

Decreasing Environmental Pollution in Superphosphate Production Using Apatite and Phosphorite Mixture

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Abstract—The enhanced need for food items is receiving more importance due to a gradual increase in the world population and, in this scenario, fertilizers play a very important role in agriculture. In this study, the production of the normal superphosphate was investigated with a continuous chamber method by adding potassium chloride to a mixture of Hibin apatite and Kingisepp phosphorite. In the experiments, the following parameters were selected: The concentration of sulfuric acid (54–66% (w/w)), the stoichiometric norm of sulfuric acid (100, 107, 110, 114% (w/w)), the ratio of apatite/phosphorite in the mixture of phosphate (95/5, 90/10, 85/15, 80/20, 75/25, 70/30, 65/35, 60/40, 55/45, 50/50 (w/w)), potassium chloride/the mixture of phosphate (1/50, 2/50, 3/50, 4/50, 5/50 (w/w)), and the reaction time (2–8 min). It was observed that by adding potassium chloride to a low-grade phosphorite and using it to substitute a fraction of high-grade apatite in the normal superphosphate production not only resulted in a high-quality product but also eliminated the waiting period for the maturation of superphosphate in the storage. The objective of this study was to produce a normal superphosphate fertilizer by using a continuous chamber method in order to accelerate the production process and to reduce the environmental pollution caused by fluoride gases by eliminating the maturation time in the storage.

Keywords—Continuous chamber method, environmental pollution, fluoride gases.

I. INTRODUCTION

THE world population gradually enhanced the need for mineral fertilizers. The global population which was threatened by a lack of soil fertility in 1850 was less than 1.5 billion; by 2050 this may have grown to 9.2 billion [1]. This scenario shows the importance of the production of fertilizers. In the next five years, the production of fertilizers will increase to 14% and achieve 184 million metric tons (with respect to 100% nutrition material), and about 50 million metric tons of which will be phosphorous fertilizers. Single superphosphate is considered as one of the most crucial and widely known sources of phosphorus in agriculture [2]. It is a well-known fact that 90% phosphate fertilizers worldwide are produced by using the high-quality apatite rock [3]. The lack of the high-grade phosphorite reserves and the low-rate production methods are two main problems that are required to be overcome in the production of phosphorous fertilizers.

A number of studies have been conducted to improve the production quality of phosphorous fertilizers by using the low-

grade minerals. The low-grade Tashkur phosphorite was used for producing the normal superphosphate investigating the content and physicochemical properties of superphosphate. It was observed that the leaching rate of phosphorite depends on the concentration and the stoichiometric amount of sulfuric acid [4]. Beglov et al. investigated the increase in the activity of the low-grade raw material of phosphate by using chemical and mechanical treatments. They showed that the activated low-grade phosphate can be used for the production of fertilizers [5]. Recebov et al. studied the production of mineral fertilizers containing phosphorous by using the low-grade Kızılkum phosphorite [6]. In this study, it was investigated that in the product, the amount of P_2O_5 decreases and the number of impurities increases with the use of the low-grade phosphorite ore. Therefore, it is important to maintain the quality of the product while using the low-grade raw materials. Petropavlovskiy investigated the methods of producing the low-grade phosphorite fertilizers. However, it is a well-known fact that the amount of P_2O_5 decreases and the number of impurities increases with the use of the low-grade raw material of phosphate. The primary objective of using the low-grade raw materials is to improve the quality of the product [7]. In other studies, the mixtures of apatite and phosphorite were used for producing the standard superphosphate [8]–[10]. Using the low-grade phosphorite in lieu of some part of apatite resulted in a decrease in the production time from 21 days to 10 days without decreasing the quality of the superphosphate obtained. The gaseous exhausts containing fluorine are emitted from the storage during the maturation period of superphosphate, which causes the environmental pollution. This pollution can be prevented or minimized by reducing the maturation period of superphosphate in the storage, which can be possible by producing superphosphate by using the continuous flow and continuous chamber methods [11]–[13]. These methods not only minimize the environmental pollution caused by fluorine-containing exhausts but also accelerate the process of production of fertilizers.

The objective of this study was to produce the normal superphosphate fertilizer by using the continuous chamber method in order to accelerate the production process and to reduce the environmental pollution caused by fluoride gases by eliminating the maturation time in the storage. It is a well-known fact that 1 kg of fluoride gas is emitted from each ton of P_2O_5 production by using the chamber superphosphate method. In addition, we also aimed to use the low-grade

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phosphorite ore replacing a fraction of the apatite concentrate to improve the quality of the product.

II. MATERIALS AND METHODS

A. The Preparation of Materials

In this study, the Hibin apatite concentrate and Kingisepp phosphorite, with a particle size of 147 μm , purchased from Russia, were used. The chemical contents of the ores and their mixtures are presented in Table I.

B. Dissolution Process

A definite amount of the mixture of apatite concentrate–phosphorite–potassium chloride was added to the solution of sulfuric acid with a definite concentration and volume and then the whole mixture was heated at 50 °C in a glass reactor. After that, this content in the reactor was stirred at a rate of 550 rpm for 8 min. As sulfuric acid and phosphate ore were mixed in the reactor, the samples were taken and analyzed after every 2, 4, 6, and 8 min. Then, the superphosphate pulp was poured into a porcelain beaker and kept in a drying oven at 110–115 °C for 1.5 h. Finally, the sample was cooled. Then, P_2O_5 and all its variants, K_2O , and moisture contents of the mixture were analyzed by using the standard methods [14]. The dissolution percentage of phosphate was determined according to the analytical data. The experimental system used in this study is shown in Fig. 1.

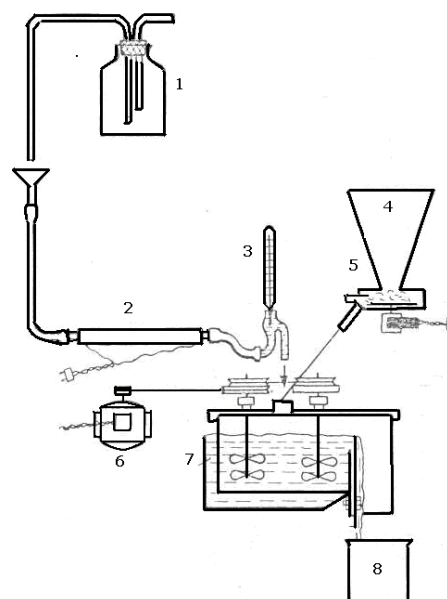


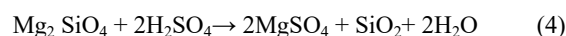
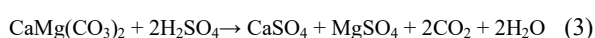
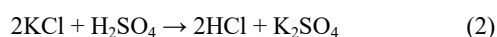
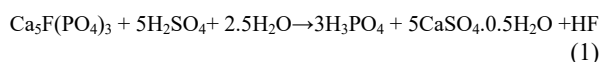
Fig. 1 Schematic representation of the production of superphosphate: The parts of the apparatus used are (1) acid flow controller, (2) heater, (3) thermometer, (4) storage bunker, (5) phosphate flow controller, (6) mixer, (7) the reactor, and (8) porcelain beaker

TABLE I
THE CHEMICAL COMPOUNDS OF THE APATITE CONCENTRATE, PHOSPHORITE ORE, AND THEIR MIXTURES

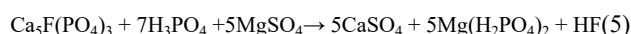
Phosphate Ores (%)		Compounds (%)							
Apatite	Phosphorite	P_2O_5	CaO	MgO	R_2O_3	CO_2	F	Insolubles	$(\text{MgO}/\text{P}_2\text{O}_5) \times 100$
100	-	39.40	52.00	0.15	0.95	-	3.17	1.10	0.38
-	100	28.00	42.00	2.50	3.00	4.60	2.50	12.00	8.93
95	5	38.83	51.50	0.27	1.05	0.23	3.14	1.57	0.69
90	10	38.26	51.00	0.39	1.16	0.46	3.10	2.14	1.01
85	15	37.69	50.50	0.503	1.258	0.69	3.070	2.71	1.34
80	20	37.12	50.00	0.620	1.360	0.92	3.036	3.28	1.67
75	25	36.55	49.50	0.750	1.463	1.15	3.003	3.85	2.05
70	30	35.89	49.00	0.855	1.565	1.38	2.969	4.42	2.38
65	35	35.41	48.50	0.973	1.668	1.61	2.936	4.99	2.75
60	40	34.84	48.00	1.090	1.770	1.84	2.902	5.56	3.13
55	45	34.27	47.50	1.208	1.873	2.07	2.869	6.13	3.53
50	50	33.70	47.00	1.325	1.975	2.30	2.835	6.70	3.93

III. RESULTS AND DISCUSSION

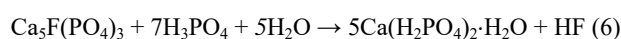
The dissolution of the mixture of apatite–phosphorite–KCl in the solutions of sulfuric acid takes place in three stages [15]. In the first stage, the following reactions occur. Therefore, the final solution contains phosphoric acid, potassium sulfate, and magnesium sulfate as:



In the second stage, some of the remaining phosphate reacts with magnesium sulfate and phosphoric acid and yields monomagnesium phosphate as:



In the third stage, the remaining phosphate reacts with phosphoric acid that was obtained in the first stage and converted into monocalcium phosphate as:



As shown above, HCl is produced along with phosphoric acid in the first stage and this accelerates the second stage because of the acidic effect of HCl. The change in the dissolution percentage of the mixture of apatite–phosphorite–potassium chloride (the ratio of KCl to a mixture of phosphate raw material = 2/25) with the reaction time is shown in Fig. 2. The stoichiometric amount of sulfuric acid (from the feedstock of 60 (w/w)) with 10% excess was used in these experiments.

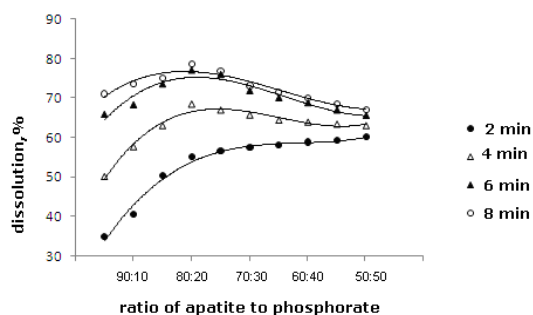


Fig. 2 The dependence of the dissolution percentage of the phosphate ore mixture on the addition of KCl versus the ratio of apatite to phosphorite

As shown in Fig. 2, the dissolution percentage increases in the first two minutes of the mixing as the amount of phosphorite in the raw material of phosphate increases, in spite of a higher P_2O_5 content of apatite than that of phosphorite. This behavior could be attributed to a larger unit surface area of phosphorite than that of apatite. The system does not follow this behavior later on.

The best value of the dissolution percentage was achieved for the apatite to phosphorite ratios of 80/20 and 75/25. This behavior may be attributed to the positive effects of magnesium oxide and carbon dioxide that are produced during the reactions [8]. There was no significant difference between the analysis of the samples taken from the reactor in the mixing times of the 6th and 8th minutes according to dissolution rates during these periods. This indicates that as the mixing time increases the dissolution rate does not change significantly. In addition, because the pulp formation in the reactor begins to get harder after 7 min of mixing, the mixing time of the reactants was considered as 6 min and after that the pulp obtained was poured into a porcelain beaker and dried in an oven.

The effect of the amount of KCl on the dissolution percentage was investigated considering the constant concentration of H_2SO_4 (60% (w/w)), the amount of sulfuric acid (10% excess of the stoichiometric amount), and the ratio of apatite/phosphorite (75/25 (w/w)) as presented in Table II. It was observed that when the mixture of apatite and phosphorite was dissolved in sulfuric acid, the dissolution percentage of the mixture of apatite and phosphorite increased from 89.52% to 94.4% depending on the amount of KCl. The dissolution occurred more rapidly when the ratio of KCl/phosphate was 2/25 (Table II). For example, although the dissolution percentage of phosphate increased 4.71% when 8 g

of KCl was added to 100 g of the mixture of apatite–phosphorite, the further addition of 2 g KCl increased the dissolution percentage by only 0.17%. The addition of KCl not only increased the dissolution percentage but also increased the potassium richness of superphosphate. In other words, when 2–10 g of KCl per 100 g of the raw material of phosphate was added to the dissolution process of the mixture of phosphate with sulfuric acid, the produced superphosphate contained K_2O ranging between 0.66% and 3.66%. Because there was no significant difference between the addition of 8 or 10 mass units of KCl to the dissolution of 100 mass units of the raw material of phosphate, 8 mass units of KCl per 100 mass units of the mixture of phosphate were used in later studies. The dissolution process of the preparation of the phosphate mixture using Kingisepp phosphorite in place of some portion of apatite was investigated with the addition of KCl. The effects of the amounts of apatite and phosphorite on the dissolution percentage of the mixture were studied considering the concentration (60% (w/w)) and the amount (10% excess of the stoichiometric amount) of sulfuric acid and the ratio of the amount of KCl to the amount of phosphate mixture (2/25) constant, and the results are presented in Table III.

Table III shows that the more the amount of phosphorite increased in the phosphate mixture with the addition of KCl, the more the dissolution percentage was achieved, and when the ratio of apatite/phosphorite was 80/20, it reached to a maximum of 94.28%. In addition, the dissolution percentage was 93.54% with a ratio of 70/30 of apatite/phosphorite, which shows that there was no significant difference. More increase in the amount of phosphorite caused a decrease in the dissolution percentage. The dissolution percentage of the phosphate mixtures without KCl was 88.19–90.01 [8]. In addition, when the amount of phosphorite in the phosphate mixtures increased from 5% to 15%, the dissolution percentage of the mixture increased from 3.45 to 6.08%.

Even if the subsequent increase in the acid concentration caused a decrease in the dissolution percentage, a higher dissolution percentage was obtained by the addition of KCl. On the other hand, the dissolution percentage of 100 g of the phosphate mixture with 8 g KCl additive was 94.23% though it was 89.52% when the concentration of sulfuric acid was 62% (w/w). In addition, Table III shows that in the chamber superphosphate production with KCl addition, the maximum dissolution percentages achieved for the ratios of apatite/phosphorite of 80/20 and 75/25 were 94.28 and 94.23, respectively. Because the dissolution percentages were approximately the same, the ratio of apatite/phosphorite was taken as 75/25 for the subsequent studies.

The dependence of the dissolution percentage of a mixture of apatite and Kingisepp phosphorite with KCl additive on the concentration and amount of sulfuric acid is shown in the chamber superphosphate production. In these studies, the ratio of apatite/phosphorite was taken as 75/25 and 4, 7, 10 and 14% excess of the stoichiometric amount of sulfuric acid, and the ratio of the KCl/phosphate mixture was taken as 2/25. Fig. 3 shows that when the concentration of sulfuric acid is

increased from 54% to 60%, the dissolution percentage of the raw material of phosphate is also increased. This behavior could be explained by the fact that the diffusion of hydrogen ions speeds up and activity increases with the addition of KCl [16], [17]. The dissolution percentages were approximately the

same in the range of 60–64% (w/w) of the concentrations of sulfuric acid. This behavior, which is advantageous from the technological point of view, makes it possible to study the concentration of sulfuric acid at a large interval for the dissolution of the mixture of apatite and phosphorite.

TABLE II

THE DEPENDENCE OF THE DISSOLUTION PERCENTAGE OF THE MIXTURE OF APATITE AND PHOSPHORITE ON KCL AMOUNT IN THE CHAMBER SUPERPHOSPHATE PRODUCTION

KCl amount added/phosphate mixture (g/100g)	Superphosphate content (%)					Moisture	K ₂ O	Dissolution Percent of Mixture of Phosphate (%)
	P ₂ O ₅ Total	P ₂ O ₅ used	P ₂ O ₅ Soluble in water	P ₂ O ₅ Free				
-	19.27	17.25	16.90	11.25		13.70	-	89.52
2	19.35	17.50	17.25	11.00		13.65	0.66	90.44
4	19.37	17.85	17.55	10.85		13.48	1.33	92.15
6	19.40	18.10	17.80	10.75		13.35	2.00	93.30
8	19.42	18.30	18.00	10.70		13.05	2.68	94.23
10	19.47	18.38	18.10	10.55		12.95	3.36	94.40

TABLE III

THE DEPENDENCE OF THE DISSOLUTION PERCENTAGE OF THE PHOSPHATE MIXTURE ON THE AMOUNT OF APATITE CONCENTRATE AND THE AMOUNT OF KINGISEPP PHOSPHORITE IN THE CHAMBER SUPERPHOSPHATE PRODUCTION

Phosphate ores (%)		Superphosphate content (%)					SP/P* (g/g)	Dissolution Percent (%)
Apatite	Phosphorite	P ₂ O ₅ Total	P ₂ O ₅ used	P ₂ O ₅ Dissolved in water	P ₂ O ₅ free	Moisture		
95	5	20.35	18.52	18.20	11.00	13.50	1.91	91.01
90	10	20.10	18.50	18.17	10.90	13.40	1.90	92.04
85	15	19.80	18.47	18.15	10.80	13.25	1.899	93.28
80	20	19.57	18.45	18.10	10.75	13.15	1.897	94.28
75	25	19.42	18.30	18.00	10.70	13.05	1.882	94.23
70	30	19.35	18.10	17.80	10.65	13.00	1.855	93.54
65	35	19.25	17.75	17.55	10.60	12.95	1.840	92.73
60	40	19.10	17.48	17.20	10.55	12.90	1.824	91.52
55	45	18.85	17.15	16.85	10.50	12.86	1.818	90.98

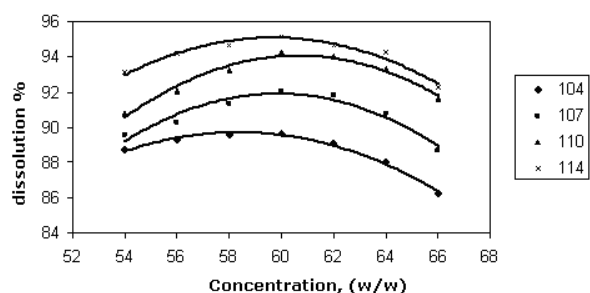


Fig. 3 Dependence of dissolution percent of KCl additive-phosphate mixture on concentration and amount of sulfuric acid

There was no significant difference between the dissolution percentages of the phosphate mixtures in the concentration range of 54-60% (w/w) in the stoichiometric amount of sulfuric acid on contrary to those of excess of 7-14% of the stoichiometric amount. In other words, the dissolution percentage changed only from 88.75 to 89.65%. Therefore, it causes calcium sulfate, monomagnesium phosphate, and monocalcium phosphate to saturate later in the reaction media because there is a more liquid phase in low concentrations of acid than that of high concentrations when sulfuric acid is in a low stoichiometric amount. As a result, the diffusion of acid to

unreacted phosphate is less blocked. This behavior shows that it is more convenient to study with low-concentration and low-stoichiometric norm acid conditions for superphosphate production. An increase in the liquid phase in higher norms of sulfuric acid causes an increase in the amount of acid. Both of these situations accelerate the reaction rate. As a result, the dissolution percentage of the phosphate mixture was obtained as 94.6–95.1% by adding KCl with acid concentrations of 56–60% and acid stoichiometric norm of 114%. The more the stoichiometric norm of sulfuric acid increased, the higher acid concentrations could be used in the superphosphate production, which positively affects the superphosphate content. The effects of the concentration and stoichiometric norm of sulfuric acid on the leaching rate of chamber superphosphate were investigated considering the ratios of the apatite/phosphorite and KCl/phosphate mixture 75/25 (w/w) and 2/25 (w/w), respectively.

Table IV shows that the dissolution percentage of the apatite–phosphorite mixture increased for all the stoichiometric norms of sulfuric acid studied when the concentration of sulfuric acid increased from 54% to 60% and a further increase in the concentration of sulfuric acid caused to decrease the dissolution percentage.

TABLE IV
THE DEPENDENCE OF THE CHAMBER SUPERPHOSPHATE CONTENT ON THE CONCENTRATION AND STOICHIOMETRIC NORM OF SULFURIC ACID

Concentration of H ₂ SO ₄ , %w/w	Total P ₂ O ₅	Content of chamber superphosphate % w/w			Moisture	Dissolution Percent of Phosphate mixture, %
		P ₂ O ₅ Used	P ₂ O ₅ soluble in water	P ₂ O ₅ free		
Norm of H ₂ SO ₄ 107% (w/w) stoichiometric amount						
54	19.37	17.35	17.00	10.25	13.85	89.57
56	19.60	17.70	17.35	10.32	13.65	90.31
58	19.82	18.10	17.85	10.45	13.40	91.32
60	19.67	18.38	18.05	10.55	13.30	92.04
62	20.25	18.60	18.22	10.67	13.20	91.85
64	20.55	18.65	18.30	10.77	13.10	90.75
66	20.85	18.70	18.35	10.90	13.00	88.69
Norm of H ₂ SO ₄ - %110 (w/w) stoichiometric amount						
54	19.05	17.30	17.00	10.50	14.00	90.81
56	19.20	17.67	17.35	10.55	13.50	92.03
58	19.35	18.05	17.75	10.62	13.25	93.28
60	19.42	18.30	18.00	10.70	13.05	94.23
62	19.75	18.57	18.27	10.80	12.90	94.03
64	19.97	18.63	18.32	10.92	12.70	93.29
66	20.35	18.65	18.35	11.05	12.60	91.65
Norm of H ₂ SO ₄ - %114 (w/w) stoichiometric amount						
54	18.80	17.50	17.25	10.80	14.20	93.09
56	19.00	17.90	17.65	10.90	13.75	94.21
58	19.17	18.15	17.90	10.98	13.50	94.68
60	19.34	18.40	18.10	11.05	13.27	95.14
62	19.65	18.60	18.30	11.15	13.10	94.66
64	19.80	18.66	18.35	11.30	12.90	94.24
66	20.27	18.70	18.40	11.45	12.85	92.26

The experimental results showed that the dissolution percentage in the reaction of the KCl additive–phosphate mixture with sulfuric acid was higher than that of KCl-free mixture at around 3.5–4.1%. In other words, the dissolution percentage increased to 94.23–95.14% in the KCl additive–phosphate dissolution. This behavior provides the opportunity to superphosphate to directly pass through the granulation process without going to the storage. Because superphosphate used in the granulation process contains an excess of free P₂O₅, it is neutralized by calcium carbonate or ammonia so that free P₂O₅ would become 2–2.3%, and then it will be granulated by being moisturized up to 15% water in the granulator. Granulation conditions such as the speed of the granulator, the granulation time, and the amount of under sieve product were selected appropriately for production conditions. The superphosphate was granulated after being neutralized with CaCO₃ or NH₃. The chemical content and

physicochemical properties of grained superphosphate are shown in Tables V and VI. The tables show that as the proportion of phosphorite increases in the raw material of phosphate, the mechanical strength of grains of superphosphate produced increases from 1.5 to 2.45 MPa and from 1.58 to 2.57, respectively. In addition, the yields increase from 83 to 93 and 84 to 93, respectively. The improvement in the physic-mechanical properties of superphosphate is explained with the strengthening of grains by using the definite amount of magnesium in superphosphate [18]. The phosphate mixture with KCl additive not only accelerated the production process by producing superphosphate, but also the low-grade phosphorite could be used in place of some portion of the apatite concentrate, the mechanical properties of granulated superphosphate can be improved, and the environmental pollution can be decreased.

TABLE V
THE CHEMICAL CONTENT AND PHYSICO-CHEMICAL PROPERTIES OF GRAINS OBTAINED AFTER SUPERPHOSPHATE FROM APATITE CONCENTRATE/PHOSPHORITE MIXTURE WITH KCL ADDITIVE NEUTRALIZED WITH CaCO₃

Phosphate ores (% w)		Granulated superphosphate content (% w)				Mechanical straight of grain, MPa	Yield of superphosphate, %	Higros-Copic Coefficient, mole/g.h
Apatite	Phosphorite	Total P ₂ O ₅	Used P ₂ O ₅	Free P ₂ O ₅	Moist.			
95	5	21.20	19.55	2.1	3.0	1.50	83	2.7
90	10	21.05	19.50	2.1	3.0	1.67	87	2.8
85	15	20.75	19.40	2.1	3.0	1.85	90	3.0
80	20	20.50	19.35	2.1	3.0	2.05	91	3.1
75	25	20.40	19.23	2.1	3.0	2.20	92	3.2
70	30	20.32	19.05	2.1	3.0	2.30	93	3.5
65	35	20.05	18.65	2.1	3.0	2.45	93	3.6

TABLE VI
THE CHEMICAL CONTENT AND PHYSICO-CHEMICAL PROPERTIES OF GRAINS OBTAINED AFTER SUPERPHOSPHATE FROM APATITE CONCENTRATE/PHOSPHORITE MIXTURE WITH KCL ADDITIVE NEUTRALIZED WITH NH₃

Phosphate ores (% w)		Granulated super phosphate content (% w)				Mechanical Straight of grain, MPa	Yield of Superphosphate %	Higros-Copic Coefficient, mole/g.h
Apatite	Phosphorite	Total P ₂ O ₅	Used P ₂ O ₅	Free P ₂ O ₅	Moist			
95	5	21.50	19.85	2.1	3.	1.58	84	2.5
90	10	21.35	19.8	2.1	3	1.75	88	2.6
85	15	21.10	19.75	2.1	3	1.95	91	2.8
80	20	20.80	19.65	2.1	3	2.15	92	2.9
75	25	20.70	19.53	2.1	3	2.29	93	3.1
70	30	20.60	19.32	2.1	3	2.42	93	3.3
65	35	20.30	18.90	2.1	3	2.57	93	3.3

IV. CONCLUSION

In this study, it was determined that by producing superphosphate from a mixture of apatite and phosphorite with the addition of KCl, the maturation stage in the storage can be eliminated and superphosphate can be produced by using a continuous chamber method. This improvement reduces the production period and the environmental pollution caused by fluoride gases by using the low-grade Kingisepp phosphorite instead of the high-grade apatite concentrate. It also makes possible to achieve 0.66–3.36% K₂O and 1.6–1.8% N in superphosphate along with P₂O₅. In addition, it helps improve the physicochemical properties of granulated superphosphate. In conclusion, the optimum results were found to be 58–64% (w/w) for the concentration of sulfuric acid, 110–114% (w/w) for the stoichiometric norm of sulfuric acid, 80/20 to 75/25 (w/w) for the ratio of apatite to phosphorite, 2/25 (w/w) for the ratio of KCl to the phosphate mixture, and 6 min for the mixing time.

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