RESEARCH OF THE COMPOSITION OF PHOSPHOGYPSUM PRODUCED DURING THE EXTRACTING OF PHOSPHANE ACID FROM ORDINARY PHOSPHORITE POWDER BY THE CLINKER METHOD

ABSTRACT

In this article, processes of washing with water of phosphogypsum that formed during obtaining extractive phosphoric acid, by clinker method, from ordinary phosphorite powder (OPP) that is a raw material of Central Kyzylkum were studied. The phosphogypsum formed by washing a sample of phosphogypsum formed in 103% concentration of sulfuric acid without mixing with water that obtained in the ratio OPP:H_2O=1,0:2,5 was found to contain 2,55% P_2O_5, 29,90% CaO and 42,45% SO_3. The acceptable sizes of washing the same phosphogypsum sample have been determined, mixing in different amounts of hot water. Phosphogypsum obtained in acceptable sizes contains 0,75% P_2O_5, 30,51% CaO and 43,58% SO_3. When washing phosphogypsum samples with water, it saves 2.5 times the amount of water and causes to reduce the amount of P_2O_5 in its composition by at least 3 times. The amount of $CaSO_4$ in the received phosphogypsum sample is increased from 79 to 86%. The samples of phosphogypsum formed without mixing with water and mixing with water were analyzed by X-ray phase analysis and their mutual salt contents were compared.

Keywords: ordinary phosphorite powder; sulphuric acid; the norm of sulphuric acid; washing water, phosphogypsum

1. INTRODUCTION

At present day, the extraction of phosphoric acid from phosphate raw materials using sulfuric acid can be divided into two directions, first one is that decomposition of phosphate raw materials with WPPA and then extraction with sulfuric acid (wet method) and second one is that Initially, phosphate raw material is treated with 93-98% sulfuric acid in the solid phase, and then phosphate acid is extracted from it with water (clinker method). The former method, the wet method, is very common around the world. This method is used in countries with almost phosphate raw materials. In these processes, calcium sulfate is formed as a precipitate and it is separated from the main suspension. Depending on the temperature and the amount of P_2O_5 and SO_4^{-2} in the solution, calcium sulfate is formed in the form of dihydrate ($CaSO_4 \cdot 2H_2O$), hemihydrate ($CaSO_4 \cdot 0.5H_2O$) and anhydride ($CaSO_4$). The main method of production of WPPA, which is relatively simple and reliable both in our country and in other countries, is the dihydrate method. It is known that phosphorites of Central Kyzylkum (Navoi region) are the main base of phosphate raw materials in our country. Many scientific studies have been conducted in our country on obtaining WPPA from various phosphate raw materials PRMs by sulfuric acid method. In this study, the main technological variables of WPPA extraction (process temperature, S : L ratio, concentration of circulating WPPA and amount of free SO_3 in WPPA) and the influence of these parameters on the values of $K_{decomposition}$, $K_{leaching}$ and K_{yield} in the sulfuric acid extraction of washed burnt phosphorite concentrate (WBPC) were studied. The optimal sizes for sulfuric acid extraction have been determined: process temperature - 85-90^{0}C, S : L ratio - 1 : (2,5-3,5), circulating WPPA concentration - 12-15% and amount of free SO_3 in WPPA – 1,5-2,5. In addition, the negative effect of free CaO in WBPC on sulfuric acid extraction was also studied. In order to eliminate this negative effect, a vacuum cooling system of sulfate-phosphate acid porridge was used, and regular research was carried out on the extraction of sulfuric acid WPPA from WBPC with the presence of ammonium sulfate, and an increase in $K_{decom.}$, $K_{leach.}$ and K_{yield} values was achieved. It has also been shown by us that it is possible to obtain WPPA from the chemically enriched phosphorite concentrate (ChEPC), which is formed during the nitric acid enrichment of CK phosphorites. The second method of WPPA production, (clinker method), is currently not used in practice around the world. However, this method has also been studied in foreign countries. In the invention presented by US scientists, phosphorite ore is treated with 98% sulfuric acid, and 65% of the total fluorine is released into the gas phase. The resulting mixture is heated in a rotating oven at 200-300^{o}C for 10-30 minutes and in this case another 25% of fluorine gas is phased out. In general, 90% of fluoride is removed from the system. 99% of total phosphorus goes to WPPA. In another invention presented by US scientists, phosphate raw materials are mixed with 98% sulfuric acid and granulated, the grains are heated at 200-240^{o}C or 350-400^{o}C to remove fluorine, and phosphoric acid is extracted from obtained mixture using water. Production of WPPA in this way has a number of advantages: high concentration of P_2O_5 and low amount of fluorine in the received WPPA. Extraction of phosphoric acid from ordinary phosphorite powder (OPP), which is Central Kyzylkum (CK) phosphorite, by clinker method, and the influence of OPP decomposition time duration on its quality indicators, as well as the processes of extracting WPPA from phosphate-acid-gypsum porridge through water and phosphoric acid solution were studied. It was shown that 8,19-9,37% P_2O_5-containing WPPA (extracted with water) and 16,57-17,39% P_2O_5-containing WPPA (extracted with 10% WPPA) were formed at the given decomposition times. The filtration rates of phosphatic-acid-gypsum porridges in water and WPPA extraction were studied. The filtration rates of phosphatic-acid-gypsum porridges in extraction with water and EFK have been studied [10]. In [11], the possibility of obtaining WPPA from washed-burnt phosphorite concentrate (WBPC) by clinker method was studied. The acceptable sizes of the extraction processes of WPPA with water have been determine. 16.01-16,93% of P_2O_5 is contained in the WPPA composition obtained in acceptable sizes. In contrast to [11], in [12], the influence of different concentrations and standards of sulfuric acid on obtaining WPPA from WBPC and 10% P_2O_5 was used in extracting WPPA `from phosphate-acid porridge.There is 25,02-25,93% of P_2O_5 in WPPA compositions in acceptable sizes. However, in the above-mentioned scientific research studies, the composition of phosphogypsums and the reduction of P_2O_5 in them were not conducted. In this scientific research, the composition of phosphogypsum formed in the process of obtaining WPPA from OPP , which is CK phosphate raw material by clinker, and the results of research on reducing the amount of P_2O_5 in it are presented.

2. MATERIALS AND METHODS

For laboratory studies, OPP with the following composition was used: 17,76% $P_2O_{5\text{total(t.)}}$; 3,15% $P_2O_{5\text{ acceptable by citric acid (ac.c.a.)}}$; 47,51% CaO; 1,79% MgO; 17,02% CO_2; 0,95% Al_2O_3; 0,73% Fe_2O_3; 3,27%SO_3; 2,26% F; 1,02% H_2O; $CaO:P_2O_5$ – 2,68 and 5,25% insoluble residue, and 98% sulfuric acid. Laboratory experiments on the break-up of OPP with sulfuric acid were carried out in a tubular glass reactor equipped with an electric motor-driven screw stirrer. This reactor was placed in a thermostat to keep the temperature constant. A pre-weighed sample of phosphorite (MM) was placed in the reactor, and then 98% sulfuric acid at 100, 103 and 105% standards was slowly added. A pre-weighed sample of phosphorite (mineralized mass) was placed in the reactor, and then 98% sulfuric acid at 100, 103 and 105% standards was slowly added. Phosphorite decay time is 30 minutes. The temperature during the decay time of phosphorite varies in the range of 80-100°C, depending on the standards and concentrations of the acid. The temperature of the reaction mass is kept at 80°C. When OPP is decomposed by sulfuric acid, the following chemical reactions occur:

$Ca_5(PO_4)_3F + 5H_2SO_4 = 5CaSO_4\downarrow + 3H_3PO_4 + \uparrow HF$ (1)

$CaCO_3 + H_2SO_4 = CaSO_4\downarrow + \uparrow CO_2 + H_2O$ (2)

$MgCO_3 + H_2SO_4 = MgSO_4 + \uparrow CO_2 + H_2O$ (3)

$2SiO_2 + 10HF = \uparrow SiF_4 + H_2SiF_6 + 4H_2O$ (4)

$R_2O_3 + 3H_2SO_4 = R_2(SO_4)_3 + 3H_2O$, R=Al, Fe (5)

Large amounts of foam is not produced because of decay time of OPP with sulfuric acid. Clinker with phosphoric acid and gypsum that obtained was mixed with 10% WPPA at a ratio of 1,0:2,5 to the original OPP for 5-10 minutes and filtered under vacuum. Wet phosphogypsum obtained was washed once in boiling water (80-90^{0}C) in unmixed (OPP:H_2O=1,0:2,5) and mixed (OPP:H_2O=1,0:(0,5-2,5)) and these samples were analyzed by specific methods [13,14]. X-rays of phosphogypsum samples were taken on a computer-controlled “Panalytical Empyrean” (Netherlands) powder diffractometer. It was performed under the influence of CuK_α radiation (Kα1= 1,5406 ´, X-ray tube current and voltage 30 mA, 30 kV). In this case, the constant rotation speed of the detector was 4 degrees/min, in steps of 0,02° (ω/2th-link), and the scanning angle was taken from 5° to 90°. The samples were analyzed in a rotating chamber with a rotation speed of 30 in a minut. The obtained radiographs were analyzed by comparison with the tables of radiometric indicators of minerals compiled by ASTM American catalog, Mikheev and Gillers [15, 16].

3. RESULTS AND DISCUSSION

The results of the laboratory experiments are presented in Table 1. From the results presented in Table 1, it can be seen that when OPP:H_2O=1,0:2,5 and phosphogypsum is washed without mixing, the amount of P_2O_5 in phosphogypsum is 2,63%, and the values of CaO and SO_3 will be equal to 29,85% and 42,50%, respectively (when the acid level is 100%). When the acid values are 103 and 105%, P_2O_5 will be equal to 2,55 and 2,52%, CaO will be 29,90 and 29,93%, and SO_3 will be equal to 42,45 and 42,40%, respectively. When the resulting phosphogypsum is washed with mixing water it is observed that phosphogypsum is further purified. For example, when OPP:H_2O is in ratio of 1,0:0,5 and an acid value is 100%, contents of P_2O_5, CaO, SO_3 will be equal to 1,01%, 30,41%, 43,44% respectively. Similar conditions are observed in 103 and 105% standards of sulfuric acid. It is observed that , As the value of the OPP :H_2O ratio decreases, that is, due to the increase in the amount of water, the content of P_2O_5 in phosphogypsum is significantly reduced, and the purity of phosphogypsum, that is, the values of CaO and SO_3 in it also slightly increase. For example, when the OPP:H_2O ratio increased from 1,0:0,5 to 1,0:2,5 at 100% sulfuric acid standard, the amount of P_2O_5 decreased from 1,01 to 0,61%, while the values of CaO and SO_3 increased from 30,41 to 31,05% and from 43,44 to 44,36% respectively. When the acid level was 103%, the content of P_2O_5 in phosphogypsum decreased from 0,92 to 0,57%, while the values of CaO and SO_3 increased from 30,34 to 30,98% and from 43,35 to 44,26%, respectively. When the rate of sulfuric acid was 105%, the amounts of the above substances decrease from 0,80 to 0,52%, from 30,28 to 30,93%, and from 43,25 to 44,19%, respectively. From the above values, it can be seen that when phosphogypsum is washed with mixing water, the amount of P_2O_5

Table 1

The main chemical composition of phosphogypsum samples formed when washed with water

The number of experiment, №	Sulfuric acid standard, %	The content of Phosphogypsum,%		
		P_2O_5	CaO	SO_3

When washed without mixing at OPP:H_2O=1,0:2,5				
1	100	2,63	29,85	42,50
2	103	2,55	29,90	42,45
3	105	2,52	29,93	42,40
When phosphogypsum is washed with mixing				
OPP:H_2O=1,0:0,5				
1	100	1,01	30,41	43,44
2	103	0,92	30,34	43,35
3	105	0,80	30,28	43,25
OPP:H_2O=1,0:1,0				
4	100	0,82	30,54	43,63
5	103	0,75	30,51	43,58
6	105	0,69	30,44	43,49
OPP:H_2O=1,0:1,5				
7	100	0,70	30,60	43,71
8	103	0,65	30,64	43,77
9	105	0,61	30,67	43,81
OPP:H_2O=1,0:2,0				
10	100	0,66	30,73	43,90
11	103	0,62	30,70	43,86
12	105	0,55	30,68	43,83
OPP:H_2O=1,0:2,5				
13	100	0,61	31,05	44,36
14	103	0,57	30,98	44,26
15	105	0,52	30,93	44,19

remaining in it is significantly reduced. It is also observed that the clarity of phosphogypsum increased from 91,38 to 93,40%. it can be concluded from the above discussion, in order to minimize the amount of P_2O_5 in the phosphogypsum samples, it should be washed the phosphogypsum samples mixed with water, and the ratio of OPP :H_2O should be 1,0:1,0. more than this ratio, that is, when there is less water, it becomes difficult to wash the phosphogypsum samples, and when there is more water, water consumption will increases and will appear solutions with less WPPA in large amounts. At the next stage, when the phosphogypsum sample was washed with boiling water without mixing in the ratio OPP:H_2O=1,0:2,5, the main salt content in it was studied using the X-ray phase method. The obtained results are presented in Figure 1. As can be seen from the results, the phosphogypsum sample mainly consists of the following substances: $CaSO_4$-79%, SiO_2-1%, $Ca_2P_2O_7$-7%, $Ca_{14,92}(PO_4)_{2.35}(SiO_4)_{5,65}$-9% and P_2O_5-4%.

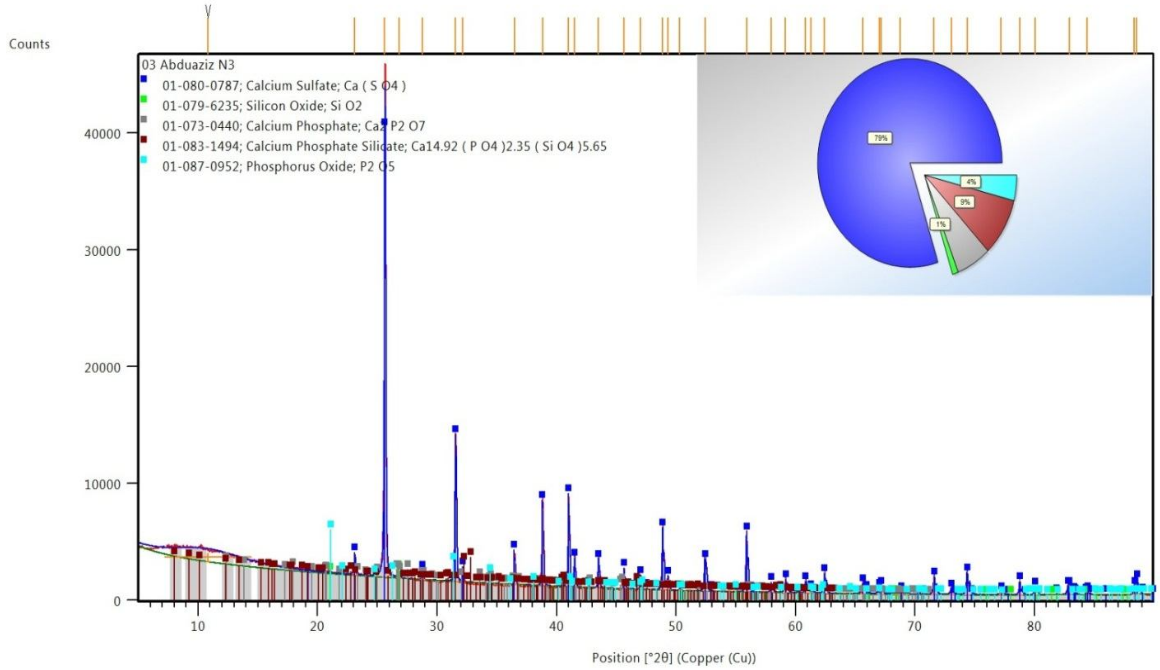

Figure 1. X-ray image of a phosphogypsum sample taken, when washed in hot water without mixing in the ratio OPP:H_2O=1,0:2,5 and its salt content.

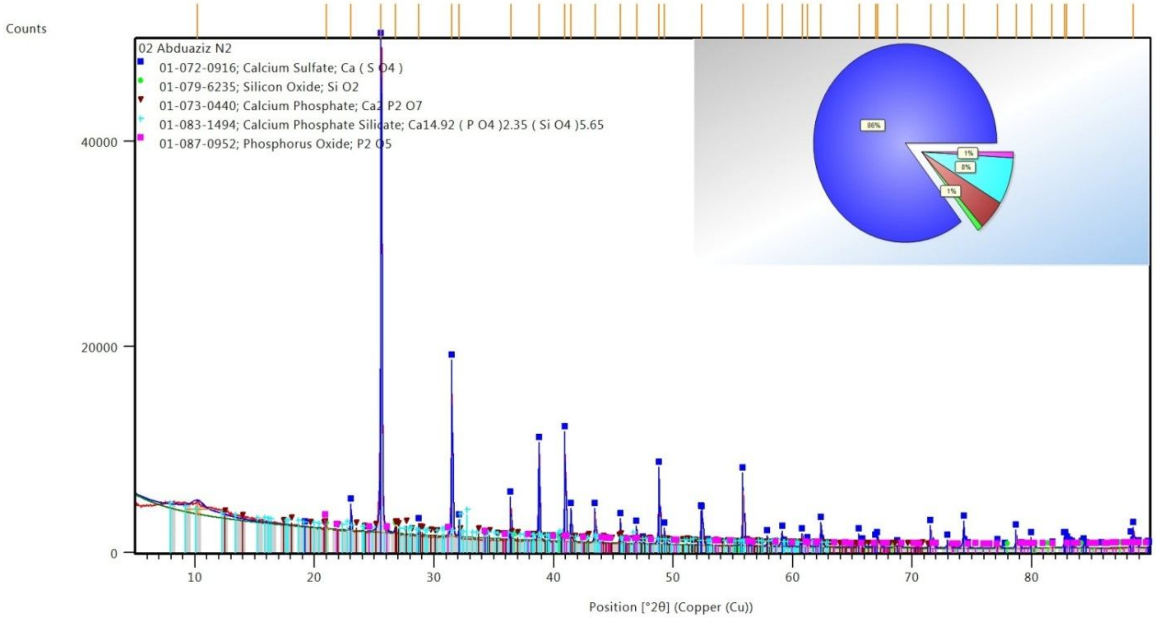

Figure 2. X-ray image of phosphogypsum sample taken, when washed in hot water mixed with OPP :H_2O=1,0:1,0 ratio and its salt content.

Figure 2 shows the main salt content when the phosphogypsum sample is mixed with OPP:H_2O=1,0:1,0 and washed with hot water, and the main salt content of this phosphogypsum sample is as follows: $CaSO_4$-86%, SiO_2-1%, $Ca_2P_2O_7$-4%, $Ca_{14,92}(PO_4)_{2,35}(SiO_4)_{5,65}$-8% and P_2O_5-1%. It can be seen in these results they, when the phosphorgypsum sample is washed in hot water with mixing , the amount of P_2O_5 decreases from 4% to 1%, and the amount of $Ca_2P_2O_7$ decreases from 7% to 4%, while the amount of $Ca_{14,92}(PO_4)_{2,35}(SiO_4)_{5,65}$ decreases by 1% and the amount of the main component $CaSO_4$ increases from 79 to 86%. This will lead to more clean phosphogypsum, and this type of phosphogypsum is more likely to be used in further processing processes.

4. CONCLUSION

The main chemical composition of phosphogypsum formed by processing OPP with sulfuric acid to obtain WPPA was studied. Phosphogypsum formed by washing a sample of phosphogypsum formed in 103% of sulfuric acid without mixing with water obtained in the ratio OPP:H_2O=1,0:2,5 contains 2,55% P_2O_5, 29,90% CaO and 42,45% - SO_3. When the same phosphogypsum sample is washed with water obtained in the ratio OPP:H_2O=1,0:1,0, the resulting phosphogypsum contains 0,75% P_2O_5, 30,51% CaO and 43,58% - SO_3. When phosphogypsum samples is washed with mixing water, it leads to save 2,5 times water and to decline at least 3 times quantity of P_2O_5 in its content. The amount of $CaSO_4$ in the received phosphogypsum sample is increased from 79 to 86%.

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