Optimization Of ADU Precipitation Process Parameters To Compensate For Detrimental Effect Of EDTA

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Abstract

Nuclear Fuel Complex at Hyderabad, India, is engaged in the manufacture of natural uranium fuel for use in all the Pressurized Heavy Water Reactors. The fuel is in the form of high-density Uranium di-oxide (UO_2) pellets clad in zircalloy tubes. The UO_2 powder is produced through the ammonium di-uranate (ADU) precipitation route.

The Precipitation process is the most critical operation in the UO_2 production process, since this is the first stage wherein the solid formation occurs and the powder morphology gets characterized. Ethylene di-amine tetra acetic acid (EDTA) is added (in ppm. quantities), to uranyl nitrate pure solution (UNPS), to chelate out rare earth elements as and when required during precipitation process.

Addition of EDTA was found to have a marked effect on the quality of the ADU precipitate produced, which in turn affected the sinterability/ metallurgical behaviour of the UO_2 powder. Studies were carried out to understand the EDTA effect and optimize the precipitation process parameters so as to ensure the sinterability of the UO_2 powder produced, with and without EDTA addition.

The observations and results of above studies are presented in this paper.

1.0 INTRODUCTION

Nuclear Fuel Complex (NFC) at Hyderabad, India is engaged in the manufacture of natural uranium fuel for use in all the Pressurized Heavy Water Reactors (PHWR). The fuel is in the form of high-density uranium di oxide (UO_2) pellets clad in zircalloy tubes. The UO_2 powder is produced through the ammonium di uranate (ADU) precipitation route. The raw material in the form of magnesium di uranate (MDU) is dissolved in commercial nitric acid to obtain crude uranyl nitrate slurry (CUNS). The CUNS is refined using solvent extraction process, with tri butyl phosphate as solvent to produce nuclear grade uranyl nitrate pure solution (UNPS) as per specification given in Table-1.The uranium in UNPS is precipitated out as ADU, by controlled addition of ammonium hydroxide in a batch reactor. The ADU slurry is filtered and dried in a Turbo drier/Spray drier. The dry ADU powder is converted to sinterable UO_2 powder by a series of thermo chemical operations of Calcination, Reduction and Stabilization in rotary furnaces.

SINTERABILITY TEST

The UO_2 powder lot produced thus, is subjected to sinterability test, wherein a sample specimen is converted to pellets by powder metallurgical operations of Pre-compaction, Final Compaction, Sintering and Center less grinding. The UO_2 powder lot gets qualified as sinterable grade, if the following criteria are met in the sinterability test:

a) Sintered density of pellet (sample quantity of pellets) should be in the range of 10.45 to 10.75 g/cc, with X bar - 3σ > 10.45 g/cc and X bar + 3σ < 10.75 g/cc.
b) Visual recovery (100% of pellets) should be greater than 70%.
c) Purity specifications should be satisfied.

2.0 ADU PRECIPITATION & SEDIMENTATION STUDIES

The ADU precipitation process is the most critical operation in the UO_2 powder manufacture since this is the first stage wherein the solid formation and the powder morphology gets characterized. It has also been established that the powder morphology of the ADU powder is retained in the U_3O_8 and UO_2 powders produced subsequently.

The feed to precipitation process, UNPS, meeting the purity criteria is taken in a batch stirred reactor and ammonium hydroxide is added in a controlled manner till the uranium is completely precipitated out as ADU. The time taken for completion of the batch is around 20 –24 hours.

After completion of the batch of ADU precipitation, sedimentation tests are carried out to determine the rate as well as pattern of settling of the ADU. About 500ml of the ADU slurry is taken in a measuring jar and allowed to settle. The level of the settled solid layer is noted every one minute and the final settled volume of the solid is noted after 5 minutes. Two different types of settling patterns as shown in Fig.-1a & 1b have been observed. The uniform pattern as shown in Fig.-1a results in a sinterable grade powder whereas the pattern observed in Fig.-1b is less likely to yield sinterable quality powder.

3.0 EDTA ADDITION

Ethylene di amine tetra acetic acid (EDTA) is added in fixed quantities to the batch of UNPS, prior to the start of ammonium hydroxide addition, to chelate out rare earth elements like gadolinium (Gd), dysprosium (Dy), thorium (Th), etc., whenever these elements are found to exceed the specification limits. EDTA forms a closed ring complex (chelate) around these elements and prevents them from getting precipitated by ammonium hydroxide. EDTA addition is occasionally necessitated due to presence of critical impurities in UNPS, in excess of the specification limits, which are in turn related to problems such as carryover of aqueous in extract in the preceding Solvent Extraction section. When the Solvent Extraction section runs smoothly UNPS of required purity is produced. For such UNPS solution EDTA is not added.

4.0 RE-OPTIMIZATION OF PRECIPITATION PARAMETERS FOR SCALED-UP EQUIPMENT

The precipitation parameters required to be re-optimized for a scaled-up precipitator. Plant scale trials were carried out, keeping constant parameters such as UNPS volume & concentration, precipitation temperature and varying parameters like flow rate of ammonium hydroxide and quantities of EDTA added. The sedimentation pattern & rate of the ADU slurries produced thus and the sinterability test acceptance data for such lots were analyzed. The data feedback was then used in varying again the flow rate of ammonium hydroxide, till ADU of required quality could be consistently produced.

Apart from the above, the precipitation parameters had to be re-optimized once again for the trials where EDTA was not added, as it was observed that maintaining the same precipitation parameters, as optimized for EDTA addition, was not resulting in sinterable grade material.

5.0 EFFECT OF EDTA ADDITION

The effect of EDTA addition is studied based on data collected from over 300 nos of plant scale precipitation trials. The data analysis is presented in Table 2 and Figures 2a to 2g. EDTA has been found to have a pronounced effect on the rate of precipitation, the final settled volumes, the sintered densities and percentage acceptance of the powder lots. Addition of EDTA has resulted in increased precipitation times, higher & wider range of settled volumes of the ADU slurry, lower sintered densities and lower % of acceptance of the powder lots.

6.0 CONCLUSION

EDTA has been found to act as retardant for the precipitation process. It also results in a wider variation in the quality of the ADU and thus the UO_2 powders. The powder metallurgical behavior of the UO_2 powders produced have been found to be adversely affected due to the addition of EDTA in the precipitation process. Further studies are required to be carried out to understand the mechanism by which EDTA affects the precipitation process.

7.0 ACKNOWLEDGEMENT

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1.0 Table 1. PURITY SPECIFICATIONS FOR
2.0 NUCLEAR GRADE UO_2 POWDER FOR PHWR FUEL

Sl.No	Element	Specification (ppm)
1	Silver (Ag)	1.0
2	Aluminum (Al)	25.0
3	Boron (B)	0.3
4	Calcium (Ca)	50.0
5	Cadmium (Cd)	0.2
6	Chromium (Cr)	15.0
7	Copper (Cu)	10.0
8	Dysprosium (Dy)	0.15
9	Iron (Fe)	50.0
10	Gadolinium (Gd)	0.1
11	Magnesium (Mg)	50.0
12	Manganese (Mn)	5.0
13	Molybdenum (Mo)	100.0
14	Nickel (Ni)	20.0
15	Silicon (Si)	30.0
16	Total EBC	<1.1

Table 2. EFFECT OF EDTA ADDITION ON PRECIPITATION AND SINTERABILITY

Sl. No.	Parameter	0 Kgs EDTA	3 Kgs EDTA	4kgs EDTA
1.	Precipitation time	13.57 hrs (Average) 10.5 – 16.49 (Range)	16.14 hrs (Average) 12.33 – 20.66 (Range)	19.43 hrs (Average) 14.45 – 26.20 (Range)
2.	Final settled volumes	62.36 ml (Average) 55 – 70 ml (Range)	68.05 ml (Average) 55 – 80 ml (Range)	77.00 ml (Average) 55 – 100 ml (Range)
3.	Sintered densities	10.64 g/cc	10.61 g/cc	10.56 g/cc
4.	% Acceptance of powder lots	100%	88.88%	82%

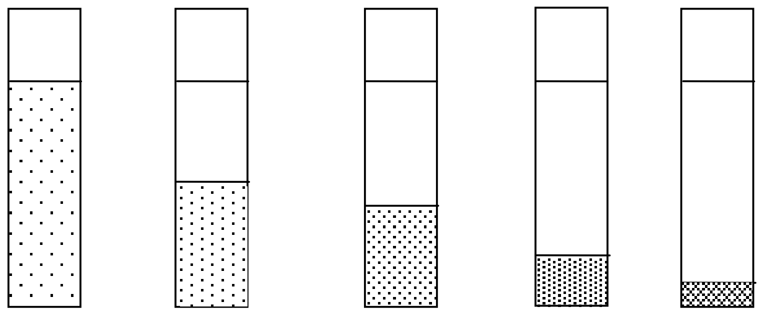

Fig. 1a. UNIFORM SETTLING PATTERN OF ADU SLURRY

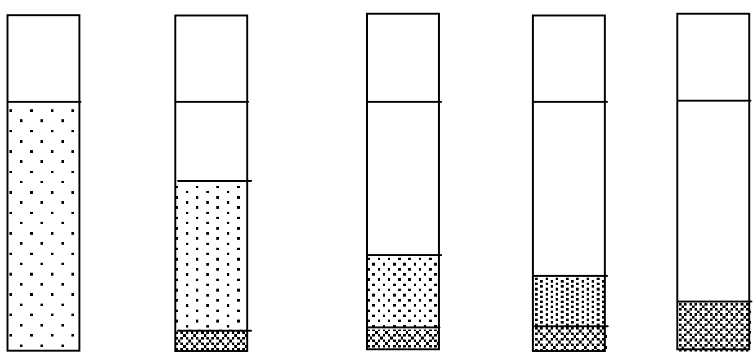

Fig. 1b. NON UNIFORM SETTLING PATTERN OF ADU SLURRY

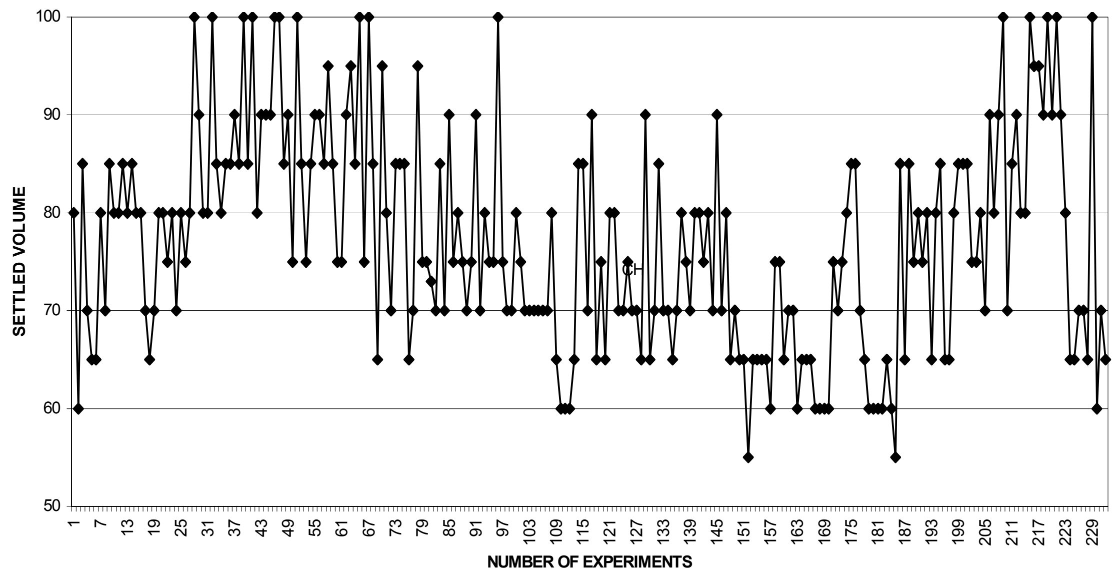

Fig. 2a. SETTLED VOLUMES FOR 4 KG EDTA ADDITION

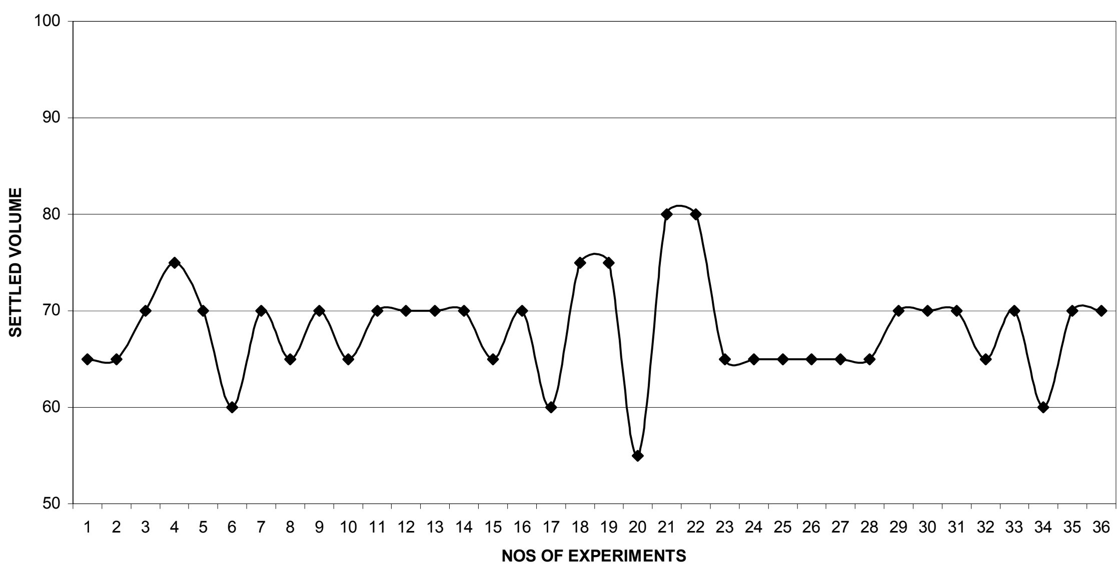

Fig. 2b. SETTLED VOLUMES FOR 3 KG EDTA ADDITION

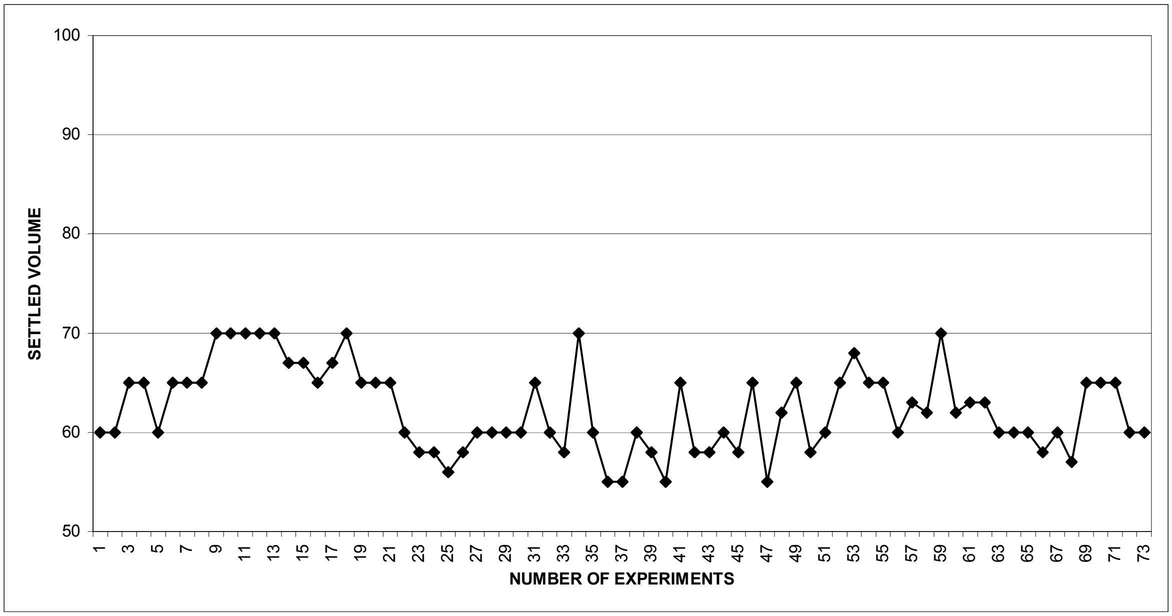

Fig. 2c. SETTLED VOLUMES WITHOUT EDTA ADDITION

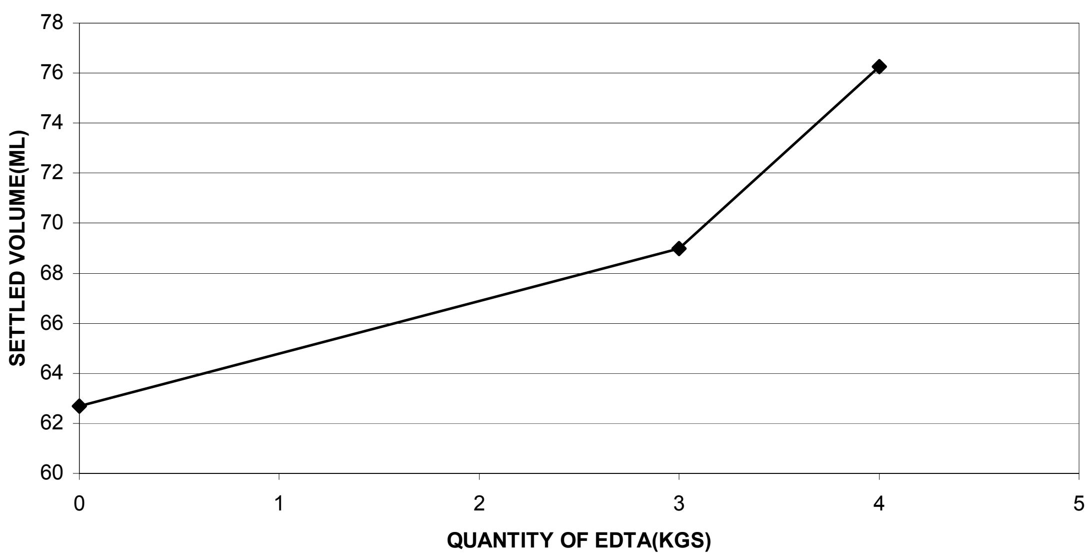

Fig. 2d. EFFECT OF EDTA ON SETTLED VOLUMES

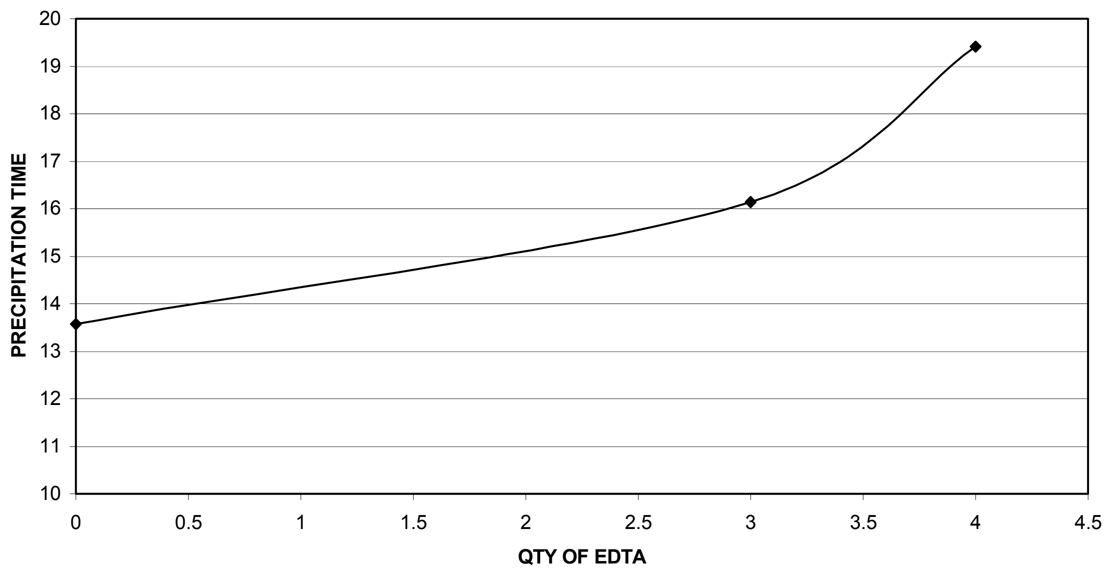

Fig. 2e. EFFECT OF EDTA ON PRECIPITATION TIME

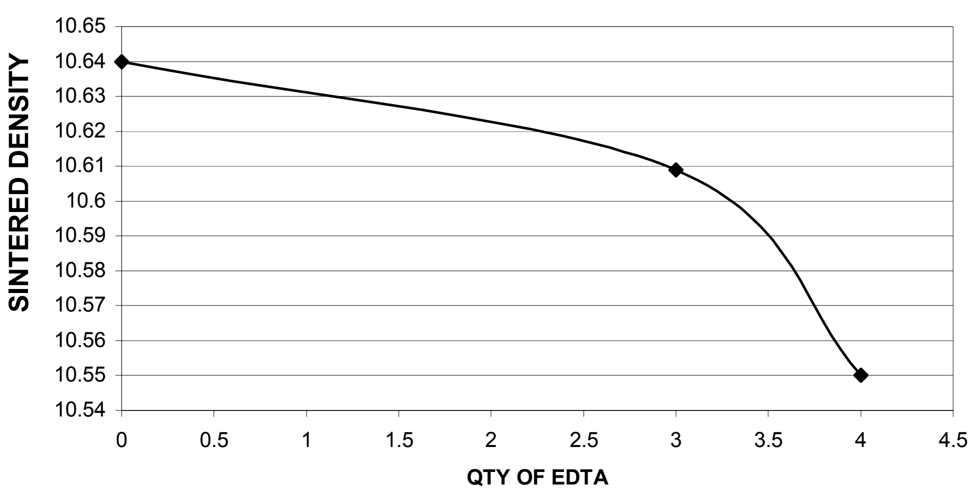

Fig. 2f. EFFECT OF EDTA ON SINTERED DENSITY

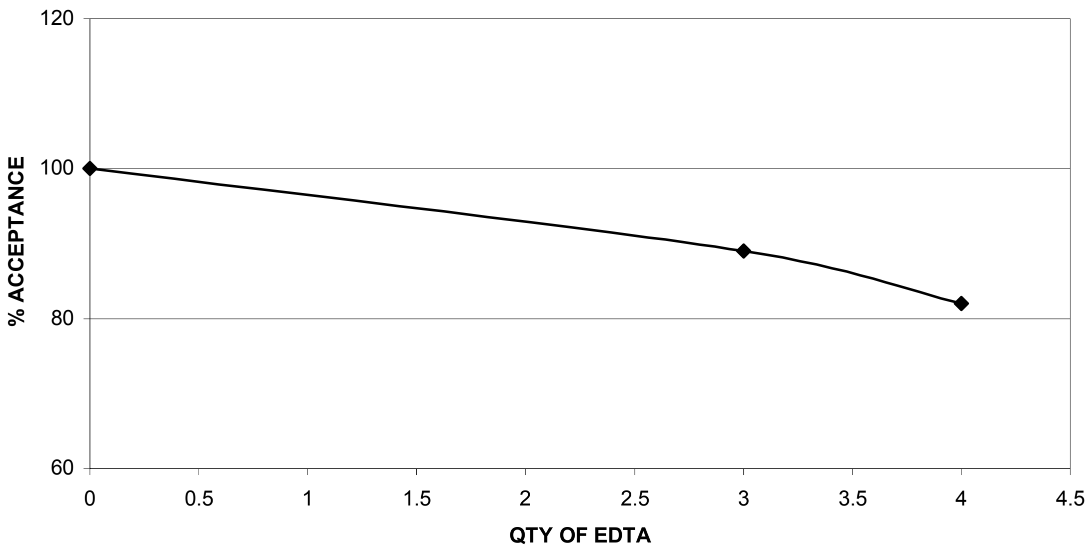

Fig. 2g. EFFECT OF EDTA ON % ACCEPTANCE OF POWDER LOTS