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OPTIMIZATION OF PROCESS PARAMETERS OF UO_2 POWDER PRODUCTION FOR HIGHER PELLET RECOVERY

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ABSTRACT –The Pressurized Heavy Water Reactor uses fuel in the form of natural UO_2pellets, produced by powder metallurgy route from sinterable grade UO_2 powder.Ex-AU route is widely accepted process for production of highly sinterablegrade UO_2 powder. The characterization of UO_2 powder is always paramount forfinal pellet recovery. Sinterability of UO_2 powder largely depends onprecipitation and subsequent heat operation namely calcination and reduction.Ammonia flow rates during AU precipitation and temperature of calcination andreduction are critical to obtain desired UO_2 powder characteristics forachieving high sinterability during pellet fabrication. The present paperdiscusses the effect of critical parameters of precipitation, calcinations andreduction on final product and successful optimization of process parametersresulting in increase of production rate by 50%.

Introduction

The fuel for Indian PHWR type reactor is high density natural UO_2 pellets encapsulated in zircollay tubes. The sintered pellets are produced through powder metallurgy route from sinterable grade UO_2 powder. Extraction and Ammonium Uranate precipitation (Ex-AU) route is one of the well-known and widely accepted process for production of sinterable grade UO_2 powder. The sinterable grade UO_2 powder implies to the powder whose powder compact gets easily sintered and shows high pellet density during pelletization operation. Sinterable grade UO_2 powder is produced by tight control of process parameters during precipitation and subsequent heat treatment operations. In the powder metallurgy process, UO_2 powder is compacted into granules to increase the flow ability and subsequently binder is added for green pellet preparation. These green pellets are sintered at high temperature up to 1700^{o}C in pusher typefurnace for getting high density UO_2pellets. These sintered pellets are checked for density and surface defects. The recovery of final pellets' quality depends on powder characteristics and pelletization parameters.

For the production of sinterable grade UO_2 powder through Ex-AU, an intermediate product 'AU' can be produced by adding either ammonium hydroxide solution or ammonia vapour. In either case the precipitation process has great influence on sinterability of UO_2 powder. In recent past vapour ammonia precipitation route has been preferred over aqueous ammonia precipitation route because of numerous advantages like elimination of handling and preparation of aqueous ammonia, reduction in batch cycle time to about 75%, increase in batch size by 10% and reduction in effluent generation, thus has resulted overall increase in through put by more than two folds. It has also high filterability which led to conservation of energy, water, steam and man-hours.

The effect of temperature and uranium concentration in mother liquor, during precipitation, was studied by L C Watson et.al [1.]. It was deduced that the precipitation temperature has least effect on sinter density of powder precipitated by vapour ammonia, when compared to linear effect of precipitation temperature on sinter density of powder precipitated by aqueous ammonia. Settling rate isa near accurate indication of precipitate quality which has great tolerance for precipitation temperature for vapor ammonia precipitation when compared to aqueous ammonia precipitation. It is observed that the rate of AU precipitation by vapour ammonia is three times faster than aqueous ammonia which is due to high polarisability of vapour ammonia which intern helps in maintaining low solubility of precipitate. The precipitates grow uniformly and rapidly, keeping nucleation to minimum even at higher pH. Settling rate, based on stroke's law,is indirect measure of particle shape, size and density. It was also observed that settling is more robust for vapour ammonia precipitation when compared to aqueous ammonia precipitation. When AU precipitated by ammonia vapor, the precipitate is free flow able and anhygroscopic in nature, leads to the high diffusivity of unionized ammonia unlike weak mobility of ammonium ion in aqueous ammonia precipitation. The AU powder produced by vapour ammonia and aqueous ammonia are having angle of repose 50^0 and 55^0 respectively which is an important aspect for downstream processing. Woolfrey [2] explained that the AU powder characteristics like composition, surface area, particle size and density are largely dependent on the precipitation conditions like pH, uranium concentration, temperature, rate of precipitation and nature of precipitant.There has been considerable argument concerning the nature of the AU precipitate. Cordfunke [[3.] , [4.] reported the presence of four distinct compounds of AU, which are as follow:

Type of AU	Composition
I	$UO_3.2H_2O$
II	$UO_3.\frac{1}{3}NH_3.\ \frac{5}{3}H_2O$
III	$UO_3.\ \frac{1}{2}NH_3.\ \frac{3}{2}H_2O$
IV	$UO_3.\ \frac{2}{3}NH_3.\ \frac{4}{3}H_2O$

It has been confirmed by XRD finding that Type I and Type III are predominant in AU precipitated at pH 3.5 and 8 respectively when uranyl nitrate solution is precipitated by vapour ammonia [5.]. Further with the experience it is well known that the thermal history of uranium-di oxide powder has significant influence on its sintering behavior. Decomposition of AU at lower temperature yields active powder having good sinterability. The rise in temperature of the decomposition of AU leads to the progressive decrease in the surface activity of the powders and requires the use of higher sintering temperature [6.]. The AU powders containing large agglomerates give sintered pellets with low densities and non-uniform microstructures [7.].

1. Experimentation

Two type of experiments were carried out:I) UNPS (U=105 gpl, FA=0.2N) was precipitatedat different ammonia flow rates and subsequently sintered pellets were produced by following standard powder metallurgy route with1hr 30min Pushing Interval(PI). II) With the optimized ammonia flow rate as established in Exp.-1, calcination temperature was varied to study the effect of PI of 1hr on sintered pellet recovery. The PI of 1hr in sintering furnace mean the residence time of boat,containing green pellets, would be 30 hrs and incase of 1hr 30 min PI, the residence time would be 45 hrs.

In the first experiment, the precipitation trialwas carried out in a semi-batch reactor in which Uranyl nitrate solution (5400 lit) is taken as batch and ammonia vapour is admitted continuously. The tank solution is agitated by three stage paddle type agitator. The uranyl nitrate solution is preheated to temperature of 58^0C before admitting vapourammonia into the reactor. Ammonia flow rate is varied to study its effect on sinterability of UO_2 powder and intern sintered pellet recovery. All precipitation trials were carried out with different ammonia flow rate like 20, 25, 30, 35, 40 and 50 kg/hr. The resulting slurry after precipitation, was filtered, dried at 300°C, calcined at 695°C temperature. Based on Specific Surface area (SSA) of calcined powder (U_3O_8), reduction temperature is adjusted to get the required SSA of UO_2powder for pelletization. The UO_2 powder was pre-compacted, granulated followed by binder/lubricant addition, finally compacted into green pellets and sintered in reducing atmosphere with pushing interval of 1 hr 30 min.

In the second experiments, UO_2powder lots produced with optimized ammonia flow ratewere studied with varied calcination temperature, pre-compacted, granulated followed by binder/lubricant addition, finally compacted into green pellets and passed through high temperature sintering furnace at pushing interval of 1 hr.

2. Results and discussion

UNPS precipitation by vapour ammonia is an acid base reaction. The prevailing acidity of UNPS will be first neutralized and then, the precipitation of AU takes place and finally the reaction is stopped at pH 8, ostensibly to recover all uranium from mother liquor. The Equation 1 shows the initial free acidity neutralization equation and Equation 2 indicates the bulk AU (Type-III) precipitation reaction. The equilibrium precipitation is desirable for consistent and reproducible quality of the precipitates and subsequent UO_2 powder. The equilibrium precipitation is confirmed by the flat curve obtained at around pH 3 in pH vs time curve given in **Figure 1**.

Equation 1: Initial Free acidity neutralization reaction

$$HNO_3(aq) + NH_3(v) \rightarrow NH_4NO_3(aq)$$

Equation 2Bulk AU precipitation reaction

$$2UO_2(NO_3)_2\,(aq) + 5NH_3\,(v) + 5H_2O \rightarrow 2UO_3 \cdot NH_3 \cdot 3H_2O \downarrow + 4NH_4NO_3(aq) + \Delta H$$

(Type III AU)

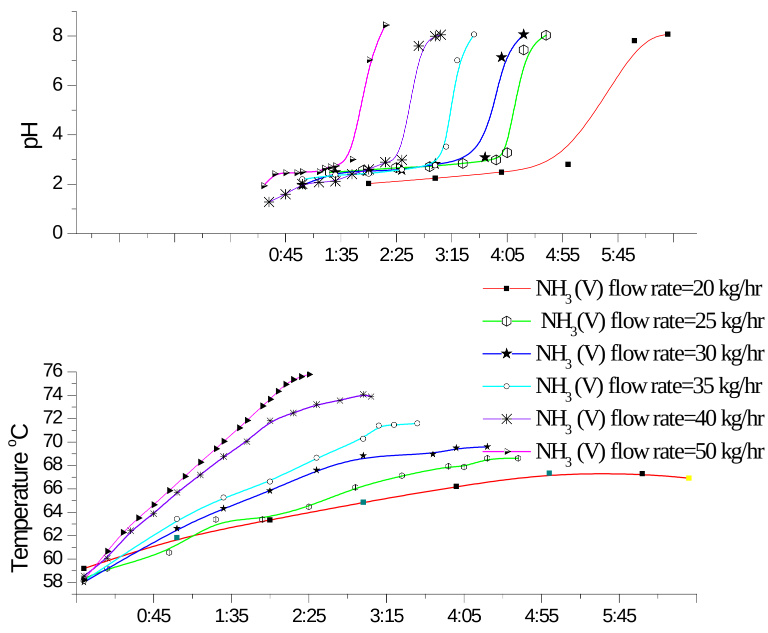

Figure 1pH and temperature profile

In this process ammonia consumption of 120 kg/ batch was measured by coriolis principle based mass flow totalizer, installed in the plant. The ammonia consumption for one batch, is stoichiometrically estimated as 119 kg from Equation 1&Equation 2 which is quite close to the measured value. This confirms the presence of type-II AU. As indicated in Equation 2, the precipitation equation is exothermic reaction wherein, temperature of solution increases with progress of reaction and goes to maximum and decrease thereafter till the end. The same is observed from **Figure 1** which indicated the end of bulk AU precipitation much before the pH 8. It is also seen that maximum temperature attained during precipitation is an increasing function of ammonia flow rate. The maximum temperatures were measured as 67.35°C and 75.78°C for ammonia flow rates 20 kg/hr and 50 kg/hr respectively.

2.1 Effect of ammonia flow rate on sintering

The precipitated ammonia slurry was filtered in rotary vacuum Pan Filter unit at flow rate of 1100 lit/hr and continusoly dried in Turbo dryer at 330°C with 2 hours residence time. The dried AU powder is calcined at 695°C temperature to produce U_3O_8 powder. Based on the resulting SSA of U_3O_8 powder, reduction temperature was set between 540 to 670°C to get the required SSA of

UO_2between 2.8-3.2 m^2/gm. The powder was pre-compacted and granules were produced. Thesegranules were mixed with 0.3% lubricant/binder. The granules added with binder is pressed in hydraulic press at the pressure between 145 to 170 bars to form green pellets. Green pellets are charged into boats made of molybdenum. Boats loaded with 25 kg of pellets are pushed inside sintering furnace at frequency of 1 boat every 1hr 30 min so that pellets will take 45 hrs of residence time inside furnace and exposed up to 1700ºC temperature. Boat after exit from furnace and sufficient cooling will be subjected to density check on sample basis by using Archimedes principle. Various lots were produced with different vapour ammonia flow rate and sintering results are given in**Table 1**. All lots have shown more than 95% recovery. As the average density results from the above table it is learned that flow rate of ammonia in precipitation has not much significant effect on sintering density. Hence, it is decided to maintain higher flow rate i.e, 50 kg/hr for increasing production and productivity since quality of pellets are met.

Table 1 Density of sintered pellets

Sı	NH_3 flow ı (kg/hr)	Average Sintered pellet dens (gm/cc)
	20	10.60
	25	10.61
	30	10.64
	35	10.61
	40	10.58
	50	10.62

2.2 Effect of U_3O_8 SSA on sintering

After finalizing the ammonia flow rate at50 kg/hrduring AU precipitation process, the effect of calcination temperature on sintering of pellets recovery for 1hr pushing interval furnace was studied. Since SSA ofU_3O_8 powder is one of the critical parameter for its quality and it depends on calcination temperature. Hence to study its effect during sintering of various powder lots with different SSA were produced. Nearly 60 UO_2 powder lots, weighing 600 kg each, were produced with 50 kg/hr ammonia flow rate are subjected to different temperature in calcination operation for getting different SSA of U_3O_8 powder.The reduction temperature is adjusted between 540-670ºC to obtain 2.8-3.2 m^2/gm SSA of UO_2 powder as per regular procedure. These UO_2 powder lots were granulated and final compacted to form green pellets and subsequently pushed inside sintering furnace having temperature up to 1700ºC at 1hr pushing interval.

Similarly results of these 60 lots were checked for pellet recovery. The acceptable density of UO_2 pellets for the PHWR lies between 10.45-10.75 gm/cc. The results of sintering recovery vs median of U_3O_8 SSA are plotted in **Figure 2** and it is observed that sintered pellet density produced from the UO_2 powder having U_3O_8 SSA 3.9 to 4.0 m^2/gm has exhibited maximum sintering recovery of

98.6 % and poor recovery above & below this range. The lower sintering recovery was observed as 64.1% between 3.0 to 3.3 m^2/gm of U_3O_8 SSA. Further exclusive trials were taken for validation.

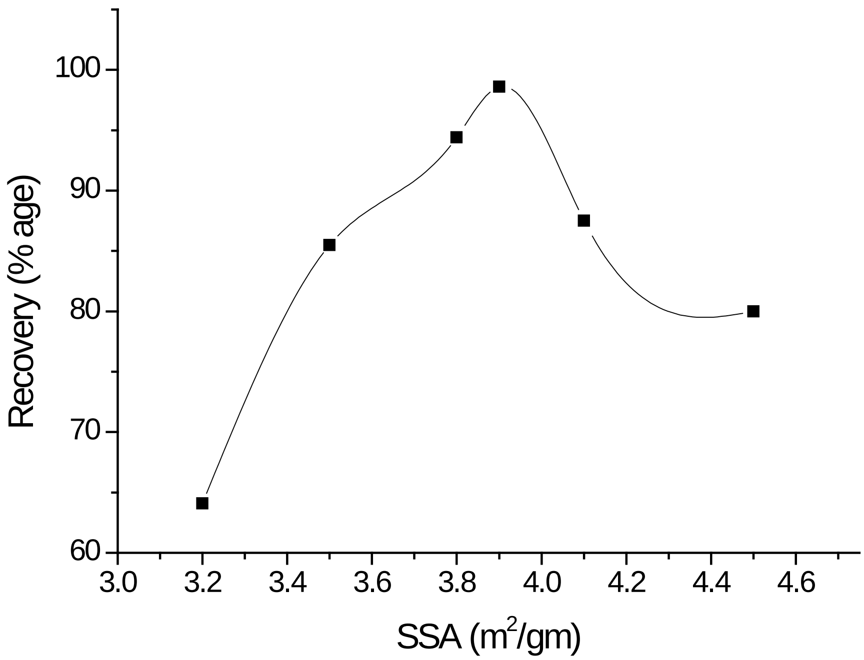

Figure 2 U_3O_8 SSA vs sintering recovery

2.3 Validation: effect of U_3O_8 SSA on sintering for higher recovery

Based on the above observation, 50 UO_2 lots were produced with 50 kg/hrammonia flow rate in precipitation and U_3O_8 SSA between 3.8 to 4.0 m^2/gm and subjected for sintering 1hr pushing interval. The results are given in**Table2**.

Table 2 U_3O_8 SSA and Sintering recovery

Sı	U_3O_8 S (m^2/gn	No of l	Sintering recov (%)
1	3.8	18	98.3
2	3.9	18	98.6
3	4.0	14	97.8

2.4 Morphology of UO_2 powder and grain structure of pellets

The SEM images (at 1,000X and 10,000X magnifications) are taken for UO_2 powder produced with

Figure 4SEM Image of UO_2 powder: 1,000X

Figure 3SEM Image of UO_2 powder: 10,000X

50 kg/hr ammonia flow rate in precipitation and controlled process parameters during heat treatment operation. Microstructure shows that primary particles of few nanometers and intermediate particles of cylindrical needle like structures which form further dendrites structure in agglomerates. SEM micrographs does not focus on primary particle but needle like structures are clearly observed. It is observed from SEM microstructures that secondary agglomeration formation is predominant for all five flow rates of ammonia.

3 standardization of pelletization operation

After optimizing the UO_2 powder production parameters, it was imperative to standardizepelletization process parameters to achieve higher sintered pellet density and higher recovery. Accordingly, batch size for binder addition was optimizedat 80 kg UO_2 granules and blending time was set at15 min for better homogeneity. Final compaction pressure was set at 170 bar withfacilitating dwell time 5 seconds. Temperature profile was optimized in sintering process to increase the residence time for surface diffusion, which generally occurs at lower temperature and similarly reduced the residence time for lattice diffusion, prevailed at higher temperature.The sintering temperature profiles for 1hr 30min and 1hr pushing intervals are indicated in **Table 3** and **Figure 5**. An attempt was made to accelerate the surface diffusion followed by lattice diffusion. Accordingly heating rate slope (°C/min) was raised to Sb = 64° from Sa =53° as indicated in**Figure** ***5***. The 30hr profile cycle was further optimized and three slops Sc_1=76°, Sc_2=48°and Sc_3=57°are embedded for higher recovery.The above optimizedpelletization parameters were adopted for regular production and achieved significant increase in average sintered pellets'density. The standard deviation of density was also reduced which indicates how precisely the process is controlled.

Table 3 Temperature profile in sintering furnace

Temperature profile	Zone-1	Zone-2	Zone-3	Zone-4	Zone-5	Zone-6
45hrs residence time (PI=1hr 30 min)	400°C	800°C	1300°C	1700°C	1700°C	1700°C
30hrs residence time (PI=1hr)***optimized***	600°C	800°C	1100°C	1400°C	1700°C	1700°C

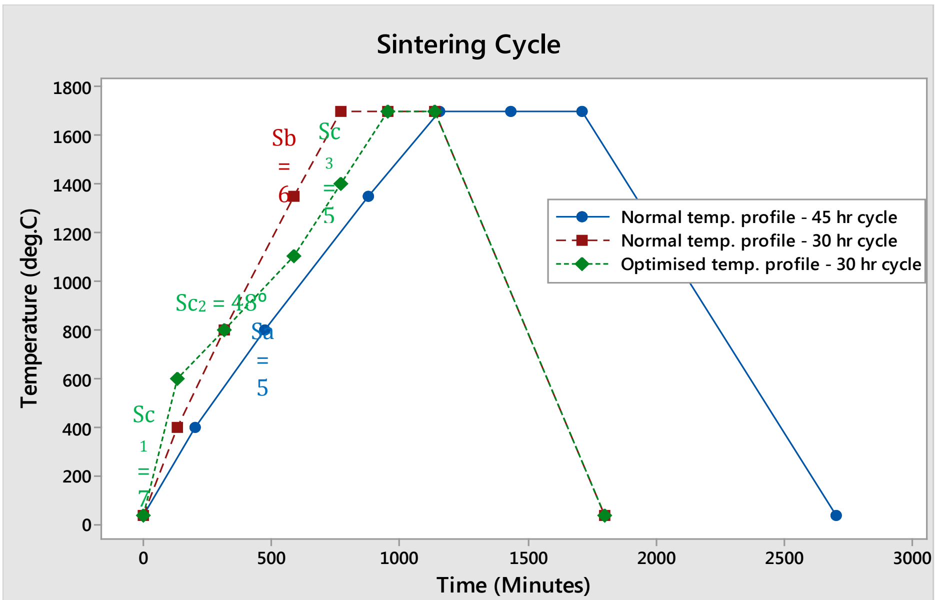

Figure 5 Optimization of sintering furnace temperature profile

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Table 4 Results of optimization

Optimized process parameter	Average sintered Density (gm/cc)	Standard deviatio (gm/cc)
UO_2 powder production	10.58	0.064
Pellet production	10.62	0.042

4 Conclusion

The effect of ammonia flow rate and U_3O_8 SSA on sintering of UO_2 green pellets were studied and following conclusions are made to achieve high sintering recovery with increased average sintered pellet density:-

- UO_2 powder production process was optimized with 50 kg/hr of ammonia flow rate in precipitation and SSA of $U_3O_8$3.9 -4.0 m^2/gm respectively.

- Optimized sintering temperature profile has 3 slopes (76^o,48^o and 57^o) to accelerate the sintering rate due to surface diffusion.

The production capacity of a sintering furnace, before optimization, was 1 boat per 1hr 30 min equivalent to 400 kg sintered pellet per day. After successful optimization of process parameters across powder and pellet production plants, the sintering is stabilized at 1hr PI and the overall production capacity of the furnace is increased to 600 kg/day, which is 50% increase without any capital investment.

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