

Processing of phosphorites and additives with researching their thermodynamical properties

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Abstract. In this article, scientific research on the production of thermophosphate fertilizers was carried out on the basis of thermo-alkaline activation of Central Kyzylkum waste phosphorite with mineralized mass and alkali metal salts, namely NaCl, KCl, Na₂SO₄, K₂SO₄, Na₂CO₃, K₂CO₃ and silica at high temperature. In this case, samples are heated in muffle furnaces at temperatures of 800°C, 900°C, 1100°C, 1200°C and for 30 min, 60 min, 120 min. The total P₂O₅, assimilable P₂O₅, total CaO and total CO₂ forms of the sintered tablets were investigated. As it can be seen from the experiments conducted with mineralized mass phosphorite, alkaline salts and quartz sand, it was found that the assimilated form of CaO, P₂O₅ and the degree of decarbonation rose with increasing temperature and time.

1. Introduction

The global introduction of agricultural chemicals has led to the formation of a powerful international industry for their production, as well as a wide network of logistics and distribution. According to the International Association of Fertilizer Manufacturers, in comparison with the 60s of the last century, the world consumption of mineral fertilizers by 2015 increased by almost 6 times. Currently, the market is one of the most monopolized. Five countries are the largest producers on it: China, the USA, India, Russia and Canada. These states account for about 60% of the total volume of agrochemical products produced [1- 3].

Since the second half of the 20th century, the world chemical industry, including the production of chemicals for agriculture, has gone from the extensive development of large-capacity industries through technical and technological renewal and structural restructuring to a resource-saving and science-intensive stage of development characteristic of the entire modern post-industrial economy. The USA, Japan and EU countries that have gone through all stages of the development of the industry are currently focused on high technologies and scientific and technical developments. Thus, according to the US Patent Office, every eighth US patent is issued in the field of chemistry. Approximately \$20 billion is spent annually on R&D. Developing countries have housed the production of products with a low degree of industrial processing, which include the large-scale production of basic mineral fertilizers [4-6].

At present, the use of certain traditional methods in the production of phosphorus fertilizers causes a number of environmental problems. The problem is that Central Kyzylkum phosphate ores cannot be used for well-known and well-known beneficiation methods (flotation, washing, de-sludging, thermal treatment and calcium oxide leaching, etc.) due to their mineralogical structure and composition. Because this type of complex and poor quality phosphate raw material is practically not used for enrichment. In addition, the obtained concentrate is associated with the formation of a large amount of liquid, solid and gaseous waste during the acid treatment process for obtaining standard fertilizer, for example, phosphogypsum, emission of fluorine gases, which requires additional environmental measures. At the same time, phosphorous concentrated fertilizers in the form of superphosphate, ammophos, etc. are convenient for transportation from the point of view of economy, but when applied to the soil, since there are many water-soluble forms of nutrients, they easily enter the nearest water bodies, poison the water with heavy metals, and cause their turbidity. As a result, the efficiency of these fertilizers is seriously affected [7-8].

In the process of enrichment of phosphorite ore of the Central Kyzylkum phosphorite complex, mineralized mass, slimy and powdery phosphorites are formed. Currently, the total volume of these waste phosphorites is 15 mln.

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reached tons. A number of scientific research works are being carried out on the development of technologies for processing these waste phosphorites into organic mineral fertilizers using unconventional methods [9-11]. In the absence of phosphorus fertilizers, attracting these unconditioned phosphorites to agricultural needs is an urgent problem.

Based on these data, in order to obtain phosphoric fertilizers with valuable agrochemical components in the country, limiting the traditional acid technology and relying on the technologies for obtaining phosphate fertilizers through the thermal activation of Central Kyzylkum phosphorites is one of the positive and promising ways to solve the problem.

In order to reduce the thermal temperature of the process of obtaining phosphate fertilizers through thermal activation, a number of works have been carried out to reduce the sintering temperature by adding salts to phosphate raw materials. The phosphate content of thermophosphate fertilizers is represented by rhenanite $\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot \text{P}_2\text{O}_5$ or CaNaPO_4 , which dissolves well in 2% citric acid, as well as calcium orthosilicate, which gives solid solutions with calcium sodium phosphate. Fluorine binds as sodium fluoride [12-13].

Alkaline decomposition of phosphates is characterized by the simplicity of the technological process and allows avoiding the consumption of acids necessary for other methods of obtaining phosphorus fertilizers, as well as the use of low-quality raw materials without enrichment, which contain relatively little P_2O_5 and important mixtures of R_2O_3 [14].

Based on the above-mentioned problems, scientific studies on the production of thermophosphate fertilizers were carried out based on the thermo-alkaline activation of the Central Kyzylkum waste phosphorite mineralized mass in the presence of alkaline salts [15-17].

2. Materials and Methods

The Before starting the research, information is found about high-temperature reactions with phosphorite and recommended alkali metal salts as NaCl, KCl, Na_2SO_4 , K_2SO_4 , Na_2CO_3 , K_2CO_3 and silica, and the thermodynamic properties based on them.

Table 1. Thermodynamic parameters of chemical substances in standard conditions

	$\text{Ca}_3(\text{PO}_4)_2$	CaF_2	NaF	NaCl	Na_2SO_4	Na_2CO_3
ΔG	-3899,5	-1175,6	-543,3	-384	-1266,8	-1048
ΔH	-4137,6	-1228	-573,6	-234,8	-1387,9	-1131
S	236	273,8	51,3	72,8	149,5	136,4
	Ca_2SiO_4	HCl	CaNaPO_4	SiO_2	SO_2	CO_2
ΔG	-112	-94,79	-1896,5	-856,7	-300	-394,38
ΔH	-1630	-91,8	-2018,3	-910,9	-296,9	-393,51
S	84	186,8	137,2	41,84	248,1	213,67

The reactions taking place in the process were calculated from the following equations.

- $\Delta G = (3 \cdot (-1896,5) + (-112) + 4 \cdot (-94,79) + (-543,3)) - ((-5075,1) + 4 \cdot (-384) + 2 \cdot (-237,1) + (-856,7)) = -495,4 \text{ KJ/ mole}$
- $\Delta G = (3 \cdot (-1896,5) + 3 \cdot (-1908,1) + 2 \cdot (-112) + 8 \cdot (-94,79) + (-543,3) + (-537,7)) - ((2 \cdot (-5075,1) + 4 \cdot 0,27 \cdot (-408) + 4 \cdot 0,61 \cdot (-384) + (-237,1) + (-856,7)) = -855,5 \text{ KJ/ mole}$
- $\Delta G = (3 \cdot (-1896,5) + (-112) + 2 \cdot (-394,38) + (-543,3)) - ((-5075,1) + 2 \cdot (-1048) + (-856,7)) = -863,84 \text{ KJ/ mole}$

Table 2. Thermodynamic characteristics of the reactions that take place for the main components involved in the thermal burning of phosphorites

№	Reactions passing in process	$\Delta G, \text{ kJ/ mole}$	$\Delta H, \text{ kJ/ mole}$
1	$\text{Ca}_5(\text{PO}_4)_3\text{F} + 4\text{NaCl} + 2\text{H}_2\text{O} + \text{SiO}_2 = 3\text{CaNaPO}_4 + \text{Ca}_2\text{SiO}_4 + 4\text{HCl}\uparrow + \text{NaF}$	-495,4	-838,4
2	$\text{Ca}_5(\text{PO}_4)_3\text{F} + 2\text{Na}_2\text{SO}_4 + \text{C} + \text{SiO}_2 = 3\text{CaNaPO}_4 + \text{Ca}_2\text{SiO}_4 + 2\text{SO}_2\uparrow + \text{CO}_2\uparrow + \text{NaF}$	-1126,2	-139,5
3	$\text{Ca}_5(\text{PO}_4)_3\text{F} + 2\text{Na}_2\text{CO}_3 + \text{SiO}_2 = 3\text{CaNaPO}_4 + \text{Ca}_2\text{SiO}_4 + 2\text{CO}_2\uparrow + \text{NaF}$	-863,84	-507

- $\Delta H = (3 \cdot (-2018,3) + (-1630) + 4 \cdot (-91,8) + (-573,6)) - ((-5365,6) + 4 \cdot (-234,8) + 2 \cdot (-285,8) + (-910,9)) = -838,4 \text{ KJ/ mole}$

2. $\Delta H = (3 \cdot (-2018,3) + (-1630) + 2 \cdot (-269,9) + (-393,51) + (-573,6)) - ((-5365,6) + 2 \cdot (-1387,9) + (-910,9)) = -139,5$ KJ/ mole

3. $\Delta H = (3 \cdot (-2018,3) + (-1630) + 2 \cdot (-393,51) + (-573,6)) - ((-5365,6) + 2 \cdot (-1131) + (-910,9)) = -507$ KJ/ mole

The calculation results are presented in Table 2.

As can be seen from the calculation results in the table, this condition with a negative value of Gibbs energy serves to predetermine the solutions to the research task of the thermal reaction.

Table 3. Calculated Gibbs energy values for reactions occurring during thermal decomposition at different temperatures

Reactions passing in process	800 °C	1000 °C	1200 °C
$\text{Ca}_5(\text{PO}_4)_3\text{F} + 4\text{NaCl} + 2\text{H}_2\text{O} + \text{SiO}_2 = 3\text{CaNaPO}_4 + \text{Ca}_2\text{SiO}_4 + 4\text{HCl}\uparrow + \text{NaF}$	-531564	-630644.2	-729724.2
$\text{Ca}_5(\text{PO}_4)_3\text{F} + 2\text{Na}_2\text{SO}_4 + \text{C} + \text{SiO}_2 = 3\text{CaNaPO}_4 + \text{Ca}_2\text{SiO}_4 + 2\text{SO}_2\uparrow + \text{CO}_2\uparrow + \text{NaF}$	-1208413	-1433653	-1658893
$\text{Ca}_5(\text{PO}_4)_3\text{F} + 2\text{Na}_2\text{CO}_3 + \text{SiO}_2 = 3\text{CaNaPO}_4 + \text{Ca}_2\text{SiO}_4 + 2\text{CO}_2\uparrow + \text{NaF}$	-926900	-1099668	-1272436

In laboratory research, samples of Central Kyzylykum waste phosphorite mineralized mass (MM), various alkaline salts and quartz are crushed to 63µm. Ground MM with different alkali salts and quartz weight ratios were obtained in stoichiometric 100% ratios relative to P₂O₅ in phosphorite. The obtained initial components are made into a pasty mass using water, the mass is made into tablets, their weight is measured and dried in a drying cabinet. Then they are heated at 800°C, 900 °C, 1100 °C, 1200 °C and 30 min, 60 min, 120 min in muffle furnaces during temperatures are also measured. Total P₂O₅, assimilable P₂O₅, total CaO and total forms of the contents of the burned tablets were studied. The total P₂O₅, absorbable P₂O₅, and total CaO values of the samples were determined spectrophotometrically on a UV-1280 spectrophotometer (Shimadzu, Japan) at a wavelength of λ =440 nm.

The results of the research showed that the amount of assimilable P₂O₅ gets up with increasing temperature, as can be seen from the experiments conducted with the samples based on mineralized mass phosphorites with chloride, sulfate, carbonate salts of sodium and quartz sand.

3. Results and Discussion

The results of the study are presented in tables 4-6. In this case, the mineralized mass in the presence of sodium carbonate and quartz sand in the presence of 30 minutes of reaction time at a temperature of 900°C has the absorbed form of P₂O₅ in citric acid relatively to the total P₂O₅. It was found that assimilation was 57.13 and 36.63% for Trilon B, and it has increased to 77.81 and 48.07% at 1200°C, respectively.

Table 4. Thermal processing of MM, SiO₂ and Na₂CO₃ in ratio 100:4,42:15,19 at different temperatures and times

№	T, °C	t, min	P ₂ O ₅ total %	P ₂ O ₅ assim. in 2 % citric acid	P ₂ O ₅ assim. ,% in 0.2M Trilone B	P ₂ O ₅ assim in 2 % citric acid /P ₂ O ₅ total *100%	P ₂ O ₅ assim in 0.2M Tr-B / P ₂ O ₅ total *100%
1	900	30	15.26	8.72	5.59	57.13	36.63
2	900	60	15.38	9.01	5.97	58,57	38.81
3	900	90	15.44	9.19	6.17	59.52	39.96
4	900	120	15.52	9.61	6.27	61.90	40.39
5	1000	30	15.64	9.89	6.35	63.23	40,60
6	1000	60	15.74	10.22	6.34	64.91	40.27
7	1000	90	15.83	10.27	6.49	64.88	41.00
8	1000	120	15.90	10.37	6.80	65.22	42.76
9	1100	30	15.98	10.28	7.69	64.31	48.11
10	1100	60	16.06	10.25	7.91	63.83	49.26
11	1100	90	16.09	11.09	7.93	68.90	49.27
12	1100	120	16,14	12.06	7.80	74,74	48.34
13	1200	30	16.31	12.69	7.84	77,81	48.07
14	1200	60	16.34	13,12	8.05	80.30	49.27
15	1200	90	16.38	13,11	8.18	80.02	49.93
16	1200	120	16.43	13,21	8.24	80.38	50.14

Furthermore, the time of reaction of mineralized mass phosphorite with sodium chloride and quartz sand was 30 minutes at a temperature of 900°C compared to total P₂O₅ and the absorbed form of P₂O₅_{assim} in citric acid. It showed that it comprised 53.42 and 34.29% for Trilon B and increased to 73.27 and 45.27% at 1200°C, respectively. In addition, absorption rates of P₂O₅ were shown to increase with increasing reaction time. For example, in the presence of mineralized mass of sodium sulfate and quartz sand, at a temperature of 1000°C and an reaction time of 30 minutes, the absorbed form is citric acid and P₂O₅ in relation to the total P₂O₅. It was found that assimilation was 60.76 and 38.69% for Trilon B, and it increased to 62.41 and 38.99% at reaction time of 60 minutes, respectively.

Table 5. Thermal processing of MM, SiO₂ and NaCl in ratio 100:4,42:17,26 at different temperatures and times

№	T, °C	t, min	P₂O₅ total %	P₂O₅ assim. in 2 % citric acid	P₂O₅ assim. ,% in 0.2M Trilone B	P₂O₅ assim in 2 % citric acid /P₂O₅ total *100%	P₂O₅ assim in 0.2M Tr-B / P₂O₅ total *100%
1	900	30	15.11	8.07	5.18	53.42	34,29
2	900	60	15,23	8.34	5.53	54.75	36.30
3	900	90	15.29	8.51	5.71	55.65	37,34
4	900	120	15.38	8.90	5.81	57.87	37.78
5	1000	30	15.57	9.24	5.93	59.34	38.08
6	1000	60	15.68	9.55	5.92	60,90	37.75
7	1000	90	15.77	9.60	6.07	60.86	38,48
8	1000	120	15.85	9.69	6.35	61.13	40.06
9	1100	30	16.01	9.70	7.25	60.58	45,28
10	1100	60	16.09	9.67	7.46	60.08	46.35
11	1100	90	16,13	10.46	7.48	64.83	46.36
12	1100	120	16,18	11.38	7.36	70.33	45,49
13	1200	30	16.50	12.09	7.47	73.27	45,27
14	1200	60	16.54	12.50	7.67	75.60	46.39
15	1200	90	16.59	12.49	7.79	75.30	46.96
16	1200	120	16.65	12.58	7.85	75.56	47.15

Table 6. 100:4,42:20,95:0,89 thermal processing in the presence of MM, SiO₂, Na₂SO₄ and coal at different temperatures and times

№	T, °C	t, min	P₂O₅ total %	P₂O₅ assim. in 2 % citric acid	P₂O₅ assim. ,% in 0.2M Trilone B	P₂O₅ assim in 2 % citric acid /P₂O₅ total *100%	P₂O₅ assim in 0.2M Tr-B / P₂O₅ total *100%
1	900	30	14.81	8.07	5.18	54.47	34.96
2	900	60	14.92	8.34	5.53	55.89	37.06
3	900	90	14.97	8.51	5.71	56.84	38,14
4	900	120	15.05	8.90	5.81	59.15	38.62
5	1000	30	15,21	9.24	5.93	60.76	38.69
6	1000	60	15.30	9.55	5.92	62.41	38,99
7	1000	90	15.38	9.60	6.07	62.42	39,47
8	1000	120	15.44	9.69	6.35	62.75	41.12
9	1100	30	15.58	9.70	7.25	62.27	46.54
10	1100	60	15.65	9.67	7.46	61.80	47,68
11	1100	90	15.68	10.46	7.48	66,71	47.70
12	1100	120	15.72	11.38	7.36	72.40	46.82
13	1200	30	15.99	12.09	7.47	75.63	46.73
14	1200	60	16.01	12.50	7.67	78.06	47.90
15	1200	90	16.06	12.49	7.79	77,79	48,52
16	1200	120	16.11	12.58	7.85	78.10	48.74

In the course of studies, the dependence of carbonate compounds in phosphorite on time and temperature was studied during reaction to phosphorite, sodium chloride, sulfate, carbonate salts and quartz sand. The results of studies showed that the degree of decarbonation increased with the increase of reaction time and temperature.

In the presence of mineralized mass of sodium carbonate and quartz sand, the degree of decarbonation is 68.54% at a temperature of 900°C in 30 minutes of reaction time, at 1000°C was 78.75% at 1200°C and 95.55% at 1200°C, it was studied that 75.64%, 85.49% and 98.67% were decarbonized in 120 minutes of reaction time, respectively.

The most positive result was observed in thermophosphates obtained on the basis of mineralized mass of sodium sulfate, quartz sand and coal. The following can be observed in these thermophosphates: P_2O_5 in citric acid and P_2O_5 in Trilon B, an increase in the range of 8.72-13.11 and 5.59-8.18% can be seen, respectively. In these ranges, the absorbable form of phosphorus in fertilizers $P_2O_{5assim}/P_2O_{5total}$ citric acid and $P_2O_{5assim}/P_2O_{5total}$ Trilon B is from 61.43 to 86.86 and 39.38 to 54.20%, respectively, and the degree of decarbonation is from 72.51 to 99.97% was found to have increased.

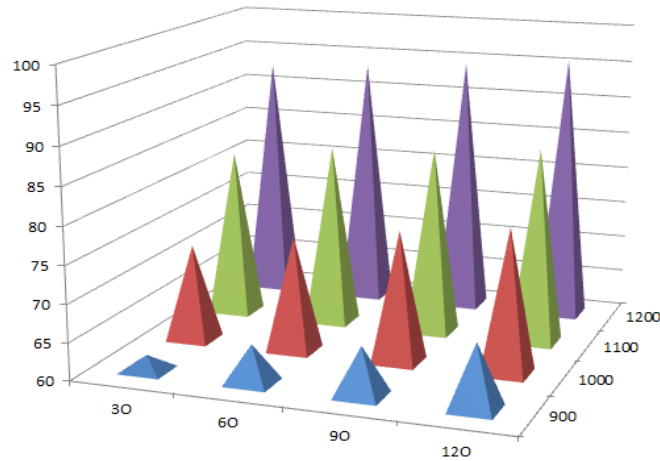


Fig. 1. Dependence of temperature and time on the degree of decarbonation during thermal processing of samples in the presence with a weight ratio of 100:4,42:15,19 mineralized mass, quartz, Na_2CO_3 and coal

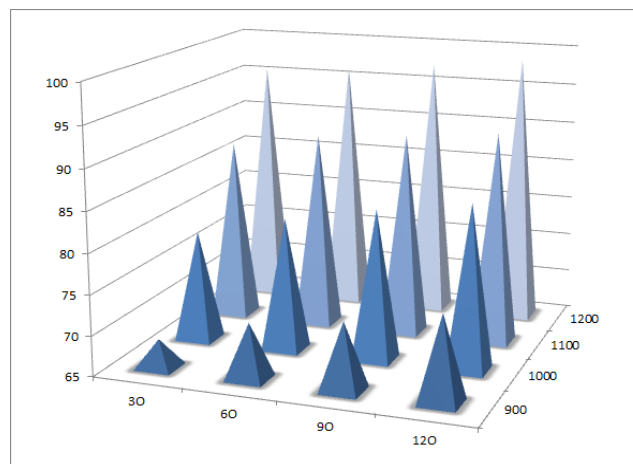


Fig. 2. Dependence of temperature and time on the degree of decarbonation during thermal processing of samples in the presence with a weight ratio of 100:4,42:17,26 of mineralized mass, quartz, NaCl and coal

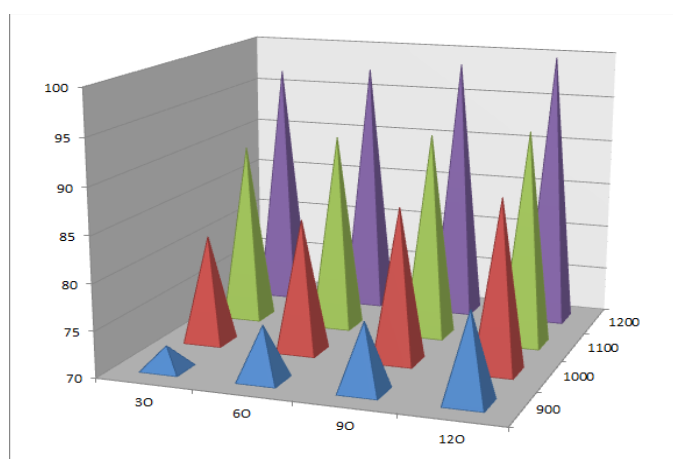


Fig. 3. Dependence of temperature and time on the degree of decarbonation during thermal processing of samples in the presence with a weight ratio of 100:4.42:20.95:0.89 of mineralized mass, quartz, Na₂SO₄ and coal.

4. Conclusions

In conclusion, the isobaric-isothermal potential values for each reaction were determined, and the thermodynamic values of the interaction reactions of the components in the mixture of sand by the combustion method were determined. In the studies of obtaining thermophosphates based on phosphorite ore, chloride, sulfate, carbonate salts of sodium, silicon oxide and coal, it was found that with increasing reaction time and temperature, the assimilable form of phosphorus in fertilizers by P₂O₅-containing citric acid and P₂O₅-containing Trilon B and the level of decarbonation were increased.

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