PRODUCTION OF MOX PELLETS FROM PLUTONIA AND MIXED OXIDE POWDERS PREPARED BY DIRECT THERMAL DENITRATION

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ABSTRACT

An important aspect of British Nuclear Fuels Advanced Reprocessing programme is the investigation of alternative finishing processes which may contribute to reducing the cost, environmental impact, and radiation dose to maintenance workers, of recycling nuclear fuel. Product finishing, the conversion of aqueous uranium-plutonium nitrate solutions into oxide, by thermal de-nitration (TDN) has potentially the minimum number of process stages and requires least effluent treatment. In the past these benefits have been marred by the relatively poor powder quality of the products, and consequent failure to meet existing specifications for pellets. This paper describes development of a variant of the TDN route which meets existing product and pellet specification.

The oxides; PuO_2, $(U,30\%Pu)O_2$ and $(U,6\%Pu)O_2$, were produced by thermal denitration of their respective di-hydrates in a rotating furnace purged with an air atmosphere. These were blended down to nominally 6 % Pu by milling with UO_2 powder. The as-produced powders were free flowing, free from fused lumps, and MOX from the powders gave high tap densities (>3 gcm^{-3}), high green pellet densities (> 7 gcm^{-3}), and high sintered pellet densities (>10.45 gcm^{-3}). The grain size in the pellets increased with increasing TDN derived component. The plutonium micro-homogeneity in the sintered pellets was excellent and the pellets gave < 0.1 w/o bulk solids residues from solubility tests.

INTRODUCTION

Thermal denitration (TDN) of uranium-plutonium nitrates is a candidate process for producing oxides suitable for use in the fabrication of mixed oxide pellets as it potentially has the minimum number of process stages and requires the least effluent treatment. Such benefits are marred by the relatively poor powder quality of urania, plutonia or mixed oxides produced by direct thermal denitration. A programme of work was undertaken to identify parameters in the thermal denitration process which influence the decomposition reactions. The aim was to achieve an understanding of the decomposition behaviour of uranium and plutonium nitrate mixtures and the powder properties that could be achieved by influencing TDN process chemistry.

The literature suggest that ceramic grade oxide can be produced by direct denitration,

- if removal of waters of crystallisation to below hemi-hydrate level is achieved before denitration
- if careful heat treatment of the denitrated product is maintained to prevent loss of surface area via thermal excursions and
- if control of the initial phase change from the liquid to solid is maintained to prevent caking.

Subsequent studies would then explore possible alternative improvements to the denitration process. Such studies have already demonstrated process improvements, the American modified direct denitration route forming a double salt with ammonium nitrate(1), the French Nitrox process (2) and Japanese microwave denitration (3) being notable examples. In addition, BNFL developed routes include TDN on a combustible matrix, denitration via reaction intermediates, and denitration of cast pellets (4).

EXPERIMENTAL

Three oxides of plutonium plus uranium were produced, containing 6, 30 and 100% of the heavy metal as plutonium from uranium and plutonium nitrate starting material. The 30% plutonium form is referred to as Masterblend (MB) and is the preferred feed for the next generation plant to minimise the requirement for powder blending in the MOX fuel fabrication stage. The uranium /plutonium mixtures were produced by adding plutonium nitrate solution to crystalline uranyl nitrate hexa-hydrate and then warmed to produce a homogeneous solution. The nitrates were then dried in a vacuum desiccator containing P_2O_5 till the weight loss was consistent with the formation of the di-hydrates. This was conducted at 50°C for the mixed nitrates but at room temperature for plutonyl nitrate. The nitrates were calcined in air at 550 °C in a rotary furnace containing a rabble bar. The 100% plutonium oxide powder was not processed further, however, the mixed oxides were reduced in 4% H_2/Ar at 700°C.

The 100 % and 30% plutonium powders were then blended down to nominally 6% plutonium enrichment with Integrated Dry route (IDR) UO_2 powder. The powders were milled and aliquots removed after specific time interval. Due to a small sample volume a ball mill was used to mill the as-produced 6% TDN plutonium batch, where as an Attritor mill was used for the other powders. The powders were uniaxially die-pressed using an Apex hydraulic press with manual die fill, cavity i.d. 9.60 mm, and sintered at 1650°C under reducing conditions. The die set plunger was machined to produce end dimples and chamfers on the pellets. Sintered densities were determined and microstructure and plutonium micro-homegeneity assessed.

Two pellet samples were submitted for solubility trials from each source of PuO_2. The pellets were dissolved to a concentration of 200 g/l heavy metal using 7 M HNO_3 and refluxed for 12 hours. The solution was then centrifuged and the clarified solution decanted. This was repeated twice more after washing with O.5 M nitric acid. The residue was washed into a platinum crucible and dried to constant weight at 200 °C. The amount of original sample not dissolved was calculated as a percentage of initial pellet weights.

RESULTS

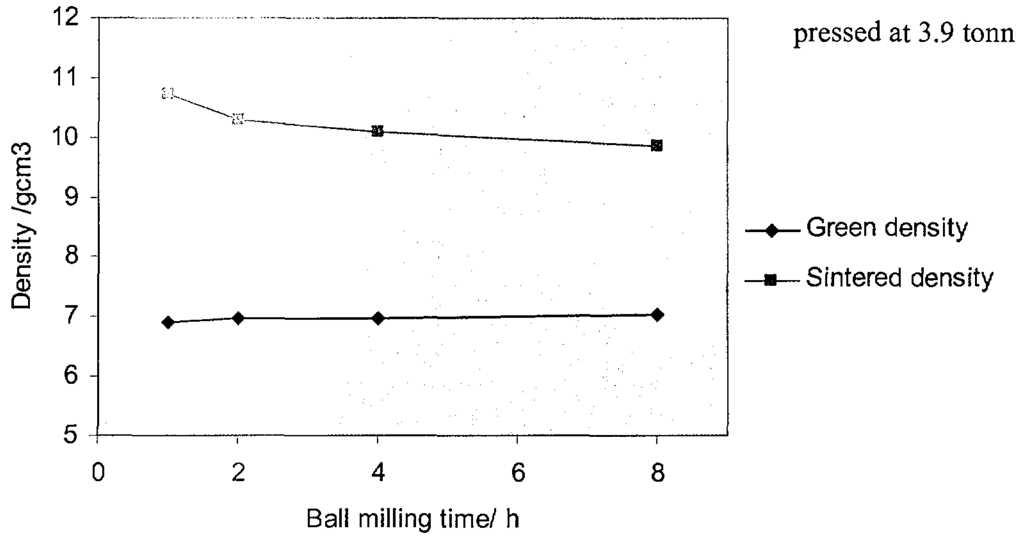
The as-produced oxides were fine free flowing powders and were without fused masses. The surface area of the 100% TDN PUO_2 and was 2.9 and 2.4 gcm^{-3} for the 30% and 6% PuO_2 powders respectively. The powder properties of the blended powders are summarised in the Tables 1.

Table 1. Powder properties of MOX from 100% and 30% TDN PuO_2

	100% TDN PuO_2			30% TDN PuO_2		
Attritor mill time /min	SSA m^2/g	Pour density g/cm^{-3}	Tap density g/cm^{-3}	SSA m^2/g	Pour density g/cm^{-3}	Tap density g/cm^{-3}
5	2.8	2.1	3.1	2.9	2.1	3.2
10	3.4	2.3	3.3	3.6	2.2	3.4
15	3.5	2.5	3.4			
20	3.8	2.5	3.5	5	2.6	3.7
30	5	2.6	3.6	4.9	2.8	4

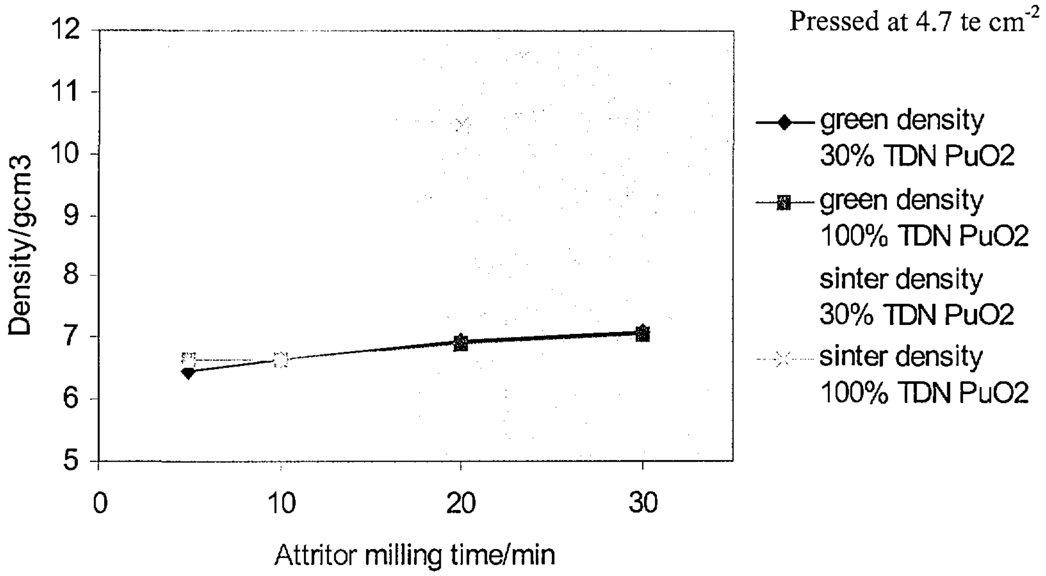
Samples of the results on pelletisation and sintering behaviour for TDN derived MOX are summarised in the Figure1 for the 6% TDN PuO_2 and Figure 2 for 30% and 100% TDN PuO_2 starting powders.

Figure 1. Compaction and sintering results of Ball milled 6% TDN PuO_2 powder



pressed at 3.9 tonnes cm^{-3}

Figure 2. Compaction and sintering behaviour of Attritor milled TDN powders



DISCUSSION

The conditions for denitration, vacuum desiccation and slow heating, were chosen to reduce the probability that melting of the lower hydrates would take place by ensuring that dehydration was virtually complete before denitration started. This is particularly important during the decomposition of the di-hydrate to ensure anhydrous heavy metal nitrate is produced rather than hydroxy nitrate species. These species by the formation of hydroxy bridges leads to the creation of sticky polymeric intermediates which are detrimental to the powder properties of the resultant oxide. The absence of fused lumps in the product was good evidence that melting had not occurred. This however, resulted in a protracted heating cycle which is not desirable for industrial application. The use of a rabble bar in the furnace also minimised lump formation. The bulk powder properties of the as-produced powders are not suitable for pellet manufacture requiring additional processing to achieve suitable die fill. The surface areas of the as-produced oxides increase with increasing plutonium content and are in the range desirable for powders to be pressed. The surface area for 100 % TDN derived PuO_2 (4.6 m^2/g) is about half that for oxalate derived PuO_2 (10 m^2/g) after similar calcination.

The surface area of the 6% TDN derived MOX increases rapidly to over 4 m^2/g after 1 h ball milling, increasing still further with subsequent milling. This is a good indicator that particles are more fragile having a low shear strength. The surface areas of the 100% PuO_2 and 30% PuO_2 derived MOX powders are lowered by the addition of IDR UO_2 but recovered by subsequent milling. The bulk powder properties of the powders increases fairly uniformly with milling time and the tap densities are typical of milled IDR, the dominant component.

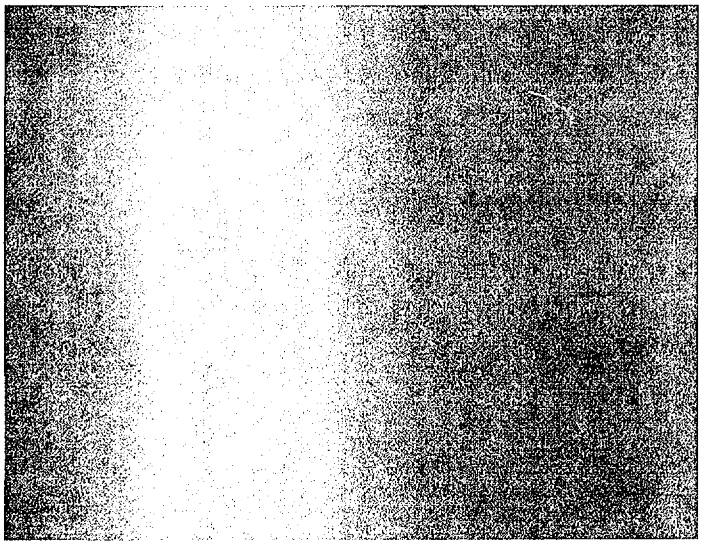
As expected, increasing green and sinter densities are achieved with increasing pressing pressures. The capping threshold was generally above 6.0 tonnes cm^{-2} pelleting pressure. Other measurements indicate that the spring back of the pellets increases with increasing pelleting pressure as expected for elastic behaviour and that the elasticity behaviour is not markedly different whether they are TDN or IDR derived powders. The proportion of TDN derived powder in the blend does not seem to have any marked effect on increase in green density indicating that TDN and IDR derived powders have similar shear properties after milling. All three powders end up with high green density pellets of about 7 gcm^{-3} after long milling. The ball milled 6% TDN PuO_2 derived MOX gives higher densities than the Attritor milled samples at short milling times and this is believed to be due to the initially higher surface area.

Figure 1 shows that for MOX from the undiluted TDN PuO_2 the sintered density decreases markedly with increasing milling time. This result was unexpected and was probably due to solarisation during sintering as a result of the high surface area of the powder. Figure 2 shows that for the pellets from Masterblend enrichment there is a marked increase in sinter density with increased mill time, whereas for the MOX composed of nearly 95% IDR derived UO_2 there is no real marked change. Thus the sintered densities appear to increase with increasing TDN derived component. The overall behaviour of the sintered densities is consistent with them increasing with milling time until some maximum is reached, after which they decrease again due to solarisation.

Macrostructure of the pellets (not shown) were fairly poor and this was believed to be due to some extent to mechanical problems with the pelleting press. However the pellet quality was consistent across all TDN components, and hence pellet quality does not appear to diminish with TDN component. The micro-homegeneity resulting from the use in MOX of 6%, 30% and 100 % TDN derived PuO_2 is excellent and a sectioned pellet from the former is shown in Figure 3. This shows a complete absence of PuO_2 rich spots. As expected micro-homogeneity improves with increasing mill time. The grain size in the pellets was also seen to increase with increasing TDN derived component. The grain size was around 4μm for a 100% TDN derived PuO_2 pellet, while the grain sizes in pellets containing a TDN derive UO_2 component are 6 to 10 μm.

The pellets from 6% TDN PuO_2 MOX after only 1 h in the ball mill gave a bulk solids residue of only 0.09 w/o from the solubility test. The pellets produced by Attritor milling 30% TDN PuO_2 for only 5 minutes gave 0.03 w/o residues and the pellets from 100% TDN PuO_2 after 5 minutes Attritor milling gave 0.06 w/o residues. These results are all low despite the short milling times and confirm the excellent micro-homogeneity displayed in the auto-radiographs.

Figure 3. Autoradiograph on a MOX pellet from 100% TDN derived PuO_2



5 min Attritor mill time
and pressed at 4.1 te cm^{-2}

CONCLUSION

High density MOX pellets of excellent micro-homogeneity have been produced in the laboratory from free flowing thermally denitrated powders after short mill times. This demonstrates that by carefully controlling the denitration process it is possible to produce ceramic grade oxide powder suitable for MOX fuel manufacture. The results with the Masterblend TDN component are particularly promising as it is the preferred finishing feed composition for the next generation of finishing plant. The conditions chosen, however, are not suitable for industrialisation and further work is required to optimise the process.

REFERENCES

1. PA Haas and WB Stines. Method for the improved decomposition of metal nitrate solutions. US patent 4 409 157, 1983.
2. R Romano. The Nitrox process for MOX production by thermal denitration. Nuclear Europe, 1986, 9, 19-21.
3. H Oshima. Development of microwave heating method for co-conversion of Pu-U nitrate to MOX powder. J. nuclear Science and Technology, 1989, 26(1), 161-166.
4. JW Hobbs. Molten salt casting of metal nitrate. UK patent application no 9901284.1, January 1999.