DRY RECYCLING OF OFF-GRADE URANIUM OXIDE POWDER FOR IMPROVING SINTERABILITY

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ABSTRACT

Nuclear Fuel for Pressurized Heavy Water Reactor (PHWR) is produced through the conventional powder-pellet route using ex-Ammonium di-Uranate (ADU) as the starting material. In order to meet the requirement of the narrow band of process parameters for obtaining high quality finished UO_2 pellet, the quality of the starting powder UO_2 has to be consistently maintained within the given specification. The Specific Surface Area (SSA), particle size, Oxygen to Uranium ratio (O/U), bulk density and chemical purity of the UO_2 powder, as well as high recovery in sinterability test are key criteria for acceptance of powder lots.

The powder lots rejected in the sinterability test, if any, has so far been recycled by wet chemical route involving HNO_3 dissolution and consumption of large quantities of chemicals which in turn results in the generation of effluents.

An alternate process of recycle by 'dry route' has been developed, which not only eliminates the above disadvantages but also contributes to improvement of productivity. The 'dry-recycle' route (DRR) has paved the way for >95% acceptability of the powder lots in sinterability tests.

The present paper describes the important aspects of DRR developed at Nuclear Fuel Complex, on an industrial scale.

INTRODUCTION

Since the last three decades, Nuclear Fuel Complex (NFC), has been manufacturing Natural Uranium Oxide Powder through ADU route[1]. The Physical and Chemical characteristics of the UO_2 powder are shown in Table-1.

Every lot of powder that meets the physical and chemical specification are subjected to sinterability-test which is designed as a predictive measure of the performance of the powder for producing acceptable quality pellets. It has been observed that, some 10 % of physically and chemically qualified powder lots do not pass the sinterability test.

The two main reasons for rejection in sinterability test are:

1. Low sintered density and wide density variations: Low sintered density of the pellets in most cases is attributed to low SSA and density variations are due to in-homogeneity in the powder.

2. Visual defect like 'Pits': 'Pits' are caused due to differential sintering of the hard agglomerates present in the powder granules.

Corrective measures to be effected on the powder lots have thus, to be directed towards improvement of those properties eg: low density and low SSA of UO_2 powder, which cause above defects. These properties are directly related to the large fraction of coarse particles in the powder lots.

From manufacturing experience and literature[2], it is known that powder characteristics are to a large extent set in the thermal conversion steps of intermediate products like ADU/AUC to UO_2. It was therefore decided to concentrate studies in the heat treatment methods of the UO_2 powder.

Literature[2] also reveals, that, UO_2 powder when re-oxidised at different temperatures, follows different paths of conversion to higher oxide and this change of composition is accompanied by corresponding re-crystallization process. Further, it is stated that repeated cycles of oxidation (400 °C) and reduction (600° C) improve the properties of the UO_2 , increasing the surface area and decreasing the bulk density. It is also reported that powder sintering could occur if this re-oxidation is carried out at temperatures $>$ 800° C and powder becomes un-reactive with low Bulk density and low S.S.A.

Based on this information, it was proposed that the rejected UO_2 powder could be re-oxidized at suitable temperature and other operating conditions so that the resulting lattice restructuring during re-conversion (once again back to UO_2) should give rise to a more homogenous and sinterable powder. A process was established after carrying out trials and many batches of powder are recycled successfully.

PROCESS DESCRIPTION

The powder lots are subjected to low temperature Oxidation (450-500°C) followed by conventional reduction in cracked ammonia atmosphere and subsequent stabilization in the presence of Nitrogen and air. The flow sheet is shown in Fig-1.

The operating conditions in re-oxidation stage are optimized to obtain the desired specific surface area. Specific surface area depends upon the physical characteristic of starting material, the atmosphere, as well as temperature of oxidation. An optimum low temperature of oxidation of about 450-500 ^{0}C results in considerable decrease in the particle size and increase in the surface area of powder due to reasons including particle- breakdown, explained later. This increase in surface area is partially retained upon re-reduction back to UO_2 also.

The variation in SSA with respect to temperature during conversion of ADU to U_3O_8 is shown in Fig.-2 and Fig:-3 shows the change in SSA after the re-oxidation process, on various lots of powder.

An O_2 partial pressure of about 20% is maintained in the furnace atmosphere during re-oxidation process which increases the rate of the reaction.

DISCUSSION

The re- oxidation reaction of UO_2 is widely studied and reported to proceed in two stages as follows[3]

$$UO_{2+x} \longrightarrow U_3O_7/U_4O_9 \longrightarrow U_3O_8$$

The two stages of the process are explained as given below (Literature [4,5]);

A. Oxidation of UO_{2+x} to tetragonal oxide. (U_3O_7/U_4O_9) : This transformation occurs at lower temperatures of around 300^{0}C, by inward movement of oxygen which diffuses into the body of UO_{2+X} particle without formation of new phase till the value 'X' reaches 2.25. The oxygen occupies the interstitial position which again tend to segregate preferentially in one portion of the lattice. This results in a tetragonal distortion of the UO_2 fluorite lattice structure. This distortion is accompanied by net shrinkage in the crystallography volume (decrease in lattice parameters or contraction of lattice) . The surface area of UO_2 powder is not altered significantly at this stage.

B. Oxidation of tetragonal oxide (U_3O_7/U_4O_9) to orthorhombic U_3O_8 : The next step of oxidation to higher state is via nucleation and growth. Nuclei of U_3O_8 start forming on the surface and begin to grow initially. These may adhere to the surface or fall from it according to the prevailing temperature and oxidizing condition. In general, the rate of oxidation, initially decreases, then becomes constant before falling to zero as complete oxidation to U_3O_8 is attained. The rate of oxidation depends on oxygen partial pressure and is inversely proportional to total pressure.

Oxidation to U_3O_8, unlike that of previous stage, is however, accompanied by re-arrangement of the lattice (as shown by DTA/TGA peaks in various studies referred above) to yield an orthorhombic or pseudo hexagonal structure. This re-arrangement results in 36% increase in the crystallographic volume as seen in the large increase in volume of the lots/batches of powder re-oxidized in the plant.

The low temperature oxidation of UO_{2+x} also results in strain within the particle which are not easily annealed out because of the poor mobility of the particle at such low temperatures. The combined effect of the initial oxidation induced particle shrinkage, increase in volume due to lattice re-arrangement and the strains resulting from these physical transformation leads to micro-cracking of the individual grains within the oxide and eventually particle breakdown occurs. The net result is, reduction in particle size leading to increase in fines percentage and also loss of hard agglomerates. Particle size change for a typical lot is shown in Table-2.

The repeated handling of the powder in the furnace also improves the homogeneity of the powder. All the desired aims of the re-working operation are thus met.

The physical processes that accompany the, chemical transformations are as follows :

1. Diffusion of the oxygen atom from bulk gas to the oxide surface.
2. Adsorption of the oxygen atom on to free reaction sites on the oxide surface.
3. Incorporation of oxygen within the oxide lattice
4. Removal of interstitial oxygen from the boundary layer into bulk of the material by diffusion through the lattice.
5. Desorption of the reaction product to leave free reaction site on the oxide surface
6. Transportation of reaction products away from the surface into bulk gas.

CONCLUSION

The process of re-oxidation of UO_2 to U_3O_8 and re-reduction of this U_3O_8 back to UO_2 thus gives the advantage of increasing the fines fraction, consequently giving the desired SSA and physical characteristics, and also making the powder more sinterable, such that 98-100 % acceptability of the powder in siterability test is assured.

Around 100 MT of the powder has been recycled by this process, in the past five to six years.

This dry route can be extended for processing other types of raw material like Depleted Uranium from re-processing plants. The starting material for heat-treatment in this case, is in the form of ADU+ U_3O_8. / U_3O_8.

ACKNOWLEDGEMENT

The authors express their deep sense of gratitude to all the staff members of Uranium Oxide Plant, New Uranium Oxide Plant and Control Laboratory of Nuclear Fuel Complex for the support in carrying out plant scale studies and establishing a short and guaranteed method of recycle.

Table – 1

UO_2 Powder Specifications

Physical Requirement

a) O/U Ratio : 2 - 2.1

b) Average Particle size : 2-3 μm

c) Specific surface Area : 2.5 - 3.5 M^2/gm

Chemical Requirement

a) Uranium Content : Minimum of 87.7% on dry weight basis

b) Moisture Content : 0.4% max. by weight of Uranium

Impurity Content			(in ppm) (Max)	Impurity Content			(in ppm) (Max)
Aluminum	(Al)	:	25	Gadolinium	(Gd)	:	0.15
Boron	(B)	:	0.3	Fluorine	(F)	:	30
Carbon	(C)	:	200	Iron	(Fe)	:	50
Calcium	(Ca)	:	50	Magnesium	(Mg)	:	50
Cadmium	(Cd)	:	0.2	Manganese	(Mn)	:	5
Chromium	(Cr)	:	15	Nickel	(Ni)	:	20
Copper	(Cu)	:	10	Silicon	(Si)	:	30
Dysprosium	(Dy)	:	0.1	Thorium	(Th)	:	200

- Any unspecified element – 100 ppm
- Any specification can go to a maximum of double the specified value provided EBC is maintained less than 1.1 ppm on uranium weight basis

The Powder should pass Sinterability Test:

a) Sintered density of the pellet : (Average -3σ) >10.45 gm/cc

b) Pellet should be free from defects like pits, cracks, chips and end caps.

c) Pellet should have good micro structure, devoid of grouped porosity, un-sintered patches etc.

Table – 2

Particle Size Distribution for a Typical Re-Processed UO_2 Lot

UO_2 Powder	Median (μ)	<10μ (%)	SA (M^2/gm)
Before Processing	13.26	24.5	2.81
After Processing	12.39	31.2	2.94

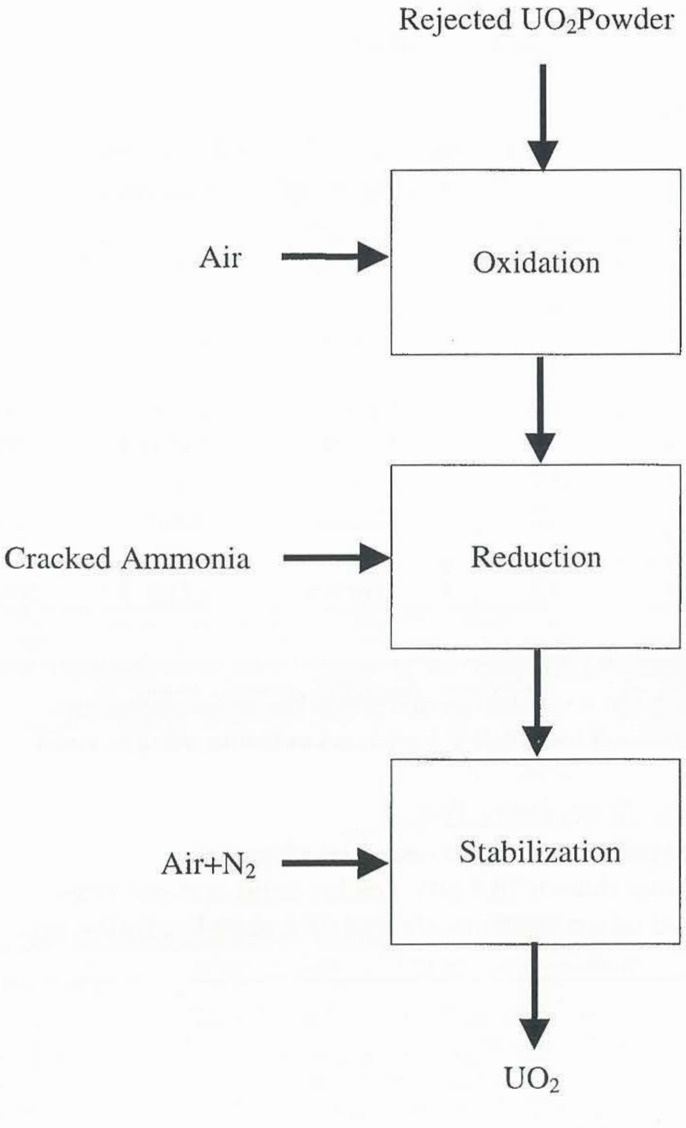

Fig.–1 Process Flow Sheet for Recycle of off grade UO_2 powder b Re-oxidation

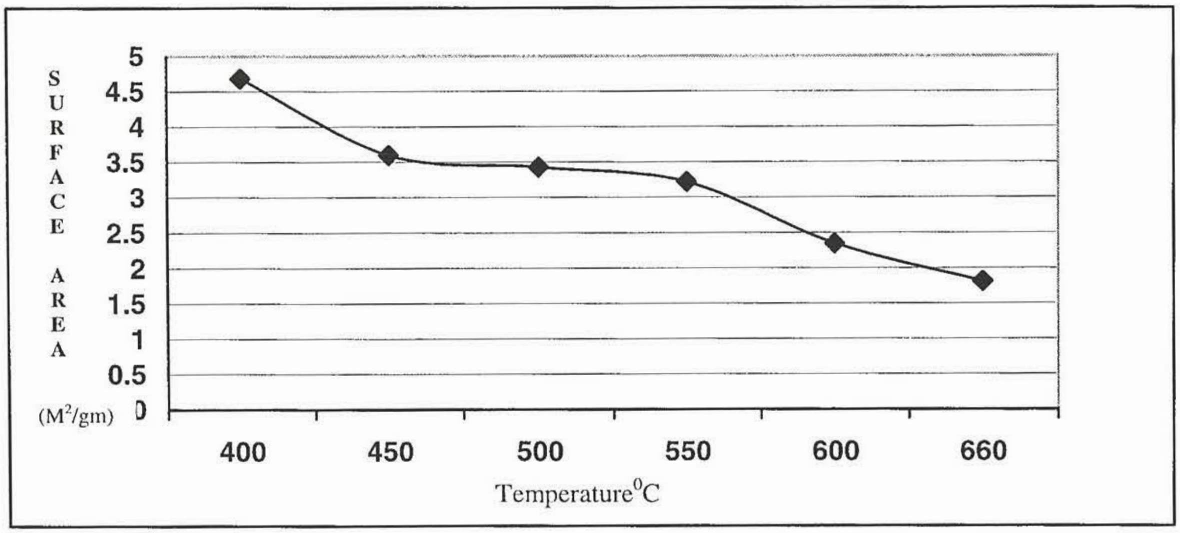

Fig.–2 Variation of specific surface area of U_3O_8 with respect Temperature

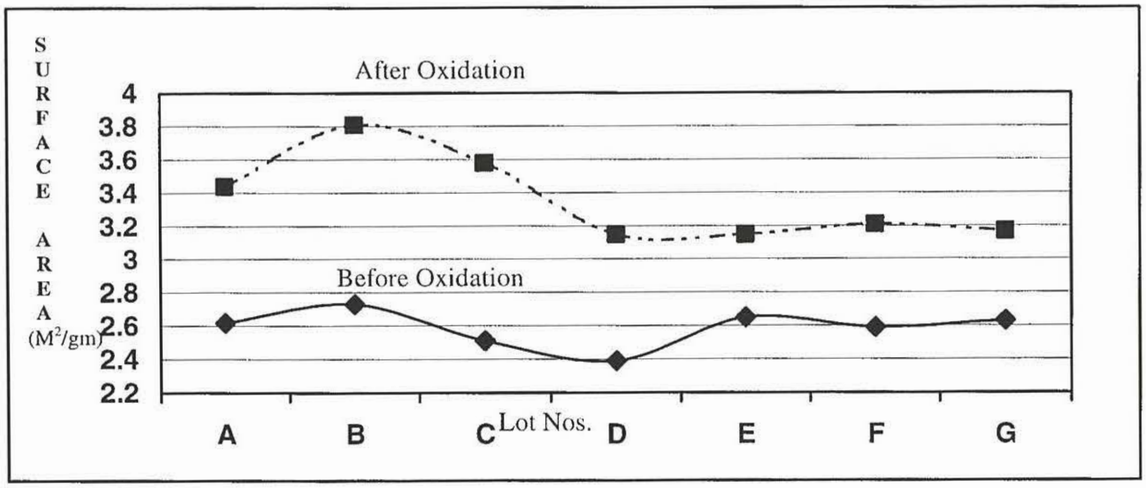

Fig.–3 Comparison of specific surface area of U_3O_8 before & after Oxidation

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