

Effect of process variables on the yield and strength of alumina hydrate precipitated from aluminate liquor

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Effects of caustic concentration, alumina to caustic ratio of aluminate liquor, quantity of seed charge and precipitation temperature on the yield of alumina hydrate has been studied under laboratory condition. Kinetic equations have been derived for the calculation of equilibrium alumina to caustic ratio under optimum conditions and correlating rate of hydrate precipitation with the initial caustic content. Effect of different precipitation parameters on the strength of alumina hydrate has also been discussed.

The precipitation of alumina hydrate (hereafter called as hydrate) from supersaturated alkaline sodium aluminate solution involves nucleation, crystal growth and agglomeration. The yield and strength of hydrate precipitated are dependent on process parameters and also to some extent on certain impurities. The important parameters are precipitation temperature profile, initial alumina to caustic ratio (RP), concentration of pregnant sodium aluminate liquor, seed ratio, precipitation time, impurity level of input seed hydrate and aluminate liquor. The attrition of alumina can occur during precipitation and/or calcination, the later being more prominent and dependant on the precipitation conditions. The strength of alumina is determined from the term attrition or attrition index (breakdown of particles) of alumina during calcination. Although the mode of calcination influences the breakdown of alumina to some extent but the crystal structure of hydrate plays a greater role. A number of reports are available on the kinetics and particle growth of alumina hydrate during precipitation from alkaline liquor with respect to precipitation parameters¹⁻³. The liquor from bauxite digestion contains alumina and other species like sodium carbonates, hydroxides, chlorides, sulphates, phosphates, vanadates, fluorides, calcium, iron, silica and ionized sodium salts of several organic compounds along with the trace elements. The concentration of these species differs from plant to plant. Different aspects of precipitation technology of alumina hydrate has been studied as a function of the above impurities^{4,5}. The kinetics of nucleation and growth of alumina hy-

drate precipitation from supersaturated aluminate liquors has also been studied⁶. Some work has been done on simulation of hydrate precipitation for continuous and batch precipitation taking plant data as well as laboratory scale experimental results⁷. It has been reported that stronger particles generally consists of a core of agglomerated particle which have cemented together by growth^{8,9}. All parameters which influence the precipitation yield and attribute to the strength of crystals are very much dependent on the precipitation process¹⁰ and the liquor quality which is again dependent on the chemistry and mineralogy of bauxite and its processing technology. The trend may remain same but the magnitude varies with the liquor and bauxite quality. In view of this, present investigation is concerned with a study on the effect of different parameters on the yield as well as strength of hydrate obtained during precipitation under laboratory conditions. The main objective is to examine the effect of precipitation parameters on the liquor productivity (yield) and to study the strength of precipitated hydrate obtained under different conditions of precipitation.

Experimental Procedure

Precipitation of alumina hydrate—All experiments were carried out by taking aluminate liquor from the Alumina Refinery of NALCO having impurities level as given in Table 1. Analysis of washed and dried hydrate, which has been used as seeding material is given in Table 2. Laboratory precipitation tests were carried out by taking one litre of aluminate liquor each time and adding

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Table 1—Characteristics of aluminate liquor

Na ₂ O (caustic)	145.2 gpL
RP	1.0
Carbonates	19.6 gpL
Chlorides	0.65 gpL
Sulphates	0.15 gpL
Oxalates	0.364 gpL
Silica	750 mgpL
Fe ₂ O ₃ (total)	20 mgpL
Fe ₂ O ₃ (soluble)	7.5 mgpL
Organics (C)	4.63 gpL
P ₂ O ₅	72 mgpL
Ga ₂ O ₃	105 mgpL
V ₂ O ₅	40 mgpL

calculated amount of seed in a constant temperature bath. The following precipitation experiments have been designed:

Seed quantity varied as 500, 600 and 700 gpL at 60°C of reaction using liquor of Table 1.

Temperature varied as 55, 60 and 65°C at 600 gpL solid content using liquor of Table 1.

Concentration of caustic varied from 140 to 150 gpL at 60°C precipitation using 600 gpL solid and RP of initial liquor as 1.0.

RP of liquor changed from 0.95 to 1.05 at 60°C precipitation using 600 gpL solid and initial caustic concentration as 145 gpL.

The ranges of variables have been chosen in such a way so that the same can be applied in an operating plant and also the findings can be useful for industrial application. Precipitation studies were conducted for 84 h under a constant temperature bath and samples drawn at regular intervals for analysis of RP. The concentration of liquors were measured by SANDA Thermotitrator (USA). The liquor productivity has been calculated by analysing the RP after precipitation, using the simple formula (applied in all alumina refineries) given below:

$$LP = C(I_{RP} - F_{RP}) \quad \dots (1)$$

where, LP=liquor productivity, gpL; C=initial caustic concentration of aluminate liquor, gpL; I_{RP}=initial RP of aluminate liquor taken for precipitation; F_{RP}=final RP of liquor after precipitation and RP=Al₂O₃ gpL and Na₂O caustic gpL.

Attrition index (AI) of alumina hydrate—Precipitation tests have been carried out under different conditions in a series of experiments at different caustic concentrations, initial RP and temperature keeping the solid content constant at 600 gpL. The washed and dried hydrate was subjected

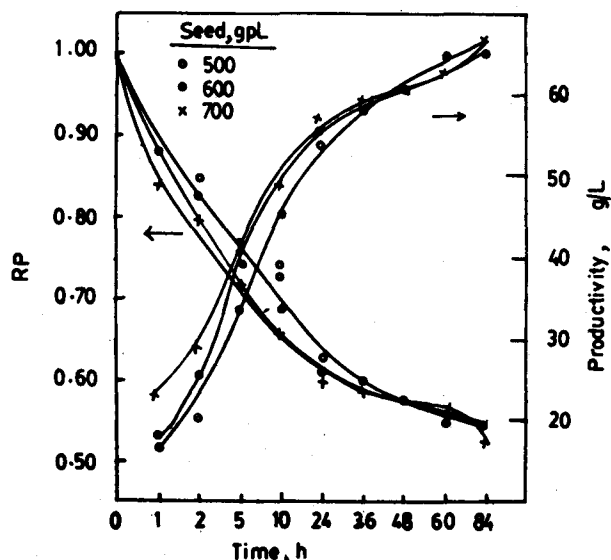
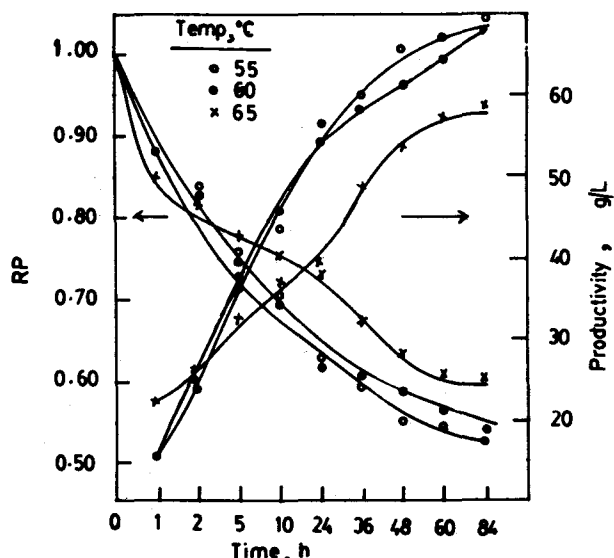
Table 2—Characteristics of seed hydrate

Physical analysis		Chemical analysis	
Grain size, microns	Wt. %	Constituents	Wt. %
- 15.5	0.1	SiO ₂	0.010
- 17.6	0.5	Fe ₂ O ₃	0.0065
- 20.2	1.0	NaO ₂ (t)	0.23
- 22.8	1.5	CaO	0.026
- 26.0	2.7	K ₂ O	0.0010
- 29.6	3.8	ZnO	0.0003
- 33.7	4.7	V ₂ O ₅	0.0009
- 38.3	7.6	MgO	0.0006
- 43.6	12.0	TiO ₂	0.0007
- 49.7	18.4	P ₂ O ₅	0.0010
- 56.6	29.7	Ga ₂ O ₃	0.007
- 64.4	39.8	Al ₂ O ₃	65.45
- 73.4	60.2		
- 83.5	76.5		
- 95.1	85.7		
- 108.3	93.4		
- 123.3	95.2		
- 140.4	99.6		
- 159.8	100		
d50, mic	71.8		
Surface area, cm ² /g	403		
LOI, %	34.5		

to attrition test before precipitation and also after calcining the product. Experiments were conducted by changing one parameter at a time. Attrition during calcination has been calculated as the difference in -45 micron percentage between hydrate and alumina, before and after calcination in a static bed furnace at 900°C. Scanning electron micrograph of the hydrate after calcination, was undertaken to observe the pattern of hydrate crystal morphology. Attrition index is a measure of particle breakdown during handling. For conducting the attrition tests a glass column of 200 cm height, having 25 mm dia was taken through which dry air (pressure of 5-6 kg/cm²) was passed at a flow rate of 460-480 liters per hour after taking 50 g of sample. The attrition index was calculated using the formula given below:

$$AI(wt\%) = \frac{(+45 \text{ micron before the test}) - (+45 \text{ micron after the test})}{(+45 \text{ micron before the test})} \times 100$$

For the purpose of grain size analysis, samples from different set of tests were analysed by employing the Elzone Particle Size Analyser, 180 XY(USA) system.

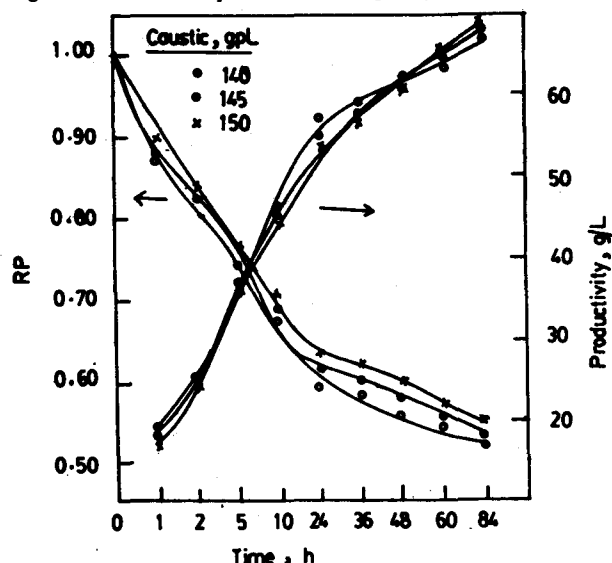
Fig. 1—Effect of seeding on precipitation of $\text{Al}(\text{OH})_3$ Fig. 2—Effect of temperature on the precipitation of $\text{Al}(\text{OH})_3$

Results and Discussion

Effect of process variables on alumina yield in precipitation

Effect of seed quantity—From Fig. 1 it can be seen that in batch precipitation the liquor productivity increases as the RP falls up to 36 h with higher seed charge, the effect being more pronounced up to 24 h. An additional amount of 4-5 g/L product has been obtained on raising the seed quantity from 600 to 700 g/L, after 24 h of precipitation. But after 36 h there was no significant increase in productivity. This is because rate of precipitation seems maximum during the initial period and it falls as the precipitation proceeds further. However, the rate of precipitation after 36 h appears to be slightly higher at lower seeding levels. Though the rate of precipitation is expected to be directly proportional to the available seed surface area, there has been no significant benefit of additional yield at higher solid content, beyond 600 g/L, which can be considered as optimum seed charge.

Effect of precipitation temperature—It is known that the rate of precipitation of alumina hydrate from a saturated aluminate liquor increases at a relatively lower temperature¹¹. However, an optimum temperature profile can be evaluated depending upon the nature of pregnant liquor and the precipitation technology involved. With 600 g/L seed charge the variation of RP and liquor productivity at different time intervals and at 55, 60 and 65°C temperatures have been analysed in Fig. 2. It can be seen that in batch precipitation after 48 h a substantial quantity (8 g/L) of hydrate could be produced by reducing the temperature from 65 to 60°C. But the increase in yield is

Fig. 3—Effect of caustic concentration on the precipitation of $\text{Al}(\text{OH})_3$

less significant on reduction of temperature from 60 to 55°C. At 55°C the productivity continues to rise to as high as more than 80 g/L when the precipitation is continued beyond 48 h.

Effect of caustic concentration—Variation in caustic concentration of aluminate liquor has generally been reported to have no significant effect on the yield of alumina¹². Higher concentration of caustic has resulted in higher production. This is mainly due to higher extraction of bauxite during digestion. But as the concentration of aluminate liquor increases beyond a certain level practically it becomes difficult to get a quality product with respect to soda content. With 600 g/L seed charge, experiment on hydrate precipitation has been carried out varying caustic concentration from 140 to 150 g/L (Fig. 3). It has been found

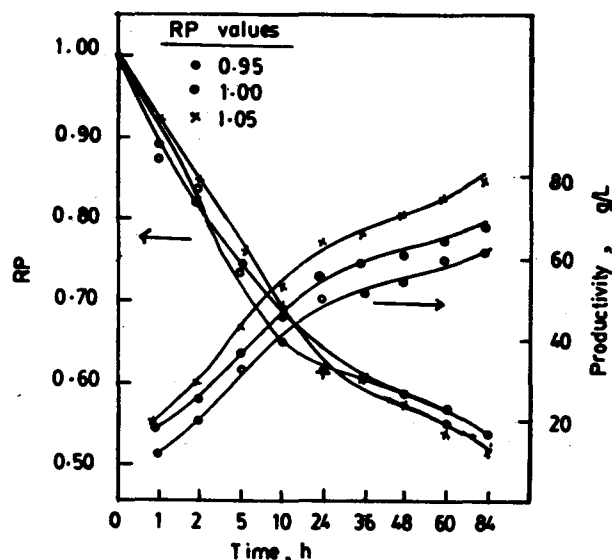


Fig. 4—Effect of initial RP on the precipitation of $\text{Al}(\text{OH})_3$

Table 3—Effect of RP equilibrium with variation of seed charge

Solids, gpL	T, °C	C, gpL C = Na_2O caustic	RP _{eq}
500	55	145.20	0.524
	55	159.80	0.581
	60	144.28	0.549
	60	152.60	0.580
	60	157.90	0.599
	65	143.37	0.594
	65	152.40	0.627
	65	156.90	0.630
600	55	145.47	0.514
	55	154.29	0.546
	60	146.58	0.534
	60	150.40	0.548
	60	154.70	0.563
	65	146.10	0.587
	65	155.5	0.543
	65	154.8	0.501
700	55	155.5	0.543
	55	144.8	0.501
	60	150.4	0.539
	60	143.6	0.523
	65	145.1	0.577
	65	154.2	0.619
	65	160.0	0.646
	65	160.0	0.646

that there has been a rise of 2-3 gpL in the productivity, at higher caustic concentration after 48 h of precipitation period.

Effect of initial RP—The rate of hydrate precipitation is directly proportional to the supersaturation of aluminate liquor. From Fig. 4 it can be seen that an additional increase of initial RP by 0.05 resulted in 8–10 g more alumina per litre after 48 h of precipitation.

Table 4—Estimation of rate constants, k

$\text{Na}_2\text{O}(\text{c})$ gpL	RP _{out}	RP _{eq}	k
139.40	0.544	0.514	0.65193
146.58	0.577	0.534	0.44017
150.40	0.595	0.548	0.39758
154.70	0.618	0.563	0.33155
160.80	0.640	0.578	0.28712

Precipitation kinetics

RP equilibrium has been determined in laboratory at different precipitation temperatures and caustic concentrations with 500, 600 and 700 gpL solids. Saturated aluminate liquor of $\text{RP}=1$ has been taken for all the three sets of test. Results are reported in Table 3. Since 600 gpL solid has been found to be optimum for better yield, a kinetic equation has been derived to correlate RP equilibrium (RP_{eq}) with temperature and caustic concentration as given below at 600 gpL seed charge.

$$\text{RP}_{\text{eq}} = \exp(3.6675 + (-1748.91 + 2.2192 \text{ C})/T) \quad \dots (3)$$

Where, T = precipitation temperature, K and C = initial aluminate liquor concentration as Na_2O caustic gpL.

The general rate equation for $\text{Al}(\text{OH})_3$ precipitation is given below:¹⁰

$$d(\text{RP})/dt = k(\text{RP} - \text{RP}_{\text{eq}})^2 \quad \dots (4)$$

and the concentration-time relationship in batch precipitation as

$$\text{RP}_{\text{out}} = \text{RP}_{\text{eq}} + \frac{\text{RP}_i - \text{RP}_{\text{eq}}}{1 + k(\text{RP}_i - \text{RP}_{\text{eq}})t} \quad \dots (5)$$

Where, k = rate constant, which is a function of total seed surface area, temperature and composition of liquor; RP = mass ratio, i.e. Al_2O_3 gpL/ Na_2O caustic gpL; RP_{eq} = RP at equilibrium; RP_{out} = outlet RP at time t , RP_i = inlet RP and t = residence time in hours and C = Na_2O caustic gpL.

From the experimental data, the rate constant values calculated using Eq. (5) for batch precipitation has been reported in Table 4. From the table the ' k ' values can be correlated to the caustic concentration by the following equation:

$$k = (-)0.01674C + 2.939237 \quad \dots (6)$$

Where ' C ' is the initial Na_2O caustic concentration of aluminate liquor, in gpL.

Attrition of alumina

From the results reported in the Tables 5, 6 and 7, it can be seen that the attrition of hydrate

Table 5—Effect of caustic concentration on attrition of alumina and hydrate

Precipitation temperature = 60°C
Initial RP of aluminate liq. = 1.0

Na ₂ O(c), g/L	Sample	Grain size micron, %						AI, %	Attrition during calcination
		-159	-110	-79	-59	-45	-30		
141.6	Hydrate	99.8	64.5	23.3	9.1	3.7	1.2	7.0	—
	Alumina	100.0	78.0	30.2	13.4	5.8	1.4	24.5	2.1
147.0	Hydrate	99.6	65.0	24.0	9.4	3.9	1.2	7.9	—
	Alumina	100.0	82.4	31.5	14.8	6.2	1.5	28.4	2.3
152.0	Hydrate	100.0	65.8	24.2	9.6	4.0	1.3	8.2	—
	Alumina	100.0	83.0	32.4	15.6	7.0	1.5	30.0	3.0

Table 6—Effect of initial RP on attrition of alumina and hydrate

Precipitation temperature = 60°C
Initial caustic content of aluminate liquor = 148.4 g/L Na₂O

RP	Sample	Grain size micron, %						AI, %	Attrition during calcination
		-159	-110	-79	-59	-45	-30		
0.970	Hydrate	100.0	64.8	24.4	9.6	4.2	1.4	12.0	—
	Alumina	100.0	82.4	32.0	15.5	7.2	1.8	30.8	3.0
1.008	Hydrate	100.0	65.2	24.0	9.4	3.8	1.2	9.6	—
	Alumina	100.0	80.4	28.4	12.8	6.3	1.4	28.2	2.5
1.035	Hydrate	99.2	64.6	23.6	9.2	3.6	1.2	8.0	—
	Alumina	100.0	76.8	28.0	12.4	5.8	1.4	23.7	2.2

Table 7—Effect of precipitation temperature on attrition of alumina and hydrate

Initial caustic content of aluminate liquor = 148.0 g/L Na₂O
Initial RP of aluminate liquor = 1.0

Temp, °C	Sample	Grain size micron, %						AI, %	Attrition during calcination
		-159	-110	-79	-59	-45	-30		
58	Hydrate	100.0	65.2	24.9	10.0	4.3	1.6	7.6	—
	Alumina	100.0	75.0	28.4	15.0	6.6	1.8	25.6	2.3
60	Hydrate	100.0	65.0	24.3	9.7	3.9	1.4	8.0	—
	Alumina	100.0	78.3	28.6	15.4	6.7	1.8	26.0	2.8
68	Hydrate	99.0	63.1	23.0	9.4	3.2	1.4	4.5	—
	Alumina	99.8	85.0	36.4	18.4	7.8	2.0	34.4	4.6

and the calcined products are generally higher with the increase in initial caustic concentration, decrease in initial RP and increase in precipitation temperature. Attrition index is more at higher temperature in case of low supersaturation of liquor as in the present case (Table 7). Precipitation at a higher temperature produces agglomerated crystals where particle breakdown during calcination seems to be high. In case of growth-type precipitation although the radial morphology of the hydrate helps in reducing the attrition during calcination but the attrition index is more. To overcome this aspect, a combination of both ag-

glomeration and growth mechanism has been adopted in modern refineries which produces pseudo-radial morphology of hydrate such as to be strong enough during calcination and the attrition index is also low. In the growth-type precipitation, frequent changes in precipitation temperature is a measure to control the fines (nuclei) generation¹³. Higher temperature reduces the generation of fines and also helps in agglomeration. While the agglomeration of fines can provide a stronger particle but that of medium sized particles produces a pseudo-mosaic structure which can break during calcination resulting in a high at-

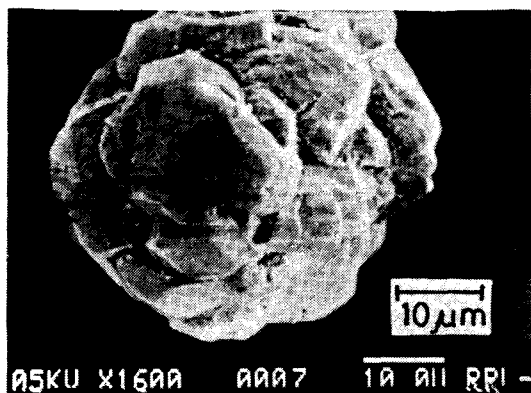


Fig. 5—Micrograph of alumina hydrate showing pseudo-mosaic morphology

trition index. The micrograph of the later type of crystals where the particles are agglomerated loosely is shown in Fig. 5.

Conclusions

In a high seed charge precipitation technology different process parameters like caustic concentration, RP of aluminate liquor, quantity of seed charge and precipitation temperature are the main factors which determine the yield and strength of hydrate. In batch laboratory tests these factors have been optimised to be 600 gpL seed, 55°C and 145 gpL caustic concentration. A kinetic equation has been developed for NALCO plant liquor. It enables estimation of high productivity

as a function of different variables. Moreover, a stronger alumina hydrate product with low attrition index can be obtained by maintaining the precipitation condition at low initial caustic concentration (140 gpL), higher initial RP of aluminate (1.05) and low precipitation temperature (55°C). Strength of the hydrate at any specific temperature is dependent on the RP of liquor.

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