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(54) Title: METHOD FOR PURIFICATION OF CALSIUM NITRATE AND PRODUCTS MADE THEREOF

(57) Abstract: The present invention relates to a method to produce purified calcium nitrate. Due to introduction of a centrifugation stage at an early stage in the process, sedimentation of water insoluble particles is prevented on a later stage of the process such that flotation can effectively be performed. Sand filtration finalizes the purification process of the present invention and thereby the amount of impurities in the liquor is surprisingly decreased. By this continuous method it is possible to achieve clearly purified calcium nitrate wherein the content of water insoluble particles is well below 150 ppm in solid calcium nitrate.



WO 2008/118024 A2

Method for purification of calcium nitrate and products made thereof

5 The present invention relates to a process for purification of calcium nitrate made from phosphate, and a purified calcium nitrate made by the process of the present invention.

Background

10 Calcium nitrate may be made by dissolving rock phosphate in nitric acid and then precipitate calcium nitrate tetra hydrate by cooling of the digestion liquor. The precipitated calcium nitrate (CN) is separated from the digestion liquor and neutralized before particulation.

15 Raw phosphate minerals e.g. apatite contain high concentrations of OH^- , F^- , or Cl^- ions in the crystal. Thus calcium nitrate crystals made from apatite usually contains impurities in the form of fluorine, phosphorous compounds. There may also be other impurities involved such as iron, aluminium etc. These impurities must be removed to obtain a calcium nitrate product suitable for technical applications i.e. as coagulant for latex, setting accelerator in concrete, for prevention of oil reservoir souring etc.

Prior art

20 Separation of solid impurities in a calcium nitrate melt/solution by settling is described in Russian patent RU2228906. Other purification methods include precipitation of fluorine and phosphorous contaminants as apatite and CaF_2 in the neutralisation step by adjusting P/F ratio and neutralising to pH 5-6, and separating the obtained precipitates in decanter centrifuges (U.S. patent 4.952.379). However, these methods do not obtain a complete separation of insoluble particles without
25 using excessive amounts of water to increase the density difference between the solid particles/precipitates and the salt solution, and/or by increasing the settling time to impractical lengths for a continuous production process.

30 U.S. patent 5 009 792 describes a flotation process for purification of aqueous salt solutions, but relies on the addition of foam forming organic components like waxes, oils and surfactants. This may be efficient i.e. for purification of a dissolved calcium nitrate product containing oil/wax coatings. However, for technical products organic components are unwanted and their use should be limited to a minimum to avoid contamination in the particulated finished product.

35 Purification by filter press or other types of filter equipment is also a known method for purification of salt solution to high levels of purity. However, for use in the purification of calcium nitrate from apatite, filters will require the use of a filter aid (i.e. diatomite) to maintain an acceptable flux through the filter cake. The amount of

filter aid limits the use of this equipment to smaller production volumes, as the filter cake must be disposed of in an environmentally sound way, and thus induces a high cost. Most filters are also operated batch-wise, which is a disadvantage in an otherwise continuous process.

- 5 Also, none of the prior art purification methods (except some filter systems) obtain a “super pure” quality; the typical content of water insoluble particles is from 400-1000 ppm.

Objective of the invention

- 10 The main objective of the present invention is to provide a method for a continuous and effective process for purification of calcium nitrate melts made by digesting raw phosphate.

A further objective is to obtain a process which obtains a reduction of the water insoluble content in the calcium nitrate melt to well below 100 ppm.

- 15 Another objective is to provide a production method which overcomes the disadvantages mentioned above.

The objectives of the invention may be obtained by the features as set forth in the following description of the invention and/or in the appended patent claims.

List of abbreviations

- CN calcium nitrate
- 20 w.i. water-insoluble

Description of the invention

- In the method used today raw phosphate is typically digested in acid in a digestion vessel, and then the digestion liquor is cooled to precipitate calcium nitrate tetrahydrate in a crystallizer unit. The formed calcium nitrate crystals are separated from the remaining liquor by filtration, washed with nitric acid and/or water, dissolved in water and neutralized by ammonia. During this neutralization process a lot of insoluble compounds are formed, like calcium fluoride, apatite, (calcium phosphates, calcium hydroxides, iron-phosphates etc.). In addition, the neutralized solution will contain insoluble materials originating from the raw phosphate, like silica and silicates. In order to purify the neutralized CN solution, water is added to reach a certain density and a flocculation agent is mixed into the CN solution. The impurities are substantially settled, but may be removed by centrifugation. The centrifugate is evaporated to correct water content and particulated (granulated or prilled). By this method a solid CN product having typically 1200 ppm insoluble material is obtained. If the solid CN product is dissolved in water a milky solution results due to these insolubles.
- 25
- 30
- 35

In order to achieve an increased purity of calcium nitrate, it was believed that an additional centrifugation after the phosphate digestion stage would reduce the amount of impurities. Trials carried out showed that the impurities were only reduced to some extent.

5 The invention is based on the surprising discovery that by placing at least one centrifuge after the digester and before the crystallizer, it becomes possible to obtain a substantially better purification by substituting the previous centrifugation unit by a flotation unit. The second purification step may be enhanced by adding a sand filtration step after flotation. By centrifugation just after digestion sludge
10 containing insoluble material from digestion unit is removed at an early stage, and it was surprising that this removal made the remaining insoluble particles float to the surface by adding flocculation agent to the neutralized CN solution. Without being bound by the theory it is believed that by removing the heavy particles, the separation in the flotation step is improved surprisingly since the flotation is less
15 disturbed.

Therefore, one aspect of the present invention relates to the method for production of purified calcium nitrate, wherein the method comprises:

- digesting a raw phosphate in nitric acid,
- centrifuging the digestion liquid to at least partly separate out solid remains,
- 20 - cooling and crystallizing the centrifuged liquid to form calcium nitrate crystals,
- filtering the crystallized solution to obtain a crystal phase,
- washing with nitric acid and/or water,
- dissolving the filtered calcium nitrate crystals in water,
- neutralizing the calcium nitrate solution by adding ammonia to an intended pH-
25 value,
- adding flocculant and floating the neutralized calcium nitrate solution,
- concentrating the purified calcium nitrate solution, and
- particulate the concentrated solution to form solid calcium nitrate particles.

30 In another aspect of the invention, there might be added a filtration step after the flotation step, for instance filtration in a sand filter.

Another aspect of the present invention relates to a purified calcium nitrate made from the method according to the present invention.

The process of the present invention is a continuous and effective process. By application of the invented sequence of process stages, it is possible to obtain
35 calcium nitrate with highly increased purity compared to the process in use today. The content of water insoluble particles will be well below 150 ppm.

The purified calcium nitrate gives a water clear solution when dissolved in water by a user.

The process and the product are environmentally friendly since the use of organic components are avoided. The process is run with a high salt concentration, which is highly advantageous as the water must be evaporated from the solution before particulation.

5 **List of figures**

Fig. 1 is a diagram of an embodiment of the method according to the invention

Fig. 2 is a diagram of an comparison example

Fig. 3 is a diagram of a second comparison example

Verification of the invention

10 The invention will now be described in greater detail by way of examples of possible embodiments of the invention. These embodiments should not be considered as a limitation of the general inventive idea of employing a centrifuge after digestion and substituting the conventional centrifuge with a flotation unit. This general inventive concept is valid for all presently known and foreseeable
15 nitrate melts.

Example of an embodiment of the method according to the invention

Apatite is in stage 1 digested in an excess in nitric acid. This step is conventional technology well known to a skilled person. Any known reactor and procedure for digesting a raw phosphate may be employed in this step, which is schematically
20 represented by box 1 in Figure 1.

After digestion, the digested liquid is centrifuged in a decanter centrifuge. This is step 2 in Figure 1. Before the centrifuge the digested liquid is cooled down to a temperature of 40 °C. The amount of digested liquid through the centrifuge is typical 20-45 m³, and the amount of sludge before the centrifuge is 3 % and after it
25 is 0,5 %. The speed on the centrifuge is 440 G-force.

The centrifuge removes a substantial amount of sludge from the digestion liquid, typical figures are up to 300 kg per m³ liquid of sand/gravel, and silicates, fluorides etc.

After centrifugation, the digestion liquid is cooled to a temperature in the range of
30 0 – 5 °C in order to crystallise calcium nitrate crystals (stage 3 in Fig. 1). The formed crystals are collected and phase separated from the liquid by filtration (stage 4). The collected calcium nitrate crystals are then washed in nitric acid and water (stage 5), and then dissolved in water to form a calcium nitrate solution (stage 6). Thereafter the CN-solution is neutralized with ammonia to a pH of 5.5 – 8 (stage 7).
35 Steps 3 to 7 are conventional technology and well known to a skilled person in the art.

After neutralization, one or more flocculants is/are added to the nitrate solution (stage 8), typically 20-30 ppm in a flocculant solution (flocculant dissolved in water).

5 Flocculant may be prepared in a flocculator. The flocculator is a tank with an effective volume of 0.87 m³, equipped with an agitator. The speed of the agitator can be varied and with that the mixing energy. In most of the tests 50 Hz was applied, which corresponds to a agitation speed of 37 rpm. Also tests with 25 and 75 Hz were done, which showed that they had no positive impact on the purification.

10 Suitable flocculants are anionic flocculants, especially high molecular weight flocculants. The flocculant may be mixed in a flocculation tank before the flotation unit. The mixing energy and the residence time are important; the mixing must be strong enough to distribute the flocculant evenly, but not too strong, as this will break the flocs. A velocity gradient (G-value) in the tank of 100 – 150 was found suitable. The residence time should not be too long, as the high temperatures may
15 decompose the polymer chains in the flocculant, preferably residence times of 8 - 12 minutes are found to be suitable. Thereafter the flocculated CN melt can be fed by gravity flow to the flotation unit of stage 9, as shear forces must be minimized to maintain the “flocs” created in the flocculation tank

20 A second dosing of flocculant M can be added just in front of the flotation unit to further strengthen the flocculants. Dosing the total quantity of flocculant solution in the feed to the flocculator only, or in the feed to the flotation unit only, deteriorated the purification.

25 Thereafter the solution is floated in stage 9. At the surface of the flotation unit, the sludge layer is removed continuously e.g. by use of rotating paddles. The sludge scraper speed had to be adjusted according to the amount of w.i. particles in the feed. Too high speed can give carry-over of flocs in the product stream as the scraper blades created turbulence beneath the sludge layer. Too low speed gave too thick sludge layer, and also carry-over of flocs.

30 In stage 9 at the entrance point to the flotation unit, dispersion liquid N can be added, from 5 – 10 vol % dispersion liquid was added, depending on the concentration of the CN melt. The dispersion liquid can be prepared in a pressurized vessel, be fed with cold water and air at 6.0 bar, preferably with either cold water saturated with air at 5 -6.5 bar, or recycled purified CN melt saturated with air at the same pressure. As the dispersion liquid is mixed with the CN melt,
35 pressure is reduced towards atmospheric pressure, and the air is released as finely dispersed bubbles in the CN melt. Air bubbles rise to the top of the flotation unit, entraining the flocs containing the w.i. particles. The level of w.i. particles was 100 - 150 ppm at the outlet of the flotation unit. The best results were with low concentration of CN melt (56 - 58 %), about 25 ppm of flocculant added at two

steps and 8 – 10 % dispersion liquid, such that 50 – 100 ppm of w.i. particles were achieved in the pure CN solution.

There is investigated as well an optional sand filtration unit as stage 10. In stage 10, the pure CN melt is optionally fed to sand filtration, preferably through an inner
5 decanter for polishing. A pilot scale sand filter was connected to a pilot scale flotation unit. Receiving purified CN melt as a feed, with w.i. content varying from 150 – 300 ppm. At a surface load of 2 – 7 m/h, the polished CN melt exiting the sand filter contained less than 50 ppm w.i. particles. The sand filter worked continuously as long as the total w.i. load was kept below 1500 g/m²h. About 10 %
10 of the CN feed melt was used as a washing-liquid for regeneration of the sand. The washing-liquid then contained about 0.1 % w.i. particles.

Preferably, the sand filters contain sand with a particle size of 1.2 – 2.0 mm. Through filtration, most of the remaining w.i. particles are filtered off. The sand filter is continuously regenerated by washing the sand with small amount of the CN
15 melt. This washing-liquid should preferably be recycled to the flotation unit.

When the process of the present invention may achieve in the resulting pure CN solution an amount of 60-70 ppm insolubles which will result in a solid CN with less than 100 ppm insolubles.

“Flocs” are defined as aggregated or coagulated particles which may be created by
20 use of flocculants.

The product stream which is purified by the stage 1 to 10 of the process of the present invention is ready for further processing as evaporation and particulation.

Comparison Example 2

With reference to fig. 2, Apatite was digested in excess nitric acid (stage 1). The
25 digested solution was cooled to 0 - 5 °C and calcium nitrate tetra hydrate crystals were precipitated (stage 3).

The CN crystals were separated by filtration (stage 4), washed (stage 5) and dissolved and diluted by water to a density of 1.49 kg/m³ at 50 °C (stage 6). The diluted CN solution was neutralized by ammonia to pH 6.5 (stage 7) and a
30 flocculant was added (stage 8) to form a CN solution A.

Part of solution A was transferred to a glass beaker and saturated with air (fine air bubbles from a glass sinter) (stage 11).

35 The air saturated solution was then allowed to rest. The flocculated particles were slowly settling to the bottom of the beaker. Almost no particles moved to the surface.

Part of the solution was centrifuged in a decanter centrifuge for removal of the insoluble and/or flocculated particles (stage 12). The centrifugate was analyzed for content of water insoluble. The centrifugate (filtrate) was found to contain 770-850 ppm insoluble particles. Visually the centrifugate was milky.

5

Comparison example 3

With reference to fig. 3, Apatite was digested in excess nitric acid (stage 1). The digested solution was transferred to a decanter centrifuge with the same velocity as in example 2 which removed most of non soluble particles (stage 2). The centrifugate was then cooled to 0 - 5 °C and calcium nitrate tetrahydrate crystals were formed (stage 3).

10

15

The CN crystals were removed by filtration (stage 4), washed (stage 5) and diluted to density 1.53 kg/m³ at 50 °C (stage 6).

The diluted CN solution was neutralized by ammonia (stage 7) and a flocculant was added (stage 8) to form a CN solution B.

20

Part of solution B was transferred to a glass beaker and saturated with air (stage 11). After 10 minutes of resting almost all the coagulated particles had moved to the surface of the solution. This was opposite to example 2, where most of the particles settled.

25

Part of solution B was transferred to a decanter centrifuge for removal of insolubles. The centrifugate was analyzed and found to contain 560 ppm insolubles. The solution is still milky but less than in example 2.

30

Evaporation and particulation of this liquid resulted in solid CN with roughly 800 ppm insoluble material.

Example 3 shows that the sole addition of a centrifugation stage to the process of prior art, did not give the degree of purification which is aimed at by the present invention.

CLAIMS

1. Method for production of purified calcium nitrate from a calcium nitrate melt comprising digesting apatite in acid (1), cooling and crystallizing the digested calcium nitrate liquor (3), filtrating calcium nitrate crystals (4),
5 washing the filtrate with nitric acid and/or water (5), dissolving with water (6), neutralizing with ammonia (7) and adding flocculant (8),
c h a r a c t e r i z e d in that it also comprises centrifugation of the digestion liquor (2) before crystallization and flotation (9).
2. Method according to claim 1,
10 c h a r a c t e r i z e d in that it comprises sand filtration (10) after addition of the flocculant.
3. Method according to claim 1 or 2,
c h a r a c t e r i z e d in that it is a continuous method.
4. Method according to any of the preceding claims,
15 c h a r a c t e r i z e d in that centrifugation (2) is done with a decanter centrifuge.
5. Method according to any of the preceding claims,
c h a r a c t e r i z e d in that the flocculant is an anionic flocculant.
6. Method according to any of the preceding claims,
20 c h a r a c t e r i z e d in that addition of the flocculant (8) is done in an flocculation tank.
7. Method according to claim 6,
c h a r a c t e r i z e d in that the velocity gradient in the flocculation tank is 100 - 150 and the residence time is from 8 to 12 minutes.
- 25 8. Method according to claims 6 or 7,
c h a r a c t e r i z e d in that the flocculant is added in 2 portions, before and after the flocculation tank.
9. Method according to any of the preceding claims,
c h a r a c t e r i z e d in that flotation (9) comprises as dispersion liquid.
- 30 10. Method according to claim 9,
c h a r a c t e r i z e d in that the dispersion liquid is cold water saturated with air at 5 - 6.5 bar.
11. Method according to claim 9,
35 c h a r a c t e r i z e d in that the dispersion liquid is recycled purified CN melt saturated with air at 5 - 6.5 bar.

12. Method according to any of claim 2 to 11,
c h a r a c t e r i z e d in that the sand used for sand filtration (10) has a
particle size of 1.2 to 2.0 mm.
- 5 13. Purified calcium nitrate,
c h a r a c t e r i z e d in that it is produced by a continuous method and has
a content of water insoluble particles < 150 ppm, preferably < 100 ppm, most
preferably < 50 ppm.
- 10 14. Purified calcium nitrate,
c h a r a c t e r i z e d in that it is produced by the method according to any
of the claims 1 to 12.
15. Product according to claim 14,
c h a r a c t e r i z e d in that the content of water insoluble particles is <
150 ppm, preferably < 100 ppm, most preferably < 50 ppm.

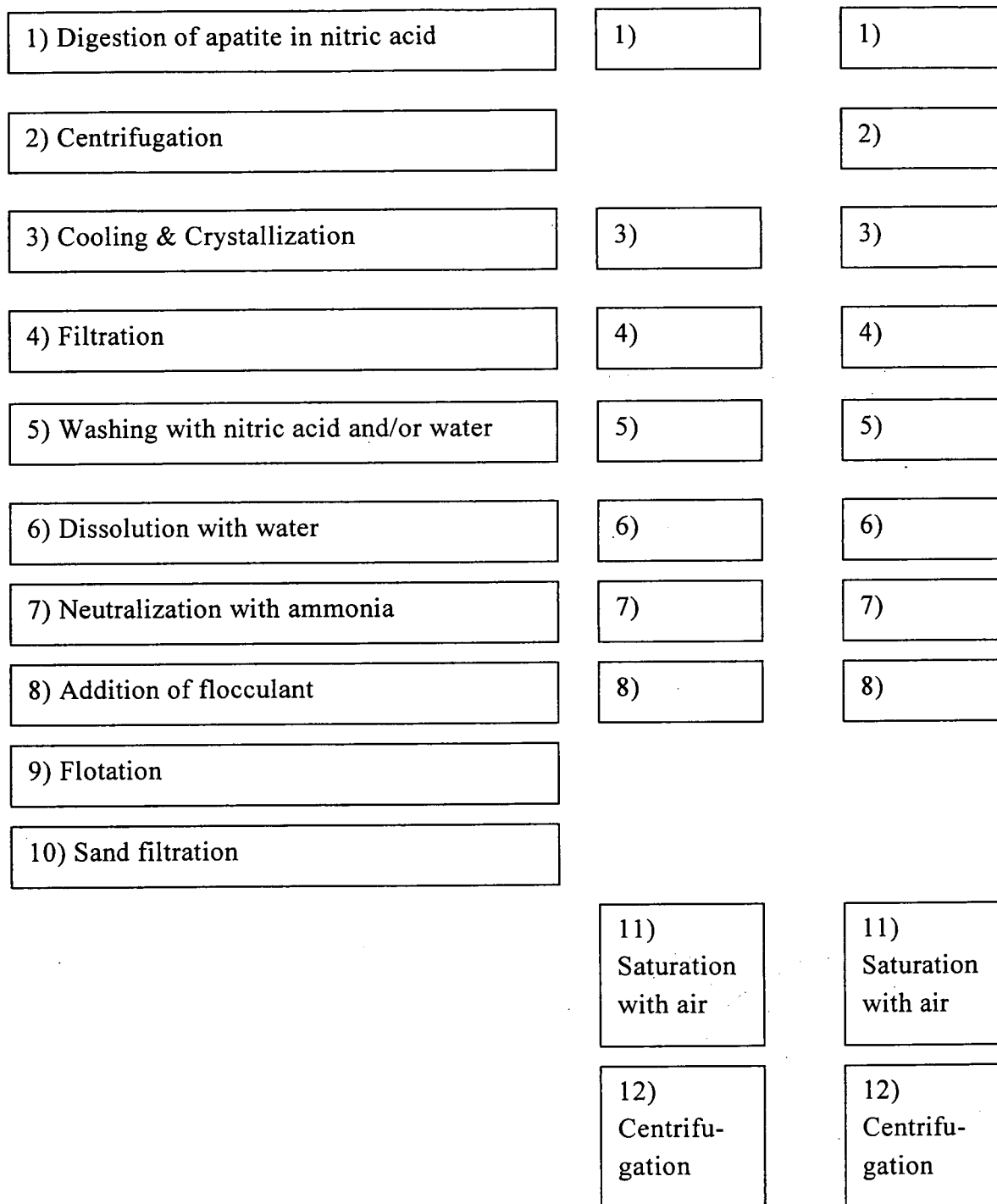


Fig. 1

Fig. 2

Fig. 3