(54) Title: ALUMINA PRODUCTION METHOD

(57) Abstract:

The invention relates to metallurgy. In particular, it relates to acidic methods of alumina production, and can be used in the course of processing low-grade aluminium-containing raw materials. This method for producing alumina includes: baking of aluminum-containing raw materials; processing of said materials with hydrochloric acid; aluminum chloride salting-out by saturating the clarified chloride solution with gaseous hydrogen chloride; aluminum chloride calcination to produce aluminum oxide, and; mother liquor pyrohydrolysis, including returning hydrogen chloride to the stages of acidic treatment and salting-out. For improving the quality of alumina and reducing power costs, aluminum chloride – precipitated in the course of salting-out – is treated with aqueous ammonia; the resulting precipitate goes to calcination, and the ammonium chloride solution is mixed with said aluminum-containing raw materials before or during baking; ammonia (released during baking) is dissolved in the water; the resulting aqueous ammonia goes to treat aluminum chloride. The ammonium chloride solution – prior to mixing with the aluminum-containing raw materials – may be subjected to stage-wise evaporation (by means of re-using heating steam.) Ammonium chloride (released during evaporation) can be mixed with the aluminum-containing raw materials.
ABSTRACT

Alumina Production Method

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Alumina Production Method

The invention relates to metallurgy. In particular, it relates to acidic methods of alumina production, and can be used in the course of processing low-grade aluminum-containing raw materials.

What is known is a hydrochloric-acid method for producing alumina by the acidic treatment of pre-calcined raw materials, clarified chloride solution evaporation resulting in the crystallization of aluminum chloride hexahydrate \((\text{AlCl}_3\cdot6\text{H}_2\text{O})\) followed by \text{AlCl}_3\cdot6\text{H}_2\text{O} calcination to produce oxide which (due to a significant content of iron and other impurities (excluding silicon) has been called ‘raw alumina’ by the authors \(\text{Metallurgist’s Guide to Non-Ferrous Metals. Alumina Production. Moscow: Metallurgiya, 1970, pp. 236-237.}\) Then, this intermediate product is processed according to the traditional alkaline Bayer method to remove iron and produce alumina of metallurgical grade.

The disadvantages of this alumina production method are as follows: complicated process flow diagram; high power costs, if said flow diagram is implemented; transfer of chlorides from the acidic cycle to the alkaline cycle, and related alkali losses (reaching 36 to 37 kg*t alumina.) Therefore, this method is not applicable in the industry.

The closest method to the claimed one is, a method for producing alumina from high-silicon bauxites by hydrochloric-acid leaching, including: baking of aluminum-containing raw materials @ up to 700 degrees C; treatment of said materials with hydrochloric acid; aluminum chloride salting-out by saturating the clarified chloride solution with gaseous hydrogen chloride; aluminum chloride calcination to produce aluminum oxide, and; mother liquor pyrohydrolysis, including returning hydrogen chloride to the stages of acidic treatment and salting-out (Elsner D., Jenkins D.H. and Sinha H.N. Alumina via hydrochloric acid

According to this method, aluminum chloride hexahydrate is separated from the solution (liquor) by salting-out with gaseous hydrogen chloride, which allows to simplify the process flow diagram, abandon the Bayer process and reduce power costs. However, the content of impurities in the final product, especially chlorine and iron, is 2 to 3 times higher than the permissible limits for metallurgical alumina.

The disadvantages of this method also include an energy-intensive method of maintaining the water balance during the process cycle by using the flash evaporation of recycled (circulated) water during the pyrohydrolysis of iron chloride and other impurity chlorides.

By salting AlCl3·6H2O out of the solution containing iron chlorides and other impurity metals, it is almost impossible to ensure high purity of the target product; calcination of such a product is the most power-consuming process. Thermal energy consumption during the calcination of aluminum chloride hexahydrate @ 1,100-1,200 degrees C is 15GJ/t alumina. Moreover, during calcination, it is very difficult to get rid of residual chlorine which has a very negative impact during the process of reducing aluminum from alumina.

The invention is based on the objective to develop a method for producing metallurgical alumina from low-grade raw materials, which allows to process low-grade high-silicon ores and waste.

The technical result is to increase the quality of alumina and reduce power consumption.

For achieving the above technical result, this method for producing alumina includes: baking of aluminum-containing raw materials; processing of said materials with hydrochloric acid; aluminum chloride salting-out by saturating the clarified chloride solution with gaseous hydrogen chloride; aluminum chloride calcination to produce aluminum oxide, and; mother liquor pyrohydrolysis,
including returning hydrogen chloride to the stages of acidic treatment and salting-out; aluminum chloride – precipitated in the course of salting-out – is treated with aqueous ammonia; the resulting precipitate goes to calcination, and the ammonium chloride solution is mixed with said aluminum-containing raw materials before or during baking; ammonia (released during baking) is dissolved in the water; the resulting aqueous ammonia goes to treat aluminum chloride.

The ammonium chloride solution – prior to mixing with the aluminum-containing raw materials – may be subjected to stage-wise evaporation (by means of re-using heating steam.)

Ammonium chloride (released during evaporation) can be mixed with the aluminum-containing raw materials.

While processing the AlCl3·6H2O crystals with aqueous ammonia, aluminum chloride undergoes pseudomorphic transformation to partially dehydrated aluminum hydroxide – boehmite (AlOOH) – including the desorption and removal (washing-off) of iron compounds to the mother liquor of ammonium chloride (which can be easily removed by washing with water.) Thus, there is an additional cleaning (treatment) process for aluminum hydroxide. The particle size of the solid phase undergoes almost no changes.

Boehmite calcination requires only 2.15GJ per 1 tonne alumina.

While treating aluminum chloride hexahydrate with aqueous ammonia, a solution of ammonium chloride is formed; this solution – compared to hydrochloric-acid solutions – has no strong corrosive impact on equipment, and can be stepwise evaporated in a group of conventional evaporators with steam heating (by means of re-using heating steam) which are widely used in the mineral salts and fertilizers industry and result in a 2-3-fold savings of heat consumed (compared to the flash evaporation of the water as per the prior art, when all the water to be used for washing the “sistoff” (insoluble residue) goes to pyrohydrolysis.)
Ammonium chloride recycling (circulation) can be efficiently carried out by adding the evaporated solution right before baking. It is also possible to recycle ammonium chloride in the form of crystals (separated in the process of evaporating the solution.)

At temperatures above 196 degrees C, ammonium chloride decomposes into gaseous hydrogen chloride and ammonia. Hydrogen chloride reacts with components of the raw materials – especially with iron – and form the corresponding chlorides. Released ammonia can be absorbed with the water and – in the form of an aqueous solution – sent to treat the AlCl3·6H2O crystals.

Separation of aluminum into the solution – by virtue of its chemical properties – takes place mainly at the stage of hydrochloric-acid treatment. Since the partial chlorination of raw materials occurs during baking, there is less pressure (load) on the hydrochloric-acid treatment facilities.

Thus, this method of producing alumina uses hydrogen chloride (hydrochloric acid) circulation (recycling) and ammonia circulation (recycling), which minimizes the consumption of reagents and heat energy.

**BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 is a flowchart showing an alumina production process according to the present invention.

Alumina is produced as follows:

Aluminum-containing raw materials mixed with ammonium chloride are sent to baking (where said raw materials undergo partial thermal activation and ammonium chloride undergoes decomposition.) Hydrogen chloride reacts with oxide components of the raw materials, and free ammonia is absorbed by the water to form aqueous ammonia. Thus, said raw materials undergo the stage of baking-chlorination.

Then – for a complete transfer of valuable components to the solution – the baked raw materials are subjected to treatment with hydrochloric acid to produce a slurry which is separated (for example, by means of filtration) into a solid phase (“sistoff” (dissoluble residue), comprising mostly silica) and a chloride solution,
where the main target component is aluminum. Separation of aluminum is carried out by introducing gaseous hydrogen chloride into the solution; hydrogen chloride displaces (or salts out) aluminum chloride hexahydrate in the form of crystals subjected to further treatment (neutralization) by aqueous ammonia coming from the baking-chlorination stage, including forming partially dehydrated aluminum hydroxide (boehmite) and an ammonium chloride solution. Boehmite is sent to calcination to produce commercial alumina. The mother liquor – after salting out aluminum chloride hexahydrate – is sent to pyrohydrolysis where hydroxides and oxides of other metals are formed (mainly, hematite) and hydrochloric acid is regenerated both as an aqueous solution and gaseous hydrogen chloride and returned to the stages of acidic treatment and aluminum chloride hexahydrate salting-out.

The ammonium chloride solution is sent to step-wise evaporation (by means of re-using heating steam.)

This method of producing alumina is illustrated with a concrete example:

The weighed quantity (100g) of raw materials containing the following main components, %: \( \text{Al}_2\text{O}_3 \) 31.5; \( \text{SiO}_2 \) 5.7; \( \text{Fe}_2\text{O}_3 \) 35.2; \( \text{TiO}_2 \) 8.5; \( \text{CaO} \) 0.22; \( \text{MgO} \) 0.2; \( \text{Na}_2\text{O} \) 0.25; \( \text{K}_2\text{O} \) 0.15; \( \text{V}_2\text{O}_5 \) 0.1; \( \text{Cr}_2\text{O}_3 \) 0.12; \( \text{SO}_3 \) 0.25; % of other impurities 17.2 was mixed with the weighed quantity (200g) of ammonium chloride. The mixture was placed in a lab tube furnace heated up to 300°C and kept therein for 3 hours. (Exhaust gaseous ammonia was passed through water.) The baked material was being dissolved in 20% hydrochloric acid @ 98°C during 3 hours. The resulting slurry was filtered, and aluminum chloride hexahydrate was crystalized from the clarified solution (by salting-out with gaseous hydrogen chloride.) The filtered crystals were treated with aqueous ammonia. According to XRD results, the solid phase produced was impurity-free boehmite (AlOOH). Boehmite, washed with water, was calcined in the muffle furnace @ 1,200°C to produce alumina. The chemical composition and granulometry of alumina met the requirements for metallurgical alumina (Γ-0).
The solution – after the salting-out of aluminum chloride hexahydrate – was subjected to pyrohydrolysis to separate iron, titanium and other minor impurities (in the form of oxides), and regenerate hydrogen chloride in the form of a hydrochloric acid solution and partially in the form of gaseous hydrogen chloride. The chlorine/ammonia solution, formed after treating the AlCl₃·6H₂O crystals with ammonia, was evaporated to separate the crystals of ammonium chloride which was also considered to be a recycled product.
Claims

1. A method for producing alumina, including baking of aluminum-containing raw materials, processing of said materials with hydrochloric acid to produce a slurry, separating the slurry into a clarified chloride solution and sinter, aluminum chloride salting-out by saturating the clarified chloride solution with gaseous hydrogen chloride, aluminum chloride calcination to produce aluminum oxide, and mother liquor pyrohydrolysis, including returning hydrogen chloride to the stages of acidic treatment and salting-out, characterized in that the aluminum chloride precipitated in the course of salting-out is treated with aqueous ammonia, the resulting precipitate goes to calcination, and the ammonium chloride solution is mixed with said aluminum-containing raw materials before or during baking, ammonia released during baking is dissolved in water, and the resulting aqueous ammonia goes to treat aluminum chloride.

2. The method according to claim 1, wherein ammonium chloride, released during evaporation, is mixed with the aluminum-containing raw materials.