



PRODUCTION OF CALCIUM NITRATE

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ABSTRACT

The article of the invention is a method of calcium nitrate production. Calcium nitrate is used in agriculture, greenhouse cultivation, water and sewage processing and in concrete additives industry. The high quality of calcium nitrate, with very low content of insoluble substances, no anti-caking agents combined with low hygroscopicity is especially needed in greenhouse and hydroponic cultivations. Additionally, the finished product should be characterized by a low content of ferrous compounds, phosphates and heavy metals.

INTRODUCTION

In the known processes of calcium nitrate fertilizer grade production, the form of the product obtained from calcium nitrate solution in a process of e.g. phosphorite reaction with nitric acid, is of great importance. It is important at the final production stages that calcium nitrate crystals have a stable form and don't contain impurities such as ferrous and fluorine compounds, which are insoluble in water and difficult to separate by the traditional methods of neutralization and purification.

A method of crystalline calcium nitrate production has been described, among others, in the patent description US 4569677. The known method is based on adding crystalline seeds to a concentrated calcium nitrate solution, which is later cooled below the crystallization temperature, so that in the final stage crystals are obtained, which are separated from the mother solution in separative processes. However, according to patent description no. WO 0183374 crystalline calcium nitrate is obtained through crystallization of the melt containing 5 moles of and 1 mol of NH_4NO_3 , while the process is carried out in a fluidized granulator, cooled with air at the temperature of 30-40°C, and relative air humidity below 30%.

Crystalline calcium nitrate has a low melting point (45-50°C), as it is a strongly hygroscopic compound, and tends to cake, which makes it difficult to store the product. To raise the melting point 6-8% of ammonium nitrate is fed into the melt, whereas the tendency of the granulate and crystals to cake is minimized by adding anti-caking agents, in either solid or liquid form



Figure 1. Crystalline calcium nitrate

The aim of the invention was to develop a method of calcium nitrate production, which would lead to a high quality product, with a stable form, no anti-caking agents, and with a low content of phosphates, fluorides and heavy metals. It has been proved that the method of calcium nitrate production according to the invention fulfils this aim.

MATERIALS AND METHODS

The method of the invention comprises firstly on the reaction in a continuous flow columns where the packing is limestone and secondly on a continuous belt crystallization of the final product. In the columns exothermic reaction takes place according to the following equation:



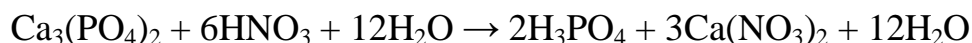
Assuming that the height of the packing is stable, and only the dosing rate of nitric acid into the reactor changes in the continuous process, the increase in the efficiency of the process is closely connected with the content of unreacted nitric acid in the reaction liquid. The correlation between the quantity of free nitric acid in the product, and the flow rate of nitric acid through the packing is an exponential function, closely related to the duration of the reaction.

Calcium nitrate is manufactured by one of these processes:

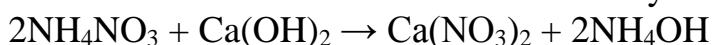
- the reaction of calcium carbonate (usually as limestone) with nitric acid:



- as a by-product of the extraction of calcium phosphate:



- the reaction of ammonium nitrate solution and calcium hydroxide:



Equipment and materials

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|---|--|
| • Weighing bottle (or small beaker) | • Watch glass |
| • Evaporating basin | • Thermometer (10 – 110 °C) |
| • 250 cm ³ beaker | • Stirring rod |
| • Bunsen burner, tripod and gauze | • Sample bottle |
| • 25 cm ³ measuring cylinder | • Spatula |
| • Filter funnel and filter paper | • 1 mol dm ⁻³ nitric acid, 25 cm ³ |
| • Hot water bath | • Calcium carbonate, 2.5 g |



Figure 2. Nitric acid for the work

Procedure of the work

1. Weigh out about 2.5 g of calcium carbonate.
2. Using a measuring cylinder, measure 25 cm³ of 1 mol dm⁻³ nitric acid into a 250 cm³ beaker.
3. Warm the acid to about 60 °C. While stirring the acid, use a spatula to add powdered calcium carbonate a little at a time, allowing the effervescence to die away between additions. Continue adding portions until there is no effervescence and some solid calcium carbonate can be seen in the beaker.
4. Filter the warm mixture into an evaporating basin. Evaporate the filtrate slowly over a hot water bath at about 60 °C until crystals form.
5. Allow the concentrated solution to cool.
6. Filter off the crystals and put the filter paper and crystals on a watch glass and dab dry with another piece of filter paper. Cover them with a piece of clean filter paper and leave them to dry at room temperature.
7. Label a sample tube with the name of the product, your name and the date. Weigh the labelled sample tube and record its mass.
8. Tip your dry product into the sample tube. Weigh the tube again. Record its mass



Calcium nitrate fertilizer is manufactured through a chemical reaction involving calcium compounds and nitric acid. The process typically begins with the selection of raw materials, where calcium carbonate (limestone) or calcium hydroxide is commonly used as the calcium source. Nitric acid, which is a strong acid and rich in nitrogen, acts as the nitrating agent. In an industrial setting, the most common method is to react calcium carbonate with nitric acid. This reaction produces calcium nitrate, carbon dioxide, and water. The overall chemical equation for this process is: $\text{CaCO}_3 + 2\text{HNO}_3 \rightarrow \text{Ca}(\text{NO}_3)_2 + \text{CO}_2 + \text{H}_2\text{O}$. An alternative route is to use calcium hydroxide, where the reaction is: $\text{Ca}(\text{OH})_2 + 2\text{HNO}_3 \rightarrow \text{Ca}(\text{NO}_3)_2 + 2\text{H}_2\text{O}$. These reactions are typically carried out in a corrosion-resistant reactor because nitric acid is highly reactive and can damage ordinary equipment.

Results of potassium nitrate and mother liquor analyzes

The name of indicators	Ca(NO ₃) ₂ content		MgCl ₂ (solution)
	Ca(NO ₃) ₂ (crystals obtained)	Ca(NO ₃) ₂ (washed crystals)	
Number of Mg ⁺ ions, at %	0.72	0.09	5.78
Number of Cl ions ⁻ , at %	2.33	0.3	14.9
Basic substance, at %	90.7	99.3	22
Humidity, at %	6.1	0.26	-

Once the reaction is complete, the mixture contains a solution of calcium nitrate and some insoluble impurities. To obtain a pure product, the solution undergoes a filtration step to remove solid residues that may be present. The clear filtrate, which contains dissolved calcium nitrate, is then concentrated by evaporating some of the water. This is usually done using vacuum evaporators to avoid excessive temperatures that could decompose the compound or waste energy.

As the solution becomes more concentrated, it is cooled gradually to encourage the crystallization of calcium nitrate, usually in the form of tetrahydrate crystals (Ca(NO₃)₂·4H₂O). These crystals are then separated from the remaining solution, often by centrifugation or other solid-liquid separation techniques.

After separation, the wet crystals are dried to reduce the moisture content. Drying is done carefully to avoid the loss of nitrate content or thermal degradation. The dried product may be granulated to improve handling, storage, and application properties.

The granulated fertilizer is then cooled and screened to ensure uniform size, after which it is packaged in moisture-proof bags since calcium nitrate is highly hygroscopic and can absorb water from the air. During the entire manufacturing process, safety precautions are essential, especially in handling nitric acid and managing the release of carbon dioxide gas. The production environment must be well-ventilated, and equipment must be corrosion-resistant. The final product is a highly soluble, fast-acting nitrogen fertilizer ideal for various crops, especially in situations where both calcium and nitrate nitrogen are needed.



Here are the advantages and disadvantages of calcium nitrate fertilizer:

Advantages:

1. Dual Nutrient Source

Provides both calcium and nitrate nitrogen, essential for plant growth and cell wall strength.

2. Highly Soluble

Dissolves easily in water, making it ideal for drip irrigation, hydroponics, and foliar applications.

3. Fast Nutrient Uptake

Nitrate nitrogen is readily available to plants, leading to quick absorption and

fast results.

4. Improves Fruit Quality

Enhances fruit firmness, shelf life, and resistance to physiological disorders like blossom end rot.

5. Reduces Soil Acidity

Unlike ammonium-based fertilizers, calcium nitrate has a neutral or slightly basic reaction in soil.

Disadvantages:

Applications

1. Hygroscopic Nature

Absorbs moisture from the air easily, making it difficult to store unless in sealed, moisture-proof bags.

2. Higher Cost

More expensive than other nitrogen fertilizers like urea or ammonium nitrate.

3. Not Suitable for All Crops

Some crops may not require extra

calcium, making its use unnecessary or uneconomical.

4. Short-Term Effect

Nitrate nitrogen is quickly leached from the soil, requiring frequent applications.

5. Handling Hazards

Manufacturing and handling involve corrosive nitric acid and reactive processes, needing strict safety measures.

Calcium nitrate fertilizer is widely used in agriculture due to its dual nutrient composition, offering both calcium and nitrogen, which are essential for plant development. It plays a significant role in improving crop quality, yield, and resistance to various physiological disorders. One of the primary applications is in high-value crop farming, especially for fruits and vegetables like tomatoes, peppers, apples, lettuce, and strawberries. These crops often suffer from calcium deficiency, which leads to problems such as blossom end rot in tomatoes and tip burn in lettuce. Calcium nitrate provides an immediate source of calcium, which helps strengthen cell walls and promotes better fruit firmness and shelf life. The nitrate nitrogen component is rapidly absorbed by plants, supporting vigorous growth and development.



In horticulture, calcium nitrate is commonly used in greenhouse production and hydroponic systems. Its high solubility in water makes it ideal for fertigation, allowing farmers to deliver nutrients directly to plant roots through irrigation systems. This method ensures precise nutrient management and minimizes losses due to leaching. In hydroponics, where soil is not used, calcium nitrate is a critical part of the nutrient solution as it supplies both nitrate and calcium in a readily available form. It is often combined with other fertilizers like potassium nitrate and magnesium sulfate to provide a complete nutrient profile.

Calcium nitrate is also used in foliar feeding, where it is sprayed directly onto the leaves. This is particularly effective in correcting calcium deficiencies quickly, especially when root uptake is limited due to poor soil conditions or environmental stress. Additionally, in alkaline or saline soils where calcium availability is reduced, calcium nitrate helps improve soil structure and displaces excess sodium, thereby enhancing root health and water penetration.

Another important application is in the prevention of certain plant diseases. The presence of calcium improves plant resistance to pathogens and reduces the incidence of issues like bitter pit in apples and internal browning in Brussels sprouts. Moreover, calcium nitrate is often used as a supplement in fertigation schedules during periods of high calcium demand, such as fruit set and development stages. It is compatible with most fertilizers except those containing phosphates or sulfates, which may cause precipitation. Overall, calcium nitrate is a versatile and essential fertilizer in modern agriculture, especially in intensive farming systems where crop quality, nutrient precision, and efficiency are critical to success

CONCLUSION

We used an excess of calcium carbonate and so the theoretical yield depends on the volume of 1 mol dm^{-3} nitric acid used.

Calculate

1. the theoretical yield of calcium nitrate-4-water, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$;
2. the percentage yield of calcium nitrate-4-water, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$.