PRECIPITATION AREA UPGRADE AT ETI ALUMINUM

Bekir Çelikel¹, Gokhan Kurşat Demir¹, Murat Kayacı¹, Meral Baygul¹, Carlos E Suarez²

¹ ETI Aluminum Inc

² Hatch Asssociates Consultant Inc

Abstract

ETI Aluminum is an integrated facility that produces sandy alumina by processing boehmitic bauxite. With the development of aluminum smelting technology and greater attention given to environmental protection, the quality requirements of alumina are much strict. ETI has initiated a study to meet smelter grade alumina specifications of its internal electrolysis customer. The old precipitation circuit at ETI alumina refinery was converted to sandy alumina. The change involved modifications to existing tanks and flows to obtain proper hydrate agglomeration. The challenge has been to improve and control particle size distribution without losing precipitation yield and product quality. ETI has been able to reduce its minus 44 micron particles from approximately 40 % to 6-8 % by means of controlling the precipitation circuit parameters such as, alumina supersaturation, seed charge, temperature and classification. Improvements in hydrate occluded soda and attrition index were obtained.

Introduction

The ETI alumina plant was designed to operate using the European Bayer Process technology with a nominal capacity of 250,000 tons per year alumina. The quality specification was always maintained in the range of 10-40% for the $-44\mu m$ fraction of the product alumina. Due to the worldwide introduction of the dry gas scrubbing process ETI's smelter requested the alumina refinery to reduce the fines content of alumina so as to improve the efficiency of the smelter operation.

The original precipitation circuit was designed using Russian (VAMI) technology to produce floury alumina, with fines (-44 μ m) around 30%. The need to increase liquor productivity also increased the generation of fines and the fluctuation in hydrate granulometry. This condition adversely affected the process control in precipitation, and resulted in operational problems at the smelter end.

The need to produce a coarser hydrate with improved crystal strength was required to improve the smelter operation so this determined the need to exercise a greater process control in the precipitation area. In order to achieve the Alumina Quality required by the

smelter, the goal to produce a relatively coarser product, $(-44\mu m \text{ fraction of about 6-8\%})$ without compromising on liquor productivity was established.

In this paper we discuss how the old precipitation circuit for the floury alumina process was converted to produce sandy alumina and the implementation of the process and operating strategies to control the precipitation circuit.

Description of the old process

ETI precipitation circuit consists of two parallel rows of 20 precipitators with a capacity of 1800 m³ and air agitated. The aluminate liquor, cooled down to a temperature of 60-63 °C in flash tanks, is mixed with the seed hydrate and transferred to the first precipitator. The liquor decomposes in a series of precipitators thus precipitating the aluminum hydroxide. Mixing of the slurry in the precipitators is carried out by means of circulating air-lifts and delivery of the slurry from one precipitator into another one is accomplished with the help of transporting air-lifts.

The decomposition of the liquor occurs in 75 hours, and the caustic module changes during the process from 1.6 to 3.5. The temperature of the hydrate slurry decreases in the precipitators from about 63 °C to about 42 °C by means of natural cooling of the precipitator walls as well as by internal jacketed piping using water as the cooling media and also by air used for slurry transfer between precipitators.

The hydrate slurry from the pump-off precipitator moves by gravity to hydroseparators, the overflow of which is delivered to hydrate thickeners. The thickened hydrate slurry and underflow of the hydroseparators are filtrated on drum vacuum filters and returned to precipitator. Part of the underflow of the hydroseparator is delivered to product filtration.

This arrangement is shown on the schematic in Figure 1

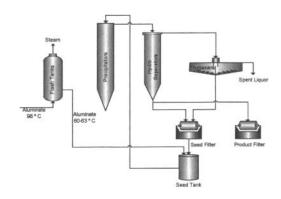


Figure 1. ETI's Old Precipitation Circuit

Higher yield and coarser alumina process

A lot of search was made in the literature for the topic dealing with the production of sandy alumina and high yield. After the review, we found that the most important parameters that affect the particle size of alumina hydrate are:

1. Nucleation

Nucleation is a special condition characterized by the spontaneous generation of crystals and the consequent rapid increase of sub-sieve particles. For a given liquor, the rate of nucleation depends essentially on the temperature and the seed surface area. Since the total seed surface area in the growth precipitators depends on the seed charge and on the seed quality (size distribution), this factor cannot be modified quickly, hence cannot be used to control the rate of nucleation in the short term. Therefore, the main parameter to adjust the nucleation rate after agglomeration in the short term is the temperature profile along precipitation. The agglomeration temperature controls this. The "ultra fines" thus formed by nucleation are so light that they are not classified and simply follow the liquor.

2. Agglomeration

Agglomeration is the quickest way to produce larger particles. In this step, small particles collide and are cemented together to produce a larger particle. Particle numbers in the precipitator dramatically decrease and the particle size distribution of the product show a coarser grain distribution than the seed in 2-8 hours. General conditions which favor agglomeration regardless of the caustic concentration are low to medium charge of fine seed, low initial molar ratio of Na₂O to Al₂O₃ (α_k), seed surfaces free from sodium oxalate and fill temperatures high enough to prevent uncontrolled nucleation.

Factors that affects agglomeration:

- Higher temperature
- Lower α_k
- Lower charge of fine seed
- Longer residence time
- Improved seed washing
- Mild agitation

3. Growth

Growth is the mechanism by which particles are enlarged by the addition of newly precipitated alumina trihydrate. Conditions which favor growth and strengthening at all caustic concentrations are similar to those which favor agglomeration that is moderate seed charges, high initial supersaturation and relatively high temperature.

Large particles produced predominantly by growth are dense and five to seven times less friable than those produced by agglomeration.

4. Yield

Within the limits allowed by the quality control requirements the productivity will be maximized by:

- Higher caustic concentration
- Higher seed charge
- Lower pump-off temperature
- Longer holding time

The yield from precipitation can be calculated quite simply.

Yield (g Al₂O₃)/ litre of circulating liquor)= [(0.962/ α_k in)- (0.962/ α_k out)].C_{in}

The yield equation shows that what we have to do to increase yield: decrease $\alpha_{k \text{ in}}$, increase $\alpha_{k \text{ out}}$ or increase C_{in} (LTP caustic concentration).

5. <u>Temperature</u>

Temperature has two effects: firstly it influences the kinetics of the decomposition reaction (higher temperature= faster agglomeration rate) and, secondly, it influences the equilibrium alumina solubility and thereby the supersaturation driving force (higher temperature= reduced supersaturation driving force and lower precipitation rate). We also know that occluded soda in the product is directly determined by the supersaturation history of the particles. We therefore try to find the combination of temperature, seed surface area and system configuration that provides the most cost effective and productive overall solution.

6. <u>Supersaturation</u>

The maximum stable concentration for any solute in a solution (such as gibbsite in sodium hydroxide) is set by its equilibrium solubility, a thermodynamic function which will depend on temperature and other factors. A solution at that concentration is said to be saturated. If the concentration is higher then it is considered to be supersaturated. This condition is often achieved by making a solution at a higher temperature and then cooling it, as we do in the Bayer process. Supersaturation is the thermodynamic driving force for precipitation and the three processes of nucleation, agglomeration and growth all depend upon it.

The equilibrium solubility for gibbsite in a pure sodium aluminate solution is given by:

A/C $(0.962/ \alpha_k) = 0.5843.Exp[6.21+(0.636.C-2487)/(T+273)]$

Where T is temperature °C and C is caustic as g/l Na_2CO_3 .

Process modifications to produce sandy alumina

Agglomeration system

Agglomeration is the important precondition for producing coarse aluminum hydroxide. In order to understand the influence of agglomeration parameters on the agglomeration process of seeded precipitation, labscale trials were conducted by varying agglomeration temperature, the molar ratio of Na₂O to Al₂O₃ (α_k), the seed load and initial size. The results show that agglomeration is enhanced when temperature is higher. The particle size of agglomerates is decreased and agglomeration efficiency varies with different seed loads. The agglomeration efficiency is higher when the supersaturations of sodium aluminate solution and seed load are balanced to each other. The seed initial size has great influence on the agglomeration efficiency.

In order to produce sandy alumina suited for the smelter operation, the following modifications and process strategies were implemented:

 Laboratory results showed that high supersaturation enhances agglomeration; so we dropped the α_k of aluminate liquors

Figure 2 shows the trend of aluminate α_k from 2007 to 2011

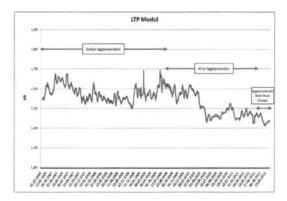


Figure 2. Aluminate Liquor α_k

- Laboratory works showed that the optimum residence time for the agglomeration is 8 to 9 hours. One Precipitation tank was converted to agglomerator and the LTP flow and fine seed quantity adjusted accordingly. The rest of the precipitators have used as growth tanks.
- Existing rotary drum filters were dedicated as fine and coarse seed filters.
- Flash tank output temperature varied due to the LTP flow fluctuations, which results in the temperature vary in agglomeration tank, hence the varies of supersaturation. This made the stable control of agglomeration impossible. To improve LTP temperature control the third barometric flash tank water control system was upgraded by adding a new control valve, restricting the water flow through the system and tuning the control system. This

contributed to a better control and less variability of agglomeration tank temperature which is set to about 72 $^{\circ}$ C.

- Incoming LTP was splitted in half as hot fill and cold fill. Hot fill temperature adjusted by flash tanks and cold fill temperature adjusted by a new plate heat-exchanger.
- In order to increase the activation of the fine seed, the washing system was started
- O. Tschamper[1] had proposed some useful indicators for agglomeration;

Degree of agglomeration = I - A / I

I= Fraction of seed (in percent) less than 45micrometers in size

A= Fraction of agglomeration product (in percent) less than 45 micrometers in size

Supersaturation/SeedRatio=Supersaturation(g/l)Al₂O₃/Se edSurfaceArea (m2/l)

Laboratory and plant on-site results have shown that the necessary degree of agglomeration may be attained without effort when the amount of fine seed in the first stage of decomposition Is fixed to keep the ratio of the supersaturation of the precipitating aluminate liquors (grams per liter Al_2O_3) to the surface area of this fine seed (square meters per liter) between 4 and 20 grams per square meter. Considering the real condition in plant, the suitable supersaturation/seed ratio is 8 to 12 as can be seen below in figures 3 and 4.

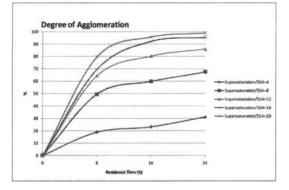


Figure 3. Degree of Agglomeration vs. Residence Time

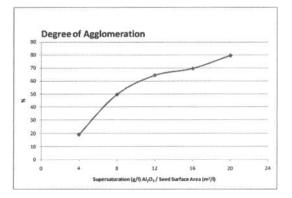


Figure 4. Degree of Agglomeration vs. SS/SSA

We have installed a PLC system that controls agglomeration by adjusting the following parameters: LTP flow x supersaturation ratio/ fine seed quantity x fine seed surface area.

- The inside cooling in the agglomerator has been stop to maintain constant temperature.
- Mild agitation is being controlled by the addition of air to the agglomerator.
- The old classification unit consists of gravity settlers for product, coarse seed and fine seed material. Hydrocyclones have been installed to improve the classification. The U/F of the Hydrocyclones feeds a pan filter to separate the product. The O/F of Hydrocyclones feed the secondaries. The U/F of secondaries feed the coarse seed filters and the O/F of the secondaries feed tertiary classifiers. The U/F of tertiaries feed the fine seed filters. The new classification system has allowed for proper separation of the different fractions of the hydrate.
- Meeting hydrate particle specifications is often in conflict with maximizing liquor productivity (yield). In this modifications a few precipitation tanks are used as the agglomeration tank which help to satisfy the product quality criteria while the conditions of the growth precipitations are set to maximize the yield. Before the improvements yield was around 85-90 g/l. After improvements we have increased pump off solids content up to 600 g/l and the pump-off temperature has been dropped to 42 °C. As a result, the yield has been increased to nearly 95 g/l while maintaining good particle size control as can be seen in figure 5.

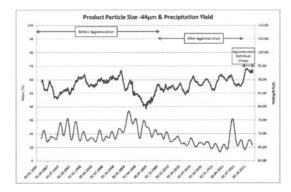


Figure 5. Product Particle Size -44 μ m & Precipitation Yield

• To improve the particle size control we have initiated new analysis which is fine seed surface area, agglomeration inlet and outlet particle size, leachable and occluded soda, agglomerator and first growth precipitator solid content. The new Agglomeration system and other precipitation equipment is shown in Figure 6

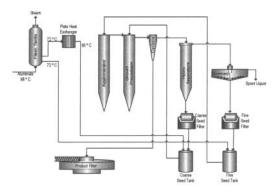


Figure 6. Agglomeration Precipitation Circuit

Dual-charge system

As we continue to see good particle size control of the product the decision was made to further increase yield. The Hot and Cold Fill initially tried at ETI did not perform as expected. Difficulties in agglomeration, given by insufficient liquor to the agglomerators for the amount of fine seed charge, made us consider a different process strategy. Since then we have reconfigured the seed charge to a "Dual-Charge" system. In this new system we started using all LTP for agglomeration and the agglomeration slurry is used to repulp the coarse seed. A second agglomerator has been put in service to maintain the residence time in the range of 8-9 hours.

The Dual-Charge is shown in Figure 7

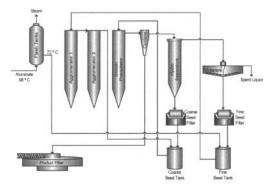


Figure 7. Dual-Charge Precipitation Circuit

The plant has seen marked improvement in the -44 fraction in the range of 5-15 % with the modifications and agglomeration parameter control of the precipitation circuit. The -44μ m in the product hydrate before agglomeration and after agglomeration is shown in Figure 8.

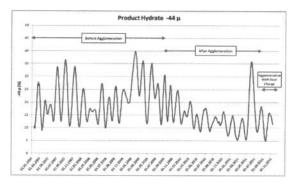


Figure 8.Product Hydrate -44 µm

Conclusions

Changing alumina specifications by new smelter requirements have initiated conversion of floury alumina production to sandy alumina production under high yield conditions.

The plant has been running since November 2009 with the improved precipitation process. The amount of variation in product particle size has been narrowed down to a very small margin compared to old floury particle size

Modifications and changes in process strategies have improved product quality, increased product capacity and brought about cost savings with little capital investment.

The understanding of precipitation theory supported by laboratory trials have allowed us to explore better plant parameters control to increase precipitation productivity while improving and maintaining product quality.

The improved understandings of the process and operation have made us aware of the significant impact caused by the variability introduced by operational events mainly in the classification area.

The strict control and monitoring of key performance indicators in the precipitation circuit has helped us tremendously in keeping the process and quality in check.

Acknowledgements

The authors would like to acknowledge The Scientific and Technological Research Council of Turkey (TÜBİTAK) for supporting R&D studies.

References

- 1. Dr. O. Tschamper, "Improvements by the New Alusuisse Process for Producing Coarse Aluminum Hydrate in the Bayer Process," TMS (1981), 103-115
- R.C. Fritschy, G.P. Brown, "Nabalco Experiences With the New Alusuisse for Producing Sandy Alumina at Gove," TMS (1983), 125-128
- J.L. Anjier, M.L. Roberson, "Precipitation Technology," TMS (1985), 367-375.
- 4. B. Garner, B. Cristol, A. Soirat, "Precipitation Particle Size Control," TMS (1999), 71-76
- Y. Xie, Q. Zhao, S. Bi, "Effect of Temperature on The Agglomeration of Hydrate," TMS (2003), 61-64
- 6. P. James, M. Jackson, "Alpart's Quality Improvements Program," TMS (2005), 83-88