

An Integrated Process for Recycling of ThO₂ Based Mixed Oxide Rejected Nuclear Fuel Pellets

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Abstract

This paper presents a study on the process engineering aspects of relevance to the industrial implementation of ThO₂ and (Th, U)O₂ mixed oxide (MOX) pellet type fuel manufacturing. The paper in particular focuses on the recycling of thorium based fuel production scrap which is an economically important component in the fuel manufacturing process. The thorium based fuels are envisaged for Advanced Heavy Water Reactor (AHWR) and other reactors important to the Indian Nuclear Power Programme. A process was developed for recycling the chemically clean, off-specification and defective sintered ThO₂ and (Th, U)O₂ MOX nuclear fuel pellets. ThO₂ doesn't undergo oxidation or reduction and thus, more traditional methods of recycling are impractical. The integrated process was developed by combining three basic approaches of recycling namely mechanical micronisation, air oxidation (for MOX) and microwave dissolution-denitration. A thorough investigation of the influence of several variables as heating method, UO₂ content, fluoride and polyvinyl alcohol (PVA) addition during microwave dissolution-denitration was recorded on the product characteristics. The suitability evaluation of the recycled powder for re-fabrication of the fuel was carried out by analyzing the particle size, BET specific surface area, phase using XRD, bulk density and impurities. The physical and chemical properties of recycled powder obtained from the sintered (Th_{1-y}, U_y)O₂ (y; 0 - 30 wt%) pellets advocate 100% utilisation for fuel re-fabrication. Recycled ThO₂ by integrated process showed distinctly high sinterability compared to standard powder evaluated in terms of surface area and particle size.

Keywords

ThO₂, MOX, (Th, U)O₂, AHWR, Recycling, Microwave, Denitration

1. Introduction

The recycling of valuable materials is important for the nuclear industry like other industrial processes. The rejects and scrap are arising in the process of nuclear fuel fabrication. The main arisings are powder and pellets from oxide or MOX production and metal swarf from production of metal fuels. The recycling of rejected nuclear fuel is a key component of the fabrication process flow sheets. The recycling comprises recovery of rejected nuclear fuel materials and their utilization for re-fabrication of the fuel. The rejected MOX fuel consists of mainly the off-specification and defective sintered pellets. Low density, under size, compositional variation and physical defects generates considerably high proportion of rejected fuel pellets. The rejected fuel pellets contain significant amount of fissile and fertile materials depending upon the composition of the fuel. Thus, judicious utilization of the feedstock materials is accomplished by recycling these rejects. The recycling assumes paramount importance for many good reasons like curtailing fuel cost, saving of natural resources, alleviating total fissile content degradation, averting personnel exposures etc. [1] [2]. The economic considerations throw a major driving force for considering the practice of recycling in the fuel manufacturing process over the alternative disposal options. Thorium dioxide or thoria (ThO₂) has gained more interest considering its resources and long-lived waste concerns. It is more abundant in the earth crust and the thorium fuel cycle generates lesser minor actinides than its uranium analogue. However, natural thorium is quasi-monoisotopic (Th²³²) which is fertile and cannot directly be used in a nuclear reactor. Thus, initial enrichment with a fissile (Pu, U²³³ or U²³⁵) is needed as nuclear fuel. India has planned ThO₂ utilization in a comprehensive way in its three-stage Nuclear Power Programme [3]. ThO₂ has been used for the initial flux flattening in Indian Pressurised Heavy Water Reactors and as fertile blanket material in the fast reactors. The third stage of power programme is built on ThO₂ based MOX fuels keeping in mind the long term deployment of thorium based reactors for sustainable energy [3] [4]. In this direction, AHWR is being set-up as technology demonstration reactor [4]. This will utilise (Th-Pu) and (Th-U²³³) MOX fuels (2.5 to 4 wt%) following a closed fuel cycle. In view of the technologically challenging issues of (Th-U²³³) or (Th-Pu) fuels in a closed fuel cycle, the once-through fuel cycle containing low enriched uranium (LEU) with U²³⁵ enrichment of 19.75% is recently proposed for AHWR [5] [6]. The proposed fuel is Th-LEU MOX having UO₂ composition from 18 to 22.5 wt% for AHWR-LEU [5].

Extensive studies were carried out for fabrication of ThO₂ or (Th, U)O₂ by standard powder-pellet route and other advanced routes in India [7] [8]. Several

attractive routes for fabrication of (Th-U²³³)O₂ fuel were developed over the years [9]-[15]. The newer routes have shown many potential advantages over the standard route. The newer methods mainly emphasized on the reduction of men-rem due to U²³² daughter products (Bi²¹², Tl²⁰⁸), radioactive dust hazard, minimizing the operations requiring shielding, ease of remotisation and fissile homogeneity in the MOX. Fresh ThO₂ and Th-LEU fuels can be fabricated in a normal facility following the standard powder-pellet route. However, fabrication of fuels from reprocessed ThO₂ or (Th, U²³³)O₂ fuel demands extensive shielding and overriding interest in the newer developed routes [9]-[15]. A few important physical characteristics of nuclear grade ThO₂ (oxalate route derived) and UO₂ (ammonium diuranate route derived) as starting feed materials for powder-pellet route are recorded in **Table 1** [16] [17]. The value in the parenthesis reports the typical property values.

Irrespective of the route followed for fabrication of fuel, a significant proportion of the total throughput (typically 15% - 20% in powder-pellet route) the off-specification fuel pellets get produced invariably in the various operations. To curtail the fuel cost, these rejects are to be recycled essentially. The recycling of rejected UO₂ based fuel is carried out by thermo oxidative [18] [19] [20], thermo oxidative-reductive [21] [22] [23], mechanical micronisation [24] and microwave dissolution-denitration [22] [25] [26] [27] [28] or by their combination.

The recycling of ThO₂ based MOX fuels is difficult as compared to UO₂ based fuels. ThO₂ having single oxidation state (+4) is a stoichiometric compound [29] and doesn't undergo oxidation like UO₂. UO₂ undergoes oxidation to U₃O₈ causing nearly 36% crystal volume increase, thereby making feasible the oxidative pulverization of sintered rejects [30]. Similarly, the reduction of ThO₂ to lower oxides is not feasible. Therefore, the dry recycling of ThO₂ sintered pellets by oxidative or oxidative-reductive pulverization is not feasible. However, the presence of UO₂ in (Th, U)O₂ opens an option for oxidative pulverisation of the matrix and hence, the recycling. Further, the comminution processes, where sintered rejected pellets are mechanically crushed are universally applicable. The micronisation down to very small size can be achieved using ball mill or attritor mill. To further improve the powder properties of mechanically micronised and/

Table 1. Important physical properties of sinterable oxide powders as starting feed materials.

Property	ThO ₂	UO ₂
Powder bulk density (g·cm ⁻³)	0.8 - 1.2 (0.85)	>0.625 (1.8)
BET Specific surface area (m ² ·g ⁻¹)	3.5 - 4.5	3.5 - 8.0
Average particle size (µm)	0.8 - 1.5	5 - 15
O: M ratio (M; Th or U)	2.00	2.00 - 2.15
Sinterability above 90% of TD	Sinterable	Sinterable

or oxidatively pulverized powder, the aqueous recycling by dissolution-denitration may be followed. The dissolution of ThO_2 requires addition of highly corrosive fluoride [31] [32] [33]. The powder may be obtained by following standard precipitation-calcination processes from thorium nitrate solution [29] [34] [35]. However, this alternative generates enormous quantities of active liquid waste. Thus, direct denitration of thorium nitrate or co-denitration of mixed thorium-uranium nitrate solutions using microwave is an attractive option. The thoria and thoria-urania powders were successfully prepared by bulk microwave denitration [36] [37] [38]. The combustion synthesis of ThO_2 and $(\text{Th}, \text{U})\text{O}_2$ solid solutions using citric acid, glycine and PVA by microwave heating have been reported [39] [40] [41] [42]. The powders so produced are highly sinterable and leave conventional methods far behind.

A little work has been reported in the literature on the recycling of ThO_2 based MOX sintered fuel rejects typically arising in fuel fabrication facilities. A dry recycling process was reported for $(\text{Th}, 14\%\text{U})\text{O}_2$ combining mechanical crushing and oxidation [43]. Addition of only 30 wt% of so recycled powder to the fresh feed material could bring the specified density. Thus, the batch Scrap Recycling Ratio (SRR) [23] obtained for fuel refabrication was 0.3 only. Mishra *et al.* [44] reports the addition of maximum 15 wt% (SRR: 0.15) of the $(\text{Th}, 30\%\text{U})\text{O}_2$ sintered rejects recycled via mechanical pulverization (crushed and attritor milled) for re-fabrication of fuel. In another method, they [44] have combined the mechanical pulverization with oxidation to bring out 100% recycling of $(\text{Th}, 30\%\text{U})\text{O}_2$ sintered rejects. This, delivered batch SRR of 1 and removed the need of fresh powder addition. Recently, an aqueous method for recycling of ThO_2 from nuclear fuel production scrap has been reported involving dissolution in triflic acid ($\text{CF}_3\text{SO}_3\text{H}$) which is recyclable for dissolution of new batches [45]. Since, MOX fuel for AHWR has $\text{UO}_2 < 5$ wt% and AHWR-LEU has UO_2 from 18 to 22.5 wt%; the methods for 100% recycling of sintered rejects in these ranges of UO_2 are to be explored essentially. The recycling of ThO_2 rejected pellets is also essential as their fabrication is carried out for fertile blanket and neutron flux flattening [3]. Usually the recycled powder possesses poor sinterability and thus requires addition of fresh powder. 100% recycling (SRR; 1) offers several advantages to the fuel fabricators mainly consistency in the process parameters, no need of separate tooling size for compaction, no need of adding fresh powder, no need of adding sintering promoters and low rejection rate [23]. Thus, work was pursued for 100% recycling of ThO_2 and $(\text{Th}, \text{U})\text{O}_2$ sintered rejects in the UO_2 range of 0 - 30 wt%.

In the present work, an integrated method was developed for 100% recycling of ThO_2 and $(\text{Th}_{1-y}, \text{U}_y)\text{O}_2$ (y ; 0 - 30 wt%) sintered rejects. The method entails conjunction of comminution processes with the aqueous processing route involving microwave dissolution-denitration for recycling of ThO_2 fuel rejects. For $(\text{Th}, \text{U})\text{O}_2$ rejects, mechanical micronisation was followed by air oxidation and microwave dissolution-denitration method. The integrated method produces

sinterable powder and can be 100% utilised for fuel re-fabrication. The recycled powder properties were compared with that of standard powders (**Table 1**). A profound effect on the powder physical properties was observed due to presence of UO_2 and by addition of PVA during denitration. The experimental work consisted of batch experiments, characterization of intermediates or products, suitability assessment of recycled powder, flow sheet development and comparative analysis. The recycled feed materials were characterized for particle size, specific surface area, phase using XRD, impurities, cake and powder bulk density. The recycled ThO_2 powder had surface area $>7 \text{ m}^2\cdot\text{g}^{-1}$ and average particle size 1 - 2 μm . The paper also recommends the scale-up perspectives of the process to cater the industrial requirements.

2. Experimental

2.1. Starting Materials

Solid cylindrical sintered pellets of ThO_2 and $(\text{Th}, \text{U})\text{O}_2$ were obtained from Oxide Fuel Section (OFS), AFFF. Depleted $\text{UO}_2(\text{U}^{235} < 0.4\%)$ was used to simulate U^{233}O_2 or LEU for experimental investigations in the fuel development programme for AHWR and AHWR-LEU. The pellets were fabricated by standard powder-pellet route. The sintered density of the pellets was above 90% of theoretical density (TD). The important properties of ThO_2 and $(\text{Th}, \text{U})\text{O}_2$ sintered pellets used in the present work are recorded in **Table 2**.

2.2. Apparatus and Instruments

2.2.1. Jaw Crusher

A Jaw crusher (M/s RETSCH, Germany) was used for mechanical crushing of the sintered pellets into coarse powder. It consists of a no-rebound hopper for feeding the sintered pellets. It has a fixed crushing arm and other movable by an eccentric drive shaft. The elliptical motion of the second arm crushes the pellets (9 - 11 mm) into the powder $<1 \text{ mm}$. A vacuum based dust collection system collects the radioactive dust formed in crushing operation. The other details of the jaw crusher can be found elsewhere [43].

2.2.2. Attritor Mill

The Attritor mill [43] consists of a vertical cylindrical stainless steel vessel,

Table 2. Typical properties of ThO_2 and $(\text{Th}, \text{U})\text{O}_2$ MOX sintered pellets.

Starting material identification	Material and composition	Diameter, Height (in mm)
SM-A	ThO_2	9 - 10, 5 - 10
SM-B	$(\text{Th}, 3.75\text{U})\text{O}_2$	9 - 10, 5 - 10
SM-C	$(\text{Th}, 10\text{U})\text{O}_2$	9 - 10, 5 - 10
SM-D	$(\text{Th}, 14\text{U})\text{O}_2$	9.7, 5 - 10
SM-E	$(\text{Th}, 30\text{U})\text{O}_2$	10 - 11, 10 - 11

central shaft and horizontal impellers made-up of hardened tool steel. The optimized size hardened chrome steel balls of diameter 6 mm were used as grinding media. The material was charged at 100 rpm into the attritor. The milling in the attritor was carried out for 40 min. at 200 rpm. The discharging of the material was carried out at 300 rpm.

2.2.3. Microwave Processing System

Indigenously developed microwave processing system of maximum microwave output power of 6 kW was used. The output power of the system can be continuously varied between 10% - 100%. The aqueous processing was carried out in a multimode applicator of volume nearly 60 liters. The microwave transmission up to the applicator is achieved through standard WR340 wave-guides from remote microwave generator. The system is equipped with real time temperature and power measurement during the processing. The other technical details of this system are described elsewhere [27].

2.3. Characterization Methods and Instruments

The bulk density of the intermediate products and powder was measured using graduated cylinder and a weighing balance following standard method [46]. The specific surface area of the powders was measured by Brunauer-Emmet-Teller (BET) physisorption model based N₂ adsorption technique [47] using Smart-SORB93[®] (M/s Smart Instruments Co., India). The O:M ratio is mole ratio of oxygen and heavy metal (where M is Th or Th+U) was determined by a thermogravimetric method involving gas equilibration technique [48]. The phase analysis was performed on EMMA[®] X-ray diffractometer (M/s GBC Sci. Eqpt., Australia) using Cu-K_α radiation. The residual carbon in the denitrated ThO₂ samples was determined by combustion following infrared absorptive measurement by CO₂ at 2349 and 770 cm⁻¹ [49]. The residual fluoride was determined in the pyrohydrolysate by fluoride ion selective electrode after pyro-hydrolysis of the sample [50].

2.4. Integrated Method of Recycling

2.4.1. Process Flow Sheet

The flow sheet for recycling of ThO₂ or (Th, U)O₂ fuel rejects by integrated method is shown in **Figure 1**. The sintered pellets were crushed using a jaw crusher to coarse powder. The coarse powder in case of ThO₂ was directly attritor milled and in case of (Th, U)O₂, it was subjected to air oxidation at 700°C for 4 h in conventional resistance furnace and subsequently for attritor milling. The attritor milling (40 min., 200 rpm) further resulted in micronisation of the coarse powder. The attritor milled powder was sieved through ASTM standard sieves.

The sieved powder (in batches) was taken for aqueous processing using microwave. It was dissolved in 16 M HNO₃ EMPARTA[®] (M/s Merck, Germany) in open quartz cylindrical vessels (height 280 mm and dia.75 mm) in microwave processing system. Several batches of 500 g of sieved powder in 1000 ml of

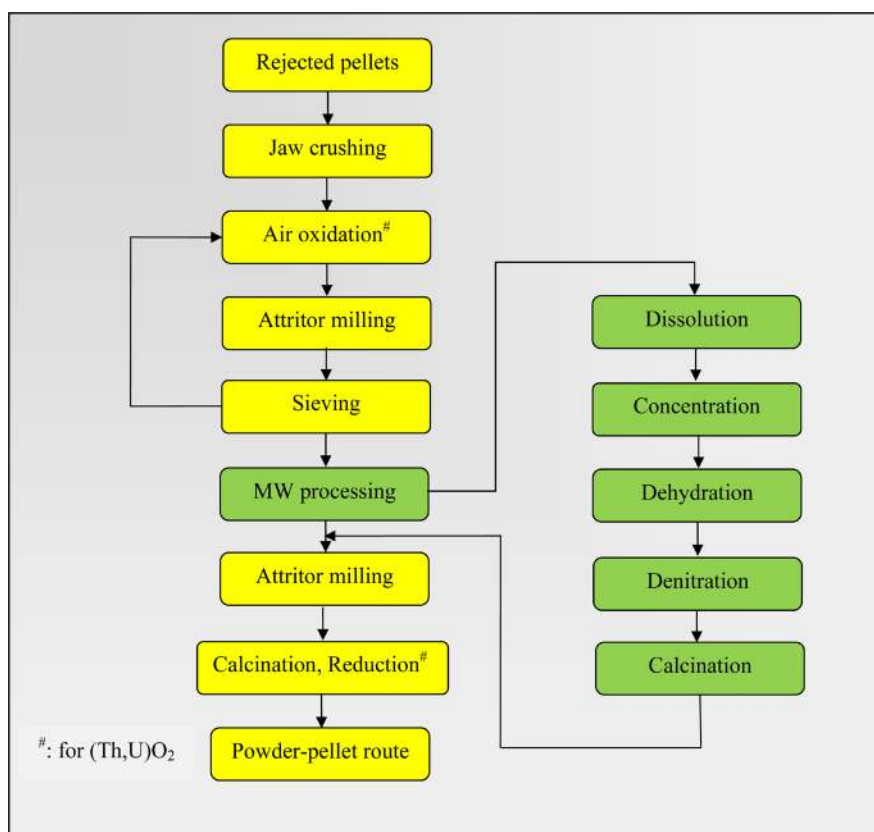


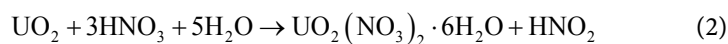
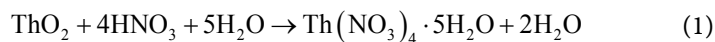
Figure 1. Flow sheet of the integrated process for recycling of ThO₂ based clean rejects.

HNO₃ were dissolved and denitrated. The typical temperature profile during microwave dissolution and denitration of a batch is shown in **Figure 2**. **Figure 2** also depicts the various stages of the process up to metal oxide conversion. The product obtained is low density, porous and dry cake of oxide or mixed oxide. The dry cake was removed from the process vessel using spatula in the form of clinkers. The clinkers were attritor milled and subjected to air calcination at 700°C, 2 h for ThO₂. The calcination and reduction (700°C, 4h) for (ThO₂, U₃O₈) was carried out.

2.4.2. Process Chemistry

1) Dissolution and Concentration

The attritor milled and sieved powder was dissolved in HNO₃ at 115°C - 120°C to form their soluble nitrates using catalyst HF as shown in Equation (1-2) [31] [32] [33] [51] [52]. The dissolved solution was further heated to concentrate and solidify by removal of excess H₂O and HNO₃. This resulted in formation of hydrated crystals of respective nitrates.



2) Dehydration and Denitration

In the process of dehydration, water of crystallisation of nitrates was removed

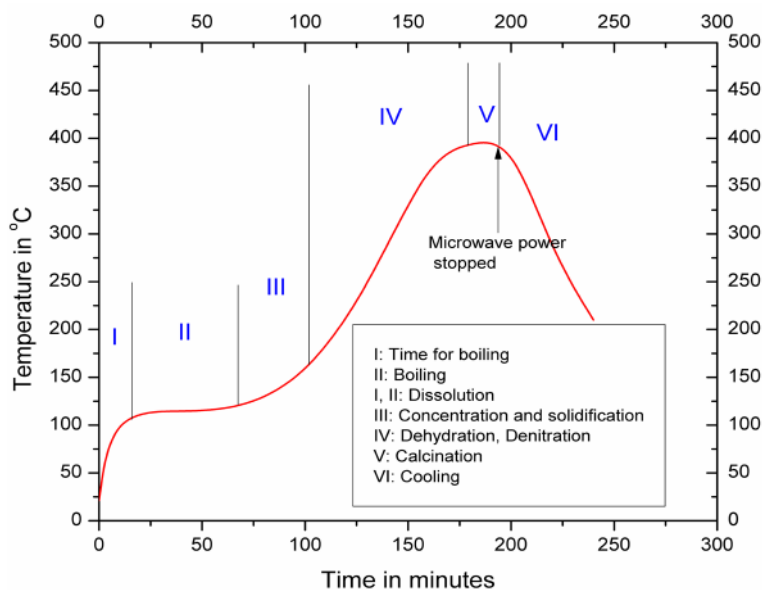
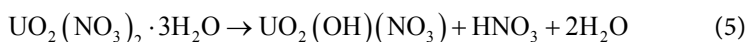
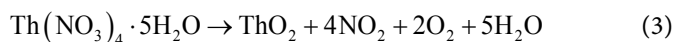


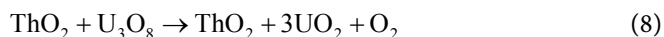
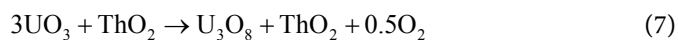
Figure 2. Temperature profile of microwave dissolution of ThO_2 and its oxidative denitration.

to get nitrates with reduced water of crystallisation above 120°C . The partially hydrated nitrates were decomposed to respective oxides or mixed oxide on further heating as described by Equation (3)-(6). The denitration reaction for thorium nitrate pentahydrate is shown by Equation (3) [53] [54]. The nitrogen dioxide (NO_2) combines with available H_2O and forms HNO_3 . After partial dehydration, the uranyl nitrate trihydrate undergoes oxidative denitration to form UO_3 through formation of uranyl hydroxy nitrate compound as shown by Equation (4-6) [25] [55] [56].



3) Calcination and Reduction

The mixed oxide product obtained after denitration was porous and was further calcined in air converting UO_3 into U_3O_8 in the same process vessel as represented by Equation (7) [57]. Another, calcination (700°C , 2 h) was carried out after attritor milling for removal of residual nitrates, H_2O , carbonaceous impurities (if any) and quantitative conversion of UO_3 into U_3O_8 . The calcined material was reduced in flowing ($\text{N}_2 + 7\% \text{H}_2$) atmosphere at 700°C , 4 h and the reduction reaction for (ThO_2 , U_3O_8) is shown by Equation (8) [58] [59]. The reduction step for calcined ThO_2 was not carried out.



3. Results and Discussion

3.1. Integrated Process for Recycling of Thoria Based MOX

3.1.1. Mechanical Micronisation

Mechanical micronisation using jaw crusher and attritor mill produces powder from the sintered pellets. The particle size and the surface area data after different stages of the integrated process (**Figure 1**) are recorded in **Table 3**. The sieve analysis was carried out for powders after jaw crushing, air oxidation and attritor milling of sintered rejects using ASTM standard sieves. The values in the parenthesis show (**Table 3**) the wt. fraction of powder in the corresponding particle size range during sieve analysis. The laser particle size analyser Cilas 1190 LD (M/s Cilas, France) was used for microwave denitrated and attritor milled powders and values recorded are average particle size (**Table 3**). The powder obtained after jaw crushing operation (**Table 3**) was compared with the sinterable grade feed powder (**Table 1**). The specific surface area and particle size were found to be poor, which may not be sintered to the densities required for an oxide fuel typically > 90% of TD. Further improvement in the powder physical properties was carried out by attritor milling. Though, the powder so obtained also showed better surface area and smaller particle size as compared to the precursors (**Table 3**). However, it cannot be recommended as sinterable grade (**Table 1**). The extended micronisation using attritor mill may be useful however, this leads to prolonged processing cycle. More importantly, the issues of concern are the impurity pick-up due to wear of attrition media and the associated radioactive dust hazard in the extended micronisation. The dust raised frequently chokes the HEPA filters calling their frequent replacement. High energy ball or attritor milling is useful however, is energy intensive. Thus, mechanically micronized powder (after attritor milling, 40 min) so obtained is not suitable as fuel feed material. Else, mechanically micronized powder can be mixed with fresh feed powders for fuel fabrication. Mishra *et al.* [44] reports the addition of maximum 15 wt% of the (Th, 30%U)₂O₇ MOX sintered rejects recycled via mechanical micronisation process (crushed and attritor milled) for fabrication of fuel.

Table 3. Typical properties of recycled powder at different stages of integrated process.

Process step	ThO ₂		(Th,14%U) ₂ O ₇	
	Particle size	Specific surface area (m ² .g ⁻¹)	Particle size	Specific surface area (m ² .g ⁻¹)
Jaw crushing	0.9 - 1 mm (>0.9)	< 1	0.9 - 1 mm (>0.9)	< 1
Air oxidation	---	---	700 - 800 μm (>0.8)	1.12
Attritor milling	180 - 250 μm (>0.9)	1.6	125 - 150 μm (>0.9)	1.7
Microwave denitration and milling	1.7 μm	3.5	1.6 μm	5.0
Microwave denitration using PVA and milling	1.5 μm	7.4	1.42 μm	7.7

3.1.2. Air Oxidation

The conventional oxidative or thermo-mechanical pulverization techniques have been employed in recycling of defective UO_2 fuel pellets for long [18]-[24]. A large (~36%) volumetric increase resulting from oxidation of face centered cubic (FCC) UO_2 to orthorhombic U_3O_8 leads to generation of internal stresses and hence pulverization of sintered compacts. The UO_2 to U_3O_8 transformation has been thoroughly studied and proceeds via formation of intermediates $\text{U}_3\text{O}_7/\text{U}_4\text{O}_9$ [30].

The oxidation of ThO_2 owing single oxidation state (+4) is not feasible like UO_2 [29]. However, presence of UO_2 in the ThO_2 matrix has caused its oxidation thus giving $(\text{Th}, \text{U})\text{O}_{2+x}$. **Figure 3** shows the increase in the % oxidation in various $(\text{Th}, \text{U})\text{O}_2$ MOX in the range of UO_2 from 0 to 30 wt%. The % oxidation was calculated using the method followed by G. Singh *et al.* [23] based on the O:M ratio of the initial and final oxidized material. It represents the percentage with respect to the theoretical ultimately achievable oxidation for a given composition. The O:M of ThO_2 is non-variable upon oxidation and taken as 2.00.

It is evident from the **Figure 3** that as UO_2 content increases in the MOX, the % oxidation increases during air oxidation (after jaw crushing). The content of UO_2 , thus steers the oxidation behavior of $(\text{Th}, \text{U})\text{O}_2$ matrix. The rate of oxidation of $(\text{Th}, \text{U})\text{O}_2$ further depends upon several factors alike oxidation UO_2 and $(\text{U}, \text{Pu})\text{O}_2$ [23] [30]. The surface area, particle size, grain size, density, temperature and oxygen partial pressure are key parameters governing the oxidation kinetics. The physical form of the MOX plays a crucial role in the oxidation process. The powder form gives more oxidation than solid pellets [23]. Thus, oxidation step was introduced after jaw crushing in the integrated process (**Figure 1**) for $(\text{Th}, \text{U})\text{O}_2$ recycling. However, oxidation process was not carried

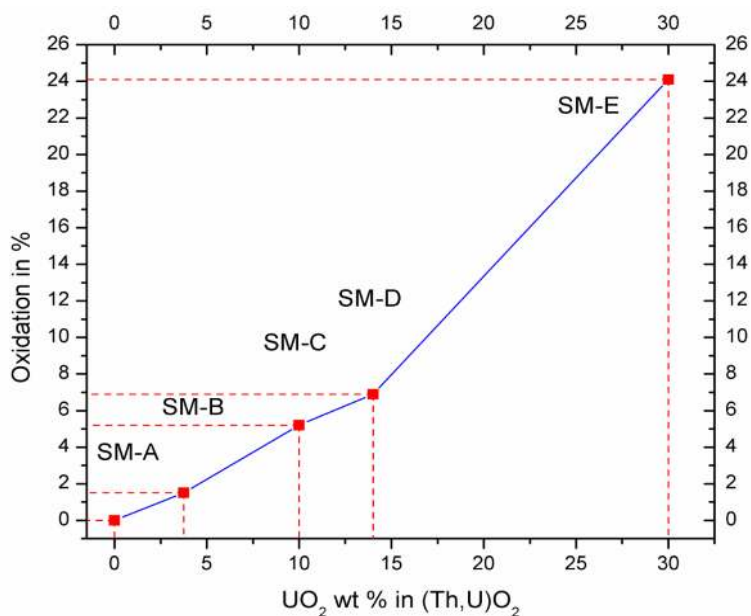


Figure 3. Variation in % oxidation as function of UO_2 content in $(\text{Th}, \text{U})\text{O}_2$.

out for recycling of ThO₂ sintered pellets in the integrated process (**Figure 1**). It is also concluded from **Table 3** that the air oxidation of jaw crushed (Th, 14% U)O₂ powder improves the specific surface area and reduces the particle size. The particle size and specific surface area of jaw crushed (Th, 30%U)O₂ were 0.9 - 1 mm (>0.9 wt. fraction) and <1 m².g⁻¹ respectively and after air oxidation were 600 - 700 μm (>0.8 wt. fraction) and 1.8 m².g⁻¹ respectively. This was attributed to oxidation of (Th, U)O₂ to (Th, U)O_{2+x} due to presence of uranium. Higher the UO₂ content in (Th, U)O₂, more is the % oxidation (**Figure 3**). This in turn improves the powder properties (surface area and particle size) and hence the sinterability. The oxidation of UO₂ to U₃O₈ decreases the density thereby increasing the surface area and reducing the particle size [30] [60]. The sinterability can further be increased by following multiple oxidation-reduction cycles [60].

3.1.3. Dissolution and Denitration Using Microwave

The applicability of microwave dissolution and denitration is based upon the microwave coupling behavior of the precursors and compounds that are formed in the course of the process. H₂O and HNO₃ are strong couplers at microwave frequency 2450 MHz [61] [62]. UO₂ and U₃O₈ are excellent microwave absorbers [63] [64]. The UO₃ and ThO₂ are weak absorbers [25] [39] [65]. However, the presence of other absorbing materials raises their temperature. As the temperature increases, UO₃ transforms to U₃O₈ which is strong absorbing material. A small amount of U₃O₈ is sufficient for transforming the entire mass of UO₃ into U₃O₈ or else a pinch of U₃O₈ is intentionally added as microwave absorbing seed [66]. The temperature raises the microwave dissipation factor and thereby the absorption increases along with the temperature [67] [68]. The microwave denitration of thorium nitrate is feasible [36] [37] [38]. The mechanical micronisation and/or air oxidation increase the surface area and thus enhance the dissolution of ThO₂ tremendously. Thus, micronized and/or air oxidized powder was used for dissolution-denitration (**Figure 1**).

The effect of various parameters influencing the powder properties of denitrated product was thoroughly studied. Based on the multi-parametric study, the optimized conditions were selected to deliver sinterable powder. The influence of the various parameters on the cake bulk density (CBD), powder bulk density (PBD) and BET surface area is depicted in **Figure 4**.

1) Effect of method of heating

The aqueous processing involving dissolution-denitration was carried out in microwave and conventional hotplate. It was found that the specific surface area in the microwave denitrated product was higher than the hot plate processed (**Figure 4(a)**). The cake and powder bulk densities were found to be lower in microwave denitrated ThO₂. This was attributed to the direct material and bulk heating associated to microwave contrary to conventional. The solidification (**Figure 2**) occurs quickly in case of microwave throughout the bulk. Thus, the evolution of gases and vapours during solidification and subsequent steps are many more times larger which forms the cake to be porous. The shape of the

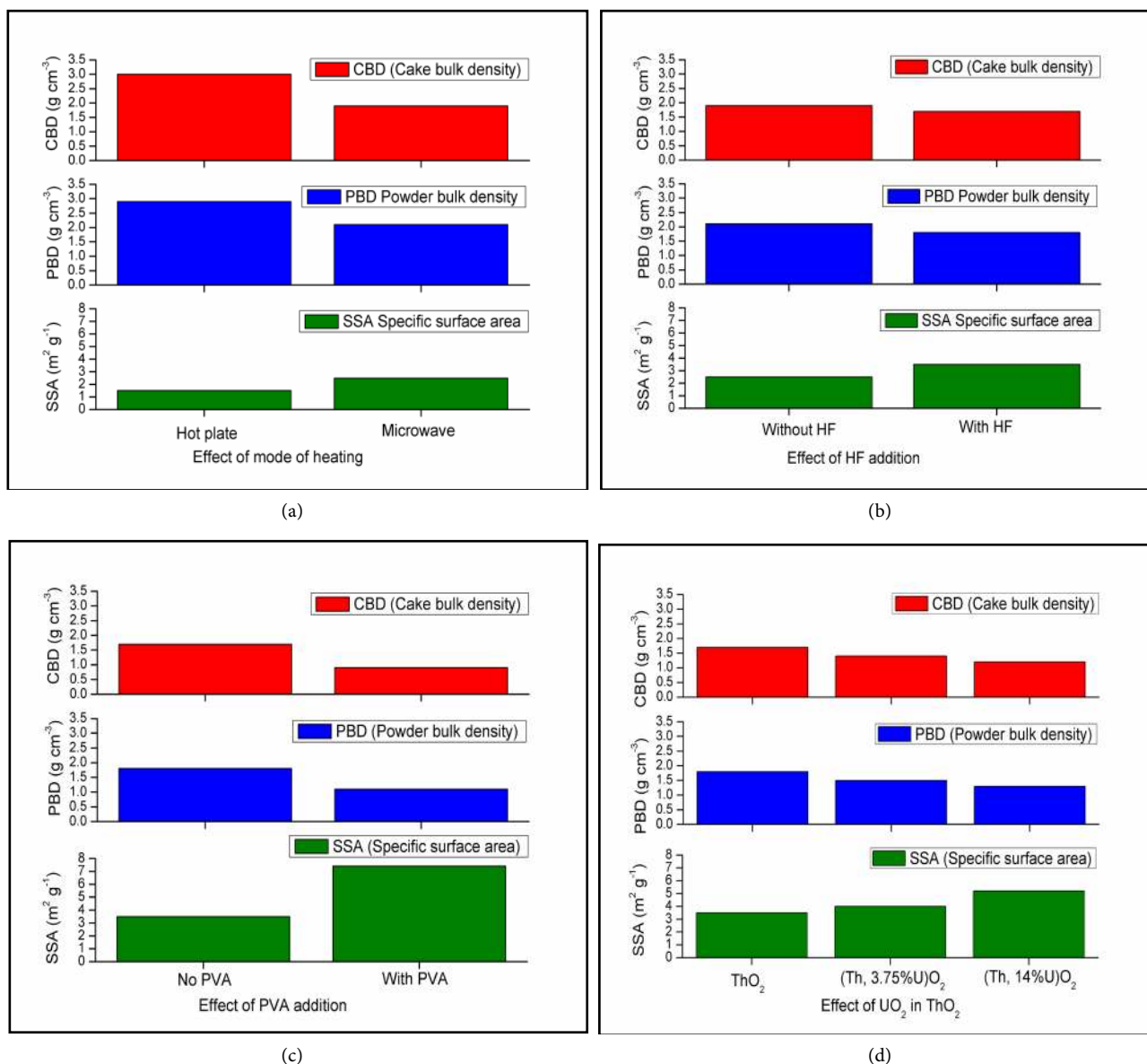


Figure 4. Influence of various parameters on the physical properties of denitrated product.

denitration process vessel plays a key role in enhancing the cake porosity [22]. Long narrow neck vessel (used in the present work) provides small area for outgoing gases and vapours (nitrogen oxides called NO_x, HNO₃, H₂O etc.). However, the heat conducts from the surface of the material in the hot plate. The solidification starts from the surface and take longer to reach up to the core of the material. Thus, there is no quick evolution of gaseous products during solidification. Therefore, the product formed in the in hot plate denitration possess high bulk density (thus, low porosity) and low surface area. The increase in the surface area in microwave denitration is due to de-agglomeration of particles because of quick evolution of gases and vapours, which prevents the nucleation and the particle size growth. These outcomes are in line with the findings by Chandramouli *et al.* [39] where they found very low specific surface area of the

ThO₂ powder synthesized via hot plate denitration. However, the surface area was higher when the denitration was performed using microwave. Thus, the microwave denitration was embedded in the integrated process (**Figure 1**) to improve the powder physical properties.

2) Effect of HF addition

To investigate the effect of completely dissolved ThO₂ on the microwave denitrated powder, the microwave dissolution of the attritor milled powder was performed in HNO₃ in the presence and absence of HF. The HF (0.025 M) in HNO₃ was added to increase the ThO₂ dissolution and. **Figure 4(b)** reveals that the dissolved ThO₂ improves the specific surface area of the microwave denitrated powder to a greater extent. The bulk densities of cake and powder were found to be lower in case of the microwave denitrated ThO₂ from completely dissolved solution. Without fluoride the solution contained undissolved and sintered ThO₂ particles which subsequent to the denitration remain in the dense form. These undissolved and dense particles are responsible for poor powder properties. Thus, complete dissolution is ascertained before concentration and solidification (**Figure 2**). Therefore, in all MOX batch recycling experiments using integrated method (**Figure 1**), HF was added for dissolution.

However, it was seen that the denitrated product without HF has slightly better surface area (2.1 m²·g⁻¹) (**Figure 4(b)**) than the starting micronized ThO₂ (1.6 m²·g⁻¹) (**Table 3**). This may be attributed to the presence of very small crystallites of ThO₂ in micronized ThO₂ powder. The ThO₂ powder with small crystallites (<56 Å) undergoes complete dissolution without fluoride [51] [54]. More the fraction of such small crystallites in the micronized powder, higher will be the extent of dissolution and subsequently the better powder properties. However, no attempt has been made to see the presence of such crystallites in the present work. The future work may be pursued in this direction.

3) Effect of PVA addition

Further improvement in the characteristics of the microwave denitrated powder was achieved by adding PVA to the completely dissolved ThO₂ (using HF). The combustion synthesis of ThO₂ from its aqueous nitrate solution using PVA has already been reported [39] [40] [41] [42]. There occurred a vigorous reaction between PVA as organic fuel and HNO₃ as oxidant. The reaction is violent because of the exothermicity of the denitration and oxidation of the PVA. The product of denitration is highly porous because of the evolution of excessive gaseous products (CO₂, NO_x etc.). PVA provides a surface for the denitration while preventing aggregation and sintering of particles, thereby helping the formation and stabilisation of the small crystallites of the powders. Thus, powder obtained has high surface area (>7 m²·g⁻¹) as shown in **Figure 4(c)** and **Table 3**. The ratio of the organic fuel and oxidant are crucial in deciding the crystallite size and hence the powder properties. The aqueous solution of PVA (8% - 10%) was mixed with aqueous thorium nitrate solution obtained after dissolution of attritor milled ThO₂ in 1:2 volume ratio in a batch of denitration after dissolu-

tion (**Figure 2**). The specific surface area and the bulk cake and powder densities of the ThO_2 so obtained are shown in **Figure 4(c)**. The large surface area of the powder obtained is in line the findings by researchers [39] [40] [41] [42]. The further studies are directed towards investigation of the effect of concentration of thorium and/or uranium, nitric acid molarity, ratio of fuel to oxidant etc. and are not in the scope of present work.

4) Effect of UO_2 in ThO_2

A profound effect on the surface area and bulk density of the denitrated product was found due to presence of UO_2 in ThO_2 as shown in **Figure 4(d)**. This is because the denitrated product contains UO_3 . The density of UO_3 is lower ($6.69 - 8.62 \text{ g}\cdot\text{cm}^{-3}$) as compared to ThO_2 ($10 \text{ g}\cdot\text{cm}^{-3}$) depending upon the allotrope formed [57]. It was reported that the microwave denitration of uranyl nitrate produces $\beta\text{-UO}_3$ [55] [56]. The studies have shown that for denitration of uranyl nitrate, the crystal structure of the oxide product depend upon temperature and heating rate with desired porous product formed at faster heating rates [69]. The calcination of UO_3 further gives voluminous U_3O_8 having density $8.326 - 8.395 \text{ g}\cdot\text{cm}^{-3}$ [54]. The surface area and bulk density of cake and powder in the microwave denitrated (Th, 14%U) O_2 are shown in **Figure 4(d)**. Thus, **Figure 4(d)** revealed that the bulk density decreases and surface area increases as UO_2 content increases in the (Th, U) O_2 .

3.2. X-Ray Diffraction Analysis

The powder X-ray diffractograms of sintered ThO_2 powder (after micronisation of sintered ThO_2 pellets; SM-A) and microwave denitrated ThO_2 powder (dissolved using HF) are shown in **Figure 5**. The analysis of the patterns shows that the peaks are sharper for sintered ThO_2 powder **Figure 5(a)** showing more crystallinity due to sintering. The XRD pattern of denitrated ThO_2 in **Figure 5(b)** indicates that the microwave denitration of thorium nitrate give well developed crystalline thoria. However, the peaks are broader than the sintered ThO_2 . The calcination was carried out after microwave denitration (**Figure 1**) to remove residual volatiles (nitrate, water etc.). This further leads to the crystal growth and improves crystallinity (giving sharper peaks) [54]. The calcination in denitrated (ThO_2 , U_3O_8) mixture additionally converts residual UO_3 into U_3O_8 quantitatively.

3.3. Suitability Assessment of the Recycled Powder

Comparison of the physical properties of the recycled ThO_2 powder (**Table 3**) and standard sinterable ThO_2 (**Table 1**) reveals that the recycled powder obtained through the integrated process (**Figure 1**) can be re-used for fuel fabrication. The recycled ThO_2 powder has specific surface area of $3.5 \text{ m}^2\cdot\text{g}^{-1}$ (direct microwave denitration) and $7.4 \text{ m}^2\cdot\text{g}^{-1}$ (microwave denitration with PVA) with average particle size $1.0 - 2.0 \mu\text{m}$. The powder properties were found to further increase due to presence of uranium (**Table 3**, **Figure 4**) in ThO_2 matrix as the case of (Th, U) O_2 .

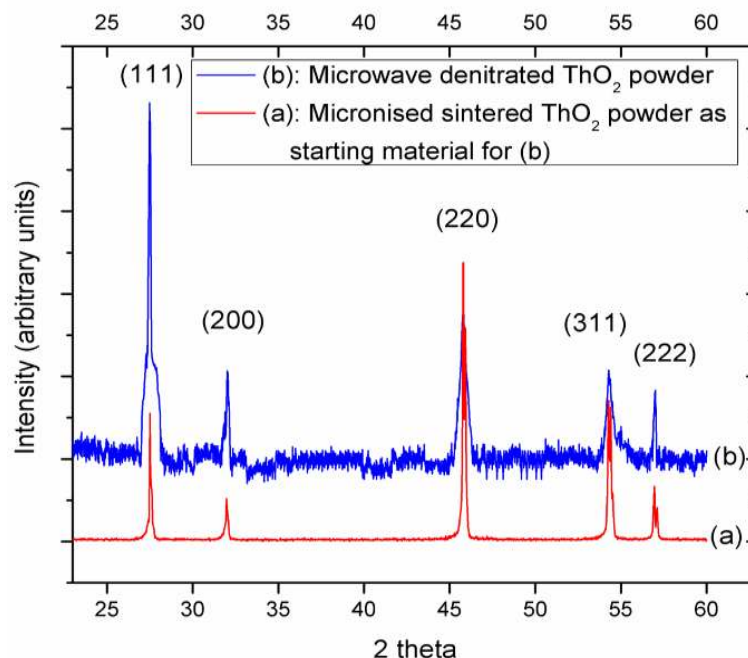


Figure 5. X-ray diffractogram of micronized sintered and microwave denitrated ThO_2 powder

The powder bulk density of the as received ThO_2 powder from oxalate route (**Table 1**) is lower ($0.85 \text{ g}\cdot\text{cm}^{-3}$) if compared to that of recycled ThO_2 with $1.7 \text{ g}\cdot\text{cm}^{-3}$ (**Figure 4(b)**). The microwave denitration with PVA further reduces the powder bulk density upto $0.9 \text{ g}\cdot\text{cm}^{-3}$ (**Figure 4(c)**). This is assigned to the platelet morphology of the oxalate derived ThO_2 where packing fraction is lesser [34] [43] [44]. The attritor milling breaks the platelet morphology converting it to spherical, thereby increasing the bulk density and surface area. The oxide or mixed oxide product in aqueous processing using microwave (**Figure 1**) is obtained in the form of clinkers. The clinkers are milled into fine powder to be used in fuel fabrication. The attritor milling is required prior to calcination and/or reduction. The morphological properties were not investigated in the present study. The future studies are being directed towards examining these aspects. However, the attritor milling of the microwave denitrated clinkers is carried out in integrated process (**Figure 1**) resulting spherical morphology of the recycled powder [34] [43] [44] and thus, higher powder bulk density ($1.7 \text{ g}\cdot\text{cm}^{-3}$).

Fluoride is essentially added for complete dissolution of ThO_2 in HNO_3 . PVA is added for obtaining improved powder physical properties during aqueous processing using microwave (**Figure 1**). The concentration of carbon and fluoride in the recycled powder is required to be measured for suitability assessment. **Table 4** records the values of carbon and fluoride in the recycled ThO_2 via integrated process (**Figure 1**). The values for standard oxalate route derived ThO_2 are also recorded for comparative evaluation. The carbon and fluoride as impurities gets decreased to acceptable levels (in the nuclear fuel) during the fuel fabrication operations as sintering ($1600^\circ\text{C} - 1800^\circ\text{C}$) and vacuum degassing.

Table 4. Carbon and fluoride in the intermediate products and final powder.

Material	Process stage	C ($\mu\text{g}\cdot\text{g}^{-1}$)	F ($\mu\text{g}\cdot\text{g}^{-1}$)
Standard ThO ₂	Calcination	756	16
Recycled ThO ₂ from SM-A	Mechanical micronisation	285	6
	Denitration with PVA and calcination	635	14

However, the fluoride is required to be in controlled amount due to its corrosive nature.

3.4. Industrial Scale-Up of the Process

The integrated process (**Figure 1**) can be easily scaled-up to feed industrial requirements. The throughput of the dry processing steps as micronisation and oxidation can be enhanced by capacity of the equipments. However, the aqueous processing possesses some concerns. The standard method of sinterable ThO₂ from sintered rejects production involving oxalate precipitation-calcination may be followed further. However, this produces large liquid wastes and is not economic (time and cost). Thus, a method is desired by the fuel fabricators which can produce sinterable grade ThO₂ consistently along with negligible waste generation, minimum processing time, simple process equipments, easy maintenance and amenable for automation and remotisation. So, microwave denitration was an obvious choice. However, the present method is developed for chemically clean sintered rejects. The impure rejects may require solvent extraction for removal of impurities post dissolution and prior to denitration. In the aqueous processing, a batch size is controlled by the criticality evaluation of the process. An additional safety factor is required to be given to operational or human errors. The recycling of ThO₂ sintered pellets by integrated process (**Figure 1**) may not require criticality safety analysis. So the batch size may be decided by equipment size and operational ease. However, this evaluation is required for aqueous processing of ThO₂-LEU and (Th, U²³³)O₂. The continuous denitration may be adapted to cater the needs on industrial scale. The microwaves directly interact the absorbing material which is required to be heated and can be projected (through waveguides) from remote generators. The maintenance required is outside the process equipments offering a huge ease to the operators. The present method is simple and fast, however, the processing time can further be reduced by adapting microwave processing comprehensively in the various operations replacing conventional heating methods. For example, air oxidation, calcination and reduction using microwave heating were reported time and cost economic [70].

4. Conclusions

An integrated process was developed for recycling the chemically clean, rejected ThO₂ and (Th_{1-y},U_y)O₂ (y; 0 - 30 wt%) sintered pellets in connection with AHWR and AHWR LEU-300 fuel. The process includes integration of three ba-

sic methodologies of recycling namely mechanical micronisation, thermal oxidation and microwave dissolution-denitration. The mechanical micronisation using jaw crusher and attritor milling of the sintered ThO₂ pellets produced ThO₂ powder which cannot be used for re-fabrication of the fuel on 100% basis due to its low sinterability as evident from its surface area (1.6 m²·g⁻¹) and particle size (180 - 250 μm). However, in (Th, U)O₂ MOX, air oxidation step was introduced between jaw crushing and attritor milling. (Th, U)O₂ with UO₂ content 3.75 wt% and 14 wt% by this combination could not produce sinterable powder. However, (Th, U)O₂ having 30 wt% UO₂ combining two methodologies delivered sinterable powder which can be recycled 100% in a batch giving SRR of 1.

To enhance the physical properties of the recycled powder obtained from the combination of comminution and/or oxidation processes, the aqueous processing using microwave dissolution and denitration was embedded in the integrated process. The microwave dissolution-denitration using HF and PVA produced highly sinterable recycled powder which can be used 100% for fuel re-fabrication. Denitration using microwave improves the powder physical properties as compared to hot plate denitration. The completely dissolved ThO₂ (using HF) results better powder properties as compared to partially dissolved ThO₂. The addition of PVA during denitration tremendously increased the specific surface area of the denitrated ThO₂ (>7 m²·g⁻¹). The presence of UO₂ in the MOX produced better recycled powder as compared to ThO₂ as starting material. The comparison of physical and chemical properties of the recycled powder via integrated process demonstrates its suitability for fuel re-fabrication.

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