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(71) Applicant: **S.A. LHOIST RECHERCHE ET DEVELOPPEMENT** [BE/BE]; rue Charles Dubois 28, 1342 Ottignies-Louvain-la-Neuve (BE).

(72) Inventors: **DU PLESSIS, Chris**; rue de l'industrie 31, 1400 Nivelles (BE). **LAMBERT, Hugues**; rue de l'industrie 31, 1400 Nivelles (BE). **GÄRTNER, Robert**; rue de l'industrie 31, 1400 Nivelles (BE).

(74) Agent: **GEVERS PATENTS**; Holidaystraat 5, 1831 Diegem (BE).

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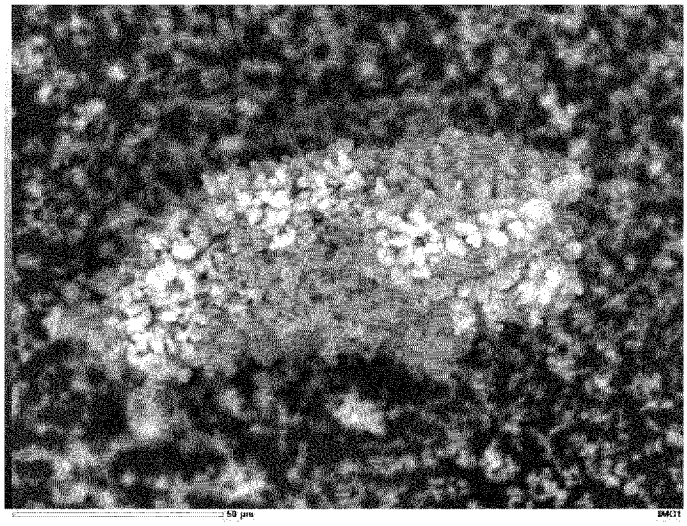


Fig. 1

(57) Abstract: The present invention describes a process for obtaining size-calibrated tri-calcium aluminate (TCA) particles comprising the steps of providing a process liquor containing sodium aluminate; providing a suspension of size-calibrated calcium hydroxide particles; mixing said selected suspension of size-calibrated calcium hydroxide particles with said process liquor to allow them to react to obtain the said size-calibrated tri-calcium aluminate particles.

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Process for obtaining size-calibrated tri-calcium aluminate particles and use of such particles in a process of alumina refining

Technical field

In a first aspect, the present invention is related to a process for obtaining size-calibrated tri-calcium aluminate (TCA) particles comprising the steps of providing a process liquor containing sodium aluminate, then providing a suspension of coarse calcium hydroxide particles and mixing said selected suspension of calcium hydroxide particles with said process liquor to allow them to react to obtain the said tri-calcium aluminate particles. In a second aspect, the present invention is related to the use of such coarse tri calcium aluminate particles in a process of purifying alumina process liquors.

State of the art

Bayer process alumina refineries typically make use of a filtration process step to remove fine suspended particulate impurities prior to the alumina precipitation step, where the so-called "green liquor" or "process liquor" containing mainly sodium aluminate is precipitated as alumina Al_2O_3 product. The filtration step to remove suspended impurities (typically fine Fe and/or Si containing solids), that have not already been removed from solution during clarification, is critical to ensure that such impurities do not contaminate the precipitated Al_2O_3 product. This impurity removal step is typically referred to as "security filtration", "impurity filtration" or "solution polishing" and is conducted in well-known pressure filtration systems (e.g. Kelly leaf filters commonly used in Australia or Diastar filters commonly used in South East Asia). These filtration systems make use of a "filter aid" bed (or cake) of particles supported by a screen, filter cloth or membrane. The filter aid is typically tri-calcium aluminate ($Ca_3[Al(OH)_6]_2$), hereinafter abbreviated as TCA, which is produced by reacting a portion of the process liquor, containing sodium aluminate $NaAl(OH)_4$ with $Ca(OH)_2$, in a molar ratio suited for the plant operation, generally from 0.5:1 to 3:1 but is specific to plant conditions. The $Ca(OH)_2$ reagent is typically added to the reactor as a slaked lime slurry, also called milk of lime, or suspension, with a solids content ranging from 12-25 % w/w. Slaking occurs when quicklime, CaO, is reacted with excess water to form a suspension of $Ca(OH)_2$.

The process feed liquor temperature is typically in the range of 95-105 °C. The slaked lime slurry is preferably at a similar temperature, or as high as practically possible, generally in the range of 70-95 °C. The TCA filter aid generation reaction is typically conducted at 95-98 °C. Although some plants use quicklime, CaO, directly in this process step, the CaO still undergoes hydration to $Ca(OH)_2$, before reacting with sodium aluminate to form TCA:

$$3Ca(OH)_2 + 2NaAl(OH)_4 \rightarrow Ca_3[Al(OH)_6]_2 + 2NaOH$$

It is important to note that it is the TCA filter aid, rather than the filter cloth that performs the filtration duty. The properties of the TCA filter aid are, therefore, critical to filtration performance. If the TCA particles are too fine, the filtration bed voids might be too small, thus slowing down the filtration process and increasing filtration backpressure. Operationally, this requires frequent back-flushing to prevent clogging, therefore causing a plant throughput bottleneck. If the TCA particles are too coarse, the voids between the particles may be too large and the

suspended impurities are not sufficiently removed during the filtration process. The ideal TCA filter aid particle size and distribution is different for each alumina refinery and is dependent upon a number of process and equipment factors, such as: the throughput rate required, the suspended impurity particle load and size, the type of filter, filtration conditions and filter cloth, membrane or screen type used.

The problem for alumina refineries is that optimal TCA filter aid particle size distribution, required to achieve filtration efficiency, cannot be controlled as a process parameter independent of the lime source. For example, US 2004/0101470 A1, paragraph [0024] describes the technical bias that the physical characteristics of the TCA filter aid are very highly dependent upon the nature of the lime particles from which it is formed. Also, Franca et al. "Some aspects of tricalcium aluminate hexahydrate formation on the Bayer process", Light Metals 2010, TMS (The Minerals, Metals & Materials Society) 2010 p.63-66., confirm the common perception that it is primarily the Calcium source that impacts the TCA particle size distribution. Thus, the TCA particle size distribution is operationally experienced as a fixed consequence of the quicklime reagent properties used, as well as a combination of other plant conditions which are known to influence particle size of the TCA..

However, this approach limits the ability to use alternative quicklime reagent sources, even if using such alternatives may have other benefits, such as higher utilization efficiency. Often the quicklime that provides satisfactory TCA particle size distribution is of a low quality and low CaO available content. The use of such quicklime increases the lime consumption due to the low utilization efficiency, not only in for TCA filter aid production but also in other parts of the Bayer process alumina refinery where lime is used.

A common experience in alumina refineries is that higher quality (i.e. higher CaO available %) and highly reactive quicklimes, generally shift the TCA towards a finer particle size distribution, without the reasons for this phenomenon being understood or articulated in scientific or patent literature. Without a suitable control mechanism, alumina refineries are restricted in their use of a lime reagent to that which provides acceptable TCA filter aid properties, even if said lime reagent other properties are sub-optimal. This is particularly problematic for alumina refineries that require coarse TCA filter aid, i.e. with a d50 larger than 20 μm. Depending on the plant installations and/or on the ore compositions, some refineries will require specific particle size distribution of TCA used as a filter aid.

There is thus a need to provide an improved process for obtaining size-calibrated tri-calcium aluminate without resorting to the use of lime reagent possessing low available CaO content. Moreover there is also a need for a process for obtaining size-calibrated tri-calcium aluminate which can be used for manufacturing coarse TCA filter aid.

Summary of the invention

In order to solve the abovementioned problems and drawbacks of the prior art, the present invention is related to a process for obtaining size-calibrated tri-calcium aluminate (TCA) particles comprising the steps of:

a) providing a process liquor containing sodium aluminate;

b) providing a suspension of size-calibrated calcium hydroxide particles

c) mixing said selected suspension of size-calibrated calcium hydroxide particles with said process liquor to allow them to react to obtain the said size-calibrated tri-calcium aluminate particles.

Tri-calcium aluminate ($Ca_3[Al(OH)_6]_2$) is hereinhafter referred to as TCA.

Sodium aluminate is hereinafter used to describe $2NaAl(OH)_4$.

By the term "size-calibrated tri-calcium aluminate particles" is meant according to the invention tri-calcium aluminate particles with an optimal particle size distribution for use as a TCA filter aid in a process of alumina refining. As mentioned above, the optimal TCA particles size is a compromise between too fine and too coarse, to provide an efficient filtration of suspended impurities while minimizing filter clogging, backpressure and throughput issues. The particle size distribution is expressed as the d50 measured by granulometry laser diffraction in methanol after sonication.

The d50 of Size-calibrated tri-calcium aluminate particles may vary according to the requirements of the plant, for example Size-calibrated tri-calcium aluminate particles may have a d50 of larger than 5 µm, preferably larger than 10 µm, more preferably larger than 15 µm, more preferably larger than 20 µm. In another embodiment of the invention the d50 of the size-calibrated tri-calcium aluminate particles may be lower than 200 µm, preferably lower than 100 µm, even more preferably less then 50 µm.

By the term "size-calibrated calcium hydroxide particles" is meant according to the invention calcium hydroxide particles having an optimal particle size distribution being a compromise between too fine and too coarse for obtaining optimal size-calibrated TCA particles.

It has been surprisingly found by the applicant that the particle size distribution of TCA particles obtained by the process according to the invention is linked to the particle size distribution of the calcium hydroxide particles by a generally linear relationship. Thus the long standing technical prejudice that highly reactive quicklimes generally shift the TCA towards a finer particle size distribution has been surprisingly overcome. The slope of the linear relationship is specific to the particular conditions, including: the solution composition, the molar ratio of $Ca(OH)_2$ to $NaAl(OH)_4$, the temperature of both the $Ca(OH)_2$ reagent and the alumina refinery liquor, the tip speed of agitation (i.e. shear force), the hydraulic residence time, the particle residence time, the extent of precipitate seeding and seed recycling. The relationship is also dependent on the quicklime properties used to produce the $Ca(OH)_2$, including its reactivity (as measured by its reaction rate with water) and its chemical composition. For all of these reasons, the precise relationship between particle size distribution of the $Ca(OH)_2$ and the TCA may be determined for each particular plant scenario. The determination of the relationship is based on generating a range of $Ca(OH)_2$ reagents with increasing particle size distributions (meaning the d25, d50 and d90 are increased), and observing the impact of using these reagents on the particle size distribution of the resulting TCA.

Preferably, the said suspension of size-calibrated calcium hydroxide particles is obtained from slaking quicklime, said quicklime having an available lime content greater than 82 %, preferably greater than 85 %, preferably greater than 90 %, more preferably greater than 92 %, more preferably

greater than 95 %, measured according to EN459-2:2010 standard. Quicklimes having an available lime content greater than 90 % are also generally referred as “high quality quicklime”.

According to the invention, it is possible to control the particle size distribution of TCA particles by controlling the particle size distribution of calcium hydroxide particles, i.e. using size-calibrated calcium hydroxide.

Size-calibrated calcium hydroxide can be produced from high quality quicklime having a content of available lime greater than 85% as measured according to EN459-2 standard, and generally presents a high reactivity with water. In turn, the use of such high quality quicklime and milk of lime derived from high quality quicklime is also advantageous for use in other components of the alumina refining process, other than TCA filter aid generation, by reducing lime reagent consumption.

In an embodiment of the invention, said suspension of size-calibrated calcium hydroxide particles is obtained from a process of slaking quicklime in the presence of a coarsening additive causing a coarsening effect on the particle size distribution of the calcium hydroxide particles obtained by said process of slaking.

In an embodiment of the invention, said suspension of size-calibrated calcium hydroxide particles is obtained from a process of slaking formulated quicklime, prepared from quicklime to which a coarsening additive has been added by spraying a solution containing a coarsening additive onto quicklime.

Preferably, said suspension of size-calibrated calcium hydroxide particles is obtained from a process of slaking quicklime in the presence of 2 w% or less, preferably, 0.1 to 1.5 w%, preferably, 0.15 to 0.8 w% and more preferably from 0.2 to 0.65 w% of a coarsening additive relative to the weight of quicklime, wherein said coarsening additive is selected among alkaline sulfates or alkaline earth sulfates.

In a particular embodiment of the invention, the said coarsening additive is sodium sulfate.

In an embodiment of the invention, said suspension of size-calibrated calcium hydroxide particles is obtained from a process wherein

- a concentrated aqueous solution of coarsening additive, in particular sodium sulfate, is provided by dissolving an amount of a coarsening additive of at least 10 w%, preferably at least 30 w% in water at a temperature of dissolution adapted to dissolve such an amount of coarsening additive;
- said concentrated aqueous solution of coarsening additive at the said temperature of dissolution is sprayed onto quicklime with an amount comprised of between 5 dm^3 and 30 dm^3, preferably between 10 dm^3 and 20 dm^3 per dry metric ton of said quicklime to obtain a formulated quicklime;
- slaking said formulated quicklime with water to provide said suspension of size-calibrated calcium hydroxide particles.

Preferably, said suspension of size-calibrated calcium hydroxide particles is obtained from a process of slaking quicklime with an amount of water such that the solid content in the milk of lime

solids content comprises between 10 and 45 % in weight of the total weight of the milk of lime preferably with a solid content in the milk of lime up to 40 %, preferably up to 35 %, more preferably up to 30 %, more preferably up to 25 % in weight of the total weight of the milk of lime.

In an embodiment of the invention, said suspension of size-calibrated calcium hydroxide particles is obtained from a process of slaking partially pre-hydrated quicklime particles having a superficial layer, at least partially superficial, of hydrated lime and a core of quicklime.

In an embodiment of the invention, said suspension of size-calibrated calcium hydroxide particles is obtained from a process of slaking quicklime in a reactor cooled at a temperature lower than or equal to 60 °C. The particles of hydrated lime obtained in such conditions are generally coarser than particles of hydrated lime obtained in conditions of temperatures comprised between 60 °C and 95 °C.

In an embodiment of the invention, said suspension of size-calibrated calcium hydroxide particles is obtained from a process of slaking quicklime in a reactor at a temperature greater or equal to 95 °C. The particles of hydrated lime obtained in such conditions are generally coarser than particles of hydrated lime obtained in conditions of temperatures comprised between 60 °C and 95 °C.

In an embodiment of the invention, said suspension of size-calibrated calcium hydroxide particles is obtained from a process of slaking quicklime to obtain a first suspension of calcium hydroxide followed by a step of particle size selection of said first suspension to remove particles of calcium hydroxide that have a particle size under a predetermined particle size and to retain the calcium hydroxide particles larger than a predetermined particle size for obtaining, possibly after dilution, said suspension of size-calibrated calcium hydroxide particles.

In an embodiment of the invention, said suspension of size-calibrated calcium hydroxide particles is obtained from a process of slaking quicklime to obtain a first suspension of calcium hydroxide followed by:

- a first step of particle size selection of said first suspension to remove particles of calcium hydroxide having a particle size smaller than a first predetermined particle size and to retain calcium hydroxide particles larger than a first predetermined particle size for obtaining, possibly after dilution, a second suspension of calcium hydroxide particles
- a second step of particle size selection of said second suspension of calcium hydroxide particles to remove particles of calcium hydroxide having a particle size larger than a second predetermined particle size greater than the said first predetermined particle size and to retain the remaining calcium hydroxide particles having a particle size comprised between said first predetermined particle size and said second predetermined particle size for obtaining, possibly after dilution said suspension of size-calibrated calcium hydroxide particles.

In an embodiment of the invention, said suspension of size-calibrated calcium hydroxide particles is obtained from a process of slurrying hydrated lime where the hydrated lime was prepared by dry hydration and its particle size was controlled by grinding and sieving to obtain the targeted size.

Preferably, said size-calibrated calcium hydroxide particles have a particle size distribution predetermined for obtaining TCA particles with a desired particle size distribution on basis of a calibration curve obtained by realizing the said steps a) to c) with at least three suspensions of calcium hydroxide of different predetermined particle size distribution.

All the embodiments disclosed herein can be used alone or in a combination thereof.

In a second aspect, the present invention is related to the use of coarse tri-calcium aluminate particles obtained by the process as disclosed herein above in a process of refining alumina from an ore comprising aluminum minerals.

In another aspect, the present invention is related to the use of coarse tri-calcium aluminate particles obtained by the process as disclosed above in a process of manufacturing TCA filter aid.

Brief description of the drawings

The figure 1 presents an image obtained by Scanning Electron Microscopy of the TCA particles obtained according to the process of invention.

Description of the invention

According to a first aspect, the present invention is related to a process for obtaining size-calibrated tri-calcium aluminate (TCA) particles comprising the steps of:

a) providing a process liquor containing sodium aluminate;
b) providing a suspension of size-calibrated calcium hydroxide particles
c) mixing said selected suspension of size-calibrated calcium hydroxide particles with said process liquor to allow them to react to obtain the said size-calibrated tri-calcium aluminate particles.

Preferably, the said suspension of size-calibrated calcium hydroxide is obtained from slaking quicklime, said quicklime having an available lime content greater than 82 %, preferably greater than 85 %, preferably greater than 90 %, more preferably greater than 92 %, more preferably greater than 95 %, measured according to EN459-2:2010 standard. Quicklimes having an available lime content than 90 % is generally also referred as “high quality quicklime”.

A typical alumina refinery process is described in the document “The chemistry of CaO and $Ca(OH)_2$”, B.I. Whittington, Hydrometallurgy 43 (1996) 13-35. An ore containing high amounts of aluminum such as bauxite is crushed and milled. The resulting product is transferred into a first tank for a pre-desilication step wherein the crushed ore is put in contact with milk of lime under agitation at temperatures about 100 °C before being transferred to a digestion tank wherein highly concentrated solution of NaOH and milk of lime is injected. This digestion step occurs under high pressure and high temperature. The resulting mud obtained after digestion is cooled and sent to a sedimentation tank to settle out the solid fraction from the liquid fraction hereby called process liquor. The solid fraction is washed with water, in a series of counter current decantation washers. One of the washer overflow eluents is sent to a tank for causticization wherein milk of lime is added to increase alkalinity by converting sodium carbonate to sodium hydroxide. In a separate process step, a small part of the process liquor is used to be reacted with milk of lime, also referred to as a

suspension of calcium hydroxide particles, to obtain tri-calcium aluminate particles which are used as a filter aid to filter the remaining process liquor. The filtered process liquor is then cooled and settled to precipitate aluminum trihydroxide in a precipitation tank. Finally, the precipitate is calcined after washing to obtain a purified Al_2O_3 Alumina product.

Since the process of refining alumina comprises different steps involving the use of milk of lime, the use of a milk of lime derived from high quality quicklime is advantageous for use in other components of the alumina refining process, other TCA filter aid generation, by reducing lime reagent consumption.

It has been found that it is possible to control the particle size distribution of the tri-calcium aluminate particles by controlling the particle size distribution of the calcium hydroxide particles. According to the invention, there are various ways to control the particle size distribution of the calcium hydroxide particles to be used for generating size-calibrated particles of tri-calcium aluminate.

In an embodiment of the invention, quicklime can be slaked in the presence of a coarsening additive causing a coarsening effect on the particle size distribution of the calcium hydroxide particles obtained by said process of slaking.

Preferably, the said coarsening additive is selected among alkaline sulfate such as sodium sulfate as a non-limitative example or alkaline earth sulfates such as calcium sulfate as a non-limitative example.

The coarsening additive can be added to quicklime before the step of slaking for example by spaying the said coarsening additive onto quicklime and then the step of slaking is performed with sufficient amount of water to obtain a suspension of calcium hydroxide particles. Alternatively or in combination with the step of spraying, the coarsening additive can be added during the step of slaking, for example in the slaking water.

Preferably, the step of slaking quicklime is realized in presence of less than 2 w%, preferably 0.1 to 1.5 w%, preferably, 0.15 to 0.8 w% and more preferably from 0.2 to 0.65 w% of a coarsening additive relative to the weight of quicklime. A minimum amount of coarsening additive is required to provide the coarsening effect on calcium hydroxide particles and a maximum amount of coarsening additive is set up to keep the suspension of calcium hydroxide particles over a certain degree of purity and to prevent the formation of too coarse calcium hydroxide particles.

In an embodiment of the invention, a suspension of size-calibrated calcium hydroxide particles is obtained from a process wherein:

- a concentrated aqueous solution of sodium sulfate is provided by dissolving an amount of sodium sulfate of at least 10 w%, preferably at least 35 w% in water at a temperature of dissolution adapted to dissolve such an amount;
- said concentrated solution of sodium sulfate at the said temperature of dissolution is sprayed onto quicklime with an amount comprised of between 5 dm^3 and 30 dm^3, preferably between 10 dm^3 and 20 dm^3 of said concentrated solution per ton of said quicklime to obtain a formulated quicklime;

- said formulated quicklime is slaked with water to provide said suspension of size-calibrated calcium hydroxide particles.

Preferably, in the step of slaking quicklime, the amount of water is adapted to provide a suspension of calcium hydroxide (or milk of lime) wherein the solid content in the milk of lime is comprised between 10 and 45 % in weight of the total weight of the milk of lime, preferably with a solid content in the milk of lime up to 40 %, preferably up to 35 %, more preferably up to 30 %, more preferably up to 25 % in weight of the total weight of the milk of lime. A minimum amount of solid content is required to provide sufficient amount of calcium hydroxide in a minimum volume of suspension and a maximum amount of solid content is preferably set up to minimize the volume of the suspension while keeping a good flowability and pumpability of the suspension.

In an embodiment of the invention, said suspension of size-calibrated calcium hydroxide particles is obtained from a process of slaking partially pre-hydrated quicklime particles having a superficial layer, at least partially superficial, of hydrated lime and a core of quicklime.

In an embodiment of the invention, said suspension of size-calibrated calcium hydroxide particles is obtained from a process of slaking quicklime in a reactor cooled at a temperature lower than or equal to 60 °C. The particles of hydrated lime obtained in such conditions are generally coarser than particles of hydrated lime obtained in conditions of temperatures comprised between 60 °C and 95 °C.

In an embodiment of the invention, said suspension of size-calibrated calcium hydroxide particles is obtained from a process of slaking quicklime in a reactor at a temperature greater or equal to 95 °C. The particles of hydrated lime obtained in such conditions are generally coarser than particles of hydrated lime obtained in conditions of temperatures comprised between 60 °C and 95 °C.

In an embodiment of the invention, said suspension of size-calibrated calcium hydroxide particles is obtained from a process of slaking quicklime to obtain a first suspension of calcium hydroxide followed by a step of particle size selection of said first suspension to remove particles of calcium hydroxide that have a particle size under a predetermined particle size and to retain the calcium hydroxide particles larger than a predetermined particle size for obtaining, possibly after dilution, said suspension of size-calibrated calcium hydroxide particles. This step of particle size selection can be done for example by cutting the said first suspension with a sieve selected from the commercially available sieves having sieve openings inferior to 125 µm (120 mesh), preferably inferior to 105 µm (140 mesh), more preferably inferior to 88 µm (170 mesh), more preferably inferior to 74 µm (200 mesh), more preferably inferior to 63 µm (230 mesh).

In an embodiment of the invention, said suspension of size-calibrated calcium hydroxide particles is obtained from a process of slaking quicklime to obtain a first suspension of calcium hydroxide followed by:

- a first step of particle size selection of said first suspension to remove particles of calcium hydroxide having a particle size smaller than a first predetermined particle size and to

retain calcium hydroxide particles larger than a first predetermined particle size for obtaining, possibly after dilution, a second suspension of calcium hydroxide particles

- a second step of particle size selection of said second suspension of calcium hydroxide particles to remove particles of calcium hydroxide having a particle size larger than a second predetermined particle size greater than the said first predetermined particle size and to retain the remaining calcium hydroxide particles having a particle size comprised between said first predetermined particle size and said second predetermined particle size for obtaining, possibly after dilution said suspension of size-calibrated calcium hydroxide particles.

The first step of particle size selection can be done for example by cutting the said first suspension with a sieve selected from the commercially available sieves having sieve openings inferior to 125 µm (120 mesh), preferably inferior to 105 µm (140 mesh), more preferably inferior to 88 µm (170 mesh), more preferably inferior to 74 µm (200 mesh), more preferably inferior to 63 µm (230 mesh). Then the second step of particle selection can be done by cutting the said second suspension with a sieve selected from the commercially available sieves having sieve openings greater than the ones of the sieve utilized in the first step of particle selection, such as sieves having openings greater than 105 µm (140 mesh), preferably greater than 125 µm (120 mesh), more preferably greater than 149 µm (100 mesh), more preferably greater than 177 µm (80 mesh).

Preferably, in the process for obtaining size-calibrated tri-calcium aluminate, the said size-calibrated calcium hydroxide particles have a particle size distribution predetermined for obtaining TCA particles with a desired particle size distribution on the basis of a calibration curve obtained by realizing the said steps a) to c) with at least three suspensions of calcium hydroxide of different predetermined particle size distribution.

In an embodiment of the invention, calcination of limestone into quicklime, can also be realized by using fuels (such as high sulfur content coal, or petroleum coke, also called petcoke) that would impart a high sulfur content (typically in the form of a sulfate or other oxidized form of sulfur) onto the quicklime product. It can be advantageous to measure the sulfur content in the quicklime and to adapt the amount of coarsening additive to be added for the step of slaking as a function of the amount of sulfur in the quicklime, such as to avoid formation of too coarse calcium hydroxide particles. It is possible to establish according to the invention a relationship between the additive concentration, the $Ca(OH)_2$ particle size and TCA particle size and that this relationship is normally different for a quicklime with a low sulfur content and a quicklime with a higher sulfur content.

Advantageously, in a process of refining alumina, size-calibrated particles of calcium hydroxide, preferably obtained from quicklime having an available lime content of more than 82 %, or even higher, can be used in different stages of the process including the step of formation of tri-calcium aluminate. Therefore, the method of manufacturing TCA particles provides not only a control method for the particle size distribution of TCA particles but also provides the possibility of using a high quality quicklime, with a CaO available content equal or greater than 82 %, to generate high quality milk of lime, thereby increasing the utilization efficiency of this reagent in all process units of the alumina refining process where it is used.

Examples

The effect of different types of milk of lime on the formation of tri-calcium aluminate has been evaluated by reacting those milks of lime with a synthetic Bayer process liquor.

Synthetic Bayer liquor can be prepared in an autoclave by heating at 180°C under stirring an aqueous mixture containing 6 mol/dm³ of NaOH, 2.2 mol/dm³ of $Al(OH)_3$, and 0.4 mol/dm³ of Na_2CO_3.

Three samples of formulated quicklime are prepared by mixing quicklime having the properties listed in table 1 with respectively 0.3 w%, 0.5 w% and 0.7 w% of Na_2SO_4 in weight of said quicklime.

Table 1

CaO Total	> 94 w%
MgO	< 2 w%
SiO2	< 0.5 w%
S	< 0.04 w%
CO2	< 1.9 w%
C	< 0.5 w%
P	< 0.03 w%
quicklime size	10-60 mm
Time of reactivity T60	< 2 min

The three said samples of formulated quicklime were crushed to <5 mm and then slaked in water at room temperature in a slaker for 20 minutes with an amount of water to obtain about 16 w% of solid content in the milk of lime.

The particle size distribution d_{50} for those three milks of lime obtained are measured by granulometry laser diffraction in methanol after sonication. The d_{50} of the calcium hydroxide particles of the three milks of lime obtained increases substantially linearly with the amount of Na_2SO_4 in the formulated quicklime. The measured d_{50} of calcium hydroxide particles are provided in table 2.

Three samples of tri-calcium aluminate are prepared from 200 ml of the synthetic Bayer process liquor as prepared above and from an appropriate amount of one of the three samples of milk of lime as prepared above such that the molar ratio of calcium to aluminum expressed in equivalent CaO to Al_2O_3 is of 1 to 9. For each sample, 200 cm³ of synthetic Bayer process liquor is heated to 80°C in a vessel preferably made of a high-strength, corrosion-resistant nickel chromium material, also known commercially as INCONEL®. Then the appropriated amount of the respective milk of lime is added in the vessel under agitation with a stirrer at 250 RPM. When the slurry reaches 95 °C, the slurry is allowed to react for 90 minutes at the same stirring rate. The slurry is then cooled to 70 °C for filtration.

The figure 1 presents an image obtained by Scanning Electron Microscopy of the TCA particles obtained according to the process of invention. It can be seen that the TCA particles are formed of aggregated crystals of dimensions below 5 µm, and that those TCA particles are larger than 15 µm, as often required for effective operation of pressure static vertical leaf filters.

The d_{50} of each of the tri-calcium aluminate samples are measured by granulometry laser diffraction in methanol without sonication. The d_{50} of the tri-calcium aluminate particles increases substantially linearly with the d_{50} of the calcium hydroxide particles of the milk of lime utilized. The values of d_{50} for the tri-calcium aluminate particles and the respective values of d_{50} of the calcium hydroxide particles utilized for the preparation of those TCA particles are presented in table 2. The amount of milk of lime utilized in the process of preparation of TCA particles is further included in table 2.

Table 2

Na_2SO_4 additive concentration (% w/w) relative to quicklime dry mass	d_{50} of the $Ca(OH)_2$ particles of the milk of lime (µm)	Amount of Milk of lime (16w% solid content) utilized for the preparation of TCA (g)	d_{50} of the TCA (µm)
0,3	92	15.7	19
0,5	110	16.6	24
0,7	144	16.7	28

This example shows that by the process according to the present invention, it is possible to control the particle size distribution of the tri-calcium aluminate particles by adding a coarsening agent and then using calcium hydroxide particles of calibrated particle size distribution to obtain size-calibrated TCA

In the quicklime utilized for the examples mentioned herein above, the content of sulfur was relatively low (smaller than to 0.04 % in weight of the quicklime).

Claims

1. Process for obtaining size-calibrated tri-calcium aluminate (TCA) particles comprising the steps of:
   a) providing a process liquor containing sodium aluminate;
   b) providing a suspension of size-calibrated calcium hydroxide particles
   c) mixing said selected suspension of size-calibrated calcium hydroxide particles with said process liquor to allow them to react to obtain the said size-calibrated tri-calcium aluminate particles.

2. Process according to claim 1 wherein said suspension of size-calibrated calcium hydroxide particles is obtainable from slaking quicklime having an available CaO lime content greater than 82,5 %, measured according to EN459-2:2010 standard.

3. Process according to any one of the preceding claims wherein said suspension of size-calibrated calcium hydroxide particles is obtained from a process of slaking quicklime in the presence of a coarsening additive causing a coarsening effect on the particle size distribution of the calcium hydroxide particles obtainable by said process of slaking.

4. Process according to claim 3 wherein said suspension of size-calibrated calcium hydroxide particles is obtained from a process of slaking formulated quicklime, prepared from quicklime to which a coarsening additive has been added by spraying a solution containing a coarsening additive onto quicklime.

5. Process according to claim 3 wherein said suspension of size-calibrated calcium hydroxide particles is obtained from a process of slaking quicklime in the presence of 0.1 to 1.5 w%, of a coarsening additive relative to the weight of quicklime, wherein said coarsening additive is selected among alkaline sulfates or alkaline earth sulfates.

6. Process according to claim 3 wherein said suspension of size-calibrated calcium hydroxide particles is obtained from a process wherein
   - a concentrated aqueous solution of coarsening additive, preferably sodium sulfate is provided by dissolving an amount of coarsening additive of at least 10 w%, in water at a temperature of dissolution adapted to dissolve such an amount of coarsening additive;
   - said concentrated aqueous solution of coarsening additive at the said temperature of dissolution is sprayed onto quicklime with an amount comprised of between 5 dm^3 and 30 dm^3 of said concentrated solution per ton of said quicklime to obtain a formulated quicklime;
   - said formulated quicklime is slaked with water to provide said suspension of size-calibrated calcium hydroxide particles.

7. Process according to any one of the preceding claims wherein said suspension of size-calibrated calcium hydroxide particles is obtained from a process of slaking quicklime with an amount of water such that the solid content in the milk of lime is comprised between 10 and

45 %, in weight of the total weight of the milk of lime, in weight of the total weight of the milk of lime.

8. Process according to any one of the preceding claims wherein said suspension of size-calibrated calcium hydroxide particles is obtained from a process of slaking partially pre-hydrated quicklime particles having a superficial layer, at least partially superficial, of hydrated lime and a core of quicklime.

9. Process according to any one of the preceding claims wherein said suspension of size-calibrated calcium hydroxide particles is obtained from a process of slaking quicklime in a reactor cooled at a temperature lower than or equal to 60 °C.

10. Process according to any one of the claims 1 to 8 wherein said suspension of size-calibrated calcium hydroxide particles is obtained from a process of slaking quicklime in a reactor at a temperature greater or equal to 95 °C.

11. Process according to any one of the preceding claims wherein said suspension of size-calibrated calcium hydroxide particles is obtained from a process of slaking quicklime to obtain a first suspension of calcium hydroxide followed by a step of particle size selection of said first suspension to remove particles of calcium hydroxide that have a particle size under a predetermined particle size and to retain the calcium hydroxide particles larger than a predetermined particle size for obtaining, possibly after dilution, said suspension of size-calibrated calcium hydroxide particles.

12. Process according to any one of the preceding claims wherein said suspension of size-calibrated calcium hydroxide particles is obtained from a process of slaking quicklime to obtain a first suspension of calcium hydroxide followed by:
    - a first step of particle size selection of said first suspension to remove particles of calcium hydroxide having a particle size smaller than a first predetermined particle size and to retain calcium hydroxide particles larger than a first predetermined particle size for obtaining, possibly after dilution, a second suspension of calcium hydroxide particles
    - a second step of particle size selection of said second suspension of calcium hydroxide particles to remove particles of calcium hydroxide having a particle size larger than a second predetermined particle size greater than the said first predetermined particle size and to retain the remaining calcium hydroxide particles having a particle size comprised between said first predetermined particle size and said second predetermined particle size for obtaining, possibly after dilution said suspension of size-calibrated calcium hydroxide particles.

13. Process according to any one of the preceding claims wherein said size-calibrated calcium hydroxide particles have a particle size distribution predetermined for obtaining TCA particles with a desired particle size distribution on basis of a calibration curve obtained by realizing the said steps a) to c) with at least three suspensions of calcium hydroxide of different predetermined particle size distribution.

14. Use of coarse tri-calcium aluminate particles obtained by the process according to any one of the claims 1 to 13 in a process of purifying alumina process liquors from an ore comprising aluminum minerals.

15. Use of coarse tri-calcium aluminate particles obtained by the process according to any one of the claims 1 to 13 in a process of manufacturing TCA filter aid.

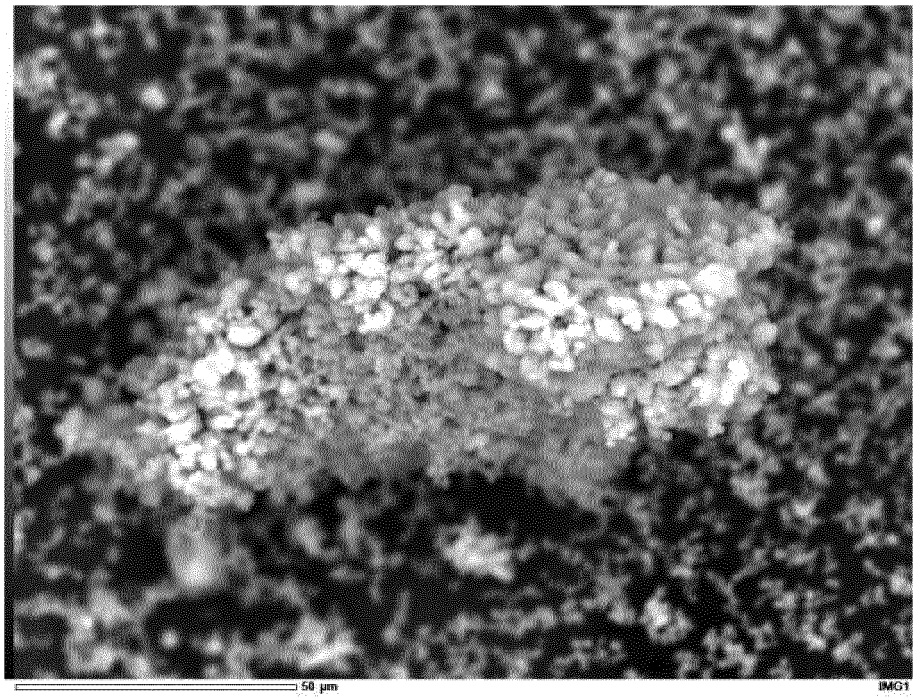


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/068757

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01F7/16 C01F11/02 C04B2/06
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01F C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 02/11856 A1 (WORSLEY ALUMINA PTY LTD [AU]; ROSENBERG STEPHEN PHILIP [AU]; WILSON DA) 14 February 2002 (2002-02-14)	14,15
A	page 2, line 21 - line 24 claims; figure 1 page 6, line 11 - line 29	1-13

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search	Date of mailing of the international search report
3 September 2019	27/09/2019

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Marucci, Alessandra

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/068757

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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