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Study on the effect of free acidity and entrained TBP in UNPS on the quality of ADU powder

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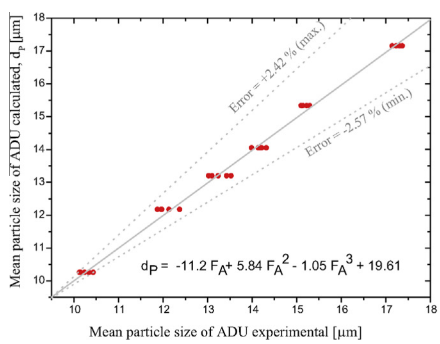
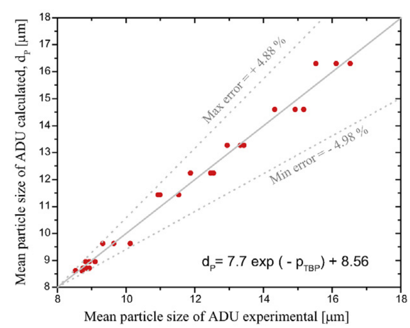
HIGHLIGHTS

- The mean particle size of precipitated ADU depends on the free acidity in UNPS.
- The mean particle size of precipitated ADU also depends on the entrained TBP in UNPS.
- As free acidity in UNPS increases, mean particle size of precipitated ADU decreases.
- As entrained TBP in UNPS increases, particle size of precipitated ADU decreases.
- Based on the experimental results two correlations were developed to find d_p of ADU.

GRAPHICAL ABSTRACT

From the experimental study it was found that mean particle size of precipitated Ammonium Di-Uranate (ADU) depends on the free acidity content and entrained TBP in Uranyl Nitrate Pure Solution (UNPS). It was found that as the free acidity as well as the entrained TBP content in UNPS increases, mean particle size of precipitated ADU decreases. Based on the experimental results two correlations were developed as shown in below figures.





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ABSTRACT

The mean particle size and size distribution of Ammonium Di-Uranate (ADU) particles, precipitated during the precipitation reaction of Uranyl Nitrate Pure Solution (UNPS) with ammonia play an important role on the sintered density of UO_2 pellets. The quality of precipitated ADU depends on number of process parameters *viz.*, pH of UNPS, concentration of uranium in UNPS, flow rate of ammonium hydroxide, temperature etc. However, the effects of the presence of free acid and entrained Tri-Butyl-Phosphate (TBP) in UNPS on the quality of ADU powder were not studied till date. Experiments were conducted to study the effect of free acidity and the presence of entrained TBP on the quality of precipitated ADU particles. It was found that as the concentration of free acid as well as the concentration of entrained TBP in UNPS increases, the particle size of precipitated ADU decreases. Based on the experimental results two correlations were developed to determine the mean particle size of ADU; one is based on the free acid content of UNPS and the other is based on the content of entrained TBP in UNPS, which is used for the precipitation. It was found that the correlated values are well fitted with the experimental data within ±3% errors for both the cases. Both these correlations are applicable when other process parameters remain constant. The experimental details and results are discussed in this paper.

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Nomenclature

A–D	constant in Eq. (6) (–)
A_1, B_1	constant in Eq. (9) (–)
C_1, C_2	constants in Eqs. (5) and (8) (–)
$C_{U,i}$	initial concentration of uranium in UNPS (mol/l)
d_p	mean particle diameter of ADU (μm)
F_A	Free acidity content in UNPS (mol/l)
$K_{d,s}$	distribution coefficient for the stripping of nitric acid from organic media (–)
K_e	equilibrium constant for extraction reaction ($mol^{-2}\ m^6$)
N_1	normality of first UNPS solution (N)
N_2	normality of second UNPS solution (N)
N_3	normality of third UNPS solution (N)
$K_{e,s}$	equilibrium constant for stripping reaction ($mol^{-2}\ m^6$)
T	temperature ($mol^{-2}\ m^6$)
Q_{AH}	flow rate of precipitant (ml/min)
V_1	volume of first UNPS solution (l)
V_2	volume of second UNPS solution (l)
V_3	volume of third UNPS solution (l)

1. Introduction

Uranium dioxide (UO_2) is the commonly used fuel in present day nuclear power reactors [1–6]. In production process of UO_2, intermediate process materials *viz.*, Magnesium Di-Uranate (MDU) and Heat Treated Uranium Peroxide (HTUP) are produced by the processing of uranium ore concentrate. MDU and or HTUP are dissolved in nitric acid and the dissolved uranium in the solution is refined by solvent extraction by using 33% Tri-Butyl Phosphate (TBP) diluted with kerosene as solvent. The extracted uranium in the loaded solvent is stripped with demineralized water to yield nuclear grade Uranyl Nitrate Pure Solution (UNPS). UNPS is reacted with ammonium hydroxide (NH_4OH) solution and converted into Ammonium Di-Uranate (ADU) by precipitation. The precipitated ADU is converted to uranium di-oxide (UO_2) powder by a series of thermochemical operations *viz.*, calcination, reduction and stabilization.

The quality of ADU powder produced during precipitation plays an important role on the sintered density of UO_2 pellets. So the process parameters followed in the process of ADU precipitation which is carried out in batch operations are very important. The quality of precipitated ADU *viz.*, size distribution, mean particle size, bulk density etc., depend on number of process parameters *viz.*, pH of UNPS, concentration of uranium in UNPS, flow rate of ammonium hydroxide, temperature etc. [2].

The UO_2 powder production steps play vital roles in the fabrication of high density UO_2 pellet for Pressurized Heavy Water Reactor (PHWR) in India. UO_2 powder is prepared either by the 'dry process' [3] or by the 'wet chemical process' [4,5]. There are different wet processes followed for the same, among these the ADU route is the most commonly followed and also well investigated [6–13]. In this process, ADU is precipitated out from UNPS by reacting with ammonium hydroxide solution in a semi-batch reactor [14]. The precipitation of ADU is the most crucial step in the production of UO_2 fuel for nuclear reactors. The quality of ADU precipitate is very important in plant operations as it affect the final sinterability of the UO_2 [14–16]. It was found that various process parameters *viz.*, uranium concentration in UNPS solution, concentration of ammonium hydroxide in aqueous solution, rate of addition of ammonium hydroxide solution, degree of agitation during precipitation and temperature affect the quality of precipitated ADU and the effect of these process parameters on the particle size of precipitated ADU were studied by many investigators [17–33].

Janov et al. [24] studied the effect of pH of the slurry after ADU precipitation on the size of the agglomerates of ADU precipitation and found that, higher the pH of slurry after precipitation, the smaller the size of the agglomerates. They also studied the settling characteristics and filterability of the ADU slurry and found that large agglomerates produced low density sintered UO_2 pellets. They also found that the washing of ADU with DM water to remove nitrate ions did not affect the properties of the UO_2 powder but extensive washing decreased the filterability of ADU slurry.

Rajagopal et al. [25] found that the physical properties of ADU, precipitated from solution obtained from solvent extraction by using dilute solvents *viz.*, methanol, ethanol and isopropanol were found to be better compared to that precipitated from aqueous medium alone and were easily filterable, compact, free flowing in nature and of larger in size than that prepared by the conventional method. They also found that the particles were uniformly distributed and not agglomerated.

Murty et al. [26] studied the precipitation of ADU in batch operation at various temperatures with different flow rates of ammonia and their effects on the characteristics of precipitated ADU *viz.*, the rate of settling, moisture content, ammonia-to-uranium mole ratio and nitrate content in precipitated ADU. They found that at low precipitation rates, dispersion of the precipitated particles was favoured at low temperature and agglomeration was favoured at high temperatures. Low precipitation rates were preferred in view of sinterability requirement of final uranium dioxide powder produced from precipitated ADU. These findings are significant to reduce the cost of energy for heating and to determine the required quantity of the precipitating agent *i.e.*, ammonium hydroxide.

Doi and Ito [5] found that precipitated ADU usually consists of agglomerated particles of size about 0.1 μm, which affect the calcination of ADU to UO_3 and its reduction to UO_2. Abdelraz [27] had suggested a scheme for possible reactions which will lead to the polymerization of UO_2^{2+} ions to $UO_2[(OH)_2UO_2]_4^{2+}$, with uranyl hydroxide, $UO_2(OH)_2$ as an intermediate compound. The reaction rate equation was derived, where apparent reaction rate constant was found to be influenced by both pH and temperature. Woolfrey [28] found that thermal decomposition of ADU in hydrogen atmosphere is affected by its initial composition *viz.*, ammonia and nitrate content and the morphology of the ADU powders. The amount of self-reduction increases with increasing combined ammonia content. The specific surface area of the decomposed powder increases with increasing total ammonia content and initial surface area of the precursor ADU.

Abdelraz [27] had studied the kinetics of polymerization of UO_2^{2+} ion to $UO_2[(OH)_2UO_2]_4^{2+}$ in the ammonia–uranyl nitrate system. They also studied the effects of pH, temperature as well as the concentration of uranyl ion. Deptula [29] found that $UO_2[(OH)_2UO_2]_4^{2+}$ ion reacts with NH_4^+ ion to form ammonium uranate and the further course of the reaction depends on how the ammonia is added. Das et al. [30] found that ammonium poly-uranate precipitated at pH 9, at equilibrium produced product at high settling rate which was easily washable and ADU particles had higher surface area of 9–10 m^2/g, compared to the surface area of 3–5 m^2/g produced at lower pH values.