



Microwave based oxidation process for recycling the off-specification (U,Pu)O₂ fuel pellets



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HIGHLIGHTS

- A process for recycling the off-specification (U,Pu)O₂ sintered fuel pellets of fast reactors was demonstrated.
- The method is a two-stage, single cycle process based on oxidative pulverization of MOX pellets using 2450 MHz microwave.
- The process demonstrated utilization of recycled powder with SRR of 1.

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ABSTRACT

This paper reports development of a process named MicroWave Direct Oxidation (MWDO) for recycling the off-specification (U,Pu)O₂ mixed oxide (MOX) fuel pellets generated during fabrication of typical fast reactor fuels. MWDO is a two-stage, single-cycle process based on oxidative pulverisation of pellets using 2450 MHz microwave. The powder sinterability was evaluated by bulk density and BET specific surface area. The oxidised powders were analyzed for phases using XRD and stoichiometry by thermogravimetry. The sinterability was significantly enhanced by carrying out oxidation in higher oxygen partial pressure and by subjecting MOX to multiple micronisation-oxidation cycles. After three cycles, the recycled powder from (U,28%Pu)O₂ resulted surface area >3 m²/g and 100% re-used for MOX fabrication. The flow sheet was developed for maximum utilization of recycled powder describable by a parameter called Scrap Recycling Ratio (SRR). The process demonstrates smaller processing cycle, better powder properties and higher oxidative pulverisation over conventional method.

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1. Introduction

The plutonium obtained from natural UO₂ fueled Pressurized Heavy Water Reactors (PHWRs) was envisaged to be used in Fast Breeder Reactors (FBRs) in the second stage of the Indian Nuclear Power Programme [1]. The plutonium as (U,Pu)O₂ mixed oxide (MOX) fuel in the commercial FBRs is now being utilized for increasing the plutonium fuel inventory following a closed nuclear fuel cycle [1]. The fabrication of high plutonia MOX fuel [2] for hybrid core of the Fast Breeder Test Reactor (FBTR) and MOX fuel for first Indian commercial fast reactor viz. Prototype Fast Breeder Reactor (PFBR) was carried at Advanced Fuel Fabrication Facility (AFFF), Tarapur, India [3]. The MOX fuel for FBTR had composition 44 wt% PuO₂ along with deeply depleted UO₂ (DDUO₂). The PFBR MOX fuel has two compositions as 21 wt% and 28 wt% PuO₂ with

DDUO₂. The PFBR first reactor core required a large number nearly 40000 fuel elements and approximately 10 t of MOX fuel [3,4]. A few important technical specifications of MOX fuel for PFBR are recorded in Table 1 and that for FBTR can be referred elsewhere [2]. The MOX fuel was fabricated by standard powder metallurgical route following compaction and sintering. The two compositions were completed in separate campaigns to avoid compositional cross mixing and hence the rejection of fuel elements.

During fabrication of MOX fuel, the fuel pellets got rejected at various process stages attributable to non-compliance of numerous physical or chemical specifications (Table 1). To name a few: sinter density, Pu agglomerates, O/(U + Pu) ratio, dimensions, impurity content, composition and physical defects like cracks, chips, blister, pits, dents, end-chipping etc. Fast reactor fuels often present certain plutonium heterogeneity and variation in O/(U + Pu) ratios. Pu heterogeneity is deleterious as it can produce local hot spots (in-pile) and difficulty in dissolution (during reprocessing). The methods used to detect and evaluate the Pu or Pu-rich agglomerates in the MOX are alpha-autoradiography and neutron

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Table 1
Important specifications of (U,Pu)₂O₇ annular MOX fuel for Indian PFBR.

Technical parameter	Specification
Outer diameter of pellet	5.55 ± 0.05 mm
Inner diameter of pellet	1.8 ± 0.2 mm
Length of pellet	7.0 mm (nominal)
PuO ₂ content (nominal)	21 ± 1% and 28 ± 1%
O/(U + Pu) ratio	1.98 ± 0.02
Total non-volatile impurity content	≤5000 ppm
Pu agglomerate	≤100 μm
Sintered pellet density	94 ± 3% of TD

radiography. The Pu based MOX fuels are fabricated hypostoichiometric O/(U + Pu) < 2.00 (Table 1) because they are more oxidizing compared to uranium fission, however this brings down their thermal conductivity significantly. Sometimes, the sintered pellet density may come below the specified limit depending upon the initial powder properties and pellet green density. Consequently, defective and unacceptable sintered MOX pellets were being accumulated. These off-specification fuel pellets are further divided in two categories as: 1) clean rejected oxide (CRO) or clean scrap and 2) dirty rejected oxide (DRO) or impure scrap, depending upon the impurity content [5,6]. We have recently reported the average shares of various MOX scrap getting generated during fuel manufacturing along with the average acceptance [7]. Among the various types of MOX scrap, the clean scrap contributed largest share nearly 20–22% of a batch throughput. Interestingly, these MOX scraps contain significant amount of Pu, demanding their efficient recycling. A recycling process involves co-recovery of UO₂ and PuO₂ and subsequently its reuse for the fabrication of fuel. The immediate recycling of Pu bearing scrap becomes essential taking into consideration the facts such as total fissile content degradation, personnel exposure associated to long term in-house storage and fresh PuO₂ demand-supply constraints to meet the production targets. Pu²⁴¹ (T_{1/2} = 14.2 years) the fissile isotope of Pu decays primarily by beta emission (99.998%) to non-fissile Am²⁴¹. Thus, Am²⁴¹ increases progressively with ageing of Pu, rendering high radiation dose (60 keV gamma), high specific alpha activity (1.184 × 10¹¹ Bq/g) and high specific heat (114 W/kg) [8,9]. Consequently, management of Pu containing MOX scrap becomes an important component of (U,Pu)₂O₇ fuel fabrication facility looking into the economic and operating personnel exposure impacts. Therefore, development of methods was pursued to efficiently and quickly recycle the MOX defective fuel pellets.

The attributes of a good recycling process are: fast processing, complete recyclability, sinterable grade powder production, multiple recyclability and minimum waste generation. In the area of recycling of the defective UO₂ fuel pellets, extensive work has been reported [10–17] and processes are established. However, comparatively lesser work has been carried out on recycling of (U, Pu)₂O₇ fuel scrap [18–24] especially containing high PuO₂ content as encountered in fabrication of fast reactor fuel. The recycling methods further are categorized as dry and wet processes. Interestingly, the dry routes of recycling offer many advantages over wet chemical processing routes like higher production rate, lesser number of process steps, no liquid waste generation etc.

Usually, powders obtained by dry route recycling has low sinterability [10,12,16] compared to fresh feed powder prepared by conventional methods [25–27]. Thus, most of the recycling methods and approaches do not employ 100% recycled powder and fresh powder addition is carried out usually to enhance the sinterability. However, fuel fabricators are working continuously to develop and evolve methods for recycling of defective fuel pellets which can deliver sinterable grade powder consistently with either equivalent or better powder characteristics as that of fresh powder.

This 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 sintering promoters and low rejection rate. The characteristics of sinterable grade UO₂ obtained via ammonium diuranate (ADU) process and PuO₂ by oxalate precipitation process are recorded in Table 2 [8,14,28–31].

The conventional method of recycling of defective UO₂ fuel pellets is based on oxidatively pulverizing them between 400 and 700 °C to obtain fine U₃O₈ powder. Recently, Mernache et al. reports a recycling process involving defective UO₂ pellets to undergo several oxidation-reduction cycles thereby obtaining sinterable UO₂ [14]. The recycled powder either U₃O₈ or UO₂ (after reduction) is blended with fresh UO₂ and can be compacted and sintered like fresh UO₂ powder. However, the fraction of the recycled U₃O₈ powder is generally not higher than 10 wt% due to poor sinterability [10,12,16] and other defects. The direct compaction and sintering of U₃O₈ is not advisable because of the large volumetric change (~36%) accompanied from orthorhombic U₃O₈ to face centered cubic (FCC) UO₂ transformation [32]. This result in lowering of density, formation of grape like pore clusters and evolution of oxygen leaving behind enormous porosities and/or cracks [12,33].

The high content of PuO₂ in a fast reactor nuclear fuel (above 20 wt%) adds more complexities in recycling of defective fuel pellets. The addition of PuO₂ to UO₂ in the MOX reduces its ability to undergo oxidation and thus making oxidative pulverisation based methods difficult. The PuO₂ is the most stable oxide of Pu and resist its further oxidation [8]. However, the dry recycling methods based upon oxidative or thermo-mechanical pulverisation of (U,Pu)₂O₇ MOX were reported by conventional heating [18–21,23]. Around 40% of the rejected MOX pellets from MICRONISSATION and MASTER BLEND (MIMAS) process are recycled using a dry process [21]. Mechanical pulverisation was coupled with oxidative in a thermo-mechanical method for dry recycling of low Pu content (<3 wt%) MOX [18]. Similarly, our recent study showed that MOX containing PuO₂ < 3 wt% was easily oxidisable [23]. The oxidation of MOX sintered pellets containing small amounts of Pu (3.2 wt%) showed appreciable degree of pulverisation between 400 and 600 °C. However, no pulverisation was observed in fast breeder reactor MOX pellets containing Pu ~30 wt% [34]. Tanaka et al. demonstrated that oxidation of MOX containing 30 wt% Pu did not disintegrate the pellet shape; however, MO₂ + x formation was observed [35]. MOX pellets containing PuO₂ > 20 wt% were unable to disintegrate into powder by conventional thermal treatment in air despite employing multiple oxidation-reduction steps and higher oxygen potential and required mechanical crushing [23].

Microwaves cause instant high temperature attributable to thermal runaways in UO₂ pellets leading to cracking of pellets during sintering [22,36]. This observation was therefore investigated for oxidative pulverisation of defective MOX pellets generated in fast reactor fuel fabrication using microwave in the present work. The direct oxidation of the off-specification MOX pellets was carried out using microwave (2450 MHz). The process was named as MicroWave Direct Oxidation (MWDO) process. MWDO is a two-stage single cycle process where in the stage-I, temperature of 800 °C was achieved rapidly with very high temperature rise rate (80 °C s⁻¹) aiming at cracking of pellets. A lower temperature for longer time (550 °C, 3 h) was kept in the stage-II of process to give sufficient time for oxidation reaction. The detailed experimental work consists of batch oxidation experiments, characterization of materials, suitability assessment of recycled powder, flow sheet development for 100% recycling, fuel fabrication and comparative analysis. The recycled feed materials were characterized for specific surface area, phase using X-ray diffractometry (XRD), bulk density and oxygen to metal (O/M) ratio. A parameter called scrap recycling ratio (SRR) was defined to describe the fraction of recycled material

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