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OPTIMIZATION OF PROCESS PARAMETERS IN PRECIPITATION FOR CONSISTENT QUALITY UO_2 POWDER PRODUCTION

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ABSTRACT- Nuclear reactor grade natural uranium dioxide powder is being produced through precipitation route, which is further processed before converting into sintered pellets used in the fabrication of PHWR fuel assemblies of 220 and 540 MWe type reactors. The process of precipitating Uranyl Nitrate Pure Solution (UNPS) is an important step in the UO_2 powder production line, where in soluble uranium is transformed into solid form of Ammonium Uranate (AU), which in turn reflects and decides the powder characteristics. Precipitation of UNPS with vapour ammonia is being carried out in semi batch process and process parameters like ammonia flow rate, temperature, concentration of UNPS and free acidity of UNPS are very critical and decides the UO_2 powder quality. Variation in these critical parameters influences powder characteristics, which in turn influences the sinterability of UO_2 powder. In order to get consistent powder quality and sinterability the critical parameter like ammonia flow rate during precipitation is studied, optimized and validated. The critical process parameters are controlled through PLC based automated on-line data acquisition systems for achieving consistent powder quality with increased recovery and production. The present paper covers optimization of process parameters and powder characteristics.

Keywords: Vapour ammonia, process parameters, Equilibrium precipitation, Ammonium urinate

Introduction

In the manufacturing of nuclear fuel for PHWR type reactor, UO_2 is produced through ex-ADU route. This route is mainly of two types: aqueous ammonia and vapour ammonia precipitation process. In recent past India has switched to vapour ammonia precipitation route from aqueous ammonia precipitation route because of advantages like elimination of handing and preparation of aqueous ammonia, reduction in batch cycle time to 75%, increase in batch size by 10% and reduction in effluent generation which has resulted through put by more than two folds. It has also improved filterability by avoiding relatively high viscous ammonium hydroxide. It led to conservation of energy, water, steam and man-hours.

The effect of temperature and uranium concentration in mother liquor was studied by L C Watson et.al [5]. It was deduced that the precipitation temperature has least effect on sinter density of powder precipitated by vapour ammonia, compare to linear effect of precipitation temperature on sinter density of powder precipitated by aqueous ammonia. The settling rate, an early indication of precipitate quality has great tolerance for precipitation temperature for vapor ammonia precipitation as compare to aqueous ammonia precipitation. It is observed that the rate of AU precipitation by vapour ammonia is three times faster than AU precipitation by aqueous ammonia. This is due to high polarisability of vapour ammonia which helps in maintaining low solubility allowing the particles to grow uniformly and rapidly and thus keeping nucleation to minimum at higher pH. Settling rate is indirect measure of particle shape, size and density based on stroke's law. It is also observed that settling rate has very less tolerance for aqueous ammonia precipitation as compared to vapour ammonia precipitation. When AU precipitated by ammonia vapor, the precipitate matrix having uranyl and hydrate molecules without ammonia molecule is free flow able and anhygroscopic in nature compared to AU precipitated by aqueous ammonia. The better flowability of the precipitate can also be attributed 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 highly related to die filling. AU gets converted to β-UO_3 at temperature 275^0C.

A literature survey by Woolfrey [2] showed that the AU powder characteristics like composition, surface area, particle size and density are largely dependent on the precipitation conditions which are mainly pH, uranium concentration, and temperature, rate of precipitation and nature of precipitant.

There has been considerable argument concerning the nature of the AU precipitate. Cordfunke [6,7] reported the presence of four distinct compounds which he designated:

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 is well known that the thermal history of uranium-di oxide powder has great 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[4].

The surface activity does not solely depend on surface area. The AU powders containing large agglomerates gives sintered pellets with low densities and non-uniform microstructures[1].

1. Experimentation:

The main feed material is Uranyl Nitrate Pure Solution (UNPS) which is prepared by extracting crude uranyl nitrate slurry using 31% TBP and kerosene mixture and subsequently is back extracted by demineralized water. Uranium concentration and free acidity was taken as ≈104 gU/l and ≈ 0.2N respectively. Another reagent, used for experiments, is anhydrous ammonia of 99.99% purity.

Precipitation trial was carried out in semi-batch reactor in which Uranyl nitrate solution is taken as batch mode and ammonia vapour is admitted continuously. Tank volume is kept constant as 5344 Lts for all experiments. The tank is agitated by three stage paddle type agitator. The liquid height to tank diameter (L/D) ratio is maintained at 0.9211. The uranyl nitrate solution is preheated to temperature of 58^0C before admitting ammonia into reactor. Ammonia flow rate is varied to study the effect on precipitation characteristics. All precipitation trials were carried out at five distinct ammonia flow rate as 20, 25, 30, 35 and 40 kg/hr. Ammonia flow rate is maintained with accuracy of ± 0.5 kg/hr to the set value with the help of closed loop flow control in PLC based SCADA system. Ammonia vapour flow is controlled by field instrument like piston/plug type flow control valves coupled with coriolis type mass flow meters. Reaction temperature is measured by highly accurate platinum type resistant temperature detector. During precipitation pH and temperature are measured and captured as reaction progresses. The pH of initial UNPS solution for all experiments are measured by glass electrode based bench pH meter and are less than 1.

2. Result and Discussion:

Batch precipitation process is an acid-base reaction starts with initial acidity neutralization and then bulk AU precipitation proceeds and finally ended with complete AU precipitation at 8 pH . The variation of pH and temperature are graphically represented as function of precipitation time in Figure 1. In Figure 1 above graph is drawn for pH verses time of precipitation. The flat region of curve indicates the bulk precipitation of AU occurs between 2.0 to 3.5 pH. The flat curve generally obtained for equilibrium precipitation only. The total ammonia consumed for all different ammonia flow rate precipitations is around 120 kg based on the initial acidity of solution which also corroborates the equilibrium AU precipitation. Equilibrium precipitation is desirable for consistent and reproducible quality of the precipitates.

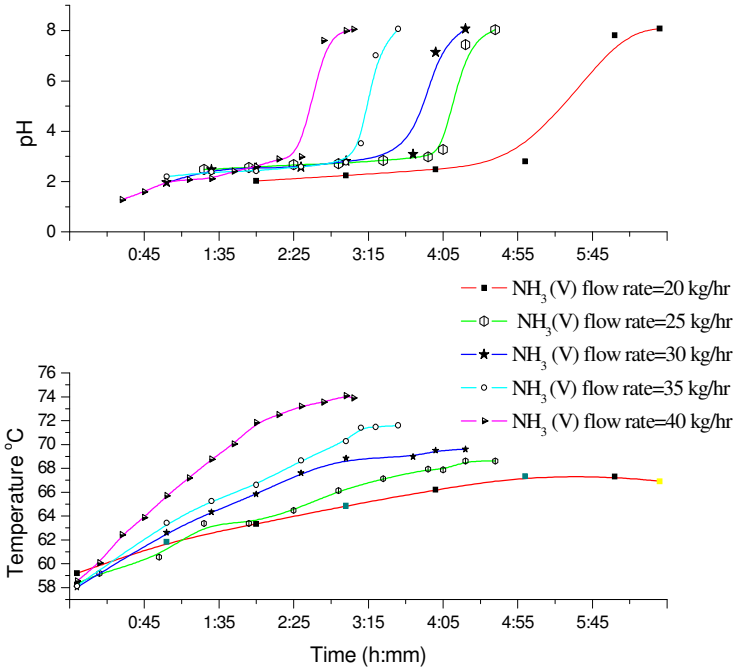

Figure 1 Progress of precipitation reaction

It is clear from graph that maximum temperature attained during precipitation is an increasing function of ammonia flow rate. The maximum temperatures were measured as 67.35°C and 74.09°C for ammonia flow rates 20 kg/hr and 40 kg/hr respectively.

2.1 Effect on settling rate:

Settling rate is a measure in deciding the quality of precipitates like specific surface area, particle size & its distribution. It has already been established that at pH 8 all uranium gets precipitated to AU of distinct type based on their precipitation condition. Jar test (Capacity 500 ml) is conducted to analyze settling characteristics of precipitates by allowing it to settle for five minutes and then settled volume of deposited precipitates is measured. All repeated experiments for different ammonia flow rates have shown almost the same settled volume in the range of 60 to 65 ml.

2.2 Effect on Bulk density of AU dried powder

Bulk density is one of the significant parameters for deciding the sinterability and visual recovery of UO_2 pellet. AU slurry is filtered in a rotary Pan Filter under vacuum of 400 mmHg and subsequently dried in Turbo dryer at temperature of 320^0C to 340^0C. The bulk density of dried AU and UO_2 powder is shown in Figure 2. It is observed that effect of ammonia flow rate on bulk density of AU and UO_2 has no appreciable changes. But there exists one to one relationship between AU and UO_2 powder's bulk density.

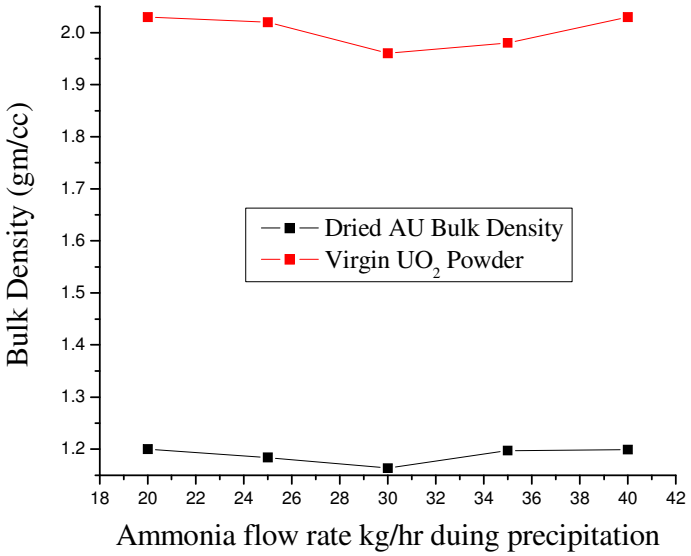

Figure 2 Variation of Bulk Density of virgin UO_2 powder and its dried AU Powder

2.3 Effect on particle size & size distribution of AU powder

Dried AU powder is checked for its particle size and distribution using laser diffraction method. It is cleared from SEM microstructures (Figure 4 to Figure 8) the size distribution by laser diffractor is actually the size of agglomerates. Various lines are plotted between percentage oversize agglomerates and AU precipitation condition (ammonia flow rate). The size distribution and its percentage against ammonia flow rates are shown in Figure 3. It is evident from the figure that size distribution is fairly same and consistent for all flow rates of ammonia.

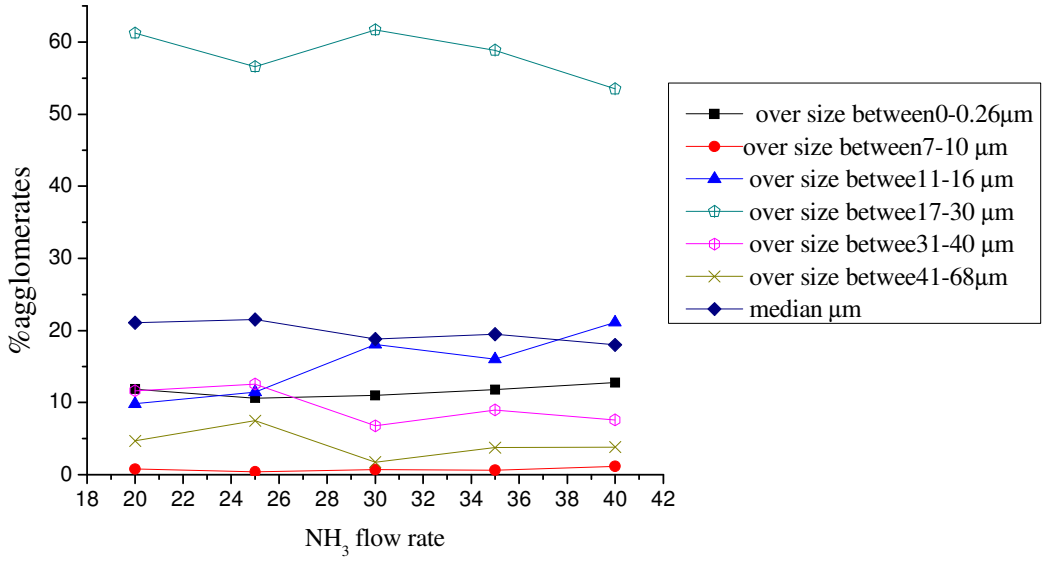

Figure 3 Quantity and size of agglomerates vs ammonia flow rate during precipitation

2.4 Effect on specific surface area of AU powder:

The dried AU powder is again heated to 100^0C to drive out the adsorbed gases to surface of AU powder for at least 1 hr. After drying the specific surface area (SSA) of every batch powder was estimated by BET method. The effect of precipitation condition on SSA is summarized in Table 1. The relation between AU powder SSA and ammonia flow rate in precipitation could not be established due to variation in AU surface area. It may be due to compositional change during drying from AU to $UO_3.xH_2O$. But a fair co-relation was found among ammonia flow rate, calcination temperature and U_3O_8 SSA. During calcination $UO_3.xH_2O$ gets converted to U_3O_8 which leads to nucleation and growth of new phase inside the same agglomerates.

Table 1 SSA at varied precipitation condition

Sr.No	kg NH_3/hr Precipitation	AU SSA(m^2/gm)	Calcination Temp(°C)	U_3O_8 SSA(m^2/gm)
1	20	10.5	693	3.9
2	25r	9.05	697	3.8
3	30	11.4	702	4.1
4	35	9.2	705	3.9
5	40	9	685	3.5

During this process many surface sites get active and pores get closed but agglomerate structure remains essentially same [1]. Similarly in present experiments as precipitation rate increases calcinations temperature was increased to obtain required SSA due to fact that with increased flow rate supersaturation in mother liquor comes down and slow down the growth of particles and agglomerates. But it is also observed that after 30 kg/hr ammonia flow rate there is significant increase in mother liquor temperature[Figure 1] which again accelerates the growth of particles and agglomerates. Hence required SSA is obtained at lower calcination temperature itself.

2.5 Effect on Morphology of AU powder:

Precipitation condition has predominant effect on morphology of AU powder which does not change significantly in subsequent operation. Hence morphology of AU powder influences the sintering behaviors at pelletization stage. The phenomenon of particle formation can be implicitly distinguished into three stages: nucleation, growth and agglomeration. Nucleation and growth are the function of super saturation. Before or after reaching end of the growth particle can form clusters or agglomerates. Agglomeration requires the collision of particles and subsequent adhesion due to attractive forces for instance van der Waals forces. Consolidation between primary particles can take place by crystalline growth from contact point.

The SEM microstructure were taken for all AU powder produced at various precipitation conditions for three magnifications 200, 1000 and 5000 and shown from Figure 4 to 8. 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.

The primary particles observed in Figure 4 (20 kg NH_3/hr) are grown as thick needle like structure. Needle like structures are seen in the agglomerate. As ammonia flow rate is increased the primary particles of needle like structures start diminishing and fluffy like structures increases in the agglomerate. At flow rate 30kg/hr (Figure 6) fluffy like particle are only predominant. But after 30 kg/hr of ammonia flow rate initiates the appearance of needle like structure again in the agglomerates. This increase can be attributed to the high temperature during the precipitation. AU precipitation is an exothermic reaction which increases the solution temperature. Again at 40kg/hr ammonia flow rate needle like structure is observed since the mother liquor temperature was soared up to 74.09^0C (Figure 1).

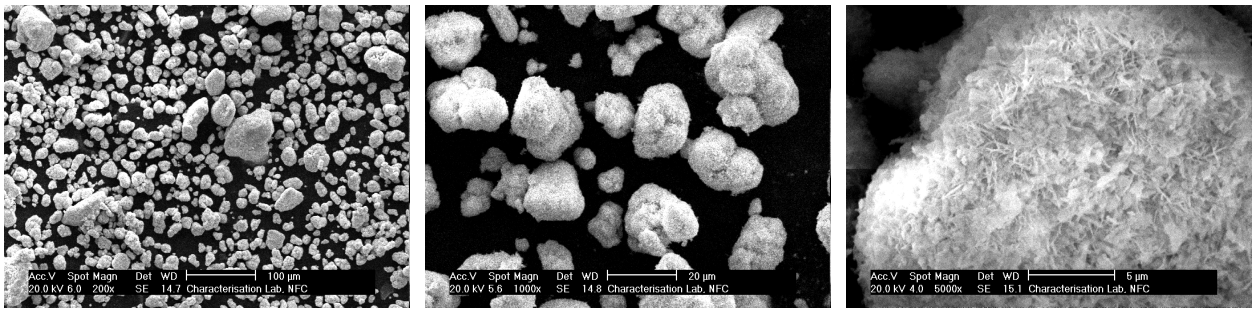

Figure 4 SEM microstructure of AU precipitated by 20 kg/hr ammonia flow rate

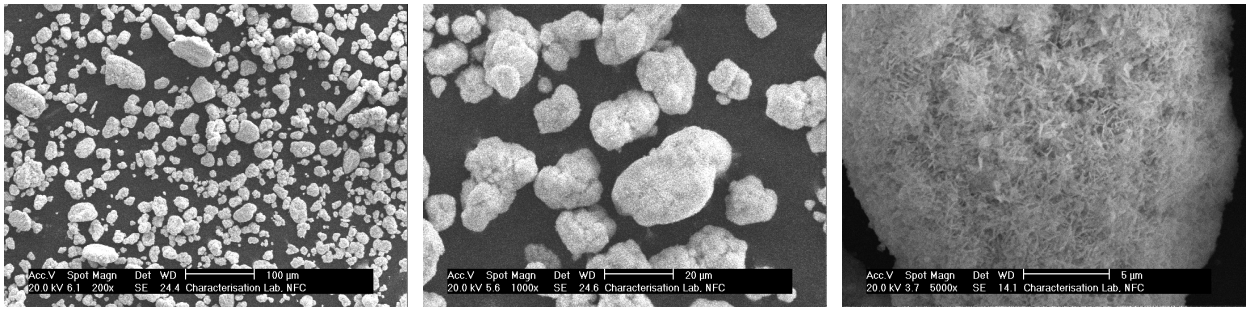

Figure 5 SEM microstructure of AU precipitated by 25 kg/hr ammonia flow rate

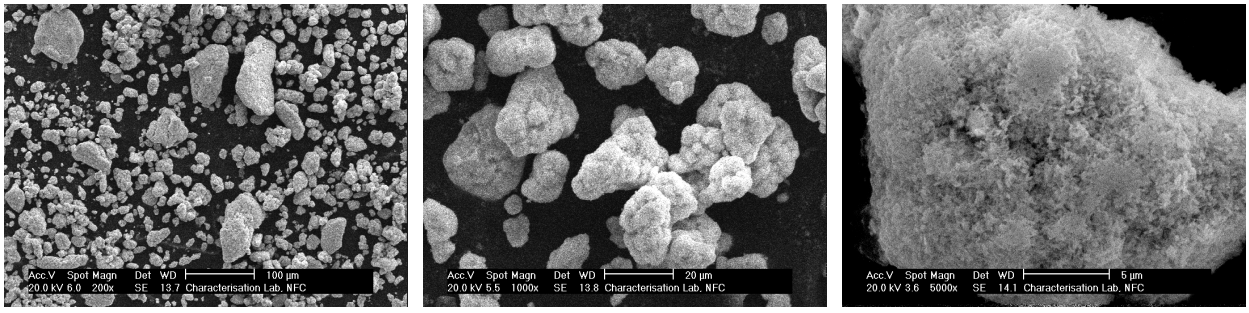

Figure 6 SEM microstructure of AU precipitated by 30 kg/hr ammonia flow rate

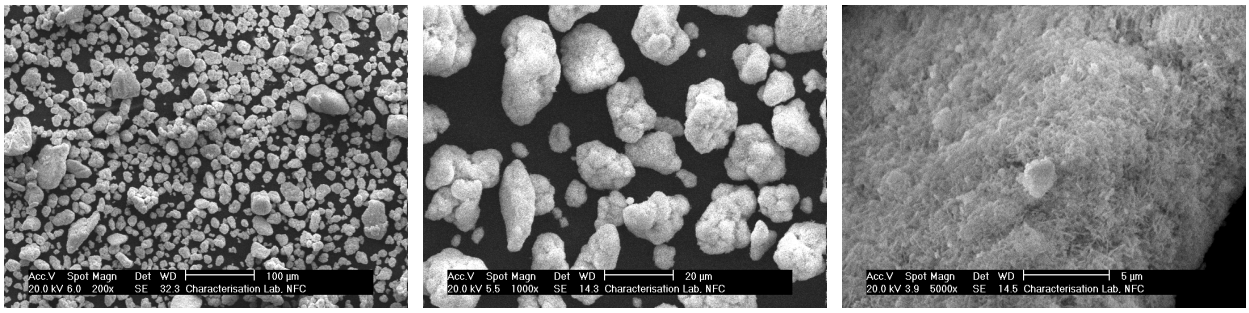

Figure 7 SEM microstructure of AU precipitated by 35 kg/hr ammonia flow rate

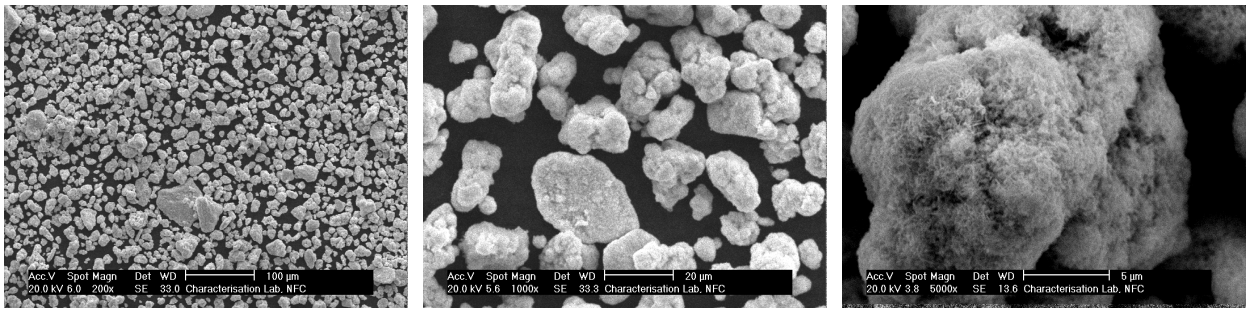

Figure 8 SEM microstructure of AU precipitated by 40 kg/hr ammonia flow rate

2.6 XRD Findings

To study the composition of AU precipitated with various flow rates, slurry was collected at 3.5 pH and 8.0 pH. Slurry was filtered and cake was dried at 100°C for 8hr. AU powder samples were subjected to XRD for compositional analysis. XRD apparatus used for study, was Regaku make bearing model No. DMAX 2200. It is observed that AU particles are not amorphous but are crystalline in nature. As per XRD studies AU powder precipitated at end pH of 3.5 shows predominantly the defraction for composition Type-I AU. Structure of type I is orthorhombic and cell dimensions are a=13.977, b=16.696 and c=14.672 where as AU powder precipitated at end pH 8 shows Type-III equivalent structure of AU. The structure of Type III is hexagonal and cell dimensions are a=14.087 and c=14.494. The AU type strongly depends on end pH.[2]. Type I AU is said to be prominent at end pH below 4.5 and Type III is observed at end more than 7.

These compositions of AU are in agreement with the literature published at various places. The Type III AU gets easily converted α-U_3O_8 (orthorhombic structure) which gives good sinterable active UO_2 powder.

2.7 Heat treatment of powder , pellet fabrication and sintering

Thermal history of powder plays an important role in determining sinterability of UO_2 powder. Dried AU powder is calcined between 695^0C to 705^0C to U_3O_8 and maintained the specific surface of U_3O_8 powder between 3.4 to 4.0 m^2/gm. Accordingly temperature of reduction furnace is adjusted between 540^0C to 600^0C to maintain specific surface area between 2.9 to 3.3 m^2/gm. Virgin UO_2 powder is granulated to increase agglomeration using roll compaction and subsequently compacted to green pellets. Sintering of green pellets is carried out at 1700^0C. Pellets produced with different precipitation condition are shown in Table 2. It is evident from the table that the powder produced at 40 kg/hr of ammonia flow rate is more compactable in nature which requires less compaction pressure, density variation more. Powder with flow rate upto 35 kg/hr exhibits more consistent behavior.

Table 2 Sintering behavior of powder

Sr.No	NH_3 (kg/hr)	Granules density(gm/cc)	Compaction pressure (bar)	Green pellet density (gm/cc)	Sintered pellet density (gm/cc)	
		average	range	range	range	average
1	20	2.60	155-160	5.75-5.85	10.46-10.75	10.60
2	25	2.69	155-170	5.76-5.86	10.46-10.74	10.61
3	30	2.74	165-170	5.74-5.83	10.46-10.70	10.64
4	35	2.65	155-170	5.71-5.83	10.22-10.70	10.61
5	40	2.70	140-145	5.75-5.89	10.35-10.63	10.55

3. Conclusion

The Effect on AU powder was studied at five different ammonia flow rates 20,25,30,35,40 kg/hr with an objective to increase recovery and production. The results of the study are summarized as :

i. There is no appreciable change in settled volume as well as particle size and its distribution with the increase of ammonia flow rate.
ii. Increase in flow rate does not have any significant effect on bulk density of AU and UO_2 powder but there exists one to one relationship.
iii. Increase in ammonia flow rate requires more calcination temperature where as low calcination temperature is adequate for 40kg/hr flow rate to achieve

consistent U_3O_8 SSA. And subsequent UO_2 powder produced needs low compaction pressure to achieve required green density as well as sintered density.

iv. Needle like structure are predominant at low flow rate whereas fluffy like structure are seen at high flow rate. However at 40kg/hr flow rate needle like structures reappears due to high temperature effect during precipitation.

v. XRD finding shows that Type I and Type III are predominant in AU precipitated at pH 3.5 and 8 respectively.

4. Acknowledgement

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