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ASSESSMENT OF THE ACIDULATION OF MAGNESIUM OXIDE FOR THE PRODUCTION OF MAGNESIUM NITRATE LIQUID FERTILIZER

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ABSTRACT

A simple an effective procedure for the synthesis of liquid magnesium nitrate fertilizer was evaluated. Analysis of variable sensitivity, mixing procedures and evolution of temperature during the reaction allowed to establish the appropriated reaction condition to produce a liquid magnesium nitrate fertilizer from the acidulation of magnesium oxide with nitric acid, that complies with the commercial specification expected in terms of pH, density and MgO percentage. In the synthesis of magnesium nitrate liquid fertilizer may be desirable that the amount of acid is less than 96% of the stoichiometric amount.

Key words: Magnesium nitrate, Liquid fertilizer, Magnesium oxide acidulation.

INTRODUCTION

The significant increase in demand of food and raw materials of vegetable origin requires the development of nutrients sources easily taken by plants to increase crop yields, which is possible through the use of fertilizers. Fertilizer is an organic or inorganic chemical substance of natural or synthetic origin, which contains one or more of essential nutrients and provide plants with the set of nutrients required for a proper development[1,2]. A mineral fertilizer is a product of inorganic origin, containing, at least one chemical nutrient needed by plants for its life cycle. Nitrogen is the main nutrient to be considered in terms of a proper fertilization; soil concentrations ranging between 200 to 250 ppm are frequently mentioned as the optimum. Economical and water soluble sources of nitrogen are potassium, calcium and magnesium salts along with ammonium nitrate or urea[3,4].

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Fertirrigation is a technique by which fertilizing substances are disseminated to plants at the same time with irrigation water; nitrogen fertilizers usually have excellent solubility in water making them a good candidate for fertirrigation[2,3,5]. The most common fertilizers in fertirrigation are liquid and solid fertilizers; liquid fertilizers are those usually supplied in the form of saturated solutions ready to use. Solid fertilizers are regularly constituted of components easily soluble in water; solubility could be a limiting factor as each compound in the fertilizer could have different solubility properties.

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

Table 1: Most common fertirrigation fertilizers

Simple		Compound	
Solution 32	8% nitric-16% urea 8% ammonium	Mono ammonium phosphate MAP	12% N, 26.5% P
Urea	46% N	Mono potassium phosphate MKP	22.5% P, 28% K
Nitric acid	12% N	Magnesium nitrate (crystals)	11% N, 15,7% MgO
Ammonium nitrate	33.5 % N	Magnesium nitrate (liquid)	6.6% N, 9.5% MgO
Phosphoric acid (liquid)	40-54% P_2O_5	Calcium nitrate	15.5% N, 19% Ca water soluble

The purpose of this study is to perform a technical evaluation of the production of a liquid compound magnesium nitrate fertilizer from the acidulation of magnesium oxide that complies with the physical and chemical characteristics of the commercial available fertilizer.

Magnesium nitrate

Magnesium nitrate hexahydrate is a crystalline solid, which crystallized deliquescent, very soluble in water and alcohol. It melts between 95-100°C, and at higher temperatures decomposes giving up nitric acid and becoming a salt low soluble in water. Magnesium nitrate is also used in industry to harden the end of the sleeves by the gas glow. It offers readily available magnesium and nitrogen to plants, which is essential for proper development[4,6,7].

Table 2: Magnesium nitrate physical and chemical characteristics

Chemical formula	**$Mg(NO_3)_2$**
Molecular weight (g/mol)	148.3
Fusion point (°C)	88.9 (hexahydrate)
Water solubility	125 g/100 mL

Commercial magnesium nitrate liquid fertilizers usually report nominal values for their most important characteristics, along with guarantee ranges; pH, density, MgO and total nitrogen weight percentage are summarized in Table 3.

Table 3: Magnesium nitrate liquid fertilizer commercial specifications

pH (20°C)	**Nominal: 6.12**	**Guarantee: 5-7**	
Density (20ºC) (g/mL)	Nominal: 1.34		
MgO (%)	Minimum: 9.75	Nominal: 10	Maximum:10.25

Magnesium nitrate can be synthesized fallowing different reactions routes, the first one correspond to the reaction of metallic magnesium with nitric acid to produce magnesium nitrate and the evolution of hydrogen. This reaction is highly exothermic.

$$Mg + 2\ HNO_3 \longrightarrow Mg(NO_3)_2 + H_2$$

The second reaction is the acidulation of magnesium oxide with nitric acid to produce magnesium nitrate and water, this reaction is also exothermic.

$$MgO + 2\ HNO_3 \longrightarrow Mg(NO_3)_2 + H_2O$$

The third one corresponds to the reaction of magnesium hydroxide with ammonium nitrate to produce magnesium nitrate, water and the evolution of ammonia.

$$Mg(OH)_2 + 2\ NH_4NO_3 \longrightarrow Mg(NO_3)_2 + 2\ NH_3 + H_2O$$

Due to local capacity of raw materials and in order to reduce safety hazard the selected reaction is the acidulation of magnesium oxide with nitric acid.

EXPERIMENTAL

Materials and methods

Technical grade purity greater than or equal to 90% magnesium oxide (particle size of 150 microns corresponding to 100 mesh and commercial nitric acid (65% weight in water), were used as reactants.

Table 4: Raw materials specifications

Reactants	Purity (%)	Particle Diameter (μm)	Mesh
MgO	90	150	100
HNO_3	65	NA	NA

Mixing procedure

The proposed reaction is exothermic and is recommended to perform a set of initial tests to establish a proper mixing procedure and a preliminary estimation of appropriate ratio of reactants to generate a product with the desire characteristic. The experimental conditions of this set of tests and the amount of product obtained are summarized in Table 5.

Table 5: Mixing procedure experimental conditions

Test	Reactants			Product
	MgO (g)	HNO_3 (mL)	H_2O (mL)	$Mg(NO_3)_2$ (mL)
1	63.3	204.98	250	364.9
2	50	175.8	150	240
3	50	195.7	200	300

Two mixing procedures were evaluated. In the first one a stoichiometric mixture of magnesium 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 magnesium carbonate water suspension under constant stirring, no filtration was required in this procedure. Temperature and pH were continuously measured during both procedures.

Sensitivity analysis

To evaluate the effect of the ratio H_2O/MgO of the initial suspension on the density of the final product four tests were performed, in each of them a different value of the ratio H_2O/MgO present in the initial suspension was used but keeping constant amount of nitric acid added.

Four tests were performed in order to determine the effect of the amount of acid added in the pH and percentage MgO of the final product, 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: MgO 2:1) and a final experiment had an amount of acid above the stoichiometric required.

Temperature time evolution

50 g of MgO were weighed in a beaker; water was added to prepare a 25% MgO suspension and then placed on a heating plate under constant stirring. Nitric acid was added at an approximate rate of 0.6 mL/min up to obtain 90 and 96% of the stoichiometric values; temperature and pH evolution of the reaction was recorded.

RESULTS AND DISCUSSION

Density and pH at 20^{o}C of the final product obtained from the procedure mixture experiments are presented in Table 6. The pH values are below or at lower end of the range reported for the commercial sample, reporting and average 17% deviation from the commercial nominal values. On the other hand, the values of density obtained are in the range reported by commercial samples with just an average 3% deviation.

Table 6: Mixing procedures experiments results

Test	pH	Density (20^{o}C)
1	4.29	1.37
2	5	1.40
3	5	1.34

A significant increment of temperature was observed during mixing procedure 1, reaching a maximum value of 110^{o}C, however, insoluble material formed even at this high temperature and the reactions required additional heating to solubilize those crystal. On contrary in mixing procedure 2 the formation of insoluble crystals was negligible requiring not additional heating. The absence of insoluble material and better temperature control (which favors the conversion) makes mixing procedure 2, a better technical option for the production than mixing procedure 1. Fig. 1 shows the results of the experiments testing the effect of the ratio H_2O/MgO in the density of the final product at constant amount of nitric acid following the mixing procedure 2. It can be observed that a moderate slope in the inverse proportionality profile of the final product density as a function of the ratio H_2O/MgO.

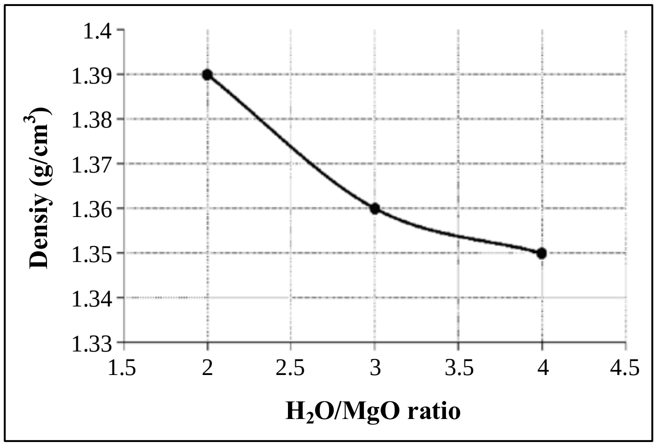

Fig. 1: Final product density as a function of the ratio H_2O/MgO

Results of the experiments testing the effect of amount of acid in the pH of the final product are presented in Fig. 2. Initially the pH profile (Fig. 2) is constant up to values of HNO_3: MgO smaller than 1.9, form that point on there is a decrease as the amount of nitric acid increases (higher values of the ratio HNO_3/MgO).

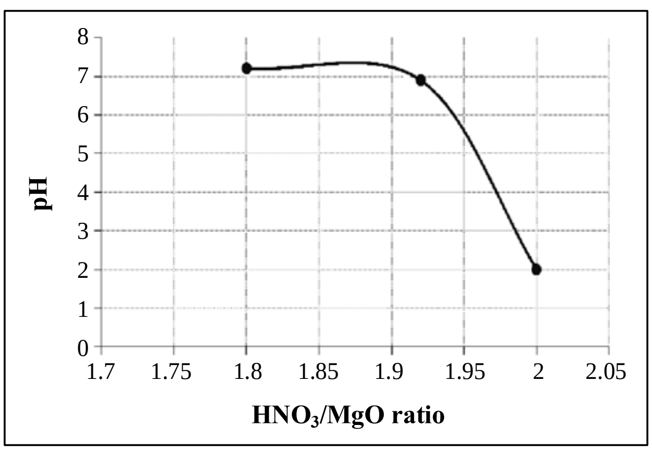

Fig. 2: Final product pH as a function of the ratio HNO_3/MgO

Figure 3 shows the results of the experiments testing the effect of amount of acid on the percentage MgO of the final product. There is an initial strong increment as the amount of acid reaches the stoichiometric value; for values above the stoichiometric the MgO percentage decreases.

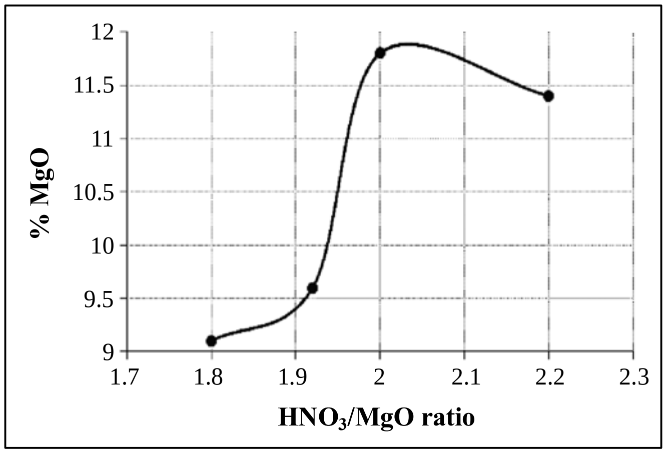

Fig. 3: Final product MgO percentages as a function of the ratio HNO_3/MgO

Results of the temperature evolution as a function of time are shown in Figure 4, with a rapid increment of temperature from 20 to 58°C in the first 20 minute of reaction, from the 20 to the 80 minutes of reaction the temperature increased just 11°C, with a final strong increment of 10°C in the last 10 minutes of reaction.

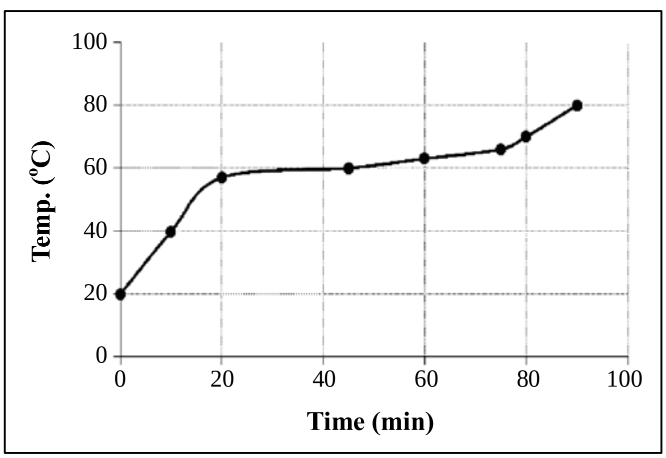

Fig. 4: Reaction temperature evolution

The complete characterization of two samples obtained from the temperature evolution experiments are reported in Table 7, along with a calculation of the yield of the reaction based on the theoretically expected amount and the one obtained experimentally. Calcium content was determined by the complexometric method. Result of sample 1 and 2 corresponds to the experiment using 96 and 90% of the acid stoichiometric values, respectively.

Table 7: Final product characterization

	pH (20°C)	Density g/mL (20°C)	MgO (%)	$Mg(NO_3)_2$ (%)	Yield (%)
Sample 1	7.0	1.36	10.3	37.6	79
Sample 2	7.7	1.36	10.88	38.2	81.1

Although pH values of sample 1 is in the upper limit of the values reported in commercial fertilizers in terms of density and MgO percentage comply with the specification expected for the product.

CONCLUSION

Liquid magnesium nitrate fertilizer from the acidulation of magnesium oxide with citric acid that complies with the commercial specification expected in terms of pH, density and MgO percentage was obtained. Analysis of variable sensitivity, mixing procedures and evolution of temperature during the reaction allowed establishing the appropriated reaction condition to produce a liquid magnesium nitrate fertilizer. In the synthesis of magnesium nitrate liquid fertilizer may be desirable that the amount of acid is above than 96% of the stoichiometric amount, obtaining yields around 80%.

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