



## HYDROCHLORIC ACID OBTAINING OF PRECIPITATE ON BASE OF PHOSPHORITE FLOUR FROM KYZYLKUM PHOSPHORITES

Shamuratova Makhinbanu Rametullaevna<sup>1</sup>, Sultonov Bokhodir Elbekovich<sup>2</sup>,  
Namazov Shafaat Sattorovich<sup>3</sup>

<sup>1,2,3</sup> *Institute of General and Inorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan*

**Abstract:** The process of direct production of fertilizer precipitate on the bases of hydrochloric acid processing of phosphorite flour of the Central Kyzylkum, containing 16.60%  $P_2O_5$ , 48.62% CaO and 13.02%  $CO_2$ , followed by neutralization of the hydrochloric acid phosphate suspension with calcium hydroxide without the filtration step of the insoluble residue are studied. Calcium chloride was leached from the precipitate suspension by double washing with water at the ratio of dry precipitate:  $H_2O=1:2.5$  and  $1:2.0$ . Optimum parameters of decomposition of phosphorite flour and precipitation with hydrochlorophosphoric acid suspension are determined. Under optimum process conditions, samples of precipitate containing 25.06-26.25%  $P_2O_{5total}$ , 21.59-22.04%  $P_2O_{5assi}$ , 27.03-28.62%  $CaO_{total}$  and 23.38-24.41%  $CaO_{assi}$  were obtained. The degree of precipitation of phosphoric acid under optimal conditions was 94.18-97.44%.

**Keywords:** phosphorite flour, hydrochloric acid, precipitate, degree of precipitation.

### I. INTRODUCTION

It is known that one of the main factors determining the productivity of agricultural crops is the use of mineral fertilizers, including phosphorus fertilizers, and this requires significant increase in their production and development of raw materials.

At the present time, three joint-stock companies in our country: «Ammofos-Maxam» (Almalyk), «Samarkandkimyo» and «Kokand superphosphate factory», produce phosphorus fertilizers.

The assortment of the production of these three enterprises is small and consists of ammophos, suprefos-NS, PS-Agro, nitrocalciumphosphate fertilizer (NCPF) and simple ammoniated superphosphate. The Kyzylkum phosphorite plant provides raw materials to factories producing phosphorus fertilizers. Since 2015, the plant annually produces 716,000 tons of washed burned phosphorus concentrate (WBPC) with an average content of 26%  $P_2O_5$ , which is phosphate raw material suitable for the production of complex highly concentrated phosphorcontents fertilizers, such as ammophos (10% N, 46%  $P_2O_5$ ) and suprefos-NS (8-15% N, 20-24%  $P_2O_5$ ). However, the volume of the WBPC can not ensure the need for production of concentrated phosphoruscontents fertilizers. It is also known that at the production of WBPC appearing phosphorecontents waste - mineralized mass and phosphorite sludge, where about 42% of  $P_2O_5$  is contained in total phosphorus, which is processed by the WBPC.

The main actual tasks in the field of production of phosphorcontents fertilizers are the following: increase in the volume of their production, expansion of their assortment, involvement in processing of poorer raw materials and decrease of the cost of production. In the conditions of an acute deficit of phosphate fertilizers due to the limited volume of high-quality phosphate raw materials, it is necessary to find effective ways of utilizing phosphorcontents waste and involving poor phosphate raw materials in the production of high efficiency phosphate fertilizers.

In connection with the sulfuric acid deficiency, in the production volume is provided process of hydrochloric acid processing of low-grade phosphorites of the Central KyzylKum with obtaining high concentrated single-phosphoric fertilizer of precipitate -  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ . Precipitate is a good fertilizer, suitable for use on all types of soils and for all crops. Apply the precipitate only for the main application. At us production of single phosphoric fertilizers, such as precipitate, enriched and double superphosphates are absent.

The hydrochloric acid process is most expedient first of all for those regions where cheap and excess hydrochloric acid is produced, for example, in the production of sodium or potassium sulfate from chlorides, in the electrochemical production of chlorine, in the hydrolysis of chlorides, etc. Under our conditions, the cheapest and most accessible reagent can become hydrochloric acid, which is a large-scale collateral product of the production of caustic soda at JSC «Navoiazot», which has very limited sales.

Earlier [1-5], we studied the process of obtaining fertilizer precipitate on the based of hydrochloric acid decomposition of the mineralized mass and phosphorite flour from the KyzylKum phosphorites, as well as from the WBPC. At the scientific works [1-3] for obtaining fertilizer precipitate used mineralized mass (14.60% of  $\text{P}_2\text{O}_5$ , 43.99% of  $\text{CaO}$ , 14.11% of  $\text{CO}_2$ , 1.58% of  $\text{SO}_3$  and 10.82% i.r.). Optimal parameters of precipitation are determined depending on the norm and concentration of hydrochloric acid, also on the nature of the precipitant. The obtained samples of precipitates under optimal conditions contents, 23.40-24.19%  $\text{P}_2\text{O}_{5\text{total}}$ , 19.31-21.38%  $\text{P}_2\text{O}_{5\text{accep.}}$  on 2% by citric acid, 26.84-28.41%  $\text{CaO}_{\text{total}}$ , 22.95-25.59%  $\text{CaO}_{\text{accep.}}$  on 2% by citric acid. The degree of precipitation in this case located from 94.01 to 98.05%. In works [4] for obtaining fertilizer precipitate was used phosphorite flour (17.09%  $\text{P}_2\text{O}_5$ , 45.36%  $\text{CaO}$ , 14.89%  $\text{CO}_2$ , 1.60%  $\text{SO}_3$  and 7.8% i.r.).

To leach calcium chloride from wet precipitate was applied in double wash with water at the ratio of dry precipitate:  $\text{H}_2\text{O}=1:2.5$  and  $1:2.0$ . Optimum parameters of decomposition of phosphorite flour and precipitation of hydrochloricphosphorus acid suspension with calcium carbonate were determined. Under optimal conditions of process obtained samples of precipitate containing 25.07-27.22%  $\text{P}_2\text{O}_{5\text{total}}$ , 22.44-22.93%  $\text{P}_2\text{O}_{5\text{accep.}}$  by citric acid, 28.09-29.57%  $\text{CaO}_{2\text{total}}$  and 24,30-25,40%  $\text{CaO}_{\text{accep.}}$  by citric acid. The degree of precipitation of phosphoric acid under optimal conditions was 94.21-97.53%. In work [5] the results of obtaining precipitate from WBPC, produced on the basis of high-carbonized phosphorites of the Central KyzylKum by thermal enrichment are given. The effect of pH on the composition of precipitates was studied. Samples of precipitates without isolation and isolation of an insoluble residue were obtained. The obtained precipitates at optimum parameters contain in their composition (mass%):  $\text{P}_2\text{O}_{5\text{total}}$  29.49-31.25;  $\text{P}_2\text{O}_{5\text{accep.}}$  by citric acid 26.24-27.62;  $\text{P}_2\text{O}_{5\text{w.s.}}$  0.42-1.52;  $\text{CaO}_{\text{total}}$  36.31-38.14;  $\text{CaO}$  by citric acid 32,23-33,94;  $\text{CaO}_{\text{w.s.}}$  1.44-2.06;  $\text{Cl}$  1.61-1.85 and  $\text{P}_2\text{O}_{5\text{total}}$  36.19-38.01;  $\text{P}_2\text{O}_{5\text{accep.}}$  by citric acid 32,75-33,45;  $\text{P}_2\text{O}_{5\text{w.s.}}$  0.40-1.41;  $\text{CaO}_{\text{total}}$  39.70-42.67;  $\text{CaO}_{\text{accep.}}$  by citric acid 35.33-38.61;  $\text{CaO}_{\text{w.s.}}$  1.25-1.96;  $\text{Cl}$  1.58-1.78, respectively, without and with the isolation of the insoluble residue. The degree of precipitation is determined and it is at the optimal parameters ranging from 98.50 to 100.0%. Material balances of the preparation of precipitates on the basis of hydrochloric acid processing of WBPC without and with the isolation of an insoluble residue are given. The above data allows us to involve and study other types of phosphate raw materials for the production of fertilizer precipitates.

In the present work, we studied the possibility of direct preparation of fertilizer precipitate on the base of hydrochloric acid processing of ordinary phosphorite flour (OPF) from KyzylKum phosphorites, followed by precipitation of hydrochloric acid phosphate extract by suspension of calcium hydroxide to pH 5.0 and separation of solid precipitate from the liquid phase (calcium

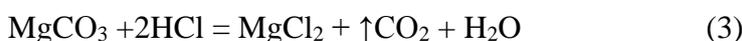
chloride solution) by the filtration method, without the step of separating the insoluble residue from the extract.

## II. EXPERIMENTAL

For laboratory experiments used high-carbonate OPF contents (wt.%): 16.60-P<sub>2</sub>O<sub>5</sub>; 48.62 - CaO; 13.02 - CO<sub>2</sub>; 1.48 - F; 0.12-Cl; 1.48-SO<sub>3</sub>; 0.70 - Fe<sub>2</sub>O<sub>3</sub>; 0.98 - Al<sub>2</sub>O<sub>3</sub>; 9.1-i.r.; CaO : P<sub>2</sub>O<sub>5</sub> = 2.93.

The decomposition of the phosphate raw material was carried out in a laboratory plant consisting of a tubular glass reactor equipped with a screw mixer driven by an electric motor. The reactor was without artificial heating, the temperature of the mixture developed to 30-35°C due to the heat of exothermic reactions. The duration of the decomposition process was 25-30 minutes.

When decomposing phosphorites with hydrochloric acid mainly occur following chemical reactions:



## III. RESULTS AND DISCUSSION

The norm of hydrochloric acid was taken 100% from stoichiometry to decomposition of CaO in the raw material. The concentration hydrochloric acid varied from 25 to 32%. The laboratory tests results are shown in Table 1.

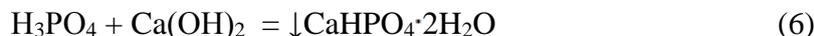
Table 1 shows the contents of hydrochloric acid pulps from phosphorite flour obtained at different concentration acids. From the data it can be seen that as the acid concentration increases, the degree of transition of the w.s. forms of P<sub>2</sub>O<sub>5</sub> and CaO to the liquid phase increases, the content of which in it is from 5.26 to 6.25 and from 15.41 to 18.30%, respectively.

**Table 1. Chemical contents of hydrochloric acid phosphate pulps**

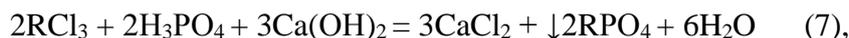
№ experiments	Content of components, mass. %						$\frac{\text{P}_2\text{O}_{5\text{w.s.}}}{\text{P}_2\text{O}_{5\text{total}}} \times 100$	$\frac{\text{Ca O}}{\text{Ca O total}} \times 100$
	P <sub>2</sub> O <sub>5total</sub>	P <sub>2</sub> O <sub>5w.s.</sub>	CaO <sub>total</sub>	CaO <sub>ws.</sub>	Cl	H <sub>2</sub> O		
Concentration of hydrochloric acid – 25%								
1	5,26	5,15	15,41	15,02	19,11	58,93	97,91	97,47
Concentration of hydrochloric acid – 30%								
2	5,97	5,85	17,48	17,16	21,69	51,74	98,16	98,17
Concentration of hydrochloric acid – 32%								
3	6,25	6,18	18,30	18,07	23,20	47,52	98,88	98,74

As the results of the experiments showed, hydrochloric acid converts a phosphate mineral into solution up to 98-99%. However, the use of a high concentration of acid contributes to decrease in the mobility of the hydrochloric acid pulp, which adversely affects its precipitation with known milk and the deterioration of its filtration. In order to avoid this negative phenomenon, it is necessary add to extraction to water. The acidic pulp was added with water in such an amount that in the suspension the moisture content was 70-80% of the total weight.

Then, the dilute hydrochloric phosphoric acid suspension was neutralized with suspension of calcium hydroxide to pH = 5.0. At the neutralizing acidic extract with calcium hydroxide, a reaction occurs between H<sub>3</sub>PO<sub>4</sub> and Ca(OH)<sub>2</sub>, which results in the formation of dicalcium phosphate and precipitates according to the reaction:



In addition, in the pulp between phosphoric acid and RCl<sub>3</sub>, the following reaction takes place:



which reduces the quality of precipitate.

To find the mass of Ca(OH)<sub>2</sub> at various rates, the following formula was used:  $m_{\text{Ca}(\text{OH})_2} = (m_{\text{H}_3\text{PO}_4} \cdot 0,755 \cdot N_{\text{Ca}(\text{OH})_2}) : 100$ , where  $m_{\text{H}_3\text{PO}_4}$  is the total mass of H<sub>3</sub>PO<sub>4</sub> in the obtaining pulp; 0.755 – ratio of the molar masses of Ca(OH)<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub> according to reaction (6). The norm of Ca(OH)<sub>2</sub> for the precipitation of H<sub>3</sub>PO<sub>4</sub> from the hydrochlorophosphoric acid pulps was 80, 90, 100, and 110%. The time of precipitation in all cases was 2.5 hours.

The neutralized pulp was then filtered out on a Buchner funnel, with discharge of 0.65 mm mer. st. through two layers of filter paper. The wet residue remaining on the filter was washed twice with hot water (90°C) at a dry weight ratio of dry precipitate : H<sub>2</sub>O = 1: 2.5 and 1: 2.0. The washed residue was dried together with the filter paper in an oven at a temperature of 90°C. Then the dried precipitate was analyzed. The results are shown in table 2. From these data it is clear that at the same concentration of hydrochloric acid, with an increase in the norm of the neutralizing agent – calcium hydroxide, an increase in the content of P<sub>2</sub>O<sub>5</sub>total, CaOtotal in samples of precipitate. For example, using 25% concentration of hydrochloric acid, an increase in the norm Ca(OH)<sub>2</sub> from 80% to 110% leads to an increase in the content of the total form of P<sub>2</sub>O<sub>5</sub> and CaO in precipitate samples from 24.02 to 26.25 and from 25.22 to 28.35% accordingly. Accordingly, the content of water forms P<sub>2</sub>O<sub>5</sub> and CaO will decrease from 1.94 to 1.05 and from 1.47 to 1.27% in the resulting samples of precipitates. A similar picture is observed for other concentrations of hydrochloric acid.

**Table 2. The main chemical contents of precipitates**

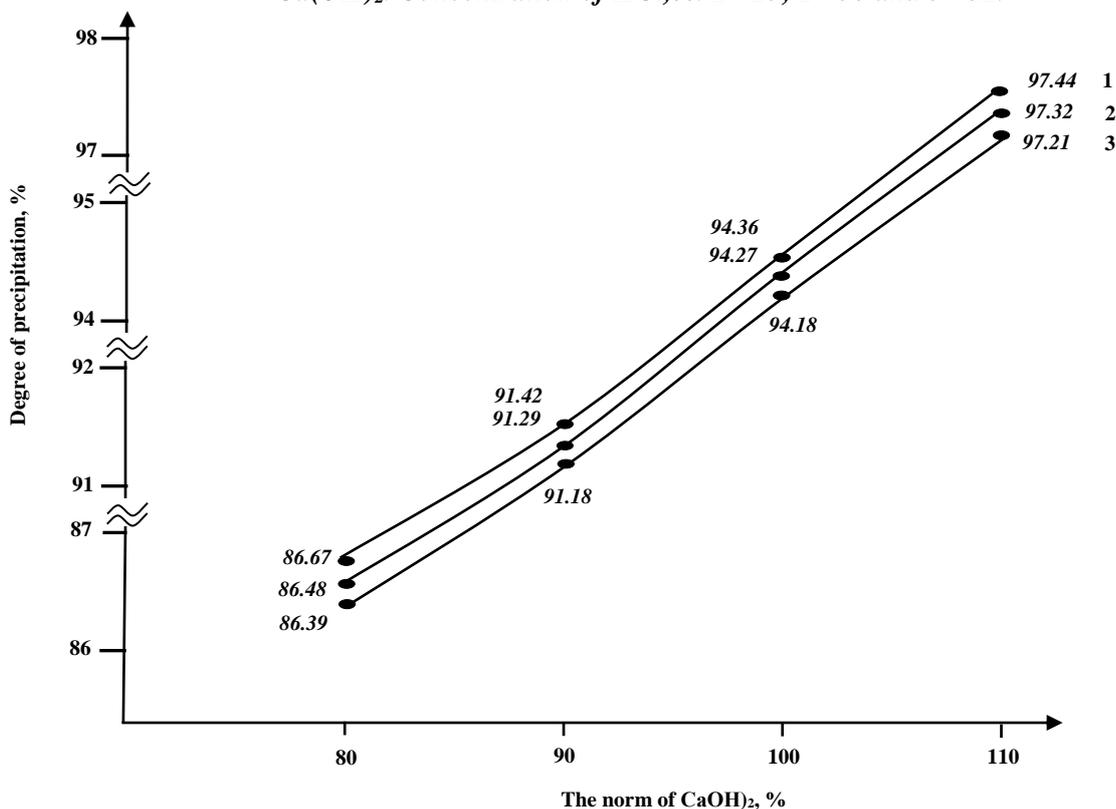
№ experiments	Norm of Ca(OH) <sub>2</sub> , %	P <sub>2</sub> O <sub>5</sub> total	P <sub>2</sub> O <sub>5</sub> accep. 2% citric acid.	P <sub>2</sub> O <sub>5</sub> w.s.	CaOtotal	CaO accep. 2% citric acid	CaOw.s.	Cl
Concentration of hydrochloric acid – 25%								
1	80	24.02	21.61	1.94	25.22	22.94	1.47	0.90
2	90	24.75	21.59	1.53	26.24	23.16	1.33	0.92
3	100	25.26	21.59	1.25	27.03	23.38	1.25	0.96
4	110	26.25	21.91	1.05	28.35	23.95	1.22	1.02
Concentration of hydrochloric acid – 30%								
5	80	23.92	21.61	1.97	25.24	23.22	1.51	0.93
6	90	24.42	21.38	1.57	26.01	23.25	1.38	0.96
7	100	25.16	21.60	1.27	27.26	23.85	1.30	1.00
8	110	26.20	22.04	1.07	28.53	24.39	1.27	1.06
Concentration of hydrochloric acid – 32%								
9	80	23.83	21.77	1.98	25.14	23.22	1.44	0.95

10	90	32	21.58	59	14	3.46	0	0
11	100	06	21.81	28	40	4.08	2	2
12	110	15	21.96	09	42	4.41	0	0

With equal norms of the precipitant, with an increase in the concentration of hydrochloric acid in the products obtained, observed slight increase of the contents  $\text{CaO}_{\text{total}}$  and conversely, a decrease in  $\text{P}_2\text{O}_5$ . For example, at the norm of precipitator – 100% using 25% hydrochloric acid, obtaining precipitate having 25.26%  $\text{P}_2\text{O}_{5\text{total}}$  and 27.03%  $\text{CaO}_{\text{total}}$  using 32% acid - 25.06%  $\text{P}_2\text{O}_{5\text{total}}$  and 27.40%  $\text{CaO}_{\text{total}}$ .

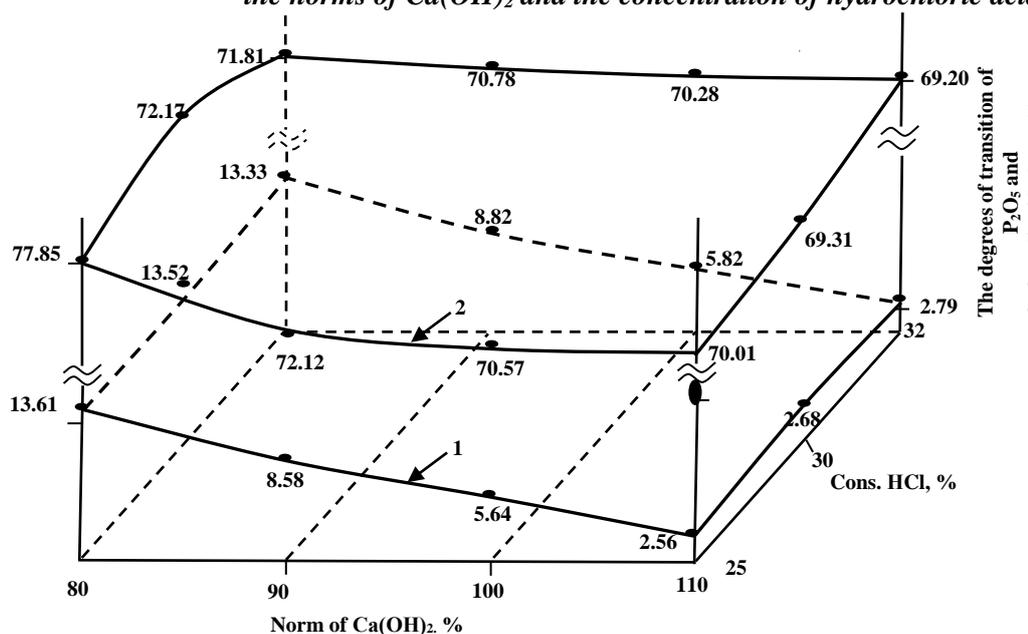
At the figure 1 shows the dependence of the degree of precipitation of the hydrochloric acid pulp on the norm of the precipitant and the concentration of the initial hydrochloric acid. It is seen from it that the higher the norm of the precipitant -  $\text{Ca}(\text{OH})_2$ , the more complete the degree of precipitation. Concentrations of hydrochloric acid have not significant effect on the degree of precipitation of phosphoric acid. The optimum norm of calcium hydroxide for precipitation can be considered 100-110% of stoichiometry. Herewith degree of precipitation is in the range of 94.18-97.44%.

**Figure 1. Dependence of the degree of precipitation of the hydrochloric acid phosphate pulp on the norm of  $\text{Ca}(\text{OH})_2$ . Concentration of HCl, %: 1 - 25; 2 - 30 and 3 - 32.**



At the figure 2 shows the degree of transition of  $\text{P}_2\text{O}_5$  and  $\text{CaO}$  to the liquid phase, depending on the norm of the precipitant and the concentration of hydrochloric acid in the form of volumetric diagram. It can be seen from the diagram that with an increase in the precipitator norm, the  $\text{P}_2\text{O}_5$  transition into the liquid phase decreases significantly, and with an increase in the concentration of hydrochloric acid, an insignificant increase in the transition of  $\text{P}_2\text{O}_5$  to the liquid phase is observed. It is also seen from the diagram that the degree of transition of  $\text{CaO}$  to the liquid phase is mainly affected by the rate of the precipitate.

Figure 2. Dependence of the degree of transition of  $P_2O_5$  (1) and  $CaO$  (2) to the liquid phase, depending on the norms of  $Ca(OH)_2$  and the concentration of hydrochloric acid.



It should be noted that the main problem in the hydrochloric acid method of obtaining fertilizer or feed precipitates from phosphate raw materials is the utilization of solution of calcium chloride, which is process waste. In Sweden [9], Boliden Chemi produces precipitate according to the hydrochloric acid technology, in which the calcium chloride solution evaporates, and is sent to cement production. In Israel [10] solution of calcium chloride is converted into magnesium chloride with the help of magnesium oxide and regeneration of hydrochloric acid is carried out. In the calcium chloride formed in our case, it can be used as an inhibitor of corrosion of reinforcement in road construction and in the manufacture of tiles for sidewalks. It can also be converted with sodium chlorate to calcium chlorate, which is the main intermediate product in the production of calcium chloride defoliant.

#### IV. CONCLUSION

The outcome of this, on the based of the results of laboratory studies, it was shown that it is possible in principle to obtain fertilizer precipitate by hydrochloric acid processing of high carbonized phosphorites of the Central Kyzylkum, followed by neutralization of the hydrochloric acid pulp by suspension with calcium hydroxide, pulp filtration and drying of the product.

#### REFERENCES

- I. Sultonov B.E., Namazov Sh.S., Zakirov B.S. *Hydrochloric acid Kyzylkum Mining Bulletin of Uzbekistan*, pp 99-101, №5, 2015.
- II. Sultonov B.E., Namazov Sh.S., Reymov A.M., Popova O.I. *The 13<sup>th</sup> Conference Inter. Sci.-pract.*, pp 29-32, Makhachkala, Russia. 2016.
- III. Sultonov B.E., Reymov A.M., Namazov Sh.S., Zakirov B.S. *Influence of some technological parameters to the process of precipitation of hydrochloric acid extract of phosphates*, *Uzbek Chem. Jour.*, pp 67-70, №2, 2016.
- IV. Sultonov B.E., Seitnazarov A.R., Namazov Sh.S. and Reymov A.M. *Hydrochloric acid processing of high-carbonate phosphorite flour of Central Kyzylkum to the fertilizer precipitate*. pp 163-168, *Chemical Industry*, № 4, 2015.
- V. Sultonov B.E., Shamuratova M.R., Namazov Sh.S., Kaymakova D.A. *Preparation of precipitate on the basis of washed calcined phosphorite concentrate*. *Universum: Technical sciences*, pp 30-36, Issue 7 (40), 2017.
- VI. Vinnik M.M., Erbanova L.N., Zaitsev P.M. *Methods of analysis of phosphate raw materials, phosphoric and complex fertilizers, food phosphates*, p 218, 1975.
- VII. State standard 12257-77, *Sodium chlorate*, *Standard agency's publishing house*, Moscow, p. 19, 1987.
- VIII. Dorokhova E.N., Prokhorova G.V. *Analytical chemistry: Physical-chemical methods of analysis*, p 302, 1991.
- IX. Fayerson G. *Foder journalen*, 19, pp 3-4, 1980.
- X. Israel Patent 32291. 1972.