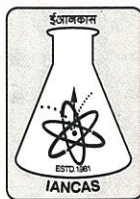


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**INDIAN ASSOCIATION OF NUCLEAR CHEMISTS
AND ALLIED SCIENTISTS**

**Advanced
Nuclear Fuels**

IANCAS
Bulletin

Editorial

The nuclear power industry has been developing and improving reactor technology for more than five decades. Several generations of reactors are commonly distinguished. Generation I reactors were developed in 1950-60s. Generation II reactors are presently in operation. Generation III reactors are currently being developed in several countries while Generation IV designs are still on the drawing board. Advanced reactors have simpler designs. They are more fuel-efficient and incorporate passive or inherent safety features to avoid accidents in the event of malfunction. They have higher availability and longer operating life (typically 60 years), higher burn-up to reduce fuel use and the amount of waste.

India is developing its own advanced technology to utilise thorium as a nuclear fuel. A three-stage program has the first stage well-established, with Pressurised Heavy Water Reactors fuelled by natural uranium to generate plutonium. Then Fast Breeder Reactors (FBRs) use this plutonium-based fuel to breed U-233 from thorium, and finally advanced nuclear power systems will use the U-233. The spent fuel will be reprocessed to recover fissile materials for recycling. The two major options for the third stage, while continuing with the PHWR and FBR programs, are an Advanced Heavy Water Reactor and subcritical Accelerator-Driven Systems. India has set a modest target of 20,000 MW of nuclear power generation by the year 2020. Nuclear fuel is the energy source for sustaining the chain reaction. For optimum performance, the fuel material should meet stringent requirements. The present bulletin provides the expert articles on advanced nuclear fuels for Indian reactors. I am thankful to Shri Arun Kumar for the enthusiastic support as the Guest Editor.

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Light Water Reactor Fuel – A Design Perspective



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Introduction

There are more than 430 commercial nuclear reactors currently operating in over 30 countries, and accounting for about one-sixth of the world's electricity generation. The nuclear energy scenario world-wide today is dominated by Light Water Reactors (LWRs), both in numbers and total power generation [1]. Of the global commercial nuclear reactors in operation, approximately 82% are the light-water-moderated and light-water-cooled reactors. There are mainly two types of LWRs. One is the Pressurised Water Reactor (PWR), in which the coolant water in the reactor core is kept under sufficiently high pressure to suppress boiling of coolant. Steam is generated in a heat exchanger and sent to the turbine for electricity generation. The other is the Boiling Water Reactor (BWR), in which

the coolant water in the reactor core is allowed to boil and the resulting steam is directly sent to the turbine. VVER is a series of pressurised water reactors developed by the erstwhile Soviet Union. The Russian abbreviation VVER stands for water-cooled, water-moderated energy reactor. All these reactor types have attained a high degree of technological maturity and have demonstrated a high level of safety and reliability. The reactor plant designs have evolved over a period of time and so has the fuel technology. The LWRs currently operating are predominantly based on the once-through fuel cycle using enriched uranium.

Since 1986, growth in nuclear capacity around the world has been about 1.5% per year. The growth in nuclear electricity generation has however been almost twice as fast, at about 2.9% per year [2]. This

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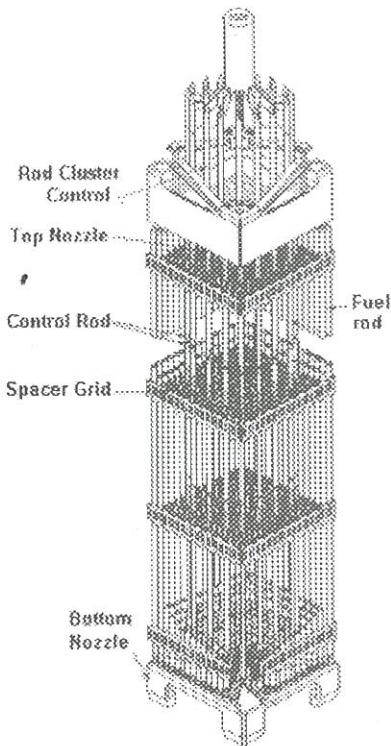


Fig. 1a

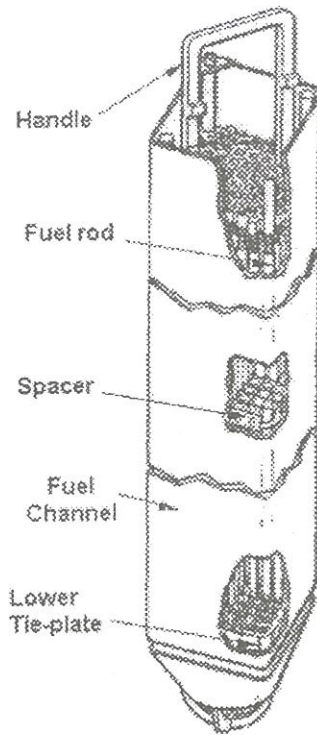


Fig. 1b

Fig. 1 Typical LWR fuel element configurations

increase is due to the improved performance and increased capacity factors of the operating plants. A number of reactors in several countries have achieved capacity factors exceeding 90%. This has been aided by, among other things, improvements in the performance and reliability of nuclear fuel. The reliable performance of nuclear fuels has a large bearing on economics of nuclear power and radiation safety. Fuel failure rates have decreased to 0.01% over the years. In addition, over the past forty years, the original burn-up levels have also doubled. The burn-up levels of LWR fuel have increased to more than 60 GWd/t, from the earlier burn-up levels of about 30 GWd/t.

This paper brings out an overview of the LWR fuels and reviews the various developments that have taken place over the years.

LWR fuel Element

The core of a large LWR contains about 200-250 fuel elements. After each cycle of reactor operation, about a quarter to a third of the highest burnup fuel assemblies are replaced with fresh fuel. The LWR fuel element essentially consists of a number of fuel rods assembled together. A typical fuel rod has uranium dioxide cylindrical pellets encapsulated in a zirconium alloy cladding tube. To obtain higher burnup, the ^{235}U enrichment has steadily increased from the traditional levels of about 2-3% and is now approaching 5%.

Typically, each fuel element in PWR is a square array of fuel rods, which are supported at intervals along their length by grid/spacers to maintain the lateral spacing between the rods. The grid/spacer consists of an egg-crate arrangement of

TABLE 1.: Salient features of fuel element for different reactors

	PWR	VVER	BWR
Fuel pin arrangement	Square array	Hexagonal	Square array
Assembly geometry	14x14, 15x15, 16x16, 17x17, 18x18	-	6x6, 7x7, 8x8, 9x9, 10x10
Average linear heat rating (kW/m)	16.6-23.8	12.9-16.7	12.8-17.9
Maximum linear heat rating (kW/m)	42.0-47.0	32.5-44.8	39.0-44.0
Rod outer diameter (mm)	9.5-10.75	8.9-9.14	9.6-11.0
Clad material	Zr-4, optimised Zr-4, Zirlo, M5, duplex	Zr1%Nb, Zr-4, E110	Zr-2, Zr liner
Clad thickness (mm)	0.57-0.64	0.57-0.63	0.6-0.87
Grid material	Zr-4, Zirlo, Optimised Zr-4, M5, Inconel	Zr1%Nb,	Zircaloy, Inconel
Discharge burnup (GWd/t)	~ 70	~ 60	~ 55
Control rod type	Rod cluster control (Operated from top)	Rod cluster control (Operated from top)	Cruciform control rod (Operated from bottom)

interlocked straps, which contain springs and dimples for supporting the fuel rods. The fuel rods have a diameter ranging from 8-12 mm and are about 4 m in length. There is 'plenum', an empty space provided above the fuel stack in the fuel rod, for accommodating the released fission gases. The fuel element also includes number of control-rod guide-tubes into which the Rod Cluster Control (RCC) assembly, containing the Ag-In-Gd control rods, is inserted from the top directly into the fuel assembly.

The fuel elements of BWR differ from that of PWR in some aspects. The fuel pin diameters and cladding thickness are somewhat larger than that in PWRs. They generally have lower enrichments and burnup and have burnable poisons mixed with the fuel matrix in a few fuel rods. The fuel element is surrounded by a square cross-section fuel channel, which forms an enclosure for the flow of the steam-water mixture. The control rods are external to the fuel assembly and are inserted from bottom in

the space (known as control cell) between the four fuel elements. Fig. 1 shows the salient features of typical LWR fuel [3].

In case of VVER, each of the fuel elements has a hexagonal geometric arrangement of the fuel rods. The peripheral region of the fuel element is made up of fuel rods with lower fuel enrichment compared to those at the center. The fuel pellet has a central hole of about 1.4-2.4 mm in diameter and this helps to decrease the internal fuel rod gas pressure and lowers the fuel center temperature. Table 1 shows salient features of fuel element configurations for different types of LWRs [4].

Fuel Design Aspects

The fuel design is to a great extent influenced by the characteristics of the reactor core, namely, the coolant, the operating temperature and pressure, the average neutron energy. An important aspect in fuel design is the choice of the fuel type to be used and the fuel rod configuration [3]. With all other things

being equal, heat transfer will be proportional to surface area. The ideal geometry for fuel would therefore be the one with high surface area to volume ratio, such as flat plate. As a finite thickness of clad is required, this configuration is not optimum for low parasitic absorption. In addition, the circular geometry tubes are more economical to manufacture and more suited to cope against internal pressure generated by fission-product gases and fuel swelling.

An optimum value of fuel rod diameter and cladding thickness is arrived at, based on material properties and the different thermal limits. The arrangement of the fuel rods in the fuel element must also satisfy the requirements set by the thermal and physics design of the reactor core. The fuel, in addition, must accommodate the stresses and strains generated, withstand metallurgical damage due to prolonged exposure to nuclear irradiation and resist effectively various other degrading mechanisms like corrosion, fretting, vibration etc. All these impose limits on fuel in terms of peak powers, fuel burn-up, residence time etc. and essentially reflect the design basis for fuel that is as follows:

- (a) The fuel element is not damaged as a result of normal and anticipated operational occurrences. 'The fuel element not damaged' indicates that the following three conditions are to be met; (i) fuel rods do not fail - Failure means that the first fission product barrier (cladding) is breached and fission gas is released from the fuel rod, (ii) fuel element dimensions remain within operation tolerances and (iii) functional capabilities are not reduced below those assumed in the safety analyses.
- (b) The number of fuel rod failures is not underestimated for postulated accidents.
- (c) Coolability of fuel is always maintained. Coolability means that the fuel element retains its rod bundle geometrical configuration with adequate coolant flow channels to permit removal of residual heat even after a severe accident.

Selection of Material

The fuel materials that have been developed for use in power reactors include metals and alloys,

oxides, carbides, hydrides, nitrides and fluorides. The configurations used include cylindrical pellets, long extruded rods (metal fuels), spherical elements (graphite matrix with coated particle dispersion fuel), cermets, coated particles and fluid fuels (molten salt reactor and aqueous homogeneous reactor).

Uranium dioxide (UO₂) is the chosen fuel material for LWRs as it offers a number of advantages compared to other forms. These include good irradiation stability, compatibility with hot coolant as well as the cladding, and ease of manufacturing. The poor thermal conductivity is the main disadvantage of UO₂, but this is offset by its high melting temperature (2800°C). High-density UO₂ pellets contain only half as much uranium as the same volume of pure uranium metal. However, uranium metal is very corrosive in hot water and it changes shape/size during irradiation in the core.

The fuel cladding provides a barrier for the release of fission products generated in fuel; avoids direct exposure of fuel from the reactor coolant and provides a structure for geometric integrity. The criteria for the selection of clad material are: it should have low affinity for neutron absorption, possess good mechanical properties (strength, toughness), must be easy and economical to fabricate, have high corrosion-resistance and have good compatibility with fuel and coolant. Zirconium alloy meets these criteria for use in LWRs. Its low neutron absorption property provides the major incentive for use in LWRs compared to stainless steel. Zirconium alloy was first used as a nuclear fuel clad material in 1951 in the first nuclear submarine 'Nautilus' in the USA. Zirconium alloys have undergone developments over the years to meet increasing demands. The composition of the various alloys used [5] is given in Table-2. Pure zirconium metal has good corrosion resistance for high temperature water but the presence of nitrogen in the metal even in small quantities reduces its corrosion resistance drastically. The effect of presence of nitrogen was overcome by the addition of tin to pure zirconium. Zircaloy-2 was obtained by adding other alloying elements like Fe, Cr, and Ni to provide better mechanical properties for use in both PWRs and BWRs. For use in PWRs, zircaloy-4 was developed by reducing Ni and increasing Fe and Cr.

TABLE 2: Composition of Zirconium alloys for clad

Alloy	Elements alloyed to Zirconium				
	Sn	Fe	Cr	Ni	Nb
Zircaloy-2	1.20-1.70	0.07-0.20	0.05-0.15	0.03-0.08	-
Zircaloy-4	1.20-1.70	0.18-0.24	0.10-0.15	0.007	-
Zr-1%Nb	-	-	-	-	1.0

It has a hydrogen pickup of about one-third of that of zircaloy-2. Zr-1%Nb is the clad material used for VVER fuel. Zr-Sn-Nb-based alloys have been developed to meet the increased demands of high burnup fuel for LWRs.

Fuel Manufacturing Process

The high density, small diameter, short length cylindrical pellets are manufactured by the conventional powder metallurgical route of cold compaction and high temperature reductive atmosphere sintering. These pellets are filled into long, thin, straight zircaloy cladding tubes and the tube is hermetically sealed at both ends by welding end-plugs to form a fuel rod. The cladding tube is made from well-characterised special alloy melts/ingots of zircaloy. The thermo-mechanical processing steps used for the fabrication are aimed at obtaining the required dimensional tolerances and optimised microstructure. The clad tubes are generally made by extrusion, multi-pass pilgering with intermediate heat treatment. The final tubes are stress relieved, straightened and ground. The fuel rods are assembled together by spacer grids, tie-plates etc. to form the fuel element. Fig. 2 shows a schematic of the fuel fabrication process for a typical LWR fuel.

A very large number of pellets and fuel rods are required to be loaded in a typical power reactor core. Hence, at all the stages of fuel fabrication, a great attention has to be paid to the quality control. The fabrication specifications are carefully formulated and enforced through rigid quality assurance procedures [5]. Quality Control is exercised through both destructive and nondestructive evaluations. For the pellets, destructive methods generally involve chemical analysis of fuel stoichiometry and impurity

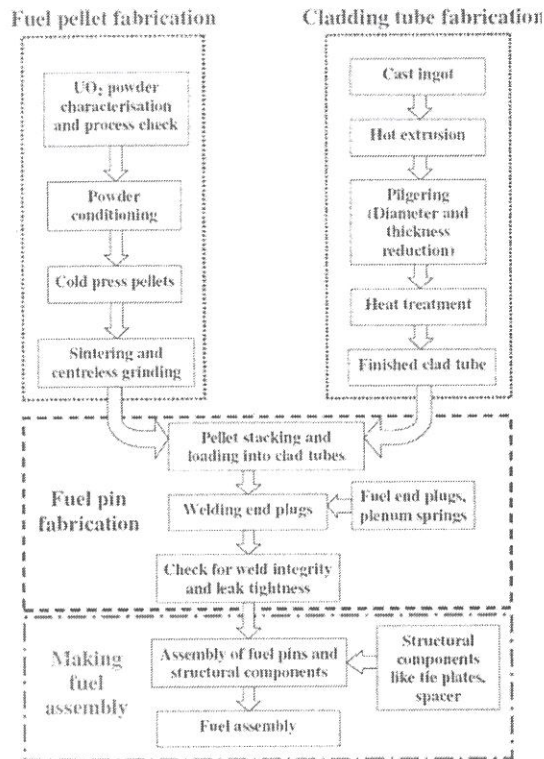


Fig. 2 Typical schematic of fuel assembly process

levels; while nondestructive methods are used to measure fuel density, open/closed porosity and dimensions. Ceramic fuel powders are characterised by measurements of surface area and absorbed gases or surface chemistry, since these strongly influence the sintered product. The tubes are subjected to ultrasonic testing and the accepted tubes are cut to final size. Non-destructive evaluation is carried out to detect the defects originating during the processing from the ingot to the final stage and destructive examination (metallography) is carried

out on sample basis at various stages of fabrication. The fuel rod is subjected to radiography of the welded end-plugs and helium leak testing.

Fuel Element Modelling and Performance Analysis

The primary aim of fuel element modelling is to provide a scientific basis for fuel design. The fuel rod behaviour is carried out by modelling the thermal, mechanical and physical processes such as densification, swelling, fission gas generation, fission gas release, irradiation damage etc. In general, a fuel performance computer code can be considered as consisting of three parts: a thermal analysis, a mechanical analysis, and a material properties component. The thermal analysis is for analysing temperature distribution and thermally induced deformation. The mechanical analysis is for analysing mechanical interaction between pellet and cladding; the evaluation of stress and strain on pellet and cladding; creep and irradiation growth; and the change in pellet-clad gap. The last part, for the material properties, includes libraries for material properties of various fuel, gas, clad and coolant materials. This is because the behaviour of nuclear fuel during irradiation is highly dependent on the physico-chemical properties of the fuel material and their variation with temperature and burn-up. These modelling codes have undergone continuous improvement and as computing power has increased over the years, it has been possible to remove pessimistic assumptions about fuel behaviour and model the important phenomena more accurately. This in turn leads to a reduction in operating margins and improved operating economics. Post Irradiation Examination (PIE) is periodically carried out, to generate feedback information, which is used by the designer, the fabricator and the reactor operator to bring about changes for improving the performance.

Fuel Failures

Fuel rod failure has an effect on reactor operations, maintenance and safety. It can occur at different times in the fuel rod lifetime [6] and usually follows a 'bath-tub' shaped time-history as shown in Figure-3. Failures due to manufacturing defects are most common, early in service life, resulting into high initial failure rate (Infant mortality period). Afterwards, failure rate drops to minimum level and

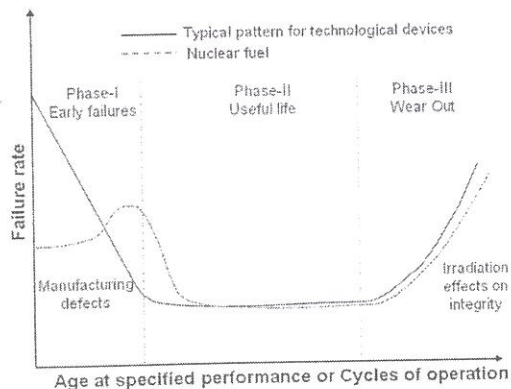


Fig. 3 Bath-tub curve for fuel failures

remains fairly constant (useful life period). The components get old with the service-life and failures again increase (wear-out period).

Some of the major fuel failures experienced in LWRs are given below:

- Clad failure by embrittlement/excessive strain from fuel swelling/fuel densification
- Internal corrosion of cladding resulting from presence of moisture, fluoride, iodine, cadmium, or hydrogen in the fuel pin
- External corrosion
- Wear and fretting of clad
- Defects in the cladding or in the welds
- Crud deposition
- Hot spots in the clad due to deposits of scale or poor heat transfer
- Fatigue failure or creep collapse
- Pellet Clad Interaction (PCI) /Stress Corrosion Cracking (SCC)

Fuel failures have been traced to several different causes as seen in Fig. 4. The primary failure causes continue to be grid-to-rod fretting in PWR designs and debris fretting in BWR designs. The most common are corrosion and crud, mechanical fretting wear (foreign material such as a piece of wire vibrating against the fuel rod surface) and PCI. These are taken care by proper selection of material, good quality control practices during manufacturing, proper fuel modelling with feedback from fuel performance analysis. The total number of

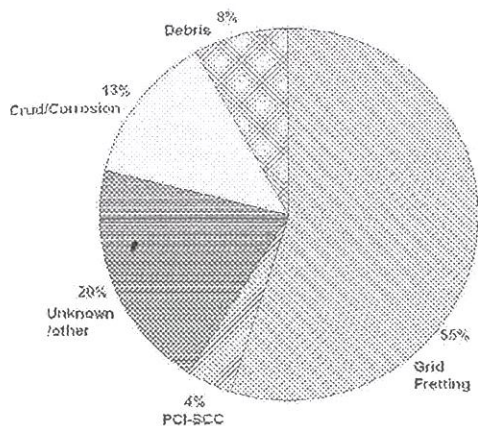


Fig. 4 Causes of fuel failures during 2000-2007 [7]

fuel failures, for both BWRs and PWRs, has been significantly brought down over the years.

Evolution of Fuel

The history of the development of nuclear fuels for power reactors dates back to the early days of the Manhattan Project. The initial impetus to the development of fuels for power reactors resulted from the construction of dual purpose reactors: the submarine thermal reactor developed by Argonne, Westinghouse, and the Naval Reactors Division of the USAEC and the plutonium-producing reactors in the UK, France, and the USSR in the early 1950s, all of which generated electricity [8]. The first commercial PWR plant in the USA was Shippingport, which operated from 1957 till 1982. It provided incentive for the development and evaluation of the zircaloy-clad UO_2 fuel rod, which is the basic fuel element for the commercial water-cooled power reactors of the world today. It was useful in establishing the failure modes and consequences for different fuel materials and designs.

During the early stages of LWR development, fuel was initially of limited reliability. As the cause and effect of the various failure mechanisms came to be understood, changes were made in the fuel design, fabrication processes and in-reactor operating procedures that led to improved fuel reliability. This in turn helped in achieving higher

reactor availability, operating longer cycles with shorter refuelling outages, steadily increasing the burn-up levels and lowering the fuel cycle costs. There was a continuous pressure on fuel designs to meet more demanding operating conditions and higher burn-ups. New cladding and structural materials with high corrosion-resistance combined with evolutionary fuel-assembly design enhancements to attain higher thermal margins, have been the key to improve fuel reliability [9]. Some of the challenges faced by fuel designers and the corresponding effective measures are described below:

- (a) During the initial years of LWR operation, in-reactor fuel densification led to clad collapse. This also had reactivity implications and resulted in local power peaking in fuel. Manufacturing methods were modified by having suitable compaction and sintering process to obtain fuel pellets which do not further densify during operation. Sample-based pellet re-sintering tests are carried out during fabrication in autoclaves at high temperatures as a part of quality control of fuel.
- (b) A dish-shaped end is provided in the fuel pellet to allow for differential thermal expansion. This was done by making suitable provisions in the tools used for cold compaction of pellets.
- (c) Zircaloy cladding is susceptible for hydriding on the internal surface due to reaction from hydrogenous impurities in the fuel rod. The fabrication changes, like improved drying of the fuel pellets, adequate quality control to remove moisture content and inclusion of a hydrogen getter inside the fuel rods, have helped to eliminate this hydriding problem.
- (d) Grinding the fuel pellets to the required size was introduced in manufacturing. This polishes the surface and improves the contact with the cladding and thus improves pellet-clad thermal conductivity.
- (e) Life-limiting effects are likely to arise in clad tube, if it has adverse textures which would lead to the radial orientation of the hydrides picked up by clad. In order to prevent this and to retain sufficient ductility during reactor

service, zircaloy clad tube manufacturing route is suitably designed to have a clad texture, which will ensure a preferential circumferential hydride platelets.

- (f) In BWRs, zircaloy-2 is a preferred material for clad from the point of view of nodular corrosion. The nodular corrosion has been limited by appropriate heat treatment and composition control of the clad. In PWRs, the amount of oxide formed on the zircaloy-4 cladding during operation, limits the average burn-up to about 45 GWd/t. Improved clad materials have been developed for fuels with higher burn-ups. Key upgrading has been provided through the LTP2 cladding (Low Temperature Processing), the Fe-enhanced zirconium liner and the development of doped pellets.
- (g) Pre-pressurising the fuel rods with helium gas (15-20 bar in PWR) has minimised the problems associated with creep collapse. In BWRs, the pre-pressurising with helium is done at about 3-7 bar and this helps to improve heat transfer between fuel, pellet and clad.
- (h) The failure of fuel-element-clad in water-reactors by the pellet-clad interaction (PCI) mechanism has been for many years an important cause of fuel failure. The initial solution to the PCI problem involved costly approach of limiting the rate of increase of reactor power. These ramp rate restrictions result in a loss of possible electrical output, and a consequent economic penalty to the reactor operator. The development of thin 'barrier' liner inside the cladding (using pure zirconium) was used for the reduction in the incidence of PCI failures. The changes in the fuel design, from 7X7 to 8X8 or 9X9 lattice (BWR), has improved fuel elements that can accommodate rapid power changes and are resistant to stress corrosion cracks. The 9X9 BWR fuel rods have lower linear heat rating than that of 8X8 rods, thereby reducing fuel temperatures and improved performance. In case of PWR also, the change in design of fuel elements containing more fuel rods having a smaller diameter (like 17x17, 18x18 lattice arrangement) has helped in improving the

operating margins and has reduced pellet-clad interaction effects.

- (i) Grid-rod fretting caused by the grid springs rubbing against fuel rods, results in wear of clad. It has been reduced through improvements in the design of spacer grids.
- (j) Debris-induced fretting failure of fuel rod has increased due to increase in reactor maintenance activities as a result of ageing of the reactors. It has been addressed through the introduction of debris filters in the fuel element bottom tie-plates and protective end-caps on fuel rods.

Recent Trends in Fuel Development

High Burnup

There is a strong economic incentive to increase the fuel burn-up in all types of reactors. Fig. 4, which presents the trends of fuel burn-up for more than two decades [10], shows that the average burn-up of LWR reactor types has doubled since 1970. For fuel, this has meant a need to endure longer operational periods and to demonstrate increased reliability.

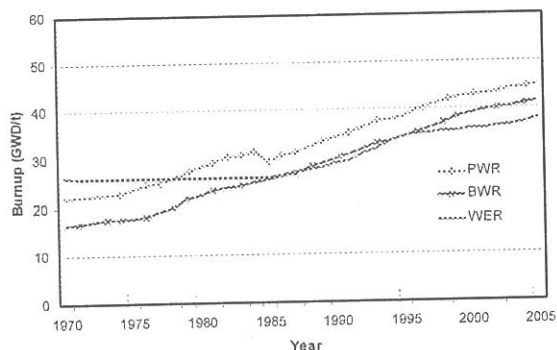


Fig. 5 Trends in fuel burn-up for different type of reactors

To achieve this increase in burnup, the U-235 enrichment of the fuel has increased typically from 2-3% to a current maximum of 4.95%. The fuel manufacturing, transport and on-site handling have been designed, built and licensed for this current maximum enrichment of 5%. To achieve the burn-up of about 100 GWd/t, U-235 enrichment of greater

than 8% will be required. It is therefore likely that further increases in burn-up will not be an immediate priority, as it will involve considerable work on issues related to criticality. It should be noted that although the main change required in nuclear fuel to obtain high burn-up is an increase in fuel enrichment, but that alone is not sufficient. It will require a series of measures like better clad material, working out fuel management strategies to take care of excess reactivity, carrying out safety and fuel performance studies. The changes are introduced to improve safety or performance margins and to ensure reliability over the extended time spent by the fuel inside the reactor.

Burnable Poison

To achieve high burn-up through the use of higher enrichments, it is necessary to control the additional reactivity of fresh fuel, especially in the currently operating reactors. For this purpose, burnable poisons are incorporated in fuel. These poisons are designed to deplete during irradiation and the poison loading/depletion rates are optimised to improve fuel utilisation. The early designs in PWRs used discrete components containing boron or other neutron absorbers alongside the fuel rods. The neutron poison is also now being added directly to fuel pellets to allow more flexibility and economy in their use. These are by boron coating of fuel pellets and gadolinium oxide doping.

Clad Material

Zirconium-based alloys have been used as a fuel rod cladding material in LWR since the early 1960s. But the need to achieve higher fuel burn-ups and higher reactor thermal efficiencies had pushed

the historically used alloys, such as zircaloy-4 and zircaloy-2, to the limits of their capabilities. These limits provided with a motivation to develop advanced cladding materials. One of the limits on PWR fuel behaviour is a constraint on the amount of oxide formed on the fuel cladding during operation. A limited amount of oxide is acceptable (<100 μm thick) and this limit is reached with standard zircaloy-4 cladding at an average burn-up of around 45 GWd/t. At first, variations in the composition of zircaloy-4 were tried and increased oxidation resistance was seen with alloys containing less tin as an alloying component. In the recent few years, there has been a significant development of clad materials with improved performance properties required for upgraded operation including new fuel management approaches and high duty reactor operation [5]. These include E110, E635 (Russian), ZIRLO™ (Westinghouse), MDA (Mitsubishi), HANA™ (Korea) and M5 (Framatome-ANP). The composition of some advanced zircaloys is given in Table 3. These recently developed alloys have led to a major reduction in oxidation of the clad during operation and have helped to meet increasing demands for achieving higher burn-up. The problem of power distortions, because of the use of fuel with higher enrichments and longer cycle times, is being addressed by careful core design and control of the water chemistry. The recommendations for control over water-chemistry have evolved over the years for all water-reactor types.

Fission Gas Release

One of the problems in increasing the burn-up is higher fission gas release. The higher quantity of fission gas is of concern because, if it is released

Table 3: Advanced Zirconium alloys used in nuclear reactor

Alloy	Composition	Remark
Optimised Zr-4	Zr-1.3%Sn-0.2%Fe-0.1%Cr-ppmSi	Suitable for high burnup PWR clad
ZIRLO	Zr-1.0%Sn-1.0%Nb-0.1%Fe	Improved alloy suitable for extended burnup (Corrosion rate of ~60% of Zr-4)
M5	Zr-1.0%Nb-0.14%Oxygen	Superior corrosion performance, improved behaviour under irradiation creep
Alloy 635	Zr-1.2%Sn-1.0%Nb-0.4%Fe	-

from the fuel pellet it can cause higher pressure inside the fuel rod, resulting in clad lift-off and thus leading to deterioration in heat transfer. There is evidence of increasing release rates of fission gas at high burn-up and many ideas are under investigation to understand and control the phenomenon. Options include adding dopants to the fuel pellet to control microstructure with the aim of reducing the release rate from the fuel during operation and also to increase the resilience of the fuel to power ramps. A high burn-up structure with high porosity has also been observed on the rim of the pellet, as the pellet burn-up exceeds 45 GWd/t. The actual quantification of the effect of this on fission gas release is undergoing further research.

Assembly Strengthening

Another issue with long residence time in a reactor is that the radiation field can cause elongation of the fuel rods and of the assembly skeleton that holds the rods in place. This elongation is constrained within the reactor and the assembly has the possibility of bending under the stresses that arise. This 'assembly bow' has been observed in both PWR and VVER reactors. The distortion of the assembly can cause local power changes and problems in insertion of control rods. This has been solved by increasing the stiffness of the fuel element and suitable changes in the design of the spring of the fuel element.

Fuel Recycling in LWRs

In the closed fuel cycle, spent fuel from nuclear reactors is reprocessed by dissolving it in aqueous medium and using the solvent extraction process for separating uranium and plutonium from the fission products and other actinides. The separated products namely the uranium and plutonium are further purified to remove the impurities for recycling it back in reactors. The separated uranium forms a major fraction of spent fuel and is designated as reprocessed uranium. Reprocessed uranium can be either used directly or after appropriate processing while plutonium is mixed with uranium for the use as MOX fuel.

Use of Reprocessed Uranium

With the present worldwide energy and environment challenges like climate change, high

fossil fuels prices and prospective future shortage, there will be an increased demand for recycling of uranium [11]. As the motivation for use of reprocessed uranium in LWRs is predominantly driven by economic factors, it has had a minor role till now in meeting the global uranium requirements for power reactors. The recycle of reprocessed uranium however is an established process accomplished through proven technologies. Reprocessed uranium has been used in LWRs on a large scale in France, Russia, Japan, Germany, Belgium and a few other countries. As reported in IAEA TecDoc-1529, about 7000 tonnes of reprocessed uranium has been recycled in LWRs worldwide till 2003. Another 3000-5000 tonnes of reprocessed uranium is expected to be recycled by the end of 2010. The reprocessed uranium obtained from LWRs has a fissile enrichment close to that of natural uranium. Its use in LWRs will therefore require further treatment and two options have been pursued. In one, the reprocessed uranium is re-enriched using the same technology used for enriching the natural uranium. While in the other option, reprocessed uranium is blended with HEU to obtain the required enrichment for use in LWRs. The radioactivity of enriched reprocessed uranium is higher than the enriched natural uranium due to the presence of ^{232}U . This requires additional shielding to protect operators during fabrication, storage and transportation. The presence of neutron absorbers ^{234}U and ^{236}U in enriched reprocessed uranium also has to be suitably compensated by having additional enrichment.

Use of MOX Fuel

Another significant development in recent times has been the use of MOX fuel in LWRs [12]. In MOX fuel, plutonium is mixed with either natural uranium or depleted uranium. The Pu content in the MOX fuel for LWRs have been in the range of about 3 to 6 wt%. Although MOX fuel resembles in many respects the UO_2 fuel, there are a few differences arising from its nuclear characteristics, thermo-physical properties and manufacturing aspects. The use of MOX in an existing reactor reduces the shut-down margin due to the higher thermal absorption cross-sections of Pu relative to those of U. The number of MOX fuel assemblies is therefore restricted to about one-third of the core and

to increase the loading of MOX fuel will require changes in the shut-down system. The MOX fuel operates at higher powers compared to the uranium fuel during the later half of its residence in core. This and its slightly lower thermal conductivity result in higher fission gas release in MOX fuels, which will have to be taken into account during design. The generation of minor actinides is also higher in the MOX fuel because the spent MOX fuel has a higher activity and generates more decay heat. The spent-fuel storage and transport has to take into account higher heat-load and the radiation shielding requirements, especially the neutron dose during transport in casks.

A number of countries have successfully demonstrated the use of MOX fuel in power reactors. In the last three decades, about 36 LWRs in Europe have been routinely using MOX fuel. Belgium, Germany and Switzerland have used MOX fuel for many years in their reactors. The fraction of the MOX in the various reactor cores has varied between 20 and 40 percent of the core. France has the greatest number of LWRs using MOX fuel. For the last two decades, twenty of its 900-MWe-class PWRs have been loading MOX fuel (up to 30 percent). Currently, French LWRs load annually about 100 tonnes of MOX fuel, which are manufactured at the Melox plant [13]. The French utility, EdF, has asked French regulators to permit an increase in the plutonium content in MOX fuel to about 8% for some of its plants. Currently, the MOX fuel is loaded and discharged under a three-year cycle while the LEU fuel uses a four-year cycle. Japan has ambitious plans to use MOX fuel in 18-20 LWRs and is expected to load about one-third of the LWR's core with MOX fuel.

India also has a large-scale programme for MOX fuel, especially for the fast reactors. There has however been a development programme of loading MOX fuel in the Indian thermal reactors [14]. A total of 14 MOX fuel elements have been loaded in twin units of TAPS-BWRs. The structural design of the MOX fuel elements was almost similar to that of the LEU fuel. The major difference was that the spacer rod in MOX fuel element was a water rod instead of a segmented fuel rod as in LEU fuel. The loading of MOX fuel on a tonnage-scale in power reactors

provided an insight into the various issues associated with the large-scale recycling of plutonium.

Conclusion

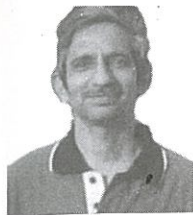
The experience gained in fuel element design, fuel management, quality control and automation in fuel fabrication has led to significant improvements in nuclear fuel cycle in recent years. The reliability of fuel has increased and fuel pin failure levels are approaching 10^{-5} - 10^{-6} levels over the life-time of the pin. The modern nuclear fuel is the result of a huge investment in research, experimental testing and operational experience. Changes have been introduced to improve safety or performance margins and the burn-ups have increased. During the earlier days, the aim was reducing the failure rate of the fuel, while today the aim is to have improved performance of the fuel with longer residence time in the reactor core. The improvement in fuel failure rates has been a very important trend over the past twenty years. There are emerging issues like proliferation resistance, safety, economics and environmental concerns. Current nuclear fuel technology is capable of meeting the requirements of the advanced reactors while maintaining the emerging safety standards. It is expected that there will be incremental improvements in fuel burn-up, giving optimum utilisation of fuel in the next decade. Future developments will pursue the goals of lowering the fabrication costs, with increased use of advanced automation techniques.

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Advances in PHWR Fuels



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Introduction

Pressurised Heavy Water Reactors (PHWR) are characterised by their use of heavy water as moderator and coolant and pressure tubes to contain the fuel and coolant. These characteristics have a significant effect on fuel. The high efficiency of heavy water as moderator (moderating ratio as high as 21000) compared to the other moderating materials (72 for light water and 188 for graphite) enables the reactor to operate with natural uranium as fuel while the pressure tube concept facilitates on- power refuelling.

Evolution of PHWR Fuel

The fuel design for PHWRs started with the selection in the early fifties of hexagonal array of 19-element wire wrap metallic uranium fuel for NPD (Nuclear Power Demonstration) research reactor in Canada [1]. The spiral wire wrap to ensure the inter-element spacing was adopted because it was judged that the spiral pattern would help to promote sub-channel coolant mixing. The decision of changing of the fuel core material from uranium metal to uranium dioxide was taken in 1955 based on successful irradiation tests of deliberately defected samples of such fuel performed in another Canadian research reactor, the NRX reactor [1]. While the lower uranium density provided by uranium dioxide relative to uranium metal resulted in a lowering of achievable burnup, uranium dioxide offered major advantages in terms of dimensional stability at high burnup and greatly enhanced corrosion resistance in

the case of failures of the external zirconium cladding of the element.

The other fuel material that was considered at the early days as fuel for PHWRs is $USiAl$ [2]. U_3Si , the delta phase of the uranium-silicon system, offers a unique combination of high uniform density (15 gm/cc) and low corrosion rate in pressurized water. However, a major obstacle was the high swelling rate in the burnup range of 1000 MWd/TeU. Even though initial studies including test irradiations were carried out, this was abandoned mainly due the success of UO_2 material.

PHWRs use 'Natural' uranium in dioxide form as fuel. 'Natural' uranium as found in the earth's crust is a mixture largely of two isotopes: uranium-238 (U^{238}), accounting for 99.3% and U^{235} about 0.7%. The isotope U^{235} is 'fissile' i.e. it undergoes 'nuclear fission' with low energy neutrons. The isotope U^{238} decays very slowly, its half-life being the same as the age of the earth (4500 million years). This means that it is barely radioactive. It is fertile i.e. it can be converted to fissile material Pu^{239} by neutron absorption and beta decay and then the resulting new element Pu^{239} can produce power by fission.

Description of PHWR Fuel Bundle

A description of PHWR plant and fuel for PHWRs is available in earlier IANCAS bulletins [3,4]. Figure 1 shows the current fuel bundle of the design used for the 220 MWe plants.

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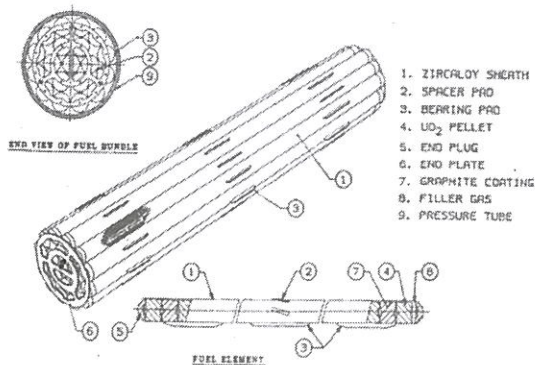


Fig. 1 19-element fuel bundle

Uranium oxide concentrate (U_3O_8) is the end product of the uranium mining stage and is passed on to fuel fabricators. Most of the world's reactors use enriched fuel. Enrichment increases the proportion of the uranium-235 isotope from its natural level of 0.7% to 3 - 4%. PHWRs use natural uranium and hence no enrichment is required. The U_3O_8 concentrate is refined and converted to uranium dioxide powder which is then converted into small cylindrical pellets by powder metallurgy route i.e. by pressing and sintering. These pellets are loaded in Zircaloy-4 (Zirconium-Tin-Fe-Cr alloy) cladding and hermetically sealed at both ends by welding with two end-plugs. Each element is provided with bearing pads/spacer pads to provide inter-element spacing. The elements are assembled in the form of a bundle by welding them to two end-plates. The elements are arranged in two/three concentric rings around a central element. These bundles are 495 mm in length. Typical fuel bundle is shown in Fig. 1. The fuel bundle structural components namely, fuel cladding, end plugs, bearing pads, spacer pads and end plates are all made of zircaloy material. Zircaloy-4 is selected for fuel element cladding and for the bundle structural components due to its low neutron absorption characteristics and better corrosion and hydriding resistance. The zircaloy fuel clad for PHWRs is of collapsible type i.e. the clad collapses over the fuel pellets, due to external coolant pressure.

These bundles are located in the pressure tubes of the coolant channel assembly. The fuel bundle generates heat by nuclear fission and this heat is transported to the primary coolant. Number of bundles in a reactor depends on reactor power and operating parameters. On-power bi-directional fuelling is carried out with the aid of two fuelling machines, one each at either end of the coolant channel.

The fuel element has been designed for maximum content of fissile material (UO_2) and a minimum content of parasitic neutron absorbing material (Zircaloy), consistent with the competing requirements for containment of fission products; and minimum resistance to heat transfer and neutron economy. The bundles are designed to generate heat by nuclear fission at heat ratings and conditions consistent with overall core design of reactor, and have to pass through any coolant channel of the reactor while being subjected to pressure, temperature and flow conditions of the coolant in the channel.

The different fuel designs used in different PHWRs in the world are described here briefly.

Nineteen-element Fuel Bundle Design

The nineteen element fuel bundles are used in the Indian 220 MWe reactors. Nineteen elements, arranged in concentric array of 1, 6 and 12 elements, are joined together by welding them to an end plate on each side to form a bundle. The bundle diameter is 82 mm and the weight is 16 Kgs. This bundle has been designed to generate a power of about 500 kWth. The limited fuel bundle type used in the first Indian PHWR, RAPS-1¹ is of 19-element wire wrap design. This fuel bundle design was same as in the Douglas Point Generating Station, Canada. On the basis of the fuel performance experience at the plants, changes have been incorporated in the fuel design, manufacturing and reactor operating guidelines from time to time [5,6]. Subsequently the helical wires (wire wrap) were replaced by skewed split spacers and short length bearings pads. In the process, the zircaloy inventory, the neutron

1. Rajasthan Atomic Power Station Units 1 & 2

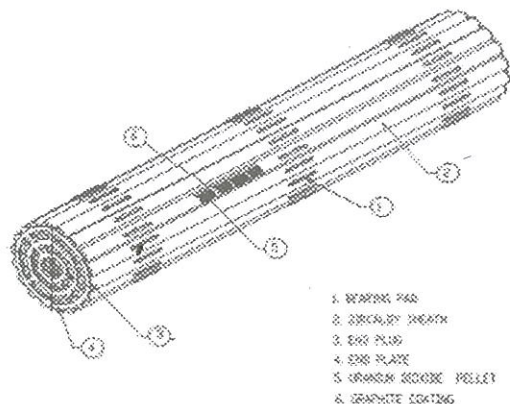


Fig. 2 37-Element Fuel Bundle

absorbing material in reactor, reduced by about 8% per bundle.

In order to overcome the fuel failures induced due to power ramps due to stress corrosion cracking of zircalloy, graphite coating on the inside surface of the cladding is carried out. The graphite coating reduces pellet clad mechanical and chemical interaction and thereby reduces the chance of fuel failure.

The UO_2 pellet shape is cylindrical with a length to diameter ratio of 1.0 to 1.2. A spherical dish was provided on both the top and bottom flat surfaces (see Fig. 1) to accommodate thermal expansion of pellet central zone. The edges of the pellet are chamfered to reduce pellet chipping.

Each fuel bundle during its stay in the reactor core has a different power Vs burnup history. The energy that can be generated by a bundle depends upon the uranium²³⁵ content in fuel, the reactor design i.e. poison material presence in the core and the depletion of U^{235} content with irradiation. The energy capability of fuel is measured by 'burnup' and the unit MWD/TeU. The PHWR bundles see an average discharge burnup of 7000 MWD/TeU. The fuel bundles are designed to go upto 15000 MWD/TeU burnup. Due to neutron flux distribution in core and due to physical heterogeneous nature of fuel, the burnup of different bundles discharged differs.

The KANUP reactor of Pakistan, also uses this type of 19-element fuel bundle [7].

Thirty-seven Element Fuel Bundle Design

The 37-element fuel bundle design (Fig. 2) is used for 540 MWe TAPS- 3&4² units and the 700 MWe PHWR power reactors. This is an extension of the closed packed 19-element fuel bundle. In this design one more ring of 18 elements has been added to get more power. All the elements are of a smaller diameter of 13 mm. The bundle has been designed to generate a bundle power of about 1000 kW. This design is used by all the PHWR operating countries, namely Argentina, Canada, China, Korea, India, and Romania.

Advanced Fuel Designs

In PHWRs, pressure tubes containing a string of short length fuel bundles and the on-power refueling, permit, flexibility in choosing different fuel designs and in-core fuel management parameters to maximize fuel utilization.

Purpose of Advanced PHWR Fuel Designs

The advances in PHWR fuel designs are governed by the desire to use resources other than uranium, improve fuel economics by increasing fuel burnup and reduce overall spent nuclear fuel waste and improve reactor safety. The international nuclear weapons control regime puts a very strong emphasis on the development non-proliferable fuel and protection of nuclear fuel from unauthorized use. This initiative will continue to shape the development of peaceful nuclear energy applications and non-proliferable fuel [8,9]. Synergism between different type of reactors i.e between fast breeder reactors, light water reactors and PHWRs for use of fuel for overall economy and reduction of spent fuel, is also an important point and place a role in new fuel development for PHWRs. The discharged fuel of fast breeder reactors will have fissile content higher than LWR input fuel and similarly the discharged fuel of LWRs have fissile content higher than PHWR input fuel i.e. natural uranium. This led to concepts namely

1. Use of thorium-based fuels, which even though is a fertile resource to be converted to fissile source, is cheaper compared to uranium and is available more abundantly in a few countries like India. The spent thorium fuels are also not amenable for proliferation.
2. Use of slightly enriched uranium (SEU) fuel which reduces the spent fuel waste.
3. Use of Reprocessed uranium from spent fuel of LWRs.
4. Use of MOX (Mixed Oxide) fuel, which again is a combination of Plutonium from reprocessed fuel and natural uranium or reprocessed depleted uranium from PHWR fuel.
5. Fuels for getting low void or negative void reactivity coefficient in PHWRs, in case of LOCA (Loss of coolant accident).
6. Fuel element assembly designs to suit these high burnup fuels and also for aging plants by improving thermal-hydraulic margins.

Increase in fuel burnup beyond 15000 MWd/TeU using higher fissile content materials like slightly enriched uranium, mixed oxide and thorium oxide in place of natural uranium in fuel elements was studied by almost all the PHWR countries [8, 10, 16, 17, 18, 22, 28, 29]. The work include reactor physics studies and test irradiation in research reactors and power reactors. Due to higher fissile content these bundles will be capable of delivering higher burnup than the natural uranium bundles. The maximum burnup studied in India with these bundles is 30000 MWd/TeU for 220 MWe PHWRs and for this the designs studied are 19-element and 22-element fuel bundles.

The different advanced fuel design concept studied by different PHWR countries are described below.

Thorium Dioxide Fuel

India's three-stage nuclear power programme has been drawn with an aim to use the large thorium resources available in the country in the second and subsequent stage of the power programme, which

envisages fast breeder reactors and advanced heavy water reactors using advanced fuel cycles [11,14]. To have operating experience of thorium, thorium fuel bundles have been designed and loaded in 220 MWe PHW Reactors [12,13]. Thorium is not a fissile material. In the reactor core, thorium converts to uranium-233 and this uranium-233 undergoes fission and generates power. The thorium dioxide fuel bundles are used in the initial core for initial flux flattening to achieve full power operation in initial phase of reactor operation. Thorium bundles in general are identical to 19 element natural UO₂ pellet fuel bundles except that the UO₂ pellets have been replaced by ThO₂ pellets. ThO₂ is having better thermal and neutronic properties compared to UO₂. Based on the properties of the thorium, the fuel bundle design was prepared, engineered and fabricated. The performance of these bundles in Indian reactors is quite satisfactory [13,15].

Thorium - Enriched Uranium mixed Oxide fuels are also studied by reactor physicists for use in PHWRs for utilizing fertile thorium resources and also to improve fuel burnup [16, 17]. This improves burnup to 50 GWd/Te and reduces fuel inventory requirements. The main challenges in this design are getting homogenous mixture and reprocessing feasibility of [16, 18, 32]. AECL is developing a Th-SEU (slightly enriched uranium) fuel with Chinese for use in their Qinshen 600 MWe PHWR plant [8, 16]. In this design, the inner 8 elements, of CANFLEX³ bundle, are of ThO₂ and outer 3 elements are of SEU. This will further reduce fuel requirement. Trial irradiation is planned in Qinshen NPP, China. The spent thorium fuels contain hard gamma emitters, due to which they are not amenable for proliferation.

Depleted Uranium Fuel Bundle

Uranium, which is having less fissile content i.e. less Uranium-235 content than naturally available, is called depleted uranium. It can be from tails coming from enrichment process or reprocessed spent fuel. These types of bundles are used as a part of initial fuel loading from RAPS-2 onwards and in that sense it is not an advanced fuel design concept. However this is a precursor to mixed oxide concept.

3. CANFLEX® is a registered trademark of Atomic Energy of Canada Limited (AECL) and the Korea Atomic Energy Research Institute (KAERI).

The bundles are used as a part of initial load fuel to get maximum reactor power, during initial days of reactor power operation in PHWRs [6, 15]. About 400 to 600 bundles of the initial core constitute depleted fuel bundles, the balance of core being natural uranium fuel bundles. These fuel bundles are similar to natural uranium fuel bundles in shape and size. The burnup achieved by these bundle is 4000 to 5000 MWd/TeU, depending upon the uranium content. They can not be used as regular refueling fuel during operation as their fissile content is less.

MOX-7 Bundles

MOX (Mixed Oxide) fuels with mixture of oxides of plutonium (from reprocessed fuel) with either uranium (natural or reprocessed depleted uranium from PHWR fuel) or with thorium was studied for loading into the operating reactors by Indians [17, 19] and Canadians [18].

The Mixed OXide MOX-7 bundle design is a 19-element cluster, with inner seven elements having MOX pellets consisting of plutonium dioxide mixed in natural uranium dioxide and outer 12 elements having only natural uranium dioxide pellets [6]. The plutonium content used is 0.4%. This makes the fissile content of inner elements 1.1% and that of outer elements 0.7%. This leads to flux flattening across the different rings of the bundle leading to generation of higher bundle power compared to natural uranium bundles.

The core average discharge burnup increases to 9000 MWD/TeHE⁽⁴⁾ with this scheme. Due to this, the fuelling rate comes down in the proposed MOX-7 / natural uranium core. Large scale utilisation of such bundles leads to substantial savings in the usage of natural uranium bundles [23]. Fifty number of MOX bundles were fabricated by NFC⁵ and BARC⁶ and loaded in the KAPS-1⁷ reactor in different locations in the year 2004 [20]. The bundles were irradiated to peak burnups of 20000 MWD/TeHE and the irradiation was successful.

SEU Fuel Bundle

Use of Slightly Enriched Uranium (SEU) fuels is planned in some units to improve mined uranium utilization, and operating economics. India has also started analysis and design works for 220 MWe PHWRs using slightly enriched uranium. This offers higher burnup and consequently less annual fuel requirement and spent fuel inventory. R&D works for design of full core of PHWRs with SEU are completed. Fuel design issues in respect of 0.9% to 1.1 % U-235 isotopic content have been reviewed. The core average discharge burnup increases to 14000 MWd/TeU with 1.1% enrichment [17]. It is possible to go upto burnups of 25 Gwd/Te. By this, fuelling costs are lowered because less uranium and fewer bundles are needed to fuel the reactor. This in turn reduces the quantity of used fuel and its subsequent waste management costs.

A few SEU bundles were fabricated by NFC and are loaded in MAPS-2⁸ unit recently for trial irradiation [15]. The channels in which SEU bundles are loaded are kept under watch and the DN Counts of these channels are closely observed. The performance of these bundles in core is satisfactory so far.

Reactor physics studies for use of SEU in PHWRs reactors was carried out in Canada also [18].

Twenty-two Element Fuel Bundle

The 22-element bundle configuration was designed for use in 220 MWe reactors [5,6]. Twenty two elements are arranged in concentric array of 1,7 and 14 elements as shown in Fig. 3. This is a flexible fuel design. It is possible to obtain considerable higher bundle power while operating within the permissible linear heat generation per unit length of an element. The bundles may give about 650 kW power. Alternatively, the design is suitable for use with advanced fuel cycles like use of MOX fuel or slightly enriched UO₂ to high burnups in 220 MWe PHWRs [15]. This design was successfully

4. Burnup of MOX bundles is specified in MWd/Te HE (Tonne of Heavy Element)

5. Bhabha Atomic Research Centre, Mumbai, India

6. Nuclear Fuel Complex, Hyderabad, India

7. Kakrapar Atomic Power Station Units 1&2

8. Madras Atomic Power Station Units 1&2

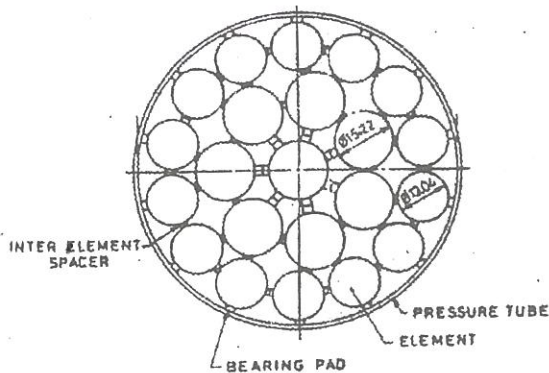


Fig. 3 22-Element Fuel Bundle

developed and test irradiated in power reactors in India [5,6].

CANFLEX² Fuel Bundle

AECL⁹, along with the Korea Atomic Energy Research Institute (KAERI), has developed CANFLEX, an advanced 43 element fuel bundle design [21]. CANFLEX fuel bundle is flexible for use with different types of fuel materials and to go for high burnups in PHWRs—using natural uranium or other advanced fuel cycles. This is similar to 22-element fuel bundle design developed by India for 220 MWe PHWR plants with one more ring of 21 elements surrounding the 22 elements. In addition, in the CANFLEX design, small buttons are provided on the elements at two planes, to improve coolant mixing and consequently provide greater operating and safety margins and extended plant life.

KAERI is now proposing, to avoid derating, CANFLEX fuel bundles, for their 640 MWe Wolsong 2,3 & 4 units loading, to improve CHF (Critical Heat Flux) margins and consequently avoid derating [22]. There are different varieties in this design.

Bruce Power, Canada has undertaken a project, called the “New Fuel Project”, to replace 37-element natural uranium (NU) fuel, presently used in all Bruce B reactors, by CANFLEX^{®1} Low-Void-Reactivity Fuel (LVRF) bundle to restore robust safety margins and to return reactors

to their rated power [24]. It has blended (Dy,U)O₂ fuel in the central pin, and slightly enriched uranium (SEU) fuel of 1.00 wt% ²³⁵U per total U in the remaining fuel pins. The inner eight pins (the central pin and the seven pins of the first ring) are slightly larger than the pins of the intermediate and outer rings. A preliminary evaluation showed that this design would achieve the same average fuel exit burnup as the current NU fuel, while it would reduce the full-core coolant-void reactivity by about 6 mk.

AECL-Canada is working on Advanced CANDU Reactor (ACR) and CANFLEX Fuel development for this reactor type. The ACR fuel is a 43-element improved CANFLEX-ACR fuel bundle, which is a negative void coefficient fuel with burnable absorber in the centre [25]. It has larger center NU pin of 20 mm OD with small percentage of dysprosium in uranium. Balance 42 elements are of same size with uniform uranium enrichment. Presently the dysprosium-uranium pin development i.e. fabrication and decay heat estimation are going on.

LWR-HWR “Tandem” cycles

DUPIC Fuel

The DUPIC (Direct Use of PWR fuel In CANDU) fuel is being developed by Koreans with collaboration with AECL [26]. This design is based on direct processing of spent LWR fuel material as PHWR fuel, without reprocessing and separating fission products and actinides generated during irradiation. The main challenge is, the fresh fuel to PHWRs is also radioactive and to be fabricated and handled remotely under shielded environment.

Reprocessed Uranium Fuel Bundle

The Uranium in spent fuel from LWRs is having fissile uranium content (^U²³⁵ content) higher than that of in natural uranium and so it can be used in PHWRs. Such designs have been worked out in India [17] and Canada. AECL, Canada has developed such designs for the Chinese [27, 28]. In the discharged fuel in addition to ^U²³⁵ and ^U²³⁸, there are other uranium isotopes namely ^U²³⁴ and ^U²³⁶ which are neutron absorbers. To compensate this

9. Atomic Energy Canada Limited

absorption, the U^{235} content is suitably increased, to get an equivalent natural uranium fissile content. The U^{232} needs to be limited from gamma activity from daughter products point of view. The proposal is to reprocess spent LWR fuel, separate the uranium in it and re-fabricate into fuel elements and bundles and reload into the PHWRs.

Weapon Grade Material

As a secondary source of nuclear fuel, down graded ex-weapon fissile materials uranium and plutonium are available for introducing into all reactors. PHWRs, having better neutron economy, are best suited to use this material [8, 9, 18]. This HEU (highly enriched uranium) can be down-graded by mixing with depleted uranium or thorium to PHWR level fissile content and can be used in PHWRs.

CARA Fuel

The Argentina Atomic Energy Commission (CNEA) is developing the CARA advanced fuel element for Argentinean PHWRs [29,30]. It is specially designed to fit the Argentinean fuel-cycle requirement for the vertical channel Atucha and horizontal CANDU 600 MWe Embalse NPP's. The CARA fuel element can be used in both reactor types keeping the same operational conditions for both NPP's. It is a one meter length 52 element fuel bundle. The fuel is 0.85% EU. The fuel is in development.

Other Fuels

Apart from the above mentioned fuel, special bundles are designed to satisfy specific reactor requirements and loaded in reactors. These are cobalt bundles, aluminum bundles and special bundles. Such concepts get generated depending upon the need.

Fuel Characteristics for Advanced Fuels

In PHWR fuel elements no plenum space is available and the cladding is of collapsible type. The additional fission product swelling and gas release due to use of high burnup fuels in PHWRs, needs to be accommodated within the fuel elements taking into account these factors. This can be done either by reducing the fuel element LHR or by modifying the

pellet parameters namely reducing fuel pellet density and increasing dish depth of the pellet [10, 31]. These parameters, are the one which could be modified in order to limit the fission gas pressure without putting much difficulty in manufacturing. To retain fission gases within the fuel matrix itself, concepts like pellets with higher grain size and soft pellets with higher creep rate are being developed for use as high burnup fuels.

Cladding Materials for Advanced Fuels

The advanced fuels with increase in burnup leads to higher residence period which means higher corrosion rate and hydrogen pickup in the zircaloy clad. The structural components have to withstand higher fretting. Also, the power ramp performance of fuel at high burnups is needed. Literature survey indicates that fully annealed cladding is expected to give better corrosion resistance and end-of-life ductility compared to presently used stress relieved cladding. Use of fully annealed cladding with thickness on the higher range within specification is to be further investigated.

The fuel elements require higher end of life fracture toughness to go for high burnups. We need new zirconium alloys which provide higher corrosion resistance, low hydrogen pickup and higher end of life fracture toughness. However, the low neutron absorption characteristic of zircaloys should be maintained as it is essential for PHWRs, i.e. the addition of new alloying elements should not lead to higher neutron absorption. The optimized zircaloys with low Tin and higher Iron content can play a roll and should be further investigated by R&D Units.

Conclusion

PHWRs containing a string of short length fuel bundles and the on-power refueling permit flexibility in using different advanced fuel designs and in-core fuel management schemes to maximize fuel utilization. The advanced fuel designs are developed by the desire to use resources other than uranium, improve fuel economics by increasing fuel burnup and reduce overall spent nuclear fuel waste and improve reactor safety. The international nuclear weapons control regime puts a very strong emphasis on the development non-proliferable fuel

and protection of nuclear fuel from unauthorized use. This initiative will continue to shape the development of peaceful nuclear energy applications and non-proliferable fuel and the rising uranium prices and depletion of uranium resources are leading to a relook into the thorium-based fuel designs and reprocessed uranium-based and plutonium-based MOX designs and are expected to play a major role in future. The requirement of synergism between different type of reactors also plays a role. In India, the fuel cycle flexibility of PHWRs is demonstrated by converting this type of technical flexibility to the real economy by irradiating different types of advanced fuel materials.

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Thorium Fuel - An Overview



Smt. Sriram Jayashree joined RED in 1989 after graduating from 32nd batch of BARC training school. She joined the Fuel Engineering Section of RED under Shri K. Anantharaman. She has been working in the field of fuel design and thorium fuel cycle development. She has been involved in the fuel design of AHWR in the initial stages. She contributed towards fuel cycle analysis detailing the fissile and fertile material inventory and its movement in AHWR fuel cycle facility. She was responsible for the design of fuel for AHWR critical facility. She was involved in the design and fabrication of natural metallic uranium fuel cluster for reference core of critical facility.

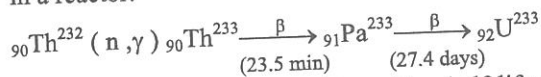
Shri K. Anantharaman is a chemical engineer from 15th batch of BARC Training School and an Outstanding Scientist of BARC. He has been working on the development of nuclear fuels for the past three decades. At present he is heading Fuel Engineering Section of RED and is responsible for AHWR fuel design. He has been involved in the thorium fuel cycle studies, advanced fuel (MOX) design for BWRs and PHWRs.



Shri U. Basak did B.E. in metallurgy and joined RMD in 1978 after graduating from 21st batch of BARC training school. His field of specialization is fabrication and characterization of ceramic nuclear fuel. He has played important role in the fabrication of mixed carbide fuel pellets for FBTR. Subsequently he has done lot of R&D on thorium-uranium fuel pellet fabrication for Advanced Heavy Water Reactor (AHWR). Presently he is on IAEA assignment at Vienna.

Thorium Fuel Cycle

The famous chemist Baron Jones Jackob Berzelius discovered the new element in 1828 and named it thorium after the powerful Scandinavian God "Thor". Thorium is much more abundant in nature than uranium. Although thorium is a fertile material, it could be considered as a mine of fissile U^{233} as Th^{232} transforms into U^{233} by neutron capture in a reactor.



U^{233} is a long-lived alpha emitter with a half-life of 1.6×10^5 years and fissionable by slow neutron ($\sigma_f = 529$ barns). However, unlike uranium fuel cycle, the thorium fuel cycle needs an external source of fissile

material to start with. This could be either U^{235} available from enrichment of natural uranium or Pu^{239} obtained from the irradiation of U^{238} or U^{235} obtained from irradiated Th^{232} . Among these three possibilities, the fissile isotope U^{233} is considered to be a superior one compared to U^{235} or Pu^{239} because of high neutron yield per neutron absorbed (η) leading to significantly higher conversion or breeding potential. Thermal neutron cross sections (in barns) of fissile isotopes of uranium and plutonium are shown in Table 1.

Thorium resources and recovery

Thorium is estimated to be three times more abundant than uranium in the earth's crust. During

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TABLE 1. Thermal neutron cross-section of fissile material

Material	σ_f (barns)	σ_c (barns)	σ_a (barns)	η
U ²³³	529	46	575	2.285
U ²³⁵	582	99	681	2.07
Pu ²³⁹	743	269	1012	2.1

the early periods of nuclear power generation (1950-1970), the interest in the utilization of thorium fuel was predominantly due to the long term availability of thorium resources. The large thorium resources are found in Australia, Canada, India and USA. The economically extractable thorium resources in some countries are shown in Table 2.

TABLE 2. Thorium Reserves in the World (Source: US Geological Survey, 2005)

Countries	Reserves (tones)	Reserve base (tones)
United States	160,000	300,000
Australia	300,000	340,000
Brazil	16,000	18,000
Canada	100,000	100,000
India	290,000	300,000
Malaysia	4,500	4,500
Norway	170,000	180,000
South Africa	35,000	39,000
Other countries	90,000	100,000
World total	1,200,000	1,400,000

Thorium occurs in several minerals as phosphates, silicates, carbonates and oxides. Among them, monazite – a phosphate bearing mineral of thorium containing 9-10% ThO₂ – is the most common. India processes monazite minerals found in the beach sands of Kerala and Orissa in large scale for the recovery of thorium concentrate as a by-product. Apart from thorium oxide, monazite

also contains more than 60% rare earth oxides. Thorium oxide powders are produced by the calcination of thorium oxalate precipitates obtained from the addition of oxalic acid to thorium nitrate solution. However, thorium metal processing is complicated as it has a high melting temperature of 2023 K.

Properties of Thoria-based Fuels

ThO₂, UO₂ and PuO₂ are iso-structural (FCC, CaF₂ type), mutually solid-soluble and have similar physical and thermodynamic properties as listed in Table 3. Thermodynamically, ThO₂ is one of the most stable oxides and does not react with many reactive metals even at high temperature. Reference cladding materials such as zircaloy and stainless steel have shown excellent compatibility with thorium-based fuels namely (Th-U)O₂ and (Th-Pu)O₂ under extreme temperature condition during irradiation. These fuels are also expected to have better irradiation performances compared to UO₂ and (U-Pu)O₂ fuels because of better structural and stoichiometric stability, higher melting point and higher thermal conductivity. The high melting point offers the possibility for high temperature operation and higher power ratings. Due to high thermal conductivity, the temperature of thoria-based fuels would be much lower than that of UO₂ and (U-Pu)O₂ fuels for the same specific power resulting in lower fission gas release. The stoichiometric stability results in less release of fission products in the coolant in the event of a clad breach.

While the above paragraph enumerates the advantages of thorium-based fuel, there are few undesirable characteristics associated with it. Thoria being highly stoichiometric, poses a problem in the spent fuel dissolution. There is also the radiological problem associated with ²³²U which is formed along with ²³³U. This causes problem in fabrication and handling of ²³³U-based fuel. Another operational difficulty with thoria fuel is due to the formation of ²³³Pa, which has a half-life of 27 days in the intermediate stage of conversion of ²³²Th to ²³³U. During a long shutdown, there is a build-up of ²³³U by decay of ²³³Pa. This addition of reactivity has to be accounted for in the reactor operation after a long shutdown and may even require reactor operation below full power to keep fuel powers within limits.

TABLE 3: Properties of UO₂, PuO₂ and ThO₂

Properties	UO ₂	PuO ₂	ThO ₂
Crystal structure	FCC, CaF ₂ type	FCC, CaF ₂ type	FCC, CaF ₂ type
Theoretical density (g/cm ³)	10.96	11.46	10.00
Metal density (g/cm ³)	9.66	10.10	8.79
Metal fraction (w/o)	88.15	88.19	87.89
Melting point, K	3123 ± 25	2623 ± 30	3643 ± 30
Thermal conductivity (W/m.K)			
773 K	4.80	4.48	6.2
1773 K	2.40	1.97	2.4
Thermal expansion coefficient, K ⁻¹	10x10 ⁻⁶ (273 – 1273K)	11.4x10 ⁻⁶ (273 – 1273K)	9.67x10 ⁻⁶ (273 – 2273K)

TABLE 4. Irradiation experiments with ThO₂ – UO₂ and ThO₂ – PuO₂ fuels

Country	Reactor	Fuel Composition	Cladding Type	Burn-up Range (atom%)
USA	Borax IV	ThO ₂ – 6% UO ₂	Al – 1% Ni	0.7 to 3.7
	Elk River	ThO ₂ – 3% UO ₂	SS 304	0.15
	MTR, ETR, NRX	ThO ₂ – UO ₂ (3 to 5%)	SS 304 & Zircaloy-2	1.5 to 15.8
	MTR, ETR	ThO ₂ – PuO ₂ (2 to 19%)	Zircaloy-2	0.69 to 3.68
	Indian Point I	ThO ₂ – UO ₂ (0 to 9%)	SS 304	4.0
	ETR, ATR, NRX	ThO ₂ – UO ₂ (2 to 25%)	Zircaloy-4	5.1
CANADA	NRU	ThO ₂ – 1.3% UO ₂	Zircaloy-2	4.0 to 6.0
	NRX	ThO ₂ – 9% UO ₂	Zircaloy-2	0.4
ITALY	Halden	ThO ₂ – UO ₂ (3 to 10%)	Zircaloy-2	0.2 to 3.6
INDIA	CIRUS	ThO ₂ – 4% PuO ₂	Zircaloy-2	2.1

International Irradiation Experience

Irradiation of thorium and thorium-based fuels in water-cooled reactors and gas-cooled reactors was mainly carried out in United States, Germany, Canada, Italy and India [2,3,4]. The summary of major irradiation experiments carried out in water-cooled reactors in different countries is listed in Table 4. Irradiation experiments with thorium-based fuels started in early fifties and were mainly carried out in United States. The earliest irradiations of

(Th-U)O₂ fuel were done in Chicago Pile No.5 at Argonne and in MTR at Idaho falls. This was followed by irradiation of aluminum clad (Th-U)O₂ fuel pins in BORAX – IV reactor and SS-304 clad fuel pins in Elk River Reactor. Thorium-uranium fuels enriched with 93% U²³⁵ was used in Indian point I, a 285 MWe PWR designed by Babcock and Wilcox. As a part of LWBR development programme, thorium and uranium fuels, clad with zircaloy-4 using the seed/blanket concept, were irradiated at Shippingport reactor (100 MWe) in order to gain

TABLE 5. Details of coated fuel particles in High Temperature Gas-cooled Reactors

Reactor system	Kernel diameter (µm)	Fuel type	Th : U	Type of coating	Remarks
AVR (15 MWe), Germany	400	(Th-U)O ₂ (Th-U)C ₂	10 : 1 5 : 1	BISO	1360 kg of thorium with HEU used and achieved burn-up 150,000 MWd/t
THTR (300 MWe), Germany	400	(Th-U)O ₂	10 : 1	BISO	Industrial scale fabrication
FSV (330 MWe), USA	400	(Th-U)C ₂	5 : 1	TRISO	25 tonnes of thorium with HEU used and achieved burn-up 170,000 MWd/t

experience in in-reactor performance of these fuel with respect to thermal conductivity, creep-behavior, fission products distribution, dimensional changes and fission gas release.

In Italy, (Th-U)O₂ fuel pellets prepared by both extrusion and sintering route and compaction & sintering method at the ITREC pilot plant for remote reprocessing and re-fabrication were irradiated at the Halden Boiling Water Reactor and evaluated for their performances. In Canada, initial irradiation of ThO₂ - 1.3% UO₂ fuel elements was carried out in CANDU (19 fuel element bundle) to investigate mainly the fuel performances with respect to thermal conductivity and fission gas release. However, in nineties, zircaloy-clad (Th-1.4%Pu)O₂ fuel-bundles (six Bruce type) fabricated in the Recycle Fuel Fabrication Facility (RFFL) of AECL were test irradiated under experiment BDL - 422 in NRU in order to investigate the suitability of thorium as matrix material for burning of plutonium (weapons grade) in heavy water reactors.

The USA and particularly Germany took a leading role for large scale utilization of thorium fuel cycle in High Temperature Gas cooled Reactors (HTGR). This included the prototype Peach Bottom (110 MWth) high temperature, graphite-moderated, helium-cooled reactor, the commercial Fort St. Vrain (330 MWe) reactor in USA, the experimental pebble bed reactor AVR (15 MWe) and THTR (300 MWe) in Germany. In these high temperature reactors, mainly the kernels of mixed oxide or carbide of thorium and uranium (HEU) coated with BISO or

TRISO coatings were used. BISO coatings are two layer coatings that consists of low density pyrolytic carbon (PyC) followed by high density isotropic PyC coating outside. TRISO coatings have four layers; the low density buffer layer followed by two layers of high density isotropic PyC with SiC layer in between. In Germany, Th-Pu based test fuel elements were also utilized in the 60 MWe Lingen Boiling Water Reactor. In United Kingdom, thorium-uranium fuel elements with 10:1 Th/U (HEU) on 'breed and feed' concept (U²³³ formed replaced U²³⁵ at about the same rate) were irradiated in Dragon reactor (20 MWth). The details of the coated fuel kernels used in the HTGRs are given in Table 5.

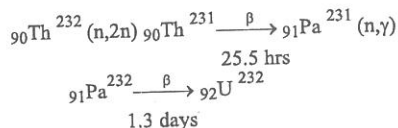
The Molten Salt Reactor (MSR) is another type of reactor concept where thorium fuels could be efficiently utilized and a conversion ratio close to one or little more (0.95-1.07) could be achieved. A prototype reactor, Molten Salt Reactor Experiment (MSRE) of 8 MWth was operated at Oak Ridge National Laboratory (ORNL) from 1965 to 1969. Based on this experience, Molten Salt Breeder Reactor (MSBR) was designed for the use of thorium-uranium fuel cycle. The fuel in MSBR is a molten mixture of UF₄, LiF, BeF₂ and ThF₄. Graphite rods suspended in the molten salt are used as moderator. The hot liquid fuel salt transfers the heat in a secondary coolant salt (8 mol% NaF and 92 mol% NaBF₄) which in turn flows to the steam generators. The molten fuel is also taken through an on-line purification system for the separation of Pa²³³ and fission products.

In Japan, Th-U (HEU) fuel was used for the criticality experiments at KURRI. A new thorium based fuels, namely thorium hydride alloyed with titanium and or zirconium, were test irradiated in JMTR (Japan Material Test Reactor) at Japan Atomic Energy Research Institute.

Large number of irradiation experiments in light water and heavy water reactors concludes that the performances of zircaloy-clad thoria-based fuels are comparable to or in some cases better than that of uranium fuels. The magnitude of fission gas release in the burn-up range of 3-6 atom% and power ratings of 370-650 W/cm are similar to that of UO₂. The irradiation-induced swelling is also low and in general the volume change of (Th-U)O₂ and (Th-Pu)O₂ fuels remain less than 1% for each atom% burn-up upto 10 atom%. ThO₂ based fuels also showed less structural changes and fission product relocation than UO₂ fuel.

Radioactivity and Proliferation Resistance

In thorium fuel cycle, apart from generation of U²³³, some amount of U²³² is also produced by (n, 2n) reaction at a neutron energy greater than 6.37 MeV.



The amount of U²³² produced along with U²³³ depends mainly on the neutron energy distribution in the reactor and the irradiation time. Thus, U²³³ always contains some amount of U²³² and the main source of radioactivity in U²³³ is due to the short lived decay products of U²³². U²³² has a half-life of 72 years and undergoes six alpha decays and two beta decays before it reaches the stable Pb²⁰⁸. The radioactivity of primary concern from U²³³ containing even a small amount of U²³² is 2.6 MeV gammas from Tl²⁰⁸ and 0.8 to 2.12 MeV gammas from Bi²¹². Due to high specific activities of U²³² (3.55x10⁸ dps/gm & ~2000 times more than U²³³) and its first daughter product Th²²⁸ (3.05 x 10¹³ dps/gm), the amount of dose increases substantially with time (Table 6) leading to the requirement of automation and remotisation of all the processes to be carried out even with the separated U²³³ in the front end of the thorium fuel cycle (fuel pellet and

pin fabrication, fuel element & assembly handling, transport etc.) in an adequately shielded facility. The easy detection of gamma activity associated with U²³³ due to the presence of U²³², remote and automated operations inside the shielded facility with almost no manual intervention, prevent any unauthorised diversion of fissile material and make the Th-U²³³ fuel cycle intrinsically proliferation resistant.

TABLE 6. Dose rates at one meter from a 1Kg sphere of U²³³ metal containing 400 ppm of U²³²

Time after separation of Th ²²⁸ and decay products (days)	Dose rate Uranium (mR/hr)
1	0.17
2	0.92
4	9.1
88	18
16	54
32	137
64	298

The total plutonium produced per MWD in Th-U fuel cycle is much less (~ by a factor of 3.2) than in the conventional uranium fuel cycle. The amount of Pu²³⁹ is also reduced and Pu²³⁸ content is almost 29 times greater than that in the weapons grade plutonium. This results in the large decay heat (0.55 KWh/g) and causes the fast degradation of the explosives. With the same intention, some amount of neptunium oxide (~1%) is also intentionally added to thorium oxide used as blanket material in fast reactor so that U²³³ gets contaminated with Pu²³⁸. The quality of plutonium produced in Th-U fuel cycle makes it unattractive for explosives leading to non-proliferation.

High burn-up capability of thorium-based fuels also increases the degree of resistance to proliferation as the improved burn-up increases the fuel cycle length, safeguarding the fissile material in the reactor itself. The longer cooling period required for the complete decay of Pa²³³ to U²³³, the high degree of chemical stability and low solubility of thoria in acid media also make the irradiated fuel extremely difficult for reprocessing. Thus the time

constraint and the chemistry of thorium act as effective barriers and reduce the risk of proliferation to a great extent.

Fabrication of Thorium-Based Fuels

Thorium-based fuels are normally used either in the form of cylindrical pellets in water-cooled reactors (LWRs, HWRs etc.) or in the form of coated particle fuel in HTGRs. Powder metallurgical route using fine powders as feed materials for pellet compaction and sintering remains the principal method [5,6] for the fabrication of high density $(\text{Th-U})\text{O}_2$ and $(\text{Th-Pu})\text{O}_2$ pellets suitable for water-cooled reactors. The other processes [7-9] which have been developed and demonstrated in laboratory-scale, keeping in mind the amenability of the process steps to automation and remotisation, are vibro-sol or sphere-pac process, sol-gel microsphere pelletisation (SGMP) route and impregnation process.

Powder-Pellet Route

Thorium, uranium and plutonium have same crystal structure and have almost similar physical and thermodynamic properties. Hence, the process flow-sheet followed for the fabrication UO_2 and $(\text{U-Pu})\text{O}_2$ pellets is also followed for thorium and thorium-based fuel pellets $(\text{Th-U})\text{O}_2$ and $(\text{Th-Pu})\text{O}_2$. However, thorium oxide is a perfectly stoichiometric compound with a very high melting point and is difficult to sinter to high density ($\geq 95\%$ T.D.) even at a sintering temperature ≥ 1923 K without any sintering aid. MgO , CaO , Nb_2O_5 etc. act as sintering aids. Pre-milled MgO -doped ThO_2 powder is mixed with either UO_2 or PuO_2 powder in a planetary ball mill / attritor before pre-compaction and granulation. Pre-milling helps in breaking off the large square shaped platelets into small sizes which in turn improve the homogeneity of powder mixtures. The granulated powders are subjected to final compaction and high temperature sintering at 1923 K for obtaining high density pellets.

Vibro-sol or Sphere-Pac Process

The vibro-sol or sphere-pac process consists of the preparation of sol-gel derived microspheres of diameter 50-1000 μm by internal or external gelation process, starting from heavy metal nitrate feed

solution. The mixed oxide gel microspheres are dried and sintered to high density ($\geq 96\%$ T.D.) which is subsequently packed in the cladding tube by vibratory compaction. This process has been used in the Babcock and Wilcox, KiloRod facility and Thorium Uranium Recycle facility (TURF) of USA for the fabrication of $(\text{Th-U}^{233})\text{O}_2$ fuel pins. The principal advantages of this process are the avoidance of the handling and generation of fine powders, less number of fabrication steps, maximum number of flexibility of operation, a high degree of micro-homogeneity of fissile species and amenability to automation and remotisation. However, the maximum achievable smear density of the vibro-sol pin is only 90% of theoretical density which comes in the way of achieving a high conversion ratio.

Sol-gel Microsphere Pelletisation Process (SGMP)

This is an advanced concept for the fabrication of high density fuel pellets retaining most of the manufacturing advantages of powder-pellet route and vibro-sol process. The SGMP process utilizes sol-gel derived dust-free and free flow calcined gel microspheres of mixed oxide as feed materials for pellet compaction and sintering. High density $(\text{Th-U})\text{O}_2$ with tailor-made microstructure suitable for thermal and fast reactors could be fabricated by SGMP process.

Impregnation Process

Pellet Impregnation Process

The pellet impregnation process has been developed for the fabrication of high density $(\text{Th-U})\text{O}_2$ pellets, particularly keeping in mind the amenability of the fabrication processes to automation and remotisation and restricting the shielded facility for fuel fabrication involving U^{233} handling area to a bare minimum. The pellet impregnation process involves first, the fabrication of low density porous ThO_2 pellets by conventional powder-pellet route followed by vacuum impregnation in uranyl nitrate solution containing U^{233} and sintering. The major advantage of this process is that a large part of the fabrication processes, including the handling of fine ThO_2 powders, is carried out in an unshielded facility and

the shielded facility is restricted to high energy gamma active U^{233} handling area consisting of impregnation and sintering facilities.

Microsphere Impregnation Technique

In microsphere impregnation technique, thorium microspheres prepared by ammonia gelation process are impregnated with uranyl nitrate solution under vacuum. The uranium impregnated thorium microspheres are calcined and reduced. Depending on the molarity of uranyl nitrate solution, a wide range of uranium loading is possible in this technique. Calcination makes the microspheres porous, which in turn becomes easily crushable and compactable. The calcined microspheres are subjected to cold compaction and high temperature sintering to get high density pellets.

Coated Particle Fuel

The fabrication of coated particle fuel used in HTGR has already been demonstrated on pilot plant scale in Germany and USA. The process involves first the preparation of kernels of thorium fuels (oxide or carbide) either through wet chemical sol-gel route or dry agglomeration method followed by coating (BISO or TRISO). The coating is generally carried out in fluidised bed by pyrolytic decomposition of hydrocarbon gas and silane vapour. The decomposition temperature, the type of gas, the cooling rate etc. are the important controlling parameters in order to obtain the desirable coating properties.

Reprocessing of Irradiated Thorium Fuels

The reprocessing of thorium-based fuel is extremely difficult compared to that of uranium or uranium-plutonium fuels as the dissolution of high density thorium-based oxide fuels is very slow in HNO_3 . The coated particle fuels have to be crushed and oxidised before dissolution. Addition of HF does enhance the dissolution rate but leads to severe corrosion problem of the dissolver material. Secondly, the partitioning of plutonium from uranium in PUREX process is much simpler as it is based on the reduction of Pu^{+4} to Pu^{+3} . However, the separation of thorium from uranium in THOREX process depends on the poor extractability of thorium in organic phase during solvent extraction.

Waste Characteristics of Thorium Fuel Cycle

Due to high chemical stability and low aqueous solubility of thorium, thorium-based fuels are also attractive as a waste form. The fluorite structure of thorium can accommodate substantial levels of actinides in other oxidation states and fission products. Thus the release of actinides is expected to be controlled by the slow dissolution rate of thorium matrix. In addition, the long-term advantage of thorium fuel cycle is that the magnitude of long-lived actinide wastes generated is less than that produced in uranium and uranium-plutonium fuel cycle. This is due to the fact that five additional neutrons are required to be captured in succession for U^{233} to reach the mass level of U^{238} and the probability of each capture decreases by a factor of ten, leading to an overall decrement in the active waste level.

Thorium Utilisation in India

The development work on thorium fuel has commenced right from the inception of India's nuclear power programme. Experience is available in all the aspects of thorium fuel cycle – mining, extraction, design, fabrication, irradiation, reprocessing, post irradiation examination and refabrication. Thorium fuel cycle is feasible in all the existing thermal reactors and fast reactors as well. In the short term, it should be possible to incorporate the thorium fuel cycle in existing reactors without major modifications in the engineered systems, reactor control and the reactivity devices. The thorium fuel cycle can be incorporated into PHWR. Physics studies have been carried out for three different cycles mainly the Self Sustaining Equilibrium Thorium cycle (SSET), the high burn-up open cycles and the Once Through Thorium Cycle (OTT) [11].

Irradiation of Thorium Bundles in PHWRs [12]

After successful use of test-fuel bundles containing high density ThO_2 pellets for flux flattening in PHWR at Madras atomic power station, India has replaced depleted uranium bundles with thorium bundles for flux flattening in PHWRs at Kakrapar and other reactors subsequently commissioned at Kaiga (I & II) and Rajasthan (III & IV). Presently thorium bundles are used in Indian PHWRs for achieving the initial flux flattening in the

TABLE 7: Irradiation of thoria bundles in PHWR

Reactor	Number of bundles
Madras- I	4
Kakrapar-I	35
Kakrapar-II,	35
Rajasthan- II	18
Rajasthan -III	35
Kaiga-II	35
Rajasthan-IV	35
Kaiga-I	35
Tarapur-III	12
Tarapur-IV	12

core. This represents a unique way of utilising thorium without any loss of burn-up in UO_2 fuel. The design of these thoria fuel bundles is almost identical to that of the uranium fuel bundles to ensure compatibility with fuel handling and thermal hydraulic aspects. Table 7 gives the number of the thoria bundles loaded in PHWRs. The thoria bundles at Kakrapar power station have been irradiated for more than 500 FPDs. One of the high burn-up thoria bundles has undergone Post Irradiation Examination (PIE) and dissolution tests. From these results the ^{232}U content of the irradiated thoria bundles has been estimated to be about 500 ppm.

Irradiation of Thoria Assemblies in Research Reactors [10]

Four thoria fuel assemblies were loaded in research reactor Dhruva during its initial days of

operation to take care of the excess reactivity of the initial core. These assemblies were similar in design to that of the natural uranium assemblies of the reactor and were successfully irradiated up to 100 EFPDs. The reprocessing of thoria fuel has been carried on aluminium-clad ThO_2 fuel assemblies known as 'J' rods irradiated in the reflector region of research reactor CIRUS. The reprocessing of these rods which had been irradiated to a level upto 1.2 Kg of U^{233} /t of thorium, and cooled for more than two years was carried out in a pilot-scale test-facility at BARC and at Indira Gandhi Centre for Atomic Research (IGCAR). The U^{233} obtained has been used for the fabrication of plate-type fuel for KAMINI reactor at IGCAR, Kalpakkam. Few numbers of thoria assemblies have been loaded in the blanket region of Fast Breeder Test Reactor (FBTR), IGCAR, Kalpakkam. A facility has also been constructed at IGCAR, primarily for reprocessing fast reactor blanket fuel.

Irradiation of Thoria-Based Mixed Oxide (MOX) Fuel¹²

Thoria-based MOX fuels and thoria fuel have been successfully irradiated in the Pressurised Water Loop (PWL) of CIRUS reactor without any failure. These tests were carried with short-length fuel pins of about 0.5 metre under simulated power reactor operating conditions. Table 8 gives details of the irradiation experiments carried in PWL, CIRUS.

Advanced Heavy Water Reactor (AHWR) [13,14]

The AHWR is a 300 MWe, vertical, pressure tube type, heavy water moderated, boiling light water cooled natural circulation reactor. The fuel consists of $(Th-Pu)O_2$ and $(Th-U^{233})O_2$ pins. The fuel cluster is designed to generate nearly 75% of energy out of U^{233} , which is bred in-situ from thorium. AHWR has adopted the well-proven pressure tube technology. The AHWR has been

TABLE 8. Details of Fuel Irradiation Tests

Fuel Design	Fuel type	Clad type	No. of pins	Peak Linear Heat Rating	Burn-up
BWR	(Th-4%Pu) MOX	Free Standing	6	40 kW/m	18.5 GWd/t
PHWR	(Th-6.75%Pu) MOX	Collapsible	2	42 kW/m	10.2 GWd/t

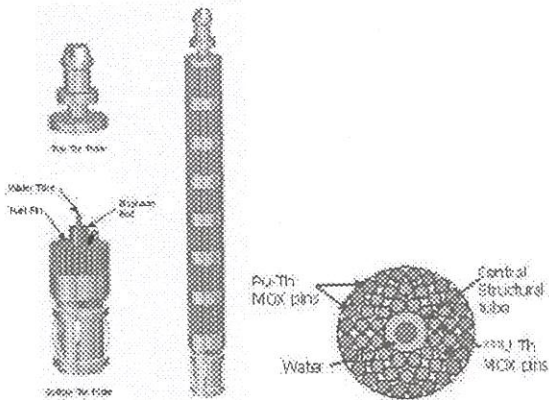


Fig. 1 Schematic of AHWR fuel cluster and cluster cross section

designed to extract most of its power from thorium-based fuel, keeping plutonium consumption as low as possible. The equilibrium fuel cycle for the AHWR is based on the conversion of naturally available thorium into fissile U^{233} driven by plutonium as external fissile feed. The AHWR has been designed to be self-sustaining in U^{233} . The fuel cycle is a closed fuel cycle, envisaging recycle of both fissile U^{233} and fertile thorium back to the reactor. Even though the AHWR is primarily designed to work with U^{233}/Th -Pu MOX fuel, the design has flexibility to accept other fuel types. The schematic of an AHWR fuel cluster is shown in Fig. 1.

The reactor core of AHWR consists of 513 lattice locations in a square lattice pitch of 225 mm where fuel assemblies occupy 452 locations. Sixty-one locations are reserved for the reactivity control devices and shut down system. The schematic arrangement of different systems in AHWR is shown in Fig. 2. The reactor has two independent, functionally diverse, fast acting shut down systems, namely, Shut Down System-1 (SDS-1) consisting of mechanical shut off rods and Shut Down System-2 (SDS-2) based on liquid poison injection into the moderator.

The reactor has a slightly negative void coefficient of reactivity. The AHWR has several passive safety systems for reactor normal operation,

decay heat removal, emergency core cooling, confinement of radioactivity etc. These passive safety features are listed below:

- Core heat removal by natural circulation of coolant during normal operation and shutdown conditions.
- Direct injection of ECCS water in the fuel cluster in passive mode during postulated accident conditions like LOCA.
- Containment cooling by passive containment coolers.
- Passive containment isolation by water seal, following a large break LOCA.
- Availability of large inventory of water in GDWP at higher elevation inside the containment to facilitate sustenance of core decay heat removal, ECCS injection, containment cooling for at least 72 hours without any active/operator intervention.
- Passive shutdown by poison injection in the moderator, using the system pressure, in case of MHT system high pressure due to failure of wired mechanical shutdown system and liquid poison injection system.
- Passive moderator cooling system to minimize the pressurization of calandria and release of tritium through cover gas during shutdown and station blackout.
- Passive concrete cooling system for protection of the concrete structure in high temperature zone.

At present the experience with thorium is very limited. In order to validate the reactor physics design of AHWR core and generate thorium data, a low power critical facility was built at Trombay [15,16]. Experiments will be conducted with AHWR type fuel clusters, thoria clusters, mixed pin (metallic uranium pin and thoria pin) clusters etc. The fuel fabrication for AHWR critical facility will be the first major fabrication exercise of the thoria-based MOX fuels. This experience will provide the initial feedback on aspects related to fuel fabrication and specification. Fuel pins of both $(Th-U^{233})O_2$ and $(Th-Pu)O_2$ will be fabricated for carrying out in-pile loop irradiation experiments.

Compact High Temperature Reactor (CHTR) [17]

Nuclear energy will be utilised in the near future for non-electrical applications or specific application areas like systems to produce hydrogen

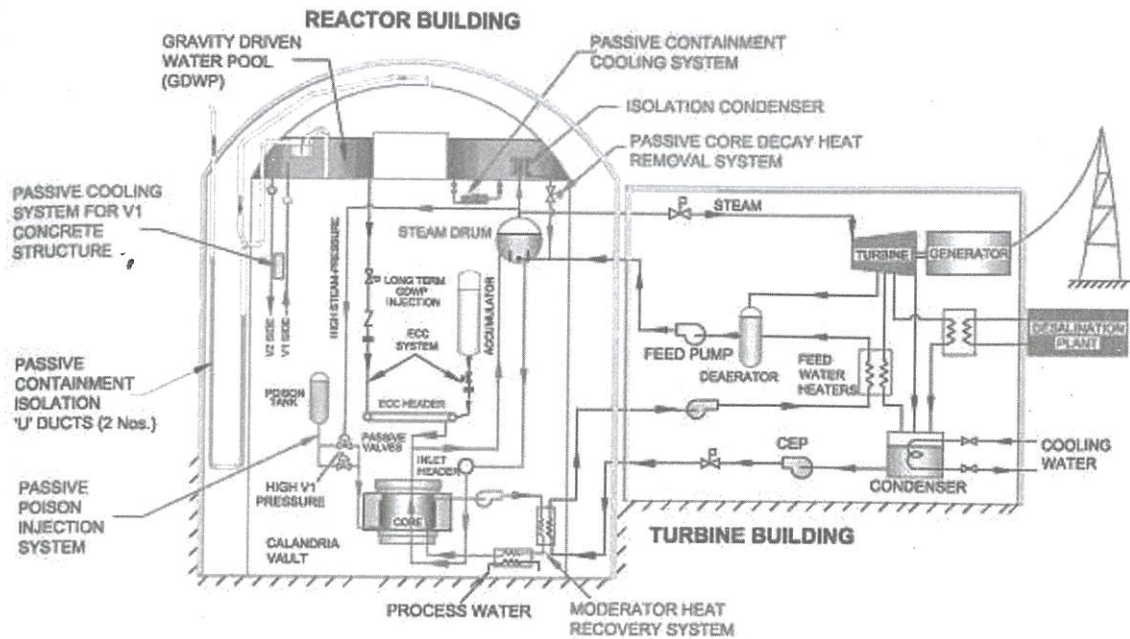


Fig. 2 Schematic arrangement of different systems in AHWR.

or hydrocarbon as a substitute for fossil fuel, compact power packs in remote areas not connected to grid system, and desalination plants to convert sea water to drinking water. For such applications, high temperature reactors using gaseous or advanced liquid metal alloy coolant would be necessary. Thorium offers special advantages in reactor design for such applications.

A Compact High Temperature Reactor (CHTR) being developed in Bhabha Atomic Research Centre (BARC) is designed on the basis of following guidelines:

- Use of thorium based fuels
- Passive core heat removal by natural circulation of liquid heavy metal coolant
- Passive power regulation and shutdown mechanism.
- Passive rejection of entire heat to the atmosphere under accidental condition
- Compact design to minimize weight of the reactor

In the current stage of design, which is illustrated in Fig. 3, the reactor core consists of nineteen prismatic beryllium oxide (BeO) moderator blocks (distributed in 1-6-12 arrangement). These

blocks contain centrally located carbon fuel tubes. Each fuel tube carries within it the fuel inside 12 equi-spaced longitudinal bores. The fuel is in the form of pellets made by TRISO coated fuel particles. The central bore of the fuel tube serves as coolant channel. Eighteen blocks of beryllium oxide reflectors then surround the moderator blocks. The beryllium oxide reflector blocks are surrounded by graphite blocks as additional reflector.

To remove heat from the reactor core, a lead-based liquid metal coolant flows by natural circulation between the top and bottom plenum, upward through the fuel tubes and returning through downcomer tubes. From the upper plenum of the reactor, heat pipes transfer heat to heat transfer interfaces of heat utilising systems. These heat utilising system interfaces provide the required environment, heat transfer area and interface hardware for energy conversion systems. The reactor has been provided with passive reactor power regulation system. The system uses core outlet coolant temperature as a driver to passively cause an extent of absorber insertion.

CHTR has been provided with four independent systems to reject entire core heat to the

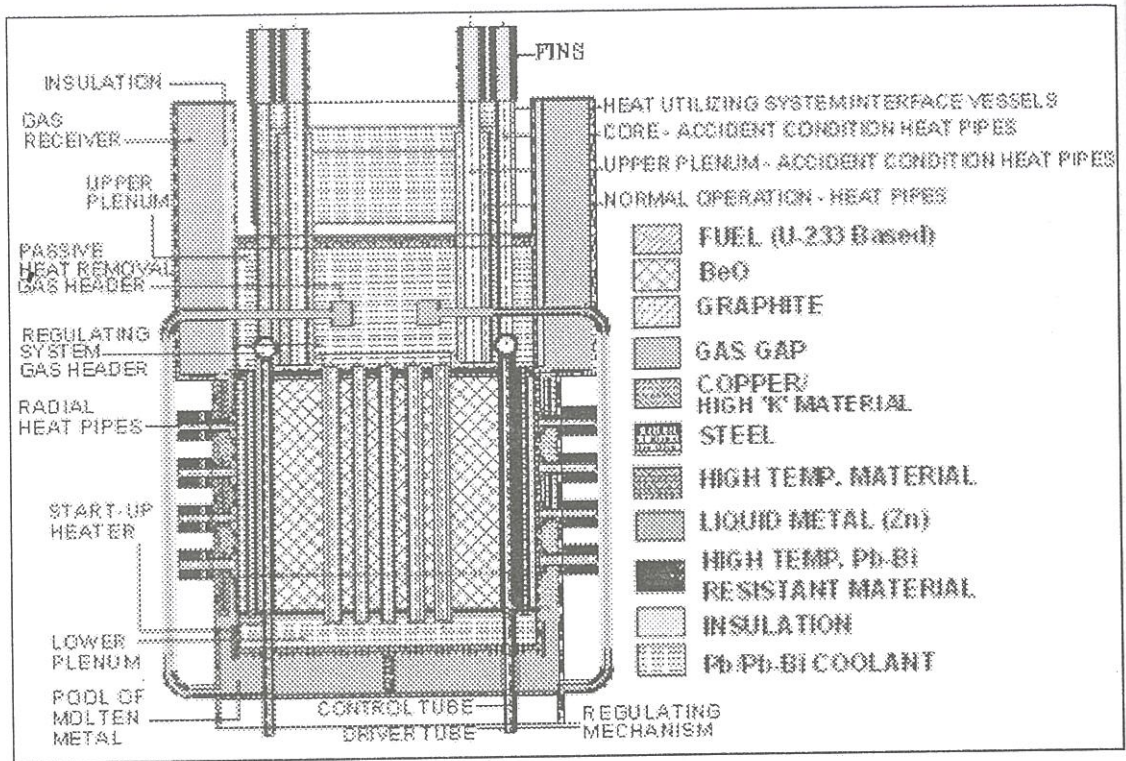


Fig. 3 Schematic of Compact High Temperature Reactor

atmosphere by passive means during postulated accident conditions at a neutronically limited peak power level. These heat removal systems, which are individually capable of removing 200 kW power each may operate together or independently to prevent the temperature of the core and coolant from increasing beyond a set point. Of these four systems, three systems use heat pipes.

Conclusion

The initial interest on thorium fuel cycle was predominantly based on the more abundant thorium reserves which have the potential of extending the fissile material resources as the fertile Th^{232} transforms into fissile U^{233} upon neutron capture. However, this could be achieved only by closing the fuel cycle. The thorium fuel cycle also experienced the difficulties in reprocessing the chemically stable thoria-based ceramic materials and the handling of separated U^{233} due to external radiation hazards associated with the presence of even a small amount of gamma active U^{232} . Therefore, the countries

having the large resources of uranium along with the thorium resources preferred to follow the well established uranium (enriched or natural uranium) fuel cycle in water cooled reactors (e.g. USA and Canada). Only HTGRs found the large scale utilization of thorium fuel cycle. But, this fuel cycle suffered a major set back in eighties due to the closure of FSV reactor in USA and the suspension of HTGRs in Germany. Only the countries like India continued with the programme on thorium fuel utilization due to limited uranium resources compared to vast thorium reserves.

Today, the stockpile of strategic materials (HEU & WPU), proliferation threat and waste management are some of the key issues before the nuclear community and these have made thorium fuel the frontrunner among other fuels including the inert matrix fuel (IMF). The chemical barriers in the back end of the fuel cycle and the radiation hazards associated with the presence of U^{232} in U^{233} along with the inherent advantage of easy detectability of beta-gamma emitting daughter products have made

the thorium fuel cycle an intrinsic proliferation resistant. Thoria is considered to be one of the most suitable matrix materials for efficient plutonium burning. The reduced generation of long lived actinide wastes is another advantage of thorium fuel cycle.

The powder-pellet route is a matured technology for the fabrication of high density oxide and mixed oxide fuel pellets industrially. However, the handling of fine powders and the involvement of large number of process steps make this technology extremely difficult for automation and remotization. In addition, the use of separated fissile material in the fabrication of pellets also poses proliferation threat to a great extent. On the other hand, the sol-gel route (vibro-sol & SGMP) and impregnation technique, though in R&D stage, appear to be most promising particularly for the fabrication of thorium-based fuels because of their process simplicity and amenability to automation and remotization, making them more cost effective. Moreover, non-separation of fissile material from nitrate solution makes these fabrication processes unattractive for any unauthorized diversion, leading to increased resistance to proliferation.

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Molten Salt Reactors Fuel



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Introduction

Historical

In the late forties, the United States initiated programmes for using nuclear reactors for defense applications. At that time the US Navy concentrated on the development of a nuclear reactor powered submarine which could stay under water for long periods of time without the occasional need for resurfacing. This required the development of a reactor which could supply high pressure steam at a few hundred degrees and this was achieved successfully. Nuclear powered submarines are, therefore, extensively deployed today by many nations. The US Air Force, started to think of nuclear energy based long range bombers that could fly for several days without refueling and the development started under the Aircraft Nuclear Propulsion Programme (ANP). This was an entirely different ball game since the nuclear reactor was to reliably heat the turbojet engine gas to more than 593°C, requiring reactor coolant temperature of about ~ 871°C. In order to minimize the requirement of shielding, to protect the crew, the reactor had to be compact with power density in the range of 3-5 kw/cc. Initially a beryllium-oxide moderated, sodium-cooled reactor with solid fuel elements was considered but it was soon realized that with these temperatures, it was difficult to conceive that the

conventional solid fuel element would not get damaged during operation. The concept of fluid fuel reactors was born to overcome this drawback [1].

Under ANP a small 2.5 MW(t) Aircraft Reactor Experiment (ARE) was constructed, with molten NaF-ZrF₄-UF₄ as fuel [2]. This reactor operated successfully in 1954 for 9 days with maximum salt outlet temperature of 860°C at full power [3]. Inconel was used for constructing the reactor vessel as well as piping and BeO blocks served as moderator. A lot of development of on various facets of molten salt reactors was carried out under ANP and a 60 MW reactor, Aircraft Reactor Test, was designed and a number of components fabricated. The Aircraft Nuclear Propulsion Programme was, however, terminated in 1957, as radiation shielding of personnel was posing problems and also the development of ICBM diminished the necessity of having bombers flying for long periods. Some major accomplishments of ANP, beside the reactor itself, include the development of i) corrosion resistant INOR-8 alloy (later known as Hastelloy N), ii) extensive database on physical and chemical properties of molten fluorides and iii) of Fluoride Volatility process for the recovery of uranium from the fuel salt.

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Molten Salt Reactor Concept

Conceptually a Molten Salt Reactor is very simple. It is a solution reactor in which a fissile material salt, dissolved in a suitable molten salt solvent, is contained in a reactor vessel. Hastelloy N (Ni with 16% Mo, 7% Cr, 5% Fe, 0.5% Si, 0.05% C) is the preferred construction material for reactor vessel, pumps, heat exchangers etc. Graphite or beryllium serves as the moderator. The reactor power is controlled by movement of control rods within the molten salt. Heat generated due to fission, heats up the fuel salt which is cooled with a coolant salt by circulating a stream of fuel salt through a heat exchanger outside the reactor. There is no need for the complex fuel element design and there is no clad which can fail. The fuel can be added to the reactor online and very little excess reactivity is required in the core, thus enhancing safety characteristics. The scenario of fuel melt down, a major safety concern in solid fuel reactors is completely absent. There is no build up of volatile fission product element in the reactor, as these can be readily removed during reactor operation. The reactor system is not pressurized since, unlike water cooled/moderated reactors, molten salts do not require pressurization to be in the liquid state, the vapour pressure at 600°C being less than 0.1 mm of Hg. In addition, the fluid fuel reactor has negative temperature coefficient of reactivity which enhances safety of the reactor.

In 1959 a Task Force, set up by the US Atomic Energy Commission (AEC), examined three fluid fuel reactor concept, namely i) aqueous homogeneous reactor, ii) molten metal reactor and iii) molten salt reactor, being developed at that time. The task force recommended that molten salt reactor (MSR) had the highest possibility of attaining technical feasibility. This was the beginning of the Molten Salt Reactor Programme at the Oak Ridge National Laboratory (ORNL) [4].

Salts for Molten Salt Reactors

Solvent Salt

Molten salt suitable for a Molten Salt Reactor MSR must satisfy a number of physical and chemical criteria [5]. The fissile concentration required in a molten salt reactor is only 1-2 per cent and the solvent salt controls the physical as well as the

chemical properties. The prominent requirement for a solvent salt is as follows:

- (i) All elemental constituents must have a low absorption cross section for neutrons having energy spectrum typical of the reactor design.
- (ii) The solubility of the corresponding fissile material salt, at the lowest possible temperature in the fuel salt loop, should be well above that required to operate the reactor.
- (iii) The solubility of fission product salts and higher actinide salts should be adequate so that these do not crystallize out during reactor operation.
- (iv) The constituents of the solvent salt should not react with the container material or the moderator.
- (v) The salt should be stable at temperatures required for producing high temperature steam and preferably have a low vapour pressure.
- (vi) The constituents of the solvent salt must be able to survive the radiation field present in the reactor core.
- (vii) The salt should have a low viscosity and good hydrodynamic characteristics for service as a heat exchanger fluid.
- (viii) The salt should facilitate online reprocessing.

Thermal neutron absorption cross sections (σ_{th}) of some elements are given in Table 1 [5]. On the basis of neutron absorption the possible anions can be nitrates, hydroxides, carbonates, fluorides, borates, silicates, phosphates and sulphates. Among these only fluorides satisfy the necessary criteria listed above. Having selected the anion we look at the possible fluoride salts. Free energies of formation and melting points of some of the salts are given in Table 2 [6]. Fluorides of Mg, Ca, Ba, Sr and Al are ruled out because these fluorides have high melting points. Fluorides of Sn, Pb and Bi are ruled out because they are less stable as compared to the fluorides of Ni, Cr, and Fe which are prominent constituents of alloys used for containing fluoride salts. Beryllium fluoride is low melting but its melt is very viscous and has low solubility for actinide fluorides. Mixtures of salts which make low melting eutectics, therefore, make suitable solvents for molten salt reactors.

TABLE 1. Elements/Isotopes suitable for MSR on the basis of neutron absorption

Isotope/ Element	σ_{th} barns	Isotope / Element	σ_{th} barns	Isotope / Element	σ_{th} barns	Isotope / Element	σ_{th} barns
N-15 N (Natural)	0.000024 1.88	O	0.0002	D H	0.00057 0.33	C	0.0033
F	0.009	Be	0.01	Bi	0.032	Li-7	0.033
B-11	0.05	Mg	0.063	Si	0.13	Pb	0.17
Zr	0.18	P	0.21	Al	0.23	Ca	0.43
Na	0.53	Cl-37 Cl (Natural)	0.56	Sn	0.6	S	0.53

TABLE 2. Free Energy of Formation (ΔG_f) and Melting Points of some fluorides

Compound (solid state)	ΔG_f 1000 K kcal/F atom	Melting Point °C	Compound (solid state)	ΔG_f 1000 K kcal/F atom	Melting Point °C
Solvent Fluorides			Solvent Fluorides (Contd.)		
CaF ₂	-125	1330	PbF ₂	-62	850
LiF	-126	848	BiF ₃	-50	727
BaF ₂	-124	1280			
SrF ₂	-123	1400	Structural metal Fluorides		
MgF ₂	-113	1270	CF ₂	-74	1100
RbF	-112	792	FeF ₂	-665	930
NaF	-112	995	NiF ₂	-58	1330
KF	-109	856	Actinide Fluorides		
BeF ₂	-108	548	ThF ₄	-101	1111
ZrF ₄	-94	903	UF ₄	-95.3	1035
AlF ₃	-90	1404	UF ₃	-100.4	1495
SrF ₂	-62	213	PuF ₃	-1043	1425

Typical examples are binary fluorides mixtures NaF-ZrF₄ (53-47 mole%) and LiF-BeF₂ (65-35 mole%) which can dissolve adequate quantities of UF₄. Detailed studies of phase behavior of fluoride salt mixtures have been reported by Thoma⁶ and Weaver et. al. [7]. Having sodium as one of the main constituents of the diluents salt is not good for the

neutron economy, but NaF systems have better solubility for UF₄ or PuF₃. Aircraft Reactor Experiment employed NaF-ZrF₄ as the solvent for UF₄. LiF containing systems are good but high cross section of natural Li (due to ⁶Li) makes systems containing natural Li not viable. Use of ⁷Li in place of natural Li overcomes this problem, albeit at a

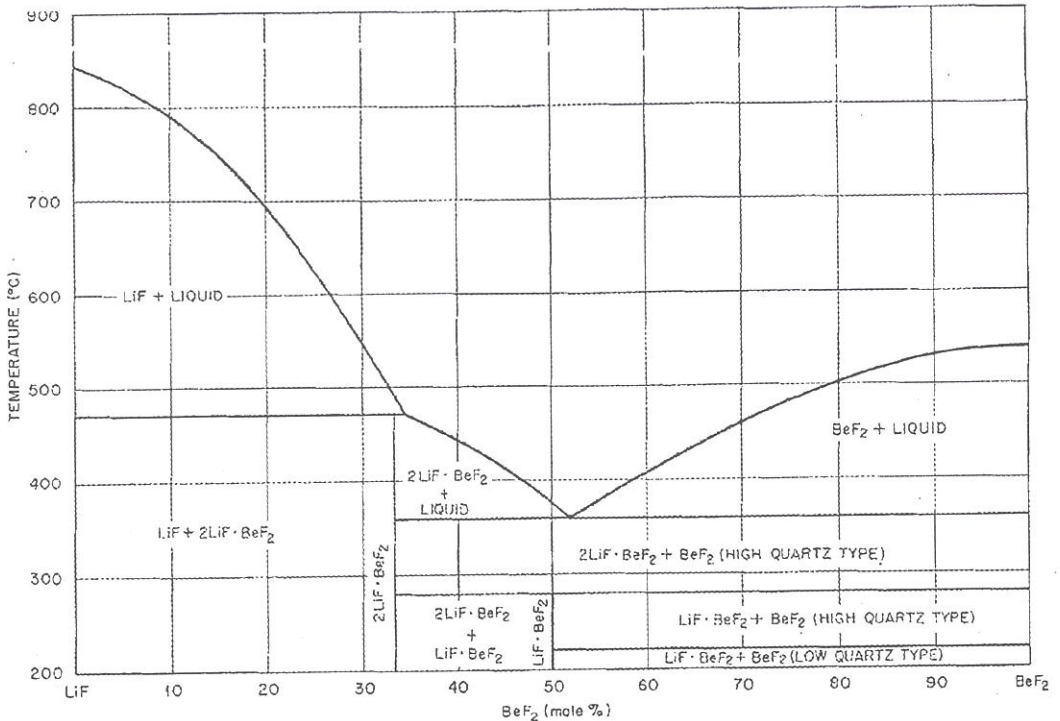


Fig. 1 Phase diagram of LiF-BeF₂ System

substantial cost. All reactor concepts, after ARE/ART are based on ⁷LiF-BeF₂ containing molten salts in view of better neutron economy. Phase diagram of this system is shown in Fig. 1. Mixtures rich in LiF concentration have fairly low viscosity, high thermal conductivity and good heat transfer characteristics. These can, therefore, serve as solvents for uranium fluoride as well as heat exchanger fluid for cooling the fuel salt.

Actinide Fluorides

Thorium Fluoride

Thorium tetrafluoride is the only stable fluoride of thorium. As thorium is a fertile material for the production of ²³³U, addition of thorium to the molten salt is beneficial. Thorium fluoride has high solubility in the fluorides considered suitable as MSR solvents. The LiF-ThF₄ system contains four binary compounds, one of which (3LiF-ThF₄) melts congruently, with two eutectics one at 570°C and 22 mole% ThF₄ and the second at 560°C and 29 mol% ThF₄. The ternary phase diagram of LiF-BeF₂-ThF₄

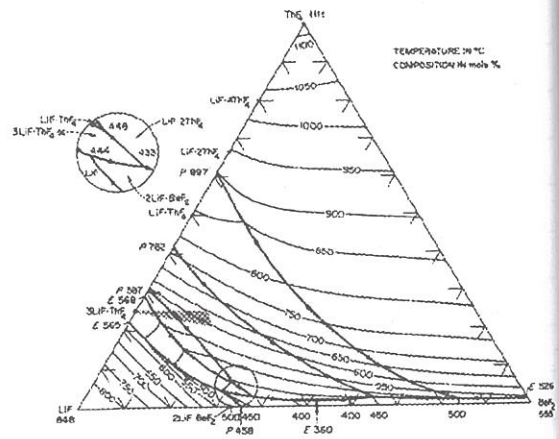


Fig. 2 Phase Diagram of LiF-BeF₂-ThF₄ System

is of relevance to the molten salt reactors and is given in Fig. 2 [7].

It is seen that a large number of ternary salt compositions have fairly low liquidus temperature.

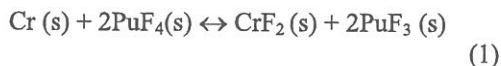
A prominent composition of interest is 72 mol% LiF-16 mol% BeF₂- 12 mol% ThF₄.

Uranium Fluoride

Two fluorides of uranium are stable in the temperature of interest to a molten salt reactor, namely: UF₄ and UF₃. Of these, UF₃ disproportionates to U+UF₄ at temperatures above 1000 K and is, therefore, not considered as fuel material. Also UF₄ has favourable properties both in terms of solubility and phase behaviour. The tetrafluoride of uranium is, therefore, always selected as fuel for MSR's.

Plutonium Fluoride

Three stable fluorides of plutonium are known: PuF₃, PuF₄ and PuF₆ [8]. Since PuF₆ is in gaseous phase at temperatures of interest to molten salt reactors, only PuF₃, and PuF₄, can be considered for use in molten salt fuel mixtures. Plutonium tetrafluoride would exhibit higher solubility than PuF₃, in fluoride solvents, but would not be compatible with Hastelloy-N. The free energy for the reaction of Cr with PuF₄, as given in Eq. 1:



$$\Delta G_f \text{ 1000 K } 0 \quad -688 \text{ kcal} \quad -148 \text{ kcal} \quad -624.9 \text{ kcal}$$

The free energy for this reaction is -84.9 kcal and it can be concluded that PuF₄ would be readily reduced to PuF₃ by chromium. The value of free energy for the reaction of Cr in Hastelloy-N and of PuF₄, PuF₃, and CrF₂ dissolved in the molten fluoride salt is also expected to be negative and reduction of PuF₄ to PuF₃ is expected. Plutonium trifluoride is, therefore, regarded as the only plutonium salt suitable for reactor with molten fluoride salts. The solubility of PuF₃ in molten LiF-BeF₂-ThF₄ has been a concern and this has been studied in detail by Sood et. al [9].

Coolant Salts

All designs for molten salt reactors have fuel and blanket circulation systems that are separated from the working fluid by an intermediate coolant system. Sodium was used as an intermediate coolant for ARE and it was proposed to use Na-K as coolant for ART. These coolants were to be used for heating

the gases of the turbojet engine and did not pose any compatibility problem. However, in the case of a civilian power reactor the salt has to heat steam. If the steam system were coupled directly to the fuel salt system by means of a steam generator, any leaks in the tubes of the steam generator would result in steam or water leaking into the fuel salt. Reactions between water and fuel salt would not be violent, but corrosive hydrogen fluoride would be generated, and uranium oxide would precipitate in the salt. Also, special provisions would have to be included in the design to prevent the fuel circulation system from being raised to the high pressure of the steam system. Molten sodium, helium, and other coolants have been considered for use in the coolant system. Sodium reacts with the fuel salt to generate considerable heat, precipitate uranium, and raise the melting point of the salt. Helium does not react with the salt but must be used at high pressure in order to obtain a good heat transfer coefficient in the primary heat exchanger. At best the heat transfer coefficient with gas is considerably less than that obtainable with sodium or salt and results in an undesirably high inventory of fuel salt and fissionable uranium in the reactor system. Therefore, in MSRE ⁷LiF-BeF₂ (66-34 mole %), was used as the intermediate coolant and provided very good service. The salt also displayed excellent compatibility with Hastelloy-N. However, the need to use enriched ⁷Li makes this coolant very expensive and not viable for a commercial power plant. Further, the melting point of this coolant is 455°C, which puts constraints on the design of the steam generator. A coolant which melts at less than 400°C would be desirable. On the basis of extensive research, eutectic composition of sodium fluoroborate and sodium fluoride {NaBF₄-NaF (92-8 mole %)} was selected as most nearly satisfying all the requirements for a coolant [10]. Pure NaBF₄ could not be selected since it does not exist in the molten state without a very high partial pressure of BF₃ gas. The eutectic composition, however, has most of the properties considered desirable for the MSBR coolant, and it can operate with a small pressure of BF₃. The melting temperature of this salt is 385°C which suits the designers even though a still lower melting point would be desirable. Thermal convection loop studies of the corrosion of Hastelloy N by sodium fluoroborate at temperatures to 607°C have indicated a low corrosion rate in the absence of contamination

of the salt by moisture, although not as low as with the MSRE coolant as with other fluoride salts, the presence of moisture greatly increases the corrosion rate. The absence of severe corrosion problems is confirmed qualitatively by experience with the circulation of sodium fluoroborate in a large test loop for extended periods. A corrosion product precipitate, Na_3CrF_6 , has been obtained from both types of loops. Its solubility is inferred to be sufficiently low that cold trapping may be required to prevent the material from interfering with operation of the coolant system by depositing on heat transfer surfaces and in other cooled regions. Molten sodium fluoroborate has been irradiated in gamma fluxes as high as 8×10^7 r/hr and found without significant effects on the salt or the Hastelloy N container and specimens.

Fuel salts for Various Reactors

Aircraft Reactor Experiment

Aircraft Reactor Experiment used $\text{NaF-ZrF}_4\text{-UF}_4$ fuel which was cooled in a heat exchanger by liquid sodium². Initially, with the sodium circulating, the fuel system was heated to 649°C and the reactor was filled with barren NaF-ZrF_4 melt. In order to make the reactor critical, uranium was added, in discrete quantities, in the form of molten $2\text{NaF}\cdot\text{UF}_4$ to the barren carrier salt. The fuel salt composition at initial criticality was approximately 52.8 mole % NaF, 41 mol % ZrF_4 , and 5.7 mole % UF_4 , and it had a melting point of 532°C. The final mixture had the composition of 53.09 mol% NaF, 40.73 mol% ZrF_4 , and 6.18 mol% UF_4 with a melting point of 538°C. The total amount of ^{235}U added to the system in order to make the reactor critical was 61.2 kg. The molten salt performed its functions without any problem and the reactor temperature could be taken to the required value of ~920°C at full 2.5 MW power. Only serious problem encountered during operation was the volatilization of ZrF_4 (vapour pressure ~30 mmHg at 860°C) which condensed on the cooler portions of the circulating system particularly the pump bowl. This experience led to a reconsideration of the using large mole per cent of ZrF_4 in the solvent salt.

Aircraft Reactor Test

Aircraft Reactor Test of 60 MW capacity was being designed in parallel with ARE operation [11]. Unlike ARE (which was a tubular design), this was a typical molten salt reactor with a spherical inconel vessel. The fuel salt was contained an spherical annulus of about 12.5 cm radial cross section and surrounded on either side by a beryllium reflector-cum-moderator. Adequate moderation of neutrons could be provided in view of the compact design. The proposed fuel was $\text{NaF-ZrF}_4\text{-UF}_4$ (50-46-4 mole%). Sodium and Na-K were to be used as coolants. Total fuel volume was 280 litres with a uranium (93.4% ^{235}U) inventory of 64 kg.

Molten Salt Reactor Experiment

Early in the aircraft development program came the realisation that the molten-salt technology offered many advantages for civilian nuclear power. Consequently a programme to investigate the use of molten fluoride reactors for civilian nuclear power applications started at the Oak Ridge National Laboratory in 1956. Three years later, enough progress had been made in this area. Following the recommendations of the USAEC Task Force on Fluid Fuel reactors, the construction of a 10 MW Molten Salt Reactor Experiment (MSRE) was authorised in 1960. This reactor used many facilities and systems erected for ART.

The reactor was designed for 10 MW(t) capacity but subsequently operated at a maximum power of 7.4 MW (t) because of the limitations of an existing salt to air heat exchanger employed in the system [12]. The solvent salt was $^7\text{LiF-BeF}_2$ instead of NaF-ZrF_4 as it had better neutron economy. Bare graphite, was chosen as the moderator in view of its good compatibility with molten fluorides. Hastelloy N, developed under ANP, was chosen as the material for construction for reactor vessel, piping, heat exchangers etc. The fuel salt was $^7\text{LiF-BeF}_2\text{-ZrF}_4\text{-UF}_4$ (64-30-5-1 mol%). Enriched uranium (33% ^{235}U) was used as fuel. The addition of ZrF_4 to the solvent salt was based on extensive studies on the stability of fluoride melts in presence of oxide impurities like, Cr_2O_3 , NiO, H_2O etc (see section 3.6) [10]. It was observed that these molten fluoride mixtures are not very tolerant to oxide impurities and precipitation of ZrO_2 and UO_2 occurs

when dissolved oxygen exceeds tens of parts per million. Fortunately ZrO_2 was the first oxide to precipitate and uranium oxide did not precipitate as long as ZrF_4 was present in the melt. So addition of ZrF_4 to the solvent salt ensured that any inadvertent leak of air/water into the system does not lead to the precipitation of UO_2 .

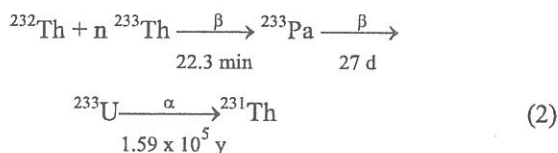
The fuel salt was cooled by a secondary salt ${}^7LiF-BeF_2$ (66-34 mol%) which in turn was cooled by air. The reactor was commissioned in June 1965 and operated successfully up to December 1969. Operation of MSRE gave a wealth of information on all facets of molten salt reactors and its trouble free performance gave an impetus to launch the development of a civilian nuclear power plant.

The MSRE was the first (and probably the only) reactor to operate on all three fissile fuels: ${}^{233}U$, ${}^{235}U$ and ${}^{239}Pu$. During its operation, enriched uranium was completely removed from the salt through fluorination by bubbling gaseous fluorine through the salt. The fluorine caused the uranium tetrafluoride to convert to uranium hexafluoride, which is gaseous, and could then be removed. In 4 days, 218 kg of uranium was separated from the intensely radioactive fission products and its activity was reduced by a billion fold. The reactor was then loaded with ${}^{233}U$ that had been made by early runs of thorium fuel at the Indian Point reactor in New York. When restarted, the MSRE was operating on ${}^{233}U$ and the ${}^{239}Pu$ that remained from the previous operation on 20% enriched uranium. Towards the last stages of operation, PuF_3 was used as the makeup fuel for the reactor.

Two Fluid Molten Salt Reactor

Success of ARE led to enhanced interest in the use of molten salt reactors for civilian nuclear power. One of initial conceptual designs was a 275 MW(e) molten salt reactor [13]. The capacity of 275 MW(e) was chosen based on the size of power plants being installed at that time. The design had some similarities to the design of ART but the reactor relied on the neutron moderation provided by the fuel salt ${}^7LiF-BeF_2-ThF_4-UF_4$ (61.8-36.9-1.0-0.3 mol%). The reason for not considering a moderator at that stage was that metallic beryllium would be too expensive for a large reactor and the behavior of graphite in molten salt mixtures was yet to be

established. The fuel region was surrounded by a blanket $LiF-BeF_2-ThF_4$ (71-16-13 mol%) which provided a thermal shield and breed some ${}^{233}U$. As in ART, sodium was proposed as a coolant. Gradually more information was generated on molten fluoride systems under MSRP. In the late sixties a large emphasis was being given to the development of breeder reactors which would permit the utilization of not only fissile ${}^{235}U$ but also the fertile isotopes ${}^{238}U$ and ${}^{232}Th$ for the production of energy. At that stage the Fast Breeder Reactor concept was in advanced stage of development and research scientists at ORNL were keen to explore the possibility of a thorium based breeder system based on molten salt reactors. The nuclear properties of ${}^{233}U$ and ${}^{232}Th$ are such that a thermal spectrum breeder reactor is a distinct possibility [14]. Further the possibility of online removal of neutron absorbing fission products would enhance breeding potential. The conversion of thorium to ${}^{233}U$ occurs via the following reaction:



After ${}^{232}Th$ absorbs a neutron, it becomes ${}^{233}Th$ and then decays (with a half-life of 22.3 min) to ${}^{233}Pa$, which has a half-life of 27 days and a sizeable thermal neutron cross section. Once formed, ${}^{233}Pa$ should be sequestered from the reactor and allowed to decay to ${}^{233}U$; otherwise it will absorb a neutron and form ${}^{234}Pa$ then ${}^{234}U$, which is not fissile. The fluid fuel nature of the molten salt reactor allows newly formed ${}^{233}Pa$ to be isolated from the fuel (or blanket), allowed to decay to ${}^{233}U$, which can be used as the fuel. This remarkable process is simply not possible in solid-fueled thorium reactors. Solid fuelled reactors rely on low neutron flux to avoid protactinium destruction, which severely penalizes their performance.

One of the first molten salt concepts to be developed for this purpose was the Two Fluid Molten Salt Reactor [15]. In this design the fuel salt containing uranium fluoride, and the blanket salt containing fertile thorium fluoride, were kept separate for easy isolation of ${}^{233}Pa$. In this reactor, energy is mainly produced in the fuel salt in the core

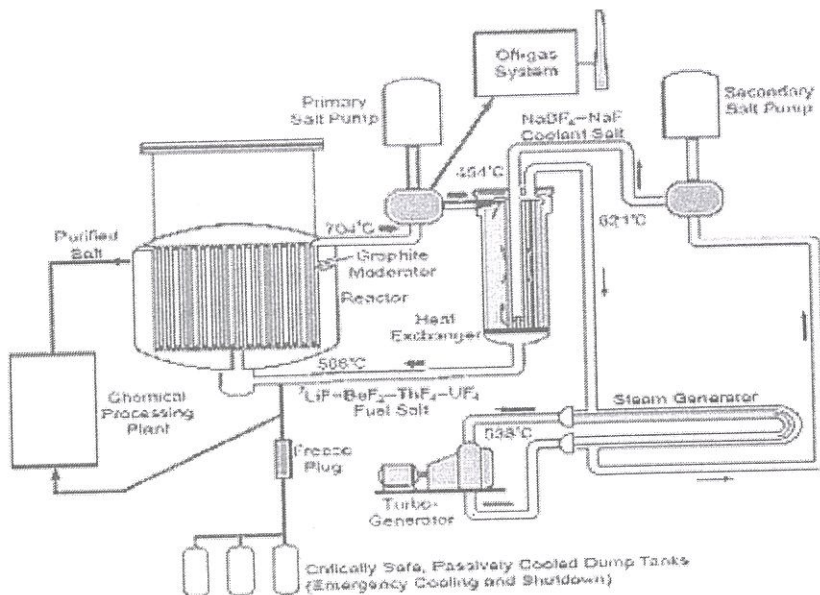


Fig. 3 Schematic of a Single Fluid Molten Salt Reactor

of the reactor and breeding occurs in a separate blanket surrounding the reactor. The fuel salt can thus be processed for the removal of fission products and the blanket salt for the removal of ^{233}Pa and ^{233}U . In the conceptual design of a Two Fluid Molten Salt Breeder Reactor, the core consists of reentry type graphite fuel elements. The fuel salt flows upward through the small passages and downward through the large central passage. The outside diameter of a fuel tube is 3.5 in., and there are 534 of these tubes spaced on a 4.8-in. triangular pitch. The tube assemblies are surrounded by hexagonal blocks of moderator graphite with blanket salt filling the interstices. The nominal core composition is 75% graphite, 18% fuel salt, and 7% blanket salt by volume.

The fuel salt is ${}^7\text{LiF}\text{-BeF}_2\text{-UF}_4$ (63.6-33.2-0.22 mol%). The molten blanket salt has a composition ${}^7\text{LiF}\text{-BeF}_2\text{-ThF}_4$ (71-2-27 mole %). Heat generated in the reactor is transferred from the fuel and blanket salts to a coolant salt $\text{NaBF}_4\text{-NaF}$ (92-8 mol%) in the heat exchangers. The coolant salt is circulated through steam generators and superheated steam so produced drives a conventional turbine generator to produce electricity. The reactor has strong negative temperature coefficient of reactivity as expansion of the fuel salt decreases the amount of fissile material

in the core. Elaborate reactor Control mechanism is, therefore, not required. The weakest link in this reactor concept was the use of graphite tubes for containing the fuel salt. Graphite is known to be dimensionally unstable under large neutron fluence expected in the core of the reactor and this would require frequent replacement of graphite tubes. Fortunately, with important developments in the process chemistry of molten fluorides, it was realised that it may not be necessary to separate fuel and the blanket salt in order to isolate the fission products and ^{233}Pa . This led to the concept of single fluid molten salt breeder reactor.

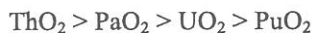
Single Fluid Molten Salt Breeder Reactor

In this concept there is only one salt in the reactor and UF_4 as well as ThF_4 are dissolved in the same salt [16]. The nominal fuel salt composition is $\text{LiF}\text{-BeF}_2\text{-ThF}_4\text{-UF}_4$ (71.7-16.0-12.0-0.3 mol%). The fuel and the blanket regions are obtained by having different fuel salt to graphite ratios in the reactor. The moderator graphite is in the form of rectangular bars with central passages for salt flow. Volume fractions of salt in the central core region and the outer core regions are respectively 0.13 and 0.37. This ratio is obtained by having different diameter of salt passages in the rectangular

moderator bars (e.g. 0.6 in & 2.6 in). NaBF₄-NaF is used as a coolant. Even though graphite is not used as a plumbing material, and the requirements of mechanical stability are much less, irradiation damage to graphite is still a concern and the design envisages a change of graphite moderator elements every four years. A typical schematic of an MSBR is shown in Fig. 3.

Effect of Oxide Impurities

Addition of a reactive oxide (e.g. H₂O) in LiF-BeF₂-UF₄ melts results in the precipitation of UO₂ [17]. If the salt also contains ZrF₄ (as in MSRE salt), and ZrF₄ concentration is significantly higher than that of UO₂, then ZrO₂ (having about 250 ppm UO₂) is precipitated instead of UO₂. Precipitation of UO₂ occurs only when ZrF₄ concentration has dropped to the level of UF₄ concentration. The oxide tolerance of MSBR fuel salt is in the range of 50-100 ppm at 600°C. Among the actinide oxides the solubility in molten fluorides decreases in the following order:



When more than one actinide fluoride is present in the molten salt, the precipitated oxide is a solid solution of the corresponding actinides. This is so since all these oxides have fluorite structure. The composition of the oxide is defined by the relative solubility of the actinides oxides in the molten salt. Pentavalent oxide of protactinium (Pa₂O₅) is very insoluble and precipitation of this oxide from the fluoride melt is one of the methods suggested for the removal of protactinium from the fluoride salt.

Operation of MSRE, from 1965 to 1969, proved that molten fluorides can be contained over extended periods without any inadvertent contamination of the fuel salt with oxide impurities due to leakage of air/water into the reactor. It was, therefore decided to do away with the addition of ZrF₄ as one of the fuel salt constituents for future reactors.

Fission Product Behaviour

Fission of each uranium nucleus in UF₄ releases four atoms of fluorine. The fission fragments generated must sequester these fluorine atoms in order to prevent the corrosion of the reactor

vessel by non-bonded fluorine/fluoride. It has been calculated that the fission products may not be able to tie up all the fluorine/fluoride released by fission. During MSRE operation it was, therefore, decided to maintain slightly reducing conditions in the fuel salt. This was achieved by reducing a small fraction (~1%) of UF₄ to UF₃ with beryllium metal suspended in the

pump bowl. Fission yields in the fission of ²³⁵U of some prominent fission products of importance in the neutron economy of a molten salt reactor are given in Table 3¹⁸. The reactor system is dynamic and, therefore, cumulative yields of members of the same mass chain are also listed above. For example, ¹³⁵I, which has high cumulative yield (6.39%), is continuously produced but as it is short lived it undergoes β⁻ decay to yield ¹³⁵Xe. The molten salt fuel is thus likely to have high concentrations of ¹³⁵I as well as ¹³⁵Xe. The latter would, of course, be readily removed by helium purging. Overall the fission products can be broadly classified into i) chemically inert elements, ii) elements which form stable salts soluble in molten salt, and iii) the so called noble metal elements which do not form very stable fluoride salts in the temperature and chemical environment (UF₄/UF₃ mol ratio ~100) in a molten salt reactor and predominantly exist in metallic state [19].

Chemically Inert Fission Products

Noble gas fission products Kr and Xe belong to this group and account for a sizeable fraction of the fission products. These would not tie up any fluorine/fluoride ions released when uranium in UF₄ undergoes fission. Also, these gases have very low solubility in molten fluorides and can be readily removed by sparging the fuel salt. In fact during the operation of ARE and MSRE it was observed that pumping action, or spraying the molten salt in the pump bowl, leads to the release of these noble gases in the pump bowl. These gases could, therefore, be removed and trapped outside the reactor. As ¹³⁵Xe, the main isotope of xenon in the fission gas, is a strong neutron poison (σ_{th} 2.65x10⁶ barns) its removal improves the neutron economy of the reactor. Also this indicates that molten salt reactors do not have to provide for xenon poisoning over-ride. In an MSBR it is proposed to introduce

TABLE 3. Cumulative Fission Yields in the Fission of ^{235}U

Nuclide	% yield (σ_{th} barns)	Nuclide	% yield (σ_{th} barns)	Nuclide	% yield (σ_{th} barns)
^{85}Br	1.30	^{132}Te	4.27	$^{141+144}\text{Ce}$	11.33
$^{85+85\text{m}}\text{Kr}$	1.59	$^{129+131+133+135}\text{I}$	16.56	^{144}Pr	5.47
^{90}Sr	5.73	$^{131\text{m}+133+133\text{m}+135+135\text{m}}\text{Xe}$	14.65	$^{144+147}\text{Nd}$	7.70
^{95}Nb	6.49	^{137}Cs	6.22	$^{147+149+151}\text{Pm}$	3.70
^{99}Mo	6.13	^{140}Ba	6.31	$^{151+153}\text{Sm}$	0.56
^{99}Tc	6.13	^{140}La	6.315	$^{151+155}\text{Eu}$	0.45
$^{103+106}\text{Ru}$	3.51				

tiny helium bubbles in the salt stream and strip them off for efficient removal of these noble gas fission products gases as well as tritium.

Chemically Reactive Fission Product Elements

Fission products Rb, Cs, Sr, Ba, Rare Earths, Y and Zr readily react with the fluorine/fluoride released after fission to form their stable fluoride salts. These elements tie up most of the fluorine/fluoride. Similarly Br and I react with some reactive fission product metallic elements.

Some of the Kr and Xe isotopes rapidly decay to form Sr, Y, Cs and Ba and accordingly variable amounts of these fission products are found in the gas phase.

Chemically Less Reactive Elements

Fission products Nb, Mo, Tc, Ru and Te have fluorides which are either volatile (NbF_5 , MoF_6 , RuF_5 , TeF_6) or unstable under molten salt reactor conditions. These fission products exist in the molten salt fuel in elemental form. With time, individual metal atoms aggregate in the molten salt to form minute colloidal particles which gradually increase in size. These colloidal particles are not wetted by the molten salt, and tend to collect at gas-liquid interfaces. These can be swept into the gas stream of the helium purge of the pump bowl as fine smoke. They also tend to plate upon the metal

surfaces of the system, and to penetrate the outer layers of the graphite moderator.

Expected Fission Product Behavior Based on MSRE Experience

Extensive samples of gas, molten salt, graphite and Hastelloy were examined during MSRE operation. On the basis of these data prediction have been made regarding the behaviour of fission products as summarised in Table 4 [19].

Table 4. Predicted Behaviour of Fission Products in Molten Salt Reactors (No Chemical Processing)

Lessons from MSRE experience

Sustained operation of MSRE, over a period of five years, has served to demonstrate the following important design features of a single-region molten-salt concept:

1. Molten salt fuel can be safely operated at temperatures of 650 -700°C.
2. The process of fission in the reactor does not lead to decomposition of the salt.
3. Reactor system components like pumps, heat exchangers and instrumentation perform as per design.
4. Remote maintenance of systems and components is possible.

TABLE 4. Predicted Behaviour of Fission Products in Molten Salt Reactors (No Chemical Processing)

Group	Elements	% Distribution in			
		Salt	Metal	Graphite	Off-gas
Noble Gases	Kr, Xe	Low	Negligible	Low	High
Stable Salt Seekers	Sr, Cs, Ba, Zr, Y, La, Ce, Nd, Pm	> 99	Negligible	< 1	Negligible
Stable Salt Seekers (Noble Gas Precursors)	Sr (Kr), Y (Kr), Cs (Xe), Ba (Xe)	Variable	Negligible	Low	Variable
Noble Metals	Nb, Tc, Mo, Ru, Ag, Te	1-20	5-30	5-30	Negligible
Halogens	Br, I	50-75	< 1	< 1	Negligible

5. Noble gas and other volatile fission products can be readily removed from the molten salt.
6. The fissile material can be added on line.
7. The reactor is self regulating and there is good response to changes in demand for power. (This feature will be slightly compromised in the single fluid MSBR).

Overall the performance of MSRE has removed many uncertainties regarding the technical viability of molten salt reactors. One issue, however, was a matter of concern. Tensile testing of Hastelloy N surveillance specimens, which had been exposed to fuel salt in the MSRE, produced cracks in the grain boundaries connecting to the salt-exposed surfaces of the specimens. Surface chemical analyses of the affected grain boundaries indicated the presence of the fission product tellurium. Similarly post irradiation examination of parts of reactor vessel and heat exchanger revealed that the grain boundaries were embrittled to depths of 5 to 10 mils in all Hastelloy N surfaces exposed to the fuel salt and to a lesser extent in material exposed to the vapour above the salt. The embrittled boundaries were opened to form visible cracks only in the heat exchanger [20]. In other parts of the system it was necessary to strain the material to form visible cracks. This intergranular cracking was clearly associated with fission products, and strong circumstantial evidence suggested that tellurium was the cause of the embrittlement. Auger analysis of the specimen revealed about 25 atom% Te, a concentration which

pointed towards the possible formation of brittle Ni_3Te_2 phase at grain boundaries [21].

Two approaches were investigated for overcoming this problem: i) Modify the chemistry of Hastelloy and ii) Modify the chemistry of the molten salt [22, 23].

Modification of Hastelloy N was already in progress at ORNL, as it was observed that the alloy is embrittled at high temperatures due to irradiation. Helium produced due to the nuclear reaction $^{10}B(n,\alpha)$ agglomerated and weakened the alloy. Presence of finely dispersed MC precipitates was expected to tie up helium atoms and prevent their agglomeration. Addition of carbide forming alloying elements was therefore investigated and this eventually led to the development of titanium modified Hastelloy N having the following composition: Ni with 12% Mo, 7% Cr, 2% Ti and 0.05% C. Significant research and industrial experience was generated on this alloy till the problem of Te based embrittlement was discovered. Unfortunately experiments proved that Ti modified alloy behaved like normal Hastelloy N as far as tellurium embrittlement is concerned. Experimental effort for other carbide forming alloying additives was, therefore, accelerated which resulted in the development of Nb modified alloys. Replacement 2% Ti by > 2% Nb was investigated in detail. Capsule tests, natural and forced convection loops as well as irradiation in Oak Ridge Research Reactor

proved that Nb modified Hastelloy is not embrittled either by irradiation or by tellurium.

In parallel, efforts to modify salt chemistry to overcome tellurium embrittlement problem was being studied. The idea was to decrease the activity of metallic tellurium by some means. A suggestion was made that if the molten salt environment is made more reducing (by increase of U(III) fraction in salt) then the following reaction is likely to occur which would decrease the Te activity.



Results of these experiments are summarised in Fig. 4. A cracking parameter was defined as a product of the frequency of cracks per centimetre and the average depth of the cracks in micrometres. It is seen that by having a U(IV) to U(III) mol ratio of about 60, it is possible to substantially decrease the cracking parameter due to tellurium attack. Already a U(IV)/U(III) mole ratio of 100 is recommended for an MSBR to overcome the oxidising effect of the fission process. Decreasing that ratio to 50 (~2% U(III)) is not going to be any problem. Uranium in the salt is not expected to react with graphite till this mol ratio approach 10. Controlling the oxidation potential of the salt coupled with the presence of chromium ions in the salt appears to be an effective means of limiting tellurium embrittlement of Hastelloy. If this is coupled with the use of Nb modified Hastelloy, the issue of tellurium embrittlement can be definitely solved.

Fuel Processing

A number of processes were developed in the Molten Salt Reactor Programme for the removal of impurities, uranium, protactinium and fission products. Before introduction in a reactor, the molten fluoride salts are treated with a gaseous H_2 -HF mixture to remove oxide impurities [24]. In ARE, uranium present in the molten fluoride salt was removed as UF_6 by treatment with fluorine. Similar process was used for the removal of 218 kg of enriched uranium from the MSRE fuel salt when it was decided to switch over to the use of ^{233}U as reactor fuel [12]. The volatilization step accomplishes a good separation from fission products like Cs, Sr, and the rare earths, fair separation from Zr, and-poor separation from Nb

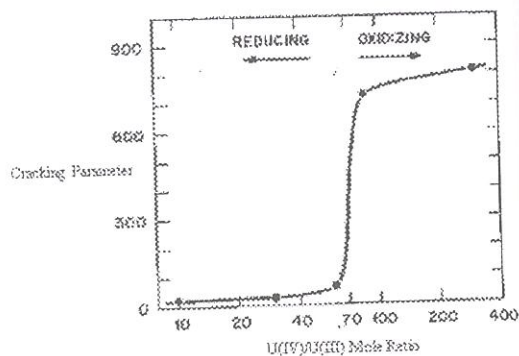


Fig. 4 Cracking behaviour of Hastelloy N exposed for 260 hrs at 700°C to MSBR salt having Cr_3Te_4 and Cr_5Te_6

and Ru. The fission products I, Te, and Mo volatilize completely from the melt. Further decontamination of the UF_6 is effected by selective absorption and desorption on beds of NaF. In MSRE, ^7LiF was one of the salt constituents, which is expensive, and it is essential to recover this salt. A vacuum distillation procedure was established for this purpose and used for recovery of ^7LiF - BeF_2 from MSRE salt [25]. A combination of fluoride volatility and vacuum distillation was one of the procedures recommended for processing of fuel from two fluid molten salt reactor [15].

The conceptual flow sheet for processing Single Fluid Molten Salt Reactor fuel is based on three processes [26]: i) Fluorination of the molten salt to remove >99% uranium as UF_6 which is purified, reduced to UF_4 and returned back to the reactor, ii) reductive extraction of the balance uranium and protactinium into liquid bismuth which is 90% saturated with Th. (Protactinium and uranium can be easily extracted from molten fluorides, whereas thorium is hardly extractable. The bismuth phase containing uranium and protactinium is hydrofluorinated to transfer uranium and protactinium back to the salt phase which is stored for protactinium decay and subsequent recovery of uranium. Bismuth phase is reused for the next step of the process.) and iii) metal transfer process in which rare earths are extracted into bismuth phase under strongly reducing conditions and then transferred to LiCl salt phase. (The process is selective and thorium does not get transferred to the salt phase.

Lithium chloride phase is then treated with Li-Bi to transfer the rare earths into the metal phase). The main constraint of the process is that bismuth is a corrosive metal and would require the use of tungsten or molybdenum equipment for reprocessing. It is possible to operate the reactor without reprocessing, at the cost of breeding. Batch reprocessing every 3-4 years by proven fluorination-cadm-distillation is also a possibility.

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Non Oxide Fuel for Fast Reactor



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Introduction

Currently thermal reactors are the main contributor to nuclear electricity generation in the world. This trend is likely to continue in the first half of 21st century even if the Fast Breeder Reactor is introduced by 2030. The scene may change in the second half of 21st century as the use of fossil fuel may have to be stopped because of green house problem and scarcity of uranium for thermal reactors. The Fast Breeder Reactors (FBRs) are likely to fulfill this gap in future. So the commercialization of FBRs is very important and is a priority job. Metallic-, carbide- and nitride fuel of mixed uranium and plutonium are being developed for FBRs besides more familiar mixed oxide fuel (MOX). The plutonium-bearing mixed oxide fuel having Pu up to 30 % has been used in different fast reactors world wide. Phenix & Super phenix reactors in France, Joyo & Monju reactors in Japan are some of the examples of the reactors which have used MOX fuel. BN-600 reactor in Russia uses enriched uranium oxide fuel. However Pu-bearing fuel is having advantage of higher breeding. In India, Prototype Fast Breeder Reactor (PFBR) is in advanced stage of construction and is expected to start in near future with MOX fuel. The advantage of the oxide fuel is its easy fabricability, good performance in the reactor and a well established reprocessing technology. Hence the early commercialisation is possible with MOX fuel and reprocessing by PUREX process. However the disadvantage of MOX fuel is its low breeding ratio

due to which the doubling time becomes very high (25 years).

The importance of recycling of plutonium has been recognized in the beginning of nuclear power development. The development of fast reactor and associated fuel cycle was started in United States in 1940s, in Soviet Union and United Kingdom in 1950s and in France and Japan in 1960s. During 1950s, it seemed that future breeder and thermal reactors would be operated in complementary way and that good breeding would be indispensable. In 1960s the experiment with high density metal fuel in the form of metallic uranium or combination of U and Pu was tried in the first generation of fast test reactors (EBR-1, EBR-II, and DFR) and first prototype commercial reactor ENRICO FERMI. The small fast reactor BR-5 in USSR was an exception as it was fuelled with PuO₂. Though the metallurgical problems related to fabrication of metallic and alloy fuel were overcome but high swelling problem, low melting temperature, risk of forming eutectic with the clad was a challenge in the continuation of this fuel. Because of these problems, high density non-oxide carbide and nitride fuel appeared to be alternative and promising choice for the fast reactor at that time. Non-oxide ceramic fuels mainly refer to carbide and nitride of uranium and solid-solution of uranium with plutonium fuel. They are also known as high density ceramic fuel or advanced fuel. Thus non-oxide ceramic fuel like mixed monocarbide and mononitride fuels have been identified as advanced fuel, almost four decades ago, because of their high heavy metal

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density, high thermal conductivity, high breeding ratio and in turn, lower doubling time and excellent compatibility with liquid sodium. However the experience on monocarbide and nitride fuel as compared to oxide fuel is very limited. India is the only country in the world which has a Fast Breeder Test Reactor (FBTR) at Kalpakkam using uranium-plutonium mixed carbide as driver fuel, though carbide fuel has been used in the form of experimental fuel pins in some of the reactors in other parts of the world. The quantity of carbide and nitride fuel fabricated so far, all over world, is very much limited. From 1990 onwards, the research and development of carbide and nitride fuel has been nearly stopped in Europe however work on these fuels is continuing in India and Japan. Around the same time work on UN fuel continued in USA as a fast reactor fuel in space shuttle, under space reactor project SP-100 of NASA.

In time to come, an important task of fast reactors will be to incinerate higher actinides. This will remove long lived isotopes of elements like Am, Np, Cm in the waste generated in LWR spent-fuel reprocessing plants to a tolerable limit.

Metallic Fuel

Metallic fuel was the first choice for fast reactors. It has the advantages of high thermal conductivity, higher metal density and higher breeding potential. Its reprocessing by inexpensive electrorefining is relatively simple. The higher coefficient of linear expansion has big advantage from the safety consideration. Because of higher metal density it offers highest breeding ratio and shortest doubling time. Cast δ -phase stabilised plutonium alloy clad in mild steel was used as fuel in the first fast reactor Clementine of Los Alamos National Laboratory, New Mexico in late 1940s. Pu-12.5%Al alloy was used in EBR-I reactor of Argonne National Laboratory, USA and breeding was demonstrated in this reactor. U-Fissium alloy fuel was first used as driver fuel in EBR-II reactor at Idaho National Laboratory in USA. Fissium is an alloy which approximates equilibrium mixture of metallic fission product elements left over by pyrometallurgical recycling designed for EBR-II. It consists of 2.5 wt% Molybdenum, 1.9 wt% Ruthenium, 0.3 wt% Rhodium, 0.2 wt% Palladium,

0.1 wt % Zirconium, and 0.01 wt % Niobium. The first metallic fuel U-5% Fissium alloy which was loaded in the EBR-II reactor had high smear density (85 to 100%) and no plenum to collect fission gas. This fuel failed at very low burn up of 3 ha% because of high swelling of the fuel due to fission product accumulation. Under irradiation the metal fuel behaves like a plastic material and the fission gases directly exert pressure on the cladding if there is no free volume to accommodate the swelling. This was the cause of the failure for high smear density fuel initially loaded in the EBR-II reactor. So this was not chosen as the main line fuel as ability of clad material to withstand high burn up conditions could not be demonstrated. The research programme to improve the performance of the metallic fuel was mainly carried out in USA and to some extent in Russian Federation. The aim was to design for the optimum fuel clad gap so that fuel gets sufficient space for swelling and becomes porous for the fission gases to get out of the fuel by inter connecting porosity. Accordingly fuel pin named Mark-II with smear density of 75% and sufficient plenum space was fabricated and loaded as driver fuel in EBR-II reactor, the composition remaining exactly same. This time the fuel could be operated up to 8 ha%. However because of lack of fabrication experience and some other technical reasons, the tests containing U-20%Pu-10%Zr alloy fuel could start only in year 1985 for the Integrated Fast Reactor (IFR). The addition of the U is done to have fertile material for breeding purpose. However, combination of Pu and U results in lowering of solidus temperature of the alloy and subsequently puts limit on the operating temperature. Addition of Zr upto 10% increases the solidus temperature. The Zr content of more than 10% leads to increase in liquidus temperature which would exceed the softening point of quartz during injection casting, leading to fabrication difficulties. The addition of zirconium also results in better chemical compatibility of fuel and the clad by reducing the inter diffusion of clad and fuel components.

Irradiation testing of U-Pu-Zr alloy has been done in USA in EBR-II whose first driver fuel was U-Fissium alloy. The metallic fuel in the reactor undergoes high swelling and gradually with burn up the gap between clad and fuel closes. The swelling accommodation can be done by introducing central

hole in the fuel rod or by giving enough space between fuel and clad.

Reprocessing of the metallic fuel can be done by PUREX process or by pyrometallurgical method which involves electrorefining. Pu, U, minor actinides and residual fission products get deposited on the cathode. This product on cathode can be used for fuel fabrication. This route of fabrication has its own advantages. As pure fissile material is not freely available, it makes the fuel proliferation-resistant. Because of the recycling of minor actinides the waste decay period to background reduces to 100 years compared to million years otherwise. Development of pyrometallurgical process is continuing in countries like Japan, USA, and Russia etc. India has also started R&D on this process.

Recently metallic fuel has been chosen by India for further development and intensive investigation. Plutonium-bearing fuel is considered to be the best fuel for the fast reactor. India has scanty resources of uranium and hence the sustenance of its fast reactor programme to breed more plutonium and in turn generate more power becomes very important. At present fast reactors have been planned to run on mixed oxide fuel but in the long run the shift towards metallic fuel is desirable. In this regard, developmental work on metallic fuel has been already started. Option is to go for either mechanically bonded binary U-Pu alloy with Zr lining or Na bonded U-Pu-Zr ternary alloy.

Mixed Uranium Plutonium Carbide and Nitride Fuel

The breeding ratio, linear power rating and specific power rating are higher for these fuels compared to oxide fuel. However there are several problems associated with fabrication of (U,Pu)₂C and (U,Pu)₂N fuel. The cost of fabrication is high as number of fabrication steps needed is more. They are pyrophoric in nature and highly susceptible to hydrolysis, hence fabrication of these fuels requires inert gas environment with oxygen and moisture maintained below 25 ppm inside glove-box. Stringent control of carbon stoichiometry has to be done to avoid formation of metallic phase and keep higher carbides within tolerable limit. Carbide fuels are generally fabricated with M₂C₃ content in the range of 5-20% in order to avoid presence of metallic phase during fabrication and to take care of burn up

related metal phase generation. Unlike oxide fuel where O/M ratio increases with burn up, in carbide fuel C/M reduces with burn up and thus there is likely hood of metal phase formation. The presence of metal phase may lead to low temperature eutectic formation with clad constituents causing clad failure. Higher limit of M₂C₃ is kept to avoid clad carburization and to avoid making the fuel more creep resistant.

The nitride fuel has its own advantages as compared to carbide fuel. It is not as pyrophoric and reactive as carbide, hence it does not need ultra high purity inert gas like N₂, Ar or He for handling. The fabrication of single phase mononitride is easier as Plutonium forms only mononitride phase and higher nitride of Uranium like UN₂ and U₂N₃ are unstable and easy to dissociate at higher temperature. A nitride fuel core gives better neutron economy than an oxide fuel core because of harder neutron spectrum. Therefore, a nitride fuelled FBR is more suited for higher conversion/breeding ratio, actinide burning, long core life, or compact core. Nitride has smaller swelling and better gas retaining capacity as compared to carbide. Further PUREX reprocessing process used for oxide fuel can be applied to nitride fuel. Large scale reprocessing of the irradiated carbide and nitride fuels has not been well established. There was less interest for nitride fuel because of difficulties in fabricating dense pellets (>90%) and its slightly lower breeding gain because of N¹⁴(n, p)C¹⁴ reaction. Further, it may be needed to use enriched N¹⁵ in the nitride fuel in order to avoid formation of beta emitting C¹⁴ from N¹⁴ during irradiation thus avoiding environmental problem during reprocessing. The nitride fuel system is currently being investigated in France and Japan. Russians have planned to use nitride fuel in their fast reactor BN-800 with sodium coolant and in BREST-300 with lead coolant.

Helium and Na bonded (material inside the gap between pellet and clad) MC and MN fuel with different cladding materials have been satisfactorily tested for more than 10% ha. Fission gas release is around 30% for this burn up but at higher burn ups (>15% ha) the release probably exceeds 50% but remains always lower than that in oxide. The swelling rate remains high in case of MC and MN fuel because of their closed packed NaCl type of

structure. So these fuels demand enough porosities /pellet-clad gap to accommodate swelling. However this leads to decrease in thermal conductivity and hence Na bonded MC and MN fuel element is better choice for utilizing the full potential of the fuel.

As stated earlier FBTR, Kalpakkam uses Plutonium rich mixed carbide fuel as driver fuel and is operating since 1985. Post irradiation examination of FBTR fuel pins has been done at burnups 25, 50, 100 & 155 GWd/t. The peak power before discharge at these burnups was 320, 320, 400 & 400 W/cm respectively. After 25 & 50 GWd/t burnup it was observed that there was no Fuel clad mechanical interaction (FCMI), negligible wrapper and cladding strain and lower fuel swelling rate. At 100GWd/t burnup it was observed that FCMI has initiated, significant increase in dimension of cladding and wrapper was there but margin was available for wrapper dilation for fuel handling. Sufficient strength and residual ductility was measured in the cladding and wrapper material. After 155 GWd/t it was observed that the gap between pellet and clad has closed throughout the length of the pin. Higher rate of increase in cladding and wrapper dimension has occurred besides substantial decrease in strength and ductility.

Fabrication of Mixed Carbide (MC) and Mixed Nitride (MN) Fuel

Fabrication of MC and MN fuel pellets involves two steps

- Synthesis of Mixed Carbide and Mixed Nitride
- Pelletisation of MC and MN fuel

MC and MN can be synthesized by various methods, some of them are:

- Arc melting of uranium, plutonium and carbon
- Production of metal powder from bulk metal by hydriding and de-hydriding followed by treatment with methane/propane and nitrogen to produce carbide and nitride.
- Carbothermic reduction of oxide powder

The synthesis by carbothermic reduction of metal oxide powder with graphite is preferred over the other two methods. In the first two methods, metal production from oxide is to be carried out first followed by the subsequent steps of carburization for

carbide synthesis. So, this involves extra step besides handling of reactive metal powder.

The classical powder metallurgy route for mixed carbide/mixed nitride fuel pellet production involves milling, pre-compaction, final compaction & high temperature sintering.

Fabrication of Mixed Carbide/Nitride Fuel in India

In India fabrication of carbide is done by carbothermic reduction of metal oxide powder with nuclear grade graphite followed by classical powder metallurgy route of pelletisation and sintering at high temperature. The flow sheet of fabrication of carbide pellet is shown in Fig.1. The fabrication of nitride is done by interaction of carbide with nitrogen at high temperature and the other steps remaining same as that of carbide pellet production.

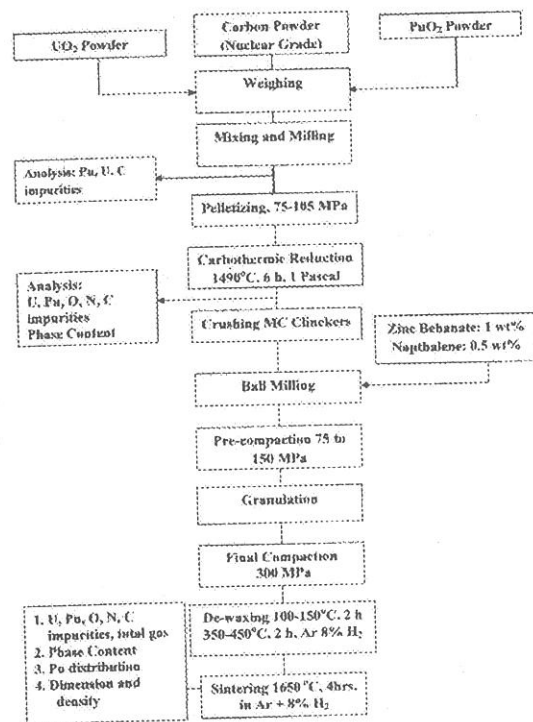
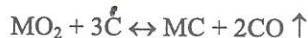


Fig. 1 Flow sheet for fabrication of (U, Pu)C pellet for FBTR

Carbothermic Reduction of Oxide Powder

It is the most convenient route to synthesise carbide. The starting material in the process is UO_2 , PuO_2 and nuclear grade graphite powder. The homogeneously mixed powder is first pelletized and then heated at $1490^\circ C$ in vacuum. The overall reaction followed during the process is as follows:



M stands for mechanical mixture or solid solution of UO_2 and PuO_2

The control of partial pressure of CO is important during carbothermic reduction. Soon it generates, it is taken out of the system in order to enhance the reaction in the forward direction. The formation of carbides is always associated with presence of some amount of oxygen and nitrogen in the MC lattice. The oxygen and nitrogen atoms present in the MC lattice act as C equivalent favoring formation of higher carbides called sesquicarbide (M_2C_3). There can be single step or two step synthesis of mixed carbide depending on the amount of C added in the initial mixture of the powder. In two step method, sesquicarbide is allowed to form first. It is then reduced by H_2 yielding relatively oxygen and nitrogen free MC. However, this requires extra step of reduction and handling of H_2 which is a risky affair due to explosion hazard. So, single step reduction for carbide production is preferred. The carbon is taken slightly less compared to stoichiometric value. The reaction is carried out in vacuum at $1490^\circ C$ for 6 hrs. The UO_2 , PuO_2 and nuclear grade graphite powder is mixed and milled for homogenisation. The mixed powder is pelletized at low pressure of 100 MPa in double compaction hydraulic press to have sufficient handling strength and at the same time enough porosity to expel the reaction gases CO_2 and CO during carbothermic reduction.

Synthesis of MN from Oxide Powder

The starting material for nitride synthesis is UO_2 , PuO_2 and nuclear grade graphite powder. As per stoichiometric calculation UO_2 , PuO_2 is taken. Nuclear grade graphite is taken 10% more than stoichiometric value. The three powders are mixed properly, pelletized at a pressure of 100 MPa and then loaded in furnace for the nitriding process to

high temperature in flowing nitrogen and hydrogen gas. For nitride synthesis, temperature of reaction is maintained around $1550^\circ C$. The formation of MN takes place as per the following reaction:



After the completion of nitriding process the product is cooled in $Ar+H_2$ atmosphere. The product is then analysed for oxygen and carbon impurity. The presence of carbon and oxygen impurity will depend on partial pressure of CO and N_2 during the course of the reaction. After preparation of MC and MN powders, the clinkers are subjected to crushing and milling. The milled powder is mixed with zinc behenate and naphthalene which act as lubricant and binder, respectively. The powder is then subjected to precompaction at 150 to 200 MPa followed by granulation through -30 mesh. The granule thus obtained is compacted to final pellet at 250 to 300 MPa. The green pellet is sintered at $1650^\circ C$ for 4 hrs to achieve requisite density of $90 \pm 1\%$ TD. For MN the sintering is done $Ar + H_2$ atmosphere. Recently few important changes have been brought out in the fabrication steps and relevant equipments to reduce the time of production as well as the man rem consumption. The mixing and milling unit has been changed to attritor from planetary ball mill. The use of liquid lubricant oleic acid instead of zinc behenate has been incorporated to avoid the de-waxing step. This in effect has reduced the total fabrication cycle time considerably.

Reprocessing of Non Oxide Ceramic Fuel

Reprocessing by PUREX Process

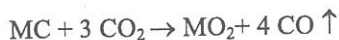
Purex process is well established reprocessing process for oxide fuel. This process has been tried for unirradiated MC and MN fuel in Russian Federation and Europe. Interfering organic complexes are likely to get formed during dissolution of carbide in the nitric acid which requires attention. In India reprocessing of irradiated carbide fuel has been successfully carried out in small scale by PUREX route. This process can be applied for MN fuel without any change. MN gets easily dissolved in HNO_3 solution. Attention has to be paid to trap $C^{14}O$ while reprocessing. This could be avoided using N^{15} instead of N^{14} .

Reprocessing by Pyrometallurgy Route

This route has been tried for reprocessing of metallic fuel in USA. This has been adapted in Russia and Japan for reprocessing of nitride fuel. In Russia reprocessing of unirradiated MN fuel has been done in hot cell under Argon atmosphere. This is done by electrochemical method. The electrolyte used is 42-45 % KCl, 42-45% LiCl, 10-16% UCl₄ at 550-620°C. Uranium and Plutonium get deposited on basic cathode while mixture of Plutonium and actinides deposit on additional cathode. Fission products such as Zr, Mo, Tl, Tc noble metals and transmutation isotope C¹⁴ remain in anodic section as insoluble particles. Alkaline and rare earth metals and also Cs, Sr are dissolved in electrolyte. The metal product on cathode is melted and used for nitride synthesis after composition correction.

Gaseous Oxidation Process

This process refers to use of oxidation of carbide and nitride by gaseous means so that after the product converts to oxide, the PUREX process can be applied for reprocessing. Issue of inorganic complex formation during carbide reprocessing can be addressed by controlled oxidation of carbide to oxide. The product in turn can be easily processed by standard PUREX route. The oxidation of carbide can be done in controlled way by using CO₂.



CO/CO₂ ratio and temperature are the important parameters to control this reaction.

Summary

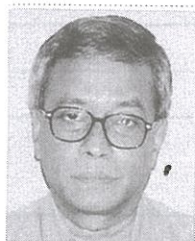
Monocarbide and Mononitride fuel for fast reactor has been studied in different parts of the world. The experience on mononitride fuel is less as compared to the monocarbide fuel. India is the only country in the world which uses mixed carbide fuel as driver fuel in FBTR at Kalpakkam. The fabrication of carbide and nitride fuel involves more steps as compared to oxide fuel fabrication. The carbide fuel fabrication essentially requires glove-box with high purity inert gas to avoid hydrolysis and to tackle pyrophoric nature of the powder. During fabrication, stoichiometry control

of carbon is important to avoid formation of sesquicarbide. Stringent control of oxygen and nitrogen in product is required to keep them within the specified limit. In India reprocessing of carbide on lab scale has been carried out successfully. This however needs to be demonstrated on industrial scale to close the fuel cycle. Nitride fuel can be reprocessed by PUREX process but the important issue is trapping the C¹⁴ produced during irradiation of N¹⁴. In Russia technological development in this regard is in advanced stage as nitride fuel is supposed to be the driver fuel for BREST-300 reactor.

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Metallic Fuel for Fast Reactor



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History

The first fuel which was used as a fuel for fast reactor was metal fuel, primarily because of its superior nuclear and thermal properties over other types of ceramic fuel e.g. oxide, carbide, and nitride fuel. Metal fuel has higher thermal conductivity and higher fissile atom density. However, this fuel could not be burn to its rated capacity because of high swelling rate during irradiation. A suitable cladding material for high temperature application was also not available at that time. As a result, no serious effort was put forward for development of metal fuelled fast reactor. Moreover, the reactor technology for use of oxide fuel was well established both in terms of its performance, commercialization of fuel fabrication process and its high burn-up potential. In the late 1970's [1] series of events cause reassessment of fast reactor technology which includes the liquid metal cooled reactor (also known as sodium cooled fast reactor) and its associated fuel cycle. One of the important event which was of serious concern was the threat of proliferation of nuclear material from the reprocessing plant for civilian reactor fuel which lead to cancellation of all reprocessing activities of the burnt fuel received from civilian reactors. In the year 1983, the Integral Fast Reactor (IFR) concept emerges at Argonne, USA which ensured safe and economic operation of nuclear reactor, solving most of the institutional problems and efforts to develop this concept continued to meet world energy demand. At the same time, it was also realized that the world

uranium reserve was limited and non-fissile. U^{238} should be used as an energy source in the centuries to come. In a nutshell, the primary or principal fuel in the reactor should be plutonium and it will simultaneously breed U^{238} to produce 'Plutonium for subsequent use as a fuel in the reactor.

Another aspect which made metal fuel option more attractive compare to other fuels was the recycling of the fuel into the reactor using a novel technique which has several advantages. The electrorefining technology was used for reprocessing the fuel when the products at the cathode contains 'Pu', 'U' and minor actinides along with residual fission products. After removal of the bulk of fission products the fuel is relatively pure for its satisfactory use in the reactor at the same time the presence of residual, fission products makes the fuel highly radioactive requiring recycling and re-fabrication steps to be carried out in hot cell. This ensures that the fuel material becomes proliferation resistance and needs further purification by PUREX process to separate 'Pu' from 'U' and other fission products.

The recycling of the fuel allows all minor actinides to remain in the fuel cycle to be fabricated as fuel and undergo fission for generation of useful energy. This essentially means that the high level waste will decay to background in 100 years instead of tens or thousands. However, although technical and institutional issues were presumed to have been

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TABLE 1. Properties of Uranium Plutonium mixed oxide, carbide, nitride, and ceramic fuels

Properties	(U _{0.8} Pu _{0.2})O ₂	(U _{0.8} Pu _{0.2})C	(U _{0.8} Pu _{0.2})N	U-19Pu-10Zr
Theoretical density(g/cc)	11.04	13.58	14.32	15.73
Melting point (K)	3083	2750	3070	1400
Thermal conductivity (W/m.K at)				40
1000 K	2.6	18.8	15.8	
2000 K	2.4	21.2	20.1	
Structure	Fluorite	NaCl	NaCl	$\alpha + \delta + \zeta$
Breeding ratio	1.1	1.2 – 1.3	1.2 - 1.3	1.5
Swelling	Moderate	High	High	High
Handling atmosphere	Air	Inert gas	Inert gas	Inert gas
Compatibility with – Clad Coolant	Average Average	Carburization Good	Good Good	Eutectics Good

solved by adapting the IFR concept it necessitated large scale demonstration to accept it fully on commercial scale. As a result, extensive research work on this fuel system was perused which includes all aspects of metallic fuel cycle during 1980 to 1992. Number of fast pin irradiation programme was planned using both U-Zr and U-Pu-Zr fuels in the USA. The details of the metal fast irradiation performance database are given in literature [2]. About 30,000 Mark-II (U-Fs) driver fuel rods, 13,000 Mark-III/IIIA/IV (U-10Zr alloy) and 600-U-Pu-Zr fuel rods were irradiated from 1964 to 1994.

Indian Scenario

India is a fast developing nation and is expected to acquire the status of a developed nation in near future. The energy demand is quite high and approximated to be 1000GW/e in terms of installed capacity in the year 2050 [3]. This can partly be met using nuclear energy from thermal or fast reactors. The thermal reactor can generate only limited amount because of limited 'U' reserve. This can, however, be achieved by effective use of limited resources of 'U' by employing FBRs. Hence development of fast reactor and their utilization for breeding of U²³³ from thorium blanket and later using it in thermal fast breeder reactors from the second and third stages of nuclear power programme

of India. Also closing the fuel cycle is also an essential requirement for the growth of nuclear power at a faster pace. The prototype fast breeder reactor (PFBR) will use mixed oxide fuel with 21% and 28% PuO₂ as the driver fuel with rated power generation capacity of 500 MW(e). However, the future fast breeder reactors (FBRs) will utilize metallic fuel because of its high breeding potential and better safety features as a result it has been decided that the first four FBRs will use mixed oxide fuel and subsequently will utilize metallic fuel. The properties of Uranium Plutonium mixed oxide carbide and nitride and metallic fuels are given in Table 1. It is evident from this table that except for some issues like high swelling rate, lower solidus temperature and fuel-clad chemical interaction metal fuel is the based option as fast reactor fuels. The issues of metal fuel could be taken care by proper choice of fuel design and specification.

Once the potential of metal fuel was understood extensive research and development work were carried out to generate database on properties of metal fuel and structural material (cladding) and to optimize fuel design parameters so that the fuel could safely reach its target burn up of 20at%. A schematic diagram of a sodium bonded metallic fuel pin is shown in Fig.1. The first metallic fuel used are U-5%Fs (Fs: Fissium; an alloy of 2.5

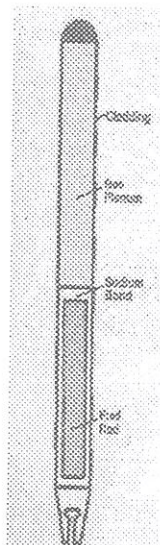


Fig. 1 Schematic diagram of sodium bonded metal fuel [Ref.5]

wt% Mo, 1.9 wt% Ru, 0.3 wt% Rh, 0.2 wt% Pa, 0.1 wt% Zr and 0.1 wt% Nb) alloy were of high smear density (85 to 100%) and failed at low burn-up because of the absence of plenum space in the fuel pin and no gap between fuel and clad. In subsequent days all the issues have been reviewed and status report prepared and published in countries like USA, Korea et.al. Some of the important references are listed [4-8].

The fuel compositions normally used are U-Pu-Zr ternary alloy where 'Pu' content varies from 15-19% and Zr 6-22%. A ternary alloy of U-19Pu-10Zr has been widely used all over the world. The issues of metal fuel as indicated in Table 1 is its low solidus temperature, high swelling rate and it is susceptible to chemical interaction with the components of cladding materials which are normally iron based alloys like austenitic stainless steel of the type SS316, D9 (Titania modified stainless steel), Ferritic Martensitic steels of the type HT9 (12Cr1Mo) or T91 (9Cr 1Mo) and ODS (Oxide dispersive stainless steel). These issues could however be overcome by choosing suitable alloy additions like V, Nb, Mo, Zr etc. [8]. These elements have been used either as an alloying element in the fuel slug or as a coating on the fuel [8]. Out of all these elements, 'Zr' was found to be the most

suitable and most of the work on metal fuel was carried out with U-Pu-Zr or U-Zr alloy. The role of Zr is as follows:

- It increases the solidus temperature
- It helps in overcoming the fuel clad chemical interaction
- Linear heat rating (LHR) of the fuel could be increased
- It stabilizes and enlarges the isotopic game phase

With this type of fuel composition the smear density of the fuel was 70%. The smear density is defined as the effective density of the fuel within the cladding. It is defined as a planar density calculated by dividing the mass of fuel (including any non-gaseous fission products) in a unit length of pin by the theoretical mass of a unit length of void less fuel of the same composition, with diameter equal to the inside diameter of the cladding [7]. Low smear density can be achieved by using highly porous fuel or a large gap between the fuel slug and cladding. Smear density increases as burn-up proceeds because each heavy metal atom that fission becomes two atoms of a less dense material.

'Zr' is a non-fissile material and its presence in the fuel slug apparently is undesirable as it also occupies fissile inventory space within the fuel core and results in some penalty on the breeding ratio. However its presence in some form is essential in order to address some of the issues of metal fuel. A new concept of a fuel design emerged where the proposed fuel will be a binary U-Pu (Pu<15%) [9] and 'Zr' will be used as a barrier layer (150 μm) which act as a shielding between the fuel and cladding; this reducing the fuel clad chemical interaction. The smear density of the fuel could vary between 80% and 75% depending upon the residence time of the fuel in the reactor or burn-up. The conceptual design of the cross-section of the proposed design of the metal fuel with and without Zr barrier is shown Fig. 2.

Fig. 2(a) shows the conventional sodium bonded pin where 'Na' acts as a thermal bond between the fuel (U-Pu-Zr) and cladding material. Fig. 2(b) shows the cross-section of a metal fuel pin with 'Zr' as a barrier layer between fuel and clad. This design could also be termed as mechanically or

metal bonded fuel design. The semi-circular groove of radius 100 μm placed diametrically opposite as the space for accommodating fuel swelling. For higher target burn-up the smear density should further be lowered down to 75% and the empty space should be provided in four grooves placed diametrically opposite. Helium gas is filled in the groove region.

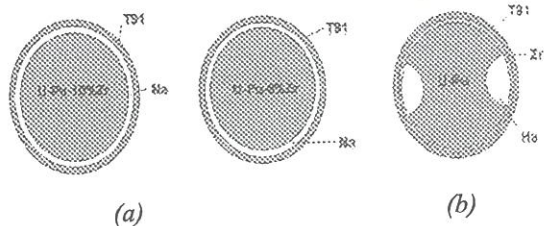


Fig. 2 Cross sections of the reference/proposed fuel pin design for U-Pu-Zr ternary and U-Pu binary metallic fuels for fast reactor [Ref. 9]

In this later concept, the binary U-Pu (<15%) fuel material is very soft at the operating temperature so that the swelling of the fuel could be accommodated in this groove region. Swelling is maximum within the first 2-3 at% burn-up. The 'Zr' bonded fuel without any 'Zr' in the fuel slug has higher breeding ratio compare to U-Pu-Zr fuel. Table 2 presents the comparative properties of U-Pu-Zr ternary, U-Pu binary fuel. From this table it is quite evident that except for the lower solidus temperature a binary U-Pu alloy has better properties than that of ternary U-Pu-Zr alloy.

'Zr' bonded fuel has the following advantage over the Na bonded fuel.

- Efficient heat transfer due to high contact conductance which reduces the risk of fuel melting and axial relocation,
- fission gas column could be located at the colder bottom of the fuel pin resulting in shorter pin length, more space for fuel/axial blanket
- No problem of highly contaminated (α , β , γ) sodium to be handled in reprocessing of the burnt fuel and waste management

TABLE 2. Properties of the U-Pu binary and U-Pu-Zr ternary metal fuels

Parameters	Ternary	Binary
Typical composition	U - 20%Pu - 10%Zr	U-15%Pu (Max.)
Density as cast (g/cc)	15.64	18.80
Recommended smear density	70%	85%
Effective fuel density (g/cc)	10.95	15.98
'Pu' loading (g/cc)	2.2	2.4
'U' loading (g/cc)	7.7	13.6
Phases present 600°C	U(α) + ζ + δ (MZr ₂)	U(α)
600-700°C	ζ + γ	β (U-Pu)
>700°C	γ	γ (U-Pu)
Thermal expansion ($^{\circ}\text{C}$) (20-500°C)	17.3×10^{-6}	18.8×10^{-6}
Solidus (s) / Liquidus (l)	1130°C (s)/ 1290°C (l)	977°C(s)/ 1022°C (l)
Thermal conductivity (W/m.K) (600-800°C)	20.4 - 25.4	29.4 - 34.6
Hardness at RT (Hv; kg/mm ²)	417 (Quenched at 500°C)	160 - 210

- Safer and simpler fuel fabrication and fuel cycle economics

Out-of-Pile Properties

The out of pile properties of metal fuel have been measured by Harbur et. al. [10]

Density

The density of U-15%Pu-10%Zr is about 15.64 g/cc. For binary U-Pu alloy (Pu<15%) density is slightly higher (18.80 g/cc) which contributes to higher fissile atom density.

Solidus Temperature

The solidus temperature for U-19Pu-10Zr alloy is greater than 1100°C. The solidus temperature could be expressed by the following relation:

$$T_{\text{solidus}} : A_0 + A_1 \cdot X_{\text{Zr}} + A_2 \cdot X_{\text{Zr}}^2 + A_3 \cdot X_{\text{Zr}}^3$$

where : $A_0 = 1408 - 1187 \cdot X_{\text{Pu}} + 967 \cdot X_{\text{Pu}}^2$
 $A_1 = 572 - 732 \cdot X_{\text{Pu}} + 4960 \cdot X_{\text{Pu}}^2$
 $A_2 = 740 + 3305 \cdot X_{\text{Pu}} - 29182 \cdot X_{\text{Pu}}^2$
 $A_3 = -624 - 3139 \cdot X_{\text{Pu}} + 36120 \cdot X_{\text{Pu}}^2$

Thermal Expansion

The mean thermal expansion for an alloy of composition U-20%Pu-1.3%Zr shows 0.4% elongation and the same for U-15%Pu-10Zr, the average co-efficient of thermal expansion was $16.3 \pm 0.4 \times 10^{-6}$ [$20^\circ\text{C} < T < 600^\circ\text{C}$] and the same for 20%Pu is $17.3 \pm 0.4 \times 10^{-6}$ [$20^\circ\text{C} < T < 550^\circ\text{C}$]. For U-15 Pu binary thermal expansion coefficient is 18.8×10^{-6} [$20-500^\circ\text{C}$]

Thermal Conductivity

Thermal conductivity of U-Zr system has been systematically measured by laser flash method by Takahashi et.al. [11] with varying Zirconium content [14at% - 91at%]. Thermal conductivity of U-Pu-Zr could be expressed by the following relation:

$$k = 16.309 + 0.027 \cdot T - 46.28 \cdot X_{\text{Zr}} + 22.98 \cdot (X_{\text{Zr}})^2 - 53.55 \cdot X_{\text{Pu}}$$

where X_{Zr} and X_{Pu} are the mole fraction of Zr and Pu respectively. This equation is valid for $X_{\text{Zr}} < 0.72$, $X_{\text{Pu}} < 0.16$ and temperature $< 1173\text{K}$. It is observed

from this equation that with increase in 'Zr' content thermal conductivity decreases. For U-Pu binary alloy thermal conductivity is higher than that of U-Pu-Zr as indicated in Table 3. The most recent thermal conductivity data is that of Byoung et.al. [8].

$$k_o = 17.5 \left[\frac{1 - 2.23 Wz}{1 + 1.61 Wz} \right] - 2.62 Wp$$

$$+ 1.54 \times 10^{-2} \left[\frac{1 + 0.061 Wz}{1 + 1.61 Wz} + 0.9 Wp \right] T$$

$$+ 9.38 \times 10^{-6} [1.27 Wp \cdot T^2]$$

where T is in °K, Wz and Wp are the weight fraction of Zr and Pu.

Hardness

Hardness of the fuel both at room temperature and higher temperature is an indication of the yield properties and creep of fuel. The fuel clad mechanical interaction (FCMI) is a very trivial issue for the metallic fuel because of high swelling rate. A soft fuel at ambient or high temperature is desirable to minimize FCMI. Hot hardness of U-15%Pu-6.8 wt% Zr and that of U-10%Zr alloy, Zr, T91 are shown in Fig. 3.

Tensile Properties

The tensile properties of U-Pu-Zr alloys with varying 'Zr' content are given in Table 3 and the time to attain 2% strain is given in Table 4. The room temperature tensile strength of the extruded material is at a minimum of 57,000 psi for U-15wt%Pu-6

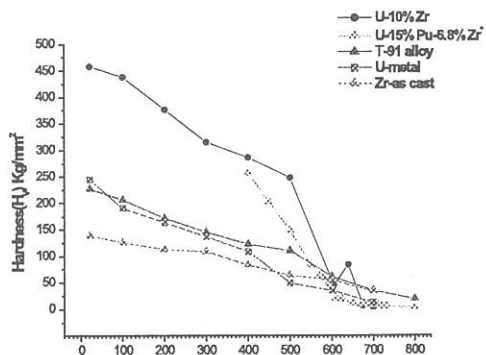


Fig. 3 Hot hardness data of U base alloys and Zr and T91 [ref.9]

TABLE 3. Tensile properties of U-Pu-Zr alloys^a

Alloy Composition Nominal wt. %			Temp °C	UTS psi	Y.S. ^b psi	Elongation %	Fabrication History	E psi x 10 ⁴
U	Pu	Zr						
75	15	10	25	70,000	-	NIL	As-extruded	2.2
			300	39,000	-	NIL	As-extruded	2.1
			350	44,000	44,000	3	As-extruded	0.9
			400	14,000	10,000	53	As-extruded	0.4
73.3	14	11.7	25	78,060	-	NIL	As-extruded	2.3
			100	80,000	-	NIL	As-extruded	1.2
72.5	15	12.5	25	95,700	-	NIL	As-extruded	1.7
			300	64,300	-	NIL	As-extruded	2.6
			350	55,700	55,000	NIL	As-extruded	2.5
			450	8,340	6,800	31	As-extruded	0.4
			525	6,740	4,100	62.5	As-extruded	0.5
71.5	15	13.5	25	84,000	-	NIL	As-extruded	1.0
79	15	8	25	97,000	-	NIL	As-extruded	2.5
72.5	15	12.3	25	61,000	-	NIL	As cast	1.4

^a Tensile test performed at a strain rate of 0.015 in./in./min..

^b Yield strength at 0.2% offset

wt%Zr which decreases to 70,000 psi for U-15%Pu-13.5%Zr. Maximum tensile strength for U-15%Pu-12.3wt% Zr in the as cast condition was 61,000 psi. U-Pu-Zr alloy behaves like a brittle material at ambient temperature. U-15%Pu-10%Zr shows some ductility at 350°C and is quite plastic at 400°C with a tensile elongation of 53%. U-15%Pu-6%Zr is quite plastic at 290°C with an elongation 11% during a short term creep test at 5660 psi. Short term creep data is given in Table 4.

Fabrication of Metallic Fuel

There are three methods of fabrication of metallic fuels [4]:

- Injection casting
- Centrifugal casting

- Continuous casting

Injection casting

In this method the feed stock is taken in a yttria coated graphite crucible which is melted in a high frequency powered pressure/vacuum induction furnace at around 1500°C. In order to minimize the volatilization loss of different species and proper mixing, 'Pu' having low melting point is kept at the bottom of the crucible followed by Zirconium and then Uranium. The lower melting U flows over higher melting Zr and also prevents volatilization loss of lowest melting species. The crucible is wrapped in Zirconia felt to insulate the heating coil. The coil is made of solid high purity and high conductivity copper. The furnace is evacuated before each injecting casting, followed by lowering

TABLE 4. Time to attain 2% strain in U-Pu-Zr alloys in the as-extruded condition

Alloy Composition Nominal wt. %			Stress psi	Time to attain 2% strain at temperature (min)			
U	Pu	Zr		290°C	350°C	400°C	500°C
75	15	10	2,000	-	-	-	20
"	"	"	3,000	-	-	-	5
"	"	"	8,000	-	-	30	failed
"	"	"	10,000	-	-	9	failed
"	"	"	11,000	-	-	3	failed
"	"	"	20,000	-	300	failed	failed
"	"	"	30,000	-	20	failed	failed
"	"	"	40,000	-	9	failed	failed
72.5	15	12.5	2,000	-	-	-	8
"	"	"	3,000	-	-	-	4
"	"	"	16,000	-	-	15	failed
"	"	"	17,000	-	-	8	failed
"	"	"	19,000	-	-	4	failed
79	15	6	1,000	-	-	-	0.3
"	"	"	5,000	30	failed	failed	failed
"	"	"	6,000	9	failed	failed	failed

of molds below the surface of the melt. After the mold is heated the chamber is pressurized with high purity Argon gas which causes the molten metal to rise through the tube. The dimension of the mold should be so chosen that after solidification the fuel slug assume the size of the fuel slug. Normal Quartz or Vycor is used as the mold which however needs to be broken to take out the mold at the same time the mold cannot be reused. Hence, this process is not very cost efficient and it produces lot of active waste (broken quest mold).

Centrifugal Casting

This method could be potentially used for fabrication of fuel slug of dimension suitable for commercial fast reactor minimizing the volatilization issues. This process is however

complicated and time consuming. The number of steps and the type of manipulation to assemble and disassemble the furnace and the mold are significant which causes low production rate per machine compared to other fabrication processes. This process was used to fabricate fuel slug of composition U-2%Zr for EBR-I which was lower than that of EBR-II (9.8mm ~ 3.3mm). This method is suitable for fabricating rod type fuel element with a surface to volume ratio of 26:1 and length to diameter of 59:1 composed of U-2%Zr alloy. The mold material is brass, copper, silver which gives smooth surface finish.

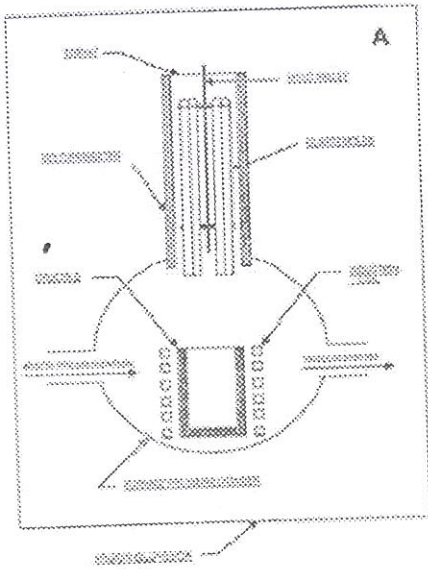


Fig. 4 Schematic diagram of the metal fuel fabrication facility [Ref. 6]

Continuous Casting

It is an advanced fabrication technique and the unique feature of this method is that it does not use a mold and the fuel slug produced is expected to have uniform properties because the solidification front (liquid/solid interface) is in quasi-steady state compare to the other two methods. It also produces very smooth and uniform surface with tolerance in rod diameter of ± 0.06 mm.

However continuous casting method has some issues like cooling rate. This is more so when casting fuel with minor actinides where there is a wide temperature difference between the solidus and liquidus temperature thereby increasing the freezing range e.g. for U-19Pu-10Zr the liquidus is at 1300°C while the solidus is 1080°C i.e. This may cause micro-shrinkage effects and loss of process control during the casting procedure. This method also needs lot of automation in order to produce fuel slugs in a commercial core without any human interaction e.g. pulling of the solid rod needs careful handling in order to avoid assembly in the length and uniformity in the diameter. Schematic diagram of the most commonly used injection casting method are given

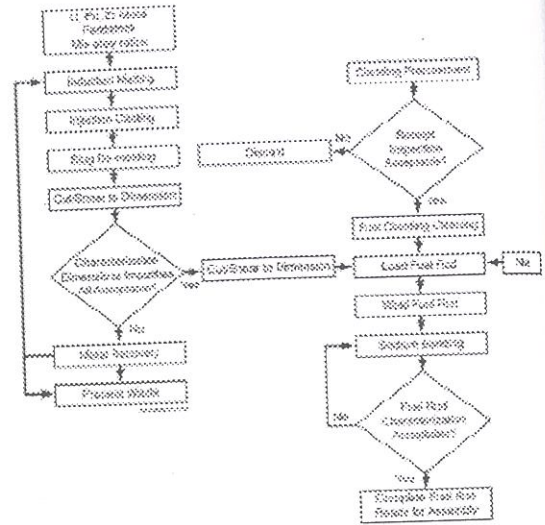


Fig. 5 Fabrication flow sheet for metal fuel fabrication [Ref. 6]

in Fig. 4 and the flow sheet for fabrication is given in Fig. 5.

Metal Fuel Performance

Steady state irradiation performance with metal fuel has demonstrated satisfactory performance and reliability of a plutonium fueled fast spectrum demonstrating burn up capability up to 20 at% under normal operating condition with modified stainless steel or ferritic martensitic type stronger steel e.g. HT9 or T91 as cladding material. The main irradiation experience of metal fuel was obtained in USA on U-Zr, U-Pu-Zr alloy evolved in Argonne national laboratory. Total no. of fuel rods which was irradiated so far is $\sim 135,000$. The details are given in Ref. [2].

The role of Zirconium as already indicated earlier was to enhance the solidus temperature of the fuel preventing centre melting at the same time zirconium gets redistributed across the cross section of the fuel. [Fig. 5] making the centre and the periphery rich in Zirconium. The enriched zirconium layer at the periphery of the fuel prevents the fuel to interact with the cladding. The Uranium distribution takes the opposite contour meaning it gets enriched where there is Zr depletion and gets

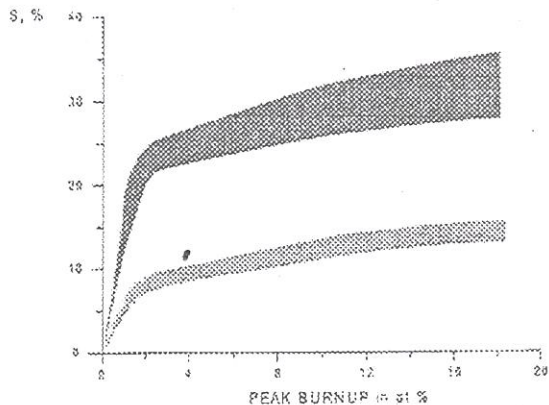


Fig. 6 Swelling behavior of U-19Pu-10Zr (light grey area) and U-10Zr and U-8Pu-10Zr fuels (dark grey area) as a function of burn up

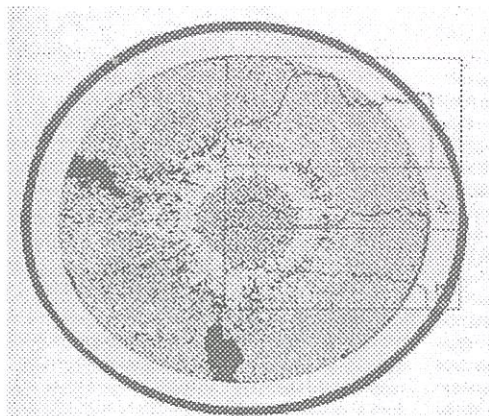


Fig. 7 Redistribution of Zr, U and Pu across the cross section of U-19Pu-10Zr alloy fuel after 3at% burn up [Ref.13]

depleted where there is Zr enrichment. It may be seen in the figure that there is no such distribution of the other species plutonium.

The zirconium concentration in the ternary fuel is limited to 10% which appears to be optimum amount. A lower percentage of Zirconium i.e. 2-6% Zr in the fuel has been reported to enhance the irradiation induced swelling. On the higher side Zirconium content has never been more than 20% because the liquidus temperature of the alloy will be higher making it difficult or impossible to use quartz mold for injection casting method which may exceed the softening point of quartz. It has been found that with every 1 wt% addition of Zr the solidus temperature increase by 13°C.

Metal fuel has been operative in fast reactors like EBR I, EBR II, Fermi and DFR where the smear density was 85% to 100%. For such a high smear density there was little or no gap between the fuel slug and the cladding material. The fuel failed within a burn up 3 at% because of severe fuel clad mechanical interaction stresses due to high swelling of the fuel. In the later designs of the metallic fuel pin the smear density was decreased to 70% which enabled the fuel pin to accommodate the very high swelling in the first few at% burn up [Fig. 6] and these pins reach a burn up of as high as 19 at%.

In the first stage of irradiation, fuel undergoes free swelling till the gap between the fuel slug and cladding is closed. Subsequent swelling which is also known as restrained swelling depends on how strong is the clad. If the cladding is not very strong it accommodates further swelling by deformation in the radial direction, e.g. the cladding made of austenitic steel swells up to 8% whereas as stronger clad like HT9 or T91 which are ferritic- martensitic type swells only 1% after about 18at% burn-up.

The reason for 'Zr' redistribution across the fuel pin is the temperature gradient from the fuel centre to the periphery and the stability of different phases (α , β , γ , etc) for U-Zr or U-Pu-Zr depends on the temperature following their respective phase diagram. 'Zr' solubility in these phases is different.

As seen in Fig. 7, 'Zr' and 'U' get redistributed but 'Pu' redistribution is not there. However pressure of 'Pu' enhances the diffusion rate. Enriched 'Zr' layer at the periphery of the fuel slug near to the cladding inner surface decreases the interaction of the fuel with the components of the cladding. The sodium bond between the fuel and clad is displaced upward when the fuel clad gap is closed after a few atom present burn-up. As a result of swelling the fuel it becomes porous and thermal conductivity of the fuel decreases, so that there is rise in fuel centre temperature by 20-70°C. However once the porosity generated within the fuel due to

swelling gets interconnected the gas is released and moves upward through liquid sodium. As a result there is some ingress of sodium into the fuel and there is gradual reversion of central temperature to the original value. This phenomenon is however not there in case of mechanically bonded fuel pin.

Fuel cladding interaction could be of two type namely fuel-clad mechanical interaction (FCMI) and fuel-cladding chemical interaction (FCCI). Fuel-clad mechanical interaction results from the swelling of the fuel. Swelling is due to generation of fission gases or fission products by irradiation. In order to reduce the fuel clad mechanical interaction sufficient space should be provided in the form of fuel-clad gap for the initial part of the swelling (upto 3at% burn-up) and the plenum space for accommodation of the fission gases. A plenum to fuel ratio of more than 1 and a smear density of about 70% is preferred. Based on this parameter a burn-up of more than 15at% could be achieved.

Fuel clad chemical interaction is also one of the major issues limiting the life of a metal fuel pin because of the formation of low melting eutectics of the type $UFe_2 - U_6Fe$. The eutectic temperature varies between $700-725^{\circ}C$ and this temperature puts a limitation on the maximum linear heat generation rate of the fuel pin so that the fuel-clad interface temperature never exceeds this temperature. 'Zr' plays very important role in retarding the fuel-clad chemical interaction. The 'Zr' rich layer formed near the fuel periphery gets stabilized with 'O', 'N'. This layer is formed more readily in austenitic stainless steel having high 'N' solubility compare to other types of alloys. 'Fe' and 'Ni' form austenitic steel and 'Fe' for ferritic/martensitic steel diffuses into this layer and forms two distinct phases. One of the phases contains 'U' and 'Pu' in it. Finally further diffusion of 'U' and 'Pu' leads to the formation of U_6Fe and UFe_2 on the cladding side of the 'Zr' layer. Fig.8 shows a typical microstructure of the presence of different compounds in the reaction layer. In the case of a mechanically bonded fuel pin there is no need of 'Zr' redistribution and the 'Zr' barrier layer ($\sim 150 \mu m$) act as a thermal bond as well as diffusion barriers right from the start of irradiation. Several studies of estimation of eutectic temperatures by Differential Scanning calorimeter and by diffusion couple test could be obtained in Ref. 12 and 13.

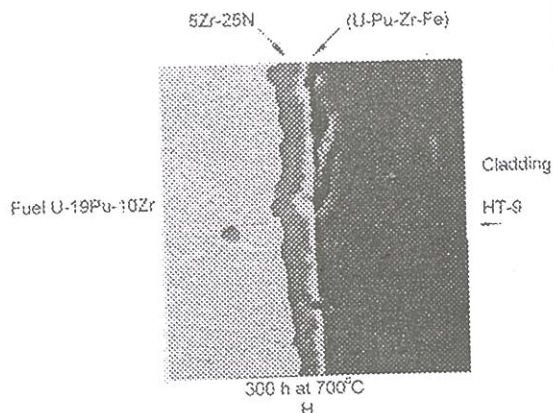


Fig. 8 Reaction layer formed at the fuel cladding interface [Ref.13]

One more key fuel performance issue arises due to the redistribution of U, Pu, Zr. The 'Zr' depleted zone formed between the fuel centre and periphery has lower solidus temperature and the fuel in no case should reach this temperature during overpower or transient condition. Moreover the fuel cladding inter diffusion is also increased by the presence of lanthanide fission product present in the fuel with increasing amount with burn-up. This could lead to the formation of lower melting temperature composition of the fuel. The detail of the metal fuel performance could be obtained in Ref. 2.

Reprocessing of Metal Fuel

Metal fuel could be reprocessed either by PUREX process or by pyrometallurgical process also known as electro refining method. For metal fuel, pyrometallurgical reprocessing of fuel is more advantageous compare to PUREX process. In the electro refining methods contains Uranium, Plutonium and minor actinides along with residual fission products. The fission product can be separated and the fuel along with minor actinides can be used for producing useful power. The major advantage of this process is that no diversion of fissionable element is possible because the fuel is highly radioactive and makes the process proliferation resistant for use of material for nuclear weapons. In the cathode the fissile material is in the form of alloy which is also radioactive. Also the

process is a batch operation and can be scaled up to the meet local requirement. Other advantages of this process is that it is economic compare to other reprocessing options, it allows all minor actinides to remain in the fuel cycle which could be reused as fuel, thus reducing the active waste.

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Fuel For High Temperature Reactors



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Introduction

For India, high temperature reactors development programme is significant mainly for non-electric applications. The requirement for high temperature reactors has originated because of a need to develop alternate energy carrier to substitute fossil fuel based transport fuel. It is well known that hydrogen production by splitting water are highly energy intensive, whether by electrolysis or by thermo-chemical process. In general, efficiencies for these hydrogen-producing processes are higher at higher temperatures. Thermo-chemical processes have been reported to have higher efficiencies (40-57%) as compared to electrolysis based processes, but need process heat at temperatures greater than 823 K [1], depending on the thermo-chemical process selected. High temperature nuclear reactors capable of supplying process heat have a large potential for sustainably supplying energy for these hydrogen production processes at required high temperature conditions.

Current design of Fuel Elements for High Temperature Reactors

World-wide High Temperature Gas-cooled Reactors (HTGRs) use two types of fuel elements, Spherical fuel elements and block (pellet/pin/ fuel compact) type fuel elements containing TRISO (TRI-iSOtropic) coated particles [2]. For spherical fuel elements, mainly used in pebble bed reactors, TRISO particles are mixed with graphite matrix in the form of powder and a binder and is then formed into a sphere of about 50 mm diameter. This sphere is then again coated with a graphite layer of 5 mm thickness so as to give an overall diameter of 60 mm. This type of spherical fuel elements (with varying dimensions) is being used by Federal Republic of Germany, Russian federation and China for their HTGR programmes. In case of a compact type fuel element, TRISO particles are mixed with graphite matrix powder and phenol binder and then heat treated to give a shape in the form of fuel compacts. These fuel compacts then can sit in the fuel bores made in moderator blocks or fuel sleeves. Typical dimensions used for fuel compacts are $\phi 12$ mm x 49 mm length by USA and annular compact used in Japan has inner ϕ 10 mm and outer ϕ 26 mm with 39

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mm length. In USA, a typical fuel compact contains two types of TRISO coated particles, one having $U^{235}CO$ (Uranium oxy-carbide) as fissile fuel and other uses natural UCO as fertile fuel. Thus for modern high temperature reactors TRISO fuel particles are the building blocks and basic component for all fuel elements.

A typical configuration of a present generation TRISO fuel particle has a $UO_2/UC_2/UCO$ kernel (spheres of the order of 0.5-mm dia). These kernels are coated with thin layers of pyrolytic carbon (pyrocarbon) and silicon carbide, which serve as tiny pressure vessels to contain fission products and fuel. The kernel initially is surrounded by a buffer layer of low density pyrocarbon. This is followed by subsequent layers of a high density pyrocarbon, SiC, and finally again a layer of high density pyrocarbon. These layers are collectively referred as TRISO coating. The coating system can be viewed as a miniature multi-shell pressure vessel that provides containment of radio nuclides and gases. This coating system is also an excellent engineered barrier for long-term retention of radionuclides in a repository environment. Fuel element design used by different countries is shown in Table 1.

A philosophy of all modern HTRs is to design the plant such that the radio nuclides would be essentially retained in the core during normal operation and postulated accidents. The key to achieving this safety goal is the reliance on ceramic-coated fuel particles for primary fission product containment at their source, along with passive cooling to assure that the integrity of the coated particles is maintained even if the normal cooling systems were permanently disrupted. Consequently, these designs mandate the development and qualification of coated particle fuels that meet stringent requirements for as manufactured quality and in-service coating integrity even for beyond design-basis accidents.

Though being the result of an intense optimisation process, the basic design of the HTR fuel elements has not been changed during the last 20 years. However, the development of coated fuel particles has experienced major changes. The Germans successfully produced and demonstrated high performance TRISO-coated fuel for their pebble-bed High Temperature Reactor (HTR)

designs in the 1980s. In 1980, the low enriched uranium cycle (LEU) was chosen in Germany for all future HTR projects instead of the previously followed high enriched thorium/uranium cycle (HEU). This decision, together with more stringent requirements for the fission product retention at elevated temperatures, led to the introduction of the TRISO-particle type where a SiC layer is sandwiched between two pyrocarbon coatings in preference to the formerly used pure pyrocarbon layers (BISO-particle type). The functional requirements of these layers have been briefly mentioned in the following paragraphs;

- (a) Low density pyrocarbon buffer layer: This porous layer acts as an absorber of fission recoils and in combination with any porosity in the kernel gives volume to accommodate fission products and kernel swelling. It also gives a mechanical separation between the kernel and the structural layers of the coating.
- (b) Inner high density pyrocarbon layer: This acts as the first structural layer. It minimizes the effects of fast neutron irradiation such as dimensional changes and provides strength to particle. This also serves as a barrier to gross diffusion of kernel material (actinides or fission products) which may affect the integrity of subsequent silicon carbide layer by corroding it. During reactor operation due to irradiation it shrinks thereby applying a compressive stress on SiC layer, thereby reduces the tensile stress on SiC layer.
- (c) Silicon carbide interlayer: This acts as a better diffusion barrier to metallic fission products than pyrocarbon. This also contains gaseous fission products released by the kernel and thus acts like a pressure vessel. It also plays an important role in the mechanical performance of the particle and because of its stability under fast neutron irradiation this layer imparts dimensional stability to the whole particle. Integrity of this layer plays a major role in maintaining integrity of whole particle. Tensile stress is introduced into the coatings due to the pressure of fission gases and CO gas as burnup proceeds. The inner and outer PyC layers undergo irradiation induced shrinkage as a result of fast neutron exposures. Consequently,

TABLE 1. Details of TRISO fuel being used in different countries [2]

Details of fuels	FRG	USA		Japan	Russia	China
		Fissile	Fertile			
Uranium enrichment fuel type	10.6% Enriched UO ₂ kernel	19.9% Enriched UCO kernel	Natural UCO kernel	6% Enriched UO ₂ kernel	8% Enriched UO ₂ kernel	17% Enriched UO ₂ kernel
Kernel, Diameter (µm)	500	350	500	600	500	501
PyC Buffer Thickness (µm)	95	100	65	60	90-100	92
Inner PyC thickness (µm)	40	35	40	30	70-80	39
SiC layer thickness (µm)	35	35	35	25-35	60	36
Outer PyC thickness (µm)	40	40	40	45	60	34
Design limit FIMA	8-10 %	26%		3.6%	10-15%	9.6%
Fast neutron fluence	2-3 x 10 ²⁵ m ⁻²	4.5 x 10 ²⁵ m ⁻²		-	2-3 x 10 ²⁵ m ⁻²	1.0 x 10 ²⁵ m ⁻²
Energy	>16 fJ	>29 fJ			>29 fJ	
Test FIMA	15 %					
Test neutron fluence	8 x 10 ²⁵ m ⁻²					
Particles protective overcoating	200 µm thick A3 graphite matrix			200 µm thick A3 graphite matrix		
Fuel Element type	60 mm Graphite sphere containing 11000 TRISO particles. The outer 5 mm is A3 matrix graphite shell. 0.5 g fissile and 6.5 g fertile content. 10% volumetric packing fraction	Hexagonal graphite block 793 mm long and 360 mm across flats having 210 fuel holes which contain 12 mm dia x 49 mm long fuel compacts and sealed. The fuel compacts are a mixture of TRISO coated fissile and fertile particles and graphite shim particles bonded by a carbonaceous matrix. 51% volumetric packing fraction	Hexagonal graphite block 580 mm long and 360 mm across flats having 31 fuel holes which contain fuel pin made of 26 mm o dia x 10 mm idia 39 mm long fuel compacts. The fuel compacts are made of 13500 TRISO coated particles bonded by a carbonaceous matrix. 30% volumetric packing fraction	60 mm Graphite sphere containing 13000- 16000 TRISO particles. The outer 5 mm is 30PG MPG-6 graphite shell. 12-15% volumetric packing fraction	60 mm Graphite sphere containing 8300 TRISO particles. The outer 5 mm is chinese graphite shell. 5 g U content. 4 % volumetric packing fraction	
Design limits for temperature C	1250	700-1250		1495	1400	1000

the outer PyC layer places a compressive load on the SiC layer, which counteracts the SiC tensile stress due to internal pressure. Inner PyC layer also acts to reduce the SiC tensile stress by tending to contract while bonded to inner SiC surface. The SiC layer fails by internal gas pressure at high burn-up irradiation condition. If inner PyC layer has failed then SiC layer can also fail by fission products corrosion.

- (d) Outer high density pyrocarbon layer: This also acts as a structural layer which improves mechanical performance by putting the silicon carbide into compression at an early stage of operation. Additionally it provides chemical protection for the silicon carbide layer and prevents its corrosion from external environment. This layer fails by tensile stress only. When the SiC layer is intact the failure of this layer usually does not occur.

Design issues for HTR Fuel

The design of fuel for HTR essentially involves the design of TRISO coated particle fuel and design of fuel compacts or spherical fuel elements. The basic design methodology is to minimise the failure fraction of fuel particles during normal operating conditions and anticipated operational occurrences by limiting the various performance parameters like stresses, peak temperatures, swelling etc. The different fuel failure mechanisms, which affect the coating integrity, have been identified. Cracking or complete damage to silicon carbide layer results in loss of mechanical strength and provides a leakage path for fission product. Some of the limiting phenomena that are unique to coated particle fuel type design are kernel migration, internal pressure due to fission gas and CO, fission product interaction and diffusion through the coatings. The coated particles need to be designed and qualified for these failure mechanisms. The design evaluations include both the analytical and the experimental evaluations. Following are some of the factors that affect the design of coated fuel particles.

Size effect of HTR Fuel Particle

The peculiarity of the coated particle fuel is the small size and spherical shape. For a fast-neutron fluence of 5.5×10^{25} n/m² at an irradiation

temperature of 1125 K, failures were observed to be about twice as high in larger 1300 μ m particle than in smaller 1050 μ m particle (16 vs 8%) in irradiation tests [3] at High-Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL). The failure rate of outer coatings on TRISO particle (caused by irradiation-induced shrinkage of coatings), increases as the particle size increases for a given neutron fluence and irradiation temperature. Decreasing the size of the particle below certain threshold poses difficulties during manufacturing especially coating processes. The conclusion that the irradiation performance of coated particles is size dependent is reinforced by the fact that zero failures were seen for regular 850 μ m fueled particles in the same irradiation test. It may not be desirable to increase the TRISO particle diameter much beyond 850 microns.

Kernel Properties

The fuel kernel, small spherical particles with a diameter of a few hundred micrometers, contains the nuclear fuel and its composition controls the basic chemistry of the particle environment. The size, shape and density of kernel also have an impact on particle behavior. The fact that kernels are in between powder and compact materials complicates the investigations. Many traditional methods of physico-mechanical and strength property investigation, such as micro hardness measurements, bending strength, etc., are not applicable to kernels due to their small size and spherical shape.

Coating Layers

The fuel kernel is surrounded by a low density, porous pyrocarbon layer called buffer layer. The thickness of buffer layer, generally the thickest layer, is limited by pressure and heat transfer. The buffer layer is not required for particle strength, but it must be able to hold the kernel away from the inner high-density pyrocarbon layer. The coatings may be thought of as pressure vessels, which are required to withstand the pressures exerted by fission product gases and expanding fuel. Because of their small size and spherical shape, the cladding can contain high pressures. Coatings have been developed which maintain their integrity during long periods of operation at high temperatures while under intense

irradiation by neutrons and fission fragments. The coating layers around the fuel kernels form the main retention barrier for fission products. Additional barriers are provided by the relatively stable lattice of the fuel kernels and by the transport and sorption characteristics of the graphitic structure.

For the inner high density Pyrocarbon layer (IPyC), there are six material and physical properties of interest to the designer of coated fuel particles; Density, Permeability, Anisotropy, Creep, Shrinkage and Strength. The stresses in the pyrocarbon are controlled primarily by the dimensional changes and creep induced by fast-neutron irradiation. The designer has to balance irradiation stability and coating contamination. The situation could be better or worst by the chlorine reactivity of the kernel.

The SiC layer is the primary fission product barrier and strength member in the coated particle fuel. For design purposes, the strength of the SiC is important as well as the strength distribution. In addition, SiC density, grain size and grain orientation as well as the trace amounts of free silicon in the layer are thought to be important. However, conclusive evidence connecting these properties to particle irradiation performance is lacking. The designer has to keep the SiC layer in compression during most of the irradiation and also has to limit the operating and accident temperatures to control SiC layer corrosion/decomposition.

The outer high density pyrocarbon layer (OPyC) is the final layer on the coated particle and is the layer that binds the particle to the fuel form. Many of the performance factors associated with the OPyC are similar to those of the IPyC, especially irradiation stability, but there are differences. The OPyC protects the SiC during fuel particle handling prior to fuel element fabrication and compresses the SiC during irradiation. It acts as a final barrier to gaseous fission product release. The properties of interest to the OPyC are similar to those of the IPyC with the exception of permeation, which is important to matrix bonding rather than chlorine transport to the kernel.

Temperature Limit

The limitation of the fuel temperature of the HTR was conservatively determined to ensure fuel integrity at elevated temperatures. The transition temperature of α -SiC (as-deposited) to β -SiC varies from 1600-2200°C. Thus, maximum fuel temperature shall not exceed 1600°C at any anticipated transient to avoid fuel failure, i.e., to permit reutilization of the fuel after anticipated transients [4]. Because of weakening of the SiC (i.e., lowering of its mechanical strength) when subjected to fast neutron irradiation at temperatures above 1000°C, the effect of burnup is sensitive to the fuel temperature history during irradiation. With increasing fuel temperature, this effect becomes even more pronounced due to deterioration of the SiC layer, which shifts the failure probability curves to higher value.

SiC Layer Thickness

SiC layer thickness should be thicker than a minimum threshold value to avoid as-fabricated SiC-failure during the compaction process. The thickness should be adequate enough to provide integrity to the fuel, in spite of suffering degradation mechanisms such as corrosion for the period of its residence in reactor core.

Packing Fraction

The packing fraction of the coated fuel particles is an important parameter that determines in part the nuclear and thermal power properties of the fuel element. The fuel packing fraction, along with the particle design and fuel enrichment, determines the fissile material density in the reactor core. The packing fraction is defined as the ratio of the volume of the fuel particles to the sum of the fuel particle volume and the matrix material volume after compaction. The packing fraction of fuel particles within a fuel compact or pebble is an important factor for performance of the fuel during normal operation [5]. At low packing fraction, the particles touching during the pressing stage dominate the particle failure rate, but with relatively mild consequences for the failure impact. A higher packing fraction allows a higher fissile material density for a given particle design and fuel

enrichment. Particle damage during manufacture is more likely at higher packing fractions.

Some of the fuel manufacturers use one more layer by resinated graphite powder i.e. over coating. The aim of the over coating is to avoid direct contact of neighboring particles, protect the particle during fuel compact fabrication integrating the particles into the matrix. Additional enrichment may be required to accommodate the required amount of the fuel material when the coated fuel particles are over coated.

Fabrication

Fabrication of the coated particle fuel involves making kernel, coating the kernels with PyC and SiC layers and then making the fuel compacts or the pebbles. The development of fabrication technology of coated particle fuel covers essentially the equipment development and the performance of experiments to develop the process for the fuel kernel preparation and the coating process in order to understand the effects of the process parameters as well as equipment details.

Kernel Fabrication

UO₂ kernels are produced using a sol-gel method known as the Gel Supported Precipitation (GSP) process or also called the external gelation. U₃O₈ powder is dissolved in nitric acid to form a uranyl nitrate solution. A casting solution is prepared by adding specific amounts of organic additives to the pre-neutralized uranyl nitrate solution. Casting is carried out in a glass column filled with the concentrated ammonium hydroxide precipitation solution. The casting solution is pneumatically fed to the nozzles at the top of the column, where a vibrator "shakes off" droplets from the feed stream. The droplets fall through air where they attain a spherical shape as a result of surface tension. The spherical droplets then pass through an ammonia atmosphere where ammonia gas is blown directly onto the droplets to create chemical reaction with the uranyl nitrate on the surface of the droplets. The uranyl nitrate precipitates as ADU in the outer layer of the droplet, forming a protective film. As the reaction continues in the casting column, ADU forms throughout the kernels with ammonium nitrate formed as a by-product. The kernels are kept

in the casting column until they are strong enough to be processed further. The diameter of a cast gel kernel is about 1.8 mm. Once casting is complete, the ageing process fully converts the gel spheres to ADU kernels, and initiates the crystal growth in the kernels. After ageing the solution, ADU kernels are washed with water, and then with alcohol. The final step is drying of kernels at 80°C under vacuum to obtain the dried ADU kernels with diameter of ~1mm and bulk density of ~1g/cc. Following the drying process, the ADU kernels are calcined in air above 400°C in a batch furnace. After calcining follows the reduction and sintering at high temperature to reduce the UO₃ to UO₂, remove remaining impurities and densify the kernels, under 100% hydrogen. The reduction of the kernels takes place between 450°C and 650°C, where after the temperature is increased to 1600°C in order to form dense, stoichiometric UO₂ kernels that have a diameter of 500 μm and density just below the theoretical value of 10.96 g/cc. The final production steps are sieving to remove any under and over sized kernels, followed by sorting to remove any odd-shaped particles.

Coatings [1, 6, 7]

Coatings on mixed-oxide, fertile and fissile kernels fulfilling are deposited by vapour in fluidized beds. The fuel kernels, produced using a sol-gel method, are coated in a vertical Chemical Vapour Decomposition (CVD) sprouted / fluidised-bed furnace by pyrolytic decomposition of hydrocarbon gas or silane (Methyl TriChloro Silane, CH₃SiCl₃ abbreviated as MTS). Various process parameters like temperature, volume of the bed, flow rates of gases, composition of the gases, contact time etc. play a major role in controlling the properties of the coatings. Mathematical models have been developed world wide for initial process parameter selection for getting required properties of coats.

The density of the layer depends on the gas concentration principally and on the deposition temperature. For the IPyC and OPyC, high-density isotropic layers, the temperature is the controlling coating parameter. The silicon carbide coating is made at about 1600°C by decomposition of a MTS flow carried in an H₂ flow. SiC is the key component of the coatings, the quality of SiC is vital to the

performance of TRISO coated particle in service. The investigation of the effect of deposition temperature on the density, surface morphology, fracture surface structure, strength and Young's modulus was carried out. The deposition temperature has a remarkable effect on the properties and so strict temperature control is necessary to secure the quality of TRISO particle. Deposition temperature should be kept in the range 1500 to 1550°C. Mechanical shocks due to violent fluidisation can cause particle failures. Once-through process development (continuous coating process) is found to be effective to reduce SiC defective fraction failures.

Fuel Compact

A typical fuel compact comprises a homogeneous packed bed of TRISO coated fuel particle held together by a carbonaceous binder. The last stage of fuel fabrication is manufacturing of the fuel compact. This step involves dispersing homogeneously required number of TRISO particles in a graphite matrix powder and binder material; and then subjecting them to various stages of compaction and heat treatment. Heat treatment temperatures are directly linked with dimensional changes of compacts, final physical properties, structure & density of graphite matrix. Heat treatment is performed under different atmospheres. Graphite matrix has to fulfill essential criteria in the fuel element such as high radiochemical purity, dimensional stability, chemical and mechanical barrier between particles, good conductivity and good strength [8].

Development of Characterization Techniques

Development and qualification of fuel elements for HTR are governed, at all stages, by the general performance requirements like optimal fission product retention capability, high mechanical strength of integral fuel element, high corrosion resistance, sufficient dimensional stability and efficient heat transfer characteristics. The integrity of the coated particle during irradiation is key to the successful deployment of high temperature reactor technology. The characterization of the coating layers in coated particle fuel is specifically unique not only in dimensional aspect but also in characteristics. However, smaller dimensions of a

spherical form would require a greater precision for their measurement. Also a statistical distribution of parameters needs development of accurate characterization methods to supply products meeting the specifications and to provide data for fuel performance & fission product models. The use of ^{233}U fuel may also require remote handling, shielding and may increase complexities. The experience is limited and the methods are newer which require validation. Since quality control of kernels and coated particles has to be performed on large quantities of small entities, elaborate sampling plans and statistical evaluation methods have to be used. Present day QA/QC methods, done manually and in many cases destructively, cannot economically test a statistically significant fraction of the large number of the individual fuel particles required. Fully automated inspection technologies with emphasis on non-destructive methods for evaluating a statistically large number of fuel particles are essential to the economical production of TRISO particles. Extensive research and development programs are being conducted by many countries [9, 10] on the fuel manufacturing and the characterization techniques.

Experimental Irradiation

As mentioned earlier, the coated fuel particle is the basic component of the HTR fuel element. The extensive international experience with a large variety of TRISO-coated fuel particles strongly indicates that SiC-based coating systems should prove adequate for a broad range of HTR applications with core outlet temperatures of at least 850°C and, perhaps, up to 1000°C (with certain core design changes to limit fuel temperatures). However, as core outlet temperatures are increased to 1000°C and higher, the ultimate performance limits of SiC-based, conventional TRISO coatings will be reached at some point. A number of candidate advanced coated-particle designs have been explored which appear to promise superior high temperature performance compared to conventional TRISO particles. The design and development of coated particle type fuel requires carrying out both in-pile and out-of-pile experiments. The as manufactured defects produced during fabrication of fuel particles or during pressing of fuel compacts/spheres can affect the integrity of the

coated particle fuel. All these have to be minimized through proper quality control measures. These will have to be followed up with a comprehensive PIE programme, the techniques for some of which may have to be developed.

Failure Mechanisms

Coated particles are designed as miniature spherical pressure vessels that contain the pressure due to fission gases and CO produced by reaction between the coatings and the oxygen liberated during fission of oxide kernels. Therefore a preliminary design goal is that the release of fission products will be sufficiently low that the radiological consequences of credible accidents are within the allowable limits. A more stringent requirement is that the release will be low enough to permit the required maintenance throughout the lifetime of the reactor. The damage to any of the coating layers could occur during fuel manufacture or irradiation; due to excessive pressure or temperature gradient in the particle during operation; degradation of the properties at higher temperatures; chemical attack of fission products etc. The mechanisms, which, alone or in combination with other mechanisms, may play a major role in the failure of the fuel particle, are explained in brief in the following paragraphs [2].

Kernel Migration

Temperature gradients in coated particle under extreme operating conditions or due to asymmetrical fuel kernel production lead to transport of carbon from hot side of the inner carbon layer to cold side of the inner carbon layer causing a fuel kernel migration towards hot side. In general, kernel migration increases with time and temperature and in oxide kernels with CO production. At high temperatures this effect was seen to play a significant role in both oxide and carbide fuel. In carbide fuel the amoeba effect is controlled by thermal diffusion of carbon in the fuel phase. The failure probability is more in prismatic core design owing to their higher power densities & thermal gradients than in pebble bed core design. This problem becomes less significant in pebble bed reactors using spherical fuel elements also because of homogeneous fuel distribution resulting in small temperature gradients. Under severest accident condition the kernel was calculated to move by 55 μm . Safety design limit was

fixed as the sum of buffer and inner PyC layer thickness. It has been reported that in UCO kernels, CO formation is suppressed and no kernel migration occurs. Mathematical models have been developed world wide to predict the distance of migration. The failure of the SiC layer due to the fuel kernel migration and then interaction with the coating is also referred as 'amoeba effect'.

Pressure Vessel Failure

Due to irradiation and high temperature, fission gases are released from the kernel of the particle. Thus the particle fuel can be considered to be a thick spherical pressure vessel. Internal pressure of the released gases and kernel swelling causes tensile stresses to build up on the coating layers. Irradiation induced shrinkage of inner and outer pyrocarbon layer results in compressive stresses to be imposed on SiC layer, which is the most important strength-providing layer. These compressive stresses reduce the tensile stresses developed on SiC coating. If the tensile stress in the SiC coating exceeds the strength of the layer, the result is an almost simultaneous failure of all the coating layers. This failure is controlled by product specification on distribution of fuel kernel diameter, coating thickness and on void volume provided in the buffer layer. Mathematical models developed in Germany, USA and Japan predict a very small (almost negligible) probability of fuel particle failure in this mode during the entire lifetime of the reactor. In oxide fuel the partial pressure of produced CO is more contributing than the partial pressure of fission gases. For carbide fuel the probability of pressure vessel type of failure therefore further reduces. Mathematical models have been developed world wide to predict this kind of failure and calculate stresses produced on the coatings.

Fast Neutron Dose Induced Pyrocarbon Cracking

In a TRISO particle, the effect of irradiation is to set in motion several slow processes which cause densification of the outer pyrocarbon coating, shrinkage on to the SiC layer and as a result creep. Subsequently the densification rate decreases, allowing the pyrocarbon to continue creeping thereby relieving the induced stress. It has been postulated by analogy with graphite that creep strain

produces micro-cracks. Once a critical concentration of micro-cracks has been reached, macroscopic fracture will occur. The onset of cracking is also accompanied by a considerable increase in the outer pyrocarbon thickness. Survival of a pyrocarbon coating is extremely dependent on the initial level of anisotropy. As a result of irradiation creep process, any initial anisotropy is increased, and depending upon the particular starting level and reactor conditions can lead to cracking. In addition to Bacon's Anisotropy Factor (BAF) other factor, which play a major role, are temperature, initial density and fluence. Mathematical models have been developed world wide to simulate this phenomenon.

Matrix/OPyC Interaction

If binding occurs between the fuel matrix material and the outer coating of the fuel particle, irradiation stresses can lead to coating failure due to the relatively high shrinkage of matrix material and the tearing away of portions of coating layers during irradiation. Such type of coating failures can be avoided by designing the fuel element so that only a weak physical coupling exists between the outer coating of the fuel particle and the surrounding matrix material, under which conditions the above mechanism is insignificant.

SiC Thermal Decomposition

The crystalline material comprising the SiC layer of the TRISO coating has a reported tendency to decompose at high temperatures. Studies have shown that phase transition of β -SiC (as deposited) to α -SiC takes place at high temperatures. This transition temperature vary from 1600 – 2200°C. Coincident formation of small pores over the entire surface of layer takes place and the material becomes disordered. This leads to rapid increase in the fission products release. Further high temperature leads to complete thermal decomposition of the SiC layer of the TRISO coating. Otherwise SiC layer shows lack of irradiation damage at high temperatures, annealing effect reduces the damages produced by fast fluence. Mathematical models have been developed to predict this behaviour.

SiC Permeability/Degradation

SiC permeability or SiC degradation depends on fast neutron fluence and burn up. This is especially important for coated particle fuel if burnup extension/push is required. Higher release of Cesium will occur if the SiC layer becomes more permeable.

Release of Fission Products and Fission Gases

Fission product release behaviour under normal operating conditions is important from safety point of view. Fission product activity is available either as coolant activity or as plate-out activity on surfaces of the primary circuit or as dust borne activity providing potentially significant exposure levels with a severe impact on maintenance procedures. The fission product isotopes of most interest from maintenance and safety considerations are those of the fission gases Krypton and Xenon, Iodine, and metals Cesium, Strontium and Silver. Particle with intact coatings are impervious to fission gases and Iodine. Fission gas release occurs only from failed fuel. These gases usually have relatively short half-lives. Only those short-lived fission product atoms lying very near the surface of the kernel can be released by diffusion before they decay. Hence fission recoil becomes important release process. Recoiled atoms stop in carbon coatings and then they are released by diffusion process. Due to the decay process fractional release of short-lived isotopes such as ^{133}I , ^{88}Kr , ^{133}Xe is only about 1% for failed fuel. For metallic fission products Ag may be released apparently from intact TRISO coatings at high temperatures. Most of these isotopes are very long lived. Hence decay is of less importance than gases. For metallic fission products diffusional release from the fuel kernel is more important than release by fission recoil. In case of oxide fuel kernel, Strontium, which forms a stable oxide, is strongly bound in oxide fuel kernels. Carbide kernels are much less retentive of metallic fission products than oxide kernels. The diffusivity of fission product metals in pyrocarbon also vary with $D_{\text{Ag}} > D_{\text{Sr}} > D_{\text{Cs}}$. Different mathematical models have been formulated for finding out the fractional release rates for fission gases as well as metallic isotopes. In UC_2 kernels rare earth fission product migration is of concern. In UO_2 kernels, Palladium is very important, as are some other noble metal fission

products. In UCO kernels, the oxycarbide form of the kernel generally ties up all fission products and limits their mobility of fission products in the UCO system. However, Pd transport has been observed in UCO fuel. The migration of silver in both UO_2 and UCO has been observed. Silver can migrate through apparently intact particles and be released into reactor coolant system where it will deposit on cold surfaces. The yields of silver and palladium are more for LEU than HEU.

Fuel and Fission Product Diffusion and Attack on the Structural Layers

SiC interlayer is used in TRISO particles to improve the retention of solid and gaseous fission products. This layer also significantly increases the mechanical strength of the particle. The benefits of the TRISO coatings are conditional upon the SiC remaining intact during the entire period of residence in the reactor. But SiC can be attacked by chemical interaction with the kernel material and the fission products. SiC corrosion can lead to an increased release of fission products. It was shown that the presence of chlorine within the particle, in combination with certain metallic fission products or uranium could lead to corrosion of the SiC layer. High temperatures increase corrosion rate. Although other metallic fission products are also involved, interaction of Palladium with SiC layer is suspected to play a major role in the corrosion process. In carbide fuel lanthanide fission products are suspected to play a similar role in corrosion. In Japan and USA failure of SiC layer is considered to take place if 50% of the SiC thickness is corroded. For the Japanese fuel the maximum Pd-SiC interaction depth was found to be dependent on the cubic root of rate of the release of Pd from kernel and a maximum penetration depth of 11 μm at the end of life was calculated. To mitigate or reduce this effect to acceptable value thermal gradients and maximum temperature should be so restricted that SiC – fission product interactions are negligible. This depth is less than 50% of SiC thickness. Most of these results have been experimentally found out.

6.1 and 6.8 mentioned above are linked strongly to the chemical composition of the fuel kernel. Thus it has been so shown that in oxide fuels SiC and ZrC lower the CO content and reduce

carbon transport. Thermo-dynamic and experimental results indicate that the effects of kernel migration and fission product diffusion are minimised by using a mixed oxide/carbide kernel.

Manufacturing Defects

As-manufactured defects produced during fabrication of coated fuel particles or during pressing of fuel compacts/spheres could impact the performance of the fuel in reactor. Some of the important defects are undetected defective particles during fabrication, particles that have failed as a result of the formation into a compact or a pebble, introduction of impurities from the graphite furnace, attack of the particles during fabrication or irradiation by impurity metals like iron.

Advanced TRISO Fuel Particle [2]

For high temperature utilisation and to have higher safety margins in design of fuel so as to have fuels with extended limits of operation and increased safety a key issue is retention of fission products and fission gases at higher temperature. Although SiC has excellent properties it gradually loses its mechanical integrity at high temperatures especially over 1700°C by thermal dissociation and transformation from β -SiC to α -SiC. The fuel temperatures are limited to, therefore, well below 1700°C during the design basis accidents in the current HTGR designs. SiC also sublimates at a temperature of 1800°C . Published literature recommends that with SiC layer, the maximum temperature of fuel can be limited to 1495°C during normal operation and 1600°C in accident conditions. Beyond this temperature release of fission products increases quite sharply. Hence one approach for higher temperature utilisation of these fuels is use of a more refractory carbide than silicon carbide. ZrC is a refractory and chemically stable candidate material for replacing SiC coating layer of TRISO fuel particles. ZrC has a melting point of 3540°C and melts eutectically with carbon at 2850°C . Fuel particles having ZrC layer instead of SiC, has been termed as ZrC-TRISO fuel particles. It has been mentioned in literature that ZrC is advantageous as compared to SiC. Some of these advantages are listed below:

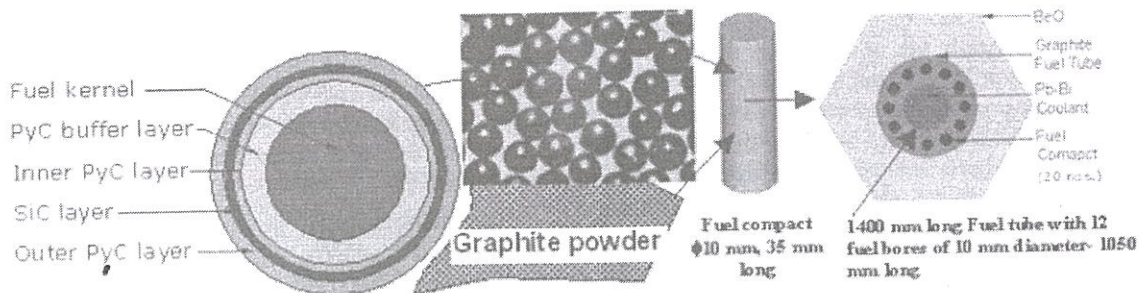


Fig. 1 Schematics of TRISO fuel particle, fuel compact, and single fuel bed for CHTR

- Improved fission products retention at high temperatures such that peak fuel temperature in normal operating and accident conditions can increase without violating safety. This will result in increased core power densities, if required.
- Increased thermal conductivity of the fuel matrix material will result in the reduction of the maximum fuel temperature for a given coolant outlet temperature.
- It can be used as a fission product and oxygen getter if deposited over the kernel and dispersed through the buffer layer.
- ZrC layer is more resistant to chemical attack by fission products such as palladium and fuel kernel.
- Above 1600°C performance of ZrC is better than SiC.
- ZrC is mechanically more stable under irradiation.
- The kernel migration or the amoeba effect is absent in particles when kernel is also given a coating layer of ZrC.
- Strong chemical resistivity against palladium corrosion.

Compact High Temperature Reactor (CHTR) Fuel

[1]

CHTR fuel consists of ^{233}U , Th, and small amount of Gadolinium as burnable poison. Thorium and burnable poisons make the fuel temperature coefficient negative, thus making the reactor inherently safe. The fuel is in the form of fuel compacts made of TRISO coated particle fuel

embedded in graphite matrix. A typical CHTR fuel bed consists of prismatic BeO moderator block with centrally located graphite fuel tube carrying fuel compacts. Schematic of fuel particle, fuel compact, and single fuel bed are shown in Fig. 1.

The details of proposed TRISO coated particle fuel for CHTR are given below:

Kernel diameter (Density: >10 gm/cc)	500 μm
Buffer low density (>1.1 gm/cc) pyrocarbon layer thickness	90 μm
Inner high density (>1.8 gm/cc) pyrocarbon layer thickness	30 μm
SiC (Density: >3.1 gm/cc) layer thickness	30 μm
Outer high density (>1.8 gm/cc) pyrocarbon layer thickness	50 μm
Total diameter of particle	900 μm

Manufacturing of kernels is an established technology in BARC, and a large number of micro-spheres have been prepared with excellent quality control. Experimental trials for TRISO coatings on surrogate materials have been carried out in BARC. There will be additional requirements like remote handling and shielding due to use of ^{233}U -based fuel material in CHTR. These are being further studied for developing manufacturing processes to meet the acceptable specification and the performance requirements of CHTR fuel.

Indian Perspectives on HTR Fuels

Indian perspective as far as fuel fabrication is concerned is important for CHTR because of use of ^{233}U . CHTR will be using ^{233}U -based TRISO coated particle fuel. This is being done for the first time in India and therefore mastering key technologies for long term use needs enormous R&D efforts in many areas of engineering, materials, related fuel cycles etc. All these activities call for multi-disciplinary expertise. The inputs and collaborations will be required from different divisions of BARC and units of DAE to get technological breakthrough, owing to the challenges in coating technologies, material development, quality control, reactor physics etc. Tests for establishing fabrication processes for kernel preparation, coating processes are required to study statistical deviation and variation of process parameters. Development of simple and quicker QC/QA procedures at different stages of the fabrication and coating process as well as for the inspection is desirable. Also novel characterisation techniques are needed because of additional requirements from ^{233}U , remote handling and shielding etc. Sufficiency of the dimensions of the kernel and different layers needs to be proved. It is required to carry out the irradiation tests with coated fuel particles over a range of fuel temperatures (700-1700°C) and for a range of burnups (2-7%FIMA) to assess performance behaviour and its correlation with fabrication parameters. These experiments are important for identifying fuel failure mechanisms, evaluation of the properties for irradiated structural materials, coating integrity evaluations, corrosion studies on coating layers and chemical behaviour of fission products.

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