Phosphoric acid activation of phosphorites of Central Kyzylkum

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The article presents a method of receiving the concentrated single phosphate fertilizers with the content of absorbable $P_2O_5$. The experiment made assumed processing of ordinary phosphate flour, washed concentrate, dust fraction, mineralized mass and thermoconcentrate of Central Kyzylkum’s phosphorites by incomplete norm of wet-process phosphoric acid. This process lasts 30 minutes at $75^\circ$C; the weight ratio of $P_2O_5$ in acid to $P_2O_5$ in raw material makes 1 : 0.3 and 1 : 0.5

Keywords: Phosphorites, acid, decarbonization, activation, fertilizer

Introduction

Phosphorite deposits of the Central Kyzylkum are the main sources of raw materials for phosphate fertilizer’s plants of Uzbekistan. Geological phosphorite manifestations are not rare for the republic. They occur at regions of: Fergana, Surkhandarya, Navoiy, Central Kyzylkum, Bukhara-Khiva and Karakalpakistan (Shayakubov, Ilyashenko, Boyko, Kudryashov, and Turanov, 1982). But the most promising in terms of practical industrial development is the region of Central Kyzylkum (Shayakubov, Mikhailov, Boiko, Kudryashov, and Zhuravlev, 1983).

Kyzylkum’s phosphorite basin covers an area of 65 thousand km². If we assume that phosphorite resources suitable for industrial application cover only 5% of this area, than their estimated reserves with an average total capacity of their layers a 2.5 m thick reaches 16.25 billion tons, or 1.95 billion tons of $P_2O_5$ (at average $P_2O_5$ grade of 12%) (Popov and Konov, 1981). The Kyzylkum’s granular phosphorite ores are identified and studied over an area of 3000 km². Calculated phosphate resources laying not deeper than 300 m reach 10 billion tons (that is equal to about 2 billion tons of $P_2O_5$). The same resources available for open pit (laying not deeper than 60 m) make 1-1.2 billion tons of ore or 200-240 million tons of $P_2O_5$ (Shayakubov, Malmatin, Yuldashev, Ilyashenko, Boyko, and Fathullaev, 1987).

At present, phosphorite’s numerous manifestations and four deposits of granular type (Dzhetymtausky, Jeroy-Sardarinsky, Tashkurinsky, and Karakatinsky) are revealed there involving more than 50% of predicted $P_2O_5$ basin’s resources.

Jeroy-Sardarinsky deposit, which projected ore’s resources are estimated to be 2.9-3.0 billion tons (or 550 million tons of $P_2O_5$), is the most studied one. Resources field approved by the State Reserves Committee of former USSR are 223.9 million tons of ore with an average grade of 19.42% $P_2O_5$ or 43.5 million tons of $P_2O_5$. These reserves are enough to satisfy the republic’s agriculture needs in phosphate fertilizers for 62 years. Just basing on these fields the Kyzylkum’s phosphorite plant appeared.

The ores of Jeroy-Sardarinsky’s deposit are characterized with following average mineral composition, %: francolite 56.0; calcite 26.5; quartz 7.5-8.0; hydromica minerals and
feldspars 4.0-4.5; gypsum 3.5; goethite 1.0; zeolite - less than 1.0; the organic matter - approximately 0.5 (Shinkorenko, Mikhailova, and Levkina, 1989). The main mineral, comprising phosphate’s grains, is fluorine carbonate apatite (francolite). Its cell’s parameters are: \( a = 9.33 \, \text{Å}, \, c = 6.89 \, \text{Å} \). It contains 33% \( \text{P}_2\text{O}_5 \), 3.5-4.0% \( \text{CO}_2 \) and 3% \( \text{SO}_3 \), isomorphically embedded into its crystal structure.

Composited sample of the phosphorite from Jeroy-Sardarinsky field contains (weight, %): 16.2 \( \text{P}_2\text{O}_5 \); 46.2 \( \text{CaO} \); \( \text{CaO} : \text{P}_2\text{O}_5 = 2.85 \); 17.7 \( \text{CO}_2 \); 0.6 \( \text{MgO} \); 2.9 \( (\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3) \); 1.5 \( (\text{K}_2\text{O} + \text{Na}_2\text{O}) \); 2.65 \( \text{SO}_3 \); 1.94 F; 0.1 CI; 7.8 insoluble residue. This raw material is not fit for processing for concentrated phosphorus fertilizers. According to standards (Andreev, Brodskiy, Zabeleshinskiy, Zorina, Klenitskiy, Kochetkov, Rodin, and Evenchik, 1987), the phosphate raw material suitable for phosphoric acid production by sulfuric extraction method (wet-process) should meet the following requirements: content of \( \text{P}_2\text{O}_5 \) not less than 24.5%, \( \text{CO}_2 \) not more than 8%, \( (\text{R}_2\text{O}_3 : \text{P}_2\text{O}_5) \) not more than 12%, \( (\text{MgO} : \text{P}_2\text{O}_5) \) not more than 7-8%; recommend value of calcium module \( (\text{CaO} : \text{P}_2\text{O}_5) \) - 1.6%; chlorine - not more than 0.04%.

If the raw material is poor with \( \text{P}_2\text{O}_5 \) content, it should be enriched. The first step is to get rid of the excessive amount of carbonates. The second one - is ore’s enrichment with flotation (Ratobylskaya, Boyko and Kozhevnikov, 1979). But Kyzylkum’s phosphate rock, along with a high degree of carbonation is characterized with thin intergrowth of phosphate minerals with calcite, therefore attempts of flotation enrichment were not successful (Amirova, 1983; Boyko, 1980; Kuzovlev, Maltsev, and Pugach, 1981).

Anyway the Kyzylkum’s phosphorite plant found the most optimal method of ore’s enrichment including its washing to chloride ions withdrawal, than burning for carbonates decomposition with \( \text{CO}_2 \) removal. So since 2006 the plant produced annually 400 thousand tons of thermoconcentrate, 200 thousand tons of washed and dried concentrate and 200 thousand tons of ordinary phosphorite flour. Their composition is the following (weight, %): for thermoconcentrate 27.26 \( \text{P}_2\text{O}_5 \), 53.36 \( \text{CaO} \), 1.3 \( \text{Al}_2\text{O}_3 \), 0.51 \( \text{Fe}_2\text{O}_3 \), 0.6 \( \text{MgO} \), 1.91 F, 2.41 \( \text{CO}_2 \); for washed and dried concentrate: 18.22 \( \text{P}_2\text{O}_5 \), 47.28 \( \text{CaO} \), 1.18 \( \text{Al}_2\text{O}_3 \), 0.6 \( \text{Fe}_2\text{O}_3 \), 0.99 \( \text{MgO} \), 2.29 F, 14.90 \( \text{CO}_2 \); for ordinary phosphorite flour: 17.20 \( \text{P}_2\text{O}_5 \), 46.22 \( \text{CaO} \), 1.24 \( \text{Al}_2\text{O}_3 \), 1.05 \( \text{Fe}_2\text{O}_3 \), 1.75 \( \text{MgO} \), 2.00 F, 16.0 \( \text{CO}_2 \);

The Kyzylkum’s phosphorite plant’s products are consumed with following local customers: the thermoconcentrate - with OJSC “Ammofos-Maxam” (Almalyq city) for production of highly concentrated nitro-phosphorus fertilizers: ammonium phosphate (10% N, 46% \( \text{P}_2\text{O}_5 \)), ammonium sulfate phosphate (15-19% N, 4-23% \( \text{P}_2\text{O}_5 \)) and “Suprefose” (8-15% N, 20-24% \( \text{P}_2\text{O}_5 \)); the ordinary phosphorite flour - with OJSC “Samarkandklimyo” (Samarqand city) for processing into nitrocalcium phosphate (6% N, 16% \( \text{P}_2\text{O}_5 \)); the washed and dried concentrate - with OJSC “Kokand superphosphate plant” (Kokand city) for production of ordinary ammoniated superphosphate (1.5% N, 12.5% \( \text{P}_2\text{O}_5 \)).

As a result, national industry produces about 169 tons of 100% \( \text{P}_2\text{O}_5 \), which is still very far from the requirements in phosphate fertilizers (518.27 tons of \( \text{P}_2\text{O}_5 \) per year) of the agriculture (Ibragimov and Beglov, 2005), so the increasing of their production is quite obvious.

It should be noticed that at production of ordinary flour phosphorite by ore crushing and dry processing there are formed so-called wastes that are still not involved in traditional mineral fertilizers industry and are stored. They are as follows: dust fraction (18-19% \( \text{P}_2\text{O}_5 \)), mineralized mass (12-14% \( \text{P}_2\text{O}_5 \)). At present, the last one has been piled up more than 6 million tons. At its washing from the chloride-ions about 30% of \( \text{P}_2\text{O}_5 \) initially located in the ore is lost with rinse water and goes into the slurry storage. So the content of \( \text{P}_2\text{O}_5 \) in dried sludge phosphorite reaches 8-10%. In a media of deficiency of qualitative phosphatic raw materials we consider being necessary to involve these wastes in agricultural practice. All the industry needs is to transform the unacceptable for plant the form of \( \text{P}_2\text{O}_5 \) into the acceptable one. But such a process based on poor Kyzylkum’s...
phosphorite ore and accordingly traditional technology (nitrogenous, sulfuric and hydrochloric acid processing of raw materials) is expensive and unprofitable. The exit out of this situation is in application of approach of phosphoric acid activation according to poor phosphate raw materials (Beglov, Ibragimov, and Sadykov, 2005). Even so the so-called un-decomposed or partly decomposed phosphates had been obtained, whose agrochemical tests showed their high efficiency (Romodina, 1981; Ostanin, 1987).

Phosphoric acid activation of phosphate raw materials involves their processing with low norm of phosphoric acid in comparison with the norm, which is required for complete decomposition of the phosphorite with the formation of monocalcium phosphate according to the reaction:

$$\text{Ca}_3\text{F}(\text{PO}_4)_3 + 7\text{H}_2\text{PO}_4 + 5\text{H}_2\text{O} \rightarrow 5\text{Ca}(\text{H}_2\text{PO}_4)_2\cdot\text{H}_2\text{O} + \text{HF}$$

Stoichiometric norm of phosphoric acid for the decomposition of each of the five types of Central Kyzylkum’s phosphorites is calculated out of the equation:

$$\text{CaO in raw material + P}_2\text{O}_5 \text{ in the acid} \rightarrow \text{Ca}(\text{H}_2\text{PO}_4)_2$$

**Experimental**

Four types of Central Kyzylkum’s phosphate raw (PR) were applied: ordinary phosphorite flour, thermoconcentrate and wastes of Kyzylkum phosphorite plant: dust fraction and mineralized mass. They were obtained at phosphorite plant except for washed concentrate which appeared after the washing of ordinary phosphorite flour with water. Chemical and disperse composition of the raw materials used in the experiments are shown in Tables 1, 2. For above mentioned activation of phosphates, the wet-process phosphoric acid (WPA), phosphate derived from thermoconcentrate of Central Kyzylkum by dehydrate way at OJSC “Ammofos-Maxam”, with content (weight, %): 18.69 P2O5, 0.26 CaO; 0.64 MgO; 0.73 Al2O3; 0.46 Fe2O3; 2.72 SO3; 1.02 F; 0.093 Cl, were applied.

<table>
<thead>
<tr>
<th>Types of phosphate</th>
<th>Content of the components of the masses, %</th>
<th>CaO : P2O5 acceptable : P2O5 total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P2O5</td>
<td>CaO</td>
</tr>
<tr>
<td>Thermoconcentrate</td>
<td>27.26</td>
<td>53.36</td>
</tr>
<tr>
<td>Ordinary of phosphorite flour</td>
<td>17.20</td>
<td>46.22</td>
</tr>
<tr>
<td>Dust fraction</td>
<td>18.54</td>
<td>44.72</td>
</tr>
<tr>
<td>Mineralized mass</td>
<td>14.68</td>
<td>40.80</td>
</tr>
</tbody>
</table>

For ordinary phosphorite flour the 100% norm of phosphoric acid (stoichiometric norm to monocalcium phosphate) reaches 1 g P2O5 in phosphate flour at 6.82 g P2O5 in acid or P2O5:5WPA = P2O5:5PR = 1 : 0.147. For the dust fraction - 1 g P2O5 in dust fraction to 6.12 g of P2O5 in acid or P2O5:5WPA = P2O5:5PR = 1 : 0.163. For mineralized mass - 1 g P2O5 in mineralized mass to 7.05 g of P2O5 in acid or P2O5:5WPA = P2O5:5PR = 1 : 0.142. For thermoconcentrate - 1 g P2O5 in thermoconcentrate to 4.96 g of P2O5 in acid or P2O5:5WPA = P2O5:5PR = 1 : 0.202. The result of treatment of phosphate raw material with phosphoric acid in the range of weight ratios P2O5 to P2O5 in the raw material in acid, from 1 : 1 to 1 : 3.33 (P2O5:5WPA: P2O5:5PR = 1 : 1 to 1 : 0.3) carried at lab’s conditions, at temperature 75°C and interaction time 30 min is offered at Table 3.
TABLE 2. PARTICULATE COMPOSITION OF RAW MATERIALS

<table>
<thead>
<tr>
<th>Size grade, mm</th>
<th>Thermoconcentrate</th>
<th>Ordinary of phosphorite flour</th>
<th>Dust fraction</th>
<th>Mineralized mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2+0.5</td>
<td>1.6</td>
<td>-</td>
<td>-</td>
<td>4.4</td>
</tr>
<tr>
<td>-0.5+0.315</td>
<td>4.8</td>
<td>1.5</td>
<td>1.5</td>
<td>10.2</td>
</tr>
<tr>
<td>-0.315+0.16</td>
<td>32.2</td>
<td>6.3</td>
<td>5.6</td>
<td>34.1</td>
</tr>
<tr>
<td>-0.16+0.1</td>
<td>25.9</td>
<td>20.3</td>
<td>5.7</td>
<td>14.5</td>
</tr>
<tr>
<td>-0.1+0.063</td>
<td>18.1</td>
<td>38.3</td>
<td>15.0</td>
<td>16.3</td>
</tr>
<tr>
<td>-0.063+0.05</td>
<td>3.3</td>
<td>17.2</td>
<td>9.8</td>
<td>4.7</td>
</tr>
<tr>
<td>-0.05</td>
<td>13.5</td>
<td>16.4</td>
<td>62.4</td>
<td>15.8</td>
</tr>
<tr>
<td>Source weight</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

TABLE 3. ACTUAL NORMS OF PHOSPHORIC ACID FOR PROCESSING OF PHOSPHATE RAW MATERIALS IN STOICHIOMETRY OF EACH TYPE OF PHOSPHATE RAW MATERIALS AND DIFFERENT RATIO P2O5WPA: P2O5PR

<table>
<thead>
<tr>
<th>Types of phosphate</th>
<th>Norm of WPA (in % from stoichiometry) at ratio P2O5WPA: P2O5PR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 : 0.3</td>
</tr>
<tr>
<td>Ordinary of phosphorite flour</td>
<td>48.9</td>
</tr>
<tr>
<td>Dust fraction</td>
<td>54.5</td>
</tr>
<tr>
<td>Mineralized mass</td>
<td>47.3</td>
</tr>
<tr>
<td>Thermoconcentrate</td>
<td>67.2</td>
</tr>
</tbody>
</table>

Results and discussion

After treatment of phosphorites with phosphoric acid the pulp was dried and products were analyzed (Vinnik, Erbanova, Zaytsev, Ionova et al., 1975). The overall data of interaction between different types of phosphate raw materials with phosphoric acid are similar (Figures 1, 2). They differ only in absolute values of the component content in the products. The first step is the decomposition of carbonates:

\[
\text{CaCO}_3 + 2\text{H}_3\text{PO}_4 \rightarrow \text{Ca(H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + \text{CO}_2
\]

This is convincingly demonstrated by Figure 1. The degree of decarbonization is a degree of removal of CO\text{2} out of raw materials treated. Even with the norm acid in a range 14-16% the stoichiometric degree of decarbonization of the phosphorites reaches the level of 61-68%. And with the norm of acid in a range from 47 to 55% of stoichiometry, the above mentioned parameter reaches the level 91-98% depending on the type of raw material. The degree of decarbonization is equal to a degree of CO\text{2} removal out of it.

Simultaneously but in a less extent the phosphate mineral is decomposed too:

\[
\text{Ca}_3\text{F(PO}_4)_3 + 7\text{H}_3\text{PO}_4 + 5\text{H}_2\text{O} \rightarrow 5\text{Ca(H}_3\text{PO}_4)_2 \cdot \text{H}_2\text{O} + \text{HF}
\]
The more acid is taken, the more complete decomposition occurs. So, for ordinary phosphate flour at a ratio of $P_2O_{5WPA} : P_2O_{5PR} = 1 : 1$ (norm acid 14.7\% of stoichiometry) a product is characterized with content (weight, \%): $P_2O_{5\text{total}} = 30.13$; $P_2O_{5\text{acceptable}} = 18.27$; $P_2O_{5\text{water-soluble}} = 1.08$ and with a degree of decarbonisation: 66.8\%. The hydrated forms of $P_2O_5$ and CaO indicate the presence of monocalcium phosphate, in a low amount. The difference between the acceptable and hydrated forms of $P_2O_5$ in the product illustrates both the contents of activated form of phosphate mineral and of the dicalcium phosphate.
The difference between the total and acceptable forms of P₂O₅ reveals un-decomposed phosphate mineral in the product.

When the weight ratio P₂O₅WP : P₂O₅PR is equal to 1 : 0.3 (norm acid 48.9% of stoichiometry) the product contains (weight, %): P₂O₅total = 42.22; P₂O₅acceptable 38.73; P₂O₅water-soluble 27.23, and its degree of decarbonization reaches 95.5%. That is, calcium carbonate left there makes about 4.5%.

Basically, the product consists of monocalcium phosphate, dicalcium phosphate and activated form of phosphate mineral. There is a high content of total, acceptable and aqua-soluble forms of P₂O₅ (P₂O₅acceptable : P₂O₅total = 91.73%; P₂O₅water-soluble : P₂O₅total = 64.49%). Such a product, concerning its composition, does satisfy the requirements of agriculture to a single phosphorus containing fertilizer.

At the ratio P₂O₅WP : P₂O₅PR = 1 : 0.5 (norm acid 29.3% of stoichiometry) the carbonates are decomposed to a degree of 87.8%, and the product contains (weight, %): P₂O₅total = 36.60; P₂O₅acceptable 28.10; P₂O₅water-soluble 14.36; P₂O₅acceptable : P₂O₅total = 76.78; P₂O₅water-soluble : P₂O₅total = 39.23. The high content of total and acceptable P₂O₅ makes it also suitable for agriculture’s application.

From the dust fraction characterized with a ratio of P₂O₅WP : P₂O₅PR = 1 : 0.5 (norm acid 32.7% of stoichiometry) the product is obtained with the degree of decarbonization 90.0% and the content of P₂O₅total 35.92%; P₂O₅acceptable : P₂O₅total = 78.40%; P₂O₅water-soluble : P₂O₅total = 45.19%. When the ratio P₂O₅WP : P₂O₅PR is equal to 1 : 0.3 (norm acid 54.5% of stoichiometry) the degree of decarbonization is 97.8% and the product contains P₂O₅total 38.70%; P₂O₅acceptable : P₂O₅total = 93.31%; P₂O₅water-soluble : P₂O₅total = 69.84%. Optimal norm of wet-process phosphoric acid appropriate for decomposition of different types of Central Kyzylkum’s rock phosphate is clearly visible at Figure 2. At this level the products must contain high level of total and acceptable forms of P₂O₅ and relative content of aqua-soluble form of P₂O₅ should be at least 50%. For example, at Figure 2-A illustrates the optimal norm of acid for the treatment of ordinary phosphate flour equal to 40% of the stoichiometric norm. This yields a product containing P₂O₅total 40%; P₂O₅acceptable : P₂O₅total = 87% and P₂O₅water-soluble : P₂O₅total = 60%.

To treat the dust fraction the optimal norm acid should be 40% of the stoichiometric norm (Figure 2-B). The product contains P₂O₅total 36%; P₂O₅acceptable : P₂O₅total = 88%; P₂O₅water-soluble : P₂O₅total = 59%. For processing of mineralized mass the optimal norm acid should be also 40% of its stoichiometric norm (Figure 2-C). Resulting product contains P₂O₅total 36%; P₂O₅acceptable : P₂O₅total = 83%; P₂O₅water-soluble : P₂O₅total = 53%. To treat the thermoconcentrate the optimal norm acid should be 30% of the stoichiometric norm (Figure 2-D). The product contains P₂O₅total 40%; P₂O₅acceptable : P₂O₅total = 66%, P₂O₅water-soluble : P₂O₅total = 50%.

Conclusion

Interaction between the ordinary phosphorite flour, dust fractions, mineralized mass, washed thermoconcentrate of phosphorites of Central Kyzylkum with not evaporated wet-process phosphoric acid taken at incomplete norm of the acid (P₂O₅WP : P₂O₅PR from 1 : 1 to 1 : 0.3) at temperature 75°C and contact time 30 minutes has been studied. Compositions of fertilizers received thus are defined. Optimum norms of phosphoric acid are determined for decomposition of phosphate raw materials at which the end product - a single phosphate fertilizer, has the high maintenance of general and assimilate forms of P₂O₅ and relative maintenance of water-soluble form of P₂O₅ there exceeds 50%. These norms at processing of the ordinary phosphorite flour, dust fractions, mineralized mass are equal to 40% from stoichiometric norm necessary for full decomposition of phosphate.
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Raw materials with formation of monocalcium phosphate, while at thermoconcentrate processing they reach 30%. Thus, the ordinary phosphorite flour, dust fraction, mineralized mass and thermoconcentrate of Central Kyzylkum are quite appropriate for production of single phosphate fertilizers by raw materials activation with phosphoric acid.

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