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PRODUCTION OF NP FERTILIZERS BASED ON THE DECOMPOSITION OF POOR PHOSPHATES USING A MIXTURE OF PHOSPHORIC AND SULPHURIC ACIDS

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ABSTRACT

The present communication reports results on the investigation of phosphate fertilizer process production. It refers to the decomposition of a phosphorite powder (18.7% P_2O_5) using a mixture of sulphuric and phosphoric acids at ratios ($SO_3 : P_2O_5$) of 1.2; 1.65; 2.6, as well as acid mixture to a phosphorite powder ratios ranging from 100:10 to 100:80. The advantages of this process in comparison with commercial ammonium sulphate-phosphate are shown. The optimal value of the acid mixture : a phosphorite powder providing granular NPSCa-fertilizers of a high content of the total and the acceptable form of P_2O_5 and CaO (more than 50% of water soluble P_2O_5 in this case) is determined. It is found that the granular fertilizers are stable enough reaching 2 MPa. The material balances in case of the acids mixtures based on the commercial way ($SO_3 : P_2O_5$ = 1.2; 1.65; 2.6) and an acid mixture : a phosphorite powder of 100 : 50 are estimated.

Keywords: phosphorites, wet-process phosphoric acid, sulfuric acid, decarbonization.

INTRODUCTION

It is well recognized that in case the phosphoric acid presence exceeds the corresponding stoichiometric amount by 5 % - 10 % in the course of formation of monobasic calcium phosphate the decomposition rate during the first stage of the process is high but starts to decrease dramatically with time. The process is brought to an end at a decomposition level of 80 % - 90 % [1]. This is especially valid in case of phosphate interaction with wet-processing phosphoric acid when a low-grade Central Kyzyl kum phosphorite, unsuitable for double superphosphate production [2], is used. The decomposition process of the raw phosphate with phosphoric acid can be intensified by using a small amount of sulphuric acid [3-6]. The method had been patented. It refers to the production of a phosphate fertilizer on the ground of decomposition of a raw phosphate with phosphoric acid in presence of sulphuric acid followed by granulation of the resulting slurry and drying of the neutralization product with ammonia [7].

To increase the amount of acceptable P_2O_5 on citric acid the decomposition process of the raw phosphate is carried out at a weight ratio of SO_3 to P_2O_5 in sulphuric and phosphoric acids amounting to 0.1-0.5 : 1.0 and $H_3PO_4 : \Sigma$ CaO, MgO, R_2O_3 in the raw material equal to 0.9 – 2.2 : 1.0. The slurry obtained is neutralized until granulation and subsequently dried. Thus the process takes place with decreased ammonia loss and fluoride compounds emission [7].

The phosphate treatment with phosphoric acid in presence of a great amount of sulphuric acid results in complete decomposition of the carbonates. This step is then followed by destroying the main mass of the phosphate particles and a change of the crystal structure of the undecomposed phosphate mineral. Thus P_2O_5 in the raw phosphate is transferred from an unacceptable form into one acceptable for the plants due to generated salts.

This proceeds during the stage of the slurry ammonization and the subsequent thermal processing.

The joint stock company (JSC) "Ammofos-Maxam" has implemented the novel type of nitrogen-phosphate fertilizer operations. The latter lead to the production of ammonium sulphate-phosphate using ammonization of a wet-processed phosphoric and sulphuric acids mixture [8]. Three grades of the product (A, B, C) are produced depending on the consumer requirements. Prior to that the properties of the phosphoric and sulphuric acids mixtures (of SO_3 to P_2O_5 ratio ranging from 1.2 to 13.5) and the composition of the ammonization products are determined [9, 10] under laboratory conditions.

The aim of the present investigation is to follow the effect of the sulphuric to phosphoric acid ratios as well as those of the acids mixture to the phosphorite powder on the phosphate fertilizer process in case of treatment of a phosphorite powder from Central Kyzyl kum.

EXPERIMENTAL

The present study was carried out in case of a sulphuric to phosphoric ($SO_3 : P_2O_5$) ratio to be 1.2; 1.65 and 2.6. After ammonization process till pH of 4.5 and a thermal treatment the ammonium sulphate-phosphate products obtained had the following composition: (i) P_2O_{5total} - 25.14 mass %; N - 16.09 mass %; $P_2O_{5acceptable}$ - 25.01 mass %; $P_2O_{5water\text{-}soluble}$ - 21.81 mass %; SO_3 - 36.08 mass % in case of $SO_3 : P_2O_5 = 1.2$; (ii) P_2O_{5total} - 20.47 mass %; N - 17.22 mass %; $P_2O_{5acceptable}$ - 20.26 mass %; $P_2O_{5water\text{-}soluble}$ - 17.56 mass %; SO_3 - 40.97 mass % in case of $SO_3 : P_2O_5 = 1.65$; (iii) P_2O_{5total} - 15.37 mass %; N - 18.26 mass %; $P_2O_{5acceptable}$ - 15.18 mass %; $P_2O_{5water\text{-}soluble}$ - 13.12 mass %; SO_3 - 45.93 mass % in case of $SO_3 : P_2O_5 = 2.6$. The mixtures were prepared using the wet-processing phosphoric acid (WPA) obtained by a dehydrated method at JSC "Ammofos-Maxam". It

Table 1. Experimental amounts used for $Ca(H_2PO_4)_2$ production in the course of wet-processing phosphoric and sulphuric acids during a phosphorite powder treatment.

Weight ratio of acid : phosphorite powder	Norm of acids mixes, (mass%)	Including		Ratio of $H_2SO_4 : H_3PO_4$, (mass%)
		H_2SO_4, (mass%)	H_3PO_4, (mass%)	
SO_3/P_2O_5 = 1,2 (14.46% P_2O_5, 17.39% SO_3)				
100:10	441	300	141	68 : 32
100:30	147	100	47	68 : 32
100 : 44.2	100	68	32	68 : 32
100:50	88	60	28	68 : 32
100:60	73.5	50	23,5	68 : 32
100:80	56	38	18	68 : 32
SO_3/P_2O_5 = 1.65 (10.79% P_2O_5, 17.83% SO_3)				
100:10	414	309	105	75 : 25
100:30	138	103	35	75 : 25
100 : 41.4	100	75	25	75 : 25
100:50	83	62	21	75 : 25
100:60	69	51.5	17.5	75 : 25
100:80	52	38.6	13.2	75 : 25
SO_3/P_2O_5 = 2.6 (6.72% P_2O_5, 14.47% SO_3)				
100:10	316	250.5	65.5	79 : 21
100:30	105	83.5	21.8	79 : 21
100 : 31.75	100	79	21	79 : 21
100:50	63	50	13	79 : 21
100:60	53	42	11	79 : 21
100:80	40	31,5	8,5	79 : 21

contained 18.69 mass % of P_2O_5, 0.26 mass % of CaO, 0.64 mass % of MgO, 0.73 mass % of Al_2O_3, 0.46 mass % of Fe_2O_3, 2.72 mass % of SO_3, 1.02 mass % of F, 0.093 mass % of Cl, and 95 mass % of sulphuric acid. A phosphorite powder from Central Kyzyl kum containing18.70 mass % of P_2O_5, 47.83 mass % of CaO, 15.3 mass % of CO_2, 1.24 mass % of Al_2O_3, 1.05 mass % of Fe_2O_3, 1.75 mass % of MgO, 2.00 mass % of F, 0.1 mass % of Cl was used for the production.

The procerdure of the batch-scale experiment was as follows: a certain amount of the acids mixture was poured into a temperature–controlled glass and a sample of the phosphorite powder was slowly added under constant stirring. The weight ratio of the acids ranged from 100 : 10 to 100 : 80. The interaction process was of 15 min duraction at 50°C.

RESULTS AND DISCUSSION

The phosphorite powder decomposition process with phosphoric and sulphuric acids takes place in correspondence with:

$Ca_5F(PO_4)_3 + 5H_2SO_4 \quad 3H_3PO_4 + 5CaSO_4 + HF$

$Ca_5F(PO_4)_3 + 7H_3PO_4 + 5H_2O \quad 5Ca(H_2PO_4)_2 \cdot H_2O + HF$

The stoichiometric amount of the acids required for mono basic calcium phosphate production is as follows: 44.2 g of a phosphorite powder are required in case of 100 g of acids mixture of $SO_3 : P_2O_5 = 1.2$; 41.4 g of a phosphorite raw are needed in case of 100 g of acids mixture of $SO_3 : P_2O_5 = 1.65$, while 31.75 g have to be used at SO_3 to P_2O_5 ratio of 2.6. The experimental amounts used are summarized in Table 1.

The acid phosphate slurries obtained are ammoniated by ammonia till reaching a pH value of 3.8 - 4.0. They are dried initially at 80°C, and then at 105°C. The granulation of the wet phosphate samples is performed in the course of the thermal treatment with the application of intensive mixing and balling. The samples dried are subjected to chemical analyses determining [11] the presence of various forms of P_2O_5 and CaO, as well as that of total N. The acceptable form of P_2O_5 is identified using citric acid and EDTA, while that of CaO – using only citric acid. The pH value of the product is obtained by measuring that of its 10 %-water suspension solution obtained by stirring for an hour.

The granule strength is tested using MIP-10-1 [12]. The data referring to the components content and the granules strength are given in Table 2, Fig. 1 and Fig. 2.

As shown by Table 2 and Fig. 1 the decomposition of the phosphorite powder with phosphoric and sulphuric

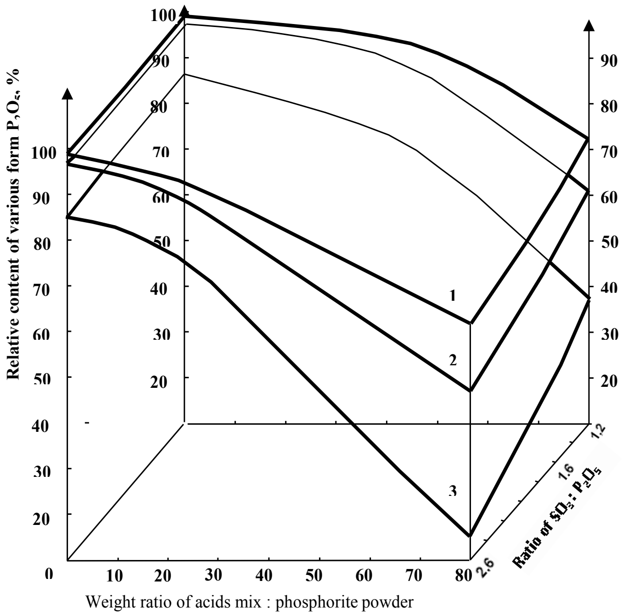

Fig. 1. Dependence of the relative P_2O_5 content determined in respect to citric acid (1), EDTA (2) and water-soluble P_2O_5 (3) versus the acids mixture: phosphorite powder weight ratios and that of SO_3/P_2O_5.

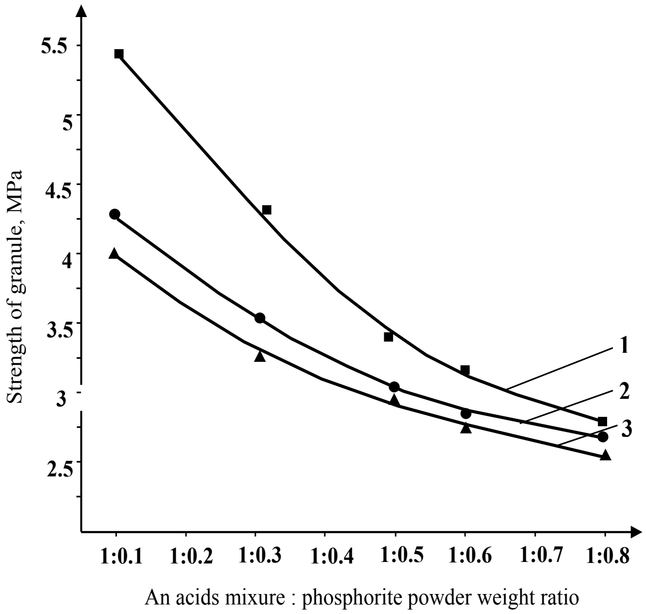

Fig. 2. Strength of the granules obtained depending on the weight ratio of the acids mixture : a phosphorite powder at SO_3/P_2O_5 : 1 – 1.2; 2 – 1.65; 3 – 2.6.

Table 2. Composition of phosphate fertilizers obtained by processing a phosphorite powder by phosphoric and sulphuric acids mixtures.

Weight of acid mix: Phosphorite powder	pH of dried products	Chemical composition, (mass%)							$\frac{P_2O_{5acceptable}}{P_2O_{5total}}$ x100 on citric acid, %	$\frac{P_2O_{5acceptable}}{P_2O_{5total}}$ x1 on EDTA %
		N	P_2O_5 total	CaO_{total}	P_2O_5 acceptable on citric acid	P_2O_5 acceptable on EDTA	P_2O_5 water-soluble	CaO acceptable, on citric acid		
Acids mix (77.56 g of WPA+22.4 g of H_2SO_4) at SO_3/P_2O_5 = 1.2 (14.5%P_2O_5, 17.37% SO_3)										
100:10	3.36	11.70	25.95	9.04	25.76	25.18	21.47	9.03	99.27	97.03
100:30	3.57	5.41	25.61	18.49	24.47	23.82	19.91	14.30	95.55	93.01
100:50	3.67	3.23	25.45	25.44	23.37	21.61	17.21	19.38	91.83	84.91
100:60	3.71	2.65	25.30	27.78	21.76	19.19	14.27	19.75	86.00	75.85
100:80	3.77	1.39	25.13	31.84	18.42	15.46	9.61	20.88	72.34	60.75
Acids mix (57.9 g of WPA+23.0 g of H_2SO_4+19.1g of H_2O) at SO_3/P_2O_5 = 1.65 (10.82%P_2O_5, 17.83% SO_3										
100:10	3.44	11.06	21.51	8.07	20.89	20.83	18.24	7.99	97.12	96.84
100:30	3.54	5.39	22.48	19.85	20.87	20.87	17.01	15.16	92.84	91.06
100:50	3.58	2.99	23.01	27.60	19.93	19.93	14.39	20.28	86.61	78.83
100:60	3.62	2.21	23.25	30.12	18.69	16.38	11.95	21.06	80.39	70.45
100:80	3.70	1.27	23.50	34.18	16.58	13.55	6.25	22.27	70.55	57.66
Acids mix (36.05 g of WPA+22.52 g of H_2SO_4+41.43 g of H_2O) at SO_3/P_2O_5 = 2.6 (6.74%P_2O_5, 17.47% SC										
100:10	3.41	10.25	17.73	10.38	17.07	16,84	14.63	10.17	96.28	94.98
100:30	3.44	4.68	19.21	22.68	16.84	16,10	13.27	17.07	86.11	84.98
100:50	3.90	2.73	19.83	29.57	15.72	13,68	9.18	21.4	79.27	68.99
100:60	4.02	2.32	20.46	32.73	14.91	12,69	7.42	20.64	72.87	62.02
100:80	4.1	1.14	21.94	37.41	13.58	10,34	3.32	22.91	61.90	47.13

acids leads to the production of concentrated phosphorus fertilizers of a high content of an acceptable form of P_2O_5 and CaO. For instance, at an acid mixture : a phosphorite powder weight ratio of 100 : 10, fertilizers of a high content of nitrogen (10.25 % - 11.70 %) are obtained. The application of a mixture of SO_3 : P_2O_5 ratio of 1.2 : 1 and an increase of the mass of the phosphorite powder from 10 % to 80 % results in a decrease of the nitrogen content of the product from 11.70 % to 1.39 %, of the relative content of P_2O_5 acceptable on citric acid ranged from 99.27 % to 72.34 %, that of CaO to be from 99.89 % to 65.58 %, and that of P_2O_5 water-soluble varied from 83.70 % to 37.76 %. It is obviously that increase of the sulphuric acid content in the mixture with phosphoric acid reaching SO_3 : P_2O_5 ratio of 1.65 and 2.6 with the simultaneous increase of the fraction of the treated phosphorite powder from 10 to 80 leads to a further decrease of the values mentioned above.

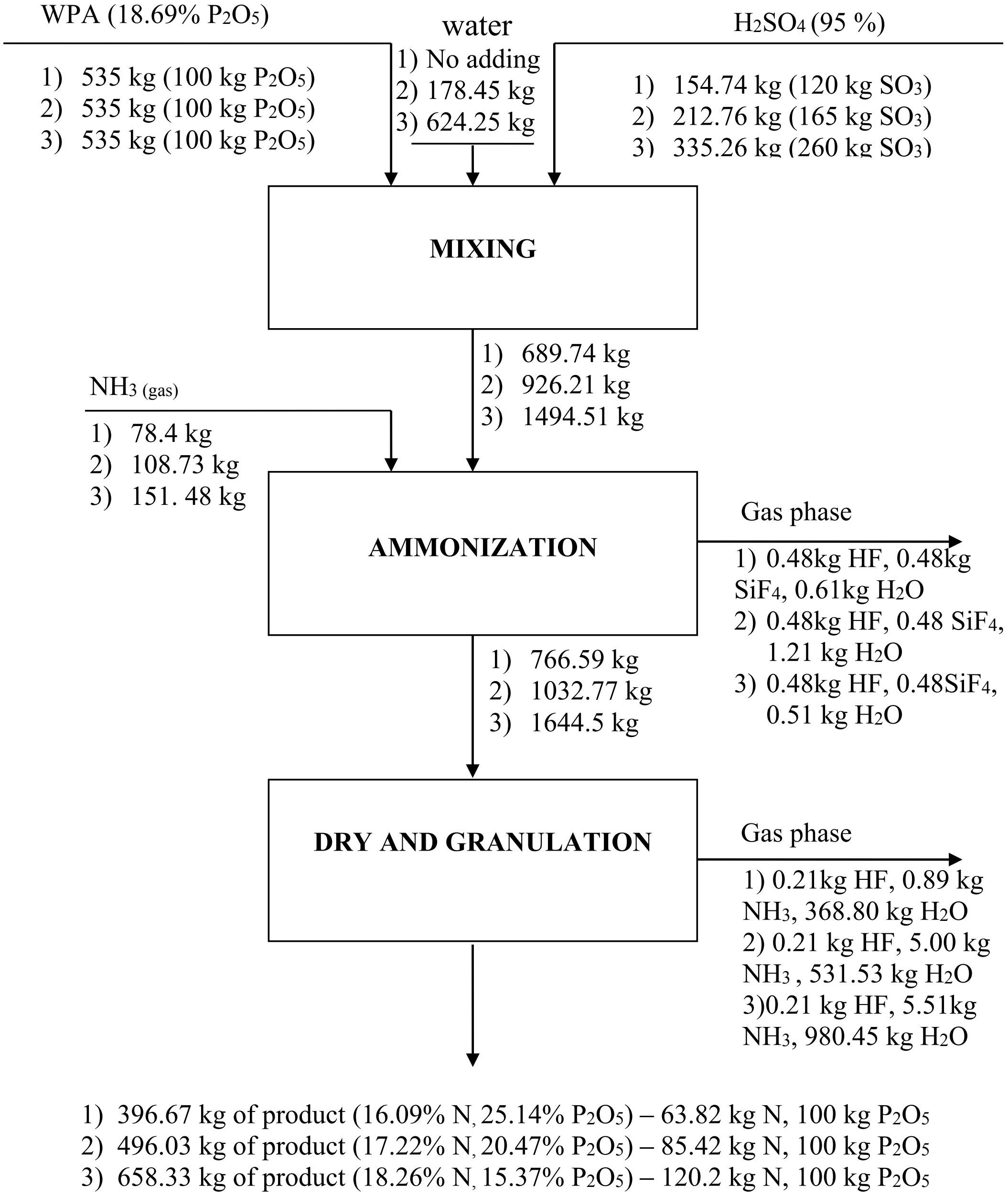

Fig. 3. A material balance of the commercial ammonium sulphate-phosphate process at SO_3/P_2O_5 ratio of: (1) – 1.2; (2) – 1.65; (3) – 2.6.

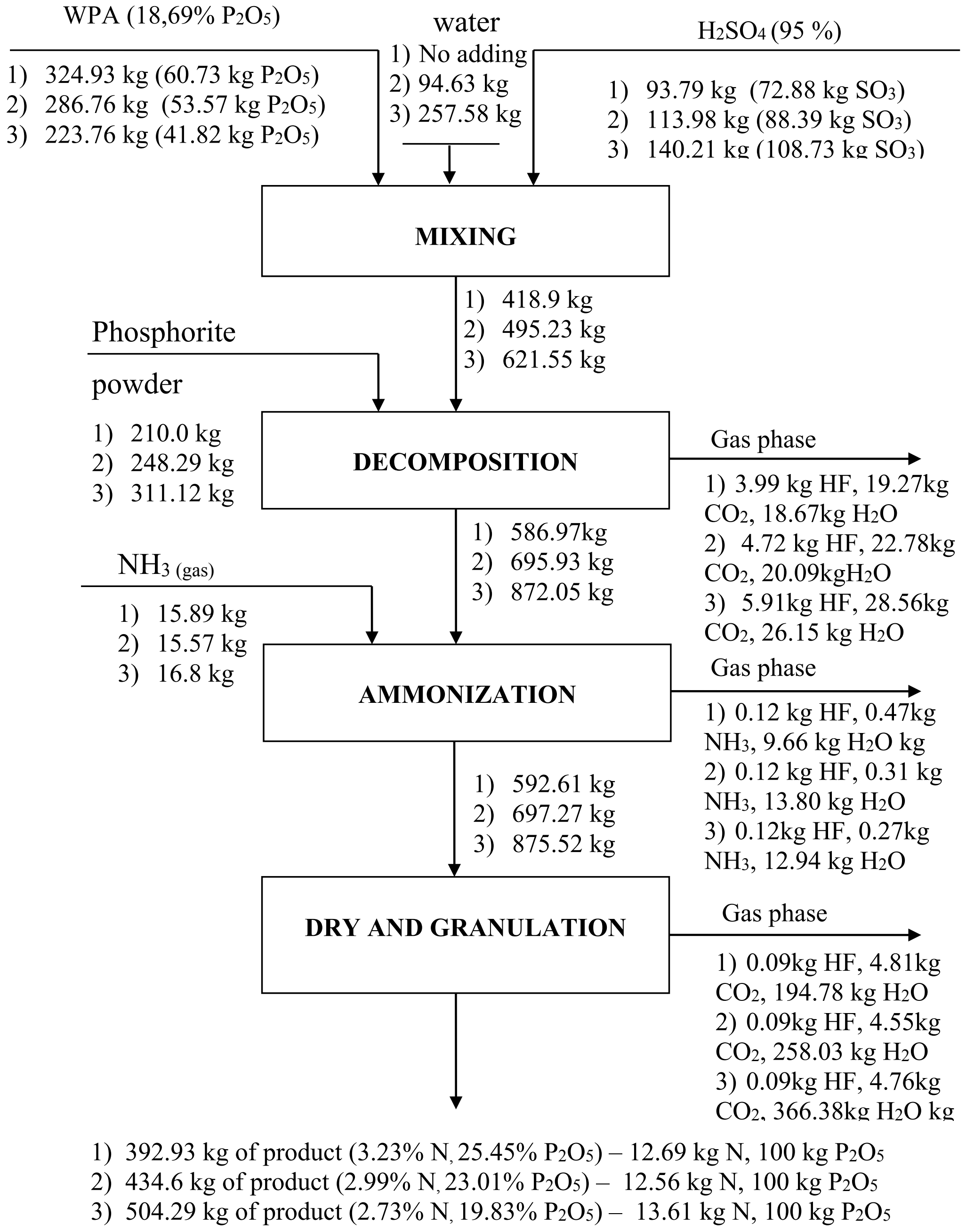

Fig. 4. A material balance of the phosphate fertilizer based on decomposition of phosphorite powder from Central Kyzyl kum in case of SO_3/P_2O_5 ratio of : (1) – 1.2; (2) – 1.65; (3) – 2.6 and an acid mixture : a phosphorite powder weight ratio of 100 : 50.

The agrochemists appreciate phosphate fertilizers of a higher content of total and acceptable form of P_2O_5 and no less than 50% of a relative content of a water-soluble form of P_2O_5. As shown above the fertilizer obtained in case of $SO_3 : P_2O_5 = 1.2$ and an acid mixtute : a phosphorite powder ratio of 100 : 60 contains $P_2O_{5totlal} = 25.30$ %, $P_2O_{5acceptable\ on\ citric\ acid} = 86.0$ %, $P_2O_{5water\text{-}soluble}$ = 56.40 %, nitrogen – 2.65 %. However, in case of $SO_3 : P_2O_5$ ratio of 1.65 and a mass fraction of the phosphorite powder of 60, the relative content of the water-soluble form of P_2O_5 in the product refers to 51.40 %. The amount of $P_2O_{5water\text{-}soluble}$ in the product exceeds 50 % (it constitutes 69.08 %) when the $SO_3 : P_2O_5$ ratio amounts to 2.6 and the acids mixture : a phosphorite powder ratio amounts to 100:30. It is worth noting that the product obtained in the course of the interaction of sulphuric and phosphoric acids mixtures with a phosphorite powder of all SO_3 : P_2O_5 ratios studied contains a large amount of an acceptable form of CaO (it ranges from 61.24 % to 99.89 %). The products obtained can be called phosphorus-calcium containing fertilizers.

Table 2 shows that the products obtained have a high strength. The most stable one is that obtained in the course of processing a phosphorite powder with an acids mixture of SO_3 : P_2O_5 ratio to be 1.2 and an acids mixture:phosphorite powder weight ratio of 1 : 0.1. The value obtained in this case amounts to 5.3 MPa. However, the increase of sulphuric acid presence in the acids mixture and that of the phosphorite powder result in strength decrease to 0.8 MPa, although it is high (2.5 MPa - 2.6 MPa) even at an acids mixture : a phosphorite powder weight ratio of 1 : 0.8.

The material balances referring to the production of 100 kg of P_2O_5 in form of three brands of ammonium sulphate-phosphate and three phosphate-containing fertilizers using phosphorite powder decomposition in case of an acids mixture : a phosphorite powder weight ratio of 100 : 50 are calculated. These balances are given in Fig. 3 and 4.

As evident from Figs. 3 and 4, some P_2O_5 in the phosphate fertilizer is exchanged on the ground of a much cheaper phosphate powder when compared with the ammonium sulphate-phosphate fertilizer produced by the conventional method. For instance, the fertilizer obtained in presence of SO_3/P_2O_5 ratio of 1 - 1.2 contains 39.27 kg of P_2O_5 introduced through the phosphate powder. The corresponding benefit amounts to 58.18 kg of P_2O_5 when SO_3/P_2O_5 ratio is equal to 1 - 2.6 It is evident that an economic advantage is obtained on the ground of using a low cost raw material.

CONCLUSIONS

The process of production of phosphorus containing fertilizers through decomposition of a high calcareous phosphorite powder in acids mixture followed by neutralization by gaseous ammonia, drying and granulation is investigated. The weight ratio of $SO_{3sulfuric}$ acid to P_2O_{5WPA} is varied from 1.2 to 2.6, while the acids mixture to a phosphorite powder weight ratio is changed from 100 : 10 to 100 : 80. It is shown that the higher sulphuric acid presence in the mixture brings about a lower P_2O_5 content of the product. The increase of SO_3/P_2O_5 weight ratio does not greatly affect the nitrogen content, while that of the ratio of acids mixture to the phosphorite powder decreases dramatically the amount of the products obtained. The optimal acids mixture to a phosphorite powder ratio of 100 : 60 was found to be $SO_3/P_2O_5 = 1.2$ and 1.65, while that of 100 : 30 corresponds to $SO_3/P_2O_5 = 2.6$. These cases lead to the production of phosphorus-calcium containing fertilizers of a high content of a total and acceptable form of P_2O_5 as well as to no less than 50% relative water soluble P_2O_5. The material balances referring to the phosphate fertilizers production are presented.

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