

The Altech Process to Produce High Purity Alumina from Kaolin Clay

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Abstract

Altech Chemicals Limited has commercialized the production of 99.99% (4N) high purity alumina (HPA) from kaolin using the hydrochloric acid process. The Altech process involves the removal of oversize silica / quartz followed by the calcination of kaolin at around 700 °C to convert the crystal structure of the clay to a more reactive form (meta kaolin) for leaching. Hydrochloric acid (HCl) is used in the leaching process. The leach reaction is exothermic and the oxide components (except silica) are converted to soluble chlorides, producing a high concentration of aluminum chloride (AlCl₃) in solution. The pregnant liquor solution (PLS), from leach residue filtration is directed to crystallization where aluminum chloride hexahydrate (AlCl₃·6H₂O or ACH) is crystallized out of solution. This is achieved by increasing the hydrochloric acid concentration of the liquor by bubbling in anhydrous HCl gas. ACH crystals are then centrifuged and washed from the solution. ACH is purified by two stages of the re-dissolution / crystallization process. The purified ACH crystals are heat treated in two stages via natural gas fired rotary kilns. The first stage involves heating the ACH to around 700 °C in order to decompose the ACH to alumina. The second stage involves heating to around 1280 °C to produce alpha alumina (α- Al₂O₃). Altech has developed the technology to produce HPA pellets for the sapphire industry as well as fine (< 1 micron) HPA powder for use in the lithium-ion battery industry. Production costs are anticipated to be considerably lower than established HPA producers - in the bottom quartile of the production cost curve.

Keywords: Non-bauxite ores, High Purity Alumina, Chloride hydrometallurgy.

1. Introduction

Altech Chemicals Limited, an Australian company is aiming to become one of the world's leading suppliers of 99.99% (4N) high purity alumina (HPA) through the construction and operation of a 4,500 tpa high purity alumina processing plant at Johor, Malaysia. Feedstock for the plant will be sourced from the Company's 100%-owned kaolin deposit at Meckering, Western Australia and shipped to Malaysia. Altech's production process will employ conventional "off-the-shelf" plant and equipment to extract HPA using a hydrochloric (HCl) acid-based process.

2. Uses of HPA

HPA is a critical ingredient required for the production of synthetic sapphire and is increasingly consumed in the manufacture of lithium-ion batteries. Synthetic sapphire is used in the manufacture of substrates for LED lights, semiconductor wafers for the electronics industry, and scratch-resistant sapphire glass used for wristwatch faces, optical windows and smartphone components. There is no substitute for HPA in the manufacture of synthetic sapphire. Lithium-ion battery manufactures require HPA as a coating for the plastic anode/cathode separator to reduce separator shrinkage and combustibility.

2.1. HPA Demand Growth Forecast

According to independent group CRU, the forecast for 4N+(99.99%) HPA, the market segment that Altech’s plant is designed to supply, is to grow at 30% per annum from 19,000 tonnes (2018) to 272,000 tonnes (2028), as illustrated in Figure 1 below. CRU estimated that HPA in powder form used in lithium ion battery separators will reach 187 kt by 2028. In addition, HPA as a pellet / bead form used in LEDs will reach 85 kt by 2028.

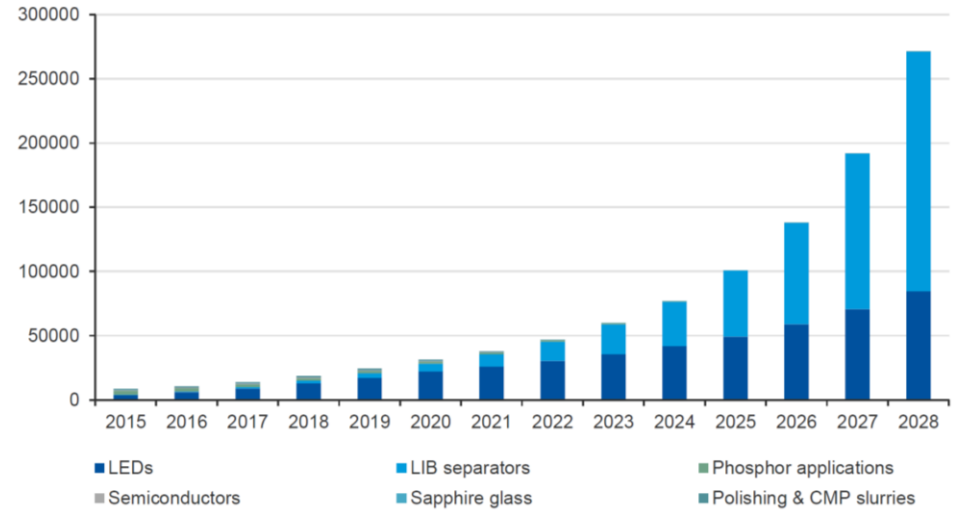


Figure 1. Total 4N+ HPA demand, 2015-2028.

Overlaying the demand profile, the report concluded an impending significant market deficit, where supply – no matter how optimistic – could not keep pace with the level of 4N+ HPA demand. The result of the analysis is an extremely large apparent 4N+ HPA short term deficit, peaking around 2021 at a deficit of around 20,000 tpa (blue bars in Figure 2). The long term supply deficit continues until 2028 and further peaks at a ~ 50,000 tpa deficit (green bars in Figure 2).

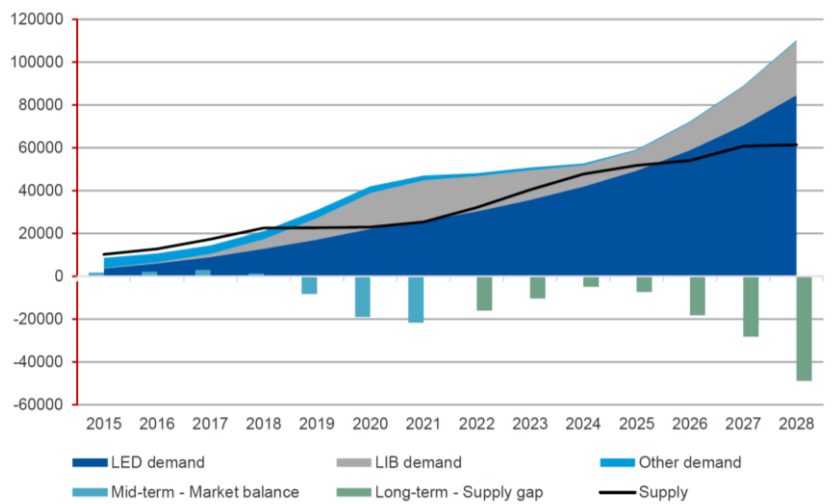


Figure 2. CRU base market balance and supply gap, 2015-2028.

The price of 4N HPA depending on quality and end applications ranges from US\$15 / kg to US\$56 / kg, but with some outlying prices significantly higher – albeit for lower volumes.

3. Process Description

There are a number of industrial methods for producing high purity alumina. One of the most common methods is hydrolysis of aluminum alkoxide. Choline hydrolysis of aluminum is another common method which involves the dissolution of aluminum powder to a hydroxide and then subsequent calcination to convert it back to an alumina (Al_2O_3) form. Altech has developed the technology to produce HPA from kaolin using hydrochloric acid, without the use of the expensive aluminum metal feed stock.

The Altech process involves the removal of oversize silica /quartz followed by the calcination of kaolin at around 700°C to convert the crystal structure of the clay to a more reactive form (meta kaolin) for leaching. Hydrochloric acid (HCl) at $\sim 3.0\%$ w/w is used in the leaching process. The leach reaction is exothermic and the oxide components (except silica) are converted to soluble chlorides, producing a high concentration of aluminum chloride (AlCl_3) in solution. The pregnant liquor solution (PLS), from leach residue filtration is directed to crystallization where aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ or ACH) is crystallized out of solution. This is achieved by increasing the hydrochloric acid concentration of the liquor by bubbling in anhydrous HCl gas. ACH crystals are then centrifuged and washed from the solution. ACH is purified by two stages of the re-dissolution/crystallization process. The purified ACH crystals are heat treated in two stages via natural gas fired rotary kilns. The first stage involves heating the ACH to around 700°C in order to decompose the ACH to alumina. The second stage involves heating to around 1280°C to produce alpha alumina ($\alpha\text{-Al}_2\text{O}_3$).

3.1. Kaolin Preparation

The kaolin is unloaded and fed into the wet screening circuit consisting of a drum scrubber, a filter and various screens. This operation ensures kaolin particle size is reduced to $< 300\mu\text{m}$ and the majority of oversize silica /quartz is removed. The purpose of this circuit is to remove the major impurity in kaolin: silica /quartz sand, which is predominantly in the form of coarse grains. This impurity is removed as the oversize in a wet screening process; consisting of a drum scrubber, a filter and a double deck screen. See Figure 3.

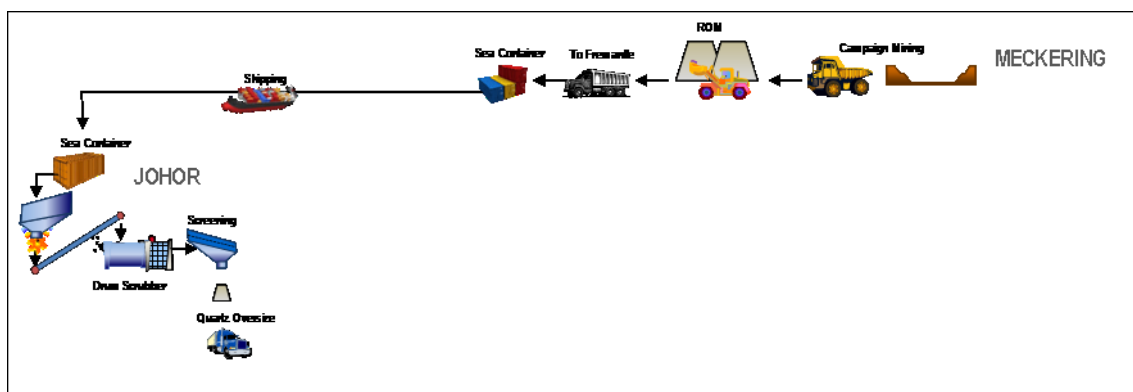
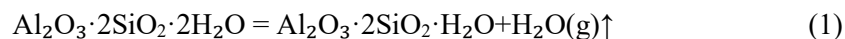


Figure 3. Removal of quartz and silica oversize.

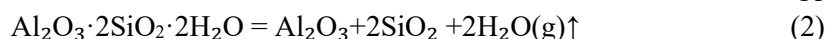
Beneficiated kaolin will be calcined at around 700°C in an indirect rotary kiln to convert the crystal structure of the clay to a more reactive form for leaching. The kiln will be indirectly fired by natural gas with associated cyclone and bag-house to collect off-gas fines. The calcine will be cooled, screened and any oversized material crushed to a particle size of $< 300\mu\text{m}$. See Figure 4.

The purpose of this circuit is to increase the reactivity of the kaolin for leaching. Kaolin, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, has a structure which is not soluble in acid. Therefore, it has to be converted

into metakaolin. Metakaolin, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot x \text{H}_2\text{O}$, has a more reactive amorphous structure, which is leachable by hydrochloric acid. To convert kaolin to metakaolin, heat is required. This transformation process has been described as the removal of structural water through dehydroxylation. This process produces a distortion or buckling effect in the Al–Si layers, which is due to the migration of the aluminium into vacant sites provided by the inter-layer spacing. This results in the change in aluminium coordination from octahedral to tetrahedral. Kaolin activation by calcination involves dehydration, according to the reaction:



Or



The chemical reaction occurs between 570 °C and 630 °C. Over-calcination results in crystallisation of the mullite phase, and sintering, resulting in losses in acid leach activity. The dehydration results in up to 14 % weight loss due to the partial or total loss of crystal water.

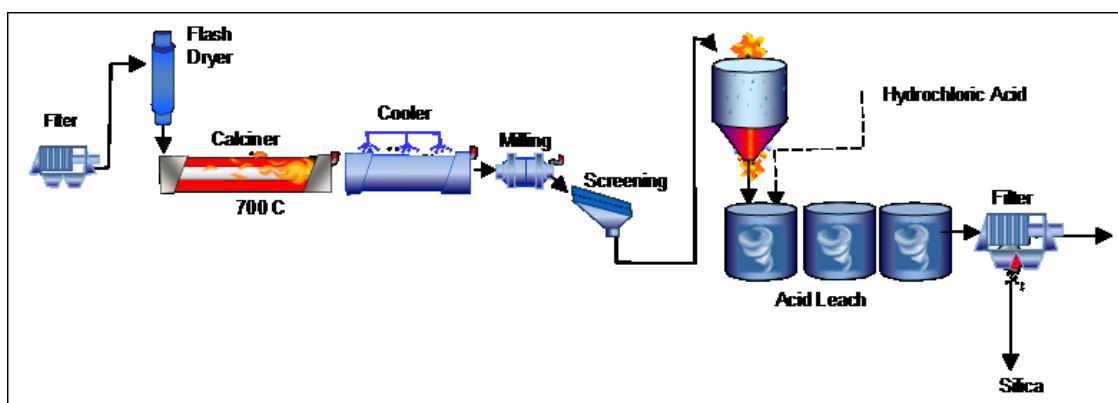
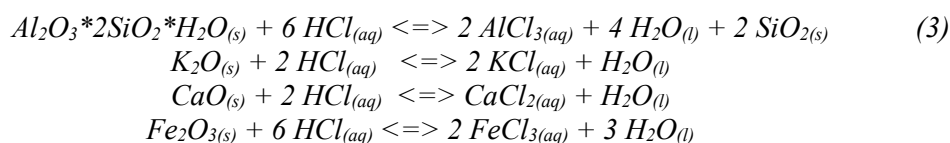


Figure 4. Kaolin calcination and acid leach.

3.2. Kaolin Leaching

Leaching follows, during which the calcine will be mixed with recycled wash liquor containing hydrochloric acid (HCl). The leach reaction is exothermic and the oxide components (except silica) are converted to soluble chlorides, producing a high concentration of aluminum chloride (AlCl_3) in solution. The leached slurry is then pumped to leach residue filtration. The silica residue slurry is filtered and the silica residue neutralized before being provided to local vendors, such as brick works or cement plants.

Kaolin calcine powder is mixed with liquor to obtain a target solids content of around 28 % w/w before the slurry is pumped into the first leaching vessel. The liquor is a combination of recycled hydrochloric acid from stage 1 crystallisation (~ 30 % HCl), a small amount of leach residue filter wash filtrate (~ 1.7 % w/w HCl). The leach reaction is exothermic and the oxide components (excluding silica) are converted into soluble chlorides, producing a high concentration aluminium chloride (AlCl_3) solution. Most of the minor impurities in the activated kaolin such as iron, sodium, potassium, magnesium and calcium etc. are also converted into their corresponding soluble chlorides. Silica is nonreactive and remains as a solid in the PLS. The reaction is as follows:



with trace amounts of basic aluminum chlorides (oxychlorides). Almost all of the chloride is liberated as HCl gas, recovered and reused in the process. The solids from the roaster fall directly into the second rotary kiln that then heats the solids further to remove the remainder of the HCl and water (H₂O) to produce HPA: highly pure alpha alumina (α - Al₂O₃). The HPA will discharge to a cooler and is then fed directly to a final acidic wash stage to remove surface trace impurities. The HPA is washed, milled using bead mills, and spray dried to produced dried HPA powder with particle size of less than 1 micron. The HPA powder is micronized to produce product of varying particle sizes, depending on the end use requirements for the lithium ion battery industry. In the other stream, the HPA is pelletized into beads and calcined in a tunnel kiln at 1600 °C to form high density HPA beads for the LED industry.

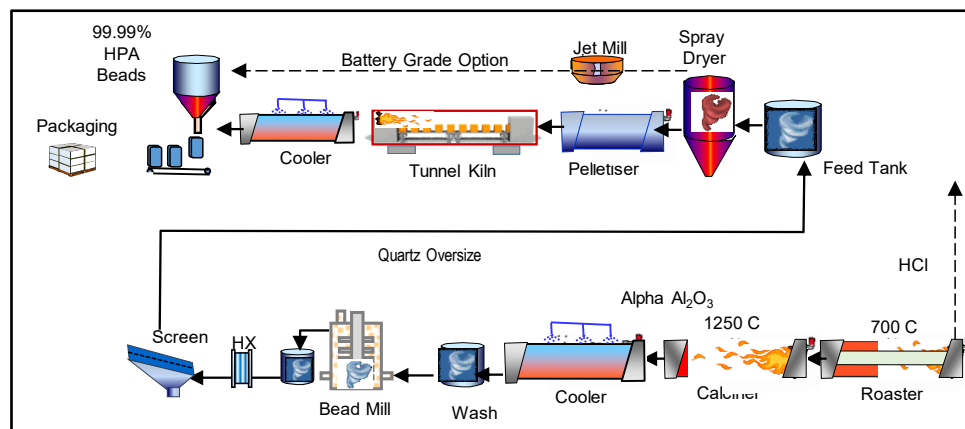


Figure 6. Alpha alumina production.

4. Sapphire Grade HPA

Altech’s sapphire grade HPA product will be 4N (99.99 %) high purity alumina (Al₂O₃) in the form of a high-density HPA bead of around 3 - 4mm in size. The higher bulk density of HPA beads (versus HPA in powder form) is preferred by synthetic sapphire manufacturers as it maximises the amount of alumina that can be placed into the furnaces and kilns used in the production of synthetic sapphire. The target loose bulk density of Altech’s high-density HPA beads will be around 2.2 t / m³.

Table 1. Sapphire grade Specification.

Sapphire Grade Spec	Chemical Content	Spec Limit
Alumina	Al ₂ O ₃	>99.99%
Silica	Si	<20ppm
Sodium	Na	<10ppm
Magnesium	Mg	<10ppm
Calcium	Ca	<10ppm
Iron	Fe	<10ppm
Copper	Cu	<10ppm
Crystal Structure		alpha
Bulk Density*	t/m ³	2.2

*Dry Basis (1110°C)



Synthetic sapphire is used in the manufacture of substrates for LED lights; semiconductor wafers used in the electronics industries; and scratch-resistant glass used for wristwatch faces, optical windows and components for smartphones and other handheld devices.

4.1. Lithium-ion Battery Grade HPA

The finishing line of Altech's proposed HPA plant is designed to produce the ultra-fine HPA used in the lithium-ion battery sector; this product may also be sold in slurry form (drums).

Table 2. Lithium-Ion Battery Grade.

Lithium-ion Battery Grade	Chemical Content	Spec Limit
Alumina	Al ₂ O ₃	>99.99%
Silica	Si	<20ppm
Sodium	Na	<10ppm
Magnesium	Mg	<10ppm
Calcium	Ca	<10ppm
Iron	Fe	<10ppm
Copper	Cu	<10ppm
Crystal Structure		alpha
Particle Size	micron	<1.0



5. Conclusion

In conclusion, Altech has developed the technology to produce HPA pellets for the sapphire industry as well as fine (< 1 micron) HPA powder for use in the lithium-ion battery industry from a kaolin feed stock using hydrochloric acid. Production costs are anticipated to be considerably lower than established HPA producers - in the bottom quartile of the production cost curve. The Company will continue to optimise and further improve the process during the commissioning and start up of the plant.