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Study Of The Process Of Heat Treatment Of Lımestone To The Process Of Obtaınıng Calcıum-Magnesıum-Contaınıng Phosphorous Fertılızers

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Abstract

The results of studies on the processing of limestone to single phosphate fertilizers are given. It is shown that in order to reduce foaming by neutralizing of extraction phosphoric acid (EPA) with limestone, it is advisable to heat treat it at a temperature of less than 800°C for at least 60 minutes. After drying, phosphate fertilizers contain at least 98,36% digestible and at least 91,94% water-soluble form of P_2O_5.

Keywords: *limestone, extraction phosphoric acid (EPA), heat treatment, decomposition, drying, phosphate fertilizers.*

The chemical industry is the basis for the sustainable development of the agro-industrial complex of the republic. Therefore, great attention is paid to its perfecting. Two potash production facilities have been built, production of sylvinite ores and phosphate raw materials of Central Kyzylkum has been mastered. The Republic will fully meet its needs for nitrogen and potash fertilizers and exports it to neighboring regions. The security of agriculture in phosphate fertilizers does not exceed 35%, which is primarily due to the inadequate supply of phosphate to phosphate production. Delivered calcined phosphate concentrate supplied to production is processed into extraction phosphoric acid and then into ammophos, supraphos, PS-Agro, and various types of heat-treated superphosphate of the SP series [1].

In the production of ammophos, the chemical energy of phosphoric acid is used completely [2]. Upon receipt of other types of phosphorus-containing fertilizers, the chemical energy of sulfuric acid is additionally used. There is no production of double superphosphate in the republic. In the production of double superphosphate-type fertilizers, about 20% of the P_2O_5 secondary phosphate raw material remains in indigestible form and is irretrievably lost. Therefore, it is of interest to use as a secondary, calcium-containing limestone raw materials. This will allow to increase the volume of phosphate fertilizers containing calcium, to reduce the loss of P_2O_5 and ammonia costs for ammoniation [3-4].

For studies, limestone was used with the composition (mass%): CaO – 54,09; MgO – 1,07; R_2O_3 – 0,19; SO_3 – 0,09; CO_2 – 43,65; H_2O – 0,29; n – 0,62 and extraction phosphoric acid of JSC Ammophos-Maxam, obtained in the dihydrate composition (mass.%): P_2O_5 – 17,23; CaO – 0,32; MgO – 0,66; Fe_2O_3 – 0,30; Al_2O_3 – 0,41; F – 1,18. Calcination of limestone was carried out in a muffle furnace, chemical analysis of the initial, intermediate and final products was carried out using known methods [5-7].

Due to the fact that during the neutralization of EPA with limestone, abundant foaming is observed, the influence of the calcining process on the technological parameters and composition of limestone is investigated. The data obtained are shown in table 1.

Table 1
The effect of calcination temperature on the chemical composition of limestone

	T, °C	Time, min	Chemical composition, mass. %							
			CaO	MgO	R_2O_3	SO_3	CO_2	H_2O	i.r	Weight loss,%
			54,09	1,07	0,19	0,09	43,65	0,29	0,62	
	100	60	54,13	1,07	0,19	0,09	43,68	0,22	0,62	0,07
	200	60	54,13	1,07	0,19	0,09	43,68	0,21	0,62	0,08
	300	60	54,16	1,07	0,19	0,09	43,71	0,16	0,62	0,13
	400	60	54,19	1,07	0,19	0,09	43,73	0,10	0,62	0,19
	500	60	54,20	1,07	0,19	0,09	43,74	0,08	0,62	0,21
	600	60	54,25	1,07	0,19	0,09	43,78	-	0,62	0,29
	700	60	54,68	1,08	0,19	0,09	43,33	-	0,63	1,08
	800	60	55,79	1,10	0,20	0,09	42,18	-	0,64	3,05
	850	60	58,02	1,15	0,20	0,10	39,87	-	0,67	6,77
	900	60	66,67	1,32	0,23	0,11	30,90	-	0,76	18,87
	950	60	79,43	1,57	0,28	0,13	17,68	-	0,91	31,9
	1000	180	96,45	1,91	0,34	0,16	0,04	-	1,11	43,92
	1050	180	96,49	1,91	0,34	0,16	-	-	1,11	43,94

From the table it is seen that with an increase in temperature at a prodding duration of 60 minutes containing calcium oxides, magnesium, one-and-a-half oxides and CO_2 increases proportionally in the degree of moisture removal to a temperature of 500°C. Starting with a temperature of 800°C, CO_2 containing decreases, while the remaining components increase. So, at a temperature of 800°C, the CO_2 content is 42,18%; CaO - 55,79; MgO - 1,1; R_2O_3 - 0,20; SO_3 - 0,09; CO_2 - 42,18 and n - 0,64. Increasing the temperature to 1000°C reduces the content of CO_2 to 0,04% and increases the content of the remaining components. Complete removal of CO_2 is observed when piercing calcium-magnesium-containing waste at a temperature of 1050°C for 60 minutes and at a temperature of 1000°C for 3 hours.

To determine the optimal temperature for calcining calcium-magnesium-containing limestone, the effect of the process duration on the foaming during the neutralization of an extraction phosphate acid containing 1% by weight of ammonium nitrate was studied. Ammonium nitrate helps to increase the solubility of calcium and magnesium phosphates in the resulting suspension. The acid norm was maintained 100% in the stoichiometry for the formation of monosubstituted phosphates of calcium, magnesium, and medium phosphates of sesquioxides at a temperature of 20–25 ° C.

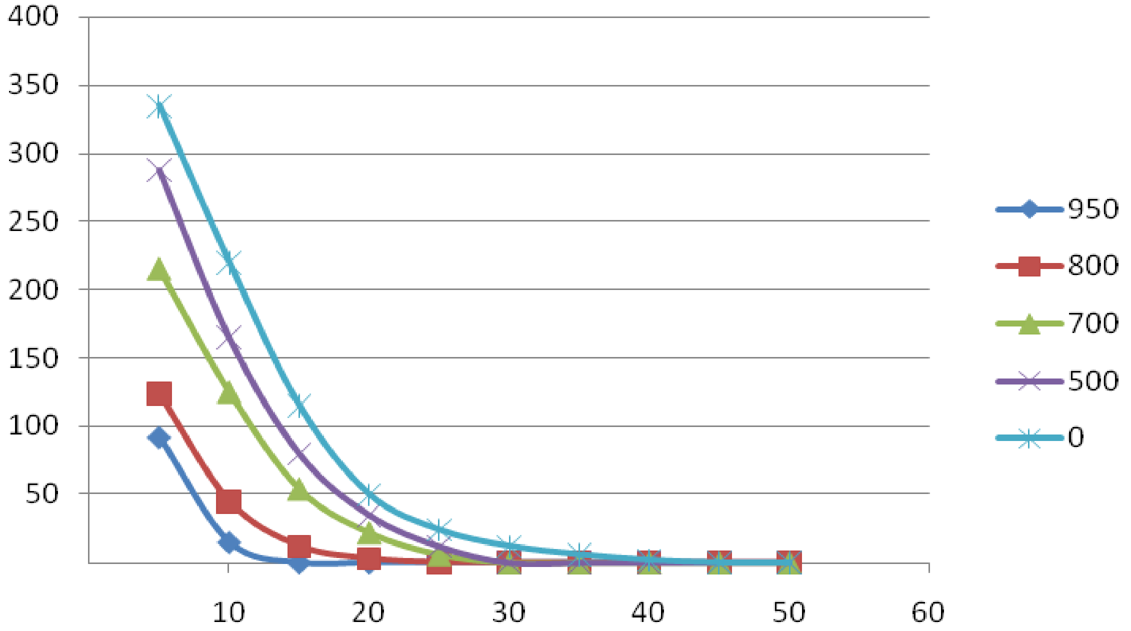

Fig. 1. Kinetics of the degree of foaming of the process of neutralizing EPA with limestone: 1 - not heat-treated; 2 - 500 ° C; 3 - 700 ° C; 4 - 800 ° C; 5 - 950 ° C.

Figure 1 shows the height of the foam in% relative to the height of the acid in the reactor before the introduction of waste. It can be seen from the figure that with the introduction of un-calcined limestone into the initial acid, the height of the foam reaches 335% within 5 minutes, and for its complete decay it takes 45-50 minutes. This indicates that it takes 2.5–3 times less time to fully quench a stable foam than it does with respect to natural calcium and magnesium carbonate raw materials. When neutralizing EPA with limestone subjected to heat treatment up to 500 ° C, the formation of a stable foam reaches 288%, the duration of its quenching is 30 minutes, and when neutralizing EPA with calcium and magnesium carbonate wastes, heat-treated at 700 ° C, the foam is 215%, and with more high temperatures 92–124%. Duration of foam quenching is 10-15 minutes.

From this it follows that in order to reduce foaming in the process of neutralization of EPA, calcium and magnesium-containing wastes of nitrogen-tour production, it is advisable to use thermally treated raw materials, calcined at 800°C for 60 minutes.

The processes of neutralizing EPA with limestone and calcination products at 800°C in the presence of 1% ammonium nitrate, as well as the processes of obtaining phosphate fertilizers containing calcium and magnesium phosphates, by evaporation and drying of suspensions were studied. The neutralization process was carried out at room temperature (20-25°C) for 30 minutes at a stoichiometric acid rate. The resulting suspension was dried at a temperature of 95-100°C. Technological parameters of the process, the chemical composition of the intermediate suspensions and final products are shown in table 2 and 3.

Table 2.

The chemical composition of suspensions, products their drying and technological indicators of the process of neutralizing EPA with limestone

Indicators	The chemical composition, wt. %	
	suspension	product
P_2O_5 (tot.)	15,64	48,05
P_2O_5 (ass.)	15,40	47,26

P_2O_5 (w.s.)	14,48	44,18
CaO (tot.)	6,76	20,77
MgO (tot.)	0,74	2,29
R_2O_3 (tot.)	1,10	3,38
SO_3 (tot.)	0,76	2,33
F	1,03	0,60
N (tot.)	0,32	0,99
H_2O	67,75	0,92
$(P_2O_{5ass.}:P_2O_{5tot.})\times100$	98,45	98,36

Table 3.
The chemical composition of suspensions, products their drying and technological parameters of the process of neutralizing EPA with products of calcination of limestone

Indicators	The chemical composition, wt. %	
	suspension	product
P_2O_5 (tot.)	15,95	47,88
P_2O_5 (ass.)	15,67	46,98
P_2O_5 (w.s.)	14,73	43,96
CaO (tot.)	6,79	20,38
MgO (tot.)	0,76	2,23
R_2O_3 (tot.)	1,11	3,33
SO_3 (tot.)	0,76	2,28
F	1,05	0,58
N (tot.)	0,32	0,97
H_2O	67,27	1,75
$(P_2O_{5\ ass.}:P_2O_{5\ tot.})\times100$	98,24	98,12

As a result of the research, suspensions were obtained, which are formed in the process of neutralizing EPA with calcium and magnesium limestone, as well as the products of their calcination composition (wt.%): $P_2O_{5\ total}$ – 15,64 and 15,95; $P_2O_{5\ ass.}$ – 15,40 and 15,67; $P_2O_{5\ w.s.}$ – 14,48 and 14,73; CaO – 6,76 and 6,79; MgO – 0,74 and 0,76; N – 0,32 and 0,32; H_2O – 67,75 and 67,27. In suspensions, the content of digestible phosphorus, i.e. the ratio ($P_2O_{5\ ass.}$: $P_2O_{5\ total}$) × 100 is 98,45% and 98,24%, respectively.

As a result of drying the resulting suspensions at a temperature of 95 ÷ 100°C, calcium and magnesium-containing phosphate fertilizers of the composition (mass%) were obtained: $P_2O_{5\ total}$ – 48,05 and 47,88; $P_2O_{5\ ass.}$ – 47,26 and 46.98; $P_2O_{5\ w.s.}$ – 44,18 and 43,96; $P_2O_{5\ ass.}$ – 2,05 and 1,96; CaO – 20,77 and 20,38; MgO – 2,29 and 2,23; N = 0,99 and 0,97; H_2O – 0,92 and 1,75. The ratio ($P_2O_{5\ ass.}$: $P_2O_{5\ total}$) × 100 is 98,36 and 98,12%, and the ratio ($P_2O_{5\ ass.}$: $P_2O_{5\ total}$) × 100 is 91,94 and 91,83%, respectively.

Thus, studies have shown the possibility of processing limestone for single phosphate fertilizers by neutralizing EPA containing 1% ammonium nitrate. To this end, it is advisable to pre-heat the limestone at 800 ° C for 60 minutes.

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