of such thorium plutonium mixed oxide fuel in WWER is the reduction in the neutron flux on the reactor vessel. LWRs using mixture of plutonium and thorium oxides have in fact, better safety characteristics compared to the one with enriched uranium oxide. Depending on the strategy of nuclear power development, the spent thorium plutonium mixed oxide fuel from WWER can be disposed or subjected to long term interim storage till the technology of reprocessing and separating  $^{233}\text{U}$  become economically attractive.

Both weapons Pu and civilian Pu could be efficiently disposed in combination with thorium as mixed thorium plutonium oxide fuel containing 20–30%  $\text{PuO}_2$  in commercial LMFBRs. In small LMFBR cores, like the demonstration type FBTR in India, the  $\text{PuO}_2$  content in (Th, Pu) $\text{O}_2$  fuel could be much higher and in the range of 70–80%.

### 3.1.2. Closed fuel cycle

Reprocessing of irradiated Th-based fuels and separation of converted  $^{233}\text{U}$  are necessary steps of closed fuel cycle. In this case, LWRs like WWER-1000 using mixed thorium plutonium oxide fuel can be considered as a converter for  $^{233}\text{U}$ . For recycling the  $^{233}\text{U}$  thus formed in LWRs (like WWER 1000), an important factor is the  $^{232}\text{U}$  content in  $^{233}\text{U}$ . For a standard burnup of 40 MWd/kg HM for a WWER-1000 fuel, the  $^{232}\text{U}$  content would be in the range of 3 000 ppm. The two recycling options [24] are as follows:

- The use of ( $^{232}\text{Th}$ - $^{233}\text{U}$ ) $\text{O}_2$  fuel.
- The use of (Depleted U- $^{233}\text{U}$ ) $\text{O}_2$  or (Reprocessed U from WWER- $^{233}\text{U}$ ) $\text{O}_2$ .

In the first option, there will be build-up of  $^{232}\text{U}$  in  $^{233}\text{U}$  in subsequent cycles whereas with the use of reprocessed uranium, two ‘dirty’ uraniums would be utilized in the same technology. The option with depleted uranium enables a smooth change over to thorium fuel cycle with minimum modification in reactor design and technology of handling spent fuel. However, the use of depleted/reprocessed uranium in combination with  $^{233}\text{U}$  is strictly speaking not pure thorium cycles since  $^{235}\text{U}$  is also being used along with  $^{233}\text{U}$  and there is a build up of  $^{239}\text{Pu}$  from the conversion of  $^{238}\text{U}$ . In addition, recycling of  $^{233}\text{U}$  with  $^{232}\text{U}$  does not utilize the main advantages of thorium fuel cycle, e.g. using the entire energy potential of thorium and excluding build-up of minor actinides and plutonium and minimizing radiotoxicity of disposed wastes. Replacement of  $^{235}\text{U}$  by  $^{233}\text{U}$  in WWER-1000 reactor fuel results in shift in water temperature co-efficient of reactivity to the positive region. On the other hand, when  $^{235}\text{U}$  is replaced by plutonium, the shift in temperature co-efficient of reactivity is in the negative region. Hence, it is possible to judiciously combine plutonium and  $^{233}\text{U}$  in the fuel composition such that the safety requirements with respect to temperature co efficient of reactivity is met. Addition of plutonium makes up for the deficiency of the reduction of  $^{233}\text{U}$ . Separate allocation of  $^{233}\text{U}$  and Pu appears to be preferable in comparison with mixed one in terms of improved efficiency in reactor control, lower neutron flux on reactor vessel and relatively simpler fresh fuel fabrication and reprocessing of spent fuel. Transition to a tight lattice in WWER-1000 raises the conversion ratio of  $^{232}\text{Th}$ - $^{233}\text{U}$  fuel but cannot convert the reactor into a thermal breeder reactor like the Shipping Port Light Water Breeder Reactor [25].

Calculations performed by Russian experts demonstrate possibility to achieve self-sufficiency in  $^{232}\text{Th}$ - $^{233}\text{U}$  fuel cycle with breeding ratio  $\geq 1.0$  in BN-800 type sodium cooled LMFBR [26]. Similar results have been reported from France also. In other type of reactors too, namely, HTGRs or Heavy Water Reactors, the calculations show the possibility of breeding ratio to approach 1.0 but not to exceed it.

In India, the vast thorium reserves are being judiciously utilized by pursuing a three stage indigenous nuclear power programme, as shown in Fig. 1, linking the ‘closed’ fuel cycles of Pressurised Heavy Water Reactors (PHWR), Liquid Metal-cooled Fast Breeder Reactors (LMFBR) and self-sustaining  $^{232}\text{Th}$ - $^{233}\text{U}$  based advanced thermal reactors [27]. In all the three stages,  $\text{ThO}_2$  is being introduced. In the first stage, namely the PHWRs, Zircaloy clad  $\text{ThO}_2$  pin assemblies are being used for neutron flux flattening of the initial core. The  $^{233}\text{U}$  obtained by reprocessing the spent  $\text{ThO}_2$  blankets from PHWRs is found to contain  $\sim 500$  ppm  $^{232}\text{U}$ . In the second stage, namely LMFBR, stainless steel 316 clad  $\text{ThO}_2$  blanket assemblies are in operation in the Fast Breeder Test Reactor (FBTR). The thoria blankets from fast reactors will produce  $^{233}\text{U}$  containing  $\sim 100$  ppm of  $^{232}\text{U}$  as reported for BN-800 [26]. The spent  $\text{ThO}_2$  assemblies from stage 1 and 2 are being reprocessed for recovery of  $^{233}\text{U}$  and recycling the same in the third stage as self-sustaining mixed ( $^{232}\text{Th}$ - $^{233}\text{U}$ ) $\text{O}_2$  in advanced water cooled thermal reactors. The Advanced Heavy Water Reactor of 300 MW(e) (AHWR 300), designed at BARC and presently being reviewed by the INPRO team of IAEA is the first major step in large-scale utilization of thorium in ‘closed’ fuel cycle. The AHWR would use Zircaloy clad 54-pin cluster of  $(\text{Th}, \text{Pu})\text{O}_2$  and  $(\text{Th}, ^{233}\text{U})\text{O}_2$  as driver fuel. During the last 3 decades, all aspects of thorium fuel cycle have been experienced in India on a laboratory scale. This includes fabrication of aluminium clad ‘J’ rods containing  $\text{ThO}_2$  pellets, irradiation of these ‘J’ rods in CIRUS research reactor at BARC, reprocessing the spent ‘J’ rods by the THOREX process for separation of  $^{233}\text{U}$  and manufacturing Al-clad, Al-20% $^{233}\text{U}$  plate fuel assemblies as driver fuel for the operating 30kWt research reactor, KAMINI at Indira Gandhi Centre for Atomic Research (IGCAR). In addition, Zircaloy clad test-pin assemblies containing  $(\text{Th}, \text{Pu})\text{O}_2$  pellets containing 4–7%  $\text{PuO}_2$  have been successfully irradiated in CIRUS to burnup of 18 000 MWd/t without any failure.



## 3.2. Nuclear systems and projects

### 3.2.1. Light water reactors

Several thorium-based fuel design options investigated in recent years [28], have demonstrated the basic feasibility of Th-based fuel cycles for light water reactor (LWRs) of current and next generation technology. Activities have focused on examining the Th- $^{233}\text{U}$  cycle as a replacement for conventional uranium-based fuels in existing LWRs, as well as a way to manage the growth of plutonium stockpiles by burning plutonium, or achieving a “net zero production,” sustainable re-cycle scenario. The fuel has to be designed to withstand very high burnup (above 100 000 MWd/kg). The fuel cycle costs are similar to those of conventional fuel. Two main implementation scenarios have been the focus of recent studies for pressurized water reactors (PWRs): homogeneous and heterogeneous. The homogeneous designs employ a mixture of  $\text{ThO}_2$   $\text{UO}_2$ , within each fuel rod, with uranium volume fraction and enrichment sufficient to obtain the required burnup and cycle length. The heterogeneous designs consider a seed-blanket approach, where U and Th fuel parts are spatially separated either within a given assembly, or between assemblies. The homogeneous studies have also considered “micro heterogeneous” schemes where the uranium and thorium fuel are spatially separated within a given fuel rod.

Two heterogeneous options have been examined under the Nuclear Energy Research Initiative (NERI) funded by the United States Department of Energy. The two approaches are: 1) the Seed-Blanket Unit (SBU, also known as the Radkowsky Thorium Fuel (RTF)) concept, which employs a seed-blanket unit that is a one-for-one replacement for a conventional PWR fuel assembly; and 2) the whole assembly seed and blanket (WASB), where the seed and blanket units each occupy one full-size PWR assembly and the assemblies are arranged in the core in a modified checkerboard array (Fig. 2).

The SBU and WASB approaches are both new fuel assembly designs, not new reactors, and are intended to be retrofittable into existing PWRs/WWERs with minimum changes to existing systems/hardware. In order to be attractive/receive serious consideration, they should also be competitive economically, and have characteristics comparable to those of existing LWRs (i.e., within the current “safety envelope”).

The improved performance is achieved by having the fuel-to-moderator ratios in the seed and blanket regions optimized to reduce Pu production in the seed, and enhance  $^{233}\text{U}$  production and burning *in situ* in the blanket. For both the SBU and WASB concepts, there is a significant reduction in the quantity and “weapons quality” of the plutonium that is produced: the production of Pu is reduced by a factor of ~3–5 relative to a standard PWR/WWER, and the plutonium that is produced has a high content of  $^{238}\text{Pu}$ ,  $^{240}\text{Pu}$ , and  $^{242}\text{Pu}$  which makes it impractical for use in a weapon. In addition, both approaches assume a once-through fuel cycle with no reprocessing, with the bred  $^{233}\text{U}$  burnt *in situ*; the  $^{233}\text{U}$  that is produced, is denatured by admixed uranium isotopes in order to force isotopic separation should extraction and use of the bred  $^{233}\text{U}$  be attempted. The residence time of the blankets (~6–9 years), and relatively high burnups, coupled with the superior neutronic performance of  $^{233}\text{U}$ , results in improved fuel utilization, as well as reductions in waste volume, decay heat and activity/toxicity.

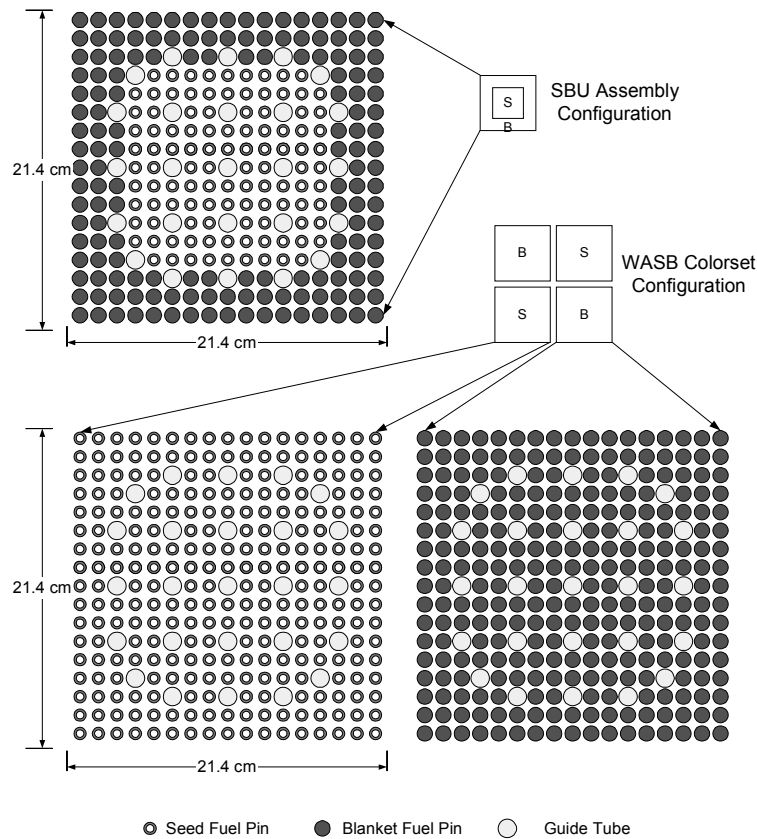


Fig. 2. Seed blanket unit (SBU) and whole seed and blanket (WASB) fuel assembly design.

### 3.2.1.1. Homogeneous/micro-heterogeneous implementation

A once through thorium-uranium dioxide ( $\text{ThO}_2\text{-UO}_2$ ) fuel cycle of no less than 25% uranium is necessary for normal PWR operating cycle lengths when the thorium is initially primed with denatured  $^{235}\text{U}$ . A homogeneous mixture of thorium and uranium will not be able to achieve the same burnup potential as the pure  $\text{UO}_2$  fuel. Spatial separation by at least a few millimeters of the uranium and thorium parts of the fuel can improve the achievable burnup of the thorium-uranium fuel. The mechanisms responsible for enhancing the achievable burnup upon spatial separation of the two fuels were evaluated. The neutron spectral shift was identified as the primary reason for the enhancement of burnup capabilities. Mutual resonance shielding of uranium and thorium was found to be a smaller factor.

A study of such micro-heterogeneous fuel designs for pressurized water reactors (PWRs), where the spatial separation of the uranium and thorium is on the order of a few centimeters was supported by a DOE-NERI. The study included three main heterogeneous geometries for the fuel: duplex pellet, axially micro-heterogeneous fuel, and a checkerboard of uranium and thorium pins in one assembly. It was found that the micro-heterogeneous fuel can achieve up to 15% higher burnup than the all-uranium fuel using the same initial  $^{235}\text{U}$ . However, denaturing of the  $^{233}\text{U}$  in the thorium portion of the fuel with small amounts of uranium significantly impairs this enhancement. The denaturing is necessary in some cases in order to reduce the power peaking in the seed-type fuel by improving the power share of the thorium region at the beginning of fuel irradiation. A combined axially heterogeneous fuel (with annular uranium fuel pellet region of 4 cm length separated by about 8 cm long region of duplex pellets where the uranium is inside the thorium) was found to meet thermal hydraulic

design requirements while still providing higher achievable burnup than the all-uranium case. However, the large power imbalance between the uranium and thorium regions creates several design challenges, such as higher fission gas release and significant axial cladding temperature gradients. The economics of manufacturing such fuel remains to be evaluated. However a reduction of plutonium generation by a factor of 3 in comparison with all-uranium PWR fuel using the same initial  $^{235}\text{U}$  content appears possible. There is also work under a NERI project examining a dispersion fuel of (Th, U) $\text{O}_2$  particles in a zirconium matrix that has high density, high thermal conductivity, and provides fission product containment.

### *3.2.1.2. Burning plutonium/transuranics*

The use of thorium-based fuels in combination with plutonium has two-fold advantages. First, the production of plutonium and higher actinides are reduced thus controlling the growth of plutonium. Secondly, the existing stockpiles of plutonium from spent nuclear fuels and dismantled nuclear weapons could be disposed off by burning the same. The viability of thorium-based fuels in PWRs for burning plutonium and transuranics are being investigated in details [35], in Europe and USA. Destruction rates and residual amounts of Pu and minor actinides (MA) in the fuel used for transmutation were examined. In general, the thorium based concepts consume approximately twice as much Pu as conventional (U–Pu) mixed-oxide fuel. Destruction of up to 1 000 kg of reactor grade Pu can potentially be burned in thorium based fuel assemblies per GWYear. Addition of MA to the fuel mixture degrades the burning efficiency. In general, evaluation of reactivity coefficients demonstrated the feasibility of designing a Th–Pu or Th–Pu–MA fueled core with negative Doppler and moderator temperature coefficients. Introduction of TRU containing fuels to a PWR core inevitably leads to lower control materials worths and smaller delayed neutron yields in comparison with conventional  $\text{UO}_2$  cores. Therefore, a major challenge associated with the introduction of Th–TRU fuels to PWRs will be the design of the whole core and reactor control features to ensure safe reactor operation.

### *3.2.1.3. Thorium utilization in a tight pitch BWR lattice*

Research on the utilization of thorium based fuels in the intermediate neutron spectrum of a tight pitch BWR lattice has been performed at Purdue and BNL as part of a DOE NERI project. This work complements the PWR–focused work described above. The focus of the work at Purdue was on the performance of thorium in tighter pitch BWR fuel lattices and to investigate whether thorium-based fuels possess advantages in intermediate neutron spectra [39]. The results of these studies showed that thorium-based fuels do have several attractive characteristics in the tight pitch lattice designs such as a more negative void coefficient, a higher fuel conversion ratio, improved non-proliferation characteristics and a reduced production of long lived radiotoxic wastes than corresponding uranium based fuels. Most high conversion light water reactors concepts fueled with plutonium in a tight pitch lattice have struggled with insuring a negative void coefficient of reactivity and have had to introduce some mechanical measures to augment neutron leakage effects such as void tubes within the fuel assemblies. One of the motivations for the Purdue work was to investigate whether thorium fuels in an intermediate spectrum possessed inherent neutronics properties that would insure negative void reactivity and thereby obviate the need for any mechanical measures to insure safe reactor operation.

### 3.2.2. *Heavy water reactors*

The advantages of using heavy water as a moderator are well understood. Its moderating ratio (the ratio of moderating ability to neutron absorption) is about eighty times that of light water, providing substantially better neutron economy than light water. For a breeding cycle, which is predicated on the availability of neutrons to breed fissile nuclides, the neutron economy of the reactor system is particularly important.

The majority of heavy-water power reactors in operation today are of a pressure tube design, employing small, simple fuel bundles and allowing on-power fuelling. The fuel bundle design greatly facilitates the production of exotic, potentially radioactive fuels. On-power fuelling permits careful reactivity management without the need for excessive neutron absorption by control devices or neutron poisons. The ability to fuel individual fuel channels also offers the possibility of independently adjusting the residence time of different fuel types in the same reactor core. All of these features could be of great benefit in the implementation of thorium fuel cycles. The current status of heavy water reactor design has been comprehensively described by the International Atomic Energy Agency [9].

Advanced heavy water designs are being pursued in Canada and India that use pressurized, boiling or super-critical light water as the coolant. These designs offer substantially reduced capital costs and allow improvements in other reactor operating characteristics. As well a, heavy water moderated, gas cooled reactor design has been examined in the Russian Federation.

#### 3.2.2.1. *Thorium fuel cycle options*

Because thorium itself does not contain a fissile isotope, neutrons must be initially provided by adding a fissile material, either within or outside the ThO<sub>2</sub> itself. How the neutrons are initially provided defines a variety of thorium fuel cycle options in HWRs that will be examined in this section. These include the following:

- The once-through thorium (OTT) cycles, where the rationale for the use of thorium does not rely on reprocessing the <sup>233</sup>U and recycling (but where reprocessing remains a future option);
- Direct self-recycle of irradiated thoria elements following the OTT cycle (no reprocessing);
- Other recycling options, ranging from reprocessing to the selective removal of neutron absorbing fission products; and
- The self-sufficient equilibrium thorium cycle, a subset of the recycling options, in which there is as much <sup>233</sup>U in the spent fuel as is required in the fresh fuel.

The OTT cycle emphasizes insitu generation as well as incineration of <sup>233</sup>U in the reactor by prudent fuel loading. However, the OTT cycle leaves behind substantial amounts of <sup>233</sup>U in the spent fuel, available for future recovery, as determined by economic or resource considerations.

High neutron economy, on power fuelling, channel design and simplicity of the fuel bundle provide a great deal of flexibility in approaches to the OTT cycle. In the original OTT concept, it was termed the ‘mixed channel’ approach, whereby channels would be fuelled either with ThO<sub>2</sub> bundles or with ‘driver’ fuel, typically SEU [45]. The driver fuel would

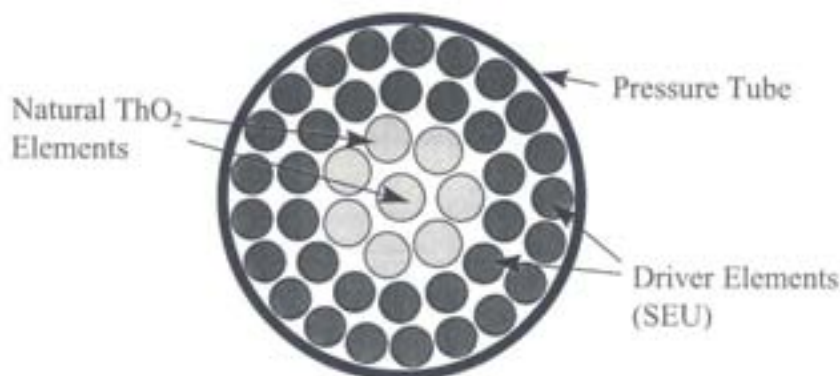


provide the neutrons required to convert  $^{232}\text{Th}$  to  $^{233}\text{U}$  in the thorium fuel. In such a system, the thorium would remain in the core much longer than the driver fuel would.

At low burnups, the thorium represents a load on the uranium, and therefore the presence of thorium causes a decrease in the energy obtained from uranium. With increasing thorium burnup, the  $^{233}\text{U}$ , which builds in, produces power, and the sum total of the energy extracted from the SEU and the thorium can become larger than that achievable with SEU alone. At still higher burnups, the accumulated fission product poisons cause the energy extracted to decrease once again. The total energy extracted will be the sum of the energy obtained from the thorium and the SEU. As the residence time of the thorium in the core increases, the energy obtained from a unit of mined uranium will first decrease, then, after passing through a minimum, will start to increase, finally becoming higher than it would have been had no thorium been present at all.

In the optimal mixed channel approach to the OTT cycle, a combination of feed rates, burnups, uranium enrichment and neutron flux level would be chosen in order that the cycle be economic (in terms of either resource utilization or monetary cost) compared with either natural uranium or SEU, without taking any credit for the  $^{233}\text{U}$  produced. Simple ‘scoping’ studies (using a lattice code) have shown that such OTT cycles do indeed exist, although their implementation would pose technical challenges to fuel management because of the disparity in reactivity and power output between driver channels and thorium channels [45]. Other driver fuels could also be considered, such as DUPIC fuel from recycled PWR fuel or MOX fuel [46].

An alternative approach has been developed in which the whole core would be fuelled with mixed fuel bundles, which contain both thorium and SEU fuel elements in the same bundle. Fig. 3 shows a CANFLEX ‘mixed bundle’ containing  $\text{ThO}_2$  in the central eight elements and SEU in the two outer rings of elements. This mixed bundle approach is a practical means of utilizing thorium in existing HWRs, while keeping the fuel and the reactor operating within the current safety and operating envelopes established for the natural uranium fuel cycle. Compared with natural uranium fuel, this option has better uranium utilization, comparable fuel cycle costs are not as low as for SEU, or for an ‘optimized’ OTT cycle using the mixed channel approach. This mixed bundle option is a practical means of utilizing thorium in operating HWRs, within the current safety and operating envelopes, and does not involve making any significant hardware changes.



*Fig. 3. CANFLEX mixed bundle.*

## Mixed bundle options

AECL has examined two mixed bundle strategies for burning thorium in existing CANDU 6 reactors [47]. In option 1, only one fuel type was used throughout the entire core, and the adjuster rods were removed. The reference fuel design for this study was a CANFLEX fuel bundle with 1.8% SEU in the outer 35 elements and natural ThO<sub>2</sub> fuel in the inner 8 elements. The initial fissile content was chosen to give UO<sub>2</sub> burnups that would be readily achievable without requiring significant development.

The second option illustrates the flexibility of existing CANDU reactors in accommodating both thorium fuel and adjuster rods. In option 2, the reactor core is divided into three regions, each containing a different type of thorium fuel bundle. The fuel in the 196 outer region channels is the same as that used in option 1. The fuel in the 124 inner region channels is identical to that in the outer region channels, except that the central ThO<sub>2</sub> element contains 6.0 wt% of gadolinium to shape the axial flux distribution. The gadolinium-doped bundles are only used in the inner, adjuster rod region of the core. The 60 outer-most channels contain thorium bundles designed to achieve burnups of over 50 MWd/kg HE. These high burnup thorium bundles use natural ThO<sub>2</sub> in all 43–fuel elements. However, the initial fissile content in the outer 35 elements is increased from 0 wt% to 1.7 wt% using 20 wt% enriched uranium. These high burnup thorium bundles are located strategically at the edge of the core in order to utilize a large percentage of the leakage neutrons to produce power. This arrangement significantly increases the amount of thorium fuel in the core and improves the overall fuel efficiency of the thorium-burning reactor.

## Direct self-recycle

Additional energy can be derived from the thorium by recycling the irradiated thorium fuel elements (which contain <sup>233</sup>U) directly, without any processing, into the center of a new mixed bundle [48]. Recycle of the central eight thorium elements results in an additional burnup of ~20 MWd/kg HE from the thorium elements, for each recycle. The reactivity of these thorium elements remains remarkably constant during irradiation for each recycle. This direct, self-recycling results in a significant improvement in uranium utilization compared with OTT: after the first recycle, the uranium requirements are ~35% lower than those of the natural uranium cycle, and more than 10% lower than those of the optimal SEU cycle, and remain fairly constant with further recycling. The cumulative uranium requirement averaged over a number of cycles is 30–40% lower than that of natural uranium fuelled CANDU reactors.

## Other recycling options

The burnup, and the energy derived from the thorium elements, could be increased even further by removal, before recycling, of the rare earth, neutron absorbing fission products from the spent fuel. Conventional reprocessing, the so-called ‘THOREX’ solvent extraction process, separates the uranium and the thorium from the fission products and other actinides. The radiation fields caused by the presence of <sup>232</sup>U (which emits α-particles) and its daughter products (particularly <sup>208</sup>Tl, which emits a 2.6 MeV γ-ray) provide a degree of self-protection and increase the proliferation resistance of recycle fuels containing <sup>233</sup>U. However, the absence of a commercial thorium recycling industry opens up the opportunity to develop a novel, simpler, more proliferation resistant recycle technology. For example, AECL has conceived a simple means of removing neutron absorbing, rare earth fission products, one which has a higher degree of proliferation resistance than the conventional thorax process and which would be much less costly. In this process, the spent fuel would be dissolved in nitric

acid and pH adjusted. Uranium and thorium precipitate at similar values of pH, levels at which the rare earth fission products remain largely in solution (precipitation of these requires a much higher pH). By adjusting the pH of the solution, the uranium, thorium and some radioactive fission products can be removed from solution, leaving the parasitic, neutron absorbing, rare earth fission products behind.

The resultant fuel would be highly radioactive, and this processing, as well as the subsequent fuel fabrication and handling, would be done remotely. This would greatly enhance the proliferation resistance of the fuel, since it would have a distinct radioactive signature for monitoring and would prove difficult to access for purposes of diversion. Moreover, the simplicity of the CANDU fuel bundle design would facilitate processing, remote fabrication and handling, and reduce the cost relative to more complex fuel designs. This recycle option would be more expensive than either the simple OTT cycle, or the direct self-recycle of irradiated thoria fuel elements into new bundles.

The benefit of removing the fission products from the spent thoria fuel can be seen from the extensive studies that were performed on thorium recycling options in the 1970s and 1980s in one study [49], a special version of WIMS–AECL was used to analyze and compare the resource utilization of various CANDU reactor fuel cycles, including once through natural uranium and SEU fuels, and recycle options based on both uranium and thorium. In these studies, a conventional reprocessing was assumed, and all fission products were removed from the recycle fissile material. The thorium cycles considered only homogeneous mixtures of ThO<sub>2</sub> and fissile material, the initial fissile material being either <sup>235</sup>U or plutonium. The <sup>233</sup>U and any remaining fissile topping material were recycled from the spent fuel, and new fissile topping materials were added to maintain burnup. A range of burnups was analyzed. The results show that for thorium cycles, the largest improvements in uranium utilization are realized in replacement reactors that inherit the <sup>233</sup>U produced in reactors that initially use thorium. For such systems in equilibrium, savings in natural uranium requirements of up to 90% (compared with once through fuelling with natural uranium) were indicated.

Thorium reactors are an important part of India's future nuclear programme, and the recycle of <sup>233</sup>U forms an essential part of ensuring a long term energy supply.

### **Self-sufficient equilibrium thorium cycle**

The ultimate uranium conserving fuel cycle would be the self-sufficient equilibrium thorium cycle, in which no fissile topping (and hence, no natural uranium) would be required in equilibrium, i.e. the <sup>233</sup>U concentration in the recycled fresh fuel matches the <sup>233</sup>U concentration in the spent fuel [50]. Further improvements in neutron economy would be required to achieve this: reducing the fuel rating to lower the flux and hence neutron capture in <sup>233</sup>Pa, increasing the moderator purity, removing the adjuster rods from the core, enriching the zirconium used in the pressure and calandria tubes to remove most of the high cross-section isotope, <sup>91</sup>Zr. However, the following studies do not give credit for such improvement.

The major shortcoming of the self-sufficient equilibrium thorium cycle is its low burnup, between 10 and 15 MWd/kg HE, which will not be economic in a cycle that requires reprocessing and remote fabrication of the <sup>233</sup>U-bearing fuel. To address this issue, a small amount of <sup>235</sup>U make-up could be added to each cycle, allowing the burnup to be increased as desired.

## High burnup open cycle

The high burnup thorium open cycle avoids the issues relating to closing the fuel cycle with reprocessing. In this cycle, the burnup is increased by trading off the conversion ratio. The thorium is enriched with  $^{235}\text{U}$  to give whatever burnup fuel can achieve. The spent fuel is not recycled (although this option would not be precluded). High burnup is equally possible with SEU, but the advantage of thorium over SEU lies in the fact that for very high discharge burnups, the initial fissile content required is lower with thorium fuel. In the case of low enrichments, SEU gives a higher discharge burnup for a given  $^{235}\text{U}$  enrichment, but with very high discharge burnups, the enrichment required for the thorium fuel is lower than that required for SEU. In theoretical assessments, pure  $^{235}\text{U}$  has been added to the thorium.

The main advantage of this thorium cycle compared with an equivalent enriched uranium cycle stems from the fact that as  $^{235}\text{U}$  is burnt, so  $^{233}\text{U}$  is built up, and as  $^{233}\text{U}$  is a superior fissile material than  $^{235}\text{U}$ , the reactivity versus burnup curve falls off more gradually with thorium than it does with enriched uranium. This means that to attain the same discharge burnup, the initial  $^{235}\text{U}$  content can be lower in the thorium cycle. To achieve a discharge burnup of around 66 MWd/kg HM (heavy metal), SEU requires an enrichment of 4.5% in a CANDU reactor, whereas thorium needs only 3.5% (in total HM). Added to this is the fact that thermal neutron absorption in thorium is about three times that in  $^{238}\text{U}$ , and that consequently the initial reactivity in the thorium core will be well below that of the SEU core for the same discharge burnup. This leads to lower reactivity swings, which is a definite operational advantage. This cycle is also an attractive method of plutonium annihilation, as it would have a very high plutonium destruction efficiency.

## Plutonium–thorium as a plutonium dispositioning option

A special application for thorium that has recently received attention is its use as a matrix material for the annihilation of weapons derived plutonium [51], [52]. This is a responsible, forward-looking strategy that uses plutonium to convert  $^{232}\text{Th}$  to  $^{233}\text{U}$ , which would be available as a future energy resource, if and when it is needed. The  $^{233}\text{U}$  would be safeguarded in the spent fuel benefiting from all the proliferation resistant features of spent  $\text{UO}_2$  or MOX fuel. As noted above, the radiation fields caused by the presence of  $^{232}\text{U}$  (which emits  $\alpha$ -particles) and its daughter products (particularly  $^{208}\text{Tl}$ , which emits a 2.6 MeV  $\gamma$ -rays), provide a high degree of self-protection and render the  $^{233}\text{U}$  unattractive as a weapons material. The  $^{233}\text{U}$  could be recovered in the future using a proliferation resistant technology, when warranted by the price of uranium and other factors.

The assessment of Pu– $\text{ThO}_2$  for plutonium management has been limited to reactor physics lattice calculations, using the multi group lattice code WIMS–AECL. Actinide inventories have been calculated using a fully coupled, multiregion WIMS–AECL/ORIGEN–S code package. Reactor calculations and fuel management simulations have not been performed. However, given the CANDU flexibility in fuel management, no technical feasibility issues are anticipated.

A somewhat different approach was taken in designing the Pu– $\text{ThO}_2$  fuel bundle for this application. To maximize the destruction of the plutonium, good neutron economy was desired. A reduction in void reactivity was also sought, to compensate for the faster dynamic behaviour of the fuel (shorter neutron lifetime and smaller delayed neutron fraction). To achieve these two objectives, the central elements in a CANFLEX bundle were replaced with a large central graphite displacer. Plutonium at 2.6% (354 g per bundle) was mixed with

thorium in the remaining 35 elements in the two outer fuel rings of the CANFLEX bundle. Enrichment grading in the outer two fuel rings would result in peak element ratings comparable to those in a 37–element bundle with natural uranium fuel. The resultant burnup was 30 MWd/kg HE, a burnup for which there is research reactor experience with Pu–ThO<sub>2</sub> fuel. Void reactivity was 8.6 mk, which is judged to be acceptable with the current shutdown system. Computer simulations also showed that using Sic instead of graphite in the central displacer reduces the magnitude of the void reactivity somewhat.

Addition of small amount of burnable poison to the central displacer would further reduce void reactivity, increase the plutonium loading per bundle as well as the absolute amount of plutonium destroyed, but would decrease the plutonium destruction efficiency. The plutonium destruction efficiency would be reduced from about 77% to 71% by poison addition that reduces void reactivity from about 8.6 mk to zero.

#### 3.2.2.2. *Advanced heavy water reactor design*

An advanced heavy water reactor (AHWR) of power 920 MWt/300 MW(e) has been designed as a forerunner of thorium-based reactors in India to maximize the energy potential of vast thorium resources (~518 000 tonnes - in terms of thorium metal). Table 2 summarizes the major design parameters of AHWR 300. Some of the salient features of this reactor are: (i) use of ThO<sub>2</sub>–based driver fuel: Zircaloy 2 clad (Th, Pu)O<sub>2</sub> and (Th, <sup>233</sup>U)O<sub>2</sub> fuel pin clusters, (ii) heavy water moderator as heat sink, (ii) boiling light water coolant, (iv) vertical pressure tube, (v) heat removal through natural circulation and (vi) on-power fuelling. The design logic and reactor physics objectives are as follows:

- The nearly 3 times higher thermal neutron absorption cross-section of <sup>232</sup>Th (7.4 barns), compared to that of <sup>238</sup>U (2.7 barns), reduces the fraction of thermal neutron absorption in coolant, moderator and structural materials, thereby, enabling to choose light water as coolant while retaining heavy water as moderator for better neutron economics.
- Heat removal in boiling mode is preferred for overall reduction of coolant quantity and improvement in steam cycle efficiency.
- The possibility of registering a positive void coefficient of reactivity with light water coolant has been countered by reducing lattice pitch, by making the lattice under moderated and by using a burnable absorber (Dy<sub>2</sub>O<sub>3</sub>) in the fuel cluster. Thus, the reactor has been engineered to obtain a negative void reactivity and in turn inherent safety.
- A vertical reactor becomes the obvious choice with boiling in channels in order to take the advantage of heat removal through natural circulation, which adds to the inherent safety of the reactor.
- The passive safety is further ensured by several engineered safety features such as a gravity-driven water pool, isolation condenser and large volumes of water that can totally submerge the core in the event of an accident.
- About 75% of the power produced in the reactor is contributed by thorium.
- The discharge burnup of the fuel is in the range of 20–24 MWd/kg.

- The Pu consumption and initial Pu inventory is kept low.
- The system is self-sustaining in  $^{233}\text{U}$ .

The AHWR core, shown in Fig. 4, has 500 lattice locations of which 452 are for fuel channels, 36 for shut-off rods and 12 for control rods. The fuel assembly in each channel has a length of 10.5 m and is suspended from the top. The assembly consists of a single long fuel cluster of length 4.3 m and two shield sub-assemblies. These sub-assemblies are held to each other through a quick connecting/disconnecting joint to facilitate handling.

Table 2. Major design parameters of AHWR

Reactor power	920 MW (Th)/300 MW(e)
Core configuration	Vertical, Pressure tube, 500 lattice locations (452 fuel channels + 36 shut off rods + 12 control rods).
Number of Fuel Clusters in the Core	452
Dimension of Fuel Cluster,	118 mm dia x 4.3 m length, 6 spacers
Number of Fuel pins in each Cluster,	54 fuel pins in 3 concentric rings
their configuration and other Components	Outer: 24 pins (Th-Pu) $\text{O}_2$ (3.25% Pu) Middle: 18 pins (Th- $^{233}\text{U}$ ) $\text{O}_2$ (3.75% $^{233}\text{U}$ ) Inner : 12 pins (Th- $^{233}\text{U}$ ) $\text{O}_2$ (3% $^{233}\text{U}$ ) Hollow Displacer Rod: $\text{ZrO}_2\text{-Dy}_2\text{O}_3$ Water Tube: Zircaloy 2, 36 mm OD x 2 mm thickness
Fissile material per cluster	$^{233}\text{U}$ : 2.3 kg; Pu: 1.75 kg.
Active fuel length (pellet stack)	3500 mm.
Clad Material	Zircaloy-2
Clad dimensions	11.2 mm OD, 0.6mm thick
Top and bottom tie plates	Stainless steel
Annual fuelling rate	102 fuel clusters
Average heat rating of fuel	10.56 kW/m.
Fuel burn up	24 000 MWd/Te.
Moderator	Heavy water
Reflector	Heavy water
Coolant	Boiling light water under natural circulation.
Total core flow rate	2306 kg/s
Core inlet temperature	261.4 °C (nominal).
Feed water inlet temperature	130 °C.
Average steam quality	17.6 %
Steam produced	405 kg/s.
Steam pressure and temperature	70 bars & 285°C.
Main Heat Transfer loop height	39 m.
Lattice pitch	270 mm: square pitch.
Pressure tube ID	120 mm.
Primary shut down system	36 nos. of shut off rods having $\text{B}_4\text{C}$ .
Secondary shut down system	Lithium Pentaborate solution injected in 32 nos. of poison tubes.

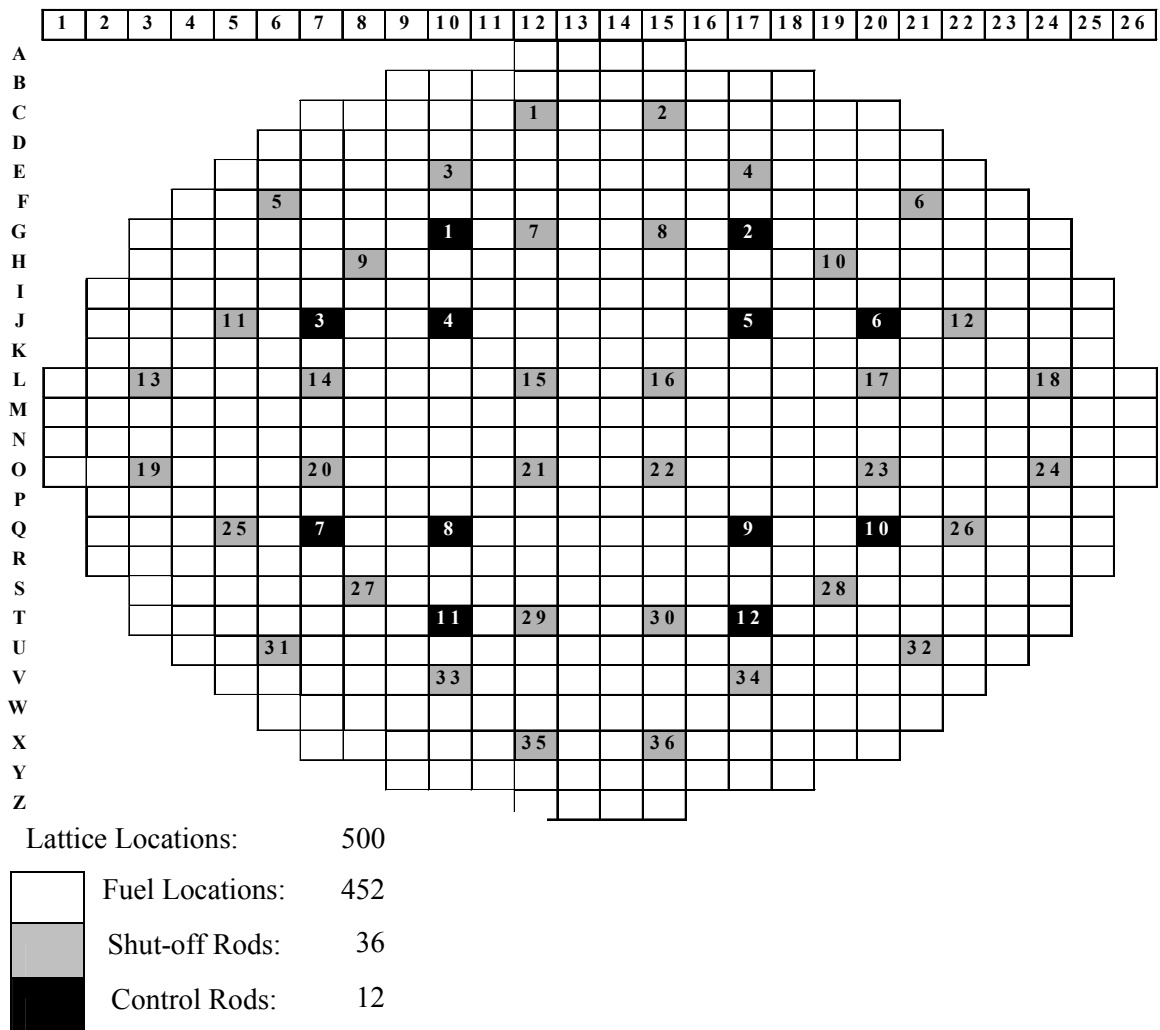
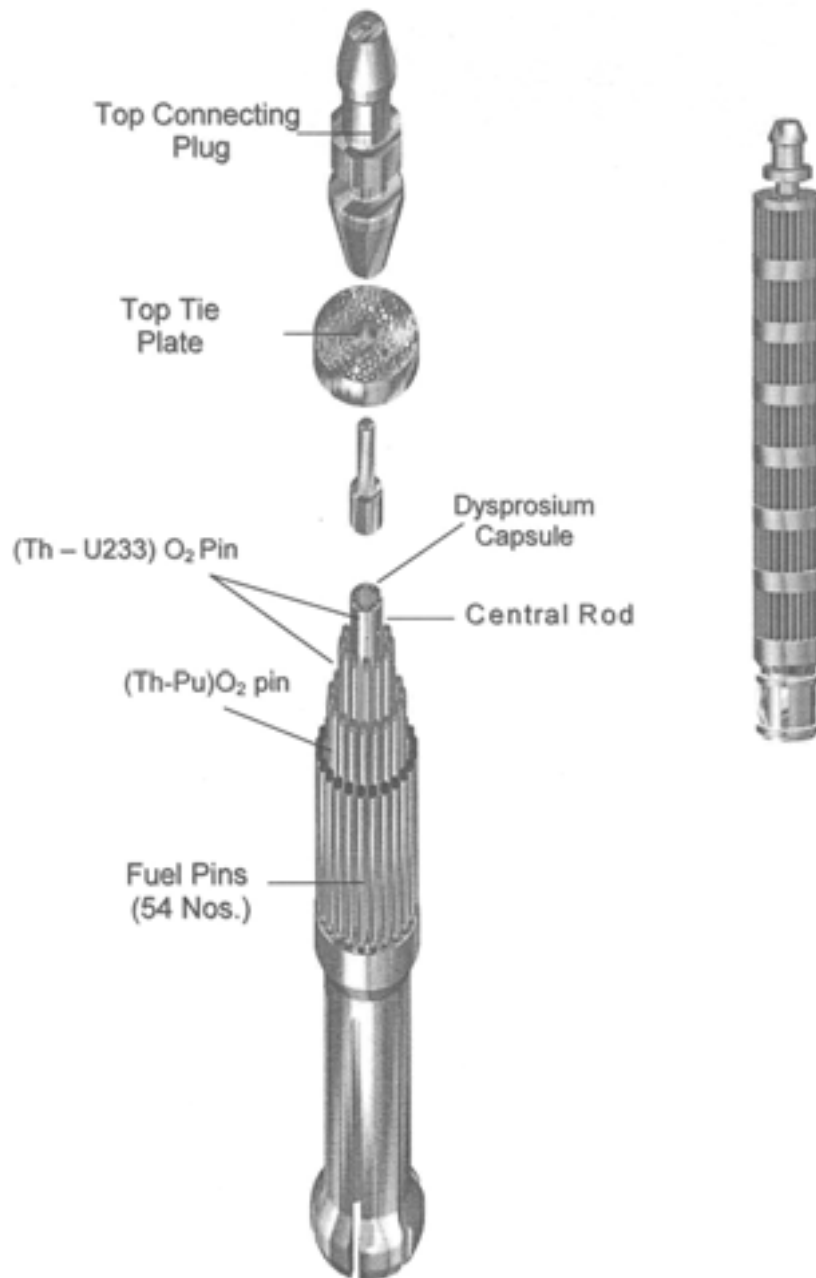


Fig. 4. AHWR core layout.

Fig. 5. shows the AHWR fuel cluster, which consists of 54 numbers of Zircaloy 2 clad fuel pins of outer diameter 11.2 mm, wall thickness 0.6 mm and a pellet stack length of 3 500 mm. The fuel pins in the cluster are arranged in three concentric rings having 12, 18 and 24 pins in the inner, middle and outer rings respectively. The 24 fuel pins in the outer ring contain high density (Th, Pu)O<sub>2</sub> pellets with 3.25% Pu. The fuel pins in the middle and inner rings contain high density (Th, <sup>233</sup>U)O<sub>2</sub> fuel pellets having 3.75% and 3% <sup>233</sup>U concentration respectively. The outer diameter of the fuel cluster is 118 mm. The fuel pins are assembled into a cluster by the top and bottom tie-plates with the central rod connecting the two tie-plates. There are 6 spacers along the length of the cluster. The hollow central rod contains ZrO<sub>2</sub>-Dy<sub>2</sub>O<sub>3</sub> and also functions as emergency core cooling system (ECCS) water injunction tube, as spacer capture rod and as tie-rod for the cluster. The dysprosium helps in achieving negative void coefficient of reactivity.



*Fig. 5. AHWR fuel cluster.*

### **AHWR and zero power critical facility in India**

A Zero Power Critical Facility (ZPCF) is being set-up at BARC, Trombay, Mumbai for reactor physics experiments to validate the physics design of the hitherto untried AHWR fuel in terms of multi-group cross-section libraries, lattice variables, pin-power distribution, simulation of reactivity devices, core flux and power distribution, void reactivity, etc. The reference core of the ZPCF will consist of 61 lattice positions of which 55 positions will be occupied by the reference fuel and the remaining 6 by the shut-off rods. The reference fuel will consist of 19-pin natural metallic uranium fuel clusters at a square pitch of 250 mm. The AHWR core will be replicated by replacing the 9 metallic natural uranium clusters in 3x3 array in the central region of the reference core by AHWR fuel clusters at a square pitch of



250 mm. The following two type of fuel clusters will be used in sequence in the core of the ZPCF:

- Set 1: 9 numbers of 54 fuel pin clusters—all the pins would be made up of (Th, Pu)O<sub>2</sub> fuel.
- Set 2: 9 numbers of 54 fuel pin clusters containing 24 pins of (Th, Pu)O<sub>2</sub> and 30 pins of (Th, <sup>233</sup>U)O<sub>2</sub>

Of the 9 clusters, experimental measurements will be made on the central fuel cluster only. The (Th, <sup>233</sup>U)O<sub>2</sub> fuel pin clusters for the CF will be assembled under water at the ZPCF site in a pool since the <sup>232</sup>U content in the <sup>233</sup>U is expected to be in the range of 500 ppm with radiation field of 0.3 to 0.8 Gy/h.

### **The advanced CANDU reactor**

Atomic Energy of Canada Limited has developed a reactor, the ACR™ (Advanced CANDU Reactor) that is an evolution from the well established CANDU 6 (over 90 reactor years of operating experience plus current construction experience). The ACR is designed to be an economical reactor choice for today with enhanced safety and reliability, while meeting expectations for sustainability. The potential for economical use of mixed oxide fuel (MOX) provides an economic means of ensuring adequate fuel supplies through recycling, thus enhancing sustainability. In the future, the ACR will be able to operate using a thorium fuel cycle.

The ACR reference design provides a design life of 40 years with an option to extend to 60 years. The design will be completed in time to have an operation start date of 2011. The ACR is a heavy water moderated, light water cooled reactor. Evolutionary changes from the CANDU 6 allow for a compact reactor core design, with the core of the 700 MW class having 284 channels, with 12 CANFLEX fuel bundles per channel. A once through fuel cycle is assumed in the reference design but the potential exists for alternative MOX, DUPIC or thorium fuel cycle options. Using light water as coolant requires some enrichment of the fuel, thus a fuel enrichment of 2% <sup>235</sup>U with 4.6% Dy in natural uranium in the central fuel element in the bundle is proposed SEU reference fuel for the once through fuel cycle. ACR is designed for operation with low-enriched fuels such as SEU at approximately 2% enrichment, for 21 MWd/kg(HM) burn up, or at up to about 4% for future operation at up to 45/MWd/kg(HM).

In particular, ACR, as designed for the reference SEU fuel cycle, can operate using MOX fuel with no design changes or operational changes. This is an important benefit, since a program of power operation can start with ACR using SEU fuel, and then, at the operator's choice of timing and degree, can move to MOX fuel with a seamless transition involving no unit downtime or power derating, or added capital cost.

As a thorium burner, the small, simple fuel bundle, fuel channel design, on-power fuelling and good neutron economy all facilitate a variety of possible fuel cycles. The lattice design provides an inherently negative coolant void coefficient for many thorium bundle design without the need to add neutron poisons to the middle of the bundle.

### **The super-critical CANDU reactor**

Looking further into the future, Atomic Energy of Canada Limited is pursuing designs for a supercritical light water reactor. In these designs, the thermal efficiency of the reactor is increased by running the coolant at much higher temperatures and pressures. The reactor coolant is operated beyond the supercritical point of light water.

This design is the next evolutionary step beyond the ACR. Increasing the temperature and pressure of the coolant breeds on the success of the ACR design. Preliminary physics calculations show that the reactor should perform well with thorium fuel cycles designed to meet a variety of user requirements.

### Heavy water moderated gas cooled ultimate safety reactor HWR–1000US

The new safety concept and the project of the heavy water power reactor HWR–1000US of 1000 MW electric power\* have been developed in the Moscow Institute of Theoretical and Experimental Physics (ITEP). The project is based on the safety concept referred to as the ultimate safety one. This means that the reactor system is designed in such a way that the large dispersal of radioactivity shall be precluded inherently and transparently following any scenarios of the fuel failures sequences, including those of core melting and destroying. These safety requirements are met by using the channel-type reactor concept whose key features are: 1) entire primary system arrangement within a multi-cavity pre-stressed concrete vessel (PCV) which retains the primary coolant pressure; 2) low temperature heavy water moderator; 3) gaseous coolant; 4) low fissile nuclides content in fuel. Combined together these features provide ultimate safety and exclusively high fuel cycle characteristics.

Large break LOCA is eliminated since the PCV basic feature is the impossibility of fragile failure. Coolant pressure is retained by PCV, and fuel channels are not loaded with the coolant pressure, that leads to considerable thinning of channel tubes and significant reduction of parasitic neutron capture. Non-slowng down gaseous coolant together with a relatively large radius of fuel channel (~ 10 cm) result in a rather high multiplication on fast neutrons. This provides a quite unique combination of a very well moderated neutron spectrum favourable for effective fissile isotopes utilization and a high fraction of fission in fertile isotopes (about of ~ 10%), thus increasing the neutron balance and hence the utilization of fuel, including the fuel with thorium (Table 3).

Table 3. Main HWR–1000US thorium fuel cycle characteristics

Parameter		Cycle type	
		Self-sustaining	With <sup>235</sup> U topping
External fissile isotopes topping	Kg/t	0	1
Fuel burnup	MWd/t	8 000	20 000
Fuel consumption at load factor 0.8	T/GW(e)/year	120	44
<sup>232</sup> U equilibrium concentration	Kg/t	0.008	0.014
<sup>233</sup> U equilibrium concentration	Kg/t	15.2	15.1
<sup>235</sup> U initial concentration	Kg/t	1.3	2.7
<sup>235</sup> U end concentration	Kg/t	1.3	1.7
Fissile isotopes loading	T/CW(e)	2.5	2.7
Processing time	Year	1	1
Processing losses	%	1	1
Breeding ratio		~1	0.96
Fissile isotopes consumption for equilibrium cycle establishing	T/CW(e)	4.0	4.4

\* Heavy Water Reactors: Status and Projected, Development, International Atomic Energy Agency, Technical Reports Series, No. 407, IAEA, Vienna (2002).

### 3.2.3. High temperature gas cooled reactor

In the past, thorium-based fuels have been successfully utilized in helium cooled high temperature gas cooled reactors (HTGRs) in Germany, USA [53], Japan and The Russian Federation. The fuels were in the form of ‘coated particles’ of  $\text{ThO}_2$ ,  $(\text{Th,U})\text{O}_2$ ,  $\text{ThC}_2$  and  $(\text{Th,U})\text{C}_2$ , popularly known as TRISO with a fuel kernel of diameter 350–500  $\mu$  with multilayer carbon and silicon carbide coatings ( $\sim 100$   $\mu$  buffer carbon layer on fuel kernel followed by inner and outer pyrolytic carbon coatings of  $\sim 40$   $\mu$  with 35  $\mu$  SiC layer in between). In Germany, two Pebble Bed HTGRs, namely AVR 15 MW(e) and THTR 300 MW(e), successfully operated till the late 1980s after which they were terminated. In Pebble Bed reactors, the coated fuel particles are embedded in graphite matrix and shaped into spherical fuel elements of diameter  $\sim 60$  mm. Coated fuel particles of mixed uranium thorium oxide and di-carbide, embedded in graphite, were also employed in the form of prismatic blocks in the helium-cooled HTGRs of USA, namely Peach Bottom (40 MW(e)) and Fort St. Vrain (330 MW(e)). The HTGR in UK, namely the Dragon reactor, has also used ‘coated fuel particles’ of mixed thorium uranium oxide and di-carbide in graphite matrix.

The US-led GIF has identified very high temperature reactor (VHTR) with helium coolant outlet temperature of 1000 C as one of the candidate nuclear energy systems deployable by the year 2025. For this, the reference reactor concept has been a 600 MWt, helium cooled prismatic block fuel of the gas turbine modular helium reactor (GT-MHR) or the pebble fuel of pebble bed modular reactor (PBMR). Th-based, ZrC coated fuel particles ‘TRISO’ of oxide, mixed oxide, di-carbide or mixed di-carbides in graphite matrix are strong candidate fuels for this type of reactor.

The HTGRs have considerable adaptability to different fuel cycles without change of active core design and main plant components and offers attractive opportunities of thorium utilization in combination with enriched uranium and plutonium [54]. The studies of fuel loads on the base of thorium with weapon quality  $^{235}\text{U}$  and  $^{233}\text{U}$ -Th fuel and also experience of Fort St. Vrain reactor operation [55] being the GT-MHR prototype showed a high effectiveness of these fuel compositions from the point of view of minimization of fissile isotopes consumption. Thus the operational conditions (ratio of fuel reloading, time between fuel reloading, limitations on an available operative reactivity margin) met the design aspects.

To use the HTGR neutron spectrum effectively in  $^{233}\text{U}$ -Th fuel ‘open’ cycle, the load of high metal component in fuel compact corresponding to moderator (carbon) to high-metal ratio ( $N_c/N_{TM} \geq 200$ ) is preferable. Compared to other fissile isotopes, in this case, the mean load of uranium in an active core as well as the consumption of uranium-233 per unit of energy generated will be least. Change over to a self-sustained fuel cycle can further lower the consumption of  $^{233}\text{U}$ . The minimum consumption of uranium in a closed fuel cycle amounts to  $\sim 0.27$  g/MW-day and this corresponds to the maximum possible load of high-metal component in fuel compact (6.1 g/compact). In comparison, the consumption of uranium in case of U-235-Th fuel is  $\sim 1$  g/MW-day. Due to various reasons (technological limitations, economical indexes), the optimum possible load of high metal component is 3 – 4 g/compact at minimum enrichment of  $\sim 4.5$  %. In case thorium is injected into the reflectors, the uranium consumption in a self-sustained fuel cycle can be reduced to  $\sim 30$  %, however due to economical reasons, this alternative will be hardly expedient. Self-sustained  $^{233}\text{U}$  reactor is not yet achieved.

### 3.2.4. Molten salt breeder reactor

Molten salt reactors (MSR) use graphite as moderator, molten fluoride salt of high boiling point ( $\geq 1400^{\circ}\text{C}$ ) with dissolved 'fissile' and 'fertile' materials as fuel and primary coolant and operate in an epithermal neutron spectrum. The core of MSR is usually a cylindrical graphite block that acts as moderator, through which holes are bored, in which the molten fluoride salt containing thorium uranium and plutonium circulates. The primary coolant, containing the fuel, flows to a primary heat exchanger, where the heat is transferred to a secondary molten salt coolant and then flows back to the graphite channel of the reactor core. The secondary coolant loop transfers the heat to the power cycle or hydrogen production facility. The operating temperature range of MSRs is between  $450^{\circ}\text{C}$ , the melting point of eutectic fluoride salts to around  $800^{\circ}\text{C}$ . In the secondary molten salt, the temperature is lower than the primary. The reactor and the primary systems are constructed of nickel-based alloys, modified Hastelloy-B and N, inconel or a similar alloy or other promising materials like Nb-Ti alloys for corrosion resistance to the molten salt. Volatile fission products (e.g. Kr and Xe) are continuously removed from the fuel salt. MSRs have a low inventory of fissile materials compared with other reactors because: (i) these are thermal neutron reactors needing less fissile inventory than fast reactors, (ii) a low fuel-cycle fissile inventory outside the reactor system, (iii) little excess reactivity is required to compensate for burnup because of fuel is added on-line, (iv) direct heat deposition in fuel/coolant that allows high power densities and (v) high absorption fission products such as Xe are continuously removed.

The 8 MWt Experimental molten salt reactor (MSRE), constructed in Oak Ridge National Laboratory (ORNL), USA in the 1960s as part of breeder reactor development programme, is the first and the only thorium-based MSR in the world. The 8 MWt MSRE had a core volume of  $<2\text{ m}^3$  and operated with a molten fuel cum coolant salt of composition  ${}^7\text{LiF}/\text{BeF}_2/\text{ThF}_4/\text{UF}_4$ , at an outlet temperature of  $650^{\circ}\text{C}$  and demonstrated: (i) the chemical compatibility of graphite moderator with fluoride salt, (ii) the removal of Xe and Kr from the fuel (iii) conversion of  ${}^{232}\text{Th}$  to  ${}^{233}\text{U}$  and in situ fission of the latter. The MSRE generated database on the physical, chemical and corrosion properties of molten salts, worked with different fuels, including  ${}^{235}\text{U}$ ,  ${}^{233}\text{U}$  and plutonium during 1965–1969 and paved the way for the conceptual design of a molten salt breeder reactor (MSBR) of 1 000 MW(e) in the mid 1970s. The graphite moderated MSBR–1000 was designed for achieving thermal breeding in  ${}^{232}\text{Th}$ – ${}^{233}\text{U}$  fuel cycle (breeding ratio  $\sim 1.06$ ) and generation of electricity using a steam cycle. The proposed fuel core had a volume of  $48.7\text{ m}^3$  with a molten salt composition of 71.7 mole%  $\text{Li}^7\text{F}$ , 16%  $\text{BeF}_2$ , 12%  $\text{ThF}_4$  and 0.3%  $\text{UF}_4$  and  ${}^{233}\text{U}$  and Th inventory of  $\sim 1\,500\text{ kg}$  and  $68\,100\text{ kg}$  respectively. The MSRE was shutdown in December 1969 and the MSBR–1000 was not constructed.

MSRs could be utilized for implementing the following Th fuel cycle options efficiently:

- 'Open' once through cycle that uses mixed  ${}^{232}\text{Th}$ – ${}^{235}\text{LEU}$  (low enriched uranium  $<20\%$   ${}^{235}\text{U}$ ) as fresh fuel, converts  ${}^{232}\text{Th}$  to  ${}^{233}\text{U}$  in situ and burns the latter in the reactor and involves no back end process that recovers 'fissile' material ( ${}^{235}\text{U}$ ,  ${}^{233}\text{U}$ ,  ${}^{239}\text{Pu}$  or  ${}^{241}\text{Pu}$ ) from the spent and discharged fuel salt.
- 'Closed'  ${}^{232}\text{Th}$ – ${}^{233}\text{U}$  thermal breeder cycle (breeding ratio:  $\sim 1.06$ ) with efficient removal of fission products (Xe/Kr) from the fuel salt outside the core, processing for  ${}^{233}\text{Pa}$  management on-line and addition of only  ${}^{232}\text{Th}$  in subsequent cycles after the first cycle.

- ‘Closed’  $^{232}\text{Th}$ - $^{233}\text{U}$ / $^{238}\text{U}$  denatured breeder cycle designed to maximize proliferation-resistance by minimal processing of the fuel salt and by addition of  $^{238}\text{U}$  to isotopically dilute and denature fissile  $^{233}\text{U}$  isotope. Though this lowers the breeding ratio marginally (slightly above 1.0) as compared to  $^{232}\text{Th}$ - $^{233}\text{U}$  ‘closed’ cycle, it ensures intrinsic proliferation resistance of the fuel cycle.

In recent years, several multinational collaborative programmes on thorium utilization in MSR have been initiated. In France, the AMSTER concept (Fig. 6) is being pursued [56]. AMSTER is a thermalized molten salt reactor working on  $^{232}\text{Th}$ - $^{233}\text{U}$  fuel cycle with an on-line reprocessing unit for removal of fission products and for feeding of heavy nuclei (U, Th, etc.) to the MSR. Russian and OECD studies have identified MSR as a potential component of thorium-based ‘closed’ fuel cycle to efficiently burn actinides and reduce the long term radiotoxicity of nuclear wastes [57]. In USA, MSBR with Multiheat Helium Brayton cycle is being examined with different thorium fuel cycle options primarily for actinide waste burning with the secondary interests of production of electricity and hydrogen and breeding and burning of ‘fissile’ fuels without separating them [58].

Molten salt (fuel & coolant,  $^7\text{LiF} - \text{BeF}_2 - \text{An.F}_4$ )

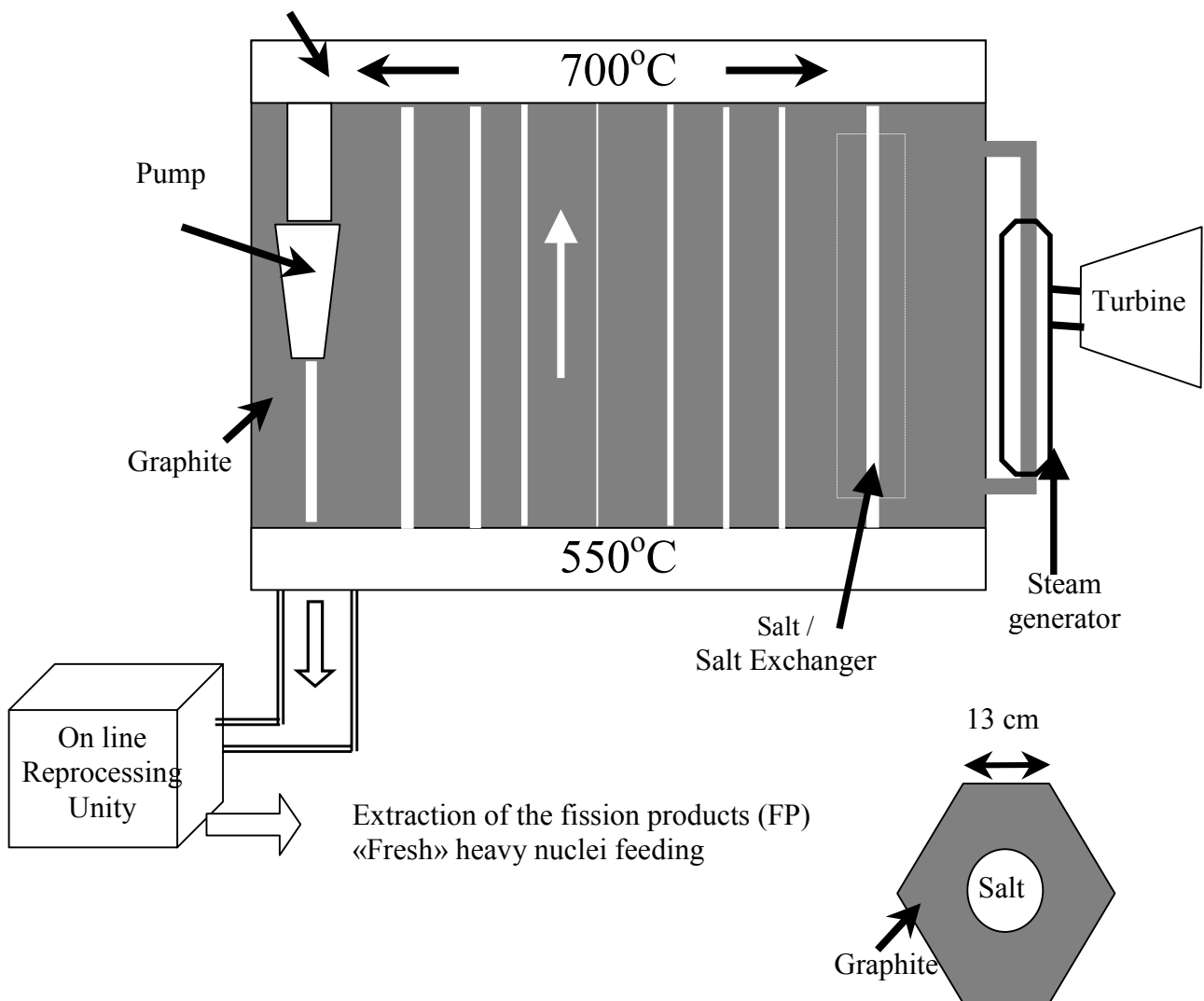


Fig. 6. Schematic of molten salt reactor.

### 3.2.5. Fast reactors

In the fast neutron spectrum,  $^{232}\text{Th}$  is less fissile than  $^{238}\text{U}$  and has a higher fission threshold energy. In addition, the  $\eta$  value increases much less with energy for  $^{233}\text{U}$  than for  $^{239}\text{Pu}$ .

Extensive investigations have been carried out in France on 'closed' thorium fuel cycle in fast neutron reactors and the following sequential approach has been proposed [15]:

- Design (Th,Pu) $\text{O}_2$  cores to burn Pu and breed  $^{233}\text{U}$  to initiate Th–U cycle in LMFBR
- Design (Th,  $^{233}\text{U}$ ) self-sustaining core with breeding ratio slightly >1.0 for multiple recycling of recovered thorium and uranium with or without other actinides.

Thorium utilization has been investigated with the reference European fast reactor (EFR: 3 600 MWt, 1 450 MW(e)) and CAPRA cores. In the EFR-like (Th,Pu) $\text{O}_2$  core (100 cm height x 405 cm diameter), the % volume fraction of  $\text{PuO}_2$  in  $\text{ThO}_2+\text{PuO}_2$  was assumed to be 20.45%, 24.95% and 29.98% in the three enrichment zones of the reactor and the isotopic composition of plutonium was assumed to be 52.54%  $^{239}\text{Pu}$ , 25.49%  $^{240}\text{Pu}$ , 9.8%  $^{241}\text{Pu}$ , 7.84%  $^{242}\text{Pu}$ , 1.96%  $^{238}\text{Pu}$  and the plutonium contained 2%  $^{241}\text{Am}$ . The EFR-like core contains axial (lower: 25 cm, upper: 15 cm) and radial (1 row of 78 assemblies) fertile  $^{232}\text{Th}$  blankets. In the CAPRA-like core, the two enrichment zones had  $\text{PuO}_2$  Vol.% in (Th, Pu) $\text{O}_2$  in the range of 43.2% and 45% with no axial or radial fertile blankets. The isotopic composition of plutonium for the CAPRA-like core was 38.95%  $^{239}\text{Pu}$ , 26.71%  $^{240}\text{Pu}$ , 13.06%  $^{241}\text{Pu}$ , 14.42%  $^{242}\text{Pu}$  and 5.5%  $^{238}\text{Pu}$  with  $^{241}\text{Am}$  content of 1.31% in plutonium. The following conclusions were drawn from these studies:

- There is ~35% decrease in sodium void reactivity of (Th, Pu) $\text{O}_2$  compared to the reference (U, Pu) $\text{O}_2$  core of EFR and even more (~65%) in a (Th, U) core. The Doppler constant is similar in (Th, Pu) $\text{O}_2$  cores and ~50% greater in (Th–U) cores than in standard (U–Pu) cores.
- Large plutonium consumptions in (Th–Pu) $\text{O}_2$  fuel, both EFR-like and CAPRA-like, compared to reference (U–Pu) $\text{O}_2$  fuel for EFR. The Pu consumptions were higher in CAPRA-like compared to the EFR-like and were 880 kg/GW(e).y and 660 kg/GW(e).y respectively.
- In EFR-like (Th–Pu) $\text{O}_2$  fuel with  $\text{ThO}_2$  fertile blanket, enough  $^{233}\text{U}$  is produced to feed a similar (Th–U) reactor after ~15 years of operation. Thus, with plutonium burning, it is possible to initiate  $^{232}\text{Th}$ – $^{233}\text{U}$  fuel cycle faster. A 'closed', self-sustaining  $^{232}\text{Th}$ – $^{233}\text{U}$  cycle is possible with indefinite recycling but with very long linear doubling time of nearly 300 calendar years without taking operating, ageing and cooling time of fuel into consideration. Hence,  $^{232}\text{Th}$ – $^{233}\text{U}$  fuel cycle is not so attractive for LMFBR for rapid growth of nuclear power programme.
- The  $^{233}\text{U}$  and  $^{232}\text{U}$  contents in EFR-like core after 1700 Effective Full Power Days (EFPD) operation + 5 years were 92.93% and 0.23% respectively. The  $^{233}\text{U}$  content in the blanket regions were much higher and 95%, 98% and 96% in lower axial, upper axial and radial blankets respectively. The  $^{233}\text{U}$  content in the  $\text{ThO}_2$  blankets of EFR-like ( $^{238}\text{Th}$ ,  $^{233}\text{U}$ ) $\text{O}_2$  core was higher than with (Th, Pu) $\text{O}_2$  core and in the range of 97.9%, 99% and >98% in the lower axial, upper axial and radial blankets respectively. These values were 90.28% and 0.22% respectively for the CAPRA-like core after 990 EFPD + 5 years.

Based on recent experimental irradiation of thorium blankets in BN-350, the Russians have reported that the  $^{232}\text{U}$  content in bred  $^{233}\text{U}$  could be brought down to extremely low levels ( $\leq 11$  ppm) by locating thorium blankets at a distance of 15–20 cm away from core border [59].

### 3.2.6. Accelerator driven system

In recent years, in various countries and at international level, the accelerator driven sub-critical system, popularly known as accelerator driven system (ADS) are being studied with specific objectives. In USA, Europe and Japan, the main objectives of ADS are incorporating inherent safety in nuclear energy systems and providing long term solutions to nuclear waste disposal by burning plutonium and minor actinides and transmutation of long lived fission products. The motivation in India is to develop ADS for safe and efficient breeding of  $^{233}\text{U}$  from the abundant thorium resources and provide sustainable nuclear energy security.

The ADS consists of three components, viz. (i) the ‘proton accelerator’, which produces protons of  $\sim 1$  GeV energy by a separate sector cyclotron (SSC) or Linac, (ii) the ‘target’ (Pb or Pb–Bi alloy) capable of releasing 20–30 spallation neutrons of emission energy below 20 MeV per accelerated proton of energy  $\sim 1$  GeV and (iii) a sub-critical reactor core of neutron multiplication factor in the range of 0.95–0.98, known as the ‘blanket’. In addition, the ADS has heat removal and electricity generation equipment.

The claims of enhanced safety characteristics are based on the fact that the ADS operates in a non self-sustained chain-reaction mode which reduces criticality concerns: the ADS is operated in a sub-critical mode and stays sub-critical, regardless of the accelerator being on or off. Moreover, the accelerator may provide a convenient control mechanism for sub-critical systems that would reduce (or even eliminate) the need of control rods. The sub-criticality itself adds an extra level of operational safety with regard to criticality insertion accidents. Among the various ADS concepts being studied, the principal ones are the (i) Energy Amplifier (EA) of the CERN Group proposed by Carlo Rubbia [60], (ii) the Waste Transmuter of Los Alamos National Laboratory advanced by Bowman [61], (iii) the ADS utilizing fast neutrons for incineration of higher actinides proposed at Brookhaven National Laboratory (Phoenix-project), now carried out in Japan as part of OMEGA programme [62] and (iv) the Russian accelerator driven technologies project [63]. Among the thermal spectrum ADS, pressurized light water reactor (PWR) with multiple spallation targets, pressurized heavy water reactors (PHWR), molten salt reactor (MSR) have been mostly studied though the fast neutron–ADS of Japanese and US designs are most suitable for burning (and not breeding) of actinides, using sub-critical fast reactor core with actinide nitride and metallic fuels. In general, for ADS–fast critical systems, the accelerator is not needed from the point of view of neutron economy but the advantages of using an accelerator are: (i) there is no initial excess reactivity and one may avoid use of control rods, (ii) the remaining reactivity swing is compensated by the accelerator, allowing to stretch the cycle and therefore reaching a high burnup, (iii) the subcritical margin leads to increased safety with less concerns regarding void coefficients and small delayed neutron fractions, which is especially relevant to minor actinide burning. The role of thorium in ADS–fast critical system is: (i) avoids production of higher actinides, (ii) limits the reactivity swing over the cycle, (iii)  $^{232}\text{Th}$  is easily converted into  $^{233}\text{U}$ , (iv) relevant if transuranic waste is absent.

The main characteristics of the selected ADS, a fast energy amplifier, is the use of a relatively small particle accelerator producing a beam having a 16 mA current of 1 GeV protons, that hit a flowing lead target for neutron production. These neutrons reach the sub-critical core, that

consists of carbon steel clad mixed thorium uranium oxide or mononitride pins with liquid lead as coolant. A liquid lead reflector encloses the core. The main objective of such an ADS is plutonium burning, clean energy generation and LWR waste incineration. The fast energy amplifier is suitable for the following core loadings containing thorium-bearing fuels:

- Mixed plutonium thorium oxide or mononitride for burning weapons-grade or civilian plutonium.
- Mixed Thorium–<sup>233</sup>U oxide or nitride for ‘clean’ energy production.
- Mixed high HEU–thorium oxide or nitride for burning HEU.

The detail studies revealed that the nitride fuel system burns slightly more Pu than the oxide fuel. The nitride fuel system produces about 20% more <sup>233</sup>U than the oxide fuel system but also a higher quantity of minor actinides. The oxide fuel energy amplifier system can incinerate 40% of the loaded Pu, while the nitride fuel system can destroy only 35%. However, taking into account the necessity of nitrogen isotopic separation [to avoid formation of radioactive <sup>14</sup>C from <sup>14</sup>N by (n,p) reaction], the mixed oxide fuel system is preferred, specially from the point of view of plutonium burning. The role of thorium based fuel in ADS and in fast critical system is more or less the same and there is no large difference in plutonium consumption.

### 3.3. Innovative fuel

The Nuclear Energy Research Initiative (NERI) project of the Department of Energy, USA has developed an innovative metal matrix dispersion, or cermet fuel consisting of (Th, U)O<sub>2</sub> microspheres (using LEU: <20% <sup>235</sup>U) of diameter ~50 micron in a zirconium matrix that can achieve high burnup in a ‘once-through’ cycle and disposed, without processing, as nuclear waste. The volume fraction ratio of fuel microspheres and zirconium matrix is 50:50. The use of mixed oxides prohibits the direct chemical separation of pure <sup>233</sup>U or <sup>239</sup>Pu. The blending of the actinide oxides helps to improve the proliferation-resistance of this innovative fuel. The high thermal conductivity of zirconium matrix enhances heat removal and keeps the fuel center temperature significantly lower compared to ‘pellet–pin’ design thereby minimizing fission product migration and fuel swelling. The metal matrix fuel has been manufactured by the novel ‘powder–in–tube–drawing’ technique, which consist of dry mixing or wet vibratory milling of zirconium powder with (Th, U)O<sub>2</sub> microspheres, loading the powder mixture in cladding tube and vibratory packing to obtain smear density in the range of 40–50% theoretical density. The tube containing the cermet powder mixture is then subjected to multiple drawing/heat treatment cycles for progressive densification of the cermet and reduction in the fuel pin diameter. The wet milling facilitates zirconium metal coating on the fuel microspheres, which enhances the ‘fission-heat’ transfer from the fuel through the metal matrix to the zirconium alloy cladding [64].

Japan is pursuing R&D activities on the innovative thorium-based hydride fuels for advanced Minor Actinides (MA) and plutonium burners with high safety characteristics [65]. The U–Th–Zr–H fuel has high thermal conductivity and consists of U–metal, Th–Zr<sub>2</sub>H<sub>x</sub> and ZrH<sub>x</sub> phases. The hydride fuel is manufactured by melting and casting ternary alloy of U–Th–Zr keeping atomic ratios of U:Th:Zr=1:4:10. Next, the alloy was hydrogenated and clad in stainless steel. The SS clad alloy fuel U–Th–Zr–H was irradiated in Japan Material Testing Reactor (JMTR) at thermal neutron fluence of 1.2x10<sup>20</sup> n/cm<sup>2</sup> at maximum pellet temperature of 554K with linear heat rate of 140 W/cm. Efforts are underway to develop thorium-based hydride fuel containing plutonium as an effective burning fuel of weapon-grade plutonium.



India has used the innovative  $^{233}\text{U}$ -bearing, Al-clad Al-20% $^{233}\text{U}$  plate fuel assemblies as driver fuel in the 30 kWt research reactor KAMINI at the Indira Gandhi Centre for Atomic Research (IGCAR) [66]. Al-clad Al-U alloy plate fuel assemblies containing  $^{235}\text{U}$  fissile material, in the form of HEU or more recently LEU, have been used in several non-power, multipurpose Material Test Reactors (MTR) all over the world. The KAMINI plate fuel elements were manufactured by the classical ‘picture frame’ technique followed by hot roll bonding. Addition of ~1% Zr to the Al-20% $^{233}\text{U}$  alloy during the melting, stabilized the relatively softer and higher uranium containing  $\text{UAl}_3$  phase and minimized the formation of the harder and lesser uranium containing  $\text{UAl}_4$  phase, which had a needle-like morphology and caused cracking during hot rolling. X-ray radiography followed by microdensitometric scan was utilized for outlining the fuel meat in the core and ensuring homogenous distribution of  $^{233}\text{U}$  in the fuel. The bonding was evaluated by ultrasonic technique. Such  $^{233}\text{U}$ -bearing fuel, after denaturing with  $^{238}\text{U}$ , could be used in place of LEU-based ( $^{235}\text{U}$ ) fuel, in MTR.

Thorium-based metallic fuel is of great interest to commercial LMFBRs with excellent safety features. The compositions under consideration are Th-20%U, Th-20%Pu, Th-20%Pu-4%U and Th-20%Pu-4%U-8%Zr. The metallic fuel pins have been manufactured by Argon National Laboratory (ANL, USA), as part of Experimental Breeder (EBR-II) fuel development programme, by induction melting of Th, U, Pu & Zr metal buttons in graphite crucibles followed by vacuum injection casting in high purity silica tubes. However, reprocessing of thorium based metallic fuel has not been attempted so far. Thermo-chemical modeling of reprocessing Th-U-Pu-Zr metallic fuel by electro-refining process has indicated that thorium will remain in anode compartment forming metallic waste together with zirconium and noble metals, while uranium-plutonium and minor actinides together with some fraction of rare earth elements can be separated and co-deposited in liquid cadmium cathode [67]. As part of inert matrix fuel development programme for incineration of plutonium, Japan has developed rock-like fuel consisting of a polyphase mixture of (Th, Pu) $\text{O}_2$  +  $\text{MgAl}_2\text{O}_4$  +  $\text{AlO}_3$  was prepared and irradiated in JPR3 reactor to burnup of 21-28% [68]. In addition, a thorium-based nitride fuel is also being developed in Japan for lead-cooled Fast Breeder Reactors for enhancement of safety, economics and breeding potential [69].

## 4. CURRENT INFORMATION BASE

### 4.1. Nuclear data and methods

Table 4 summarizes the important cross-section data of  $^{232}\text{Th}$ ,  $^{233}\text{U}$ ,  $^{235}\text{U}$ ,  $^{238}\text{U}$ ,  $^{239}\text{Pu}$  and  $^{241}\text{Pu}$  in thermal and epithermal neutron spectrum. In these energy regions, the neutron capture cross-section of  $^{232}\text{Th}$  is nearly two and half times higher than that of  $^{238}\text{U}$  but the resonance integral for the capture cross-section of  $^{232}\text{Th}$  (85.6 barns) is lower than that of  $^{238}\text{U}$  (278 barns) [70]. A high capture rate in the fertile material implies that in thorium-based reactor, there is a need for higher feed enrichment, though in well moderated reactors like the Heavy Water Reactors,  $^{232}\text{Th}$  will always be a better fertile material than  $^{238}\text{U}$  and breed fissile material more efficiently. Of the three ‘fissile’ materials,  $^{235}\text{U}$ ,  $^{239}\text{Pu}$  and  $^{233}\text{U}$ , in the thermal and epithermal region, the  $\eta$  ratio (neutron yield per fission to neutron absorbed) of  $^{233}\text{U}$  is the best as shown in Figure 7. Further, the fission products from  $^{233}\text{U}$  are less poisoning than those from  $^{235}\text{U}$  or  $^{239}\text{Pu}$ . The criticality characteristics of  $^{233}\text{U}$  lie approximately between those of  $^{235}\text{U}$  and  $^{239}\text{Pu}$ .

Table 4. Summary of neutronic properties of 'Fissile' ( $^{233}\text{U}$ ,  $^{235}\text{U}$  &  $^{239}\text{Pu}$ ) and 'Fertile' ( $^{232}\text{Th}$  &  $^{238}\text{U}$ ) isotopes in thermal [average over Maxwellian spectrum at 300°C (0.05eV)] and Epithermal region

Nuclear Data	$^{232}\text{Th}$	$^{233}\text{U}$	$^{235}\text{U}$	$^{238}\text{U}$	$^{239}\text{Pu}$	$^{241}\text{Pu}$
Thermal						
Cross-section (barns)						
Absorption $\sigma_a$	4.62	364	405	1.73	1045	1121
Fission : $\sigma_f$	0	332	346	0	695	842
$\alpha = \sigma_c / \sigma_f$		0.096	0.171		0.504	0.331
$\eta_{\text{th}}$		2.26	2.08		1.91	2.23
Epithermal Resonance	0	764	275	0	301	
Integral (RI) barns						
( $\propto$ dilution)						
$\text{RI}_a$	85.6	882	405	278	474	740
$\text{RI}_f$		746	272		293	571
$\alpha = \text{RI}_c / \text{RI}_f$		0.182	0.489		0.618	0.296
$\eta_{\text{epi}}$		2.10	1.63		1.77	2.29
Neutron Yield $\nu$		2.48	2.43		2.87	2.97
Delayed Neutron Yield $\beta$		0.0031	0.0069		0.0026	0.0050
Capture:						
2 200 m/s value	7.6	54	100	2.7	267	
Resonance integral	85	140	144	275	200	
Neutron/fission (on average)		2.5	2.4			2.9

In reactors with harder neutron spectrum like the HTGRs, the segregated fuel geometry allows more neutrons to slow down through the resonance energy region thereby reducing the probability of capture. For such dispersed fuel configurations,  $^{232}\text{Th}$  is again a better fertile material. The fission cross-section of both  $^{232}\text{Th}$  and  $^{238}\text{U}$  is zero up to neutron energy of 0.1 MeV. For  $^{232}\text{Th}$ , the value of fission cross-section remains zero up to 1.0 MeV and only above 1.4 MeV neutron energy, the fission cross-section is in the range of 0.01. However, for  $^{238}\text{U}$ , the fission cross-section is already significant at energies below 1.0 MeV. Hence, in  $^{238}\text{U}$ - $^{239}\text{Pu}$  fuelled fast reactor, nearly 15% of the fissions take place in  $^{238}\text{U}$ , whereas in a  $^{232}\text{Th}$ - $^{233}\text{U}$  fuelled fast reactor, only 2% of the fission takes place in  $^{232}\text{Th}$ . In thermal neutron spectrum, the fission of  $^{232}\text{Th}$  in both thermal and fast neutron spectrum is of minor importance. Hence, fast fission of  $^{238}\text{U}$  is of significance in both thermal and fast reactors.

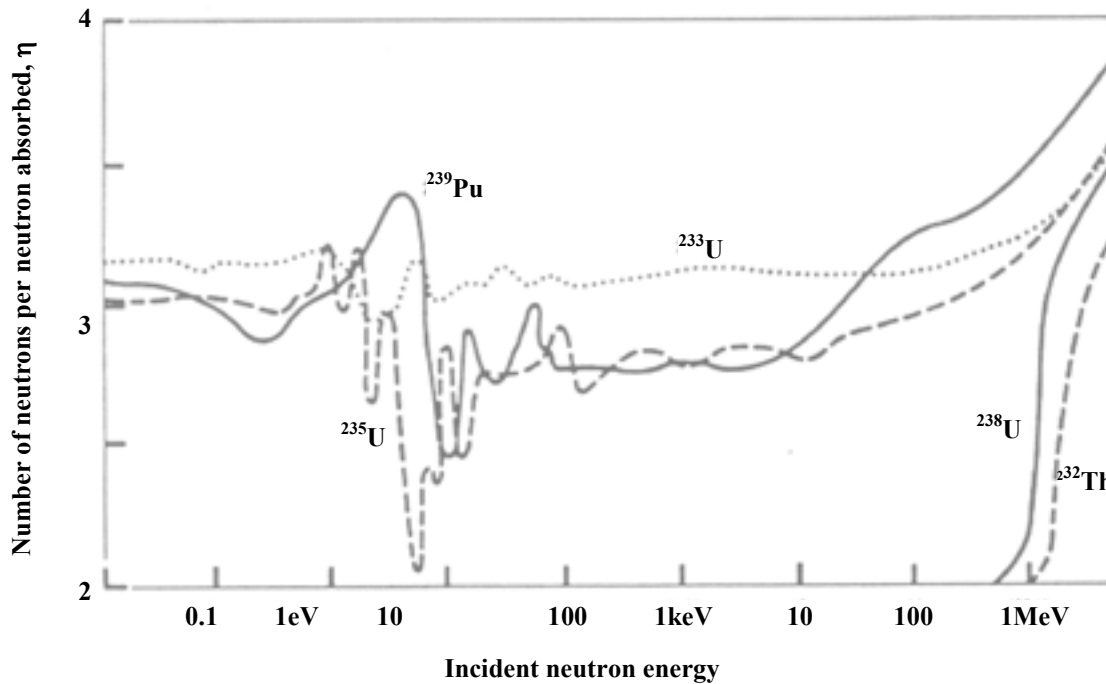


Fig. 7. Neutron yield per neutron absorbed [71].

In thermal neutron spectrum,  $^{233}\text{U}$  is the best fissile material because of its much lower neutron capture cross-section (54 barns) compared to that of  $^{239}\text{Pu}$  (267 barns) and  $^{235}\text{U}$  (100 barns), even though  $^{239}\text{Pu}$  produces a higher number of neutrons per fission than  $^{233}\text{U}$ . In addition, the higher plutonium isotopes build up to a greater extent than the higher isotopes of  $^{233}\text{U}$  because of the higher capture cross-section of  $^{239}\text{Pu}$  and its higher isotope like  $^{240}\text{Pu}$ . Hence,  $^{232}\text{Th}$ - $^{233}\text{U}$  cycle is likely to consume less fissile material, net per fission compared to  $^{238}\text{U}$ - $^{239}\text{Pu}$  though in case of the former, a higher fissile inventory would be required. The delayed neutron fraction ( $\beta_{eff}$ ) of  $^{233}\text{U}$  and  $^{235}\text{U}$  is 0.31% and 0.69% respectively. Thus, the uranium cycle ( $^{235}\text{U}$ -based) is relatively more benign than thorium ( $^{233}\text{U}$ -based), at least in the beginning of the cycle. Later,  $^{239}\text{Pu}$ , which has a  $\beta_{eff}$  value of 0.26%, builds up in the uranium cycle and the average delayed neutron fraction decreases.

The database for Th-U and Th-Pu systems are significantly scanty and less reliable compared to the well-established U-Pu system. Presently, in most cases, the nuclear data files JENDL-3.2 and ENDF/B-VI(Rev.5) of IAEA/NDS are used which consists of both evaluated and experimental data. These need to be revalidated. The following Table shows the accuracy of the nuclear data needed for Fast Reactors in a one-group approximation. The experimental data are insufficient, and the scatter of the results of measurements exceeds the estimated measurement errors in most cases. Lately, in Japan, some measurements of neutron induced fission cross sections of  $^{229}\text{Th}$  and  $^{231}\text{Pa}$  have been made which are summarized in Fig. 8.

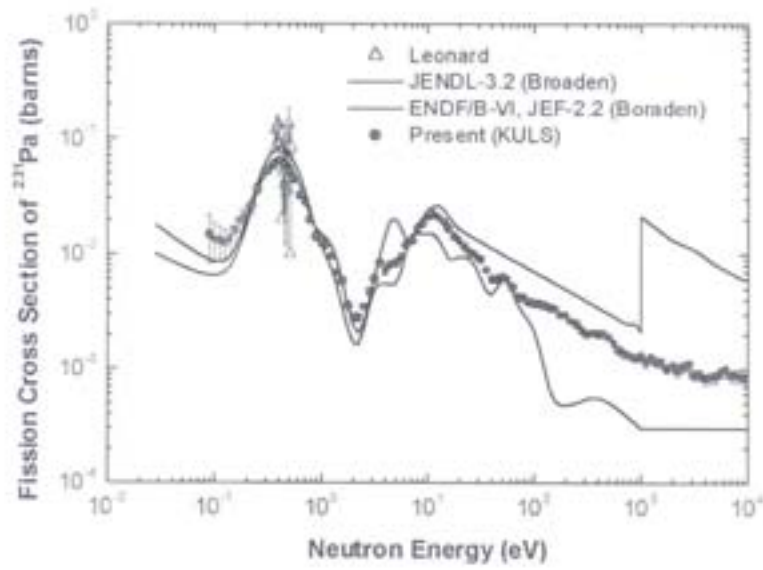
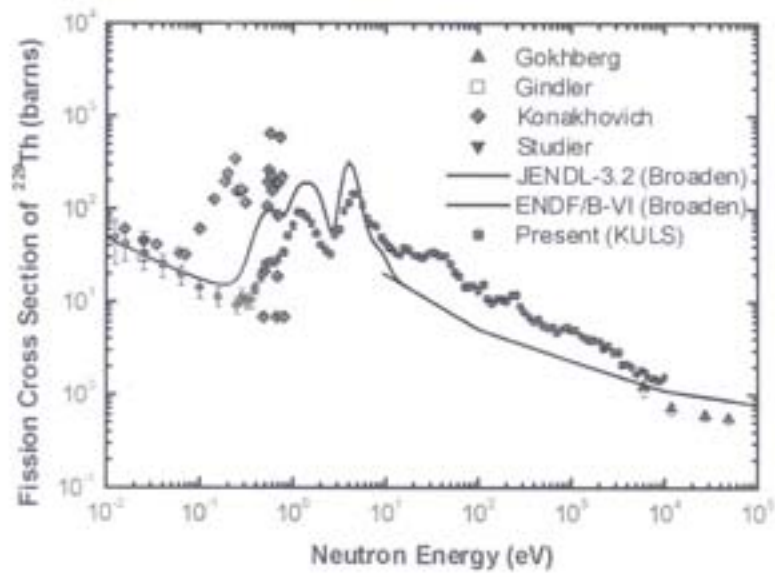


Fig. 8. Comparison of measured and experimental/evaluated fission cross-section data of  $^{229}\text{Th}$  and  $^{231}\text{Pa}$  at different neutron energy.

The following Table 5 shows the nuclear data accuracy requirements for fast reactors in a one group approximation [72].

Table 5. Nuclear data accuracy requirements for fast reactors in a one group approximation [72]

Reaction cross-section	<sup>233</sup> U	<sup>232</sup> Th	<sup>234</sup> U	<sup>232</sup> U	<sup>231</sup> Pa
$\sigma(n,f)$	1	1	5	25	20
$\bar{v}$	0,5	1	3	-	-
$\sigma(n,\gamma)$	3	2	5	75	20
$\sigma(n,n')$	5-10	5	10	-	-
$\sigma(n,2n)$	10	10	15	-	50
$\sigma(\text{tot})$	2	-	5	-	-
$\sigma$ for formation of <sup>1</sup> H, <sup>3</sup> H, <sup>4</sup> He	15	15	20	-	-
Basic role in the reactor	Chain reaction	Chain reaction, <sup>233</sup> U production	Chain reaction, <sup>235</sup> U production	Back-end	Back-end

#### 4.2. Fuel properties and irradiation behaviour

Table 6 summarizes the major materials properties of ThO<sub>2</sub>, UO<sub>2</sub> and PuO<sub>2</sub> of relevance to nuclear fuels [73]. ThO<sub>2</sub>-based mixed oxide fuels are expected to have superior thermophysical properties, such as higher melting point, better thermal conductivity and lesser release of fission gas as compared to UO<sub>2</sub>-based mixed oxide. Recently, the FRAPCON-3Th modeling of thorium-based fuels has led to the conclusion that for LWR application, the fuel performance improves when using a homogeneous thorium-uranium fuel matrix. For high burnup, the fission gas release, the fuel swelling, and the fuel centerline temperature are lower for mixed thorium-uranium oxide compared to the standard UO<sub>2</sub> pellets.

As part of thorium-based fuel development programme for fast breeder reactors, the thermophysical properties of mixed thorium-plutonium oxide pellets of both thorium and plutonium-rich compositions were evaluated in India. The plutonium-rich mixed oxide pellets contained 70–80% PuO<sub>2</sub> which could be considered as candidate fuel for small LMFBR core like the operating fast breeder test reactor. The thorium-rich compositions contained 20–30% PuO<sub>2</sub> which could be considered as alternative fuel for large LMFBRs like the forthcoming Prototype Fast Breeder Reactor (PFBR-500). The mixed oxide pellets were prepared by “powder-pellet” route involving mechanical mixing of ThO<sub>2</sub> and PuO<sub>2</sub> powders followed by cold pelletization and high-temperature sintering [74]. Small amount of Nb<sub>2</sub>O<sub>5</sub> (0.25wt%) or CaO (0.5wt%) powder were used as “sintering aid” and admixed with the powder during co-milling. The sintered pellets were evaluated in terms of density, oxygen-metal ratio and microstructure. The important thermophysical properties evaluated for these fuels are:

- Thermal diffusivity and in turn thermal conductivity as a function of temperature:
- Coefficient of thermal expansion in different temperature ranges:
- Hot-hardness as a function of temperature and in turn “indentation creep”.

Table 6. Comparative physical properties of UO<sub>2</sub>, PuO<sub>2</sub> and ThO<sub>2</sub> fuels

Property	U	UO <sub>2</sub>	Pu	PuO <sub>2</sub>	Th	ThO <sub>2</sub>
Crystal structure	- Orthorhombic [RoomTemp(RT). up to 935 K] - Tetragonal (935 K- 1045K) - B.C.C (1045 K – MP)	FCC (CaF <sub>2</sub> type)	6 Phases Important Phases: - Monoclinic (RT upto 392 K) - F.C.C. (583 K– 723 K) - B.C.C. (745 K – MP)	FCC (CaF <sub>2</sub> type)	- F.C.C (RT-1673K) - B.C.C. (1673 K- MP)	FCC (CaF <sub>2</sub> type)
Melting point (MP), K	1405	~3123	913	~2623	2025	~3643
Theoretical Density, g/cm <sup>3</sup> at 298K	19.05	10.96	19.86	11.46	11.68	10.00
Thermal conductivity Wm <sup>-1</sup> K <sup>-1</sup>						
773 K	30	4.80	30	4.48	43.1	6.20
1773 K	-	2.40	-	1.97	-	2.40
Co-efficient of thermal expansion (K <sup>-1</sup> )	14.2x10 <sup>-6</sup> Randomly oriented Polycrystal (30-600 K)	10x10 <sup>-6</sup> (298- 1223 K)	56x10 <sup>-6</sup> (main value α-phase)	11.4x10 <sup>-6</sup> (298- 1223 K)	11.9x10 <sup>-6</sup> (30-600K)	9.67x10 <sup>-6</sup> (298- 1223 K)

The thermal diffusivity “α” is usually measured by the laser flash technique. The thermal conductivity “k” at a particular temperature is computed from the measured value of α at that temperature, utilizing the following relation:

$$k = \alpha \times \rho \times C_p$$

where ρ is the density and C<sub>p</sub> the specific heat of the material at that temperature.

The experimental thermal conductivity data of hypo-stoichiometric and stoichiometric mixed thorium-plutonium oxide up to 1850 K, recently generated in BARC, India, by employing the “Laser-flash” technique for measurement of thermal diffusivity, are summarized in Fig. 9 & Fig. 10. As expected, for the F.C.C./CaF<sub>2</sub> type ThO<sub>2</sub>-based mixed oxides, the thermal conductivity was found to progressively reduce with temperature.

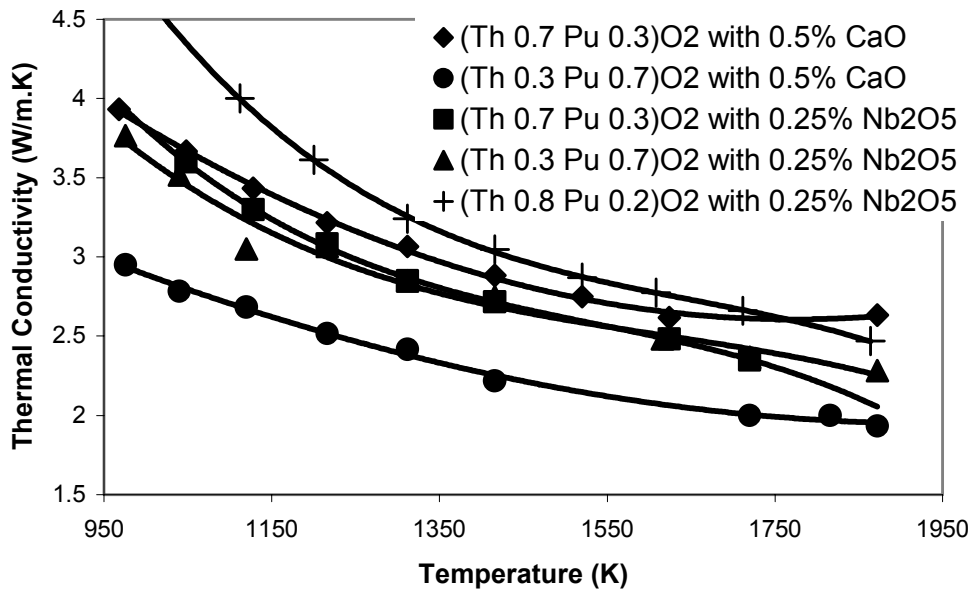


Fig. 9. Thermal conductivity of high density mixed thorium plutonium oxide pellets with Nb<sub>2</sub>O<sub>5</sub> or CaO “sintering aid”.

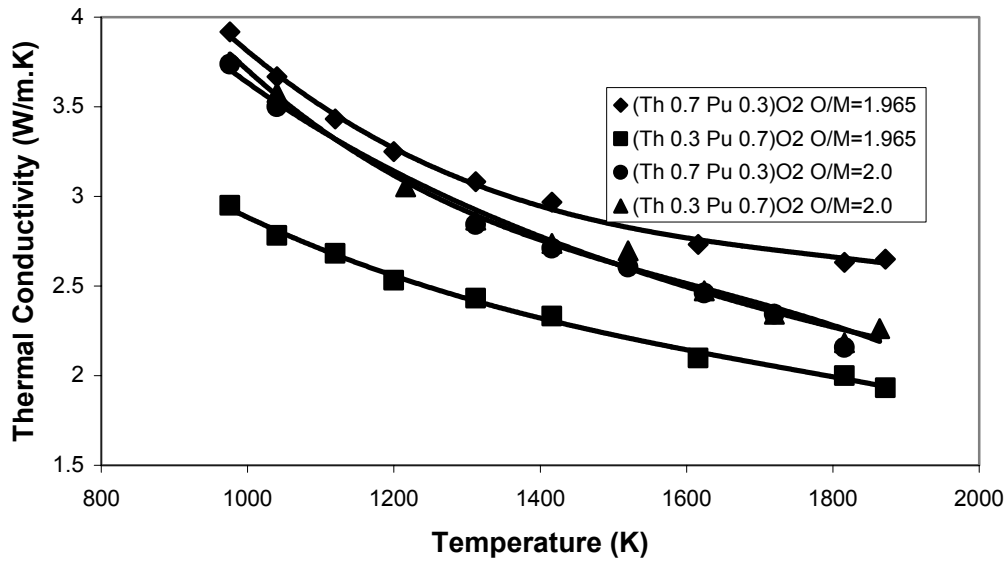


Fig. 10. Inter-comparison of experimental data on thermal conductivity of thorium and plutonium rich (Th,Pu)O<sub>2</sub> pellets with two different oxygen to metal ratios.

These experimental data match well with the thermal conductivity of Th,UO<sub>2</sub> pellets recently computed by Loewen et al using modified sub-routine FTHCON of FRAPCON-3 code as shown in Fig. 11.

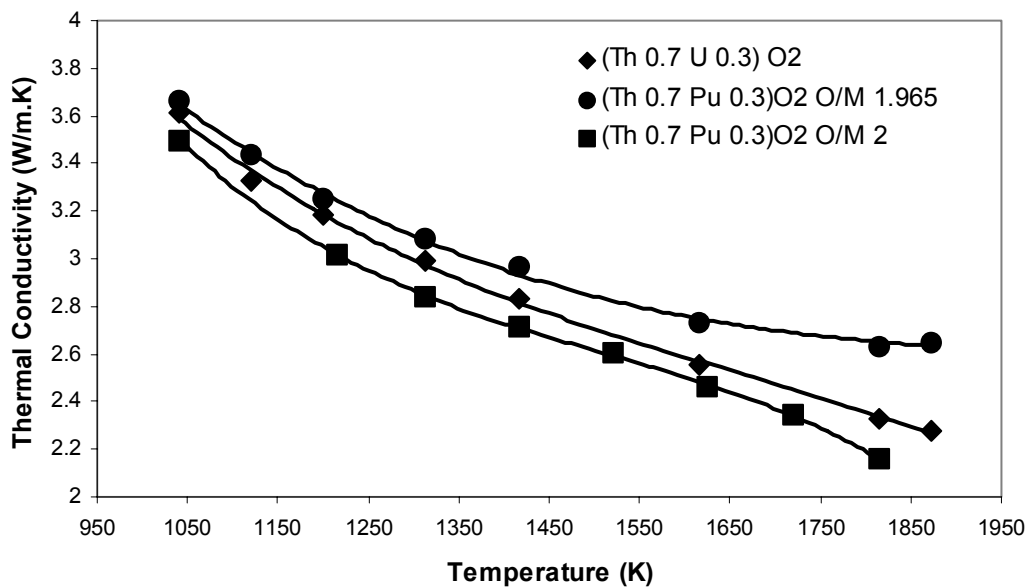


Fig. 11. Inter-comparison of experimental thermal conductivity data of  $(Th,Pu)O_2$  of different oxygen to metal ratio with computed data (FRAPCON-3Th) of  $(Th,U)O_2$  containing the same amount of  $ThO_2$  in both cases.

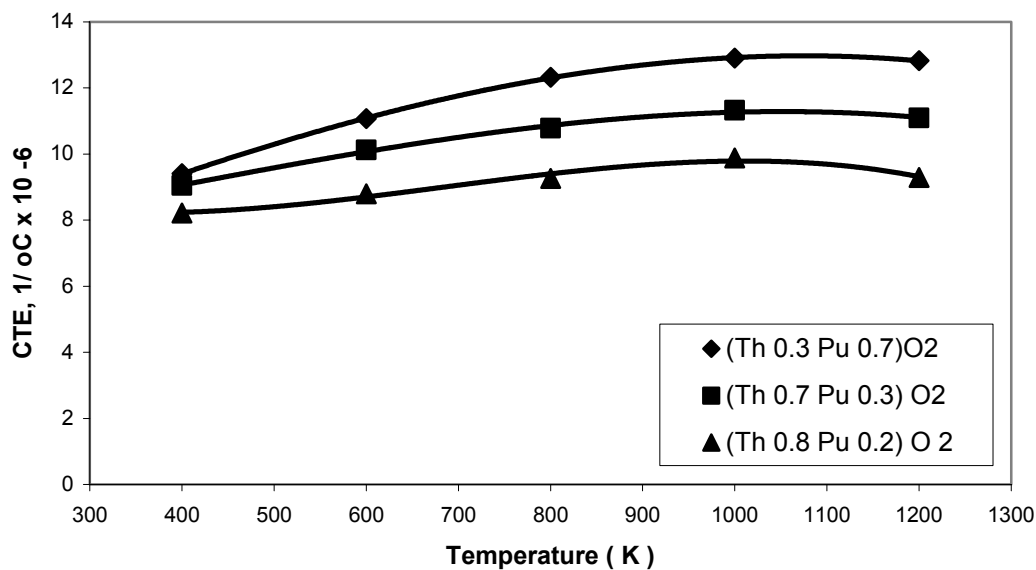


Fig. 12. Coefficient of thermal expansion data of  $(Th,Pu)O_2$  (with 0.25%  $Nb_2O_5$ ).

The coefficient of thermal expansion of mixed Th–Pu oxide were evaluated by a high-temperature dilatometer and is summarized in Fig. 12.

The hot hardness data of the mixed Th–Pu oxide was evaluated at BARC up to 1600 K. The hardness values of Th & Pu rich mixed oxides was found to decrease with increase in temperature, as expected, and as summarized in Fig. 13. The data were more less similar for both thorium and plutonium compositions.



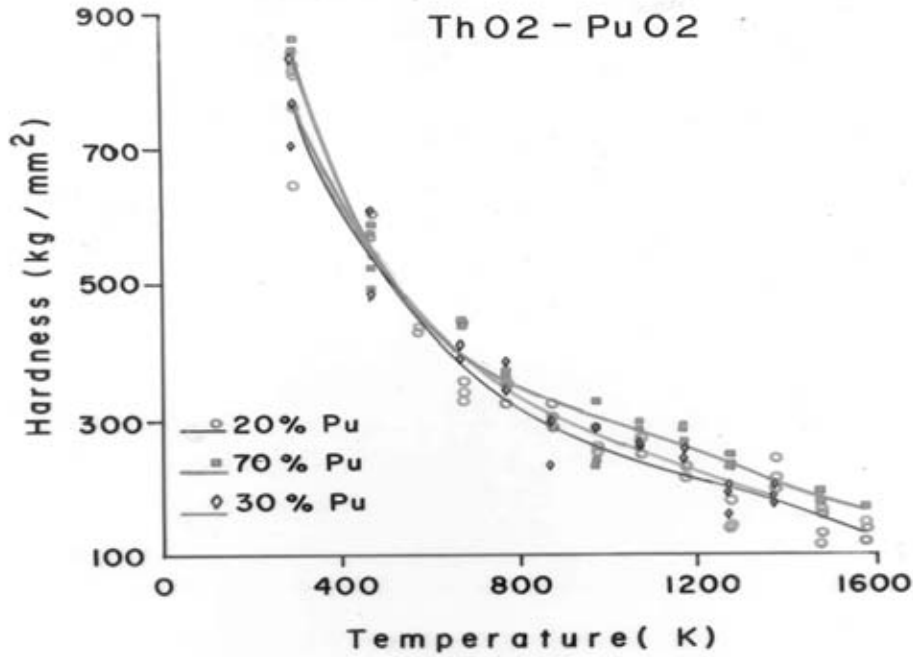


Fig. 13. Hot indentation hardness data of (Th,Pu)O<sub>2</sub> pellets containing 20%,30% & 70% PuO<sub>2</sub>.

In the PHWR 220 MW(e) units in India, 35 nos. of Zircaloy-4 clad 19-element pins of ThO<sub>2</sub> are utilized neutron flux flattening of the initial core during start-up. During the last few years ThO<sub>2</sub> bundles have been utilized for this purpose in seven units of PHWR 220 including the two units each at Kakrapar Atomic Power Station (KAPS 1&2), Kaiga Atomic Power Station (KGS 1&2), Rajasthan Atomic Power Station (RAPS 3&4) and in RAPS 2 after mass coolant channel replacement. So far, some 232 thoria bundles have been successfully irradiated in the operating PHWR upto a maximum power of 408 kW and burnup 13 000 MWd/Te HM without any failure [75].

In-pile irradiation of Zircaloy-clad (Th,Pu)O<sub>2</sub> fuel pins have been successfully carried out in the pressurized water loop of CIRUS research reactor. A six-pin cluster of free-standing Zircaloy-2-clad ThO<sub>2</sub>-4%PuO<sub>2</sub> was successfully irradiated upto a burnup of 18.4 MWd/kg. Subsequently, two additional 6-pin clusters of collapsible Zircaloy-2-clad pins containing high density ThO<sub>2</sub> and ThO<sub>2</sub>-6.75%PuO<sub>2</sub> were successfully irradiated upto a burnup of 15 000 MWd/Te without failure. The peak pin-power rating was 40kW/M [76].

#### 4.3. Spent fuel isotopics, radiotoxicity and decay heat

Thorium based fuel cycle does not produce minor actinides (Am, Np, Cm) but are associated with isotopes like <sup>232</sup>U and <sup>228</sup>Th, with relatively short half life and other radionuclides like <sup>231</sup>Pa, <sup>229</sup>Th and <sup>230</sup>U, which would have long term radiological impact. In addition, there would be fission products like <sup>129</sup>I and <sup>135</sup>Cs, which give the highest contribution to the total dose on short term basis and activation products like <sup>59</sup>Ni and <sup>94</sup>Nb. The residual heat of spent Th/U MOX fuel is more than that of UOX fuel mainly because of the <sup>232</sup>U and daughter products.

Table 7 summarizes the decay heat of selected plutonium and uranium isotopes in uranium and thorium fuel cycle respectively. The radiological impact of thorium fuel cycle is shown in

Fig. 14 [8]. In UOX, the residual heat is due to transuranium radionucleides, in particular the Pu isotopes. The residual heat of Th/Pu MOX is 30% lower than Th/U MOX. In both cases, the influence of fission products in the residual heat is minor and the Pu isotopes are mainly responsible for the residual heat. For Th/Pu-MOX fuel, the influence of  $^{232}\text{U}$  and its decay products is negligible in comparison with Th/U-MOX. The maximum residual heat is obtained after about 30 years for Th-based fuels and 40 years for U-based fuels. The radiotoxicity of Th/Pu or U/Pu MOX from PWR is comparable with UOX fuelled MOX for the same fuel burnup. The reduction of radiotoxicity is possible only if the minor actinides are also extracted for incineration.

In the ‘once-through’ thorium fuel cycle in thermal reactors, there is always a need of topping fissile material for extended burnup in order to get the maximum benefit from in-situ  $^{233}\text{U}$ . For this purpose, the best topping material is  $^{233}\text{U}$  as it would minimize formation of minor actinides. However, highly enriched uranium (HEU) topping material would also lead to similar radiotoxicity in terms of minor actinide contents in the spent fuel. However, if MEU or LEU is used as topping material, then there would be additional contributions to radiotoxicity mainly from the plutonium isotopes and the minor actinides. The ‘seed-blanket’ Radkowsky concept [9] where each fuel assembly consists of a uranium seed and a thorium blanket, could minimize the radiotoxicity of spent fuel to some extent. From the point of view of plutonium burning in PWR in ‘open’ thorium cycle, nearly two times more plutonium can be burnt as compared to U/Pu–MOX core minimizing the radiotoxicity of spent fuel.

Table 7. Specific radiation rates for selected actinides

Nuclide	D, Dose Rate (Gamma) at 1m $\mu\text{Sv/h/g}(t=1\text{s})$	H, Heating Rate W/g	N, Neutron Emission Rate/ g/s
Pu-238	1.81	5.65E-01	2.94E+03
Pu-239	1.52E-02	1.93E-03	2.53E-02
Pu-240	2.61E-02	7.05E-03	1.20E+03
Pu-241	1.76E-01	4.00E-03	5.0E-02
Pu-242	3.17E-04	1.16E-04	2.01E+03
Am-241	3.12E+02	1.12E-01	1.19
U-232	1.97E+01*	7.06E-01	1.84E-04
U-233	8.16E-03	2.79E-04	-
U-234	2.69E-03	1.78E-04	9.78E-03
U-235	1.30E-03	5.71E-08	4.00E-03
U-236	1.52E-05	1.75E-06	7.17E-03
U-238	8.63E-08	8.45E-09	1.67E-02

\*Dose rate from U-232 strongly time dependent.

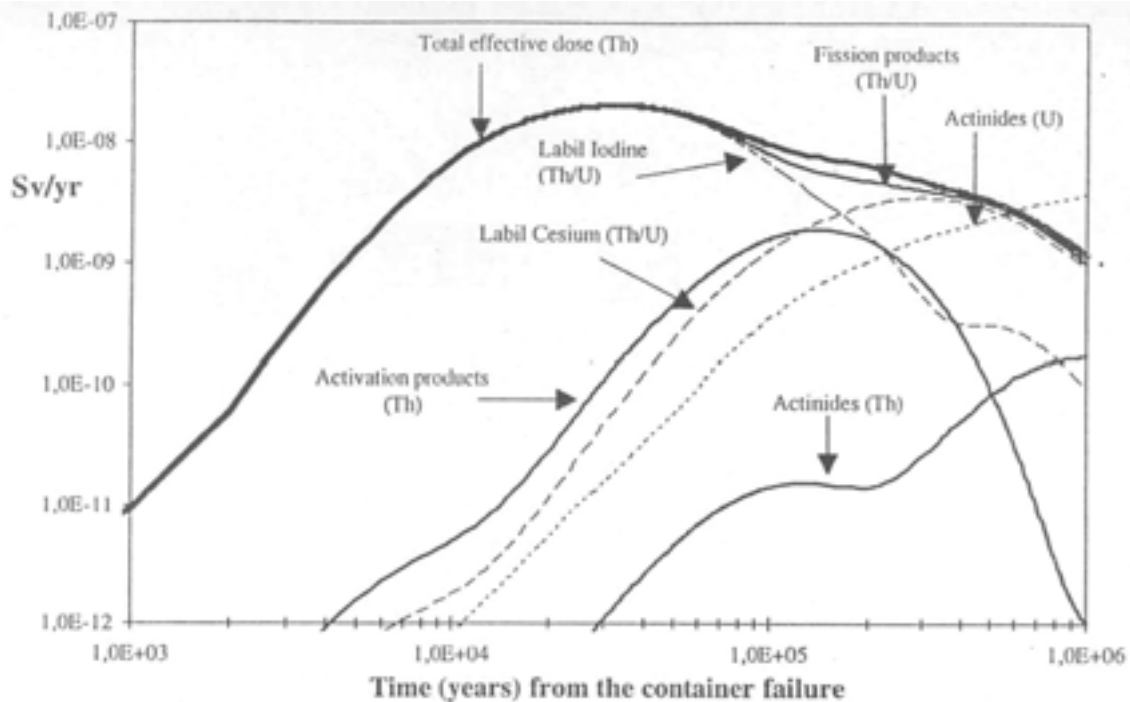


Fig. 14. Radiological impact of thorium fuel cycle [77].

In the ‘closed’ thorium fuel cycle in fast reactors with Pu and minor actinides, the amount of Pu burning will be much larger and appreciable amounts of  $^{233}\text{U}$  would be produced which could be utilized for starting new thorium-fuelled thermal reactors or ADS cycle.

## 5. FRONT END ISSUES AND CHALLENGES

### 5.1. Resources, mining and milling

Thorium is widely distributed in nature with an average concentration of 10 ppm in earth’s crust in many phosphates, silicates, carbonates and oxide minerals. Natural thorium is present as nearly 100%  $^{232}\text{Th}$  isotope. In general, thorium occurs in association with uranium and rare earth elements (REE) in diverse rock types: as veins of thorite, thorianite, uranothorite and as monazite in granites, syenites, pegmatites and other acidic intrusions. Monazite is also present in quartz-pebble conglomerates sand stones and in fluvial and beach placers. In addition, thorium is also found as an associate element with REE bearing bastnaesite in carbonatites.

The present knowledge of thorium resources in the world is limited and incomplete because of the relatively low-key exploration efforts arising out of insignificant demand. Apart from its main use in nuclear energy, as ‘fertile’ material, thorium finds limited application in non-nuclear areas, mainly as thorium nitrate for gas mantles and to a very limited extent as thorium oxide refractory, catalyst (for synthesis of either methane or mixtures of saturated and unsaturated hydrocarbons from mixtures of CO and  $\text{H}_2$ ), thoriated tungsten welding rods and in magnesium-based alloys.

The largest known reserves of thorium are contained in the beach and inland placer deposits of monazite, a mixed phosphate mineral with chemical formula:  $(\text{RE}/\text{Th}/\text{U})\text{PO}_4$ . Monazite is

a primary source of light REE and thorium and a secondary source of phosphate and uranium. The total known world reserves of thorium in the Reasonably Assured Reserves (RAR) and Estimated Additional Reserves (EAR) categories are in the range of 2.23 million tonnes and 2.13 million tonnes respectively as shown in Table 8.

Table 8. Estimated thorium reserves (tonnes of Th metal) [78]

Country	RAR	EAR
Australia	19 000	-
Brazil	606 000	700 000
Canada	45 000	128 000
Greenland	54 000	32 000
Egypt	15 000	309 000
India	319 000	-
Norway	132 000	132 000
South Africa	18 000	-
Turkey	380 000	500 000
United States	137 000	295 000

In the RAR category, the deposits in Brazil, Turkey and India are in the range of 0.60, 0.38 and 0.32 million tonnes respectively. The thorium deposits in India has recently been reported to be in the range 0.65 million tonnes.

Table 9 summarises the average composition of monazite in different countries of the world [79]. The world's reserve of monazite is estimated to be in the range of 12 million tonnes of which nearly 8 million tonnes occur with the heavy minerals in the beach sands of India in the States of Kerala, Tamil Nadu, Andhra Pradesh and Orissa.

Table 9. Composition of monazite concentrates in wt %

Countries	ThO <sub>2</sub>	U <sub>3</sub> O <sub>8</sub>	(RE) <sub>2</sub> O <sub>3</sub>	Ce <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	SiO <sub>2</sub>	Other oxides
India	8.88	0.35	59.37	(28.46)	27.03	0.32	0.36	1.00	/
Brazil	6.5	0.17	59.2	(26.8)	26.0	0.51	1.75	2.2	/
Florida Beach Sand USA	3.1	0.47	40.7	-	19.3	4.47	-	8.3	/
South Africa monazites rock	5.9	0.12	46.41	(24.9)	27.0	4.5	0.42	3.3	/
Malaysia	8.75	0.41	46.2	(23.2)	20.0	-	2.2	6.7	/
Korea	5.47	0.34	65.0	24.7	-	0.35	0.19	4.08	/
Italy	11.34	15.64	35.24		31.02				6.76
Sri Lanka	14.32	0.10	53.51		26.84				5.03

Production of monazite on a commercial scale was initiated in the 1950s by Brazil, India and USA as a source of REE and thorium. Till early 1990s, Australia was the largest producer of monazite followed by India, Brazil, South Africa and China. The total annual production was in the range of 15 000 tonnes. However, presently only India and China are the main producers of monazite and the annual production has come down to the level of 5 000 tonnes.

The two main sources of thorium that could be considered are:

- monazite itself; and
- old residues, amounting to some 25 000 tonnes of ThO<sub>2</sub>, originating in the rare earth extraction process from monazite.

Thorium concentrate and nuclear grade ThO<sub>2</sub> are produced from monazite by involving the following process steps:

- Extraction and pre-concentration of beach sands.
- Conversion of ore (beach sand concentrates) to monazite.
- Conversion of monazite into thorium concentrate, uranium concentrate and rare earth
- Storage of thorium concentrate in suitable form or conversion of thorium concentrate to nuclear grade ThO<sub>2</sub> powder.

The mining and extraction of thorium from monazite is relatively easy and significantly different from that of uranium from its ores. Most of the commercially exploited source of monazite is from the beach or river sands along with heavy minerals. The overburden during mining is much smaller than in the case of uranium and the total radioactive waste production in mining operation is about 2 orders of magnitude lower than that of uranium. The so-called Radon impact is also much smaller than in the uranium case due to the short lifetime of thoron as compared to that of radon, and needs therefore, much simpler tailings management than in the case of uranium, to prevent long term public doses. As far as occupational doses are concerned, there is no need to control ventilation with respect to Rn<sup>220</sup> inhalation because monazite extraction is done in open pit. However, the inhalation and ingestion dose factors are high for thorium and thoron.

Monazite deposits are formed by weathering of parent rock, followed by the gravity concentration of heavy minerals in sand-beds through the actions of wind and water in the coastal areas of tropical countries. The individual heavy minerals, namely ilmenite, rutile, monazite, zircon, sillimanite and garnet are separated from each other by methods depending up on physical properties i.e., specific gravity, magnetic susceptibility, electrical conductivity and surface properties. Fig. 15 shows the flowsheet for separating monazite from heavy minerals in beach sands [80]. The electrically conductive ilmenite and rutile constituents are first separated using high-tension separator. Next, the non-conducting monazite, which is heavy and moderately magnetic, is isolated from non-magnetic sillimanite and zircon and magnetic garnet by the use of high intensity magnetic separators and air or wet tables. The resulting concentrate contains 98% monazite.

The monazite is finely ground and in most countries dissolved in 50–70% sodium hydroxide at ~140°C and subjected to a series of chemical operations, including solvent extraction and ion exchange processes to obtain pure thorium nitrate, which is precipitated in the form of thorium oxalate and subjected to controlled calcinations to obtain ThO<sub>2</sub> powder. In India, until recently, the monazite used to be alkali leached, the rare earth used to be separated as mixed chloride and the thorium stored in the form of thorium hydroxide in concrete silos. The hydroxide cake contained around 35% ThO<sub>2</sub>, 7% rare earth oxide, 0.6% U<sub>3</sub>O<sub>8</sub> and nearly 28% insolubles and moisture. Recently, a project entitled “**thorium retrieval, uranium recovery and restorage of thorium oxalate**” (THRUST) has been completed for processing monazite in such a manner that all the thorium present is separated in pure thorium oxalate form (99% purity) which is much easier to handle, store and retrieve to prepare mantle grade thorium nitrate or nuclear grade thorium oxide as and when required. In addition, the major fraction of uranium present in monazite is also separated in the form of crude uranium concentrate. Fig.

16 summarizes the process steps being followed in India for preparation of pure thorium oxalate for long term storage in concrete silos [79].

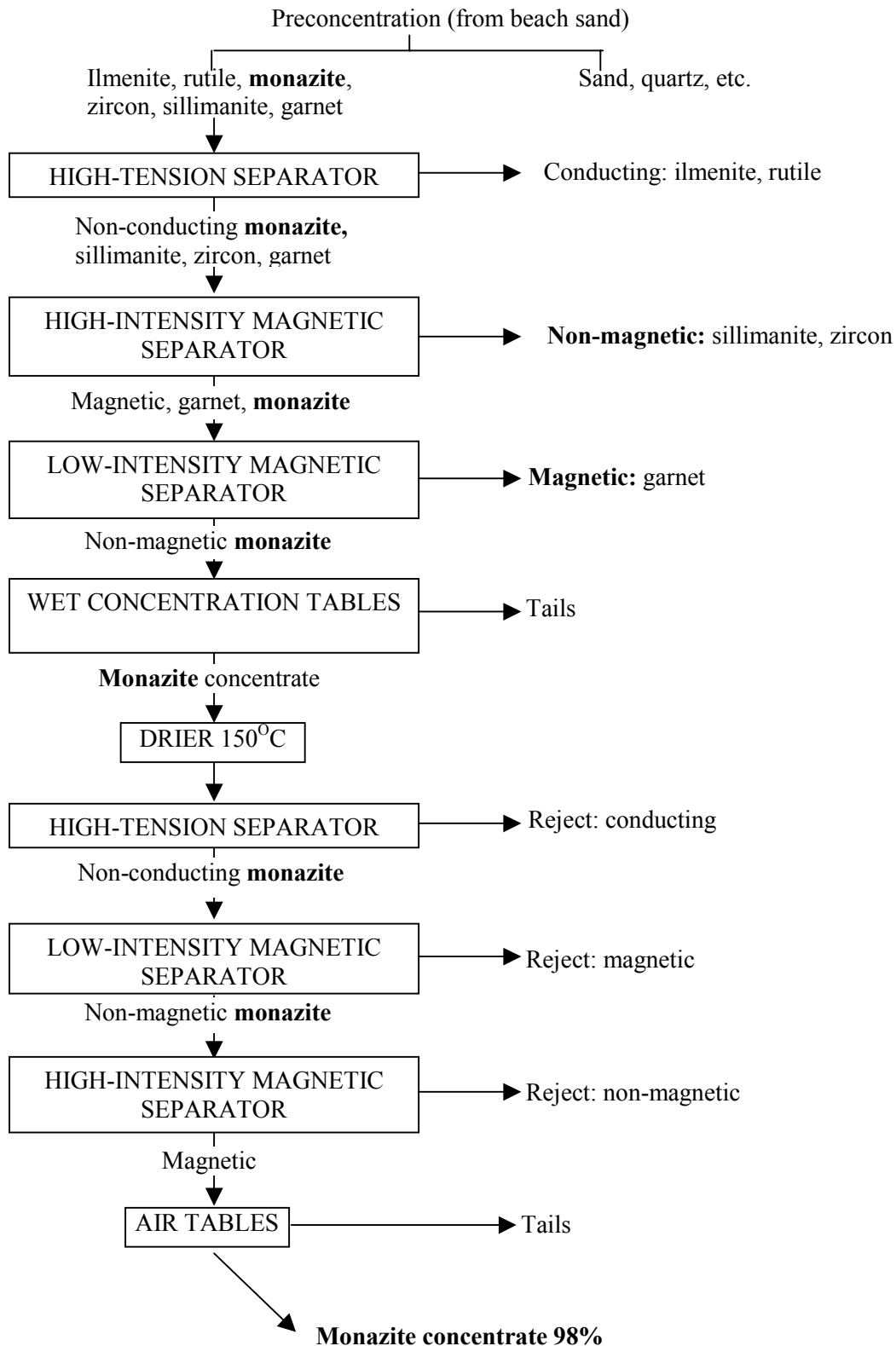


Fig. 15. Typical flow sheet for separating monazite from heavy minerals in beach sand [80].

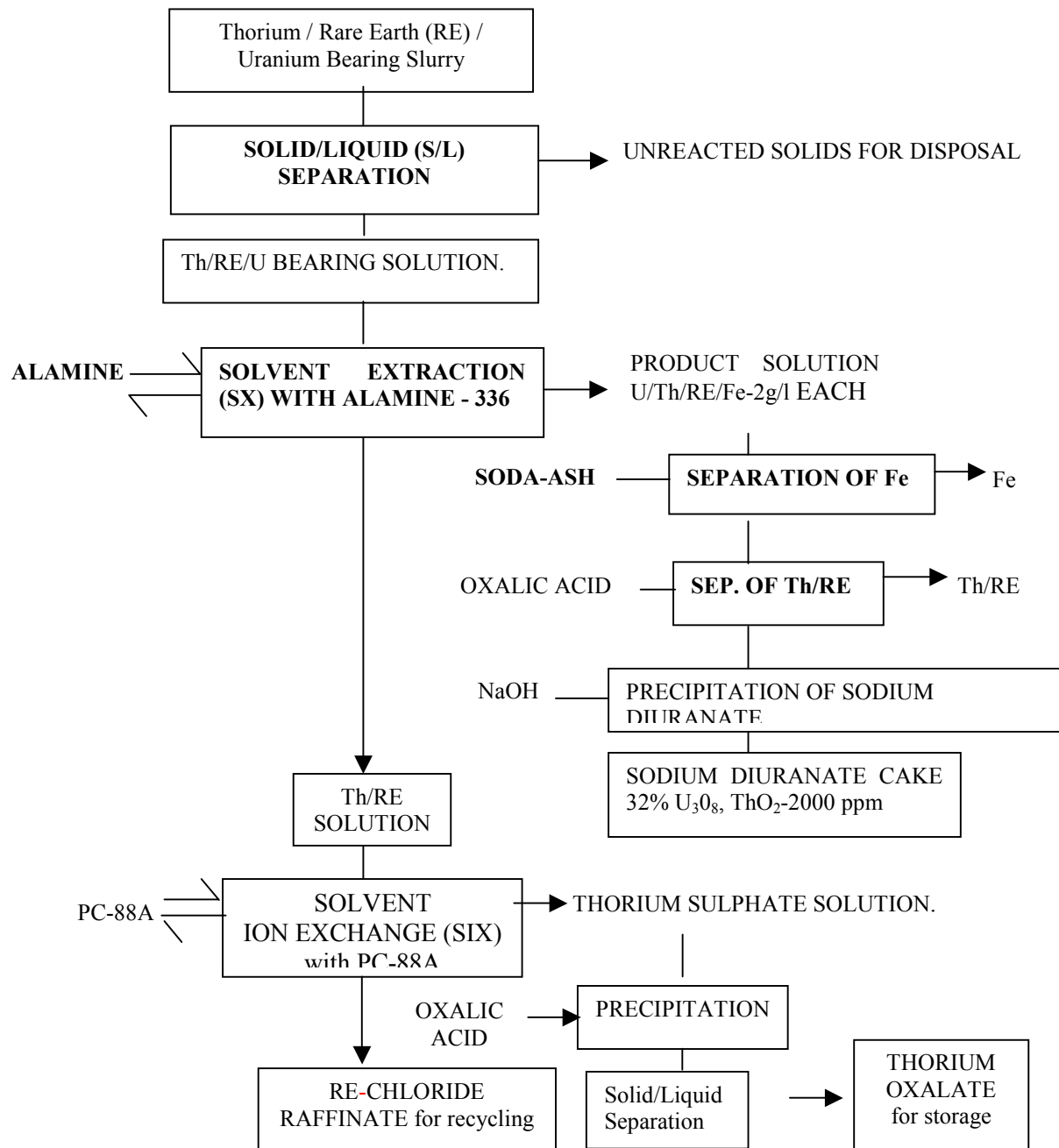


Fig. 16. Recent techniques of processing monazite in India [79].

## 5.2. Types of fuels and fuel elements

There is a big diversity of thorium-based nuclear fuels and fuel elements depending on the type of reactor. Except for the molten salt breeder reactor (MSBR), which uses mixed fluoride in liquid form as fuel and primary coolant, all other reactors use solid fuels in the form of tiny “ceramic fuel microspheres” (100–1000  $\mu$ ), “ceramic fuel pellets” or “metallic alloy fuel rods”. Table 10 summarizes the thorium-based fuel and fuel elements used in experimental and power reactors.

Table 10. Types and geometry of thorium-based fuels and fuel elements

REACTOR TYPE	COMPOSITION	FUEL SHAPE	FUEL ELEMENT
High temperature Gas cooled reactors	ThO <sub>2</sub> , (Th,U)O <sub>2</sub> , ThC <sub>2</sub> , (Th,U)C <sub>2</sub> ( <sup>235</sup> U or <sup>233</sup> U)	Microspheres 200-800 μ coated with multiple layers of buffer & pyrolytic carbon and SiC	Mixed with graphite and pressed into large spheres (~60 mm) for Pebble-Bed Reactor or fuel rods for HTGRs with prismatic fuel elements
Light water reactors	ThO <sub>2</sub> , (Th,U)O <sub>2</sub> , (Th,Pu)O <sub>2</sub>  (<5%Pu, <sup>235</sup> U or <sup>233</sup> U)	<ul style="list-style-type: none"> <li>• High-density Sintered Pellets</li> <li>• High-density Microspheres</li> </ul>	<ul style="list-style-type: none"> <li>• Zircaloy clad Pin Cluster encapsulating Pellet-Stack</li> <li>• Zircaloy clad 'vipac' Pin Cluster encapsulating fuel microspheres</li> </ul>
Heavy water reactors			
PHWR	ThO <sub>2</sub> for neutron flux flattening of initial core		
AHWR	(Th,U)O <sub>2</sub> (Th,Pu)O <sub>2</sub> (<5%Pu, <sup>235</sup> U or <sup>233</sup> U)	High-density Sintered Pellets	Zircaloy clad Pin Cluster encapsulating Pellet-Stack
Fast reactors	<ul style="list-style-type: none"> <li>• ThO<sub>2</sub> blanket</li> <li>• (Th,U)O<sub>2</sub> &amp; (Th,Pu)O<sub>2</sub> (~25%Pu, <sup>235</sup>U or <sup>233</sup>U) fuels</li> <li>• Th metal blanket</li> <li>• Th-U-Zr &amp; Th-U-Pu-Zr fuels</li> </ul>	<ul style="list-style-type: none"> <li>• High-density Sintered Pellets</li> <li>• Injection-cast Fuel Rods</li> </ul>	<ul style="list-style-type: none"> <li>• Stainless steel (SS) clad Pin Cluster encapsulating Pellet-Stack</li> <li>• SS clad Pin Cluster encapsulating Fuel Rods</li> </ul>
Molten salt breeder reactor	Li <sup>7</sup> F + BeF <sub>2</sub> + ThF <sub>4</sub> +UF <sub>4</sub>	Molten salt liquid form	Circulating molten salt acting as fuel and primary coolant

### 5.3. Fuel fabrication

Selection of process flowsheet and the mode of fabrication to be employed for either first cycle or recycled fuel would depend to a great extent on the radiotoxicity, quantity and form of the fuel material. Fuels containing naturally occurring 'fissile' <sup>235</sup>U in combination with 'fertile' <sup>238</sup>U or <sup>232</sup>Th, emitting only alpha particles of relatively low specific activity, can be manufactured by the so-called 'contact operations' where the operator has direct contact with the fuel material. However, process operations that involve generation and handling of fine powders of <sup>235</sup>U, <sup>238</sup>U or <sup>232</sup>Th bearing fuels are carried out in ventilated enclosures for minimizing radioactive aerosol. The enclosures need not be hermetically sealed for handling <sup>235</sup>U, <sup>238</sup>U or <sup>232</sup>Th bearing materials, if they are not pyrophoric. Glove box operations are those requiring hermetic sealing of equipment and are essential for handling highly radiotoxic plutonium and <sup>233</sup>U-bearing materials. Often in such facilities, light beta-gamma and neutron



shielding and semi remote operations are necessary. Remote operations are those requiring heavy shielding and a high degree of automation and remotisation. During the last 4 decades, several countries have manufactured thorium based oxide and non-oxide fuels in both 'particulate' (microspheres) and 'pellet' forms by employing contact-, hooded-, glove box-, semi-remote- and remote operations.

ThO<sub>2</sub>, ThO<sub>2</sub>-UO<sub>2</sub> and ThO<sub>2</sub>-PuO<sub>2</sub> fuels have been manufactured in both 'particulate' (microspheres) and 'pellet' forms for use in water cooled reactors in the form of 'vi-pac' and 'pellet-pin' elements respectively. For fabrication of 'vi-pac' pins, high density fuel microspheres of 1, 2 or 3 size fractions (typically 1000 μ, 100 μ and 10 μ) are 'vibratory compacted' into fuel cladding tubes to obtain fuel elements of controlled 'smear' density. The high density pellets are loaded in fuel cladding tube and encapsulated to obtain 'pellet-pin' fuel elements for water cooled reactors. High-density fuel 'microspheres' of ThO<sub>2</sub>, (Th,U)O<sub>2</sub> or (Th,U)C<sub>2</sub> have been manufactured for High Temperature Gas cooled Reactor (HTGR). The 'microspheres' are subjected to multi-layer coatings of pyrolytic carbon and silicon carbide, known as BISO or TRISO particles, and compacted in graphite matrix. The HTGR fuel is either in the form of spherical balls (known as Pebbles) or prismatic bars.

ThO<sub>2</sub>, UO<sub>2</sub> and PuO<sub>2</sub> are isostructural (FCC, CaF<sub>2</sub> type), completely solid soluble and have very similar thermodynamic and thermophysical properties. The manufacturing processes of thorium based fuels are, therefore, similar to that of the well-established processes for fabrication of UO<sub>2</sub> and mixed oxide fuels. However, as mentioned earlier, a special feature of <sup>232</sup>Th-<sup>233</sup>U fuel cycle is the high gamma dose associated the daughter products of <sup>232</sup>U, which is always associated with <sup>233</sup>U and the high specific radioactivity of <sup>233</sup>U. Hence, handling of <sup>233</sup>U bearing materials, like <sup>239</sup>Pu and its higher isotopes, require remote and automated operation in hot cells or shielded glove boxes. The process flowsheets for fabrication of <sup>233</sup>U or Pu bearing fuels should preferably be dust-free and amenable to remotisation and automation.

The major fabrication campaigns reported, so far, for ThO<sub>2</sub>-based water cooled reactor fuels are based on the conventional 'powder-pellet' route, involving cold pelletisation of fine powder or powder mixtures, followed by sintering. The 'powder pellet' route is suitable for fabrication of high-density fuel pellets but has the disadvantage of 'radiotoxic dust hazard' as it involves handling of fine fuel particles. Further, fine powders have poor flowability, which makes automation and remote fabrication somewhat difficult. The alternative 'vibro sol' or 'sphere pac' process involves preparation of dust-free and free flowing sol gel derived fuel microspheres, which after high temperature treatment produces very high-density fuel microspheres. Such fuel microspheres of 1, 2 or 3 size fractions are vibro packed in fuel cladding tube to obtain fuel pins having controlled smeared density. The 'vibro sol' route is highly suitable for remotisation and automation but has the limitation of maximum achievable smeared density of only 90%T.D., which makes it less attractive for use as a water cooled reactor fuel.

The following techniques have been developed so far for manufacturing ThO<sub>2</sub> and thorium based mixed oxide fuels:

- (1) **'Powder-pellet' route:** for preparation of high density fuel pellets, using ThO<sub>2</sub>, UO<sub>2</sub> and PuO<sub>2</sub> powders as starting materials; the fuel pellet stacks are encapsulated in cladding tubes.

- (2) **‘Vibro-sol’ route**: for preparation of fuel microspheres using nitrate solutions of uranium, plutonium and thorium as starting materials and adapting ‘ammonia external gelation’ or ‘ammonia internal gelation’ process for obtaining hydrated gel microspheres; the microspheres are sintered and vibro packed in cladding tubes followed by encapsulation.
- (3) **‘Sol-gel microsphere pelletisation’**: using dust-free and free-flowing sol gel derived oxide fuel microspheres for direct pelletisation and sintering.
- (4) **‘Impregnation technique’**: where (a) partially sintered ThO<sub>2</sub> pellets of relatively low density ( $\leq 75\%$  theoretical density) or (b) ‘porous’ ThO<sub>2</sub> microspheres are vacuum impregnated in uranyl nitrate (‘U’ as <sup>233</sup>U) or Pu–nitrate solution followed by calcination and sintering to form high density ThO<sub>2</sub>-based mixed oxide fuel pellets, which are encapsulated in cladding tubes.

### 5.3.1. Powder-pellet route

The ‘powder-pellet’ route has been extensively used in the past for carrying out the manufacturing of ThO<sub>2</sub>, (Th, U)O<sub>2</sub> and (Th, Pu)O<sub>2</sub> fuel pellets of controlled density and microstructure using ThO<sub>2</sub>, UO<sub>2</sub> and PuO<sub>2</sub> powders as starting material. The essential steps are milling, granulation and binder addition, cold pelletization and sintering. Thoria powder derived from the ‘oxalate’ process has been used in major ThO<sub>2</sub>-based fuel production campaigns. The ex-oxalate ThO<sub>2</sub> powder has a flat, square platelet morphology, which requires pre-milling for making it ‘sinteractive’. The alternative route of ‘direct denitration’ of thorium nitrate tetra-hydrate produces less sinterable ThO<sub>2</sub> powder with low specific surface area and large oxide crystallites and has, therefore, been given up. Since ThO<sub>2</sub> has a very high melting point ( $\sim 3350^\circ\text{C}$ ), the sintering has to be carried out at temperatures higher than  $2000^\circ\text{C}$  to obtain high-density pellets. However, with small addition of ‘sintering aids’ like Nb<sub>2</sub>O<sub>5</sub>, high-density ThO<sub>2</sub> pellets could be obtained by sintering in air at temperature as low as  $1150^\circ\text{C}$  [81]. Small addition of divalent metal oxide, like CaO and MgO, also enhances the diffusion of Th<sup>+4</sup> by creating anion vacancies [2]. Recently, U<sub>3</sub>O<sub>8</sub> was found to be a favourable ‘sintering aid’ [82]. Addition of around 2% U<sub>3</sub>O<sub>8</sub> was found to enhance the densification of ThO<sub>2</sub> and high density (96% T.D.) pellets could be obtained by sintering in air at  $1100^\circ\text{C}$ . This will pave the way for manufacturing high density (Th,U)O<sub>2</sub> pellets without the addition of dopants like CaO, MgO or Nb<sub>2</sub>O<sub>5</sub>.

In USA, the Nuclear Materials and Equipment Corporation (NUMEC) and the Bettis Atomic Power Laboratory were involved in industrial scale manufacturing of high density ThO<sub>2</sub> and (Th,U)O<sub>2</sub> pellets for use as blanket and seed materials respectively in Shipping Port Light Water Breeder Reactor (LWBR), Borax IV Reactor, the Elk River Reactor and the Indian Point Reactor. In most of the campaigns, CaO or MgO was used as sintering aid.

In India, some 15 metric tonnes of high density ThO<sub>2</sub> pellets have so far been manufactured by powder pellet route mostly at Nuclear Fuel Complex(NFC), Hyderabad and to a limited extent at BARC for use in the following research and power reactors :

- (a) CIRUS and DHRUVA research reactors at BARC: In the form of Al-clad ‘J’ rods containing ThO<sub>2</sub> pellets for CIRUS and as 7–pin cluster containing ThO<sub>2</sub> pellets for DHRUVA. Some 3 tonnes ThO<sub>2</sub> pellets have been irradiated in these reactors;
- (b) PHWRs: In the form of Zircaloy clad 19–element ThO<sub>2</sub> bundles for neutron flux flattening of the initial cores of PHWRs during start-up. Each assembly contains around

14 kg of ThO<sub>2</sub> pellets. So far, some 7 tonnes of ThO<sub>2</sub> pellets have been manufactured for PHWR 220 units. Some 232 nos. of ThO<sub>2</sub> bundles have been used in eight PHWR 220 units in Kakrapar Atomic Power Station (KAPS 1&2: 70 nos.), Kaiga Atomic Power Station (KGS 1&2: 70 nos) and Rajasthan Atomic Power Station (RAPS 3&4: 70 nos. and RAPS 2: 18 nos. after retubing). Initially, four ThO<sub>2</sub> bundles were irradiated in Madras Atomic Power Station (MAPS), Kalpakkam.

- (c) LMFBR: In the form of stainless steel 316 clad, ThO<sub>2</sub> blanket material for Fast Breeder Test Reactor (FBTR) at IGCAR, Kalpakkam. So far, some 5 tonnes of ThO<sub>2</sub> pellets have been manufactured and delivered for use as axial and radial blanket assemblies for FBTR. Each radial and axial blanket assemblies contain some 12.25 kg and 4.4 kg of ThO<sub>2</sub> pellets respectively. Presently, 54 radial blankets of ThO<sub>2</sub> are in FBTR core.

Sinterable grade, high purity ThO<sub>2</sub> powder is being supplied by the Indian Rare Earths Limited (IREL) from their “Monazite Processing and Thorium Plants”. BARC has also played an important role in the initial phase of ThO<sub>2</sub> pellet fabrication campaigns. The ThO<sub>2</sub> powder is subjected to grinding followed up pre-compaction-granulation, cold pelletization, high temperature sintering in air and centreless grinding. Both MgO and Nb<sub>2</sub>O<sub>5</sub> dopants were found to enhance the densification of ThO<sub>2</sub> pellets.

ThO<sub>2</sub> and (Th, U)O<sub>2</sub> (containing <10% UO<sub>2</sub>) pellets have been successfully sintered to high density pellets (≥95% T.D.) in both air and reducing atmosphere. Small addition (~0.25%) of Nb<sub>2</sub>O<sub>5</sub> was also found to be effective in improving the densification of ThO<sub>2</sub> pellets particularly when the sintering is carried out in air. A sintered density of 96–97% T.D. could be achieved by low temperature sintering of Nb<sub>2</sub>O<sub>5</sub>-doped ThO<sub>2</sub> pellets at 1150<sup>0</sup>C in air. Nb<sub>2</sub>O<sub>5</sub> doped ThO<sub>2</sub> pellets required higher sintering temperature (1 700<sup>0</sup>C) in H<sub>2</sub> or N<sub>2</sub>+H<sub>2</sub> atmosphere to achieve high density (96-97% T.D.).

(Th,Pu)O<sub>2</sub> pellets of controlled density and microstructure have been manufactured by the ‘powder pellet’ route using ex-oxalate ThO<sub>2</sub> and PuO<sub>2</sub> powders as starting materials, as part of thorium fuels development programme for water cooled thermal reactors and fast reactors. Two numbers of Zircaloy clad six-pin clusters of (Th, Pu)O<sub>2</sub> containing 4% PuO<sub>2</sub> and 6.75%PuO<sub>2</sub> have been manufactured earlier in BARC in two different campaigns and successfully irradiated in the Pressurised Water Loop (PWL) of CIRUS research reactor simulating the operating conditions in PHWRs to maximum burnups of 18.4 MWd/t without any failure [83].

Process flowsheets have been developed for manufacturing ThO<sub>2</sub>-30%PuO<sub>2</sub>, ThO<sub>2</sub>-50%PuO<sub>2</sub> and ThO<sub>2</sub>-75%PuO<sub>2</sub> pellets of controlled density and microstructure using small amounts of CaO (0.5wt%) or Nb<sub>2</sub>O<sub>5</sub> (0.25wt%) as ad mixed dopants for enhancing the densification of these mixed oxide pellets [74]. The Nb<sub>2</sub>O<sub>5</sub> and CaO-doped pellets were sintered in air at 1 350<sup>0</sup>C and in Ar+8%H<sub>2</sub> at 1 650<sup>0</sup>C respectively. The ThO<sub>2</sub>-30%UO<sub>2</sub> pellets showed a single-phase microstructure. The microstructure of ThO<sub>2</sub>-50%PuO<sub>2</sub> and ThO<sub>2</sub>-75%PuO<sub>2</sub> showed a two-phase microstructure consisting of FCC (Th, Pu)O<sub>2</sub> and BCC ThO<sub>2</sub>-Pu<sub>2</sub>O<sub>3</sub> phases. These thorium-based fuels are considered as better candidates compared to (U, Pu)O<sub>2</sub> or inert matrix fuels as a carrier for disposition of weapons-grade plutonium in ‘once-through’ fuel cycle in fast reactors from the point of view of negative fuel temperature coefficients. The discharged fuel will be ‘proliferation-resistant’ because of the presence of the 2.6 MeV hard gamma of thallium 208, a decay product of <sup>232</sup>U associated with <sup>233</sup>U and can be stored for long times because of the inherent inertness of ThO<sub>2</sub> matrix.

Two clusters of  $\text{ThO}_2$ -4% $\text{PuO}_2$  and  $\text{ThO}_2$ -6.75% $\text{PuO}_2$  have been test irradiated to burnup of 18 000 MWd/t without any failure. These pellets are manufactured by the ‘powder-pellet’ route using  $\text{ThO}_2$  and  $\text{PuO}_2$  as starting materials. The powders are subjected to co milling followed by cold-pelletisation and sintering.

### 5.3.2. *Sol-gel processes*

The ‘powder-pellet’ route involves generation and handling of fine powder or particles (<1 micron) of the fuel and is hence associated with the problem of ‘radiotoxic dust hazard’. Further, fine powders are not free flowing and pose problems in remote and automated fabrication. In addition, microhomogeneity of fissile and fertile species in mixed oxide is not fully obtained since the oxide powders are mechanically mixed and the time of high temperature sintering is inadequate for complete solid solution formation. The alternative ‘sol gel’ processes avoid generation and handling of fine powders and involves use of liquids and dust-free and free-flowing microspheres. The process is amenable to automation and remote operations in hot cells or shielded glove boxes and is ideal for manufacturing thorium-based highly radiotoxic  $^{239}\text{Pu}$  (associated with  $^{240}\text{Pu}$ ,  $^{241}\text{Pu}$ ,  $^{242}\text{Pu}$  and  $^{238}\text{Pu}$ ) and  $^{233}\text{U}$  (associated with  $^{232}\text{U}$ ) bearing oxide and non-oxide (carbide) fuels. In addition, excellent microhomogeneity is ensured in case of mixed oxide, mixed carbide or mixed nitride fuels since nitrate solutions of Th and U or Pu are mixed in the liquid stage. Further, since the starting materials of sol gel processes, namely, nitrate solutions of uranium ( $^{233}\text{U}$ ), plutonium and thorium, are end products of reprocessing plants, the equipment for sol gel processes could be easily annexed with reprocessing plant for refabrication of thorium-based fuels.

Sol-gel derived  $\text{ThO}_2$  and  $(\text{Th}, \text{U})\text{O}_2$  microspheres have been prepared in the past for manufacturing fuel microspheres of controlled density for: (i) ‘vi-pac’ fuel pins, where usually high density fuel microspheres of two or three size fractions (typically 1000  $\mu$ , 100  $\mu$  and 10  $\mu$ ) are vibro compacted in fuel cladding tube to obtain fuel pins of controlled ‘smear’ density, (ii) for coated fuel particles for HTGR, where high density fuel microspheres are subjected to multi layer coating of pyrolytic carbon and silicon carbide, popularly known as TRISO and BISO particles, which are embedded in graphite matrix, (iii) direct pelletisation and sintering, popularly known as ‘Sol-gel microsphere pelletisation’ (SGMP) process; soft, low density ‘porous’ fuel microspheres are suitable for SGMP process. For preparation of  $\text{ThC}_2$  and  $(\text{Th}, \text{U})\text{C}_2$  fuel microspheres, for use in HTGR, the sol gel process is modified for obtaining microspheres containing an intimate mixture of oxide/mixed oxide and carbon. These microspheres are subjected to carbothermic synthesis in vacuum or high purity flowing argon atmosphere to obtain high density carbide or mixed carbide microspheres.

In the early-mid 1960s, sol gel microspheres of  $(\text{Th}, ^{233}\text{U})\text{O}_2$  were prepared in USA in Babcock and Wilcox unshielded pilot plant at Virginia and at semi-shielded Kilorod facility at Oak Ridge National Laboratory (ORNL), Tennessee [84], [85]. The sol gel microspheres of the mixed oxide were prepared from mixed thorium nitrate and uranium nitrate solution by steam pyrolysis in a batch denitrator. The ORNL sol gel process based on dehydration reaction was replaced by the more efficient ‘ammonia gelation’ processes, developed in Europe in the 1970s, which cause rapid gelation of droplets of sols or solutions of the nitrates of U, Th or Pu either ‘externally’ by ammonia gas and ammonium hydroxide or ‘internally’ by an added ammonia generator such as hexa methylene tetra amine (HMTA). Table 11 summarizes the popular sol gel routes utilized for preparation of  $\text{ThO}_2$  and  $\text{ThO}_2$ -based mixed oxide microspheres [86].

Table 11. Principal sol gel routes for preparation of hydrated gel microspheres of oxides of U, Th and Pu

Process	Materials prepared	Laboratory/country
External gelation	ThO <sub>2</sub> , UO <sub>2</sub> and (Th,U)O <sub>2</sub>	NUKEM, FRG [86]
External gelation of thorium (EGT)	ThO <sub>2</sub> and (Th,U)O <sub>2</sub>	KfA, FRG [87]
Internal gelation	ThO <sub>2</sub> and (Th,U)O <sub>2</sub>	KfA, FRG [88]
Internal gelation	ThO <sub>2</sub> and (Th,U)O <sub>2</sub>	BARC, India [89]

### 5.3.2.1. Ammonia external gelation process

The external gelation of thorium (EGT) [87] has several advantages over the other sol gel processes and is ideally suitable for remote manufacturing of highly radiotoxic ThO<sub>2</sub>-based <sup>233</sup>U or Pu bearing ‘microspheres’ in hot cells. The EGT process utilizes simple and reliable equipment and a few chemicals like ammonia and ammonium hydroxide, which are not flammable and have high radiolytical stability and produce a minimum of waste. The EGT process takes full advantage of the gelation features and sol gel chemistry of ThOH<sub>4</sub>, unlike other gelation processes, which use gel-supporting polymers or apply the buoyant force of an organic environment. The gel particles thus produced can be washed within a short time using small quantities of water that can be dried in minutes in a simple continuous manner.

Fig. 17 shows the major steps of EGT process developed in Germany. First, the ‘sol’ is prepared by controlled addition of gaseous ammonia through a hollow, rotating disperser shaft immersed in a jacketed and water heated glass vessel containing the nitrate solutions of thorium and uranium or plutonium. The solution is constantly monitored for pH and viscosity during the pre-neutralization step for preparing the ideal ‘hydro-sol’. An optimum ‘sol’ has pH in the range of 3.25 to 3.50 and viscosity  $3 \times 10^{-2}$  Pa.s. Droplets of the ‘sol’ are introduced through a electromechanical vibrator with a horizontal jetting nozzle inside a containment box that houses 2 horizontal ammonia gas pipes and the gelation bath. Thus, the droplets pass through a curtain of NH<sub>3</sub> gas and quickly coat themselves with a gel-skin before falling into the NH<sub>4</sub>OH gelation bath. The diameter of the nozzle bore and nozzle frequency control the diameter of the hydrated gel-microspheres. The gel microspheres containing NH<sub>4</sub>NO<sub>3</sub> are washed with 1% NH<sub>3</sub> for removing ammonium nitrate. The washed microspheres are dried in humid air on a continuous belt drier at 200<sup>0</sup>C to obtain gel microspheres of excellent sphericity. The EGT process could be tailored to obtain oxide or mixed oxide microspheres of high density suitable for: (a) ‘vibratory compaction’ in fuel cladding tubes and (b) preparation of ‘coated fuel particles’ for HTGR or for low-density ‘porous’ easily crushable microspheres suitable for direct pelletisation and sintering to high density fuel pellets. Figure 18 describes schematically the EGT process, which has been adapted for preparation of thorium based oxide, mixed oxide, carbide and mixed carbide microspheres of controlled density. The only waste of the process is the wash water containing NH<sub>4</sub>NO<sub>3</sub>, which could either be completely decomposed into the gases NO<sub>x</sub>, N<sub>2</sub>O, N<sub>2</sub> and H<sub>2</sub>O or reconverted to ammonia and nitric acid, which can be recycled.

The EGT process was extensively utilized in Germany for manufacturing high density ThO<sub>2</sub> and (Th, U)O<sub>2</sub> microspheres in the diameter range of 400-500 micron for manufacturing coated fuel particles for the HTGRs in Germany, namely AVR and THTR. However, without changes of process and equipment, microspheres in the diameter range of 100-800 micron could be easily produced.

The EGT process has been adapted with some modification for preparing ‘porous’ microspheres of ThO<sub>2</sub>, (Th,U)O<sub>2</sub> and (Th,Ce)O<sub>2</sub> (Ce for simulating Pu) in the diameter range of 100-800 micron suitable for direct pelletisation and sintering.

#### 5.3.2.2. *Ammonia internal gelation process*

The ‘ammonia internal gelation’ process was first reported by KEMA Laboratories, Netherlands for preparation of UO<sub>2</sub> microspheres. The KEMA ‘internal gelation process’ was modified in India for preparation of ThO<sub>2</sub> and (Th,U)O<sub>2</sub> microspheres [90]. The internal gelation process is based on the hydrolysis of hexa methylene tetra amine [HMTA: (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>], which releases ammonia rapidly at 90°C or above. The nitrate solutions of thorium and uranium or plutonium are mixed with HMTA at around 0°C and urea to form the feed solution. Droplets of the feed solution are gelled into spherical particles by contacting them with hot silicon oil at 105–110°C, which is an inert and immiscible medium. The ammonia released from HMTA cause the precipitation of the metal ion into a hydrated oxide gel. The properties of the gel depend on the composition of the feed solution, the temperature of the gelation medium and the contact time of the droplet with gelation medium. Thorium nitrate solution is expected to behave like a tetra-basic acid during hydrolysis and would therefore require larger quantities of HMTA compared to dibasic ion like UO<sub>2</sub><sup>++</sup> or PuO<sub>2</sub><sup>++</sup>. The HMTA requirement was reduced by partial denitration of thorium nitrate solution by using formaldehyde (13 m aqueous solution). The addition of urea was also found to enhance the acid neutralization power of HMTA.

Extensive work has been carried out in BARC [89] to study the gelation behaviour of partially denitrated thorium nitrate solution with HMTA and urea on the basis of which a gelation field diagram has been developed, which outlines regions of opaque gel formation that yield good quality ThO<sub>2</sub> and (Th,U)O<sub>2</sub> microspheres containing up to 10mole% uranium. Unlike that of UO<sub>2</sub>, good quality ThO<sub>2</sub> and ThO<sub>2</sub>-based microspheres can be obtained in very narrow region with precise control of the composition of feed solution. The stream of the feed solution was forced through a stainless steel capillary at a constant flow rate and broken into droplets of uniform size with the use of electromagnetic vibrator. The droplets gelled in a few seconds and were collected at the belt separator. The gelled product was first washed several times with carbon tetrachloride to remove silicone oil and then several times with 2-3 M ammonium solution to remove any unreacted HMTA and urea as well as ammonium nitrate formed during gelation. The washed gel particles were dried in air oven and heated to 1 250–1 650<sup>0</sup> C to form spherical microspheres in the diameter range of 100-400 micron.

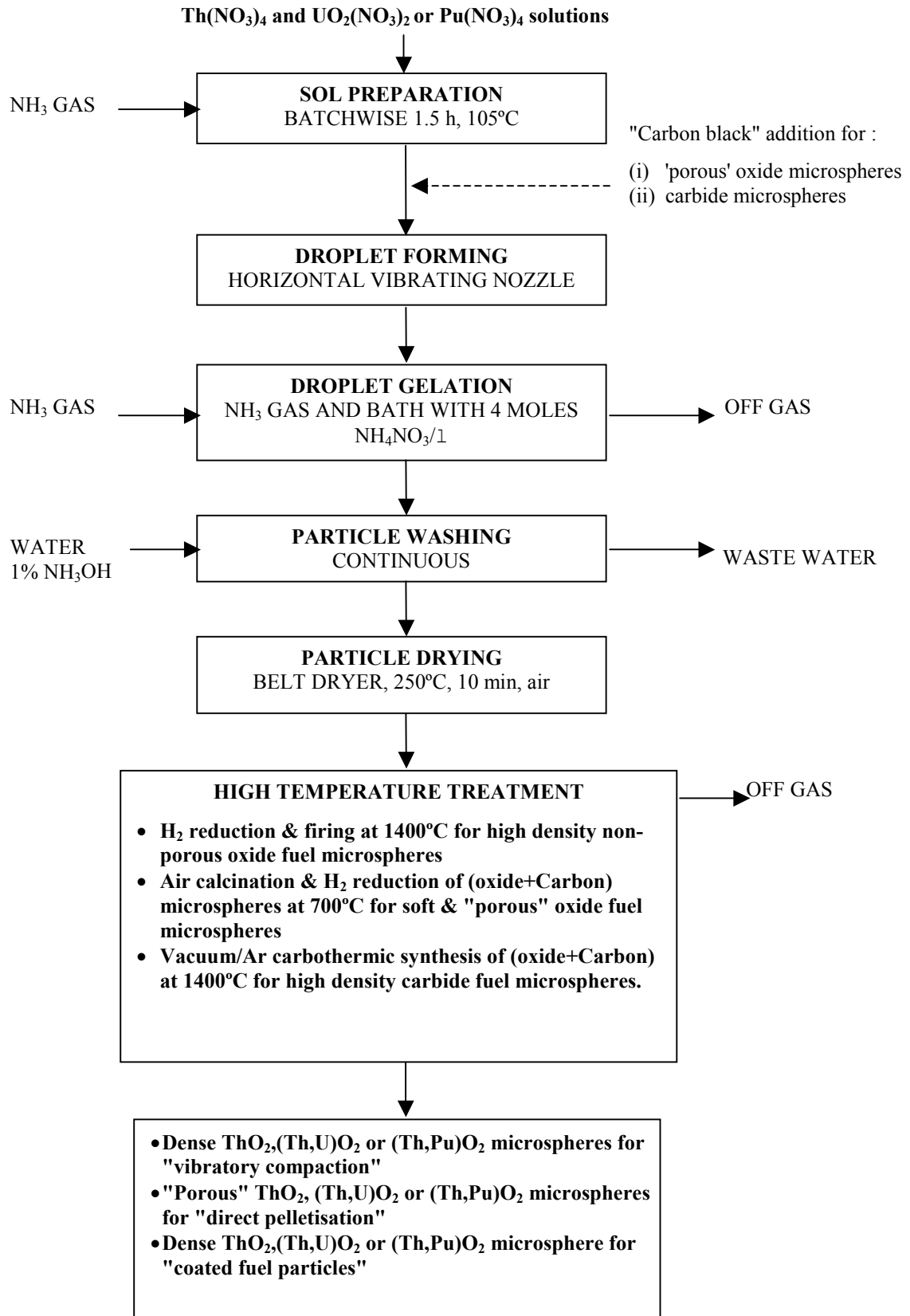


Fig. 17. Flowsheet based on KfA-EGT process of Germany for preparation of Th based "oxide" & "non-oxide" fuel microspheres for fabrication of "pellet-pin", "vipac pin" and "coated fuel particles".

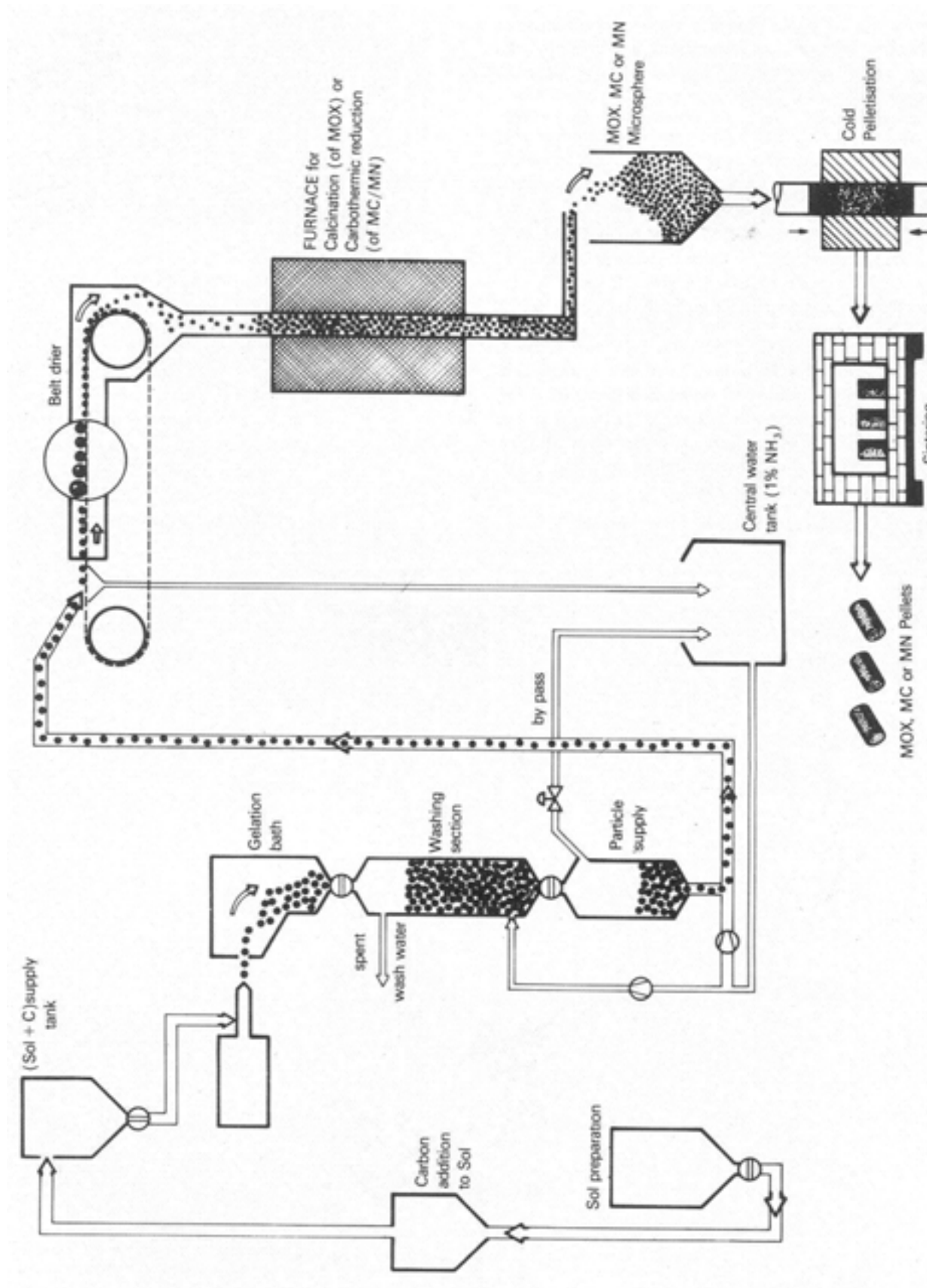


Fig. 18. Flowsheet for 'ammonia external gelation of thorium' process for production of sol gel derived Th based oxide and carbide fuel microspheres for: (a) Pelletization (SGMP) (b) Vi-pac pins (c) Coated fuel particles for HTGR.



By the ammonia internal gelation process, it is possible to produce ThO<sub>2</sub> and ThO<sub>2</sub>-based mixed oxide materials for the following specific requirements:

- (i) hard and high density microspheres suitable for manufacturing 'vi-pac' fuel or 'coated fuel particles' (for HTGR); and
- (i) soft, porous and easily crushable microspheres for direct pelletisation and sintering of fuel pellets.

However, the major disadvantages of the process are: (i) the narrow range of stable feed solution composition that would yield good quality microspheres, (ii) the use of more number of chemicals and inflammable organic materials and (iii) excessive washing cycles and waste generation.

### **5.3.3. Vibratory compaction**

'Vi-pac' fuel pins of Zircaloy clad (Th, <sup>233</sup>U)O<sub>2</sub>, containing 3%<sup>233</sup>UO<sub>2</sub>, have first been successfully manufactured on a pilot plant scale in USA, in the 1960s, in the unshielded glove-box facility of Babcock and Wilcox (B&W) Company, and the shielded Kilorod set-up of Oak Ridge National Laboratory (ORNL) [84], [85]. In the B&W facility, the fuel is deactivated by removing the first daughter product of <sup>232</sup>U i.e., Th<sup>228</sup> and is then refabricated rapidly before the increase in the <sup>232</sup>U daughters and the associated gamma activity. The maximum <sup>232</sup>U content in the unshielded facility of B&W was 42 ppm. A total of 192 fuel rods of 10 feet length were vibratory compacted in the glove box line. The Kilorod facility has been designed for semi remote operations with the capability of handling of <sup>233</sup>U containing up to 200 ppm <sup>232</sup>U and with frequent decontamination up to 600 ppm <sup>232</sup>U. In all, some 980 kg of (Th, <sup>233</sup>U)O<sub>2</sub> microspheres have been vibratory compacted into 1100 clad fuel pins in the smear density of 88–91%T.D. Based on the successful experience of the Kilorod facility, two remote fabrication facilities for handling highly radioactive <sup>233</sup>U-bearing material, namely Thorium Uranium Recycle Facility (TURF) at ORNL and Programma Ciclo Uranio Torio (PCUT) at CNEN, Italy were set-up but not utilized because of the change in programme [91]. In FRG, as part of the heavy water moderated thorium breeder reactor programme, a few 'vi-pac' (Th, U)O<sub>2</sub> fuel containing HEU with 93% <sup>235</sup>U were fabricated in the 1960s for irradiation-testing experiments [92].

### **5.3.4. Impregnation technique**

The impregnation technique is an attractive alternative for manufacturing highly radiotoxic <sup>233</sup>U or Pu -bearing thoria based mixed oxide fuel pellets, remotely in a hot cell or shielded glove-box facility, taking advantage of the chemical inertness of ThO<sub>2</sub>. In this process, the relatively less radioactive natural ThO<sub>2</sub> is first prepared in an unshielded area in the form of 'low density pellets' (≤80%T.D.) with 'open porosity' or sol gel derived 'porous microspheres'. The ThO<sub>2</sub> pellets or microspheres thus prepared are impregnated in uranyl nitrate (<sup>233</sup>U) or plutonium nitrate solution of molarity in the range of 1 to 3, in a shielded facility, followed by sintering in case of the pellets or cold pelletisation followed by sintering in case of the microspheres to obtain ThO<sub>2</sub>-based mixed oxide pellets of high density and excellent microhomogeneity, particularly when the impregnation was carried out in nitrate solutions of low molarity (0.5 to 1.0). The solid solution between ThO<sub>2</sub> and UO<sub>2</sub> or PuO<sub>2</sub> is formed during the sintering step. Thus, fine <sup>233</sup>U or Pu bearing powders are avoided and handling of these materials is restricted only in certain parts of the fuel fabrication plants. Process steps like precipitation of ammonium di uranate or plutonium oxalate, calcination,

mixing, grinding, granulation, etc., which are associated with ‘radiotoxic dust hazard’, are eliminated.

Figure 19 [74], [93] schematically shows the flowsheet of the ‘impregnation technique’ developed in India. Use of microwave during impregnation for local heating of the partially sintered low density ThO<sub>2</sub> pellets or ‘porous microspheres’ facilitates expulsion of entrapped gas and impregnation operation. Annular ThO<sub>2</sub> pellets are suitable for enhancing the impregnation operation, leading to uniform distribution of <sup>233</sup>U or Pu in sintered pellets. With ‘pellet impregnation’ technique, it was possible to prepare high density (Th, U)O<sub>2</sub> pellets containing up to 2.5% U and with ‘microsphere impregnation’, it was possible to produce (Th, U)O<sub>2</sub> containing up to 20% U.

### 5.3.5. *Sol-gel microsphere pelletisation*

Sol gel microsphere pelletisation (SGMP) is a novel concept for fabrication of oxide and non oxide ceramic nuclear fuel pellets of controlled density and microstructure by using sol gel derived dust-free and free flowing fuel microspheres, rather than fine powder derived granules, for compaction of fuel pellets and sintering. The advantages of SGMP process are as follows:

- radiotoxic dusts and aerosols are not produced and process losses are minimized;
- dust free and free flowing nature of microspheres facilitate remote and automated fuel fabrication inside shielded glove boxes or hot cells;
- high microhomogeneity in case of mixed oxide, carbide and nitride fuels since nitrate solutions of Th, U and Pu are mixed and used as starting materials;
- possibility of controlled density and tailored microstructure of fuel pellets; and
- the process is ideal for manufacturing highly radiotoxic thorium-based and <sup>233</sup>U and Pu bearing fuel pellets for nuclear power reactors.

The SGMP process has been successfully developed initially in Germany and later in India for manufacturing high density ThO<sub>2</sub>, (Th, U)O<sub>2</sub> and (Th, Ce)O<sub>2</sub> (Ce for simulating Pu) pellets containing uniform distribution of closed spherical pores in the ideal diameter range of 2–5 micron. The EGT process of Germany was modified for obtaining dust free and free-flowing ‘porous’ ThO<sub>2</sub>-based oxide and mixed oxide microspheres, which could be easily pelletised by cold compaction and sintered to high density pellets. For this, the following three major modifications have been made [94]:

- (i) using thorium nitrate, mixed thorium uranium nitrate or mixed thorium plutonium nitrate solutions of relatively low molarity (1-1.2 M).
- (ii) addition of ‘carbon black’ pore former to the ‘sol’ prior to gelation and later removing carbon by controlled air calcinations at 700°C to obtain ‘porous microspheres’ The porous microspheres have very low crushing strength and lose their individual identity during pelletisation and also facilitate uniform pore size, shape and distribution in sintered pellets.
- (iii) addition of around 1wt% Ca(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O to the heavy nitrate feed solution to obtain 0.4% CaO as ‘sintering aid’ in the fuel microspheres.

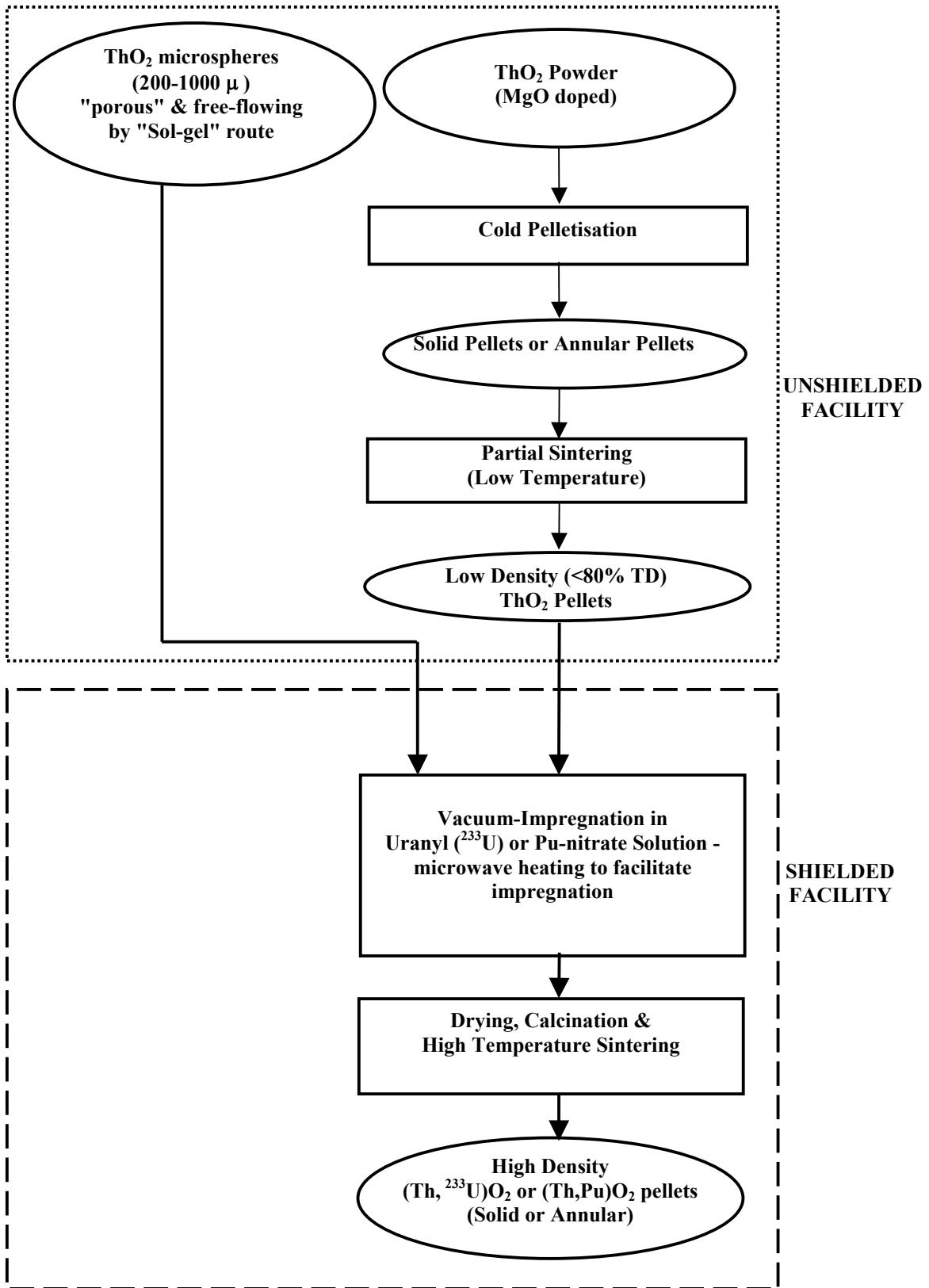
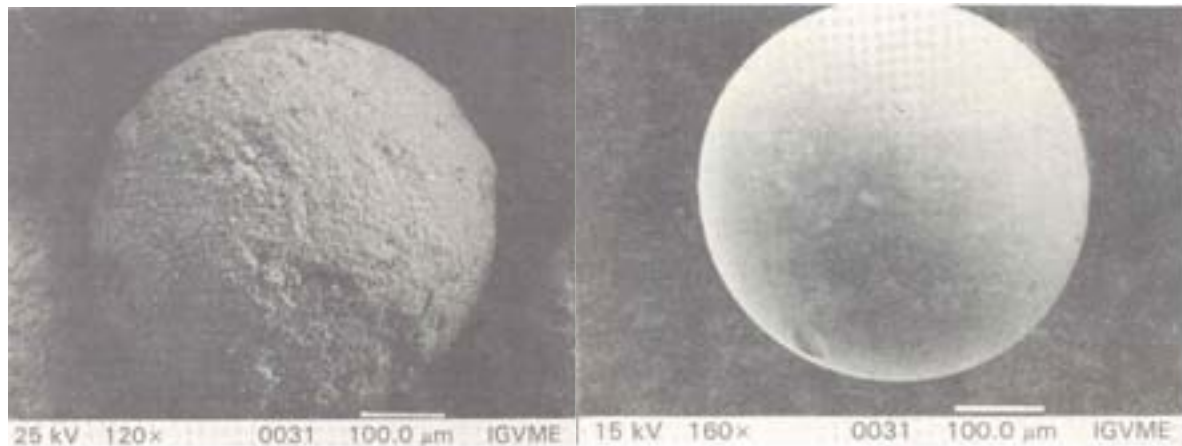


Fig. 19. Process flowsheet based on "Impregnation Technique" for manufacturing high density  $(\text{Th}, {}^{233}\text{U})\text{O}_2$  and  $(\text{Th,Pu})\text{O}_2$  fuel pellets.

Without the use of carbon black pore former, the EGT process leads to ‘non-porous’ microspheres on calcination, which retain their individual identity during pelletisation and sintering and lead to low-density oxide pellets with open porosity and a ‘black-berry’ microstructure because of densification within the microspheres and not between them during the sintering process. Fig. 20 shows the microstructure of sintered (Th, U)O<sub>2</sub> pellets prepared from ‘porous’ and ‘non-porous’ microspheres.



*Fig. 20. Microstructure of sintered (Th,U)O<sub>2</sub> pellets prepared from (a) ‘porous’ and (b) ‘non-porous’ microspheres.*

For preparation of high density microspheres of ThC<sub>2</sub> or (U,Th)C<sub>2</sub>, ultra fine carbon black particles are uniformly mixed with the ‘hydro-sol’ of the oxide prior to gelation. After gelation, hydrated gel microspheres containing an intimate mixture of oxide and carbon black are obtained, which are subjected to carbothermic synthesis in vacuum or flowing argon at around 1400°C to obtain high density reaction-sintered microspheres of the carbides or mixed carbides suitable for ‘coated fuel particles’ for HTGR.

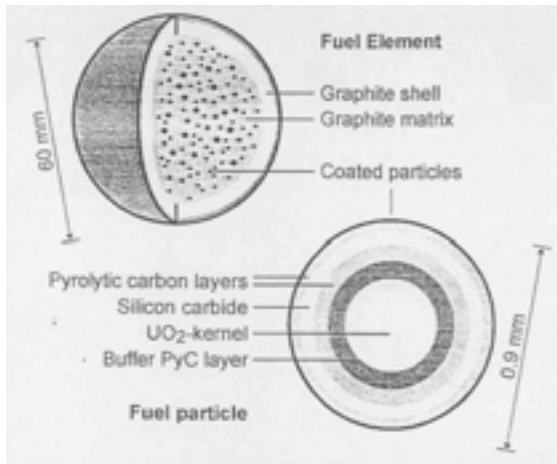
In India, the ammonia internal gelation process has been adapted for preparation of hydrated gel microspheres of ThO<sub>2</sub> and ThO<sub>2</sub>+UO<sub>3</sub>, which after controlled calcination leads to the formation of soft and easily crushable microspheres, which could be directly pelletised and sintered. HMTA is used as an ammonia generator and silicone oil at ~100°C is being utilized as an inert gelation bath. Addition of pore former is not necessary. However, as mentioned earlier, in the internal gelation of thorium process, it is necessary to have a precise control of the composition of feed solution and process parameters in order to prepare good quality microspheres and to restrict the molarity of the feed solution in the narrow band of 1.0–1.4M [89].

### **5.3.6. Coated fuel particles**

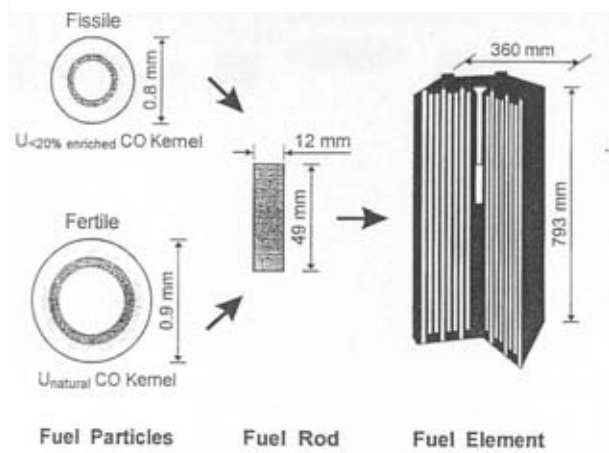
The higher melting point of thorium oxide and di-carbide as compared to their uranium counterparts, make thorium-based ceramic coated fuel particles in graphite matrix, an ideal choice of fuel for HTGRs, where the objective is to have a high coolant outlet temperature (750–900°C) and more particularly high fuel surface temperature (900–1100°C) and a compact core. R&D and manufacturing of coated fuel particles for HTGRs are underway for more than three decades in several countries. The core of an HTGR essentially consist of tiny, multilayer coated fuel particles, popularly known as TRISO, of ThO<sub>2</sub>, (Th, U)O<sub>2</sub>, ThC<sub>2</sub> or (Th, U)C<sub>2</sub> dispersed in graphite matrix and shaped in different forms depending on the design.

Two major directions for the fuel element designs have emerged, namely the German spherical fuel element design pursued in Germany (used in AVR and THTR reactors), Russia (VGM) and China (HTR 10) and the block type US design that have been utilized in USA [Peach Bottom Unit 1 and Fort St. Vrain (FSV)], UK (Dragon) and Japan (HTTR). In the German design, kernels of  $\sim 500 \mu$  of 'fissile' and 'fertile' materials, surrounded by layers of carbon buffer ( $\sim 95 \mu$ ), inner pyrocarbon ( $40 \mu$ ), silicon carbide ( $35 \mu$ ) and finally outer pyrocarbon ( $\sim 40 \mu$ ) as shown in Fig. 21(a), are homogeneously distributed in graphite matrix and shaped in the form of fuel element balls of diameter 60 mm with a 5 mm fuel free zone in the outer shell [53]. In HTGRs, the coated layers confine fission products released from the 'fissile' or 'fertile' kernels. The pyrolytic carbon (PyC) layers essentially retain Kr and Xe, whereas the silicon carbide layer is effective in retaining solid fission products, e.g. Cs, Sr, Ba, Ag, etc. SiC is an ideal coating material because of its low thermal neutron absorption cross-section, high ability for retention of solid fission products, good irradiation stability, high thermal conductivity, high strength and no thermal creep up to  $1900^\circ\text{C}$ . The disadvantage of high brittleness of SiC is overcome by embedding in dense PyC coatings, for which these particles are called TRISO. Earlier, the 'fissile' and 'fertile' kernels were coated with only PyC and were known as BISO particles. The reference fuel sphere contains approximately 11 000 TRISO coated 'fissile' particles. The active core of the German THTR reactor consist of 360 000 such spherical fuel elements. The modular HTGR of Russian Federation and China are also Pebble-Bed type reactors containing spherical fuel elements like the German HTGR. The US fuel element [Fig. 21(b)] is a hexagonal graphite block, 793 mm in length and 360 mm width across the flat surface contain some 102 coolant channels of diameter 15.9 mm and 210 fuel holes, which are filled with TRISO fuel compacts of diameter 12 mm and sealed. The active core of 350 MW(e) steam cycle HTGR consists of 660 graphite fuel elements and the core of 600 MWt direct cycle GT-MHR consists of 1020 elements. The FSV initial core required about 20 000 kg of HEU,  $(\text{Th}, \text{U})\text{C}_2$  and  $\text{ThC}_2$  TRISO coated particles assembled into some 1 500 hexagonal prismatic fuel elements. For Cores 1&2 of Peach Bottom Unit 1, some 3 500 kg of BISO coated HEU  $(\text{Th}, \text{U})\text{C}_2$  particles were manufactured and assembled into more than 48 000 annual fuel compacts in cylindrical fuel elements. The Japanese design [Fig. 21(c)] consists of block-type fuel, similar to the 'pin-in-block' design of the Dragon HTGR fuel of UK. Each hexagonal block, 550 mm in length and 360 mm across the flat surface, has 31 or 33 fuel holes, each containing an annular fuel pin, which consists of 14 fuel compacts in a graphite sleeve. A fuel compact made of graphite matrix powder with the shape of an annular cylinder, 30 mm height, 26 mm outer diameter and 10 mm inner diameter, contains 13 500 TRISO coated fissile particles. The HTTR active core is composed of some 70 000 fuel compacts.

(a) German Design



(b) US Design



(c) Japanese Design

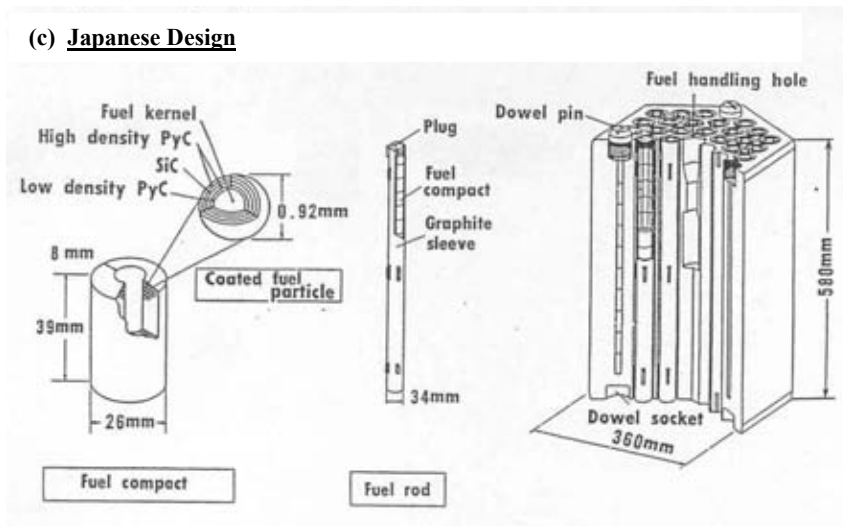


Fig. 21. Reference design of coated fuel particles and fuel elements for high temperature gas cooled reactors.

Manufacturing of HTGR fuel element is carried out in 3 steps, namely preparation of ‘fertile’ ( $\text{ThO}_2$  or  $\text{ThC}_2$ ) and ‘fissile’ [ $(\text{Th}, \text{U})\text{O}_2$  or  $(\text{Th}, \text{U})\text{C}_2$ ] containing LEU or  $^{233}\text{U}$ ] kernels, multilayer coating to form TRISO particles and fabrication of fuel elements in the form of spherical balls or prismatic blocks. The spherical fuel kernels are prepared by ‘ammonia external or internal gelation’ process starting with nitrate solution of thorium and uranium followed by reduction at  $900^\circ\text{C}$  and sintering at  $1500^\circ\text{C}$  to form high density fuel microspheres. For preparation of the carbide fuel particles, carbon-black is added to the sol prior to gelation and the hydrated sol containing a homogenous mixture of oxide and carbon particles are subjected to reaction sintering at  $\sim 1400\text{--}1500^\circ\text{C}$ . The coating is carried out in fluidized bed reactor using different hydrocarbon gas and methyl trichlorosilane (MTS:  $\text{CH}_3\text{SiCl}_3$ ) as per the sequence shown in Fig. 22. The buffer layer is coated in the temperature range  $1100\text{--}1400^\circ\text{C}$  using a mixture of argon and acetylene ( $\text{C}_2\text{H}_2 + \text{Ar}$ ). The inner pyrolytic carbon layer is coated at  $1370\text{--}1470^\circ\text{C}$  using a mixture of  $\text{Ar} + \text{C}_3\text{H}_6$ . The SiC layer is coated at  $1500\text{--}1570^\circ\text{C}$  using methyl trichlorosilane (MTS:  $\text{CH}_3\text{SiCl}_3$ ), a source for Si and C. Argon and hydrogen are used as the carrier gas along with MTS for the SiC coating. In recent years, ZrC coating is preferred for higher burnup in place of SiC. The process parameter for the outer pyrolytic carbon (PyC) layer is the same as that of inner PyC layer.

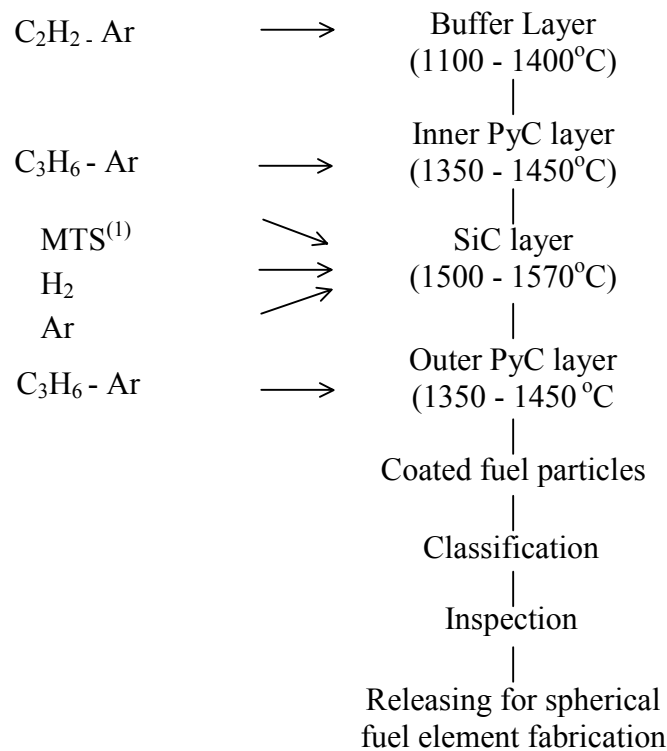


Fig. 22. Flowsheet for multi-layer coating of fuel particles for high temperature gas cooled reactor.

The coated fuel particles are embedded in carbon matrix and graphite shim. The carbon matrix consisting of 47% petroleum pitch, 38% filler, 10% octadecanol and 5% polystyrene is injected into a mould at  $160^\circ\text{C}$ . On cooling, the compact solidifies after which it is carbonized

at 900°C to decompose organic compounds and to obtain a solid carbon contact. Thereafter, the compacts are heated at 1 650°C for stabilization.

The spherical fuel element is formed in a rubber mould, under quasi-isostatic pressing condition with pre-pressing pressure of 30 MPa and final forming pressure of 300 MPa. The spherical fuel elements thus formed is first carbonized at ~800°C and later heat treated at 1 950°C.

## 6. BACK END ISSUES AND CHALLENGES

### 6.1. Back end issues

The back end of the thorium fuel cycle has several unique issues and challenges, both for 'open' and 'closed' cycles, which need to be addressed and resolved before thorium could be introduced in commercial nuclear power reactors. First, it is essential to know the inventories of radionuclides in spent Th-based fuels having 'fertile/fissile' combinations like  $^{232}\text{Th}/^{235}\text{U}/^{238}\text{U}$ ,  $^{232}\text{Th}/^{239}\text{Pu}$ ,  $^{232}\text{Th}/^{233}\text{U}$  and  $^{232}\text{Th}/^{233}\text{U}/^{238}\text{U}$ , the residual heat associated with these fuels, their radiological impact and the quantities of thorium, uranium, plutonium and transuranic elements, including minor actinides (MA) and long lived fission products. As such,  $^{232}\text{Th}$ - $^{233}\text{U}$  fuel cycle does not produce plutonium and minor actinides (Np, Am and Cm) in significant amount, at least for the first recyclings. However, there are other radionuclides such as  $^{231}\text{Pa}$ ,  $^{229}\text{Th}$  and  $^{230}\text{U}$ , which may have long term radiological impact. In general, there is lack of experience and know-how on the back end issues of: (i) high burnup once-through Th- $^{235}\text{U}/^{238}\text{U}$  and Th-Pu cycles and (ii) multiple recycling of Th, U and Pu. In addition, the common challenges for uranium and thorium fuel cycles like annihilation of long lived radionuclides by transmutation into stable or short lived products are also to be resolved.

For reprocessing of spent Th-based fuels, the wet chemical route developed in Oak Ridge National Laboratory (ORNL) [95] in the mid 1950s, namely the THORium-uranium EXtraction (THOREX) process, based on solvent extraction separation of uranium and thorium from fission products by means of tributyl phosphate (TBP), has so far been the most viable route for recovery of uranium. Figure 23 shows the schematic diagram of the THOREX process. So far, reprocessing of spent thorium fuel has been carried out only in a few countries [96], [97] based on THOREX process mostly on laboratory or pilot plant scale. In India, a small laboratory facility was set-up at BARC in 1970, where thorium metal and oxide elements irradiated at CIRUS were reprocessed to obtain high purity  $^{233}\text{U}$  containing less than 5 ppm  $^{232}\text{U}$ . The  $^{233}\text{U}$  from the solvent extraction plant was further purified by anion exchange. The THOREX process is yet to attain the maturity of the commercial and well-established Plutonium URanium EXtraction (PUREX) process for reprocessing spent uranium or mixed uranium plutonium fuels.

Some of the major problems in the back end of thorium cycle are as follows:

**The protactinium problem:** In the conversion chain of  $^{232}\text{Th}$  to  $^{233}\text{U}$ ,  $^{233}\text{Pa}$  is formed as an intermediate, which has a relatively longer half-life (~27 days) as compared to its counterpart  $^{239}\text{Np}$  (half-life: 2.4 days) in the uranium fuel cycle. As a consequence, it is necessary to have a cooling time of at least 12 months (more than 10 half-lives of  $^{233}\text{Pa}$ ), prior to reprocessing, in order to complete the decay of  $^{233}\text{Pa}$  to  $^{233}\text{U}$  and avoid loss of any  $^{233}\text{U}$  fissile material. Normally, Pa is passed into the fission product waste in the THOREX process. This could have long term radiological impact because of the formation of  $^{231}\text{Pa}$ , an  $\alpha$ -emitting isotope of



protactinium in the thorium burnup chain with a relatively long half-life ( $3 \times 10^4$  years). Attempts of extracting Pa together with U and Th by the  $\text{HNO}_3$ -TBP/ Kerosene solvent extraction route has not been successful. However, selective adsorption of protactinium in Vycor glass with subsequent elution, preceding the extractive separation process, has been reported to be successful. Nearly 98% of protactinium could be separated by this novel method.

**The  $^{232}\text{U}$  problem:** In irradiated  $^{232}\text{Th}$  and mixed  $^{232}\text{Th}$ - $^{233}\text{U}$  and  $^{232}\text{Th}$ - $^{239}\text{Pu}$  fuels,  $^{232}\text{U}$  is also formed along with the bred  $^{233}\text{U}$ , as shown in the 'thorium burnup chain' in Fig. 24. The  $^{232}\text{U}$  is mainly generated from thorium as a result of the 6.37 MeV threshold (n, 2n) reaction and also from the (n, 2n) reaction with  $^{233}\text{Pa}$  and  $^{233}\text{U}$ .  $^{232}\text{U}$  emits alpha particles and has a half-life of 73.6 years. Radiation hazard mainly arises due to build-up of the gamma emitting, short-lived daughter products of  $^{228}\text{Th}$ , namely  $^{212}\text{Pb}$ ,  $^{212}\text{Bi}$  and  $^{208}\text{Tl}$ , as shown in Fig. 25, particularly  $^{208}\text{Tl}$ , which emits 2.6 MeV gamma radiation.  $^{232}\text{U}$  cannot be chemically separated from the recovered  $^{233}\text{U}$ . Likewise,  $^{228}\text{Th}$  cannot be chemically separated from the recovered thorium in the reprocessing plant. As a result, both  $^{233}\text{U}$  and  $^{228}\text{Th}$ , which are recovered from reprocessing the spent thorium fuel cycle cores, develop high-energy gamma radiation fields on standing. Hence, remote reprocessing and refabrication are needed. The  $^{232}\text{U}$  generation depends upon the fast neutron flux at the thorium assembly position in the reactor and the time of irradiation. Hence, thorium or thorium-based fuels irradiated in fast reactors are likely to contain higher quantities of  $^{232}\text{U}$ . In a harder spectrum of LWRs, the  $^{232}\text{U}$  production will be in the range of 2 000 to 3 000 ppm at typical exit burnups. In a well thermalized spectrum like PHWR, the  $^{232}\text{U}$  content in an irradiated thorium assembly is expected to be in the range of 500 to 1 000 ppm. In the BN-350 fast neutron reactor, the  $^{232}\text{U}$  content in irradiated thorium blankets has been significantly minimized by locating the thorium blankets some 15 to 20 cm away from the core border. The  $^{232}\text{U}$  content was only 2 to 11 ppm in  $^{233}\text{U}$  obtained by irradiation of thorium blanket away from the core in BN-350, until about  $1.3\text{g}^{233}\text{U}$  per kg of thorium was obtained [59].

**Dissolution problem in  $\text{HNO}_3$ :** Unlike uranium oxide and plutonium oxide, thorium forms only the dioxide, which is very stable. Uranium dioxide dissolves rapidly in nitric acid in a molarity range 6 to 13,  $\text{ThO}_2$  and  $(\text{Th,U})\text{O}_2$  or  $(\text{Th,Pu})\text{O}_2$  containing higher percentages of thorium (>80%) cannot be dissolved with pure  $\text{HNO}_3$ . A small amount of HF addition to nitric acid is essential for the dissolution of the relatively inert  $\text{ThO}_2$ -based fuels. However,  $\text{ThC}_2$  or  $(\text{Th,U})\text{C}_2$  can be directly dissolved in  $\text{HNO}_3$  without using fluoride ions as catalyst. The use of fluoride ion enhances the corrosion of stainless steel equipment and pipings. This problem is mitigated by the addition of small amounts of aluminium in the form of nitrate to complex the excess fluoride thereby limiting the concentration of free fluoride ion. The so-called THOREX reagent [13 M  $\text{HNO}_3$  + 0.05 M HF + 0.1 M  $\text{Al}(\text{NO}_3)_3$ ] developed by the Oak Ridge National Laboratory (ORNL) in the 1950s [95] has so far been the best for dissolution of Th-based metallic fuel,  $\text{ThO}_2$  and  $\text{ThO}_2$ -based mixed oxides. Conventionally, the spent thoria or thoria based mixed oxide fuel is dissolved with agitation in boiling THOREX solution at around 393K under atmospheric pressure. Using THOREX dissolvent at 473 K under about 9 atmospheres of inert gas pressure drastically increases the rate of fuel dissolution. Irradiated fuel in general has been found to dissolve faster, probably because of the disturbed crystal lattice. Recent experimental studies [76], [98] with unirradiated  $\text{ThO}_2$  pellets have shown that addition of ~1.5% MgO during pellet fabrication and use of microwave heating facilitate dissolution of  $\text{ThO}_2$  and addition of 0.03 M NaF in place of 0.05 HaF also enhances the dissolution rate.



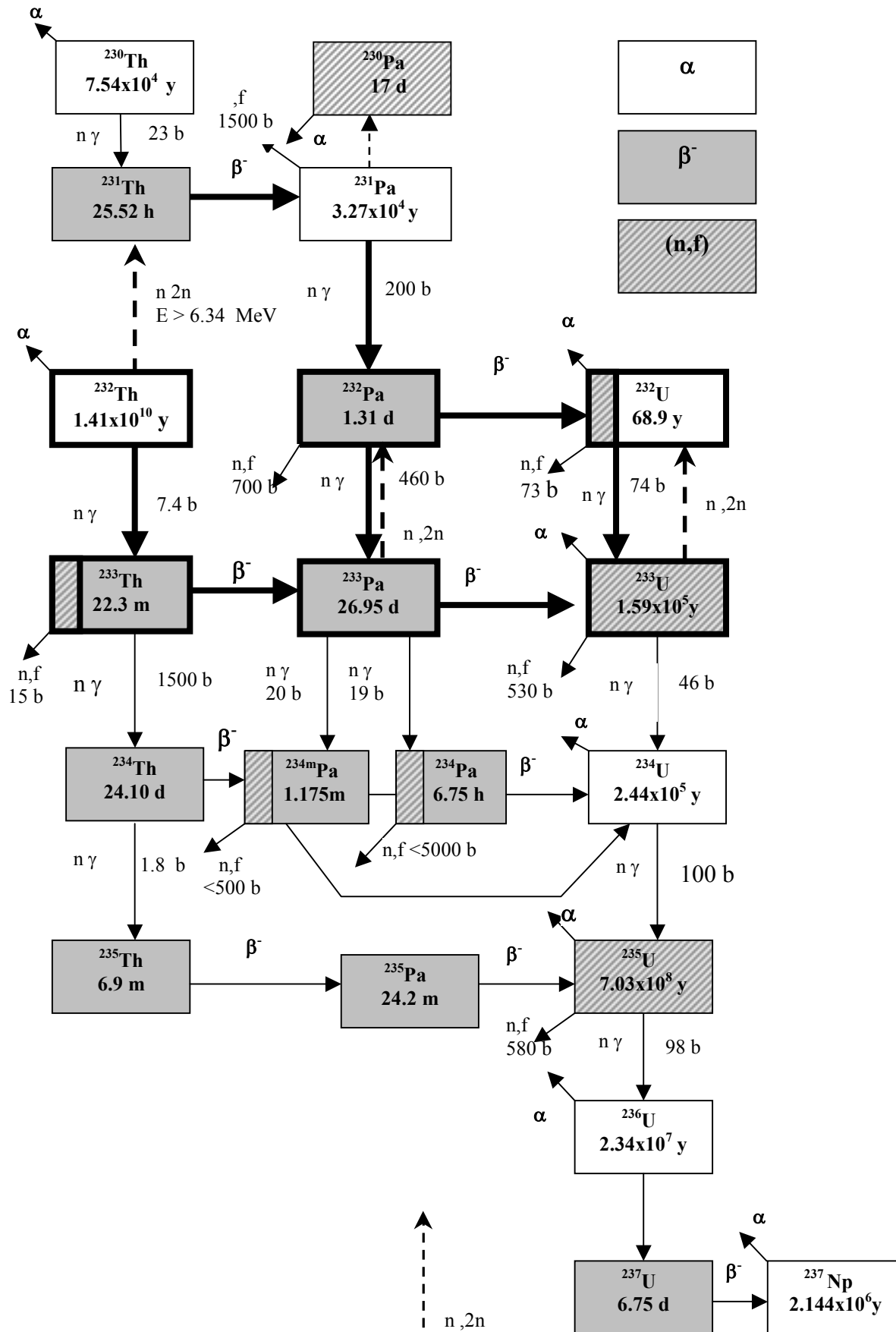


Fig. 24. The thorium chain.



The first step in reprocessing of spent fuel is the ‘head end’ treatment. This step is distinctly different for graphite matrix HTGR fuel elements containing ‘coated fuel particles’ as compared to Zircaloy or stainless steel clad LWRs, PHWRs and LMFBRs fuels in the form of ‘pellet-pin’ or ‘vi-pac’ pin assemblies. For HTGR fuel elements, which consist of nearly 98wt% graphite, the primary objective is to remove the bulk of graphite from heavy metals and the fission products. The reference and the only qualified and advanced ‘head end’ process for HTGR fuel elements is based on ‘crush-burn-leach’ route [99], where the fuel blocks and spheres are subjected to dry mechanical crushing to sizes in the range of 0.5 mm to several millimeters followed by fluidized bed burning of all carbon particles to form CO<sub>2</sub> in the off gas along with tritium and volatile fission products like krypton, iodine and xenone, etc. The off gas is subjected to further treatment and the <sup>14</sup>C is completely or partially retained by absorbing CO<sub>2</sub> in a Ca(OH)<sub>2</sub> slurry to form solid Ca(CO)<sub>3</sub>, which is stored as long lived low-level radioactive waste. The head end treatment of thorium based fuels from LWRs, PHWRs and LMFBRs are more or less similar to spent UO<sub>2</sub> or (U, Pu)O<sub>2</sub> fuels from these reactors and begins with ‘chop-leach’ process, which involves mechanical decladding followed by dissolution in nitric acid.

The major steps in reprocessing spent thorium fuel following the THOREX route are as follows: (i) head-end process for separation of irradiated fuel from associated materials such as fuel cladding or graphite, (ii) dissolution in boiling THOREX solution: 13 M HNO<sub>3</sub> + 0.05 M HF + 0.1M Al (NO<sub>3</sub>)<sub>3</sub>, (iii) Th/U/Pu partitioning by solvent extraction and separation of fission products, (iv) further purification of uranium by ion exchange or co-precipitation of (Th, U) or (Th, Pu) salts and (iv) waste treatment and disposal. So far, no alternative method capable of replacing the THOREX process has been developed, though a few alternative extractants have been explored in laboratory studies.

### **6.2.1. Head end processes**

The first step in ‘reprocessing’ is chemical or mechanical decladding of the irradiated fuel elements for the actual chemical separation and purification process. For aluminium-clad thorium metal or oxide fuel from research reactors, NaOH and NaNO<sub>3</sub> are used for chemical decladding, whereas for Zircaloy or stainless steel clad thorium oxide or mixed oxide fuels from water cooled and fast reactors respectively, mechanical ‘chop-leach’ process is usually employed. The head end treatment procedures of HTGRs consists of two main steps, namely disintegration of graphite structurals followed by separation of heavy metal from graphite. Fig. 26 summarizes the alternative head end treatment procedures for spent HTGR fuel (7). The qualified technique consist of mechanical crushing and grinding for fuel disintegration and quantitative burning of all carbon to form carbon dioxide in the off gas leaving spent heavy metals in the form of ash consisting of thorium, uranium and other non-volatile fission products. The oxidizer off gas contains CO<sub>2</sub>, CO, O<sub>2</sub>, N<sub>2</sub>, volatile fission products and particulate matter. The off gas is cooled and passed through sintered metal filter in cyclone separator. Most of the particulate matter is removed by the separator and sintered metal filter and recycled back to the oxidizer. The off gas from the cyclone is passed through silica-gel adsorber for removing ruthenium to cesium and through absolute filters to remove particulates and finally discharged to the reactor stack by exhaust fans. The off gas is monitored for radiation and particulate matter.

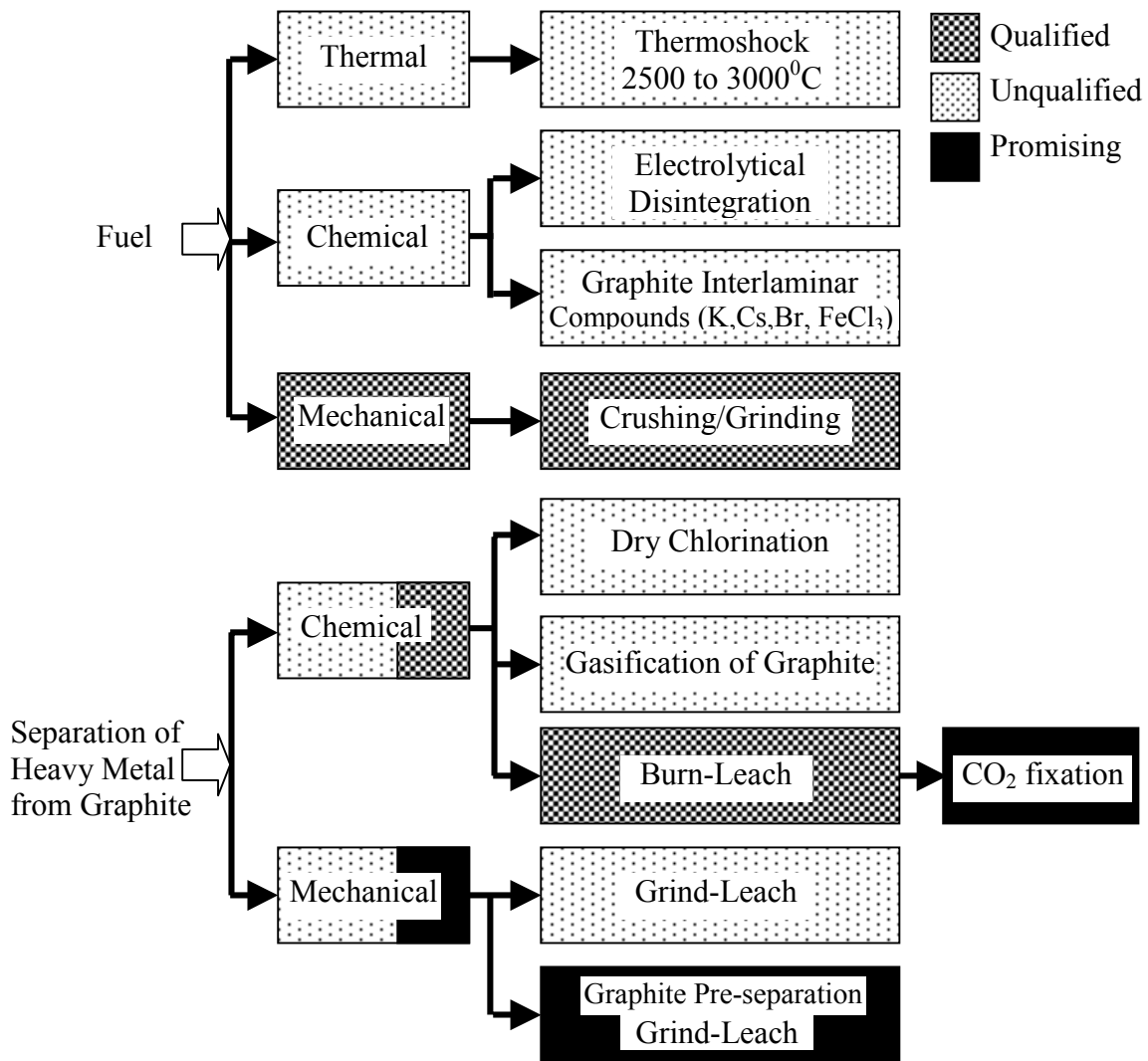


Fig. 26. Different head end treatment processes for multilayer coated fuel particles in graphite matrix for HTGR.

Prior to the leaching operation, the decladding of SS or Zircaloy clad fuel elements are mostly carried out by the following methods:

- Mechanical removal of the cladding material by cutting, shearing, grinding and crushing, popularly known as chop leach, shear-leach and grind leach.
- Chopping the fuel element rods in single or bundle shear, popularly known as the chop-leach process.
- Chemical de-cladding:

SS cladding: by DAREX or SULFLEX process using 5 M HNO<sub>3</sub> + 2 M HCl and 5 M H<sub>2</sub>SO<sub>4</sub> respectively or by Dry Fluorination with HF-O<sub>2</sub> mixture.

Zircaloy cladding: by ZIRFLEX using 6 M NH<sub>4</sub>F + 0.5 M NH<sub>4</sub>NO<sub>3</sub> or Dry Fluorination/Chlorination.

- Joint Dissolution of cladding with fuel using ZIRFLEX or SULFLEX for zirconium and SS clad fuels respectively.

### 6.2.2. Dissolution and solvent extraction

The dissolution of irradiated thorium-based fuel in nitric acid is slow for which a fluoride ion catalyst is required. The presence of fluoride ion cause corrosion problem in stainless steel equipment and piping in the reprocessing plant for which aluminium nitrate is added to the dissolver. The aluminium addition is kept to the minimum because it passes through the plant with the fission products and adds to the radioactive waste. For dissolution of thorium, the standard THOREX solution consisting of 13 M HNO<sub>3</sub> + 0.05 M HF + 1 M Al(NO<sub>3</sub>)<sub>3</sub> is universally used and till date better or alternative solution has not been developed. The dissolution could be marginally enhanced by microwave heating and addition of 0.03 M NaF along with HF. ThO<sub>2</sub>-based irradiated sintered pellets containing MgO dopant (~1.5%) are reported to dissolve faster compared to un-doped pellets. The product solution from dissolver unit, with acid concentration in the range of 8–9 M HNO<sub>3</sub>, is subjected to filtration or centrifugation for removing any undissolved solids. For solvent extraction process, Tributyl Phosphate (TBP) is the most common extractant, which is used in combination with hydrocarbon diluent, e.g. usually Shell Sol–T, dodecane or n-paraffin for reprocessing spent thorium-based fuel. The relative volume fraction of TBP and the diluent are selected depending on whether <sup>233</sup>U alone or both Th and U or all U, Th and Pu are to be recovered.

In the THOREX process, the use of strong salting-out agent is indispensable to achieve satisfactory thorium extraction rates and thorium yields. A relatively high acid concentration in the scrubbing part of the extraction process ensures almost quantitative thorium extraction. However, high HNO<sub>3</sub> concentration favour the extraction of some fission products and thus deteriorate the achievable decontamination factors. An acid deficient feed solution would be of advantage since a high acid concentration favours radiolysis of TBP. However, in the region of low acid concentrations, particularly for high burnup fuels, undesirable precipitation of fission products like zirconium occur. A high acid feed solution prevents this problem. The following three schemes can be adopted for the THOREX process:

#### 6.2.2.1. INTERIM 23 process separation of only uranium

In most countries, the so-called INTERIM 23 process [100] has been used in the past, where partitioning of thorium is omitted and the uranium is selectively extracted with 1.5 to 5% TBP in Shell sol–T diluent, which gives relatively good decontamination factors. The objective of the INTERIM 23 process is to extract only the uranium in the organic phase and the thorium is passed into the aqueous waste stream raffinate together with the fission products. Next, the organic phase is scrubbed with 1 to 2 M nitric acid to remove the co-extracted thorium. The final thorium contamination depends on the number of scrubbing stages and their efficiency. The <sup>233</sup>U from the organic phase is finally stripped with acidified water to recover the extracted uranium as shown in Fig. 27. However, the uranium thus separated contains significant amount of thorium as impurity. The <sup>233</sup>U product used to be further purified by anion exchange process in hydrochloric acid medium. The anionic chlorocomplex of uranium in 8 M hydrochloric acid is absorbed on the anion exchanger leaving the cation thorium in the effluent. The uranium product eluted with dilute nitric acid is precipitated as di-uranate and calcined to uranium oxide. The anion exchange process has certain disadvantages like: (i) change over from nitrate medium to chloride medium, (ii) corrosion of equipment, (iii) gasing of column due to high concentration of HCl, and (iv) poor decontamination factor from the corrosion product iron. These difficulties could be resolved by adapting any one of the

following alternatives: (a) cation exchange process in nitric acid for preferential sorption and separation of tetravalent thorium using gel type Dowex 50 WX8 (100 to 200 mesh) or Dowex 50 WX4 (50 to 100 mesh) resin. The cation exchange method is suitable for continuous processing in pilot scale operation, (b) anion exchange in acetic acid medium for selective sorption of uranium as its anionic acetate complex though this method has also similar problems like the one involving hydrochloric acid medium, (c) precipitation and separation of thorium from uranium as thorium oxalate.

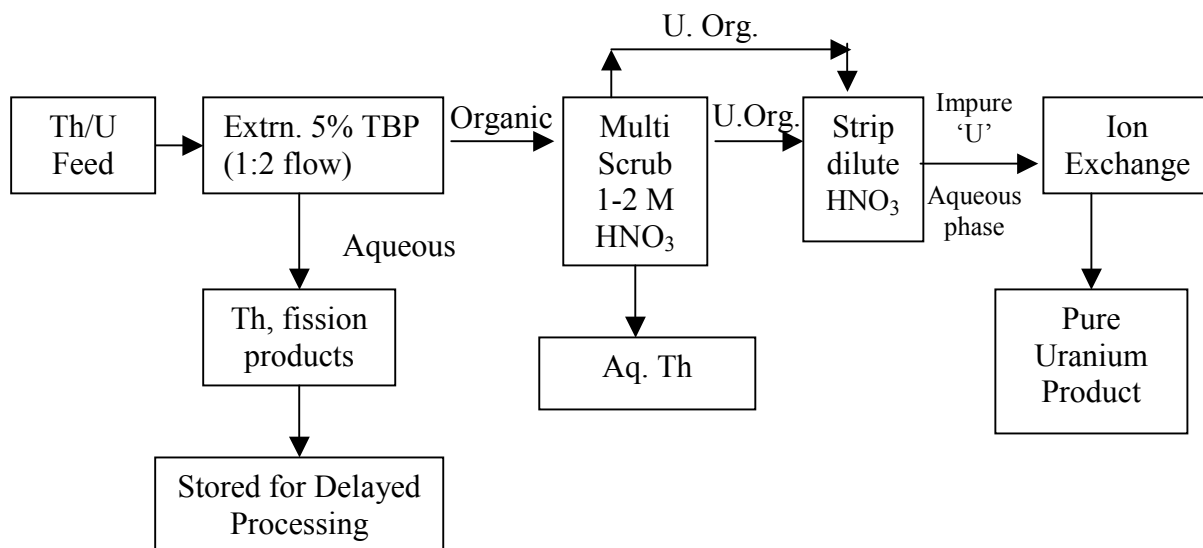


Fig. 27. Process flowsheet for extraction separation of only uranium from irradiated thorium or thorium based fuel.

#### 6.2.2.2. Two stream reprocessing for uranium and thorium

For extraction of thorium along with uranium, TBP-based processes with higher percentage of TBP (30 to 42.5%) and paraffin/dodecane diluent has been used to extract thorium along with uranium leaving the fission products in the aqueous phase as raffinates. For separation of uranium from Thorium after co-extraction in high percentage of TBP, the control of acidity is important for selective stripping. A higher acid strip ( $> 0.3\text{M}$ ) is used to remove the bulk of Thorium while very low acid is used to strip the Uranium left in the organic phase.

In the THOREX process, control of the acidity of the feed solution is important. The feed adjustment is made by dilution with water. In most cases, an acid deficient solution is used for the TBP-HNO<sub>3</sub> solvent extraction in order to have relatively high decontamination factors in terms of the fission products. However, low acid concentration has the disadvantage of poor Th yields and crud precipitation because of hydrolysis. This is disadvantageous particularly for high burnup fuel, containing higher percentages of fission products (e.g. Ru, Zr, Nb, Pa, etc.), because it leads to precipitation. On the other hand, a high acid concentration favours radiolysis of TBP. Merz and Zimmer [101] have discussed in length about reprocessing of high burnup thorium-based fuel.

One of the problems encountered in this route is the third phase formation due to poor solubility of Th-TBP complexes in the diluent use. The third phase formation depends on the initial thorium content, salt content and acidity of the aqueous and organic phases, the temperature of extraction, the concentration of TBP and the nature of the diluent. In order to avoid third phase formation, the solvent loading of TBP phase with thorium is restricted to



values much lower than what is normally employed in the case of uranium. Alternatively, aromatic diluents like decalin (deca hydronaphthalene), in place of dodecane, Shell sol-T or n-paraffin, can be used to increase the loading of thorium in TBP without third phase formation. Amides are also being considered as potential candidates for the selective extraction of uranium, based on its superior uranium-thorium separation factor. In general, for 30% TBP flowsheet with 1–3 M HNO<sub>3</sub>, as feed acidity the organic loading is in the range of 28–35 g/l. For 42.5% TBP flowsheet, the organic loading is ~55 g/l. Results using acid deficient thorium flowsheets have also been reported where aluminium nitrate has been used as salting out agent. The use of nitric acid alone as salting agent results in large reduction in waste volumes and is hence more favoured. For selective stripping of uranium and thorium from the organic phase, high acid strip (above 0.3 M) is used to remove the bulk of thorium, while very low acid is used to strip the uranium left in the organic phase.

Alternatively, if the irradiated Th-based fuels are long cooled ( $\geq 2$  years), the <sup>233</sup>U is first separated from the bulk of thorium by 5% TBP flowsheet and then the thorium is removed by 30% TBP using the conventional flowsheet. During the extraction of uranium, the fission product pick up by 5% TBP would be low and hence the downstream contamination would be low. The thorium could be processed at a subsequent stage after cooling thereby minimizing the contamination and radiation problems due to fission products and residual <sup>228</sup>Th.

For co-processing and enhancement of uranium thorium ratio a 5–10% TBP extraction scheme can be used as shown in Fig. 28 (10). In this case, all uranium would be extracted into TBP phase and the tailored quantity of thorium could be co extracted with uranium by judicious choice of TBP concentration in the extractant. The thorium and uranium thus loaded in the organic phase can be stripped together and further co-processed. The volume of 5% TBP to be handled will depend mainly on the amount of uranium to be recovered.

#### 6.2.2.3. *Three stream reprocessing of irradiated (Th,Pu) fuel*

The irradiated (Th, Pu) fuel will consist of thorium, uranium, plutonium and the fission products. The three-stream process is a combination of THOREX and PUREX processes. In the first step, the 5% TBP flowsheet is followed to extract uranium and plutonium in the organic phase, leaving the thorium and the fission products in the aqueous phase. After scrubbing and stripping, the mixed (U–Pu) nitrate solution is further processed according to the PUREX flowsheet for separation of U and Pu in the form of nitrate solutions, which could be further processed for obtaining UO<sub>2</sub> and PuO<sub>2</sub> powders for storage. The aqueous solution containing thorium and fission products from the first step is then subjected to solvent extraction using 30% TBP for extracting the thorium in the organic phase, leaving the fission products in the aqueous phase. The thorium is then scrubbed and stripped in the aqueous phase by using dilute nitric acid after which the thorium nitrate is precipitated in the form of thorium oxalate by addition of oxalic acid. The thorium oxalate is calcined in air to form ThO<sub>2</sub> powder.

So far, only limited investigations have been carried out on the three-stream process. In the acid-deficient THOREX process, during dissolution, large quantities of nitrous gases are produced which stabilizes <sup>+4</sup>Pu, which is extractable, and <sup>+5</sup>Np, which is not extractable. As a result, all Np go to the aqueous phase alongwith the fission fragments, whereas Pu is extracted jointly with Th and U. During re-extraction, 90% of Pu is distributed to the Th stream and 10% to the U stream [103]. Further investigation is needed to optimize the process chemistry of 3–stream route to separate and recover U, Pu and Th in pure form.

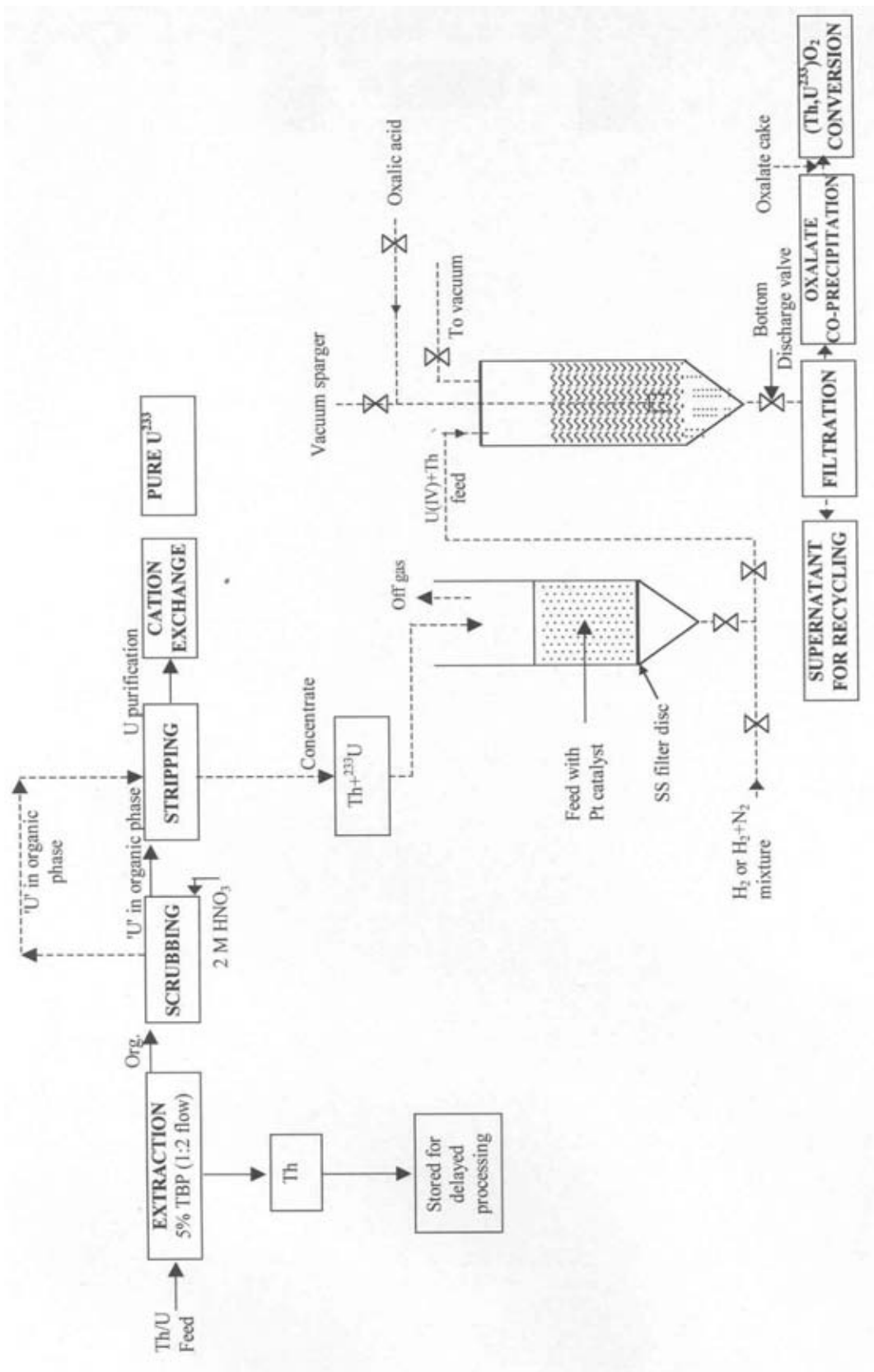


Fig. 28. Modification of THOREX process for co-extraction and co-precipitation of U and Th oxide [9].

### 6.3. Waste management

Thorium-based fuel cycle does not produce plutonium and minor actinides like Np, Am and Cm but is associated with other radionuclides such as  $^{231}\text{Pa}$ ,  $^{229}\text{Th}$  and  $^{230}\text{U}$ , which may have long term radiological impact. The chemistry of THOREX process is somewhat different compared to that of PUREX. If thorium is not to be recycled because of its radioactivity, its disposal becomes an additional problem. The presence of sulphates, phosphate and fluorides in the raffinates of the reprocessing plants could have considerable corrosion problem at the high temperatures during the vitrification process. In addition, more than 20% of the fluoride are likely to volatilize. The fluoride problem could be minimized by using calcium and fixing the fluoride as  $\text{CaF}_2$ . The THOREX route is expected to generate some 50-70% more glass volume compared to the PUREX process.

### 6.4. Disposal of thorium fuels

#### 6.4.1. Introduction

Thoria-based fuels are appealing from a waste-management perspective because  $\text{ThO}_2$  is chemically stable and the highest oxidation state of thorium unlike that of  $\text{UO}_2$ , which oxidizes to  $\text{U}_3\text{O}_8$  and  $\text{UO}_3$ . In addition,  $\text{ThO}_2$  is almost insoluble in groundwater. To analyze and appreciate the waste disposal issues of thorium based fuels, an intercomparison of the physical properties of  $\text{UO}_2$  and  $\text{ThO}_2$  is essential. The disposal of spent  $\text{ThO}_2$ -based fuel should match the scenario of direct disposal of spent  $\text{UO}_2$  fuel bundles in corrosion-resistant container, surrounded by a clay-based buffer material, within a vault excavated deep in granite [104]. Taylor et al [105] has made a detailed comparison of the factors affecting the disposal of  $(\text{Th}/\text{Pu})\text{O}_2$  and  $\text{UO}_2$  fuels.

#### 6.4.2. Chemistry of thorium

##### 6.4.2.1. Redox chemistry

By far the most important chemical difference between  $\text{ThO}_2$  and  $\text{UO}_2$  is that thorium is present in its maximum oxidation state, Th(IV), whereas uranium is not. Under oxidizing conditions,  $\text{UO}_2$  can be converted to the comparatively soluble uranyl cation,  $\text{UO}_2^{2+}$ , and its derivatives. This reaction and the corresponding reduction dominate the geochemistry of uranium, and an understanding of the kinetics of oxidative dissolution of  $\text{UO}_2$  is central to the performance assessment of irradiated  $\text{UO}_2$  fuel as a waste form, so long as the uranium or other fissile component is either present in solid solution or is effectively encapsulated by thorium. Oxidative dissolution of the matrix is not an issue with thorium fuel. Redox conditions could affect the leachability of  $^{233}\text{U}$  from irradiated thorium, but this leachability would be limited to surface dissolution and is unlikely to be a major concern.

The inertness of thorium to oxidation is also relevant to interim dry storage of irradiated fuel before geological disposal. The maximum acceptable temperature for dry storage of spent  $\text{UO}_2$  fuel from CANDU-PHWRs in air is typically 150 to 175°C, because at higher temperatures oxidation of  $\text{UO}_2$  to  $\text{U}_3\text{O}_8$  in defected elements can cause powdering of the fuel matrix and splitting of the fuel cladding [106]. Matrix oxidation is not an issue with thorium based fuels. Moreover, the thorium structure can easily accommodate oxidation of minor solid-solution components such as U and Pu. Thus fuel oxidation is unlikely to be a concern during dry storage of thorium based fuels, and hence the maximum storage temperature would be limited by some other factor, probably cladding degradation [107].

#### 6.4.2.2. *Aqueous chemistry*

The solubility of crystalline thoria in aqueous solution at 25°C and pH>5, in the absence of complexing agents, has been estimated at  $10^{-14}$  mol/kg, or 2 parts per quadrillion [108]. The release of actinides and those fission products that are retained by the thoria matrix is expected to be limited by the solubility of ThO<sub>2</sub>. Such release would be exceedingly slow in an engineered disposal vault of the type envisaged for CANDU UO<sub>2</sub> fuel. No credible aqueous or geochemical process has been identified that would greatly accelerate ThO<sub>2</sub> fuel-matrix dissolution under disposal conditions [105].

#### 6.4.2.3. *Compatibility of actinides with thoria*

Thoria crystallizes with the fluorite structure, as do all other actinide dioxides. Extensive solid-solution formation occurs between these oxides, and the fluorite structure can also accommodate substantial levels of actinides in other oxidation states, such as Am(III) and U(VI), as well as many fission products. Thus no phase segregation of actinides is expected to occur within the fuel, either during operation or after disposal, and it is reasonable to assume that release of actinides will be controlled by the slow dissolution rate of the thoria matrix, provided that the fuel is initially homogeneous.

### 6.4.3. *Fission-product segregation*

Calculated environmental releases and subsequent radiation doses arising from a CANDU UO<sub>2</sub> fuel disposal vault are dominated by the "instant" release of soluble and mobile fission products (in particular, <sup>129</sup>I) from the fuel-to-sheath gap of the fuel. Grain boundary inventories may also be released rapidly, as compared with matrix dissolution. It is likely that similar findings would emerge from a detailed assessment of thoria fuel disposal, especially given our expectation of extremely slow matrix dissolution. Therefore, it is important to consider the irradiation history and microstructural behaviour of the fuel, and to have reliable information on the segregation of mobile fission products to the gap and grain boundaries in thoria fuels.

#### 6.4.3.1. *Grain growth and fission-product segregation*

Grain growth in the central region of fuel pellets is a major cause of fission-gas release to the fuel-to-sheath gap, because the gases and other incompatible elements are swept from their original resting places in the fuel matrix and become concentrated at the grain boundaries. There, they form features such as fission-gas bubbles and noble metal particles [109]. Interlinkage of fission-gas bubbles on grain-boundary intersections eventually creates tunnels that permit venting of other fission products to the fuel-cladding gap. Thorium oxide is a somewhat better thermal conductor than UO<sub>2</sub> is; it also has a higher melting point and slower cation diffusion. Therefore, for a given power rating and fuel geometry, it would be expected to run cooler and undergo less grain growth.

Fission gas release rates are expected to be somewhat smaller for thoria based fuels than for UO<sub>2</sub> fuels that have comparable geometry, microstructure and power history. This conclusion is based on the lower diffusion rate for xenon in ThO<sub>2</sub> than UO<sub>2</sub> [110], [111] and the smaller burst release in ThO<sub>2</sub> [112]. The expected low fission-gas release rates from thoria based fuels are supported by in-pile experiments on ThO<sub>2</sub> and (Th/U)O<sub>2</sub> fuel assemblies. Goldberg et al. [113], [114] measured fission-gas release in a set of 51 thoria based fuel rods over a range of linear powers, burnups and compositions. They gave an expression for the rate of fission- gas

release, which suggests that rates are significantly lower than for  $\text{UO}_2$  under comparable operating conditions.

In many cases, the segregation and hence the leachability of volatile, non-gaseous fission products, such as cesium and iodine, is correlated with fission-gas release [115], [116], and thus the release of these fission products is expected to be lower for a thoria based fuel than for  $\text{UO}_2$ . Jones et al. [117] reported low fission-gas releases for  $(\text{Th}/\text{U})\text{O}_2$  fuels, and they also noted that fission-product release from defected thoria elements was 1 to 2 orders of magnitude lower than for  $\text{UO}_2$ . Experimental data obtained by Matzke [118] supports this notion; he found that the release of Br, Cs and Rb from thoria was generally slower than from  $\text{UO}_2$ .

#### *6.4.3.2. Diffusion properties of thoria*

Diffusion of fission products in  $\text{UO}_2$  and  $\text{ThO}_2$  remains poorly understood, but generally appears to involve U or Th ion vacancies. High-temperature, out-of-pile annealing experiments on lightly irradiated or ion-implanted samples appear to be consistent with modestly lower fission-product diffusion rates in  $\text{ThO}_2$  than in  $\text{UO}_2$ —roughly paralleling the difference in cation lattice diffusion [109], [118], [119], [120], [121]. Fission-product migration in-reactor involves further complexity; indeed, Matzke [109] has suggested that 5 different diffusion coefficients are required to model fission-gas transport! Nonetheless, the overall trend is evidently maintained; under equivalent operating conditions, fission-product segregation and release tend to be lower for  $\text{ThO}_2$  than for  $\text{UO}_2$  fuels.

#### *6.4.4. Reactor operation*

Reactor operation also affects fission-product release. At the linear power ratings typical of CANDU reactors, grain growth in natural  $\text{UO}_2$  fuel is slight. At similar power,  $\text{ThO}_2$  fuels should exhibit little or no grain growth. CANDU reactors have flexibility in fuel management and fuel design that can ensure that  $\text{ThO}_2$  fuels would operate at similar or lower linear power ratings, compared with the corresponding ratings of current  $\text{UO}_2$  fuel. For example, the 43-element CANFLEX bundle reduces peak ratings by about 20% compared with the peak power ratings of the 37-element bundle [122]. Hence there is a real possibility that  $\text{ThO}_2$  fuel could be operated with minimal fission-gas release.

#### *6.4.5. Conclusions*

The high degree of chemical stability and the low solubility of thoria make irradiated thoria based fuels attractive as waste forms for direct geological disposal. Moreover, there are good reasons to expect lower fission-gas releases (and correspondingly lower gap and grain-boundary inventories of other fission products) in thoria fuels than in  $\text{UO}_2$  with comparable power history. To realize these beneficial qualities of thoria based fuels, an appropriate fuel-fabrication process must be utilized to achieve an acceptable degree of microscopic homogeneity. Detailed PIE and leaching studies of thoria based fuels, coupled with a thorough understanding of their physical and chemical properties, are needed to support these preliminary conclusions.

## 7. PROLIFERATION RESISTANCE

### 7.1. Background

The choice of nuclear power as a major contributor to the future global energy needs must take into account acceptable risks of nuclear weapon proliferation, in addition to economic competitiveness, acceptable safety standards, and acceptable waste disposal options. The main goal is to strengthen the proliferation resistance of the civilian nuclear fuel cycle such that it remains the less preferred route to nuclear weapon development. The primary link between civilian nuclear power and nuclear weapons is nuclear material, i.e. materials, which either are, or could be processed into, weapon-usable material.

The general proliferation risks associated with civilian nuclear power systems include:

- misuse of nuclear **materials** through its diversion or theft,
- misuse of **facilities**, equipment, and technology,
- transfer of nuclear **skills** and technology.

Non-proliferation or proliferation-resistance is assessed by analyzing the diversion “barriers” associated with a given nuclear system. The proliferation resistance of a given system is not an absolute value. It is, therefore, important to develop a methodology that can compare existing and proposed reactor/fuel cycle systems with respect to their proliferation resistance.

### 7.2. An assessment of proliferation resistance—general approach

An overall methodology should provide an integrated assessment that combines the effectiveness of:

material/technical features—designated as *intrinsic* barriers; and

safeguard/institutional measures—designated as *extrinsic* barriers.

Material barriers are those material qualities that make it difficult to produce a nuclear explosive and may be related to isotopic composition of the material, isotopic separation/processing required, radiation hazard and signature, and detectability and difficulty of movement of the mass/bulk required.

Additional intrinsic barriers are related to the elements of the fuel cycle itself, difficulty of gaining access to materials, or misuse of facilities to obtain weapon-usable material. These and other features of a given fuel cycle may be described as **attributes** of a given system. A systematic accounting of such attributes may serve as a framework for a methodology-integrated assessment of the proliferation resistance.

The Nuclear Energy Research Advisory Committee (NERAC) of Department of Energy, USA has summarized the relative importance of various barriers to a selected threat as shown in Table 12.

Table 12. Relative importance of various barriers to a selected threat

	Sophisticated State – Overt	Sophisticated State - Covert	Unsophisticated State - Covert	Subnational Group
<b>Material Barriers</b>				
Isotopic	Low	Low	High	High
Chemical	Very low	Very low	High	High
Radiological	Very low	Low	Moderate	High
Mass and Bulk	Very low	Low	Low	Moderate
Detectability	Very low	Low	Moderate	High
<b>Technical barriers</b>				
Facility Unattractiveness	Very low	Low	Low	Moderate
Facility Accessibility	Very low	Low	Low	Moderate
Available Mass	Moderate	Moderate	High	High
Diversion Detectability	Very low	Moderate	Moderate	Moderate
Skills and Knowledge	Low	Low	Moderate	Moderate
Time	Very low	Very low	Moderate	High
<b>Institutional Barriers</b>				
Safeguards	Moderate	High	High	Moderate
Access and Security	Very low	Low	Moderate	Moderate
Location	Very low	Very low	Low	Low

The first two types of barriers (material and technical) are intrinsic and the last barrier (institutional) is extrinsic. The NERAC report suggests several guidelines/comments for implementation of the proliferation resistance assessment methodology:

- barriers are not absolute, but are engineering challenges that may be overcome by a combination of technology and weapon design,
- barriers do not act independently, and the effect of multiple barriers can be greater than the sum of their individual effects,
- the barriers approach avoids the difficulty of the risk-based method, which requires quantitative (numerical) risk probabilities,
- the barriers approach requires only an assessment of the relative effectiveness of individual barriers, resulting in qualitative and transparent comparisons of various systems concepts and options,
- effectiveness of different barriers can not be aggregated into a single parameter,
- qualitative effectiveness of a barrier is graded in five categories:
  1. ineffective or very low – I,
  2. low – L,
  3. medium or moderate – M,
  4. high – H, and
  5. very high – VH.

A consistent comparison of different systems requires consideration of all steps of the fuel cycle. Many of the barriers, related to mining, milling, and conversion, as well as, extrinsic barriers, have similar proliferation resistance characteristics for all fuel cycles, and thus, do not significantly affect relative comparisons of most fuel cycles.

Table 12. given in the Appendix presents a full matrix of various barriers for a generalized fuel cycle. To compare different options the comparative effectiveness of each barrier, divided in categories must be considered and graded into one of the five categories listed above.

### 7.3. Thorium fuel cycle

In order to address the impact of introducing Thorium-based fuel cycles, two prevalent factors should be clearly stated:

- Utilization of Thorium-based fuel will influence mainly the **material** barriers,
- Material barriers are important for the proliferation threats posed by the **covert** effort undertaken by an **unsophisticated state** and a **subnational** group. This statement is based on the assumption that technical barriers will be less effective for the proliferation threat posed by a sophisticated country.

The light water reactor (LWR) with the once-through fuel cycle is likely to remain the main technology direction in the near term, with heavy water reactors as a secondary route. Thus, the **LWR once-through cycle may serve as a “reference” case** for assessment of evolutionary improvements in the proliferation resistance of more advanced reactor designs and fuel cycles, such as Thorium-based fuels.

The proliferation resistance advantages of the Thorium-based fuels are realized through:

- extended fuel burnup, which could result in the reduction of the quantity and quality of plutonium (Pu) produced, reduction in the number of refuelings, and the number of spent fuel assemblies, and
- significant reduction in the quantity and quality (isotopic composition) of the discharged fuel as a result of a partial replacement of  $^{238}\text{U}$  by  $^{232}\text{Th}$  as a fertile component of the fuel.

### 7.4. Proliferation resistance effect of introducing Th-based fuel

The fissile material weapon quality is evaluated by considering three properties:

- The critical mass is different for different isotopic composition of Pu;
- weapon yield degradation due to pre-initiation caused by spontaneous fission neutrons; and
- weapon stability degradation caused by heat emission.

Thorium-based fuel may be introduced in all reactor systems of current technology and advanced designs. With respect to LWR's there are two main design options: a homogeneous mixture of  $\text{ThO}_2$  and  $\text{UO}_2$  and several heterogeneous designs, where Th and U parts of the fuel are spatially separated. Several fuel cycle performance parameters related to the proliferation resistance are summarized in Table XIII.



Table 13. Proliferation resistance parameters

	PWR	Th-Homogeneous	Th-Heterogeneous
Total Pu Discharged, kg/GW(e)-year	250	150	70-90
Spontaneous Fission Source, (crit.mass-sec) <sup>-1</sup>	1.6*10 <sup>6</sup>	3.0*10 <sup>6</sup>	4.0*10 <sup>6</sup>
Decay Heat Emission, watts/crit.mass	90	200	350

**Note:** The data in the table are **approximate**, representative values derived on the basis of several homogeneous and heterogeneous Th-based designs.

As an example, the qualitative assessment of the proliferation barriers presented below is related to the heterogeneous Th-based fuel design (seed blanket). Table 14 presents an example of the qualitative comparison of the standard (all-U) fuel cycle with the Thorium-based fuel cycle for the LWR reactor of current technology.

Table 14. Comparison of proliferation resistance of all-Uranium vs. Thorium cycles for LWR (subnational group threat)

	All-U fuel	Th-based fuel
<b>Material Barriers</b>		
Isotopic	High	Very High
Chemical	High	High
Radiological	High	Very High
Mass and Bulk	Moderate	Moderate
Detectability	High	Very High

Thorium produces through a nuclear reaction the fissile isotope <sup>233</sup>U. <sup>233</sup>U has been determined to be at least as efficient as <sup>235</sup>U as a weapon material. Therefore, a relatively small amount of natural (or enriched) uranium can be added to thorium in order to dilute the generated <sup>233</sup>U below the proliferation level of 12%, thus creating an effective barrier to diversion of <sup>233</sup>U.

It should be noted that grading of the all-U case presented in Table 14 is based on the values adopted in the NERAC report and **should be considered as a guideline only**. The justification of the corresponding values for the Th-based case are discussed below:

Isotopic barrier grade increased from high to very high,

Amount of fissile material in spent fuel decreased by a factor 2–4,

Critical mass for Pu composition is increased by 30–50%,

Fresh fuel enrichment below 20%, i.e. low enrichment,

Spontaneous neutron generation is increased by a factor of 2–2.5,

Heat-generation rate (<sup>238</sup>Pu) is increased by a factor of 2.5–4,

Radiological barrier grade increased from high to very high,

$^{238}\text{Pu} + ^{240}\text{Pu} + ^{242}\text{Pu}$  content increased by a factor of 1.5–2,

$^{232}\text{U}$  present only in Th-based fuel,

Detectability barrier grade increased from high to very high,

Passive delectability increased due to an increase in spontaneous fission,

Hardness and uniqueness of the radiation signature increased ( $^{232}\text{U}$ ).

The objective of thorium fuel cycle should be to ensure ‘proliferation-resistance’ of ‘fissile’ material and at the same time produce minimum quantities of ‘radiotoxic waste’. The radiotoxicity of the waste can be significantly reduced if the bred  $^{233}\text{U}$  is separated and recycled but the disadvantage associated with this strategy is that  $^{233}\text{U}$  is ‘fissile’ and constitutes the proliferation problem. The  $^{233}\text{U}$  can be rendered proliferation-resistant through mixing with  $^{238}\text{U}$  and denaturing. However, on recycling such denatured fuel, a new source of radiotoxicity is introduced in the fuel cycle. The proliferation/toxicity dilemma of thorium-based fuel cycle can be resolved in combination with one of the following family of accelerated driven Energy Amplifiers (EA) [18]:

completely thermalized neutron (graphite moderator)–EA (T–EA),

partially thermalized neutron (pressurised water moderator)–EA (PW–EA), and

fast neutron (lead cooled)–EA (F–EA).

$^{232}\text{U}$  is always present in ‘fissile’  $^{233}\text{U}$  and has the daughter product  $^{208}\text{Tl}$ , which emits highly penetrating 2.6 MeV gamma photons. The fractional quantity (ppm) of  $^{232}\text{U}$  in the recycled uranium from spent thorium fuel from different EA as function of burnup is shown below:

Burnup	T-EA	PW-EA	F-EA
40 GWd/t	200 ppm	3100 ppm	500 ppm
80 GWd/t	200 ppm	5000 ppm	900 ppm
160 GWd/t	not applicable	not applicable	2200 ppm

Fig. 29 shows the dose rate from 5 kg (approximate critical mass)  $^{233}\text{U}$  containing 100, 1 000 and 10 000 ppm  $^{232}\text{U}$  at various time interval after chemical separation and the LD–50 line indicating 50% chance of death following one hour exposure. The gamma activity provides adequate barrier to diversion, particularly when the  $^{232}\text{U}$  content is in the higher range. However, the presence of  $^{232}\text{U}$  will pose problem during reprocessing and refabrication because of the need of very thick lead shielding to reduce the gamma dose. The lead shielding thickness in cm necessary to reduce the gamma dose rate at 1 m distance to 2.5  $\mu\text{Sv/h}$  from 1 kg  $^{233}\text{U}$  with various concentration of  $^{232}\text{U}$  as a function of the ageing time after chemical purification is given below:

$^{232}\text{U} / ^{233}\text{U}$	Ageing time in days				
	10	30	100	400	4000
100 ppm	6.75 cm	10.4 cm	13.3 cm	16.4 cm	18.4 cm
1 000 ppm	12.1 cm	15.5 cm	18.4 cm	21.5 cm	23.5 cm
10 000 ppm	17.2 cm	20.8 cm	23.5 cm	26.0 cm	28.1 cm

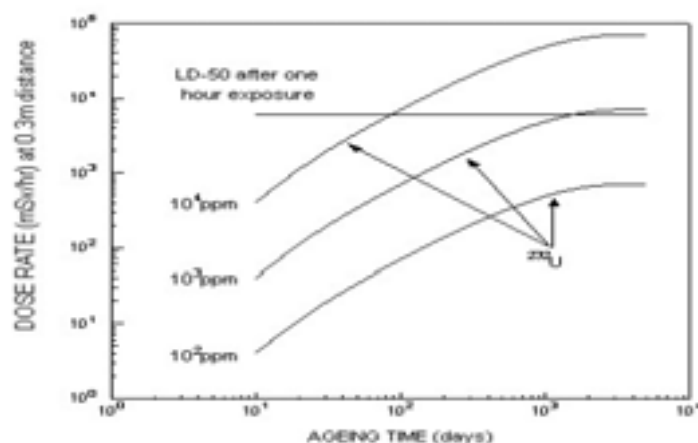


Figure 11. Dose rate as a function of ageing time from 5kg of recycled  $^{233}\text{U}$  contaminated with  $^{232}\text{U}$ .

Fig. 29. Dose rate as a function of ageing time for 5 kg of recycled  $^{233}\text{U}$  contaminated with  $^{232}\text{U}$ .

In contrast to uranium-fuelled reactors ( $^{238}\text{U} + ^{235}\text{U}$ ), where there is no natural denaturant for plutonium isotopes,  $^{238}\text{U}$  is an effective denaturant for the bred  $^{233}\text{U}$  in thorium ( $^{232}\text{Th}$ ) cycle. A possible solution to safeguard the reactor grade  $^{233}\text{U}$  is to denature with  $^{238}\text{U}$ . Denaturing the reactor-grade uranium with an equal quantity of  $^{238}\text{U}$  should be regarded as the lower limit for non-proliferation. The resulting radiotoxicity is a factor 50 lower than that obtained by using  $^{238}\text{U}$  as the breeder fuel in a T-EA or a PW-EA.

Depending on which EA system is used, different levels of the isotopes  $^{232}\text{U}$  will be produced. Through its high gamma active  $^{208}\text{Tl}$  daughter product, one will require shielding in any recycling/fabrication stages. However, this gamma activity will also allow one to monitor movements of the material and possible diversion.  $^{232}\text{Th} / ^{233}\text{U}$  offers potentially significant advantages over  $^{238}\text{U} / ^{235}\text{U} / ^{239}\text{Pu}$ , in terms of lesser transuranic actinide waste and adequate proliferation-resistance.

## 8. ECONOMIC ASPECTS OF TH-BASED FUEL CYCLES

### 8.1. Background

Introduction of Th-based fuel cycles into operating and near-future nuclear power plants may be considered as an evolutionary development driven mainly by the objective of enhancing the intrinsic proliferation barriers. The superior neutronic properties of  $^{233}\text{U}$  and improved long term fuel storage stability offer additional motivation for utilization of Th-based fuel.

The economics of the nuclear fuel cycle, i.e. an overall fuel cycle cost (OvFCC) should be considered as a design constraint: any novel fuel cycle concept should be competitive with the existing slightly enriched all-uranium cycle. This design constraint and its impact on evaluation of possible Th-based fuel options are discussed in this section.

### 8.2. Fuel cycle cost model

The **levelized fuel cycle cost** is calculated in mills/kWh by equating the net present value of the entire fuel cycle cost and the net present value of the total electricity output of the power plant over its lifetime, where both have been discounted to the same time point. The total fuel cycle cost is a sum all cycle transactions, where a unit cost and a specific lead/lag time relative to the start of the power production of a given batch are assigned to each transaction as shown in Table 15.

Table 15. Fuel cycle transactions

Transaction	Units	Unit cost (\$)	Lead/lag time (y)
Natural Uranium	kg heavy metal (HM)	25	1.0
Thorium	kg HM	50	0.5
Conversion	kg HM	6	0.5
Enrichment	kg separating working unit	80	0.25
Fabrication ( $\text{UO}_2$ )	kg HM	250	0.25
Fabrication ( $\text{ThO}_2\text{-UO}_2$ )	kg HM	300	0.25
Waste Disposal	kg HM	420	5.0

The recommended fuel cycle cost data in Table 15 is based on the following:

**unit costs and lead times** should be considered as typical values, used for comparative analysis only, and not as actual industrial data,

Conversion, enrichment, and fabrication **Process losses** are assumed to be zero, since these are often incorporated in the unit price. An **optimal enrichment process tails** assay, which is necessary for the fuel cycle requirements calculations, is obtained using the following approximate correlation:

$$x_w|_{opt} = \left( 2.425 + 1.925 \frac{C_{NU} + C_{Conv}}{C_{SWU}} \right)^{-1},$$

where  $C_{NU} + C_{Conv}$  = unit cost of 1 kg of NU in the form of  $\text{UF}_6$  and

$C_{SWU}$  = unit cost of 1 kg-SWU.

Unit **cost of fabrication** of the ThO<sub>2</sub>–UO<sub>2</sub> mixture is (arbitrarily) increased to account for possible modification of the fuel fabrication facilities and licensing.

The waste disposal fee for the once-through fuel cycle is assigned 1 mill/kWh according to the present US law. This is basically a tax on energy production, which ignores completely one of the advantages of the Th-based cycle, i.e. a higher discharged burnup and a corresponding reduction of the disposed weight per unit energy. Therefore, it is suggested here to extend the fuel cycle cost model by estimating the waste disposal cost in units of \$/kg H.M.

The **waste disposal cost** = 420 \$/kg H.M. was obtained based on the following assumptions:

Waste disposal fee = 1 mill/kW h,

Thermal efficiency = 0.331,

Initial fuel enrichment = 4.5% <sup>235</sup>U,

Discharged burnup= 52 GWd/t H.M,

Dry-fuel storage cask for on-site storage of 24 PWR assemblies = \$1.2M.

The fuel cycle cost per unit of electricity generated is calculated as the present value of the cash outlays divided by the present value of the electricity generated.

For a **homogeneous design option** a discounting period is chosen as the number of years/cycles (possibly as a plant lifetime), and then all transactions are discounted to beginning of the first cycle.

For a **heterogeneous design option** there are two separate fuel material flows: seed fuel (usually enriched U or Pu) and blanket (thorium spiked with some enriched uranium). The fuel management scheme, inter refueling intervals and accumulated burnup are different for each fuel flow. Therefore, the **calculation of the fuel cycle cost is performed for a period of one blanket lifetime (T<sub>b</sub>)**, which resides in the core for N successive seed reloads.

All transactions are discounted to the beginning of the blanket (and 1<sup>st</sup> seed) irradiation reference point. **Continuous compounding** is used to present worth the transactions.

Levelized electricity cost is calculated according to the following formula:

$$e_f = \frac{\left( \sum_i C_i^{\text{blanket}} e^{x\Delta t_i} + \left[ \sum_i C_i^{\text{seed}} e^{x\Delta t_i} \right] \left[ 1 + e^{-x\frac{T_b}{N}} + e^{-x\frac{2T_b}{N}} + \dots + e^{-xT_b} \right] \right)}{E \times \frac{1 - e^{-xT_b}}{xT_b}}$$

where: T<sub>b</sub> – Blanket lifetime, years

E – Total electric energy (kWh<sub>e</sub>) produced during period T<sub>b</sub>

Δt<sub>i</sub> – Lead time before start of irradiation of transaction “i”

x – discount rate

$C_i^{\text{Seed}}$  – direct cost of transaction “i” for seed

$C_i^{\text{Blanket}}$  – direct cost of transaction “i” for blanket

At the beginning of the blanket irradiation only 1/3 of all the seeds residing in the core are refueled, while 2/3 of the seed assemblies were loaded into the core during previous blanket cycles. In addition, at the blanket discharge time point only 1/3 of the seed assemblies are discharged while 2/3 will continue to produce energy during the next blanket lifetime.

The **costs of those partially burned seed assemblies** are incorporated into the total fuel cycle cost in the following manner:

- a. for the steady state condition, the two seed batches that reside in the core at the beginning of the blanket irradiation are identical to the last two seed batches that remain partially burned at the end of the blanket irradiation,
- b. the requirements and direct costs of all of these seed batches are known. It is assumed, for the sake of simplicity without introducing significant error, that these fuel assemblies have a linear depreciation rate,
- c. thus, the credit for once and twice burned seed assemblies at the end of the blanket irradiation will be 2/3 and 1/3 of their direct costs respectively, then discounted back to the reference point. Similarly, the expenses associated with once and twice burned seed assemblies that are present in the core at the beginning of the blanket irradiation can be calculated as 1/3 and 2/3 of their direct costs respectively.

**The energy produced** by the core is calculated as:

$$E = \left( \sum_i E_i \right) \times P \times \eta$$

where:

- $E_i$  -  $i$ -th cycle energy, effective full power hours,  
 $P$  - core thermal power, kW,  
 $\eta$  - plant thermal efficiency (fraction).

**The capacity factor** (CF) and the fuel cycle length are not independent parameters. If the cycle calendar length,  $T$ , is fixed (e.g. 18 months) then the CF is simply the effective full power days (EFPD) divided by calendar length:

$$CF = EFPD / T \text{ (days)}$$

In the present study, the capacity factor is determined based on a 45 days refueling interval and a 5% forced outage rate during operation.

### 8.3. Fuel cycle cost for Th-based cycles

The fuel cycle cost model presented in the previous section was applied to several Th-based homogeneous and heterogeneous designs. It should be noted, that the results of the

calculations are quite sensitive to the choice of unit costs, especially for the enrichment and fabrication transactions. The results presented in this section and basic conclusions are characteristic for the data set chosen in this report.

Table 16 presents estimated fuel cycle cost for three fuel options: the reference UO<sub>2</sub> cycle compared with homogeneous and heterogeneous design options. The last column includes the back end contribution calculated as presented above.

Table 16. Levelized fuel cycle costs, mills/kW h

Fuel Design Option	Fuel Cycle Length, months	Front End only	Front and Back End
Heterogeneous	18	3.60 – 3.80	4.15
Homogeneous	18	6.05	6.58
PWR**	18	3.22	4.22

\*4.5% initial fuel enrichment, 51.6 MWd/kg discharge burnup, 3-batch core.

#### 8.4. Summary

The fuel cycle model described in this section was applied to different Th-based fuel options, including homogeneous and heterogeneous designs. The main conclusion is that the homogeneous mixture of U and Th used in a once-through cycle results in a significantly increased fuel cycle cost. The main reason is that the Th part of the fuel is always “sub-critical” penalizing the discharged burnup, and consequently natural uranium and enrichment requirements. The heterogeneous fuel design (seed and blanket), which allows separate fuel management for the U and Th parts of the fuel, results in a slightly higher OvFCC for the front-end and lower OvFCC, when back end savings related to Th utilization are included.

## 9. FUTURE PROSPECTS AND RECOMMENDATIONS

Since the commissioning of the first prototype power reactor in the world in the mid 1950s, for generation of electricity, nuclear power has developed during the last five decades and blossomed as a matured technology with some 441 reactors in operation in 32 countries with installed capacity of ~358 GW(e) and generating some 16% of global electricity. Many of the world’s nations, both industrialized and developing, believe that nuclear energy, a non-greenhouse gas-emitting source of primary energy, will play a greater role in the 21<sup>st</sup> century and beyond. The future reactor types and fuel cycle options in different countries will depend on resource utilization, environmental impact, safety, public acceptance and energy politics including energy security and sustainable energy supply. Two international projects, namely the IAEA-initiated INPRO and the US-led GIF and a European Union project MICANET are underway to expand and extend the benefits of clean, safe and cost effective nuclear energy for generation of electricity, desalination of sea-water and production of hydrogen, as a non-carbon based energy source, for the transportation sector. Both INPRO and GIF programmes aim at judicious utilization of natural uranium and thorium resources and the stockpiled military and civilian plutonium fissile material in inherently safe reactors and fuel cycle facilities, with adequate short and long term strategies for management, interim storage and safe disposal of nuclear waste and augmentation of proliferation-resistance and physical protection of nuclear materials to avoid their diversion or misuse for non-peaceful purpose.

During the pioneering years of ‘Atoms for Peace’ programme, from the mid 1950s to mid 1970s, there was considerable interest in the industrialized nations, particularly in USA and Germany to utilize thorium, which is 3 to 4 times more abundant in nature than uranium, to supplement uranium reserves. Natural thorium is primarily present as the ‘fertile’  $^{232}\text{Th}$  isotope, which has to be converted in a reactor to ‘fissile’  $^{233}\text{U}$  by means of neutron capture followed by two  $\beta^-$  decays, through  $^{233}\text{Pa}$  with a half life of 27 days. Thorium has been used in combination with  $^{235}\text{U}$  and to a limited extent  $^{233}\text{U}$  and  $^{239}\text{Pu}$  in several experimental and prototype high temperature gas cooled reactors, LWRs, and in a molten salt breeder reactor. However, the initial enthusiasm on thorium fuels and fuel cycles was not sustained among the developed countries due to new discovery of uranium deposits and their easy availability.

Thorium fuels and fuel cycles have all through been relevant to India because of limited uranium resources of very low grades (0.04–0.04%  $\text{U}_3\text{O}_8$ ) but easily available and vast source of monazite, containing 8–10%  $\text{ThO}_2$ , in the beach sands. One of the major aims of the ambitious and expanding nuclear power programme in India is thorium utilization in all the three stages of the indigenous nuclear power programme with ‘closed’ fuel cycle linking pressurised heavy water reactors, liquid metal cooled fast breeder reactor and  $^{232}\text{Th}$ – $^{233}\text{U}$ –fuelled self sustaining advanced reactors. In PHWRs, Zircaloy clad  $\text{ThO}_2$  pin assemblies is being used for neutron flux flattening of the initial cores during start up. In fast breeder test reactor, stainless steel clad  $\text{ThO}_2$  pin assemblies are used as blanket. For the third-stage, an Advanced light boiling water cooled Heavy Water moderated Reactor of 300 MW(e) (AHWR 300), vertical pressure tube type, has been designed with  $(\text{Th}, \text{Pu})\text{O}_2$  and  $(\text{Th}, ^{233}\text{U})\text{O}_2$  driver fuel. Such ‘closed’ nuclear fuel cycle will burn plutonium and simultaneously breed  $^{233}\text{U}$ , which could provide the fuel for a new generation of low-actinide-waste producing energy system working on  $^{232}\text{Th}$ – $^{233}\text{U}$  cycle. A 30 kWt research reactor KAMINI fuelled with Al–20%  $^{233}\text{U}$  alloy is in operation at IGCAR since 1996.

In recent times, there has been renewed interest in several developed countries on thorium fuels and fuel cycles and their utilization in LWR, PHWR, ACR, HTR, Fast Reactors, MSBR and ADS. The major benefits are proliferation-resistance, longer fuel cycle and higher fuel burnup through ‘in-situ’ use of bred-in  $^{233}\text{U}$ , improved waste form characteristic, reduction of plutonium inventories and ‘fissile’ materials. In the ‘closed’  $^{232}\text{Th}$ – $^{233}\text{U}$  fuel cycle, one of the major concerns is that the separated  $^{233}\text{U}$  could be diverted and used as a weapon material though  $^{233}\text{U}$  is easier to detect than  $^{239}\text{Pu}$ , due to the presence of  $^{232}\text{U}$  and its strong gamma emitting daughter products  $^{208}\text{Tl}$  as a by-product. This problem could be resolved by denaturing  $^{233}\text{U}$  with the addition of 8–10 times  $^{238}\text{U}$  and making the fuel proliferation-resistant. Reprocessing and refabrication of  $^{233}\text{U}$  bearing fuels require remote operation inside heavily shielded hot cells because of the strong gamma radiation associated with the daughter products of  $^{232}\text{U}$ . For refabrication of Th-based ceramic fuels, the reprocessing and fuel fabrication plant should be co-located and process flowsheets amenable to remote operation like the ‘Sol-Gel-Vibro-Compaction’ or ‘Sol-Gel-Microsphere-Pelletisation’ (SGMP) should be implemented in place of the classical ‘powder’ route for minimizing radiotoxic dust hazard and facilitating automation in order to keep personnel exposure to a minimum.

### **Future prospects**

The future prospects of thorium fuels and fuel cycles in different nuclear energy systems are summarized as follows:



(a) **LWRs:**

- (i) ThO<sub>2</sub> and (Th, <sup>235</sup>U)O<sub>2</sub> (LEU) ‘pellet-pin’ fuel assemblies, the ‘Radkowski seed blanket thorium fuel’ of high burnup and in ‘once-through’ cycle.
- (ii) Cermet fuel consisting of fuel microspheres of (Th, <sup>235</sup>U)O<sub>2</sub> (LEU) in zirconium matrix
- (iii) (Th, Pu) ‘pellet-pin’ fuel assemblies for burning civilian and weapons plutonium in ‘once-through’ high burnup fuel cycle.

(b) **HTGR:**

Multilayer coated fuel particles (in some cases using ZrC coating in place of SiC) of Th-based mixed oxide or dicarbide in graphite matrix for very high temperature gas cooled reactors of the Pebble–Bed or Prismatic Block type, primarily with the objective of delivering high temperature (800–1000°C) process heat for generation of hydrogen based on thermochemical iodine sulphur process (I–S).

(c) **Heavy water moderated reactor:**

- (i) High burnup 43–element CANFLEX (9 inner elements of ThO<sub>2</sub>) pin assemblies in combination with slightly enriched uranium oxide pins (34 outer elements) in advanced CANDU reactor (ACR) on ‘once-through’ basis.
- (ii) High burnup 54–elements fuel assemblies containing thirty (Th, <sup>233</sup>U)O<sub>2</sub> fuel pins in two inner circles and twenty four (Th, Pu)O<sub>2</sub> pins in outer most circle for AHWR working on self-sustaining mode.

(d) **Fast reactors:**

(Th, Pu)O<sub>2</sub> ‘pellet-pin’ fuel assemblies operating on ‘once-through’ open cycle mode for burning weapons or civilian plutonium and simultaneously making the spent fuel proliferation-resistant because of the formation of <sup>232</sup>U by (n,2n) reaction of <sup>232</sup>Th.

(e) **MSBR:**

Mixed fluoride molten salt fuel (and primary coolant) of composition <sup>7</sup>LiF/BeF<sub>2</sub>/ThF<sub>4</sub>/UF<sub>4</sub> for self sustaining <sup>232</sup>Th–<sup>233</sup>U fuel cycle (the initial core would use LEU).

(f) **ADS:**

Thorium fuelled energy amplifier (EA) of completely thermalised EA (T–EA), partially thermalized Pressurized Water moderated EA (PW–EA) and Fast neutron lead cooled EA (F–EA).

## Recommendations

- (i) In front end of fuel cycle, thorium resources identified, so far, are a factor of three lower than those reported for uranium, in spite of the fact that thorium is three times more abundant in nature than uranium. Activities on exploration and prospecting of thorium minerals need to be augmented all over the world.
- (ii) For most efficient use of thorium resources, self-sustaining, proliferation resistant and ‘closed’ <sup>232</sup>Th–<sup>233</sup>U fuel cycle should be developed on an industrial scale for thermal

neutron reactors like MSBR, HTGR and AHWR. Such fuel cycle will generate minimum quantity of low actinide waste, the radiotoxicity of which would be much lower than the existing reactors working on  $^{238}\text{U}$ - $^{235}\text{U}$ / $^{239}\text{Pu}$  fuel cycle for the first 50 000 years of disposal.

- (iii) Civilian and weapons-grade plutonium could be burnt efficiently by introducing (Th, Pu) $\text{O}_2$  fuel in 'once-through' open cycle in either fast reactor, LWR or CANDU-PHWR. The spent fuel would be proliferation-resistant due to the presence of strong gamma emission from the daughter products of  $^{232}\text{U}$  formed by (n,2n) reaction with  $^{232}\text{Th}$ .
- (iv) Utilizing (Th, LEU) $\text{O}_2$  fuel in 'once-through' open cycle in LWRs involving Radkowski seed blanket concept or as cermet fuel in zirconium matrix. Alternatively, utilizing (Th, LEU) $\text{O}_2$  fuel in 'once-through' open cycle in ACR involving 43-element CANFLEX bundle with 9 inner pins of  $\text{ThO}_2$ .
- (v) Developing ADS with subcritical thorium assembly as a breeding fuel for minimizing transuranic actinide waste. The reference Energy Amplifier (EA) concepts are T-EA, PW-EA and F-EA.
- (vi) For fabrication of highly radiotoxic plutonium and  $^{233}\text{U}$ -bearing (with  $^{232}\text{U}$ ) thorium based ceramic fuels, the dust-free 'Sol-Gel-Vibratory-Compaction' or 'Sol-Gel-Microsphere-Pelletisation' (SGMP) processes, amenable to remotisation and automation, should be developed on an industrial scale.
- (vii) For reprocessing of spent Th-based fuel, the thrust areas should be further modification of THOREX process in order to have two stream (U and Th) or three-stream (U, Pu and Th) routes for separation of  $^{233}\text{U}$ , Pu and thorium. The proliferation-resistance of  $^{233}\text{U}$  could be further improved by denaturing with the addition of  $^{238}\text{U}$ .
- (viii) In the area of long interim storage and disposal of high active wastes, though  $\text{ThO}_2$  and (Th, U) $\text{O}_2$  are known to be more stable than  $\text{UO}_2$  or (U, Pu) $\text{O}_2$  in oxidizing environments such as ground water or hot air, further experimental data is needed to confirm this assumption.



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## GLOSSARY

ACR	advanced CANDU reactor
ADS	accelerated driven system
AHWR	advanced heavy water reactor
AHWR 300	advanced heavy water reactor of 300 MW(e)
AMSTER	actinide molten salt transmuter
CANDU	CANadian Deuterium natural Uranium reactor
CF	capacity factor
DUPIC	direct use of spent PWR fuel in CANDU
EAR	estimated additional reserves
EBR	experimental breeder reactor
ECCS	emergency core cooling system
EFPD	effective full power days
EFR	european fast reactor
EGT	external gelation of thorium
F-EA	fast energy amplifier
FBTR	fast breeder test reactor
GIF	generation IV International Forum
GT-MHR	gas turbine modular helium reactor
HEU	high enriched uranium
HLLW	high level liquid wastes
HM	heavy metal (uranium, plutonium etc), usually as before irradiation
HMTA	hexa methylene tetra amine
HTGR	high temperature gas cooled reactor
HTTR	high temperature engineering test reactor

HWR	heavy water power reactor
HWR-1000	US heavy water moderated gas cooled ultimate safety reactor
I-S	iodine-sulphur
INPRO	innovative nuclear reactors and fuel cycle programme
JMTR	Japan material testing reactor
KAPS	Kakrapar Atomic Power Station
KGS	Kaiga Generating Station
LEU	low enriched uranium
LMFBR	liquid metal cooled fast breeder reactor
LOCA	loss of coolant accident
LWBR	light water breeder reactor
LMFBR	liquid metal cooled fast breeder reactor
LWR	light water reactor
MA	minor actinides
MEU	medium enriched uranium
MICANET	<b>Michelangelo Network</b> competitiveness and sustainability of nuclear energy in EU
MOX	<b>mixed</b> uranium plutonium oxide
MSBR	<b>molten</b> salt breeder reactor
MSRE	experimental molten salt reactor
MTR	material testing reactor
MTS	methyl trichloro silane
MWt	megawatt thermal
NERAC	nuclear energy research advisory committee
NFC	Nuclear Fuel Complex at Hyderabad, India
NUMEC	nuclear materials and equipment corporation

OMEGA	options making extra gains from actinides (Japanese initiative)
OTT	once through thorium
OvFCC	overall fuel cycle cost
PBMR	pebble bed modular reactor
PCUT	Programma Ciclo Uranio torio at CNEN, Italy
PCV	pre stressed concrete vessel
PFBR	prototype fast breeder reactor
PHWR	pressurised heavy water reactor
PUREX	plutonium URanium EXtraction
PW-EA	pressurised water energy amplifiers
PWL	pressurised water loop
PWRs	pressurised light water reactor
PyC	pyrolytic carbon
RAPS	Rajasthan Atomic Power Station
RAR	reasonably assured reserves
REE	rare earth elements
RTF	Radkowsky thorium fuel
SBU	seed blanket unit
SEU	slightly enriched uranium
SGMP	sol gel microsphere pelletisation
SSC	separate sector cyclotron
Sv	sievert (unit of radiation dose)
T-EA	thermalized energy amplifiers
TBP	tri butyl phosphate
T.D	theoretical density

THOREX	THORium uranium EXtraction
THRUST	<b>thorium retrieval, uranium recovery and restorage of thorium oxalate</b>
THTR	thorium high temperature reactor
TPB	tri butyl phosphate
TRISO	triply coated ceramic particle fuel
TRU	transuranium
TURF	thorium uranium recycle facility at ORNL
USBM	US bureau of mines
VHTR	very high temperature reactor
WWER	Russian pressurised water reactor
W-Pu	weapons grade plutonium
WASB	whole assembly seed and blanket
ZPCF	zero power critical facility

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