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ThO_2 and $(U,Th)O_2$ processing—A review

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ABSTRACT

India is one of the few countries committed to expansion of nuclear power. In view of the abundance of thorium relative to uranium, thorium cycle is under serious development and implementation. Both ThO_2 and $(U,Th)O_2$ are used. Fine powders of the same are mostly prepared through the aqueous chemical route, pressed and sintered. Extrusion and hot impact densification are also being used. Sol-gel method and other alternatives are also being pursued with the advantage of automation and remote operation. Relevant papers on the thorium cycle with emphasis on processing methods and related aspects are reviewed here.

Keywords: Thorium Dioxide; Uranium Dioxide; Thorium Fuel Cycle; Thoria Urania Processing

1. INTRODUCTION

Sustainable development is the development that meets the needs of the present generation without compromising the needs of future generations. To attain this goal, one of the imperatives is to adopt nuclear power. In spite of the disaster at Fukushima, nuclear power remains a clean viable alternative to fossil fuels that have wreaked havoc on the environment by way of global warming, climate change, melting ice caps and rising sea levels.

Alternative nuclear technologies have been suggested as a means of delivering enhanced sustainability with proposals including fast reactors, the use of thorium fuel and tiered fuel cycles. The debate as to which is the most appropriate technology continues, with each fuel system and reactor type delivering specific advantages and disadvantages which can be difficult to compare fairly. Eastham *et al.* [1] came up with a novel method for rapid comparative quantitative analysis of nuclear fuel cycles. Its framework includes metrics such as fuel efficiency, spent fuel toxicity and proliferation resistance. The method rapidly identifies relative cycle strengths and weaknesses and has significant scope for use in project planning and cycle optimization.

One option suggested especially for the Asia Pacific Region is the use of pressure tube reactors (PTRs) with fuel channels that can be tailored to many fuels and fuel cycles [2]. These include development of indigenous recycling and thorium-based options, not only to extend global energy resources, avoid depletion and associated price increases, but to enhance energy security and reduce dependence on imported fuels.

The information on thorium and thorium fuel cycles has been well documented in the publications of IAEA and of others [3-15]. Thorium fuels complement uranium fuels and ensure long term sustainability of nuclear power. Thorium is 3 to 4 times more abundant than uranium and widely distributed in nature as an easily exploitable resource. In recent times, the need for proliferation-resistance, longer fuel cycles, higher burn up, improved waste form characteristics, reduction of plutonium inventories and in situ use of bred-in fissile material has led to renewed interest in thorium-based fuels and fuel cycles in several countries.

Rodriguez and Sundaram [16] reviewed the nuclear and materials aspects of the thorium fuel cycle. The Indian perspective of thorium fuel cycles hinges on the scarcity of uranium and abundance of thorium in the country. Its use requires reprocessing to separate the fissile ^{233}U for sustained operation using ^{232}Th-^{233}U. Irradiated thorium assemblies have been reprocessed and the separated ^{233}U was used for test reactor KAMINI, at Kalpakkam, India. The thorium fuel cycle technologies that are being developed for the Advanced Heavy Water Reactor (AHWR) will be useful for the large scale utilization in the third stage of Indian nuclear power program [17,18].

2. THORIA AND THORIA MIXED FUEL

$Th_xU_{1-x}O_{2+y}$ binary compositions occur in nature, uranothorianite, and as a mixed oxide nuclear fuel. As a nuclear fuel, important properties, such as the melting point, thermal conductivity, and the thermal expansion coefficient change as a function of composition. Additionally, for direct disposal of $Th_xU_{1-x}O_2$, the chemical durability

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[*] Retired.

changes as a function of composition, with the dissolution rate decreasing with increasing thoria content. UO_2 and ThO_2 have the same isometric structure, and the ionic radii of 8-fold coordinated U^{4+} and Th^{4+} are similar (1.14 nm and 1.19 nm, respectively). Thus, this binary is normally expected to form a complete solid solution [19].

The use of thoria requires addition of fissile materials and these can be in the form of enriched uranium (^{235}U), plutonium or uranium (^{233}U) obtained from reprocessing of thorium fuel. The fabrication aspects of these three MOX fuels differ from one another. The (Th-^{235}U) MOX fuel can be fabricated like the conventional uranium fuel and the (Th-Pu) MOX fuel can be fabricated inside glove box like that of well established (U-Pu) MOX fuels. The fabrication of (Th-^{233}U) MOX fuel however requires a considerable technological development. The fabrication activities right from handling and storage of material to the manufacturing processes used must be able to accommodate the higher level of radiological activity due to the presence of ^{232}U in the recycled urania. The major radiation source is its hard gamma emitting daughter products ^{208}Tl and ^{212}Bi. The fabrication activities have therefore to be structured to ensure low material hold-up and quick recycling of the reprocessed materials to keep the radioactivity dose levels as low as possible and also calls for a high level remotisation and automation.

The feasibility of using advanced fabrication techniques like Pellet Impregnation, Advanced Agglomeration, Sol-Gel Micro-sphere Pelletization or Vibropac that are more amenable to remotisation are also being explored [20]. ThO_2 containing around 4% $^{233}UO_2$ along with ThO_2-3 to 4 % PuO_2 is the proposed fuel for the Indian Advanced Heavy Water Reactor [21].

3. FABRICATION PROCESSING

Thorium oxide has been sintered by several researchers [22-26].

High specific surface area fine powders are needed since surface energy reduction is the driving force in sintering. Fine ThO_2 powders are obtained by precipitating Thorium as oxalate. Fine UO_2 powders are obtained by precipitating U as ammonium diuranate. Researchers at Battelle Memorial Institute [27] found that of the thorium oxalate precipitation variables-temperature, agitation, and digestion time, temperature has the most effect upon particle morphology, surface area, crystallite size, and sinterability of the derived thoria powder. Most sinterable thorium oxide powder was obtained by precipitating thorium oxalate at 10˚C followed by digestion. Pellets of 96% TD were obtained without resorting to milling. Simultaneous separate introduction of the oxalic acid and thorium nitrate solutions into the continuous precipitation reactor produces precipitated particles which are agglomerates of inter-grown crystals distinctly different from the particles precipitated by direct strike. In the production of thorium oxide powder from oxalate, the decomposition and calcining heat cycle must include enough time between 300˚C and 400˚C to thoroughly decompose the oxalate hydrate.

Altas *et al.* [28] prepared thoria urania by co precipitation at 10˚C. The oxalate was found to be isomorphous and not occluded type. The oxide powders were compacted to 37% TD. On sintering at 1100˚C in carbon dioxide, 81% TD was achieved.

Nanocrystalline thoria was synthesized on laboratory scale at Kalpakkam [29-31]. A master sintering curve for ThO_2 was developed by Kutty *et al.* [32].

Researchers at the University of Paris [33] obtained $U_{(1-x)}Th_xO_2$ sintered pellets from crystallized $U_{(1-x)}Th_x(C_2O_4)_2\cdot 2H_2O$ precursors precipitated at low temperature. They considered two different chemical routes for the synthesis of $U_{1-x}Th_xO_2$ solid solutions, both based on the initial precipitation of crystallized precursors from a mixture of hydrochloric solutions containing the cations and oxalic acid. In the first route, called "open system", the oxalic acid was added drop wise into the actinides solution stirred in a beaker, and heated at 323 K under ultrasonic agitation. In the second method, called "closed system", the mixture was placed in a closed PTFE container set in a digestion bomb then heated in an oven for a week at 403 K. In both conditions, the so-obtained precipitates were separated from the supernatant by filtration or centrifugation, washed several times with deionized water and ethanol, dried at about 343 K overnight then finally ground in an agate mortar. The expected $U_{1-x}Th_xO_2$ mixed oxide powders were finally obtained after heating above 673 K.

The precipitation of thorium-uranium (IV) oxalate dihydrates then their conversion into dioxides above 500˚C allowed optimizing the reactivity of the powders. The great increase in the specific surface area observed through the heat treatment of the precursors was linked to the departure of the volatile compounds and to the subsequent strains generated in the bulk of the grains, leading to the formation of pores and cracks and/or to the partition of the grains into sub-micron particles. This operation then allows the benefit from the wet chemistry methods in terms of cationic homogeneity and high reactivity without need for grinding, which could be penalizing in nuclear processes [34].

Optimal operating conditions for the sintering of the samples were determined through dilatometric studies under argon atmosphere from room temperature to 1500˚C (heating rate of 5˚C/min) achieving densities of 94% to 99% TD. The use of hydrothermal conditions in precipitation improved the cationic distribution in the sintered samples.

Joseph *et al*. [35] investigated in detail the thermal decomposition of thorium oxalate.

The US Department of Energy carried out the most comprehensive compilation of literature on ThO_2 [36] under the title "Thorium dioxide—Properties and Nuclear Applications". Idaho National Engineering and Environmental Laboratory presented results of a detailed study of advanced proliferation resistant, lower cost, uranium-thorium dioxide fuels for LWRs [37].

At Japan Atomic Energy Research Institute [38], ThO_2 powder of specific surface area 4.56 m^2/g was ball milled to 9 m^2/g, compacted at 2 to 5 t/cm^2 without binder and sintered at 1550˚C to get densities in the range 96% - 98% TD.

In the ionic crystal lattice of urania or thoria, it is the cation that is the slower moving species. Sintering being a diffusion controlled process, speeding up the cation will also promote sintering. Matzke [39,40] determined that the diffusion of uranium in UO_2 and ThO_2 is enhanced by several times in the presence of niobium. At Nuclear Fuel Complex, India, it was found that doping by Nb_2O_5 lowered the sintering temperature of ThO_2 to 1150˚C [41,42]. Without the additive, the same thoria powder could be sintered at a higher temperature of 1600˚C. The low temperature sintering result was later reconfirmed by researchers at Indira Gandhi Centre for Atomic Research, Kalpakkam [43].

The specifications for thoria based pellets for the LWBR program of USA [44], based on irradiation tests, define the requirements of high density and high integrity and are optimized to achieve high thermal conductivity and to minimize creep, fission gas release, in-pile densification, chipping and fuel-clad interactions. A fuel pellet fabrication route-consisting of 1) powder blending (dry mixing of thoria and Urania); 2) micronising (fluid energy milling) to activate and homogenize the ThO_2-UO_2 mixture; 3) liquid/solid agglomeration by adding binder; 4) lubricant addition; 5) compaction; 6) pretreatment for removal of binder and lubricant; and 7) single fire sintering—has been developed to produce pellets of the required quality; the process is claimed to be easily adaptable for remote handling.

The sol-gel process for producing microspheres of mixed oxides of Th and U is a more attractive method for manufacturing fuels in the thorium cycle because it 1) is amenable to remote operation; 2) minimizes the number of processing steps for powder preparation; 3) minimizes dust production; and 4) greatly reduces holdup of fissile material in process equipment. In the SOLEX process for (UO_2-ThO_2) microsphere production developed at the Oak Ridge National Laboratory [45], feasibility has been demonstrated using both depleted uranium and ^{233}U.

Recycle fuel containing ^{233}U must be fabricated behind heavy shielding because of the high-energy gamma radiation of the daughter products arising from the decay, of the ^{232}U that contaminates the ^{233}U. The reference fabrication method for the production of $(Th,U)O_2$ recycle fuel is the conventional powder-compaction/sintered-pellet route. Since this process has several dusty operations and requires complex equipment, there is an incentive to develop simpler fabrication methods that are more suited to remote operation. Atomic Energy of Canada Limited has been engaged in a recycle fuel program to develop and evaluate alternate ways of producing $(Th,U)O_2$, fuel by remote fabrication. The extrusion of sol-gel derived pastes is one of several methods studied [46]. Crack free extruded $(Th,U)O_2$ slugs with high density (9.7 Mg/m^3) have been produced from sol-gel pastes with a moisture content of 16%, prepared from ThO_2, denitrated at 600˚C, and mixed with 0.4% organic binder. The slugs were finally sintered at 1600˚C in a H_2, atmosphere.

French engineers have developed equipment for Hot Impact Densification process [47] which has the advantages of fast heating and molding, close shape tolerances eliminating subsequent grinding, use of coarse feed powder with reduced dust generation and solubility in the PUREX process.

Nuclear fuel pellets are typically fabricated using a rotary press with multiple tool stations by uniaxially pressing in double action dies at the rate of several hundred pellets per minute. A number of problems, however, are associated with uniaxial die pressing that may lead to pellet rejection. These are: 1) Cracking due to end capping and/or laminations; 2) Density variation within the pellet; and 3) Die wear leading to lack of dimensional control. In addition, as-sintered pellets have a slightly hour-glass shape due to non-uniform packing of the powder compact and therefore require post-sinter machining.

An alternate route for fabrication of green pellets is by using dry bag isostatic pressing of fuel rods and subsequent cutting of the above rods into pellets.

Dry bag isostatic pressing (DBIP or "isopressing") is used for mass production of ceramic parts, for instance, spark plugs, automobile oxygen sensors and ceramic rods and tubes. It is a method to mold powder into a green part by introducing granulated powder into a polyurethane mold and hydrostatically pressing it through a master bag within the high-pressure vessel. It distinguishes itself from "wet bag isostatic-pressing" by the fact that the mold does not contact the hydraulic fluid directly but through the master bag and so can be rapidly filled, inserted, pressed and taken out again. This method is suitable for mass production of simple shaped products with its labor-saving automatic operation. For the manufacturing of nuclear fuel pellets, a single rod may be cut into 20 - 30 pellets depending upon the pellet length requirement. DBIP can be automated all the way from powder filling the mold to product removal. The main advantage of using isostatic pressing over uniaxial pressing for nuclear fuel production is that much more uniform pellet densities are achievable [48].

Yamagishi and Takahashi prepared high density thoria urania pellets by sol-gel microsphere pelletizaion [49].

Mathews and Hart followed a concept that combines the front end of the gel-sphere flow sheet with the back end of the standard pelletizing flow sheet [50]. The gel-sphere process is used as a nitrate-to-oxide conversion step that directly provides an ideal press feed material. The use of microspheres as press feed eliminates three major dust generation steps from the pelletizing process-powder milling, slugging, and granulation. The potential for low dust buildup means lower radiation levels, less exposure to operators, and easier equipment maintenance than with conventional pelletizing. The spheres have better flow properties than powders, so transport problems should be reduced, and consistent die fill should be achieved. At the same time, the fuel retains the familiar pellet configuration and is anticipated to exhibit irradiation behavior similar to conventional pellet fuels.

Coated Agglomerate Pelletization (CAP) [51-53] and Powder oxide Pelletization (POP) and co precipitation route have been developed at BARC, Mumbai [54].

More recently, a new fabrication technique Impregnated Agglomerate Pelletization (IAP) has been developed for making (Th,U)O_2 pellets [55,56]. It is a useful technique for fabrication of highly radioactive (Th,^{233}U)O_2 fuel for AHWR. It reduces powder handling, man-rem, number of process steps requiring shielding. Improvement in microstructure and homogeneity of (Th,U)O_2 pellets fabricated by IAP process has been observed. Results from IAP process are claimed to be better than CAP route and comparable with POP route.

In the IAP process, ThO_2 is converted to free flowing spheroids by powder extrusion route in an unshielded facility which are then coated with uranyl nitrate solution in a shielded facility. The dried coated agglomerate is finally compacted and then sintered in oxidizing/reduceing atmosphere to obtain high density (Th,U)O_2 pellets. Fabrication of (Th,U)O_2 mixed oxide pellets containing 3 - 5 wt% UO_2 was carried out by IAP process.

Glodeanu [57] listed the key process parameters in the fabrication of high density thoria urania pellets as comminution of the starting powders by dry ball milling and intimate mixing. The surface area of the powder mixture increased as the co milling time was increased, but saturated after 10 hours. Sintered densities of ~97% TD were reached in the entire range of thoria urania compositions.

Researchers at Kalpakkam found that deagglomerating thorium oxalate resulted in sinter-active powder [58]. V. Chandramouli *et al.* [59] carried out Microwave synthesis of solid solutions of urania and thoria. This method involves the denitration of the mixture of uranium and thorium in the presence of polyvinyl alcohol using a microwave oven. They also investigated combustion synthesis of thoria [60].

4. HOMOGENEITY AND DENSITY

While it is easy to achieve homogeneity in small scale operations, it becomes increasingly difficult as the size of the batch is increased to tonnage level. It is necessary to choose the right equipment for preparing intimate mixtures of mixed oxides. The type of the mixing machine chosen depends on the powder characteristics. Free flowing powders may mix readily in a double cone or V type tumbling mixer, where as ribbon mixer may be more appropriate for powder mixtures which do not flow. ThO_2 and UO_2 powders prepared through the aqueous chemical route are usually nonflowable. The efficiency of mixing in different types of mixing machines will have to be evaluated statistically from results of several samples [61].

In the sintering of UO_2 containing 1.5% Gd_2O_3, low sintered densities were attributed to the presence of Gd_2O_3 powder in large agglomerate form in the starting powder mixture. The stability of a void is related to its size by $p = 2\gamma/r$, where p is the pressure acting on a void towards closure, γ is the surface tension and r is the radius of the void. If r is large, p will be small and vice versa. If the Gd_2O_3 agglomerate size in the powder mixture or compacted green pellet is large, when the Gd_2O_3 dissolves in the UO_2 matrix, it would leave a large sized void, which would be difficult to close. On the other hand, if the agglomerate size of the Gd_2O_3 is small, the void left on dissolution would be small and close easily in the course of sintering [62].

A similar reasoning will be applicable to ThO_2-UO_2, PuO_2-UO_2 and other mixed oxides. Hence the starting powder mixture has to be free from large agglomerates of the minor component. Intimate mixtures are usually obtained by co precipitation or co-milling using either jet or ball or hammer mills. However, the use of such machines has to be accompanied by leak tight containment and other measures to keep airborne radio active particles at acceptable levels.

5. CONCLUDING REMARKS

Several methods have been published for the preparation of thoria urania powders. However, aqueous precipitation method appears to be most common, well tested and reliable.

Several types of sintering including microwave sintering have been developed. However, sintering at high temperatures in reducing atmosphere seems to be the most favored production route.

While sintering in a dilatometer provides an insight into the sintering process, reproducibility on a large scale can come only from the experience from large scale production.

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