

Process and Design Optimization for Producing Low Soda Alumina

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Abstract

Hindalco alumina refineries operate on conventional Bayer process to produce alumina mainly for aluminum production and part of it is sold as a specialty alumina. Generally, specialty alumina requires Na₂O less than 0.25% for use in touchscreen panels for mobiles, tablets, televisions, etc. In Bayer process the control of the product quality is majorly dependent on the process parameters such as seeding strategy, precipitation temperatures, and time. In the present study in-depth analysis of the precipitation process was carried out with focus on the optimization of the process parameters and streamline SOP to achieve the desired product quality. Alumina precipitation was studied at lab scale by varying the different parameters viz: temperature profile, precipitation time, seeding, etc. Detailed product characterization was carried out to understand the partitioning and form of sodium in with aluminum hydrate precipitate. The best operating conditions were identified which could result in reduction in Na₂O impurity in final product. The CFD simulations of agglomerator tanks were also carried out to study the swirling flow pattern generated as well as possible bypass of the pregnant liquor due to inlet and outlet design configuration. In order to quantify & minimize this bypassing, residence-time distribution (RTD) analysis was performed on the existing design and compared with different inlet outlet design modifications. The lab study helped in optimizing the process parameters like precipitation temperature profiles, seeding strategy and precipitation time to achieve the % Na₂O less than 0.25%, while CFD study provided solutions to reduce the extent of bypassing from 14% to 5% for pregnant liquor. The results are discussed in detailed with in this paper.

Keywords: Low soda alumina, Precipitation experiments, Agglomeration and growth, CFD modelling, RTD study.

1. Introduction

The Bayer's process produces hydrate and alumina, which is refined from raw bauxite ore in an energy intensive process that uses substantial amounts of caustic soda as the dissolving agent. The basic refining process has remained unchanged, where the productivity and the product quality heavily depend upon the quality of the raw material, process stability and control. In order to use alumina at various non-metallurgical applications, product specifications vary in terms of impurities present in alumina, the particle size distribution (PSD) and hardness, etc. Soda is one of the major impurities which affects the final product quality, hence it has limitation factor for various product specifications. Soda in hydrate exists in two forms: lattice soda and soda adsorbed on the surface of hydrates, which can be controlled by an efficient hot water washing method. While the control of soda in lattice requires special efforts during the crystal formation stage to

prevent impurities from being trapped in the crystal lattice. Diluting the solution, raising the temperature, controlling the seeding strategy by varying particle size of seeds, as well as seed loadings can slightly reduce the soda content [1]. The process of producing saturated liquor remains the same for metallurgical as well as non-metallurgical applications. The method of achieving super saturation and the use of seeding with various PSD decides the level of impurities and PSD of the final alumina tri-hydrate. Consistently producing lower soda impurities of less than 0.25 % in alumina is a challenge for the plant's operating team. In general, a trade-off exists between the soda content, the particle size distribution and the productivity. It is important to optimize and balance various variables in the agglomeration and growth of alumina hydrate to achieve lower soda levels. Hence, current study was carried out with objective to find out process parameters for achieving the desired % Na₂O in alumina. This study utilizes experiment and modeling approach to attain the process parameters for desired alumina quality.

2. Technical Approach

The precipitation experiments were designed and carried out in lab scale precipitator by varying pregnant liquor (PGL) temperature, PSD, fine and coarse seed loading. The retention time and the precipitated hydrate products were analyzed using X-ray Fluorescence (XRF) and Malvern particle size analyzer for % Na₂O and PSD, respectively. The design of the first plant agglomerator and the turbulence generated due to its inlet and outlet configuration resulted in probable short circuiting of fluid to the next agglomerator. The design analysis was performed using the CFD modelling approach and ANSYS Fluent 16.0 as a tool to converge the solution in steady state. Fluid bypass was quantified using a residence time distribution approach in transient simulation employing inert tracer.

2.1 Precipitation Experiments

The experimental setup consists of a water bath for indirectly heating/cooling the slurry with a precise temperature and time controller in order to maintain the desired temperature gradient during the precipitation time. This installation facilitates the adjustment of a start and end temperature as well as a cooling rate to carry out precipitation of alumina tri-hydrate using the pregnant liquor and the seedings. The setup consists of 12 tanks which ensure the proper mixing of the pregnant liquor and the seeds in all the tanks. The pregnant liquor (PGL) required for the precipitation was arranged from Bayer processing plant and the caustic concentration was adjusted to remove any effects for all of the DOE experiments. The seedings used for the experiments were collected in a single lot from Bayer processing plant to maintain the same seed morphology and the impurities. All 12 tanks can be simulated with different seeding inputs as well as different retention times, This facility also ensures the easy discharge of the slurry volume after the desired time for the individual tanks. Input seeds were analyzed for particle size distribution, impurities and SEM analysis for morphology of the seed structure. Experiments (DOE) were designed as shown in Table 1 in order to study the effect of different input variables like retention time, PGL temperature, seed charge and seed ratio on productivity of alumina and the % of Na₂O impurity addition in alumina hydrate. In addition to the DOE experiments, a few sets of experiments with total time duration of 6 hours and sampling at the frequency of 30 minutes were carried out to study the process of agglomeration and soda occlusion in details during the agglomeration step. Samples collected during all experiments were washed with hot water and filtered multiple times to ensure removal of surface soda as well as oven dried for removal of surface moisture. Further, these samples were analyzed for % Na₂O and particle size distribution. For the caustic measurement in liquor standard titration methods were used. The samples collected during agglomeration steps were analyzed using a scanning electron microscope (SEM) for the particles size distribution of impurities, as well as structure and morphology. The results of all experiments will be discussed.

Table 1: Design of experiments for precipitation at the lab scale facility.

Sr. No.	Variables	Levels
1	Temperature [C]	3
2	Seed charge & seed ratio (g/l)	6
3	Time (H)	3
	Total Experiments	54

2.2 CFD modelling approach

The agglomerator design is an air agitated tank which generates swirl flow inside the tank with tangential inlet at top region. This inlet acts as source of momentum to achieve mixing in the tank. The PGL liquor and seed slurry enters the tank from top and outlet is overflowing into the next tank, which is located near to PGL inlet pipe as shown in Figure 1 - existing design.

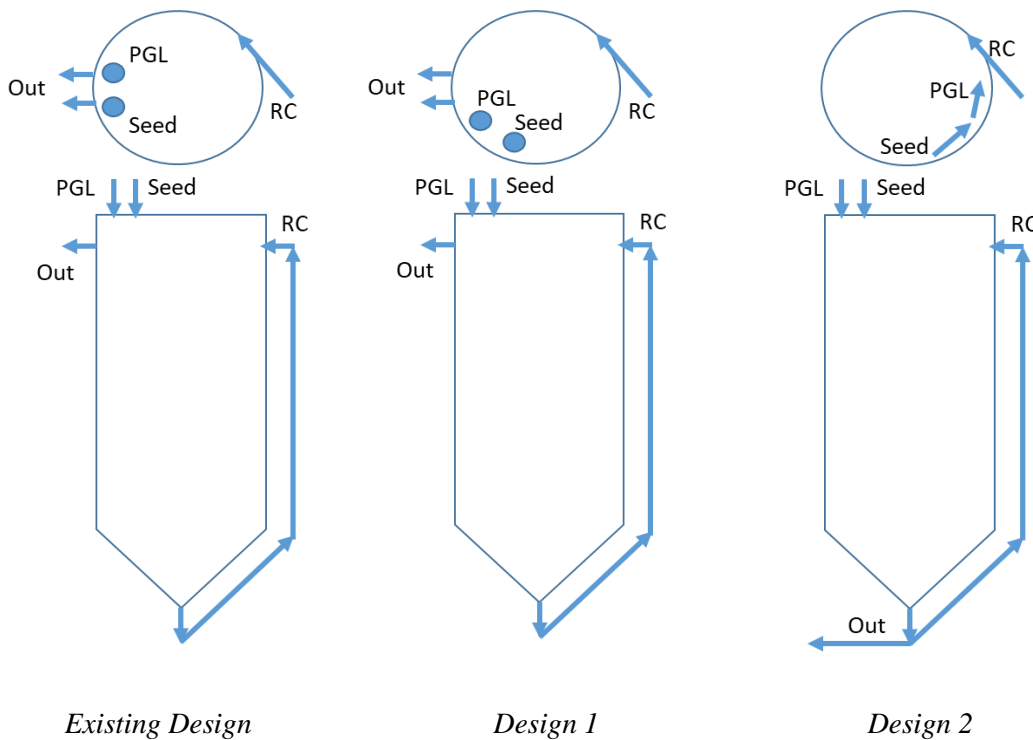


Figure 1. Existing design and design modifications attempted during CFD analysis

This configuration lead to the possibility for bypassing the supersaturated pregnant liquid from agglomerator to the precipitation tanks. Hence, the agglomeration efficiency will be affected resulting in higher nuclei formation and disturbing the product particle size distribution. To overcome these possibilities a design assessment of agglomerator was done using a CFD modelling approach to quantify and minimize bypassing of super-saturated pregnant liquor. Even though CFD simulation is becoming increasingly popular among hydrometallurgy industries [3, 11, 14]; few publications are available specific to the Bayer process. Woloshyn et al., [14], successfully modelled the slurry hydrodynamics as a single phase in alumina process digesters to assess the influence of vessel aspect ratio and inlet configuration for the selection of preferred vessel geometry. The pregnant liquor and seeds during precipitation represent the same fluid conditions of liquor and solids as those of alumina processing digestors. Hence, for the present analysis, the flow of the pregnant liquor and the seeds slurry was assumed to be a homogeneous and non-settling slurry. The geometry and the tetrahedral meshing were performed using ANSYS-Design 16 modeler and numerical simulations were carried out using ANSYS-Fluent 16.

Turbulence was modeled using a single-phase Reynolds stress model (RSM). In this model the continuity equation 1 is solved while Equation 2 is the momentum conservation equation, which is solved in the model for predicting the flow pattern inside the tank. Equation 3 represents the turbulent viscosity equation solved for Reynolds stresses. In the previous work [13, 2], the effectiveness of the RSM model was proven both for the flow pattern and turbulent mixing predictions. The agglomerator with swirl flow generates anisotropic turbulence and predictions of the Reynolds stress model (RSM) are accurate compared to the k-e model, because the RSM model solves the Reynolds stress tensor matrix, while the k-e model assumes flow to be isotropic and solves only diagonal components of the Reynolds tensor matrix.

$$\nabla(\rho u) = 0 \quad (1)$$

$$\frac{\partial}{\partial t} (\rho u'_i u'_j) = -\nabla p + \nabla \tau \quad (2)$$

$$\tau = \mu \left(\nabla u + (\nabla u)^T - \frac{2}{3} \delta \nabla \bullet u \right) \quad (3)$$

Residence time distribution study is an effective method to identify non-idealities in the reactors. The RTD study uses an inert tracer whose physical properties are the same as those of the slurry, ensuring the tracer will follow the fluid flow. In all continuous unit operation/processes, as soon as the pulse tracer is introduced into the vessel, the pulse spreads with respect to the nature of the flow pattern and finally it exits the outlet of the tank. The tracer concentration is measured at the outlet as well as within the tank at strategic locations based on the flow dynamic study. These locations are selected where low velocity regions are observed within the tank w. r. t. time for complete analysis. The two main important parameters to be observed are the mean residence time, and the variance of the tracer (E), [7]. The deviation from the plug flow is characterized by the number of dispersions. The “E” curve in the subsequent discussion is taken from Equation (4). For the estimation of RTD, the following transport equation (5) for the concentration *c* (scalar) was simulated.

$$E = \frac{1}{\sqrt{4\pi(D/uL)}} \exp \left[-\frac{t_m(1-(t/t_m))^2}{4t(D/uL)} \right] \quad (4)$$

After computation of the velocity information and the turbulence characteristics, the tracer blending process was modeled by solving the conservation Equation (5). Here, the dispersive transport of the tracer due to turbulent movement in the reactor is explained by the turbulent diffusivity. A simple dispersion model is used to predict the axial dispersion. The first term on the right side of Equation 5 will be zero because a non-diffusive tracer is used during the study. In addition, the second term indicates the external source term, which will become zero since the tracer is a one-time injection.

$$\frac{\nabla(\rho_{sl} C_t u)}{dt} = \nabla(DC) + S_t \quad (5)$$

The “E” is the normalized distribution function for exit age. The purpose of keeping it normalized is that the flow distribution inside the reactors at different scales can be compared directly. Rousseaux et al., [11], validated their CFD based RTD with lithium ion tracer experiments for thickeners at plant. The thickeners in the Bayer process exhibit similar slurry conditions, in which the solids are suspended and indicate some dead pockets or short circuiting within the thickener.

The successful validation of RTD predictions shows the capabilities of the CFD modelling approach for metallurgical slurries.

3. Results and Discussion

3.1 Optimization of hydrate precipitation kinetics

Agglomeration of the process studied using 6 h experiments with sampling at 30 min intervals where samples were analyzed for soda occlusion as well as precipitation/agglomeration rate. The results are plotted in Figure 2. The x axis represents the time and the primary y axis is % Na₂O, while the secondary y axis is the rate of precipitation/agglomeration. From Fig. 2 it can be observed that during the initial 30 min to 1 h there is a very high rate of precipitation, as well as higher rate of soda absorption in hydrate. The major reason behind the high rate of precipitation is a higher supersaturation of the alumina hydrate present in the liquor with a relatively lower surface area of seeds available for the cementation of the hydrate.

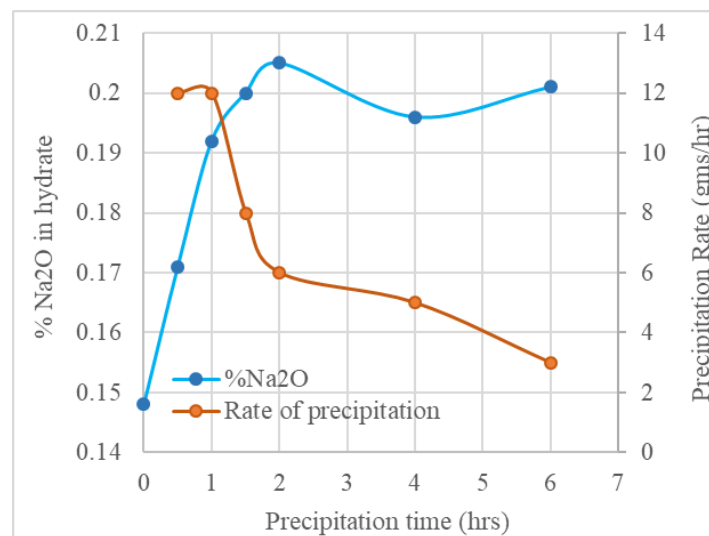


Figure 2. Rate of precipitation/ agglomeration experiments for soda occlusion

Figure 3 shows the SEM analysis of the seeds before precipitation and the hydrate after 30 min of precipitation. It can be observed that, for the finest fractions less than 37 microns of the hydrate has a higher cementation and a higher soda pickup. This nature of higher soda pickup for the finer fraction can be explained by the fact, that during the experiments, a higher supersaturation at the initial moment favors the higher precipitation rate. Theory as well as literature [8] reported that, the soda content in the hydrate is higher when higher precipitation rates are present in the process. Hence, it is extremely important to control the initial rate of precipitation of 1~1.5 h to control the soda content in hydrates. A total of 54 laboratory-scale controlled precipitation experimental data sets are presented in Table 2, where the operating parameters are normalized for temperature and retention time (N), which is the ratio of final precipitation time and initial precipitation temperature. Also, the specific surface area of seeds (SSA) is another variable. SSA is calculated on the basis of the seed in grams used for the set multiplied by the specific surface area (m²/g).

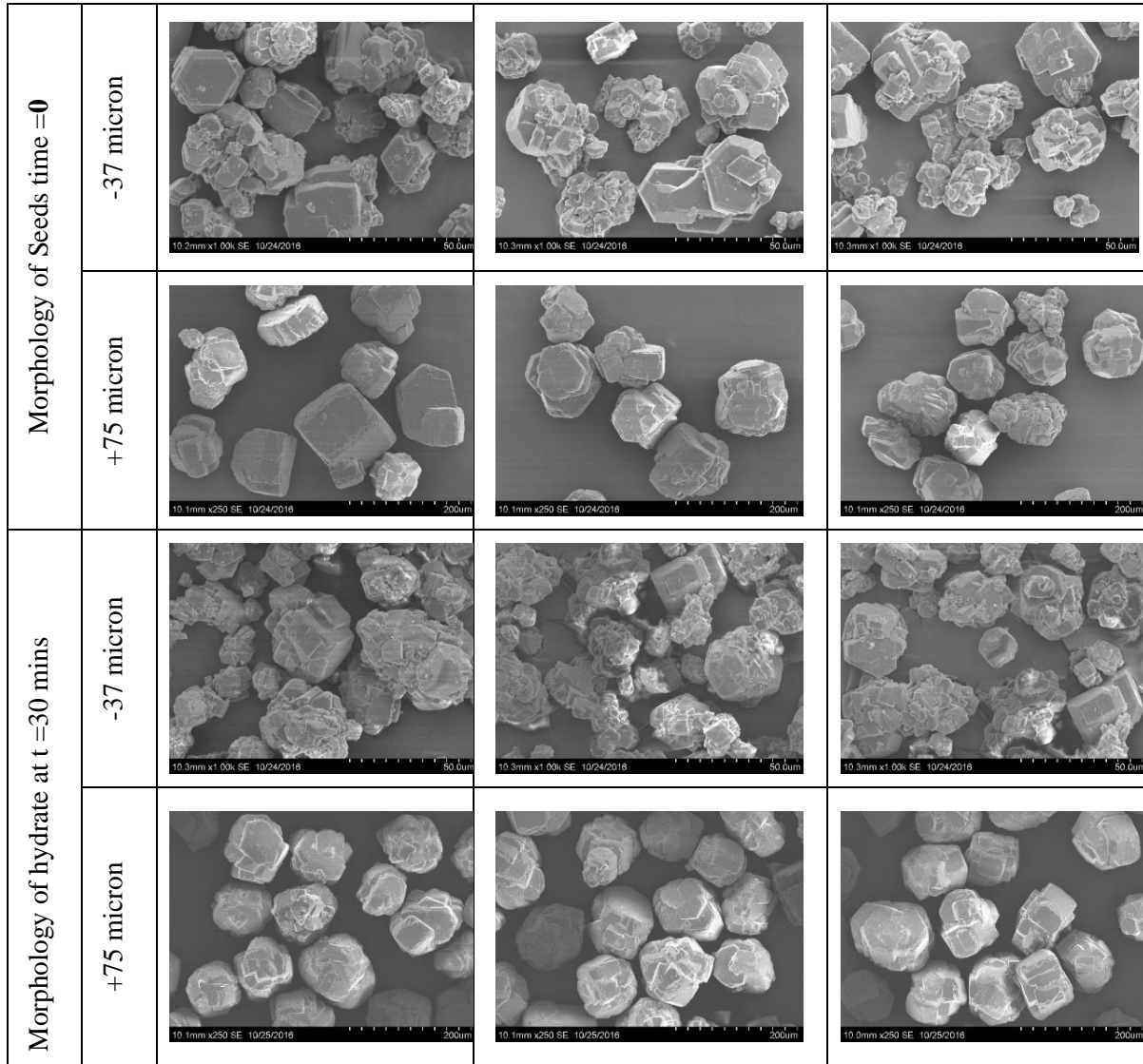


Figure 3. Growth and change in particle morphology of aluminum hydrate particles during agglomeration.

Supersaturation is a function of temperature and caustic concentration, which is an extremely important parameter and driving force for precipitation, as well as the control of impurity during the process. From Table 2 it can be clearly observed that, sets 46, 50 and 52 show the lowest soda occlusion in the alumina after precipitation. The reasons behind the lowest soda in these sets are the operating conditions. All of three data sets show lower supersaturation and SSA relatively higher than the rest of the experiments. Secondly, the ratio (N) which incorporates the effect of the initial precipitation temperature, and the precipitation time is more than 0.3 conditions of lower supersaturation. The higher SSA and Ratio (N) reveal vital information for the operational variable, which can be simplified as higher starting temperature with a higher residence time as well as a higher seed area for achieving lower soda occlusion in the alumina trihydrate.

Table 2. Controlled variable and impurities in alumina for all DOE

Test No	Ratio (N)	SSA (m ²)	Supersaturation (g/l)	%Na ₂ O Alumina	Test No	Ratio (N)	SSA (m ²)	Super saturation (g/l)	%Na ₂ O Alumina
1	0.30	12.39	75.47	0.287	28	0.34	11.81	70.09	0.267
2		13.50	75.47	0.274	29		7.75	70.09	0.289
3		10.85	75.47	0.298	30		8.44	70.09	0.280
4		11.81	75.47	0.286	31	0.39	12.39	71.87	0.283
5		7.75	75.47	0.313	32		13.50	71.87	0.269
6		8.44	75.47	0.298	33		10.85	71.87	0.304
7	12.39	75.47	0.290	34	11.81		71.87	0.275	
8	13.50	75.47	0.283	35	7.75		71.87	0.322	
9	10.85	75.47	0.296	36	8.44		71.87	0.275	
10	0.35	11.81	75.47	0.283	37	0.28	12.39	66.63	0.275
11		7.75	75.47	0.313	38		13.50	66.63	0.280
12		8.44	75.47	0.310	39		10.85	66.63	0.287
13	12.39	74.96	0.292	40	11.81		66.63	0.278	
14	13.50	74.96	0.280	41	7.75		66.63	0.302	
15	10.85	74.96	0.284	42	8.44		66.63	0.257	
16	0.40	11.81	74.96	0.280	43	0.33	12.39	66.63	0.336
17		7.75	74.96	0.305	44		13.50	66.63	0.274
18		8.44	74.96	0.293	45		10.85	66.63	0.280
19	12.39	70.09	0.275	46	11.81		66.63	0.249	
20	13.50	70.09	0.263	47	7.75		66.63	0.286	
21	10.85	70.09	0.287	48	8.44		66.63	0.269	
22	0.29	11.81	70.09	0.263	49	0.37	12.39	60.81	0.284
23		7.75	70.09	0.307	50		13.50	60.81	0.248
24		8.44	70.09	0.296	51		10.85	60.81	0.258
25	12.39	70.09	0.284	52	11.81		60.81	0.249	
26	0.34	13.50	70.09	0.266	53		7.75	60.81	0.252
27		10.85	70.09	0.296	54		8.44	60.81	0.258

3.2 Flow Pattern Study

The study includes the three different cases with varying the inlet and outlet configuration, i.e., 1- Existing design; 2- Design 1; 3- Design 2. Simulated results fully converged with residual of mass and momentum to be less than 10⁻⁰⁶ CFD were analyzed and velocity vectors were plotted using ANSYS CFD-Post 16 in Figure 4. It can be observed from Figure 4 that tangential entry of re-circulatory flow makes a swirling downward flow around the periphery of the tank, The PGL flow and fine seed flow enter in perpendicular direction, which results in chaotic unstructured turbulent flow inside the tank, as shown for the existing design in Figure 4. The different inlet configuration was simulated with PGL and seed slurry relocated by 45° as shown in Figure 4 - Design 1; this resulted in higher and lower velocity pockets as can be seen in vector plot in Figure 4 - Design 1.

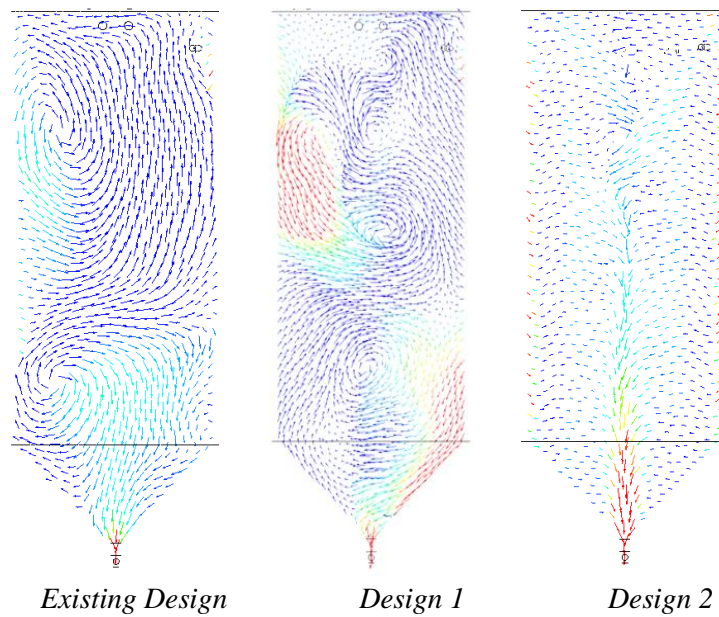


Figure 4 Flow pattern in agglomerator existing design different design modifications

Design 2 is to move the PGL flow and seed flow from the perpendicular top inlet to the tangential inlet just next to the recirculatory flow in a sequential fashion, as well as an overflow outlet located at the conical bottom, as shown in Figure 1 - Design 2.

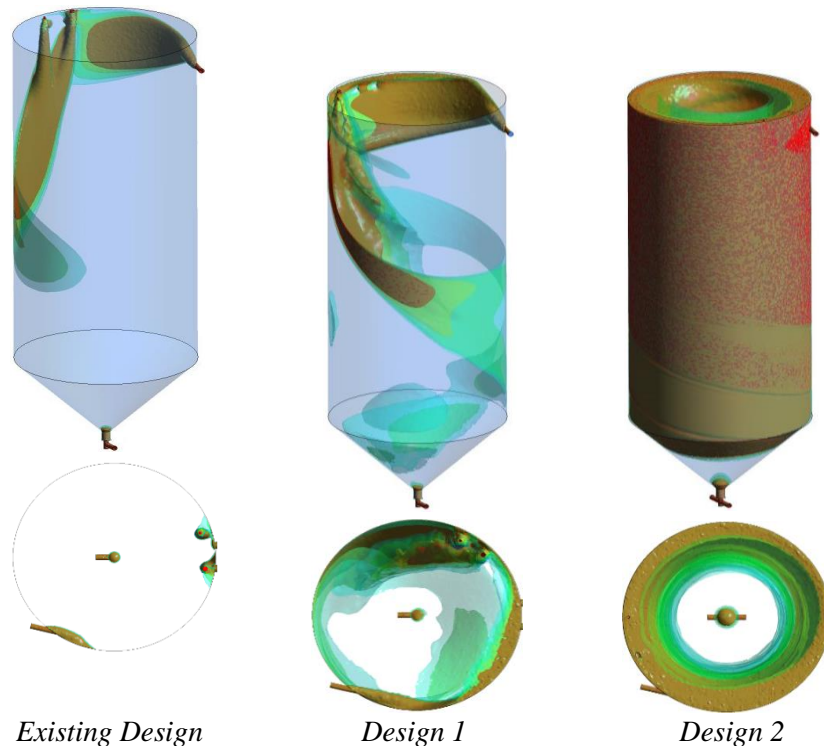


Figure 5. Spatial distribution of liquor in agglomerator for all simulated cases

The flow pattern generated in Design 2 is characteristic swirl flow in downward direction with strong pull at the bottom. This strong pull is extended till 2/3 height of the tank. The central pull from conical bottom is missing in Design 1 and in existing design when compared with the Design

2. In order to visualize the swirl flow and swirl strength inside the tank, multiple iso-surfaces were created and displayed as a velocities contours, as shown in Figure 5 for all simulated cases. The spatial distribution of liquor in existing design as well as Design 1 is very poor. The presence of stagnant zones is observed when compared with Design 2. The design case 2 shows the better spatial distribution, i.e. higher velocities in characteristic flow pattern among all simulated cases. Further, in order to distinguish between these cases and quantifying the extent of mixing and bypassing of fluid, residence time distribution study was also performed. Results will be discussed in the next section.

3.3 Residence Time Distribution Study

The residence time distribution study was performed on fully converged flow simulations for all the designs. The inert tracer was injected through PGL inlet having similar physical properties as that of PGL and tracer equation was solved at time step of 0.5 sec for 20000 sec. The tracer should be inert since it should not react/diffuse with the slurry when mixed inside the tank. The concentration of the tracer was measured at different strategic locations based on critical analysis of flow pattern inside the tank as well as outlet of the tank. The measured concentration data was used to calculate the exit age distribution using Equation 5 and plotted against the normalized time as shown in Figure 6. It can be observed from Figure 6 - Design 2 that E- curve starts little late for the normalized “0” value, which indicates the slurry spends some time inside the tank. The industrial well-mixed tanks show the distorted behavior like Design 2 in Figure 6, - Design 2 which confirms the good mixing in agglomerator. While existing design and Design 1 E-curve show the early exit of fluid, (nearer to normalized time the “0” tracer is measured at the outlet), which indicates the short circuiting of the fluid. It can be observed that E curve shows long tail for the existing design, Design 1 cases against Design 2, which indicates the presence of dead zones inside the tank which is harmful for the mixing phenomenon.

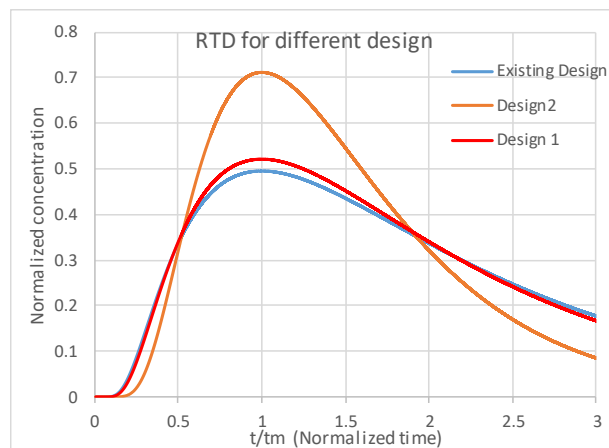


Figure 6. Exit age distribution curves for all simulated cases

The mean retention time, dispersion numbers and % of PGL bypassing at different time for all the simulated cases is presented in Table 3. The % by-passing is the y intercept of E curve at calculated normalized time for the individual cases.

The mean retention time is the average time spent by the PGL and the seeds inside the agglomerator, so the mean retention time should be closer to the actual retention time. It can be observed from Table 3 that, Design 2 gives the highest mean retention time among all the cases, which is close to the retention time (ratio of volume by volumetric flow). Dispersion number is the ratio of the dispersive flow to the convective flow and it indicates the extent of mixing in the tank. The smaller the number the better is the distribution of mixing.

Table 3. RTD results and mean residence time for all simulated cases

No	Design	Mean Retention time (sec)	Dispersion No	% bypassing of PGL at different time					
				10 min	20 min	30 min	40 min	50 min	60 min
1	Existing Design	6276	0.316	4.5 e^{-5}	0.09	1.21	4.2	8.74	14.06
2	Design 1	6250	0.317	9.1 e^{-4}	0.34	2.45	6.44	11.37	16.44
3	Design 2	7100	0.167	1.2 e^{-10}	3.6 e^{-4}	0.05	0.56	2.36	5.96

Table 3 clearly indicates the better mixing in Design 2 than that of other simulated cases. The inlet and outlet configuration of existing design results in bypassing of 14 % PGL liquor (before 60 min) to next agglomerator, which is maintained at lower temperature. When this PGL enters the next tank at lower temperature, the super saturation increases drastically. Hence, the rate of precipitation increases and results in increased soda in hydrate. While Design 2 inlet - outlet configuration of Design 2 results in ~ 5% bypass of PGL, the existing design will result in a higher soda content in hydrate than that of Design 2. The top region of the agglomerator includes all the PGL inlets, fine seed and re-circulatory flow and it needs to be mixed intensively, i.e. higher values of the dispersion number.

4. Conclusions

The initial period of higher precipitation rate determines the major proportion of the % Na₂O content association with alumina tri-hydrate. This is due to the increased level of local supersaturation and resulting in a higher precipitation rate in the initial time. The precipitation kinetic experiments clearly show the importance of higher PGL temperature, higher seed load and higher fine seed fraction as well as higher retention time to achieve lower % Na₂O values in alumina. The optimum conditions are supersaturation of 60.8 g/l, total seed surface area of 13.50 m² and ratio (N) of 0.37. CFD simulations of all designs attempted revealed that Design 2 performed well in terms of minimizing the percentage short circuiting of both supersaturated liquid and seed slurry. The bypassing of inlet feed is reduced to 5 % (Design 2) from 14% (existing design). The product quality in terms of lower soda (<0.25 %) in alumina can be achieved by maintaining the above-mentioned process key ratio/ supersaturation.

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