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# BENEFICIATION OF LOW-GRADE PHOSPHORITES BY HUMIC ACID

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**ABSTRACT**
This paper presents the results of research on the beneficiation of Akzhar phosphorites (Kazakhstan) by humic acid synthesized from brown coal. The results of scanning electron microscopy studies of microstructure and IR spectroscopic data suggest the feasibility of using humic acid as a leachable reagent for the beneficiation of low-grade phosphorites. The operating parameters of leaching by humic acid were determined. The obtained data complement the theory of using organic acids to remove carbonate impurities in the composition of phosphorites, and also provide scientific justification for further application in production.
**Keywords:** Low-grade Phosphorite, Humic Acid, Beneficiation, Carbonate Impurities.
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## INTRODUCTION

Today, the phosphorus industry is experiencing a shortage of high-quality phosphate raw materials. Due to the reduced content of the main components in phosphorites, processing most of the raw materials using traditional technologies is inefficient. The search for new technological solutions that allow low-grade phosphates to be enriched with a high content of $P_2O_5$ is one of the urgent problems of enterprises in the phosphorus industry.

The Karatau phosphate basin is the main source of raw materials for the production of phosphorites in Kazakhstan. At the global level, it belongs to large phosphorous deposits. The reserves of phosphorous rocks in the Karatau basin for $P_2O_5$ amount to about 700 million tons. According to the main content of phosphorus pentoxide, deposits are usually classified into high-grade (25-32%), ordinary (20-24%) and low-grade (below 20%). The main deposits are Zhanatas, Koksu and Kokzhon. In recent years, the first two fields have been depleted, as they have been exploited since the mid-twentieth century. The use of low-grade phosphorites is not possible due to the technical inconsistency of raw materials. Research on the enrichment of Kazakhstan's phosphorites is not at the proper level. Flotation methods have been studied in the past, but enrichment methods are not currently used[1].

Similar problems of raw material enrichment concern scientists in other countries. For example, one of the promising methods of chemical enrichment was studied in Egypt, where organic acids were used as a leachable reagent. According to these studies, oxalic acid was a strong reagent for the phosphorites of the Abu Tartour deposit. According to the results, the content of phosphorus pentoxide increased from 21.8% to 28% [2]. The use of organic acid has yielded results in China[3] and Uzbekistan.[4]

The mechanism for leaching phosphorites with organic acids is based on the selective addition of calcium and magnesium with organic acid at low temperatures and concentrations. In this case, the removal of phosphates by organic acids does not occur. Consequently, due to the removal of calcium and magnesium, the phosphate component increases.[3]

One type of organic acid is humic. Humic acids are usually obtained from peat and brown coal.[5] Having a polyfunctional and irregular structure, humic acids are often used for the production of fertilizers[5-7], land reclamation[8], and medicine.[9]

## EXPERIMENTAL

### Material and Methods

Humic acid was synthesized from brown coal of the Lengerdeposit (Southern Kazakhstan) according to


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the Interstate Standard[10]. Humic acid extraction is performed using sodium hydroxide, and then hydrochloric acid is used to precipitate humic acids. The resulting humic acid had a pH=0.8.

Phosphate rock from the Akzhar deposit with the following chemical composition was selected for beneficiation (Table-1):

Table-1: Elemental Composition of Akzhar's Phosphate Rock

| C | O | F | MgO | $Al_2O_3$ | Si | $P_2O_5$ | S | $K_2O$ | CaO | $Fe_2O_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 10% | 32,5% | 1.5% | 2% | 1% | 17% | 14% | 0.1% | 0.3% | 21% | 0.55 |

**General Procedure**

The process of leaching phosphates by humic acid was carried out according to the scheme (Fig.-1):

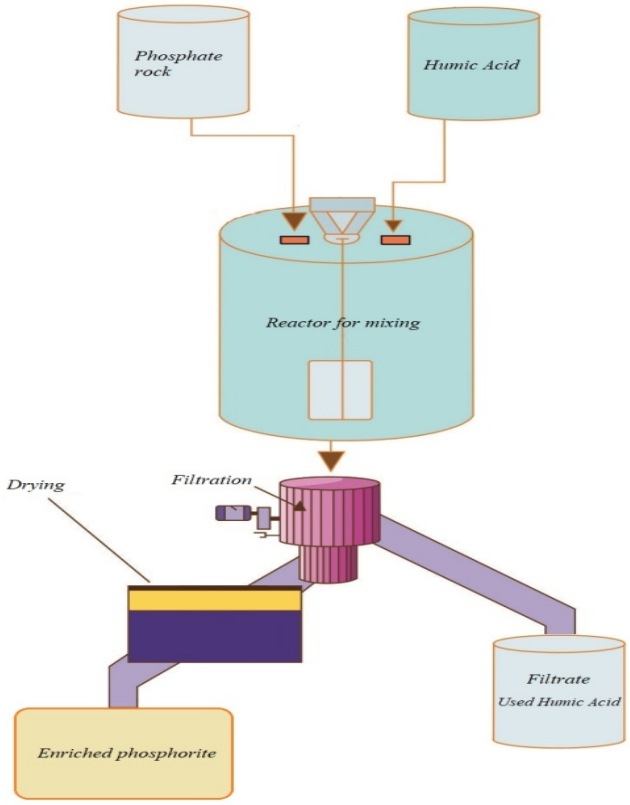


Fig.-1: Scheme for Enriching Low-grade Phosphorites by Humic Acid

To study the physical and chemical characteristics of the raw material and the resulting product, the methods of the scanning electron microscope and FTIR were used.

## RESULTS AND DISCUSSION

Leaching of phosphate rock by humic acid was carried out in temperature ranges from 35 to 65ºC. The results are shown in Table-2 and Fig.-2.

Table-2: Results of Leaching by Humic Acid

| 60 min | | | | |
|---|---|---|---|---|
| t, ºC | 35 | 45 | 55 | 65 |
| $P_2O_5$, % | 14.72 | 14.83 | 14.80 | 14.87 |
| 90 min | | | | |
| t, ºC | 35 | 45 | 55 | 65 |
| $P_2O_5$, % | 16.08 | 16.25 | 16.38 | 16.85 |
| 120 min | | | | |
| t, ºC | 35 | 45 | 55 | 65 |
| $P_2O_5$, % | 16.53 | 18.45 | 23.07 | 22.89 |

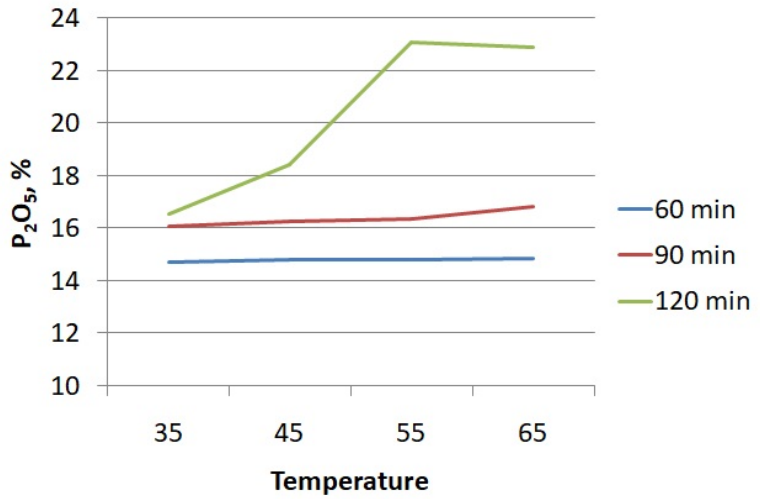


Fig.-2: Dependence of Phosphorus Pentoxide Content of Temperature

As you can see in Fig.-2 the optimal temperature is $55^0$C and the leaching time is 120 min, at which the content of phosphorus pentoxide increased to 23.07%. This ability to grow the content of $P_2O_5$ is based on its acidic property. The structure of humic acids contains oxygen-containing functional groups. The presence of carboxyl and phenolic groups increase their reactivity.[11]

The mechanism of phosphorite enrichment with organic acids is related to the primary leaching of carbonates rather than phosphates[3]. At a temperature of $65^0$C or more, slight entrainment of phosphates in the solution was detected. The chemistry of the leaching process can be represented as follows:

$$CaMg(CO_3)_2\ (s) + Hum\text{-}COOH\ (aq) = Hum\text{-}COOCaMg\ (aq) + CO_2\ (g) + H_2O \qquad (l)$$

As a result, humic acid attaches itself to the salts of carbonates to form humic acid salts in the form of calcium and magnesium humates. To describe this process, used data obtained by the method of a scanning electron microscope (Fig.-3) and an IR-Fourier spectrometer (Fig.-4 and 5).

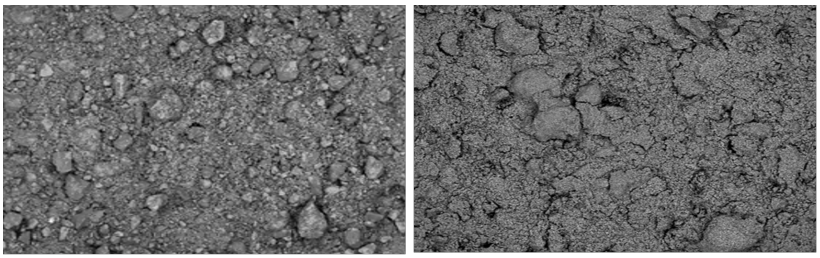


Fig.-3: Microstructure of Akzhar Phosphate Rock before and after Leaching with Humic Acid

Following the figure above, the structure of phosphate rock becomes more amorphous and the presence of calcium-containing compounds is much less.

Based on the data of IR spectroscopic study, it is clear that the compounds of carbonate type (calcite, dolomite, siderite), and as isomorphic inclusions of carbonate are expressed with a lower intensity. Absorption spectra with wavelengths of 1020-1090 $cm^{-1}$ characterize the presence of silicate compounds with Si-O-Si valence bonds. Absorption spectra in the region of 800-802 $cm^{-1}$ are typical for silicate compounds in the valence state Si-O-Ca and Si-O-Al. There are also noticeable valence fluctuations of the OH group observed in the absorption region of 3080-3700 $cm^{-1}$. Diffraction waves in the 1080-1090$cm^{-1}$ region are typical for organosilicon compounds of the Si-O-C, Si-O-Si type.

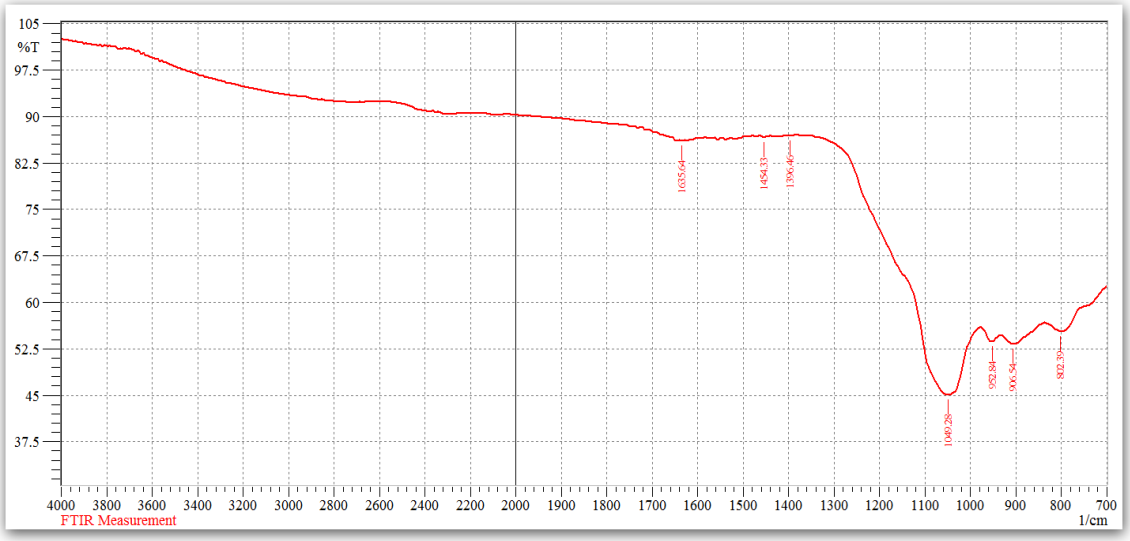


Fig.-4: IR Spectroscopic Data of Akzhar Phosphate Rock before Leaching

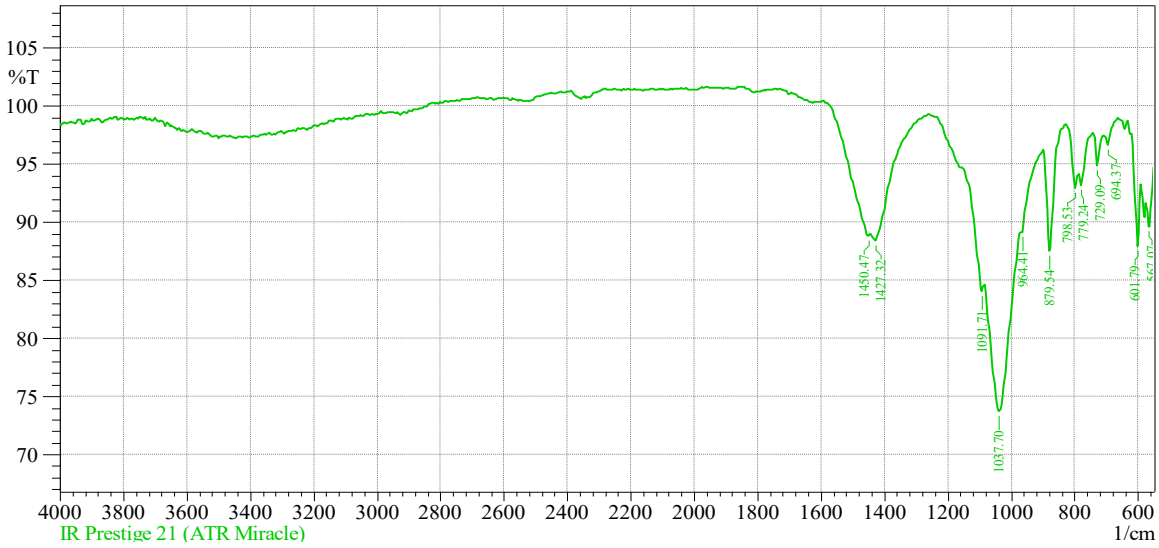


Fig.-5: IR Spectroscopic Data of Akzhar Phosphate Rock after Leaching

## CONCLUSION

Thus, using humic acid synthesized from brown coal, it is possible to increase the content of phosphorus pentoxide by removing impurities in the form of carbonates. In our case, the $P_2O_5$ growth was from 14% to 23.07%. At the same time, the optimal parameters were as follows: temperature-55ºC and time-120 min. The use of humic acid is characterized by high efficiency, low cost, and simple operating conditions. However, the possibility of regenerating the used humic acid and its corrosive effect remains open for future research.

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