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Study of crystal growth and effect of temperature and mixing on properties of sodium diuranate

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ABSTRACT

Almost 30–40% of total uranium deposits in India are in the form of carbonate and bicarbonate. Uranium in the ore is leached by alkali and then precipitated with NaOH as sodium diuranate (SDU). Morphology of SDU particle has been observed using high resolution SEM and it has been observed that the SDU particles consist of nano scale circular platelets, which are connected with each other to form primary agglomerates and further connected to form secondary agglomerate. Effect of temperature and mixing on SDU particle size distribution (PSD) and crystal structure have been studied. It was observed that the mean particle size reduces with an increase in the impeller power number. But no changes were observed in crystal structure with a change in the impeller design. Further, the mean particle size was found to be reduced with an increase in temperature.

1. Introduction

The rising demand for uranium in the power reactors requires intensive exploration to look for more workable uranium ore deposits and techno-economic process for exploitation. Uranium deposits in India are of low grade and are relatively smaller in extent as compared to those present in the worldwide commercial practice (Suri et al., 2009). Almost 30–40% of total uranium deposits in India are in the form of carbonate and bicarbonate along with gangue minerals like calcite, dolomite, pyrite and quartz. India has deposits of uranium as carbonate ore in the host rock of alkali (dolomite and calcite) containing 0.048% U_3O_8 and hence considered as lean resource of uranium (Suri, 2008). The presence of high amounts of calcite and dolomite (60–65%) limits the acid leaching route since most of the acid used gets spent in the neutralization of these preponderant gangues requiring a very high acid consumption (Padmanabhan and Suri, 2007). The run of mine (ROM) ore, after conventional crushing and grinding is thickened, repulped and subsequently subjected to alkali leaching by sodium carbonate and sodium bicarbonate solutions. The leached slurry is then filtered and washed. The filtrate, called leached liquor (LL) containing sodium uranyl carbonate, after clarification, is subjected to precipitation as sodium diuranate (SDU) with an addition of sodium hydroxide. SDU slurry is thickened and then filtered. The cake is finally dried to get the SDU powder. The knowledge of particle size distribution (PSD) and morphology of SDU is very important for the design of thickener, filter and dryer. Morphology and PSD of powder are very important physical attributes of powder which also controls further processing and material handling of the powder. These properties of SDU depend on kinetics of SDU precipitation process. Reaction, nucleation, growth, agglomeration and breakages are the steps in the overall process of precipitation. The most significant factors affecting the kinetic parameters are reaction kinetics, degree of supersaturation, flow field pattern, mixing, residence time, temperature, concentration, and suspension density (Rane et al., 2014a). One of the major challenges in industrial precipitator is to control the particle size distribution and morphology and to predict the influence of vessel geometry, configuration, operating conditions, and the effect of scale on the process behaviour. A complex variety of different processes occur in crystallizers, such as reaction, nucleation, crystal growth, attrition and agglomeration of crystals, fluid dynamics, and heat and mass

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transfer. Some of these processes are not yet well understood in spite of their need for design and operation of large-scale precipitator/crystallizers.

Kim et al. (2009), Mellah et al. (2006), Biswas et al. (2014) reported effect of reaction chemistry on SDU precipitation by producing SDU by different routes. Kim et al. produced high yield uranium precipitate from carbonate medium using H_2O_2 solution. Recovery of uranium as ammonium uranyl carbonate (AUC) from uranyl carbonate solution by ammonia was studied by Mellash et al. Biswas et al. used H_2SO_4 to decompose CO_3^{2-} and HCO_3^- ions in aqueous medium and NaOH/MgO as precipitating agents. No literature has been published on morphology of SDU. Doi and Ito (1964), Janov et al. (1972), Manna et al. (2012a; 2012b) have reported the morphology of similar compound ammonium diuranate.

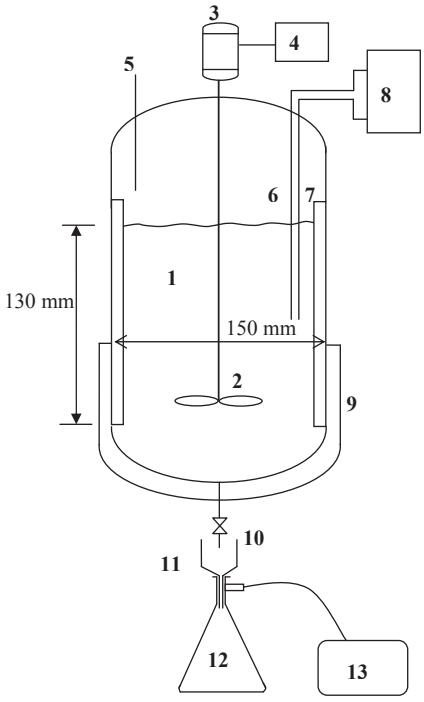
Rane et al. (2014b) reported that fluid dynamics or mixing plays an important role in precipitation process, hence determining particle sizes and morphology. Parameters like reactor and impeller shapes, aspect ratio of the reactor vessel, number, type, location and size of impellers, degree of baffling, etc., provide effective handles to control the performance of stirred reactors (Rane et al., 2014a). There is practically no information available in the published literature on effect of mixing on the properties of SDU. Though there is several published literature studies on the effect of mixing on the properties of product produced by reactive precipitation or crystallization, most of these were concerned with $BaSO_4$ precipitation. Leeuwen et al. (1996), Jaworski and Nienow (2003) and Wong et al. (2001) revealed that the impeller speed had a small effect on crystal size and morphology. Pohorecki and Baldyga (1983) observed a decrease in the mean particle size with an increase of impeller speed for batch precipitation. Tosun (1988) observed that the particle size first decreases and then increases with an increase in the impeller speed. Fitchett and Tarbell (1990) found that the nucleation rate to decrease and particle size to increase with increased extend of mixing. Aslund and Rasmuson (1992) studied benzoic acid precipitation and reported that an increase in mixing intensity in the vicinity of feed point favour the production of larger crystals.

When the uranium concentration in the leached liquor is very less (<800 mg uranium per litre), the precipitate obtained has very small average particle size which causes problems in filtration and reduces the recovery of uranium. Therefore, it was thought desirable to undertake a systematic investigation to understand the uranium recovery during precipitation and to study the effect of mixing and temperature on particle size distribution (PSD) and crystal structure of SDU.

2. Experimental

Experimental set up for SDU precipitation by reaction of LL with 8 (N) NaOH is shown in Fig. 1. Experiments were performed in an agitated 2.5 l (liquid volume) glass reactor (1) with a dished bottom. The reactor was of 150 mm inner diameter and fitted with 4 number of equispaced 15 mm width baffles. Three types of impellers (2) were used for the study: (i) six bladed disc turbine (DT), (ii) six bladed 45^O pitched blade turbine (PBT) and (iii) three bladed hydrofoil (HF). Pictorial images of these impellers are shown in Fig. 2. In all the three cases, impeller sweep diameter was 0.4 times the tank inner diameter. The reactor was provided with muffle electrical heater (9), pH electrode (6), temperature indicator (Pt 100 RTD) (7) and flush bottom valve.

The pH of solution was continuously monitored using pH meter (8). After completion of precipitation, 100 ml slurry was taken for study of settling characteristics and rest of the slurry was filtered in Buchner funnel (11) using 542 Whatman paper (pore size 2.7 μm). Filtrates were collected separately and samples were analysed for



1. Glass Reactor with baffles	8. pH Meter
2. Impeller	9. Muffle Heater
3. Motor	10.Flush bottom valve
4. VFD	11. Buchner Funnel
5. NaOH feed line	12. Conical Flask
6. pH Electrode	13. Vacuum Pump
7. PT 100 RTD	

Fig. 1. Experimental set up.

uranium concentration. The cake was washed with demineralised water and dried in an oven at 100° C for 6 h. Morphology, crystal structure and PSD were studied. Morphology of SDU was observed using high resolution "Scanning Electron Microscope" (SEM). The SDU powder was coated with very thin (40–50 nm) gold layer by magnetic scattering technique to prevent charge deposit during the study of morphology. The SDUs were characterized by X-Ray Diffraction using an Inel diffractometer with Cu K_α radiation ($\lambda = 1.54056$ Å). A list of instruments used for analysis is given in Table 1.

3. Results and discussion

3.1. Study of growth of SDU particle during precipitation

In order to investigate the formation and growth of SDU particles, 250 ml of 8 (N) NaOH was added to 2.5 L LL at the starting of reaction. The LL contained 740 mg uranium per litre of solution in the form of uranyl carbonate. During precipitation process samples (aliquot) were withdrawn after regular intervals. The collected samples were immediately filtered and then washed. The pH and