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Influence of Technological Parameters on the Properties of Granulated Dolomite

Alfredas Martynas SVIKLAS*, **Rasa ŠLINKŠIENĖ**

Faculty of Chemical Technology, Kaunas University of Technology, Radvilėnų pl. 19, LT-50254, Kaunas, Lithuania

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The main parameters of dolomite phosphorization and the successive granulation of the product in a laboratory pan granulator were studied. The physico-chemical properties of granulated dolomite such as size of granules, moisture content, granules crushing strength and chemical composition (CaO, MgO and P_2O_5) were measured. Dependence of granules size percentage distribution of product on the amount of dolomite treated by phosphoric acid under various granulation conditions was determined. The main parameters of phosphorization were determined and the main physico-chemical properties of granulated dolomite were examined too. The results of investigation allow optimizing the process of reaction of dolomite with phosphoric acid in order to obtain a granulated product containing calcium, magnesium and phosphorus for using in agriculture.

Keywords: dolomite; phosphoric acid; granulation; physico-chemical properties; granules crushing strength; granules size percentage distribution.

INTRODUCTION

In recent decades there has been a growing need for the inclusion in fertilizers of nutrients other than the primary elements, nitrogen, phosphorus and potassium. Calcium and, to a lesser extent, magnesium are main secondary elements which are present in many of the commonly used fertilizers.

The usual materials containing calcium (and magnesium) are limestone (principally calcium carbonate), dolomite (a double carbonate of calcium and magnesium), or dolomite limestone which is mixture of the two minerals.

In addition to secondary nutrients that are incorporated in granular mixtures, secondary nutrient materials are also used for direct application and bulk blending [1 – 3].

Powder materials are normally used for direct application for correction of soil acidity only [4 – 6]. In making solid mixtures using powder dolomite it is difficult to obtain good mixing of small amount of additives with the other fertilizers materials and segregation may take place in handling.

Particle size distribution is very important property for fertilizers handling and using. Usually fertilizers bulk blending requires granules of 1 mm – 5 mm size. These particle size materials are also excellent secondary nutrient sources for direct application. Granulation of dolomite and other minerals in the absence of additives is very difficult [7]. Effect of process parameters on the crush strength of granular fertilizers is described in [8].

Well know process of dolomite treatment with nitric acid [9 – 11] and corresponding results are used for production of liquid fertilizers.

An interaction of dolomite with sulphuric acid was investigated for granulation of dolomite [12]. Only the preliminary results of dolomite interaction with phosphoric acid were obtained [13].

The aim of the research was to optimize the process of reaction of dolomite with phosphoric acid in order to obtain the granulated product containing calcium and magnesium and enriched with primary nutrient – phosphorus.

MATERIALS AND EXPERIMENTAL METHODS

The dolomite waste fraction up to 0.5 mm particle size, coming from Petrasiunai in Lithuania showed the following elemental composition (% (w/w): 28.81 CaO; 19.98 MgO; 1.71 Fe_2O_3; 0.10 Al_2O_3; 2.10 SiO_2; $1.76 \cdot 10^{-2}$ Mn; $2.71 \cdot 10^{-2}$ Zn; $1.54 \cdot 10^{-3}$ Cr; $3.34 \cdot 10^{-4}$ Cu; $.2.81 \cdot 10^{-4}$ Ni; $8.51 \cdot 10^{-4}$ Co; $2.50 \cdot 10^{-4}$ Mo; $9.79 \cdot 10^{-5}$ Cd; $4.69 \cdot 10^{-6}$ Pb; $< 1 \cdot 10^{-6}$ Se; $< 1 \cdot 10^{-6}$ Hg. These data are similar to results of other investigators [14].

For phosphorization process the phosphoric acid with concentration 85.5 % produced in Lithuanian joint-stock company "Lifosa" was used. The content of calcium and magnesium in dolomite was measured by complexometric titration, phosphorus by photometric analysis [15] and concentration of micronutrients in dolomite – by atomic-absorption electrothermopyrographic spectrometry with spectrophotometer "Perkin Elmer Zeeman 3030" [16, 17]. Physical properties of the products were evaluated by standard methods: particle size distribution was measured by conducting a "screen analysis" (sieve analysis) on a representative sample and granule strength involved determination of the crushing strength of individual granules using calibrated crushing test machine [15].

A laboratory pan granulator (diameter (D) 0.5 m, pan edge height (L) 0.08 m, speed 28 rpm and inclination of axis (α) 52°) was used for granulation of dolomite (Fig. 1).

Temperature of mixture granulation was 35 °C – 40 °C with the moisture 4 % – 10 % and drying temperature 65 °C during 1.5 h.

*Corresponding author. Tel.: +370-37-300169; fax.: +370-37-300152.
E-mail address: *alfredas.sviklas@ktu.lt* (A. Sviklas)

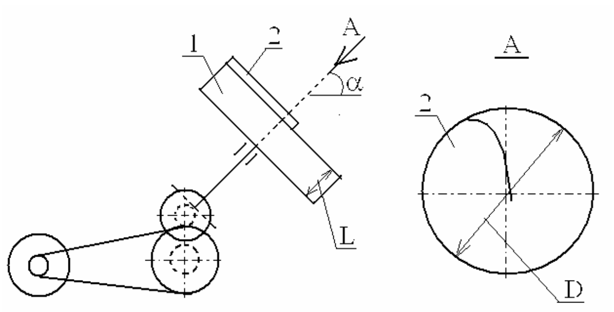


Fig. 1. Laboratory pan granulator: 1 – granulators pan; 2 – reciprocating scraper

RESULTS AND DISCUSSION

The plasticity of salts and minerals is important property for granulation, but it is difficult to measure or define quantitavely. Due to law plasticity it is very difficult to granulate dolomite. On the other hand, superphosphates (calcium dihydrophosphates) have good plasticity and mixtures containing them are easily granulated. Calcium phosphates may be obtained using treatment of dolomite by phosphoric acid. An interaction between dolomite and phosphoric acid occurs according to the following equations [18 – 20]:

$$CaCO_3 + 2H_3PO_4 \xrightarrow{H_2O} Ca(H_2PO_4)_2{\cdot}H_2O + CO_2\ ; \tag{1}$$

$$MgCO_3 + 2H_3PO_4 \xrightarrow{H_2O} Mg(H_2PO_4)_2{\cdot}H_2O + CO_2\ ; \tag{2}$$

$$CaCO_3 + H_3PO_4 \xrightarrow{H_2O} CaHPO_4 + H_2O + CO_2\ ; \tag{3}$$

$$MgCO_3 + H_3PO_4 \xrightarrow{H_2O} MgHPO_4 + H_2O + CO_2\ ; \tag{4}$$

$$3CaCO_3 + 2H_3PO_4 \xrightarrow{H_2O} Ca_3(PO_4)_2 + H_2O + CO_2\ ; \tag{5}$$

$$3MgCO_3 + 2H_3PO_4 \xrightarrow{H_2O} Mg_3(PO_4)_2 + H_2O + CO_2\ . \tag{6}$$

Depending on the ratio between dolomite and phosphoric acid, various calcium and magnesium phosphates are obtained. The best plant availability occurs when dihydrophosphates (1, 2) as well as hydrophosphates (3, 4) are used for fertilization and phosphates (5, 6) are sparingly soluble.

Samples, corresponding to the end amount of 5, 10, 15, 20 and 25 % of dolomite were treated by phosphoric acid in stoichiometry ratio 1 : 1 and mixed with the rest (95, 90, 85, 80 and 75 %) of the dolomite. Mixture of dolomite was granulated at different water spraying conditions and physico-chemical properties of granulated product were measured. Both wet and dry dolomite was used in the reaction and additionally water was sprayed directly in the granulator.

Five series of dolomite treatment and granulation were investigated (Table 1): I – both the dolomite treated by phosphoric acid and the rest dolomite were dry and have been mixed with water during the granulation; II – the dry dolomite treated by phosphoric acid, and the rest wet dolomite have been granulated in the absence of water; III – the dry dolomite has been treated by phosphoric acid and mixed with the rest wet dolomite and the water has been sprayed during the mixture granulation; IV – both the dolomite treated by phosphoric acid and the rest dolomite have been wet and water has been not used during the mixture granulation; V – both the dolomite treated by phosphoric acid and the rest dolomite have been wet and additionally water has been sprayed during the mixture granulation.

The granules size percentage distribution of granulated dolomite is mainly depending on the ratio of dolomite and phosphoric acid (Table 1). When 5 % and 10 % of dolomite was treated by phosphoric acid, dependence of size distribution on the granulation series is insignificant.

When 15 % and 20 % of dolomite was treated by phosphoric acid (Table 1) a dependence of size distribution from the production series type was determined. For example, when water was sprayed on the granulation mixture at the I, III, V series the granules of 3 mm – 5 mm diameter contains of 40 %, and up to 20 % when granulation mixture at II, IV series was no sprayed by water.

A similar dependence exists at the production series when granules with 1 mm – 2 mm and 2 mm – 3 mm diameter of dolomite are evaluated.

As low amount (5 %) of treated dolomite, the formation of fine granules (< 1 mm and 1 mm – 2 mm) takes place about 35 % – 50 % from total amount of production. By increasing the amount of treated dolomite up to 25 %, large granules (3 mm – 5 mm) prevail in granulated product.

Dependending on component ratio, the reaction between phosphoric acid and dolomite occurs 15 min – 90 min. The main properties of granulated product such as a size of granules, moisture, granules crushing strength, the granules size distribution of product and chemical composition (CaO, MgO, P_2O_5) were measured and are given in the Table 1 (stoichiometry ratio of dolomite and phosphoric acid 1 : 1). As shown in the Table 1 granular product range in size was 4 mm, a crushing strength was equal 1.15 kg/gran – 4.35 kg/gran, and humidity varied from 0.03 % up to 0.54 %. The best physico-chemical properties of granulated dolomite were obtained when the amount of treated dolomite with phosphoric acid is equal 20 % – 25 % and moisture content in the mixture is maintained from 4 % to 10 %. Granulated dolomite contains 22.99 % – 27.27 % of CaO, 15.46 % – 18.88 % of MgO and product was enriched by phosphorus from 4.0 % up to 16.39 % of P_2O_5.

Dependence of granules crushing strength on the diameter of granules and the amount of the dolomite treated by phosphoric acid in stoichiometry ratio 1 : 1 under I series conditions is shown in Fig. 2.

As shown in Figure 2, the crushing strength of granules depends on the diameter of granules and amount of treated dolomite by phosphoric acid and varies in the range from approximately 0.8 kg/gran up to 5.0 kg/gran. The crushing strength value of granulated product (4 mm – 5 mm diameter) containing part of dolomite treated by phosphoric acid 15, 20 and 25 percent, correspond to

Table 1. The physico-chemical properties and chemical composition of granulated dolomite

Series	Fraction composition, %					Mixture moisture, %	Granules (4 mm diameter) crushing strength, kg/gran	Granules moisture, %	Chemical composition, %		
	<1 mm	1 – 2 mm	2 – 3 mm	3 – 5 mm	>5 mm				CaO	MgO	P_2O_5
5 % dolomite was treated by phosphoric acid											
I	40.44	32.50	20.95	4.67	1.44	4.0	2.20	0.05	27.22	18.88	4.00
II	43.97	35.40	14.96	3.49	2.18	4.5	1.15	0.03			
III	43.40	34.34	15.64	4.43	2.19	6.5	1.45	0.06			
IV	45.35	33.65	13.77	3.88	3.35	5.0	1.65	0.07			
V	49.22	29.64	16.52	2.94	1.68	8.0	2.05	0.04			
10 % dolomite was treated by phosphoric acid											
I	35.67	30.26	29.11	1.94	3.02	4.5	2.30	0.22	25.80	17.89	7.58
II	21.33	27.74	25.87	15.23	9.83	5.0	2.25	0.11			
III	22.19	26.27	31.54	12.92	7.98	7.0	2.00	0.10			
IV	22.26	35.65	26.19	11.66	4.24	5.5	1.60	0.47			
V	16.33	27.09	30.80	18.33	7.45	8.5	2.10	0.05			
15 % dolomite was treated by phosphoric acid											
I	15.18	19.79	22.70	33.42	8.91	5.0	3.15	0.43	24.51	16.99	10.81
II	17.31	30.14	28.79	13.85	9.91	5.5	3.65	0.20			
III	14.10	11.29	11.29	40.17	23.15	7.5	3.05	0.09			
IV	23.19	36.86	21.90	9.85	8.20	6.5	3.40	0.11			
V	12.33	10.81	14.53	39.07	23.26	9.0	3.45	0.16			
20 % dolomite was treated by phosphoric acid											
I	4.70	20.04	26.88	39.46	8.92	5.5	3.90	0.54	23.35	16.19	13.73
II	8.40	23.68	27.67	20.88	19.37	6.0	4.00	0.12			
III	7.64	15.49	13.85	34.71	28.31	8.0	4.05	0.11			
IV	14.87	19.10	27.04	24.72	14.27	7.0	4.00	0.09			
V	10.10	9.23	25.39	30.61	24.67	9.5	3.60	0.09			
25 % dolomite was treated by phosphoric acid											
I	2.15	13.35	14.18	51.47	18.85	6.0	4.20	0.18	22.99	15.46	16.39
II	7.75	4.19	13.43	58.49	16.14	6.5	4.15	0.19			
III	5.26	8.22	9.81	55.24	21.47	8.5	4.35	0.17			
IV	12.54	10.36	27.23	32.86	17.01	7.5	3.90	0.26			
V	10.36	8.90	22.09	29.14	29.51	10.0	4.10	0.15			

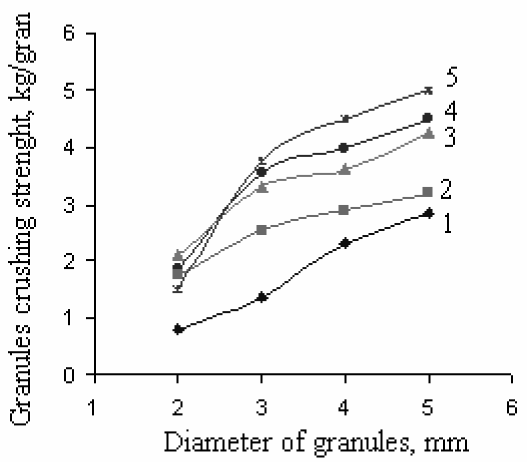


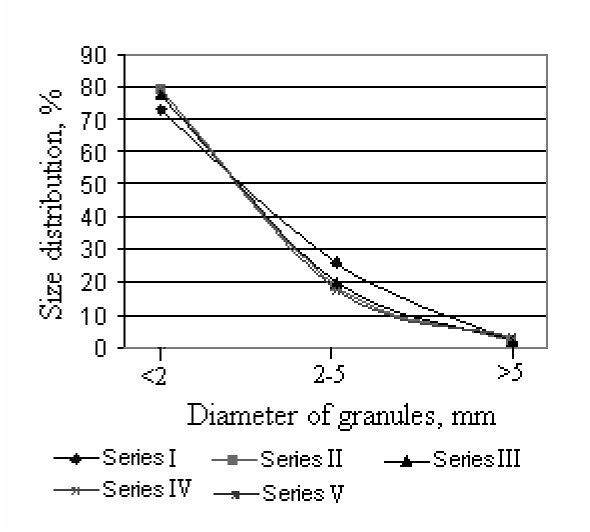
Fig. 2. Dependence of crushing strength value of granules on the diameter of granules and the amount of the dolomite treated by phosphoric acid: 1 – 5; 2 – 10; 3 – 15; 4 – 20; 5 – 25 %

fertilizers quality requirement. The highest crushing strength – 5.0 kg/gran (Fig. 2, curve 5) is obtained for 5 mm granules containing 25 % of dolomite treated by phosphoric acid.

Content of market product (2 – 5 mm diameter granules) obtained under different conditions at various amounts of treated dolomite is presented Fig. 3. As shown in Figure 3, the market fraction content is directly depending on the amount of dolomite treated by phosphoric acid and on the granulation method is insignificant.

As shown in Figure 3, a, the main part of granulated product, when 5 % of dolomite was treated by phosphore acid, contains a fine granules (< 2 mm of diameters) and this part is equal 70 % – 80 %. A market fraction part contains accordingly up to 20 % – 30 % of product.

A fraction distribution of the product when 10 % of dolomite was treated by phosphoric acid is shown in Fig. 3, b. A market fraction part was increased up to 30 % – 50 % of product and fine parts (< 2 mm of diameter)



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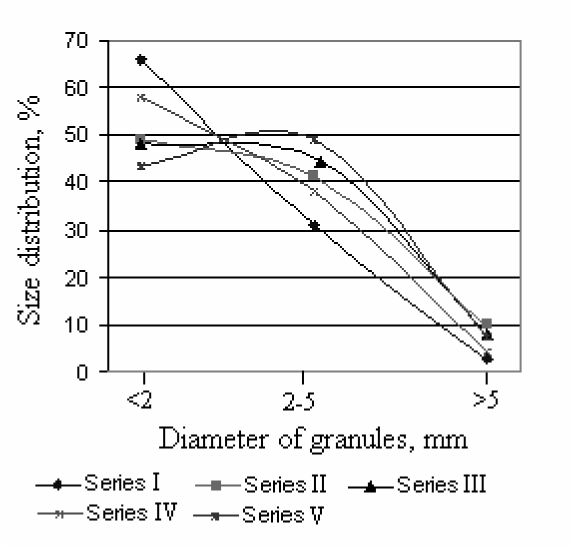

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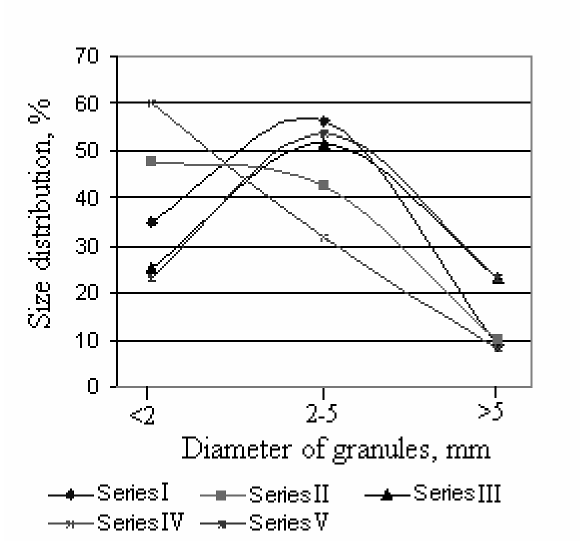

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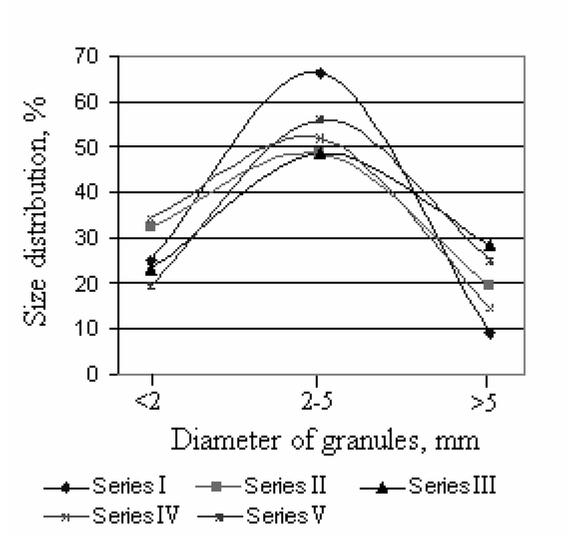

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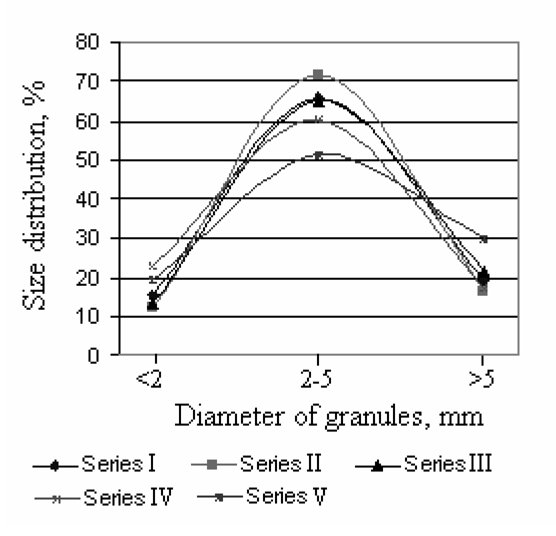

e

Fig 3. Content of market (2 mm – 5 mm diameter of granules) product obtained under different conditions at various amounts of dolomite treated by phosphoric acid (%): a – 5; b – 10; c – 15; d – 20; e – 25 contains up to 70 %. A market fraction part of product increases significantly up to 60 % when 15 % of dolomite was treated by phosphoric acid (Fig. 3, c). In this case, a product contains 25 % – 45 % of fine fraction.

The better fraction composition when 20 % of dolomite was treated by phosphoric acid in the product was obtained (Fig. 3, d).

The market size granules are the main part and contains 50 % – 65 % of product. Recycle part (< 2 mm of diameter) is equal approximately 25 % and oversize granules (> 5 mm of diameter) contains 10 % – 30 % of product. Similar results of fraction distribution when 25 % of dolomite was treated by phosphoric acid are obtained.

Dependence of fraction distribution of granules from the production method, when 5, 20 and 25 % of dolomite was treated by phosphoric acid is insignificant.

The greater dependence of fraction distribution and productions method is found when 10 % and 15 % of dolomite was treated by phosphoric acid and granulated product was obtained (Fig. 3, b and c).

The greater part of market fraction of product may be produced when granulation mixture was sprayed by water (I, III and V series) and 20 % – 25 % of dolomite was treated by phosphoric acid.

CONCLUSIONS

The main parameters of dolomite phosphorization and granulation process were determined, and physico-chemical properties of the product were measured.

The granulated dolomite may be enriched by primary nutrient phosphorus containing up to 16.39 % P_2O_5 and it is an advantage to compare with untreated dolomite.

Crushing strength directly depends on the granule diameter and the amount of dolomite treated by phosphoric acid. The highest crushing strength (5.0 kg/gran) is obtained when diameter of granules is equal 5 mm and containing 25 % of dolomite treated by phosphoric acid.

The granules size percentage distribution of product mainly depends on the ratio of dolomite and phosphoric acid.

The market product fraction (2 mm – 5 mm diameter) of granulated dolomite mainly depends on the amount of dolomite treated by phosphoric acid.

The best fraction distribution of product when 20 % – 25 % dolomite was treated by phosphoric acid and granulation mixture was sprayed by water.

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