

CHEMICAL ENRICHMENT OF LOW-GRADE PHOSPHORITES OF CENTRAL KYZYL KUM

Bokhodir E. Sultonov, Shafoat S. Namazov, Bakhtiyar S. Zakirov

*Institute of General and Inorganic Chemistry
of Academy of Sciences of Uzbekistan,
77a, st. Mirzo-Ulugbek, 100170, Tashkent, Uzbekistan
E-mail: bse-chemist-68@mail.ru*

Received 06 January 2014

Accepted 11 April 2014

ABSTRACT

With the purpose of obtaining phosphorus-concentrates suitable for highly-concentrated fertilizers manufacture a process of chemical enrichment of mineralized mass of phosphorites of Central Kyzylkums was investigated. Some technological parameters of the process studied are determined. The phosphorus-concentrates obtained under optimum conditions of chemical enrichment contain (mass %): P_2O_5 23.73 - 24.53, CaO 39.15 - 38.86, CaO_{aqua} 1.98 - 2.17, CO_2 2.49 - 2.26, $CaO:P_2O_5 = 1.51 - 1.60$. They meet all requirements known for the corresponding wet sulfuric acid extraction resulting in phosphorus containing fertilizers production. Their application leads to ca 30 % decrease of sulfuric acid input and phosphogypsum wasted.

Keywords: poor phosphates, mineralized mass, washed calcined phosphorus-concentrate, nitric acid, calcium module, degree of decarbonisation.

INTRODUCTION

The production of phosphate fertilizers is currently limited by raw material's supply. The stable operation of the enterprises producing phosphate fertilizers depends primarily on the quality of the phosphate raw materials. Poor phosphates deposits of Central KyzylKum are the main source used by the phosphate chemical fertilizers producing enterprises at the Uzbekistan Republic. The average phosphorite sample of Jeroy Sardar field contains (mass %): P_2O_5 16.2, CaO 46.2, $CaO:P_2O_5 = 2.85$, CO_2 17.70, MgO 0.60, (R_2O_3) 2.90, (R_2O) 1.50, SO_3 2.65, F 1.94, Cl 0.1, 7.8 of insoluble residuum. This phosphate rock is not suitable for sulfuric and nitric acid extraction because of low concentration of P_2O_5 , high carbonate content and calcium module value [1]. The latter value is recommended to be 1.6 units. It is so because the higher CaO to P_2O_5 is in raw phosphate material, the greater amount of the acid reagent requires. That is why the raw materials have to be enriched.

There are several ways of phosphate raw materials enrichment. The most common one is that of flotation. But its application in this case is extremely difficult because of the close physical and chemical properties of phosphate, calcite and their close "germination" (mixing). The electro-surface properties of these minerals indicate that those materials separation is difficult as well.

The thermal method of enrichment is acceptable in case of high carbonates content in the phosphate raw material. It is used at the Kyzyl-Kum's phosphate plant. It provides raw material's washing up from chloride ions and carbonates removal. However, at phosphorite rock's sorting and classification at the plant, a large amount of waste is formed. It contains balance sheet ore, the so-called mineralized mass, which is not yet involved in mineral fertilizers production. Each year more than 300 thousand tons of mineralized mass are stored. Nowadays, the amount of such wastes accumulated in terraces exceeds 6 million tons [2]. In our opinion, such man-caused terraces provide a reserve for increase of the phosphate

fertilizers production. The average composition of the mineralized mass is as follows (mass %): 14.68 P_2O_5 , 40.8 CaO, 1.17 Al_2O_3 , 1.37 Fe_2O_3 , 0.53 MgO, 1.85 F, 12.84 CO_2 , CaO: P_2O_5 = 2.78.

To increase its supply of highly qualified phosphorus-concentrate the Kizilkum's phosphorite plant needs to increase its power in terms of mine's ore and production of washed calcined phosphorus-concentrate. By 2014 the plant will increase its production capacity from 400 to 716 thousand tons per year with an average P_2O_5 content of 26 % and calcium module close to 2.0 - 2.1. Thus the volume of extra-balanced ores will be increased to result in a rise of the mineralized mass.

The poor Kyzyl-Kum's phosphorites are enriched by treatment with dilute solutions of nitric acid, sulfuric acid and nitrate solutions of calcium nitrate and magnesium [3 - 5]. The disadvantages of these methods refer to foam and large amounts of acid wastes formation as well as with difficulties of diluted solutions utilization.

We studied [6] in details the process of chemical beneficiation of phosphate rocks from Central Kyzyl-Kum by means of their decarbonisation with nitric acid. The latter was used at a norm of 80 - 110 % calculated on the carbonates. This stage was followed by liquid phase's separation and wet cake's washing with 5 - 10 % calcium nitrate solution. The main weaknesses of this process is the low yield of P_2O_5 (65 %) and the formation of an waste solution containing calcium nitrate requiring essential capital costs for its disposal.

Currently, the Institute of General and Inorganic Chemistry of Uzbekistan, Academy of Sciences, conducts targeted research to improve the nitric acid method of KyzylKum's phosphates enrichment. The aim is to have almost 100 % of P_2O_5 in the phosphorite concentrate improving the filterability of nitro-phosphate suspension and a relatively more concentrated solution of calcium nitrate. The present paper reports the results of the laboratory studies of mineralized mass enrichment.

EXPERIMENTAL

Mineralized mass used was of the following chemical composition (mass %): P_2O_5 15.29, CaO 43.12, CO_2 14.72, SO_3 1.62, CaO: P_2O_5 = 2.82 and 58.78 % of nitric acid.

The nitric acid amount was determined in accordance with:

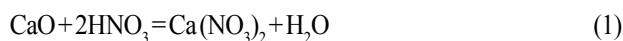
$$m_{HNO_3} = \frac{m_{in.phosph.} \cdot \omega(CaO) \cdot 2,25 \cdot N_{HNO_3}}{58,78}$$

where

$m_{in.phosph.}$ is the mass of the initial phosphorite,

$\omega(CaO)$ is the mass fraction of CaO,

N_{HNO_3} is the norm of HNO_3 and 58.78 (%) is the concentration of HNO_3 , 2,25 is the ratio of the molar masses of HNO_3 and CaO in the reaction:



The norm of nitric acid according to CaO stoichiometry was varied in a range from 40 to 60 %. The interaction of the phosphate raw material (PRM) with nitric acid was performed at 35 - 40°C in a glass reactor equipped with stirrer. The reactor was charged with nitric acid and a suitable amount 25 g of PRM. The latter was fed in portions within 3 - 4 min. Partial decomposition and decarbonization of the phosphate raw materials occurred in the reactor. After 20 minutes the resulting pulp was treated with gaseous ammonia under pH control (getting pH 3) to avoid P_2O_5 transition into a liquid phase. 10 % of calcium nitrate solution stayed at vigorous stirring in the reactor. The weight ratio of phosphorus to calcium nitrate solution was in the range of 1: (2.0 - 3.0). The resultant slurry was separated by filtration under vacuum. The wet phosphorite concentrate was washed with water in a weight ratio of PRM : H_2O = 1:1.5. The wet phosphor-concentrates was dried at 100 - 105°C. The dried precipitate and the filtrate were subjected to chemical analysis by conventional procedures [7]. The degree of decarbonization was calculated according to:

$$\omega = \left(1 - \frac{m_1 \cdot \omega_1 CO_2}{m_2 \cdot \omega_2 CO_2} \right) \cdot 100\%$$

where

m_1 is a samples's mass;

m_2 – the initial weight of phosphorite,

$\omega_1 CO_2$ – the mass fraction of CO_2 in the phosphor-concentrates obtained;

$\omega_2 CO_2$ – the mass fraction of CO_2 in the source of phosphorus.

The washing degree of phosphorus-concentrates was

calculated according to:

$$\varphi = \left(1 - \frac{m_{\text{phos.concen.}} \cdot \omega_{\text{CaO}} \cdot 2,93}{m_{\text{in.phosph.}} \cdot \omega_{\text{CaO}} \cdot N_{\text{HNO}_3} \cdot 2,93 - m_{\text{NH}_3} \cdot 4,82} \right) \cdot 100\%$$

where

$m_{\text{phos.concen.}}$ is a samples's mass;

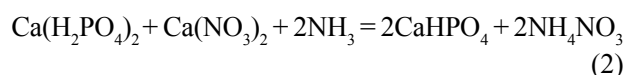
$m_{\text{in.phosph.}}$ is the mass of the initial phosphorite;

$\omega(\text{CaO})$ is the mass fraction of CaO in the initial phosphorite;

N_{HNO_3} is the norm of HNO_3 ;

m_{NH_3} is the mass of NH_3 ;

4.82 is the ratio of molar mass of $\text{Ca}(\text{NO}_3)_2$ and NH_3 in the reaction:



2.93 is the ratio of the molar masses of $\text{Ca}(\text{NO}_3)_2$ and CaO. The water form of CaO in the phosphor-concentrate obtained was defined by a conventional procedures [7].

RESULTS AND DISCUSSION

The laboratory tests results are shown in Table 1. It is seen that P_2O_5 content in the samples of phosphor-concentrates increases with the increase of nitric acid's concentration. For example, at a ratio of PRM:solution $\text{Ca}(\text{NO}_3)_2 = 1:2.0$ and 40 % norm of HNO_3 the content of $\text{P}_2\text{O}_{5\text{total}}$ in the phosphor-concentrate is equal to 21.39 % and at 60 % norm the content is close to 24.38 %. Under these conditions calcium module decreases from 1.95 to 1.64, the extent of washing of phosphor-concentrates from calcium nitrate is in the range of 90.43 - 92.45 %. Similar trends are observed at different ratios PRM : solution of $\text{Ca}(\text{NO}_3)_2$.

At the same norm with an increase of the ratio HNO_3 PRM : solution of $\text{Ca}(\text{NO}_3)_2$, i.e. with the increase of the amount of circulating calcium nitrate solution, there is some increase in the content of P_2O_5 and calcium module decrease. For example, at a rate of 45 % of

Table 1. Chemical composition of phosphorus-concentrates.

Ratio PRM: $\text{Ca}(\text{NO}_3)_2$	P_2O_5 total.	P_2O_5 acceptable by citric acid	P_2O_5 acceptable by EDTA	CaO total	CaO acceptable by citric acid	CaO water solubility	N total	CO_2 total	CaO: P_2O_5	The extent of removal of $\text{Ca}(\text{NO}_3)_2$, %, from phosphorus- concentrates"
Norm of HNO_3 40 % for CaO										
1:2,0	21,39	9,28	6,02	41,71	18,25	1,95	0,97	2,76	1,95	90,43
1:2,5	21,64	9,45	6,14	41,32	18,20	1,84	0,92	2,71	1,91	91,07
1:3,0	21,92	9,64	6,27	40,77	18,08	1,71	0,86	2,67	1,86	91,81
Norm of HNO_3 45 % for CaO										
1:2,0	22,92	10,05	6,58	41,49	18,64	2,02	1,01	2,65	1,81	91,53
1:2,5	23,10	10,19	6,65	40,42	18,24	1,90	0,95	2,60	1,75	92,10
1:3,0	23,33	10,42	6,84	39,66	17,96	1,78	0,89	2,56	1,70	92,67
Norm of HNO_3 50 % for CaO										
1:2,0	23,57	10,61	7,10	40,31	18,61	2,12	1,07	2,54	1,71	92,03
1:2,5	23,73	10,71	7,18	39,15	18,13	1,98	0,99	2,49	1,65	92,61
1:3,0	24,08	10,93	7,31	38,53	17,93	1,86	0,93	2,45	1,60	93,16
Norm of HNO_3 55 % for CaO										
1:2,0	24,18	10,91	7,32	40,21	18,58	2,19	1,11	2,40	1,66	92,56
1:2,5	24,34	11,02	7,39	39,00	18,10	2,08	1,03	2,38	1,60	92,98
1:3,0	24,64	11,22	7,52	38,01	17,72	1,98	0,98	2,33	1,54	93,40
Norm of HNO_3 60 % for CaO										
1:2,0	24,38	11,04	7,40	40,10	18,59	2,28	1,15	2,31	1,64	92,45
1:2,5	24,53	11,16	7,48	38,86	18,14	2,17	1,09	2,26	1,58	92,86
1:3,0	24,78	11,30	7,59	37,48	17,54	2,06	1,03	2,22	1,51	93,29

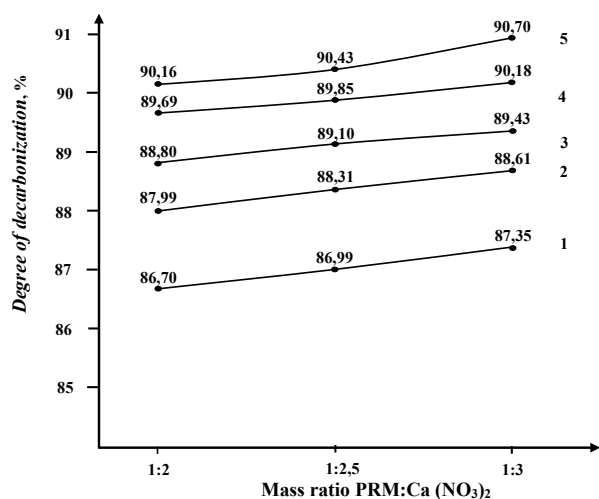


Fig. 1. Extent of decarbonization at various rates of nitric acid. Norm of HNO₃: 1 - 40 %; 2 - 45 %; 3 - 50 %; 4 - 55 %; 5 - 60 %.

nitric acid, if the ratio of PRM : solution of Ca(NO₃)₂ is increased from 1:2.0 to 1:3.0, the content of P₂O₅ increases from 22.92 to 23.33 %, CaO_{water} and calcium module decrease from 2.02 down to 1.78 % and from 1.81 down to 1.70, respectively. The extent of washing of phosphor-concentrate from calcium nitrate increases from 91.53 to 92.60 %. At other norms of nitric acid, a similar picture is obtained, but with a higher norm of HNO₃ in all obtained samples of phosphor-concentrates CaO_{water solubility} content in the form of calcium nitrate is increased. If we vary HNO₃ norm between 40 and 60 % at the selected mass ratios PRM:solution of Ca (NO₃)₂, the extent of washing of phosphor-concentrate varies in the interval of 90.43 – 93.40 %, but at an acid's norm of 60 % the degree of phosphor-concentrates washing from calcium nitrate decreases though insignificantly. This is probably due to Ca(NO₃)₂ formation. It is known that Ca(NO₃)₂ is a hygroscopic substance so a large amount of Ca(NO₃)₂ causes phosphor-concentrate tracking and can lead to a number of technical difficulties during the processing of acid fertilizer production. Therefore, it is impractical to increase the rate of HNO₃ aiming to increase the quality of phosphor-concentrates. Figure 1 shows the extent of decarbonization of phosphorites depending on the rate of nitric acid at different ratios of phosphorus : a solution of Ca(NO₃)₂.

It is seen that the extent of decarbonization of phosphorites is mainly affected by the rate of nitric acid; at the same time the ratio of phosphorus:solution of Ca(NO₃)₂

does affect it marginally. For example, at nitric acid's rate of 40 % and at investigated ratios PRM : solution of Ca (NO₃)₂ 1:(2.0 - 3.0) the degree of decarbonization increases in the range from 86.70 to 87.35, i.e. only with 0.65 %. The increase of nitric acid's norm from 40 up to 60 % contributes to the increase of the degree of decarbonization from 86.70 to 90.16, from 86.99 to 90.43, from 87.35 to 90.70 %, in case of PRM : solution of Ca(NO₃)₂ 1:2.0; 1:2.5; and 1:3.0, respectively.

We suppose that the decarbonization extent is lower when compared ratio of theoretical one because calcium carbonate is present in three forms: calcite cement - "exocalcite" to the calcite relics preserved from substitution of phosphate within phosphatized shell - "endocalcite", carbonate group isomorphically included in the crystal lattice of the mineral phosphate [8]. Therefore in the course of decarbonization, some of the "endocalcite" and the carbonate groups are isomorphically included in the crystal lattice to remain in the enriched phosphor-concentrate.

The results obtained provide to determine the optimal conditions of the enrichment process: HNO₃ norms 50 – 60 % and the mass ratio of PRM : solution of Ca(NO₃)₂ = 1:2.5. The phosphor-concentrates composition, depending on the HNO₃ rate, changes (mass %): P₂O_{5 total} from 23.73 to 24.53; P₂O_{5 acceptable} by citric acid from 10.71 to 11.16; P₂O_{5 acceptable} by EDTA from 7.18 to 7.48; CaO_{total} from 39.15 to 38.86; CaO_{acceptable} by citric acid from 18.10 to 18.14; CaO_{water solution} from 1.98 to 2.17; CO₂ from 2.49 to 2.26; N from 0.99 to 1.09. The obtained phosphor-concentrates are quite suitable for the production of concentrated phosphate fertilizers.

CONCLUSIONS

The fundamental possibility of obtaining of chemical phosphorite concentrate through interaction of phosphate mineralized mass of Central Kyzyl-Kum's region with a concentrated nitric acid is experimentally verified. Under optimal conditions of chemical enrichment, the phosphor-concentrates obtained meet the requirements for sulfuric acid extraction. The advantages of the method proposed are as follows:

- Possible recycling of phosphates of Central Kyzyl Kum to obtain chemically enriched phosphor-concentrates containing 23-24 % of P₂O₅.

- A significant reduction of heat and power costs;
- Maximum decrease of calcium module ($\text{CaO} : \text{P}_2\text{O}_5$) to 1.5 - 1.6 against values of 2.0 - 2.1 in the washed phosphor-concentrates;
- During the processing of chemically enriched phosphor-concentrate the saving of scarce sulfuric acid reaches at least 30 %, while the volume of phosphor-gypsum obtained as a waste decreases to 30 % too.

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