CHANGES IN UO_2 POWDER PROPERTIES DURING PROCESSING VIA BNFL'S BINDERLESS ROUTE

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Abstract

The Short Binderless Route (SBR) has been developed for Mixed Oxide fuel production in BNFL's MOX Demonstration Facility (MDF) and the Sellafield MOX Plant (SMP). It is a compact process which enables good homogenisation of the Pu/U mixture and production of free flowing press feed material. The equipment used to achieve this consists of an attritor mill to provide homogenisation and a spheroidiser to provide press feed granules. As for other powder processes, the physical properties of the UO_2 powder can affect the different process stages and consequently a study of some of these effects has been carried out. The aims of the work were to gain a better understanding of the process, to consequently optimise press feed material quality and to also maintain powder hold-up levels in the equipment at a minimum. The paper considers the effects of milling processes on powder morphology and powder surface effects, on the granulation process and also on powder and granule bulk properties such as pour, tap and compaction densities. Results are discussed in terms of powder properties such as powder cohesivity, morphology and particle size. UO_2 powder derived from both the Integrated Dry Route (IDR) and the Ammonium Di-Uranate (ADU) Route are considered. Small (1 kg) scale work has been carried out which has been confirmed by larger (25 kg) scale trials. The work shows that IDR powder with differing morphologies and ADU powder can be successfully processed via the SBR route.

1. INTRODUCTION

It is well established that powders derived using different production routes may exhibit different properties and behaviour even though they have the same chemical composition. For example, uranium dioxide powders derived from dry and wet routes can possess different particle sizes, particle morphologies, specific surface areas and have slight differences in chemical composition, hence they can exhibit different behaviour. Additionally each stage in the processing of fuel can change the properties and hence, the resultant powder behaviour. It is important to understand how the fundamental powder properties can affect the different stages in the processing of nuclear fuels such as granulation, pressing and sintering. In this study three UO_2 powders with different morphologies were initially characterised and then further characterised after processing using the Short Binderless Route (SBR) which has been developed for Mixed Oxide fuel production. The data obtained were used to obtain an understanding of the powder behaviour and support the development of the SBR and its application in BNFL's MOX plants. Both Integrated Dry Route (IDR) and Ammonium Diuranate (ADU) derived UO_2 powders were studied.

2. EXPERIMENTAL

Three uranium dioxide powders, which were derived from powder processes used by BNFL Fuel Division at the Springfields site, were studied. The first two materials were prepared by the Integrated Dry Route (IDR) using different kiln conditions to provide one powder of 'plate like' particle morphology (IDR_P) and one of 'sphere like' particle morphology (IDR_S). The third powder was prepared via the Ammonium Diuranate route (ADU) in the BNFL Springfields Enriched Uranium Residues Recovery Plant (EURRP).

Each powder sample was characterised, before and after milling, using the following techniques. Powder pour densities were determined by measuring the volume of a known mass of material (lOOg) in a tared measuring cylinder. Tap densities were determined by tapping the measuring cylinder until the powder volume remained constant and this volume was recorded. For both measurements the bulk density values were calculated by dividing the mass (g) by the volume (cm^3). The Specific Surface Area of each powder was measured using a gas adsorption technique, iron levels were determined by atomic absorption and particle size was determined by Coulter Counter analysis. The powder morphologies were examined at high magnification using a Scanning Electron Microscope (SEM).

In each milling experiment a 1 kg batch of powder, containing 0.1 wt % zinc stearate lubricant, was milled in a 5.7 Litre attritor mill pot with a steel ball charge. Powder batches were milled up to 40 minutes with samples taken for characterisation, using the techniques listed above, after 20 minutes and 40 minutes. Granules were prepared by tumbling the powder with a further 0.1 wt % zinc stearate lubricant. The granules were compacted to pellets with an Apex press using a 10 mm diameter cylindrical steel die. Green pellet densities were calculated from mensuration results prior to sintering pellets at 1750°C for 5 hours in pure Hydrogen. No pore former was added to the material prior to sintering. Pellet sintered densities were measured using a water immersion technique.

3. RESULTS AND DISCUSSION

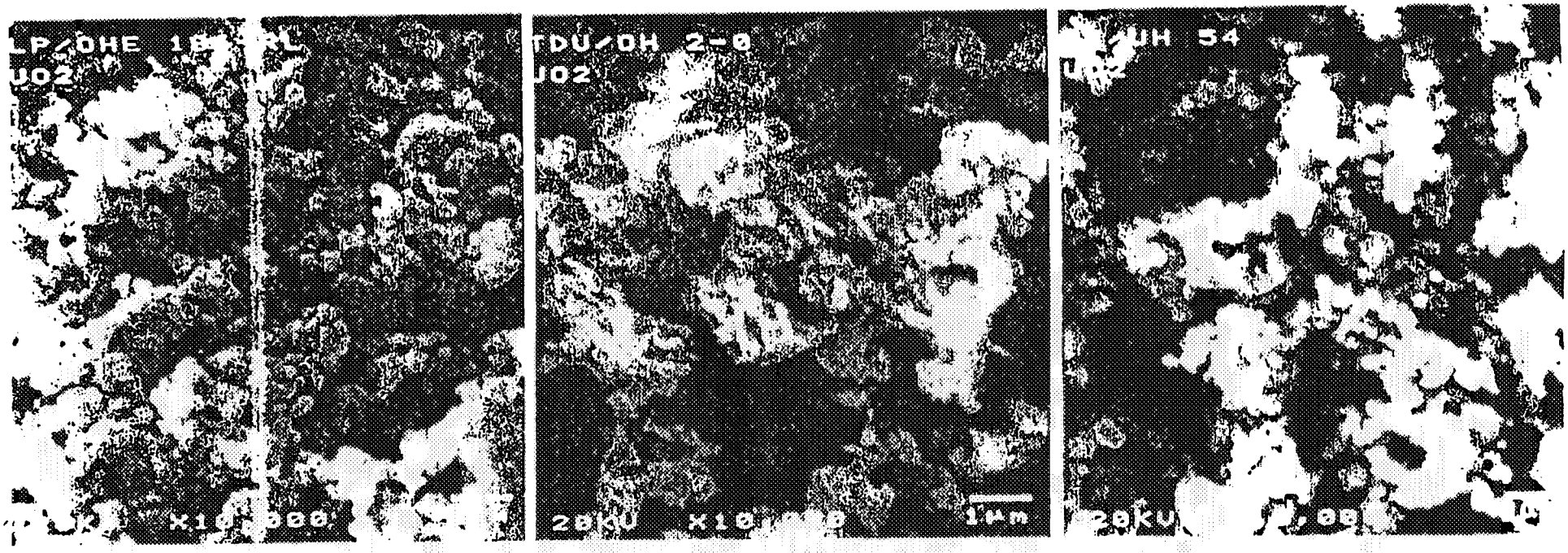
3 .1 EFFECT OF MILLING ON POWDER CHARACTERISTICS

The morphology of each unmilled powder can be seen in Figure 1 a. The IDRs and ADU powders appear similar, each consisting of small (less that 1 μm) rounded particles. The IDR_P powder possessed a definite 'plate-like' morphology with individual particles approximately 1 μm in size.

Table 1 gives results of the Coulter counter analysis results which show that the mean particle sizes for each powder are very similar prior to milling. All of them lie within the range 3.53-3.72 μm. Following milling, in the case of the IDR powders, the particle sizes have apparently increased which is not a very likely occurrence. It could indicate that the newly milled powders have loosely agglomerated during the analysis and given higher results than expected. The SEM micrographs taken after milling and illustrated in Figure lb, indicate a much smaller powder particle size than those recorded by the Coulter Counter analysis. These results could be due to the known tendency of these powders to agglomerate following milling, as demonstrated in spheroidisation.

Table 2 gives results of powder pour and tap densities and granule flow rates. Figures 2 and 3 show pour and tap densities versus milling time. In all cases the powders showed a large increase in pour and tap density following milling for 20 minutes and spheroidisation. In the case of the IDR powders a further slight increase occurred on milling for 40 minutes while the ADU material showed a very slight decrease. The results indicate that extent of milling had an effect on powder and on granule properties. While there was a broad spread in initial pour and tap densities for the three powders there was only a slight difference in the values after milling for 40 minutes.

Pour and tap density is a measure of how powder particles pack together and the properties are affected by parameters such as particle size, shape, and agglomeration. Agglomeration and irregular



IDRs UO_2 IDRp UO_2 ADU UO_2

FIG. 1a SEM Micrographs Unmilled Powders

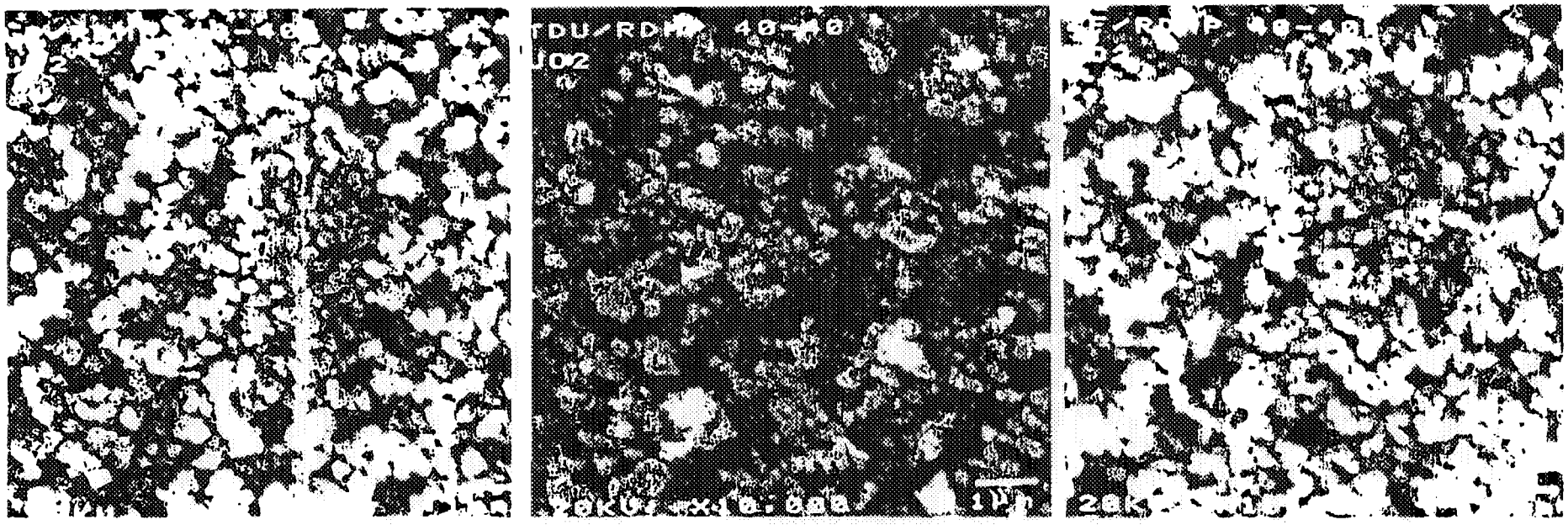


FIG. 1b SEM Micrographs Milled Powders

TABLE 1 Powder Particle Size Analysis by Coulter Counter for Given Milling Time

	Mean Particle Size / μm for given Milling Time / min		
	0	20	40
ADU	3.53	4.29	3.38
IDR_P	3.65	3.90	4.63
IDR_S	3.72	3.63	6.44

TABLE 2 Results of Granulation Trials Pour and Tap Densities and Granule Flow Rate

	Results for given milling time / min								
	0			20			40		
	Pour/ g cm^{-1}	Tap/ g cm^{-1}	Flow/g s^{-1}	Pour/ g cm^{-1}	Tap/ g cm^{-1}	Flow/g s^{-1}	Pour/ g cm^{-1}	Tap/ g cm^{-1}	Flow/g s^{-1}
ADU	1.71	2.43	no flow	3.16	4.04	35.68	3.11	3.71	36.87
IDR_P	0.80	1.39	no flow	3.08	3.66	38.51	3.33	3.88	35.87
IDR_S	1.60	2.03	23.08*	3.11	3.57	38.83	3.22	3.82	41.08

* Flow occurred in only one of three trials

particle shape are detrimental to achieving high packing densities and can affect the pelleting process. It appears that the powder particle characteristics, initially present in the powders, and which can lead to differences in pour and tap densities are minimised after milling suggesting that the milling process has reduced the number of powder agglomerates, in all the powders studied. The SEM micrographs of the milled powders also suggest a less agglomerated structure and show that, in the case of the $IDR_{(P)}$ powder the morphology of the particles is modified with the plates becoming more rounded.

Figure 4 shows the powder specific surface area (SSA) versus milling time, this indicates that for each powder the SSA increases with extent of milling. This also supports the theory that agglomerate breakdown is occurring during the milling process. Throughout the milling cycle the $IDR_{(P)}$ and the ADU powders exhibited very similar SSA values whereas the values for the $IDR_{(S)}$ powder was consistently lower.

As expected, the iron levels increased with prolonged milling however, the level of iron pick-up was well within existing specification levels and is not a problem to the successful application of the SBR in the fabrication plants.

3 .2 EFFECT OF MILLING ON GRANULE CHARACTERISTICS

Table 2 shows pour and tap density and flow results for the granulation trials on unmilled and milled powders. The unmilled powders showed no signs of granulation after tumbling for 1 hour and pour and tap densities were consistent with unmilled material which had not been granulated. Pour densities were, as expected, higher for milled powders after granulation, indicating the fact that granulation had taken place. Only one unmilled powder (IDRs) showed any tendency to flow whereas all milled materials had good flow properties.

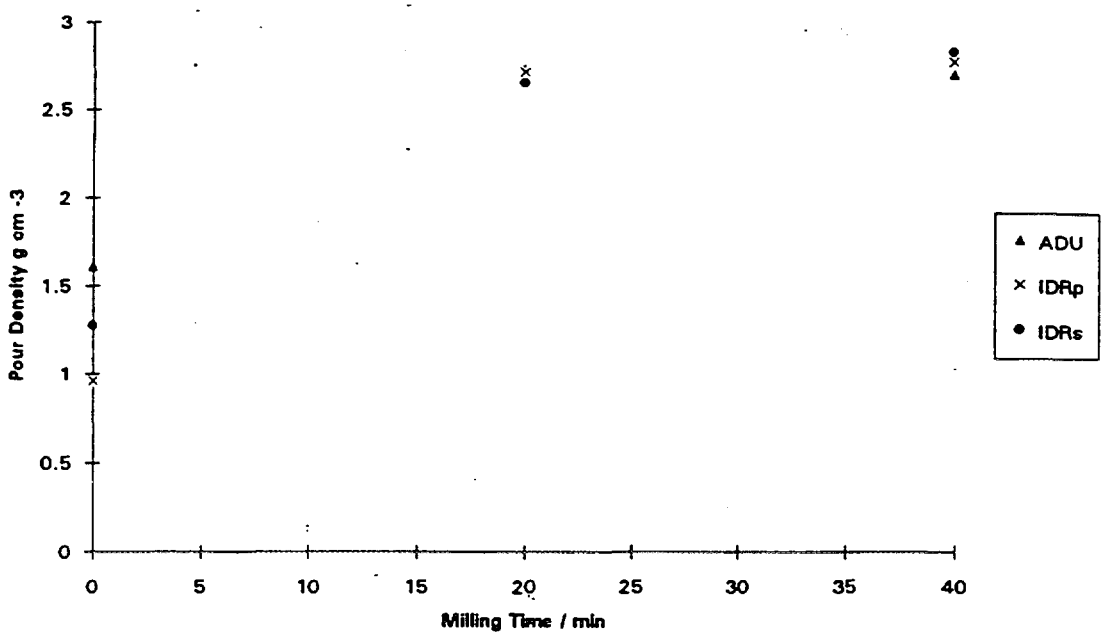


FIG. 2 *Powder Pour Density as a function of milling time*

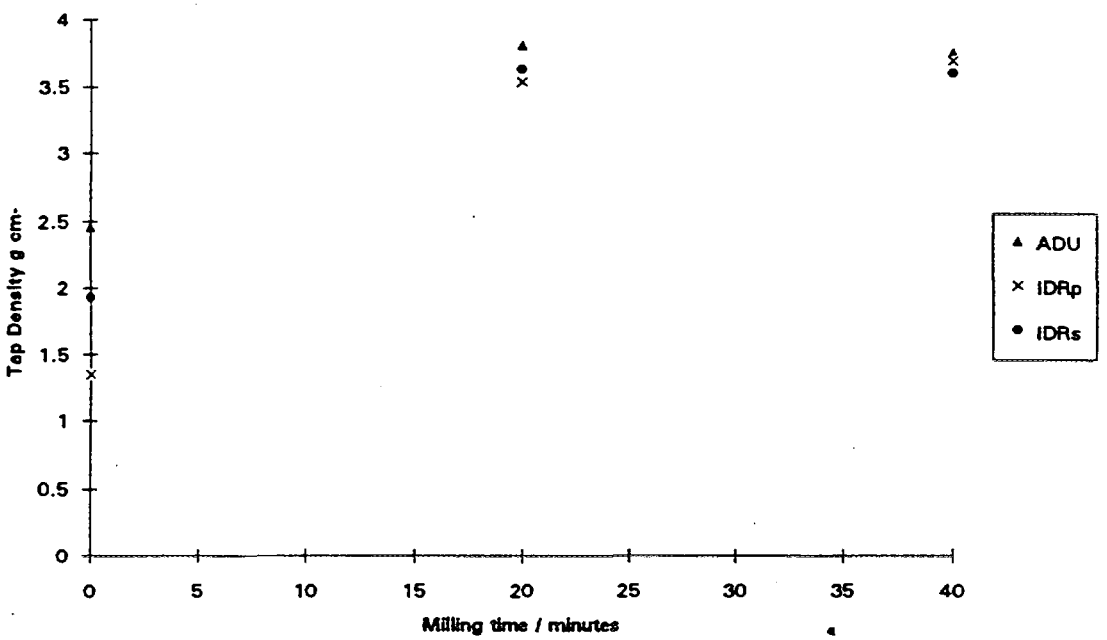


FIG. 3 *Powder Tap Density as a function of milling time*

Granules produced by spheroidisation build up by powder rolling over itself and agglomerating. The powder particles behave as nuclei, and 'pick-up' material via a 'snowball' effect to form larger granules. The granulation results show that the milled powders are the more cohesive and form stable free-flowing granules via the spheroidisation process. This is consistent with the fact that the milled material has a higher surface area and contains newly cleaved surfaces increasing the opportunity for interparticle bonding via Van der Waal's forces.

3.3 EFFECT OF MILLING ON POWDER COMPACT CHARACTERISTICS

Table 3 shows the compaction properties of each powder before and after milling. All powder green densities quoted were for pellets pressed at the same load of 4 tonnes cm^{-2}. The results confirm that the milling operation gives rise to increased green density for the same pressing load. Where granules were pressed at the same load there was a difference of between 0.68 - 0.95 g cm^{-1} in the green density achieved for unmilled powder and powder milled for up to 40 minutes. The greatest difference was shown using the IDRp example confirming the biggest change in powder morphology occurred in this example during milling. It is noticeable that after only 20 minutes milling the green density of pellets produced from each powder was similar.

3.4 EFFECT OF MILLING ON POWDER SINTERING CHARACTERISTICS

The densities of the sintered pellets produced from all compacts are shown in Table 4. For the unmilled powders, the ADU powder exhibited a much lower sintered density than IDR. Milling produced an increase in sintered density for all powders, with the largest increase observed in the ADU powder.

4. PLANT SCALE BEHAVIOUR

Plant scale trials (25kg) have shown that the most important difference between milled and unmilled material is the increased cohesive and adhesive nature of milled material, which, together with changes in ambient humidity may cause powder to adhere to surfaces of equipment. To overcome this, dry inert process gases and very highly polished process surfaces are used in the plant. The phenomena and trends observed in the lkg scale trials have generally been confirmed in large-scale trials.

TABLE 3. The Green Density Achieved for Granule Compaction at 4 Tonnes cm~2 for Given Milling Time

	Green Density / g cm^{-2} for given milling time / min		
	0	20	40
ADU	6.02	6.57	6.70
IDR_P	5.77	6.54	6.72
IDR_S	6.06	6.59	6.73

TABLE 4. Sinter Density Results for Green Compacts Pressed at a Load of 4 Tonnes cm 2

	Sinter Density / g cm^{-2} for given milling time / min		
	0	20	40
ADU	10.56	10.69	10.72
IDR_P	10.71	10.78	10.80
IDR_S	10.75	10.81	10.79

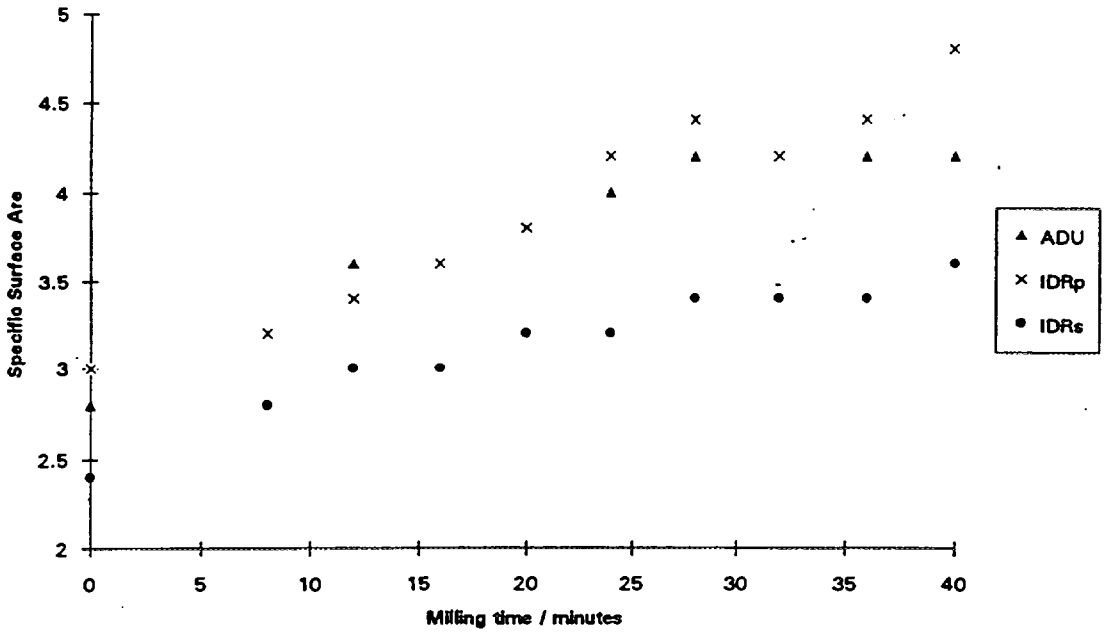


FIG. 4 Change in Powder Specific Surface area with milling time

5. CONCLUSIONS

Experimental studies have demonstrated how the milling of powders affects particle morphologies and subsequent behaviour of powder during pellet fabrication. The properties of powders changed most during the initial phase of milling but the change was less marked after further milling. All powders were successfully processed via the Short Binderless Route, producing good quality green and sintered pellets. The results support the use of ADU derived UO_2 in the SBR process.