ИЗВЕСТИЯ ВЫСШИХ УЧЕБНЫХ ЗАВЕДЕНИЙ.
Т 65 (12) Серия «**ХИМИЯ И ХИМИЧЕСКАЯ ТЕХНОЛОГИЯ**» 2022
V 65 (12) **ChemChemTech** 2022

DOI: 10.6060/ivkkt.20226512.6672

УДК: 66.022.389

СУЛЬФАТНЫЕ ДОБАВКИ ДЛЯ ИНТЕНСИФИКАЦИИ ФИЛЬТРАЦИИ НИЗКОСОРТНОЙ ФОСФОРИТНО-АЗОТНОКИСЛОЙ СУСПЕНЗИИ

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В процессе вскрытия фосфатных пород и извлечения основного компонента методом кислотной экстракции необходима стадия выделения нерастворимого остатка из полученных суспензий с помощью фильтрации. Это обеспечит повышение концентрации питательных элементов в продуктах переработки природных фосфоритов, используемых в качестве модельных минералов. Нерастворимый остаток на фильтровальной перегородке является фильтрующим слоем, плотная структура которого препятствует эффективному процессу разделения системы жидкость-твердое. С целью интенсификации процесса фильтрации азотнокислотной суспензии на основе низкокачественного высококремнистого фосфорита Полпинского месторождения исследовано влияние сульфатных добавок: серной кислоты, сульфата аммония и сульфата калия на структуру осадка и, соответственно, время фильтрации суспензии и промывки осадка. Содержание вводимых добавок варьировали в интервале 10 - 30 масс. %. Результаты исследования микроструктуры осадков – вертикального сечения и их поверхности, полученных с помощью метода сканирующей электронной микроскопии, позволили установить, что введение исследуемых добавок приводит к увеличению порозности слоя за счет образования крупных друз из монокристаллов дигидрата сульфата кальция – гипса. Это улучшает фильтрационные свойства слоя осадка, сокращая время фильтрования и промывки. Следует отметить, что при прочих равных условиях, эффективность добавки сульфата калия выше в сравнении с добавками серной кислоты и сульфата аммония. Ее преимущество заключается не только в улучшении реологических свойств суспензий, но и наличии калия в системе в качестве питательного компонента при переработке азотнокислотной вытяжки на комплексные удобрения. Экспериментально установлена эффективная концентрация сульфата калия в системе 20 масс. %. При этом обеспечивается максимальное значение скорости фильтрования суспензии 0,537 $м^3/(м^2·ч)$, что в 1,08 и 1,03 раз выше в сравнении с фильтрованием суспензий, содержащих сульфат аммония и серную кислоту, соответственно. Выявленная тенденция распространяется на скорость промывки осадков - максимальное значение соответствует 0,750 $м^3/(м^2·ч)$, что превосходит соответствующие образцы сравнения в 1,1 и 1,15 раз.

Ключевые слова: низкокачественные высококремнистые фосфориты, азотнокислые суспензии, интенсификация фильтрования, осадок, структура

SULFATE ADDITIVES FOR INTENSIFICATION OF THE FILTRATION OF LOW GRADE PHOSPHORITE-NITRIC ACID SUSPENSION

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In the process of opening phosphate rocks and extracting the main component by acid extraction, a stage of isolation of the insoluble residue from the obtained suspensions by filtration is necessary. This will ensure an increase in the concentration of nutrients in the products of processing natural phosphorites used as model minerals. The insoluble residue on the filter baffle is a filter layer, the dense structure of which prevents the effective process of separating the liquid-solid system. In order to intensify the filtration process of nitric acid suspension based on low-quality high-siliceous phosphorite of the Polpinsky deposit, the effect of sulfate additives: sulfuric acid, ammonium sulfate and potassium sulfate on the structure of the sediment and, accordingly, the filtration time of the suspension and washing of the sediment was studied. The content of the administered additives varied in the range of 10 - 30 weight %. The results of the study of the microstructure of sediments – vertical cross–section and their surface obtained using the scanning electron microscopy method allowed us to establish that the introduction of the studied additives leads to an increase in the porosity of the layer due to the formation of large druses from single crystals of calcium sulfate dihydrate - gypsum. This improves the filtration properties of the sediment layer, reducing the filtration and washing time. It should be noted that, all other things being equal, the effectiveness of potassium sulfate additives is higher in comparison with sulfuric acid and ammonium sulfate additives. Its advantage lies not only in improving the rheological properties of suspensions, but also in the presence of potassium in the system as a nutrient component during the processing of nitric acid extract for complex fertilizers. The effective concentration of potassium sulfate in the system was experimentally established at 20 weight. %. At the same time, the maximum value of the filtration rate of the suspension is 0.537 $m^3/(m^2 \cdot h)$, which is 1.08 and 1.03 times higher compared to the filtration of suspensions containing ammonium sulfate and sulfuric acid, respectively. The revealed trend extends to the precipitation washing rate - the maximum value corresponds to 0.750 $m^3/(m^2 \cdot h)$, which exceeds the corresponding comparison samples by 1.1 and 1.15 times.

Key words: low-quality high-siliceous phosphorites, nitric acid suspensions, filtration intensification, sediment, structure

Для цитирования:

Почиталкина И.А., Кондаков Д.Ф., Макаев С.В., Сибирякова И.Б., Костанов И.М. Сульфатные добавки для интенсификации фильтрации низкосортной фосфоритно-азотнокислой суспензии. *Изв. вузов. Химия и хим. технология*. 2022. Т. 65. Вып. 12. С. 30–36. DOI: 10.6060/ivkkt.20226512.6672.

For citation:
Pochitalkina I.A., Kondakov D.F., Makaev S.V., Sibiryakova I.B., Kostanov I.M. Sulfate additives for intensification of the filtration of low grade phosphorite-nitric acid suspension. *ChemChemTech* [*Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*]. 2022. V. 65. N 12. P. 30–36. DOI: 10.6060/ivkkt.20226511.6672.

INTRODUCTION

Apatite and phosphorite ores are the source of phosphate fertilizers and other phosphorus-containing compounds. Apatite deposits mostly have magmatic origin, and phosphorites are usually minerals of sedimentary origin. Both types of ores contain apatite group minerals with the general formula $3Ca_3(PO_4)_2{\cdot}CaX_2$, where X is fluorine, chlorine, or hydroxyl group [1-3]. Phosphorite processing is usually more energy and cost-intensive than apatite processing because of the presence of insoluble residues, mostly quartz and other silica-based compounds, typically found in the sedimentary minerals.

Digestion of phosphate raw materials with mineral acids (sulfuric, nitric, hydrochloric, phosphoric), called acidulating, is the main industrial method to produce phosphate fertilizers, and it is also used to extract phosphoric acid [4, 5].

Despite the fact that the acidulating with sulfuric acid is the most common wet process, the nitric acid acidulating is also used on a fairly large scale. Depending on the further treatment of nitric acid extracts [5], this method can produce simple phosphorus and nitrogen fertilizers as well as complex fertilizers containing several nutrients with a wide range of their ratios. In the latter case, the nitrogen from nitric acid passes into the bulk of the fertilizer [6, 7]. For a number of reasons, a shortage of high-grade sulfur and, as a result, sulfuric acid was predicted in the world in the early 1950s. This fact, along with a possibility to cover higher capital costs of nitric acid by manufacturing complex fertilizers, also gave impetus to a wider utilization of nitric acidulation of phosphate raw materials both in the US [8] and in Europe [9].

A specific feature of the processing of low-grade phosphate rocks with high silica content is the need to remove an insoluble residue from heterogeneous nitric acid extract by filtration in order to increase the concentration of nutrients in the resulting fertilizers [10]. The aim of this study is to investigate ways for the intensification of the filtration process.

MATERIAL AND METHODS

The object of the study was the phosphorite from Polpino deposit in the Bryansk region of the Russian Federation, which is an example of low-grade deposits with high content of α-quartz (up to 34% SiO_2) [11, 12], therefore the technology requires its removal from nitric acid extract by filtration.

The precipitate formed on the filter during the separation process plays the role of the main filtration layer (filter cake), and the filtration rate depends on its structure. It has long been known that sulfuric acid or sulfates can be used to remove excess calcium from the reaction system during nitric acidulating of phosphate raw materials, and it is used in the technology of mineral fertilizers to increase the content of water-soluble form of phosphorus in resulting products [13-15]. This method was projected onto the studied systems with the aim to change the chemical composition of the liquid phase and the crystalline structure of the precipitate.

Based on literature data [16] and our own studies of the influence of physicochemical factors on the crystallization kinetics of poorly soluble calcium salts and their crystal structure [17, 18], we suggested that the addition of sulfate anion to the acid extract will provide the binding of a certain amount calcium cations from liquid phase into sulfate. They crystallize into insoluble microparticles relatively fast and act as seeds, thereby ensuring the growth of the precipitate particles. This in turn increases the porosity of filter cake, which will solve technological problem of increasing the rate of subsequent filtration. Also, this method will increase the ratio of water-soluble forms of phosphorus in the fertilizer. In addition, it was assumed that clay impurities, which form a colloid, would also adhere to the insoluble microparticles, therefore an increase in the fraction of the crystalline precipitate in the filter cake and an increase in the filtration rate were also expected.

To confirm these hypotheses, four groups of model nitric acid suspensions of Polpino phosphorite with three different sulfate additives were prepared: sulfuric acid as well as ammonium and potassium sulfates. Phosphorite sample masses were constant for all model systems (12.0000 g), and 40 wt. % solution of nitric acid was added with 20 wt. % excess over the stoichiometric ratio of the decomposition of phosphorite to phosphoric acid. The reaction was carried out in a stirred thermostat at a constant temperature of 25 °C until the complete decomposition of phosphorite occured. The degree of decomposition was controlled by photometric determination of P_2O_5 concentration in the liquid phase. The decomposition time was usually 15-17 min, after that the sulfate additives were introduced into the suspension. The so-called concentrations of additives ω_{add} were calculated not from the total mass of the sample but based on the CaO content in phosphorite [11, 12]:

$$\omega_{add} = \frac{m_{add}}{(m_{add}+m_{CaO})}\cdot 100\% \qquad (1)$$

where m_{add} is the mass of the additive, m_{CaO} is the mass of CaO in the phosphorite sample.

The suspensions were thermostated with stirring at 18 °C (filtration temperature) immediately prior to filtration. The experiment consisted of a separation of a known volume of suspension on a Buchner funnel with a diameter of 90 mm covered with Whatman Grade 1 qualitative filter paper and determination of the filtration time. Filtration was carried out to the last drop. Then the crystallized precipitate was washed with the same amount of distilled water, also thermostated at 18 °C in advance, and the washing time was determined.

To obtain verifiable experimental data of the filtration process, the same conditions were maintained: the laminar flow of fluid through the pores of the precipitate layer and through the filter openings under constant vacuum of 0.044 MPa, created by a water aspirator and controlled by a spring pressure gauge.

The precipitates on the filter obtained after separation of the suspension were dried to a constant mass at a temperature of 100 °C and sent for examination by instrumental analysis methods. By the SEM method, using the JSM-6510 LV device (JEOL, Japan) equipped with a low vacuum system (JEOL Ltd., Japan), JEOL with low vacuum system, made by, micrographs of precipitation (voltage – 15 kV, magnification multiplicity x100 and x1000) with preliminary Pt spraying on the samples under study were obtained.

The phase composition of precipitation was determined using the D8 Advance X-ray diffractometer (Bruker, Germany), shooting conditions: CuKa radiation, Ni filter, LYNXEYE detector, geometry of reflection shooting. Phase identification was performed using the Bruker EVA program and the ICDD PDF-2 database.

RESULTS

Five parallel model mixtures were prepared for every experimental point, and the filtration and washing time (τ) were determined for each of them. The results were statistically processed, the averaged times (τ_{av}) were calculated, and the corrected sample standard deviations (s) were also determined. The value of the Student coefficient for five parallel experiments was 2.78. The standard errors of the experimental results (δ) were calculated for a confidence level of 0.95, and based on that, the relative errors (β) were calculated. The results of parallel experiments on filtering and washing of a model suspension without additives and their statistical analysis are presented in Table 1.

Table 1

The result of filtering and washing of a nitric acid model suspension without additives

***Таблица 1.* Результат фильтрации и промывки модельной суспензии азотной кислоты без добавок**

Sample	τ, s	τ_{av}, s	s, s	δ, s	β, %
Filtering of the suspension					
1	57	57.8	0.837	1.04	1.80
2	58				
3	57				
4	58				
5	59				
Water washing					
1	45	43.4	1.34	1.67	3.84
2	42				
3	42				
4	44				
5	44				

Table 2

The result of filtering and washing of a nitric acid model suspension with various sulfate additives

***Таблица 2.* Результат фильтрации и промывки модельной суспензии азотной кислоты с различными сульфатными добавками**

Additive	Filtration time, s	Water washing time, s
10 wt. % H_2SO_4	58 ± 1	43 ± 2
15 wt. % H_2SO_4	57 ± 1	44 ± 1
20 wt. % H_2SO_4	53.4 ± 0.7	42 ± 3
25 wt. % H_2SO_4	58 ± 2	44 ± 1
30 wt. % H_2SO_4	58 ± 1	43 ± 2
10 wt. % $(NH_4)_2SO_4$	58.6 ± 0.7	46 ± 2
15 wt. % $(NH_4)_2SO_4$	62 ± 1	41 ± 1
20 wt. % $(NH_4)_2SO_4$	68 ± 2	38 ± 1
25 wt. % $(NH_4)_2SO_4$	72±2	42± 1
30 wt. % $(NH_4)_2SO_4$	72 ± 4	45 ± 1
10 wt. % K_2SO_4	58 ± 1	47 ± 3
15 wt. % K_2SO_4	58 ± 3	47 ± 3
17.5 wt. % K_2SO_4	56 ± 2	38 ± 2
20 wt. % K_2SO_4	53 ± 3	38 ± 2
25 wt. % K_2SO_4	64 ± 3	40 ± 1
30 wt. % K_2SO_4	69 ± 8	40 ± 6

The filtration time of the model suspension without additives was 58 ± 1 s, and the washing time was 43 ± 2 s with 95% probability.

Similarly, five parallel experiments were carried out on filtering and washing of each model suspension with different concentrations of sulfate additives (sulfuric acid, ammonium and potassium sulfates). The statistically analyzed results of these experiments are presented in Table 2.

The experimental data demonstrate that the addition of ammonium sulfate into the mixture increases the filtration time, which can be explained by the deterioration of the rheological characteristics of the ammoniated pulps in comparison with acidic pulps, as we showed earlier [19]. However, the dependence of the washing time on the concentration of the ammonium sulfate additive exhibits a minimum corresponding to 20% of the additive. Most likely, at this concentration of the additive, the porosity of the precipitate layer increases due to aggregation of small particles and their enlargement during crystallization of calcium sulfate, with SiO_2 microparticles acting as seeds.

The addition of up to 10-15 wt. % of sulfuric acid into the mixture does not lead to a change in the filtration and washing time (duration stays within the experimental error). But the filtration and washing parameters begin to slightly improve with further increase in the sulfuric acid concentration, reaching a minimum at 20 wt. %, that is, at the same concentration as in with ammonium sulfate additive.

Addition of 20 wt. % of K_2SO_4 leads to a decrease in filtration time by 8.65%, which may be explained by an improvement in the rheological characteristics of the suspension due to ability of a potassium ion to increase the fluidity of the suspensions [20]. It should also be noted that the addition of potassium sulfate in an amount of 17.5-20.0% leads to a decrease in washing time by 12.9%, that is, to a result that is very similar to the effect of addition of an ammonium sulfate in an amount of 20%.

The values of the suspension filtration rates, presented in the Table 3, were calculated using the masses of the filtrate, filtration time and diameter of the funnel.

Table 3

The filtration rate of model suspensions for the optimal amount of sulfate additives

Таблица 3. **Скорость фильтрации модельных суспензий для оптимального количества сульфатных добавок**

Additive	Filtration rate, $m^3 \cdot m^{-2} \cdot h^{-1}$	Water washing rate, $m^3 \cdot m^{-2} \cdot h^{-1}$
Without additive	0.490	0.653
20 wt. % H_2SO_4	0.503	0.672
20 wt. % $(NH_4)_2SO_4$	0.524	0.706
20 wt. % K_2SO_4	0.537	0.750

SEM micrographs (Fig.) show the surface of the precipitates. It can be seen that the most densely packed structure corresponds to the precipitate formed from nitric acid extract without additives, and the precipitates formed with sulfate additives are thicker but less dense. The differences in cross-sections of filter cake formed in the presence of sulfate additive are obviously more pronounced than the differences in micrographs of their surface. Every surface has a fraction of plate-like crystals corresponding to $CaSO_4 \cdot 2H_2O$, but the structure of the precipitate formed with potassium sulfate additive is distinguished by the presence of larger druses from single plate-shaped crystals and a higher porosity of the layer, compared to counterparts, which confirms the technological results of the investigated filtration process.

Comparison of the dependences of the suspension washing time on the concentration of the additives confirms the hypothesis of enlargement of the insoluble microparticles by the rapid crystallization of calcium sulfate on their surface. In this case, the maximum effect is achieved by the introduction of sulfuric additives at a concentration of 20 wt. %, which is also confirmed by the scanning electronic microscopy data. It should be noted that the effect of the additive is bigger when sulfates are introduced as neutral salts instead of sulfuric acid, and this behavior does not depend on the nature of the salt. According to the results of the X-ray analysis of the samples, it was found that the sediments are mainly SiO_2 with a high crystallinity alpha quartz structure [00-046-1045] and $CaSO_4 \cdot 2H_2O$ with a gypsum structure [01-074-1904].

Potassium sulfate is the most promising additive for the production of concentrated fertilizers from low-grade phosphate rock using filtration of an inert insoluble residue. An addition of 20 wt. % with respect to CaO contained in Polpino phosphorite reduces the filtration time by ~ 1.1 times, providing the maximum efficiency of the filtration process, and it also corresponds to the minimum washing time of the solid phase, therefore this concentration should be considered optimal.

CONCLUSION

An analysis of the experimental dependences of nitric acid suspensions made from model low grade silica rich phosphorite allows us to conclude that there is a multivariable dependence of the filtration rate on the concentration of sulfate additives. The filtration rate is affected both by the filterability of the precipitate layer and by the rheological characteristics of the filtered pulps.

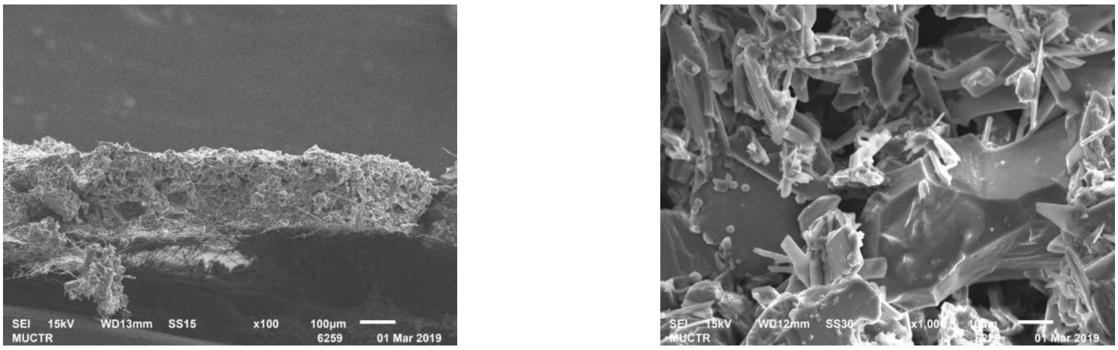
Potassium sulfate is deemed the most effective additive, providing the biggest decrease in the filtration time and significant decrease in washing (by 1.1 and 1.15 times, respectively, for 20 wt. % K_2SO_4), simultaneous removal of calcium and insoluble residues and also introducing potassium into the system as a component of the resulting complex fertilizer.

Instrumental studies of samples were carried out with the involvement of the equipment of the Center for Collective Use of the D.I. Mendeleev MUCTR under the state contract No. 13.CCP.21.0009.

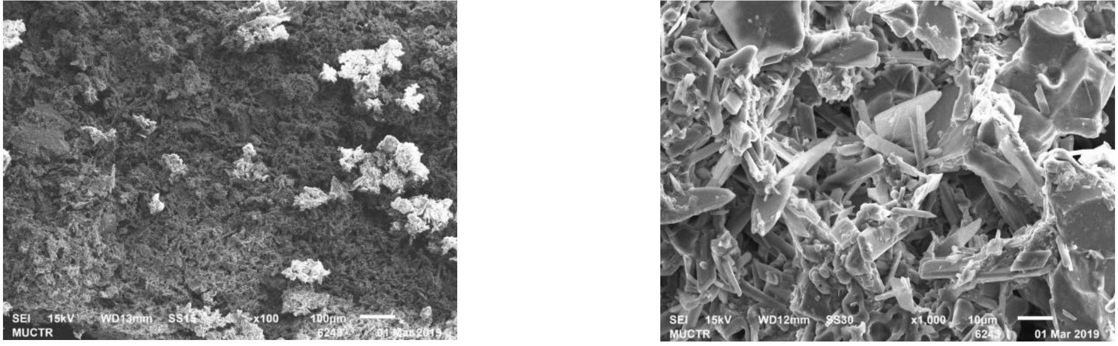
The authors declare the absence a conflict of interest warranting disclosure in this article.

Инструментальные исследования образцов проводились с привлечением оборудования Центра коллективного пользования ФГБНУ им. Д.И. Менделеева МУЦТР по госконтракту №13.ГПК.21.0009.

Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.



a (without additives) b (without additives)



c (H_2SO_4) d (H_2SO_4)

Fig. SEM micrographs of the cross-section of the filter cake and the surface of precipitate after filtration of the acid suspensions of Polpino phosphorite without any additives (a,b); with the addition of 20 wt.% of H_2SO_4 (c,d). Scale: a,c– X100; b,d– X1000

Рис. СЭМ-микрофотографии поперечного сечения фильтровальной корки и поверхности осадка после фильтрации кислых суспензий фосфорита Полпино без добавок (a, b); с добавлением 20 мас.% H_2SO_4 (c,d). Масштаб: a, c– X100; b, d– X1000

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Поступила в редакцию (Received) 18.05.2022
Принята к опубликованию (Accepted) 09.09.2022