OPTIMIZATION OF PRECIPITATION PROCESS OF CHINESE REFINERY

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ABSTRACT
Precipitation profiles of Chinese refineries are generally characterized by high solid content, high caustic concentration and growth only process plus relatively loose product quality target control. Usually diasporic type bauxite is exploited and processed in China due to the formation under an oriental natural environment. Processing this type of bauxite requires digestion conditions with high temperature (+260 °C) and high caustic concentration (+410 g/L, expressed as Na_2CO_3) to achieve good alumina extraction efficiency. Furthermore, extremely large circulation of seed (+800 g/L, 1st precipitator) is adopted to give high productivity and "adequate" product quality.
This study reports typical precipitation process and key performance indicators (KPIs) used in Chinese alumina refineries. It highlights the influence of several factors such as slurry solid concentration, interstage cooling profile and seed moisture on precipitation yield and rate. An objective process used in China has also been stated and forms a basis for presenting optimized precipitation profile which is currently applicable and unique to diasporic bauxite refining in China.
Keywords: Precipitation, Caustic Concentration, Solid Content, Product Quality

Notation and units
Caustic concentration appeared in this paper is expressed as Na_2CO_3 unless otherwise stated.

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1. INTRODUCTION AND BACKGROUND

Generally in China, refineries are characterized by high temperature, high caustic concentration in digesting bauxite, at the same time high solid content, high caustic concentration and growth only process in precipitating hydrate as well.

1.1 Diasporic Bauxite

More than 50 alumina refineries were built in China by the end of October 2014. Nearly 30 of them reach the capacity of 700kt/a, and circa 20 of them achieved over 1000kt/a. Practically 90% of the refineries are processing the type of Chinese diasporic bauxite which was formed in relative high latitude area with lower ambient temperature and also less amount of rainfall comparing with gibbsite concentrated in tropical region. The figures listed in Table 1 indicate that the diasporic bauxite is characterized by high alumina (+60% wt.) and silica (+8% wt.) content, a small amount of calcium and titanium, a little iron substitution, a low level of inorganic and organic carbon.
Mineralogy studies and digestion performance experiments in chalco laboratories indicate that diasporic bauxite contains neither boehmite nor gibbsite, majority of silicon enters kaolinite and very little forms quartz. The standard digestion experiment also shows that diasporic bauxite favors high temperature (+260 ℃) and high caustic concentration (+410 g/L) as condition for achieving good alumina extraction efficiency. As

consequence, liquor that reports to precipitation possesses high-purity that would lower alumina saturation slightly, but high caustic concentration at the same time which will significantly increase saturation thus lead to low supersaturation.

Table 1: Chemical Composition of Diasporic Bauxite

Bauxite	Shanxi	Henan
% Al_2O_3	63.85	68.50
% Na_2O	0.12	0.52
% SiO_2	12.77	6.52
% CaO	0.72	0.85
% Fe_2O_3	3.38	6.45
% TiO_2	3.00	2.46
% CO_2	0.68	0.78
% LOI	13.56	13.07
% Others	1.92	0.85
Total	100.00	100.00

1.2 High Caustic Concentration

Correspondingly, green liquor used around the refineries employs high caustic concentration of circa 290 g/L after dilution and clarification. This level is much higher than most western countries (circa 240 g/L) that adopt an 'agglomeration plus growth' process. Usually, alumina concentration difference between actual and saturated (also known as the square of '$A_{actual.}$-$A_{eq.}$') plays an essential but primary driving force in hydrate crystal precipitation even if at the same time influenced by many other operating factors such as residence time, impurity contamination, seed classification, temperature profile, etc.

1.3 High Solid Content

Besides, high solid concentration (over 800 g/L) which was also known as high circulation was employed with the aim to conduct compensation for liquor supersaturation loss due to caustic concentration and obtain higher yield. Under some unusual circumstances, like periodic fining of product or losing of calcination capacity, for instance, the solid phase rising by up to even more than 1000 g/L in the 1st precipitator feed can be found in some refineries. Operating at high solid content level will cause a series of problems that related not only to CAPEX & OPEX of the refinery but also to the product quality. Because larger circulation requires wider pipe as well as bigger pump and equipment like disk filter, more power consumption is needed to keep the entire system running. Meanwhile, the lack of holding time due to the large circulation will poison the crystal which may need dozens of hours to reach optimum size, moreover, a high frequency of particle collision will result in both poor performance of sticking and appearance of terrible fine particles (the probable cause of periodic fining) under continuous agitation.

1.4 Product Quality

Typical product quality index listed in table 2 indicate that commonly in China alumina product has the feature of marked high -45μm content and abrasion index that run counter to Smelter Grade Alumina requirement.

Table 2: Typical Product Quality Index in China

No.	Description	Value	Unit
1	-20μm	2.1	%
	-45μm	16.4	%
	+150μm	1.6	%
2	Angle of Repose	27.4	degree
3	Abrasion Index	22.2	%
4	α-AL_2O_3	4.5	%
5	Bulk Density	1	g/cm^3
6	Specific Surface Area	80.6	m^2/g

2. PRECIPITATION PROCESS AND KPIS

Figure 1 shows a rough but typical process flow diagram of precipitation employed by almost all refineries of China. It indicates a fact that the biggest difference from western country lies on a single stage operation without distinguishing fine

seed for agglomeration, coarse seed for growth.

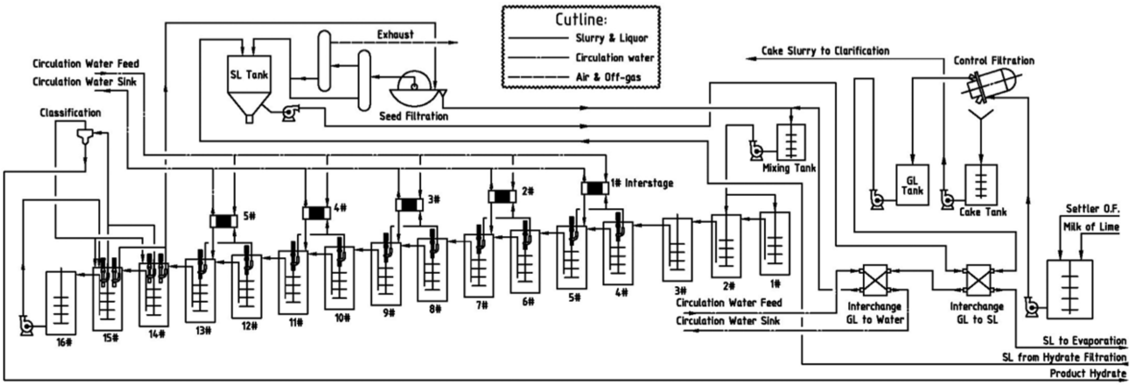

Figure 1: Typical Process Flow Diagram of Precipitation Employed in Chinese Refineries

The precipitation row usually employs 15 to 20 precipitators in series that would provide total residence time of circa 40 to 45 hours related to the high seed charge of greater than 800 g/L (1st precipitator feed). 5~10 stages of wide-channel plate heat exchangers provide totally circa 10 degrees temperature drop to maximize liquor productivity. The cooling profile with average temperature drop of 1.3~2℃ for each interstage can be found. Size and strength of the particles are less important in comparison with the pursuit of liquor productivity, which can usually achieve high precipitation rate of more than 50% with +90 g/L green liquor yield.

Usually, the classification is designed with a single stage of hydro-cyclone. To meet both the requirement of facility operating condition and product hydrate flow rate, only circa 10 percent of the pump-off slurry mixed with spent liquor would be sent to feed the cyclone, achieving solid content of 550 to 650 g/L. The underflow of the cyclone (900 to 1000 g/L) would then be pumped to product filtration and washing, the overflow goes back to the pump-off tank. The remainder of the slurry flow by gravity to seed preparation unit.

3. ISSUES AND PROPOSED SOLUTIONS

Take a typical and existing process including 20 precipitators (with 10 interstages cooling) as an example and study basis, various issues are stated, solutions are proposed. The BaseCase conditions are listed in Table 3.

Table 3: BaseCase Conditions

Items		Value	Unit
Green Liquor	Qv	1240.5	m^3/h
	T	71	℃
	Molar Ratio(MR)	1.467	——
	Caustic	292.71	g/L
	Seston	0.0103	g/L
Seed	SSA	0.049	m^2/g
	Moisture	18	%
Precipitator	Volume	5080	m^3
Interstage	Each	1.3	℃
Row Feed	Solids	950	g/L
	T	59.54	℃

Benefits can be seen from Figure 2, that Annual Production rate advances possibly by a series of ways such as interstage cooling increase, seed circulation increase, seed moisture decrease, green liquor molar ratio decrease, green liquor caustic concentration increase and green liquor flowrate increase. But the last three factors are subject to external conditions as digestion, clarification and control filtration, etc.

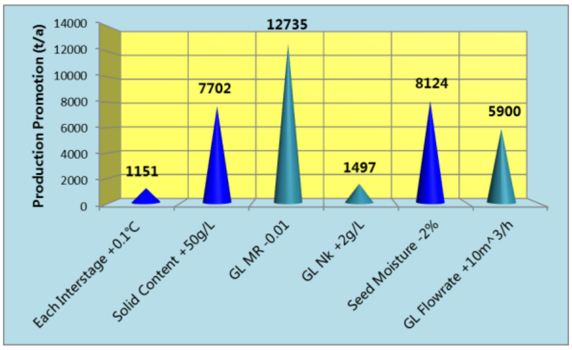

Figure 2: Production as a function of various factors

3.1 Interstage Cooling Profiles

The alumina refineries promote production and precipitation rate (which shown as below) by enhancing interstage cooling to compensate for supersaturation loss.

$$Precipitation\ Rate = \frac{MolarRatio_{SpentLiquor} - MolarRatio_{GreenLiquor}}{MolarRatio_{SpentLiquor}} \times 100\%$$

Figure 3 shows the trend of alumina production and precipitation rate vary along with the each enhancement of interstage cooling by 0.1℃. The green liquor condition, precipitation feed slurry temperature and solid content were controlled to be the same.

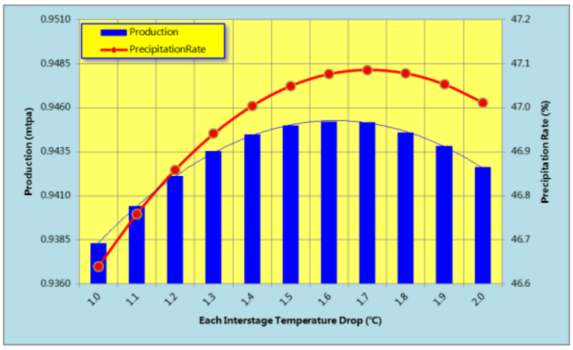

Figure 3: Production & Precipitation Rate VS Cooling

The curve in Figure 3 also indicates an inflection point that total cooling should be governed within certain limits. Due to the large circulation, further cooling leads to greater precipitation and more production, and thus higher pump-off molar ratio. The hydrate seed carring spent liquor with higher molar ratio would raise the initial molar ratio of the feed slurry, thus push the starting point of precipitation further. Once the influence of 'pull up' suppresses the interstage cooling benefit, alumina production and precipitation rate will be empoisoned, as shown in Figure 3, the curve begins to descend down at the point which corresponding to 1.7℃ of each interstage.

Another evidence lies on the particle growth that shown in Figure 4. Despite very low growth rate (less than 1um during 35h) compared to the process with agglomeration and growth, yet a diameter of hydrate difference between feed and pump-off can be observed.

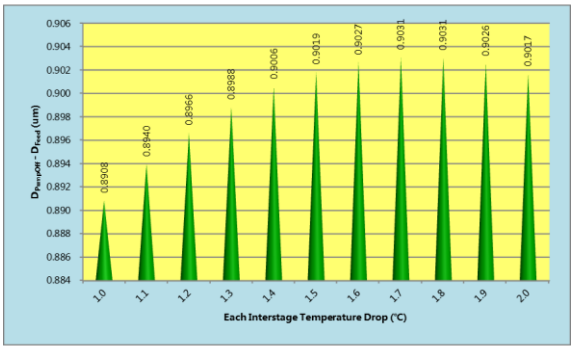

Figure 4: Particle Size Distribution VS Interstage Cooling

The advantage of enhancing cooling is easy to see but the conclusion can also be made that for different precipitation conditions an optimum cooling point should be ascertained.

3.2 Solid Concentration

In China, refineries can contribute adequate production by large seed circulation that usually up to 900g/L, sometimes +1000g/L. As shown in Figure 5, feed solid concentration promotion indeed driving up liquor productivity because of the increase of available particle surface area. When feed solid concentration was increased to certain level, an inflection point also appears in the same way of interstage cooling. Production and precipitation rate continuously decrease with seed added, and also +1200g/L nearly reaches

the solid content limit of existing precipitation tanks with agitation.

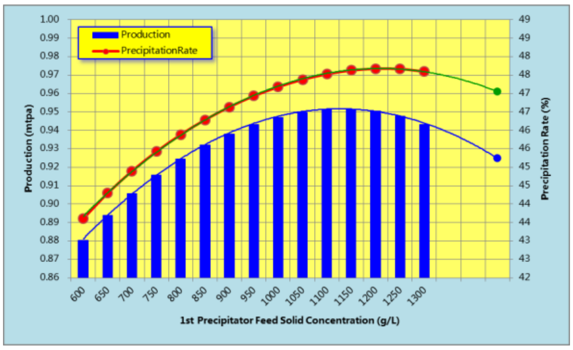

Figure 5: Production & Precipitation Rate VS Solid Content

Green liquor temperature should be elevated because of the large circulation carrying much more cooled medium which lead to downward deviation of optimum original temperature. Under the same feed slurry (Temp.= 59.54℃) conditions, the increase of solid content (from 600 g/L to 1300 g/L) brings only 1.25℃ spent liquor temperature drop but requires 30.77℃ green liquor temperature elevation for balance (as shown in Figure 6). That means less heat can be gained by spent liquor through HID and also higher steam consumption of evaporation unit.

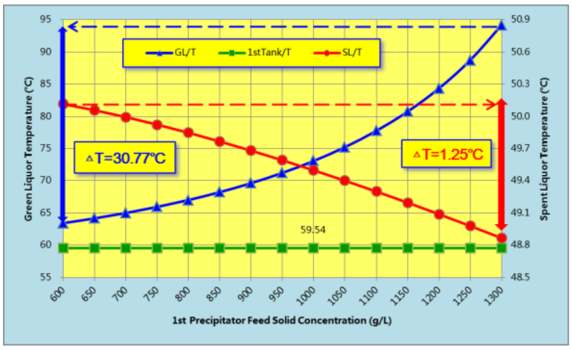

Figure 6: Liquor Temperature VS Solid Content

Another disadvantage of elevating seed charge lies on the loss of holding time, and in turn lack of growth rate. Figure 7 shows average particle SSA against holding time. When solid content was elevated to 1000g/L, the pump-off solid has a SSA of only 0.0484m^2/g, which cuts down 0.0008m^2/g comparing with the feed.

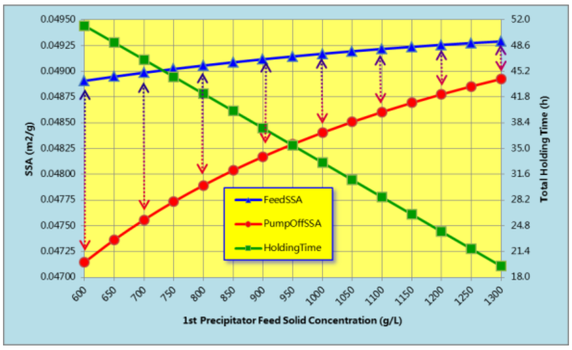

Figure 7: SSA & Holding Time VS Solid Content

Growth only stage determines high seed charge as the guarantee to achieve production, but also highlights disadvantages such as lack of holding time, probability of collision, increase of agitation transportation power, etc. So under the existing process, proper solid operating range is needed.

3.3 Seed Moisture

Decreasing seed moisture totally contributes to production, precipitation rate, benefits process operation. It can be learned from Figure 8 that 8124 t/year production raise could be obtained by 2% seed moisture reduction, at the same time 0.35% precipitation rate promotion.

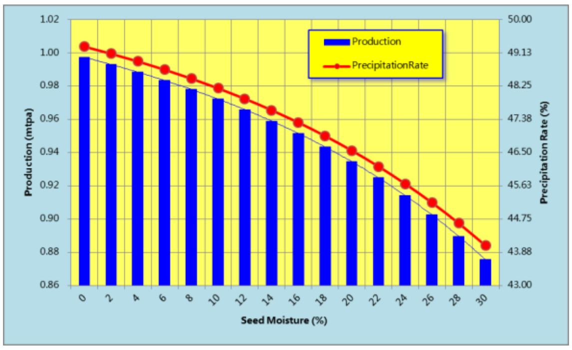

Figure 8: Production & Precipitation Rate VS Seed Moisture

Figure 9 shows seed moisture against molar ratio and holding time. It clearly indicates the influence of the spent liquor carried by seed on

the initial molar ratio of precipitation series. Another benefit of lower moisture was further holding time, in fact, a reduction of 2% seed moisture could bring additional 1.6h.

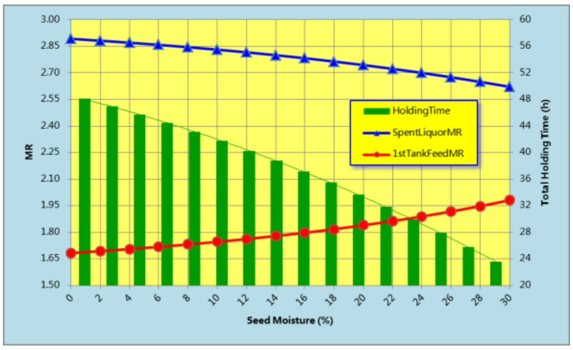

Figure 9: Molar Ratio & Holding Time VS Seed Moisture

Generally Chinese refineries can maintain 20% seed moisture under steady operating conditions using ‘vertical disk filters’. Facility of this kind characterizes large capacity, high operation rate and relative loose operating conditions. The good performance requires smooth Particle Size Distribution with coarse crystals which can be achieved as well by moisture reduction as shown in Figure 10. Both holding time and initial supersaturation increase result in about 0.04um growth rate promotion against 2% moisture reduction during existing conditions.

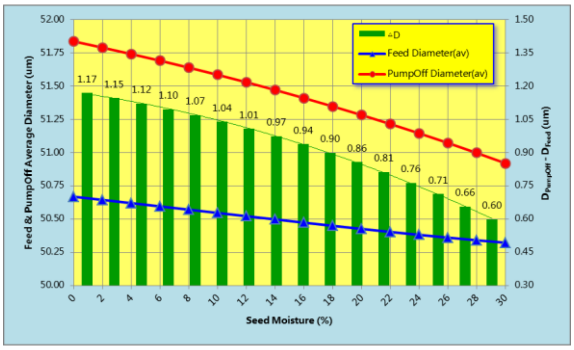

Figure 10: Particle Diameter VS Seed Moisture

4. RECOMMENDATIONS AND OUTLOOK

This study only discussed the influence of some internal factors on precipitation, and then came to the conclusion that for the existing condition, proper interstage cooling profile (1.7℃ each stage), optimum feed slurry solid concentration (~900g/L) and as low seed moisture as possible would achieve maximum benefit of production, precipitation rate and alumina quality.

5. ACKNOWLEDGEMENTS

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