



Evaluation Of A Synthesis Process For The Production Of Calcium Nitrate Liquid Fertilizer

M Rodríguez¹ and H Zea^{1*}

¹Departamento de Ingeniería Química y Ambiental, Universidad Nacional de Colombia, Bogota, Colombia.

Abstract: a simple and effective procedure for the synthesis of liquid calcium nitrate fertilizer was proposed; analysis of variable sensitivity, mixing procedures and evolution of temperature during the reaction allowed to establish the appropriated reaction condition to produce a liquid calcium nitrate fertilizer that complies with the commercial specification expected in terms of pH and density. In the synthesis of calcium nitrate liquid fertilizer it may be desirable to use an amount of acid less than 96% of the stoichiometric, as the pH and the percentage of CaO could be lower than expected.

Keywords— Calcium nitrate, liquid fertilizer, Calcium carbonate.

Introduction

Given the key role agricultural production has worldwide and the constant increment in fertilizers consumption, the development of alternative fertilizers is a constant need of the productive sector; these developments must get the maximum benefit of available raw material. Nitrogen is the main nutrient to be considered in terms of a proper fertilization; there are many nitrogen water soluble and economical raw materials. Soil concentrations ranging between 200 to 250 ppm are frequently mentioned as the optimum. Typical nitrogen sources are potassium, calcium and magnesium salts along with ammonium nitrate or urea; many of these salts are highly soluble in water and are easily transferred to the soil.

The purpose of this study is to perform a technical evaluation of the production of a liquid compound calcium nitrate fertilizer that complies with the physical and chemical characteristics of the commercial available fertilizer. Due to the local capacity of raw materials the selected reaction to evaluate is the neutralization of calcium carbonate with nitric acid.

Fertilizers

Fertilizer is a chemical substance organic or inorganic, natural or synthetic intended to provide plants with the set of nutrients required for a proper development. A fertilizer must contain one or more of essential nutrients. A mineral fertilizer is a product of inorganic origin, containing at least a chemical plant needs for its life cycle. The most important feature of any fertilizer is that it should have a high solubility in water, thus can be dissolved in the water irrigation and the nutrients could have passive and active absorption in the plant, through the flow water.

Among the many criteria used to classify fertilizer water solubility and the irrigation technique stand as the ones with higher impact in the simplicity of use by the final consumer. Fertirrigation is a technique by which fertilizing substances are distributed to plants simultaneously with irrigation water; nitrogen fertilizers

usually have high solubility in water making them an excellent candidate for fertirrigation¹⁻³. The most common fertilizers in fertirrigation are:

- Liquid Fertilizers: usually supplied in the form of saturated solutions ready to use.
- Solid fertilizers: constitute of components readily soluble in water; solubility could be a limiting factor as each compound in the fertilizer could have different solubility in water.

Fertilizers could also be classified by number of nutrients included: simple fertilizers contain only one nutrient, meanwhile (Table 1) compound fertilizers will contained two or more nutrients (Table 2).

Table 1 simple fertirrigation fertilizers

Solution 32	8% nitric-16% urea 8% ammonium
Urea	46% N
Nitric Acid	12% N
Ammonium Nitrate	33.5 % N
Phosphoric acid (liquid)	40-54% P ₂ O ₅

Table 2 compound fertirrigation fertilizers

Potassium nitrate	13% N, 38% K
Potassium sulfate	43% K, 18% S
Mono ammonium phosphate MAP	12% N, 26.5% P
Mono potassium phosphate MKP	22.5% P, 28% K
Magnesium nitrate (crystals)	11% N, 15,7% MgO
Magnesium nitrate (liquid)	6.6% N, 9.5% MgO
Calcium nitrate	15.5% N, 19% Ca water soluble

Calcium nitrate

Calcium nitrate is highly hygroscopic and soluble in water when heated⁴. Liquid calcium nitrate provides nitrogen, essential for the growth and development of crops, necessary for the synthesis of chlorophyll and plays an important role in the photosynthesis process as well as being a major component of vitamins and energy transfer systems of plants. Calcium helps to reduce soil acidity⁵.

Table 3 Calcium nitrate physical and chemical characteristics

Chemical formula	Ca(NO ₃) ₂
Molecular weight (g/mol)	164.09
Melting point (°C)	561
Water solubility	121.2 g/100 ml

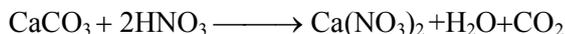
Commercial calcium nitrate liquid fertilizers usually report nominal values for their most important characteristics, along with guarantee ranges; pH, density, CaO % and Ca(NO₃)₃ % on a commercial calcium nitrate liquid fertilizer summarized in Table 4.

Table 4 Calcium nitrate liquid fertilizer commercial specifications

pH (25°C)	Nominal:6.35 Guarantee: 5-7
Density (20°C) (g/ml)	Nominal: 1.490 Minimum: 1.477
CaO (%)	Minimum:16.75 Nominal: 17.00 Maximum:17.25
Ca(NO ₃) ₂ (%)	49.7

Calcium nitrate was the first synthetic fertilizer known as Norge saltpeter, usually produced by dissolving limestone in nitric acid and neutralizing the resultant liquor with powdered limestone or lime. This process continues in use but now ammonia is used to neutralize.

The reaction occurring in the process is:



CO₂ and water vapors produced are removed, any entrained droplet is removed by a purification system. Commercial grade calcium nitrate contains approximately 5-7% ammonium nitrate, which is obtained by neutralizing the free acid remaining ammonia or nitrate solution with addition of fresh ammonia. If the product is required in crystals, the calcium nitrate solution is sent to an evaporator to obtain the appropriated conditions for crystallization. If calcium nitrate is used to produce liquid fertilizer, the evaporation step is not necessary. Some inert or other components of the calcium source used that do not react with nitric acid must be removed by filtration. Calcium nitrate is also a byproduct of the acid treatment of phosphoric rock process (Oda Process)^{1,2,4,6}.

Solutions of calcium nitrate can also be obtained by absorption in lime slurry of the fumes from nitric acid plants. Initial nitrate-nitrite solution becomes a pure calcium nitrate solution by an analogous reaction. Nitrate produced is used directly for the production of fertilizers, or is converted into ammonium nitrate^{3,5,7,8}.

Materials And Methods

Commercial nitric acid (65% weight in water) and calcium carbonate technical grade purity greater than or equal to 90%, particle size of 37 microns corresponding to 400 mesh, were used as reactants.

Table 5 Raw materials specifications

Reactants	Purity %	Particle Diameter (μm)	Mesh
CaCO ₃	96	37	400
HNO ₃	65	NA	NA

Mixing procedure

The proposed reaction is highly exothermic and is recommended to perform a set initial tests to establish the proper mixing procedure and a preliminary estimation of appropriate ratio of reactants to generate a product with the desired characteristic; the experimental conditions of this set of tests are summarized in Table 6.

Table 6 Mixing procedure experimental conditions

Test	Reactants			Product
	CaCO ₃ (g)	HNO ₃ (mL)	H ₂ O (mL)	Ca(NO ₃) ₂ (mL)
1	85.3	376.2	90	210
2	50	190.1	150	233
3	50.5	159.7	50	150

Two mixing procedures were evaluated, in the first one a stoichiometric mixture of calcium oxide and nitric acid was prepared by slowly adding the oxide to the acid contained in a beaker, a final filtration stage was necessary for this procedure and it was made under vacuum, the density of the resulting solution was adjusted with water. In the second mixing procedure nitric acid in excess was slowly added to a calcium carbonate water suspension under constant stirring, no filtration was required in this procedure. Temperature and pH were continuously measured during both procedures.

Sensitivity analysis

Two set of experiments were performed to determine the effect of the amount of nitric acid and the ratio H₂O/CaCO₃ of the initial suspension on the characteristics of the final product.

In order to analyze the way in which the ratio $H_2O/CaCO_3$ of the initial suspension affects the density of the final product, four tests were performed, in each one a different value of the ratio $H_2O/CaCO_3$ in the initial suspension was used, to which a constant amount of nitric acid was added.

In order to analyze the way in which the amount of acid affects the pH and percentage CaO of the final product, four tests were performed, in two of them the amount of acid added was below the stoichiometric value, a third test had an amount of acid added equal to the stoichiometric (corresponding to molar ratio $HNO_3:CaCO_3$ 2:1) and a final experiment had an amount of acid above the stoichiometric required

Temperature time evolution

50g of $CaCO_3$ were weighed in a beaker, water was added to prepare a 50% $CaCO_3$ suspension and then placed on a heating plate under constant stirring. Nitric acid (63.7 ml) was added at an approximate rate of 0.3 mL/min; temperature and pH evolution of the reaction was recorded.

Results and Discussion

Final pH and density at 20 °C of the material obtained from the procedure mixture experiments are presented in Table 7. The pH values are in the range reported for the commercial sample, however all of them are under de nominal values (average and minimum deviation of 14% and 7%). In terms of density both procedures were capable to reproduce the density reported for commercial samples.

Table 7 Mixing procedures experiments results

Test	pH	Density (20 °C)
1	4.85	1.40
2	5.9	1.26
3	5.6	1.40

An important increment of temperature was observed during mixing procedure 1, reaching a maximum of 80 °C. Even this high temperature, insoluble material formed, the reactions required additional heating to solubilize those crystal. On contrary in mixing procedure 2 did have just a minor temperature change and did not require additional heating, since the formation of insoluble crystals was negligible. The absence of insoluble material and better temperature control (which favors conversion) make mixing procedure 2 a better technical option for production than the mixing procedure 1.

Results of the experiments testing the effect of the ratio $H_2O/CaCO_3$ in the density of the final product at constant amount of nitric acid following the mixing procedure 2 are presented in Figure 1, it can be observed a slope with inverse proportionality profile of the final product density as a function of the ratio $H_2O/CaCO_3$; a strong decrease of density is observed for the values below an up $H_2O/CaCO_3$ equals 2, above this value the decrease rate is smaller.

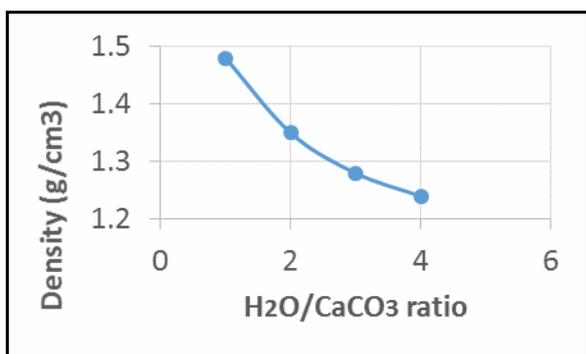


Figure 1 Final product density as a function of the ratio $H_2O/CaCO_3$

Results of the experiments testing the effect of amount of acid affects the pH and percentage CaO of the final product are presented in Figure 2 and 3. Initially the pH profile (Figure 2) is constant up to values of

$\text{HNO}_3/\text{CaCO}_3$ smaller than 1.9, from that point on there is a decrease as the amount of nitric acid increases (higher values of the ratio $\text{HNO}_3/\text{CaCO}_3$).

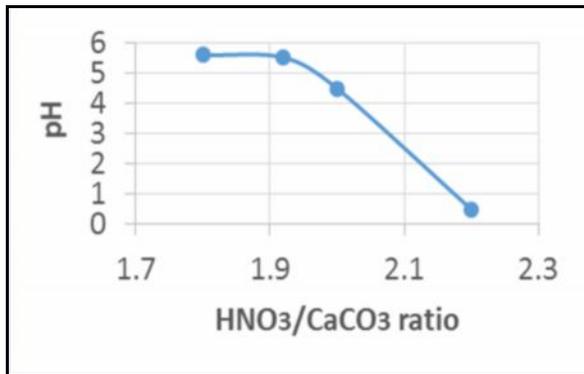


Figure 2 Final product pH as a function of the ratio $\text{HNO}_3/\text{CaCO}_3$

In term of the CaO percentage in the final product there is an initial increment as the amount of acid reaches the stoichiometric value; for values above the stoichiometric the CaO percentage decreases.

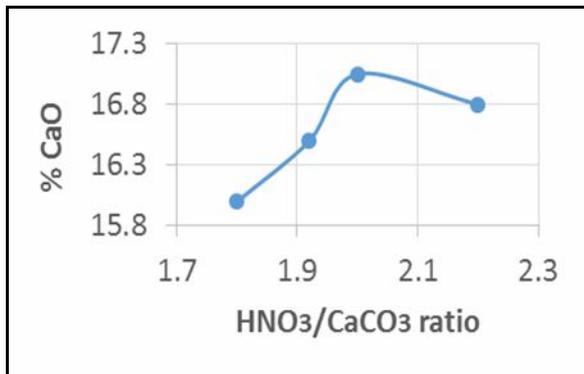


Figure 3 Final product CaO percentage as a function of the ratio $\text{HNO}_3/\text{CaCO}_3$

Results of the temperature evolution as a function of time are shown in Figure 4; there is a rapid increment of temperature from 17 to 35 °C in the first 10 minutes of reaction, after those initials 10 minutes it takes the reaction 50 minutes to reach the maximum temperature registered (approximately 46 °C), from that point on the temperature was almost constant up to the end of the experiment.

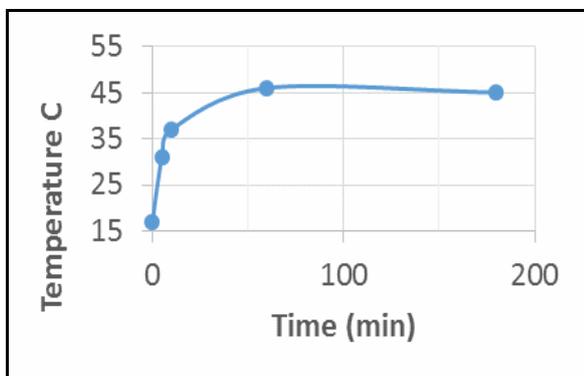


Figure 4 Reaction temperature evolution.

The complete characterization of two samples obtained from the temperature evolution experiments are reported in Table 8 and 9. Calcium content was determinate by the complexometric method. Finally a calculation of the yield of the reaction based on the theoretically expected amount and the one obtained in the experimental runs is reported in Table 9.

Table 8 Final product characterization

	pH (20 °C)	Density g/ml (20 °C)	CaO %
Sample 1	5.8	1.48	16.4
Sample 2	6.0	1.48	16.0

Table 9 Final product yield

	% Ca(NO ₃) ₂	Yield
Sample 1	45.4	93.8
Sample 2	42.3	88.5

Conclusions

A simple and effective procedure for the synthesis of liquid calcium nitrate fertilizer was proposed; analysis of variable sensitivity, mixing procedures and evolution of temperature during the reaction allowed to establish the appropriated reaction condition to produce a liquid calcium nitrate fertilizer to comply with the commercial specification expected in terms of pH, and density. In the synthesis of calcium nitrate liquid fertilizer may be desirable that the amount of acid is less than 96% of the stoichiometric required, as the pH and the percentage of CaO could lower than the expected when using values above the stoichiometric. In terms of density of the final product the used relationship of water to carbonate in the initial suspension (1:1) is appropriated. Under the synthesis condition proposed the reaction yield is around 90 %.

References

1. Azeem, B., et al., *Review on materials and methods to produce controlled release coated urea fertilizer*. Journal of Controlled Release, 2014. 181(0): p. 11-21.
2. Parvizi, H., A.R. Sepaskhah, and S.H. Ahmadi, *Effect of drip irrigation and fertilizer regimes on fruit yields and water productivity of a pomegranate (Punica granatum (L.) cv. Rabab) orchard*. Agricultural Water Management, 2014. 146: p. 45-56.
3. Rahman, M.M., et al., *Production of slow release crystal fertilizer from wastewaters through struvite crystallization A review*. Arabian Journal of Chemistry, 2014. 7(1): p. 139-155.
4. Adams, J.R. and A.R. Merz, *Hygroscopicity of Fertilizer Materials and Mixtures*. Industrial & Engineering Chemistry, 1929. 21(4): p. 305-307.
5. Pierre, W.H., *Nitrogenous Fertilizers and Soil Acidity: I. Effect of Various Nitrogenous Fertilizers on Soil Reaction I*. 1928. p. 254-269.
6. Nawrocki, A. and R. Olszewski, *Method of calcium nitrate production*. 2007, Google Patents.
7. Perry, R., *Perry's Chemical Engineers Handbook*. . Mc -Graw Hill. Séptima Edición., 1997(New York.).
8. Rabie, D.R.H., W.R. Morris, and J.P.G. Eygelaar, *Method for producing calcium nitrate granules*. 2006, Google Patents.
