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METHOD FOR PRODUCING A FIRE RETARDANT AGENT WITH NITRIC ACID SOLUTIONS OF VARIOUS CONCENTRATIONS

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Abstract: The purpose of this work is to study the content of nitrate ions in the manifestation of the fire retardant effectiveness of the product of nitric acid processing of low-grade phosphorites for the fire protection of cellulose materials. To achieve the goal of this study, a method was used to study the features of the processes of processing low-grade phosphorites with solutions of nitric acid in various concentrations. To study the effect of concentration (C_{HNO3} = 5, 10, 20 %) on the solubility of samples (dust fraction (DF)), phosphorite layer-1 (FL1), phosphorite layer -2 (FL2), mineral mass (MM) low-grade phosphorites and extraction of main flame retardant components Σfire retardant component experimental studies were carried out in the liquid phase. The following methods were used in the research process: chemical elemental analysis, microprobe analysis, infrared spectroscopy, potentiometry, viscometry, special methods for determining the flammability and fire protection of materials.

Keywords: Microprobe analysis, infrared spectroscopy, fire retardant component, potentiometry, viscometry, exocalcite, endocalcite.

Introduction. In the modern world today, through the effective use of mineral raw materials, waste from the mining and chemical industries, mineral fertilizers of particular importance for the national economy, astringents, synthetic detergents and fire retardants are obtained.

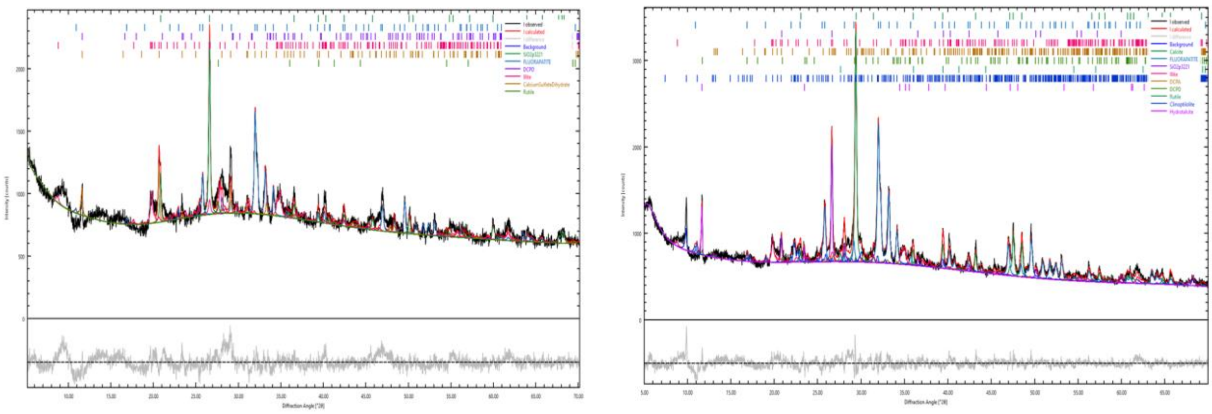
In this regard, special attention is paid to the necessary increase in their main component (P2O5-10-15%) through improving enrichment processes, organizing an effective process of low-temperature decorbonization, purification of fluorine-containing impurities, extraction of rare earth metals, as well as the creation and implementation of technologies for obtaining new types of inorganic products from silicate and aluminate by-products [1]. Therefore, in recent years, scientists and specialists have been engaged in scientific research aimed at creating methods and technologies for processing and obtaining materials based on these little-used raw materials to obtain inorganic materials for non-traditional purposes [2].

Every year, chemical industry enterprises offer new technologically advanced flame retardant formulations, but today half of the total proposed volume is inorganic compounds that have been tested for decades. These compounds include: boric acid, borax, Al and Mg hydroxides, red phosphorus, polyphosphates and ammonium sulfate [3-4].

Analysis of scientific and patent information on the use of various substances to reduce the flammability of polymer materials shows that fire retardants mainly include inorganic and organic substances that contain in their molecules elements such as halogens, phosphorus, nitrogen, boron, metals, groups with one or another combination of their compounds, combined flame retardant composition [5].

Methods. The interaction of samples of low-grade phosphorites with a 5% (10 and 20%) solution of nitric acid was carried out at a ratio of S:L = 1:3, by dissolving 50 g of low-grade phosphorites in 150 ml of HNO_3 solution, ϱ = 1.031 g/cm^3, (ϱ = 1.054 and ϱ = 1.115 g/cm^3) at 25-40 ^oC, for 60 minutes, pH = 2.7 (measurement carried out using a FIVE/Easy pH/mV device with a combination electrode LE438 (t^o=80^{o}C, pH = 0-14).

Studying by microprobe analysis made it possible to clarify the changes occurring from a chemical and mineralogical point of view, it can be noted that in processed samples of low-grade phosphorites, one of the common rock-forming minerals is calcite. Its content varies from 10 to 60%, the predominant share (up to 80-90%) is concentrated in the cement solid inclusion, in which microgranular calcite firmly grasps the phosphate components from the outside ("exocalcite"), as one of the forms of mixed carbonates - dolomite-calcite minerals. Another morphological variety of carbonate mineral is “endocalcite,” which is found inside phosphate grains and represents relics of primary calcite. These morphological varieties of carbonates behave differently in chemical and technological processes. In Fig. 1. An X-ray pattern of samples of low-grade phosphorites processed with 20% HNO_3 is shown.



a) b)

a) processed phosphorite layer 1 b) processed phosphorite layer 2.

Figure 1. X-ray diffraction pattern of a sample of low-grade phosphorites processed with 20% nitric acid:

The study of the solid phase by X-ray phase analysis (Fig. 1) showed the presence of various mineral components found in the composition of processed samples of low-grade phosphorites with nitric acid, such as in the phosphorite layer-1 sample the presence of fluorapatite $Ca_5(PO_4)_3F$ (34.1%); rutile - TiO_2 (2.4%); gypsum - $CaSO_4 \bullet 2H_2O$ (9.4%);

illite - $(K,Na,Ca,H_3O^+)(Al,Fe,Mg)_2(Si_3Al)O_{10}(OH)_2{\cdot}(H_2O,K^+)(x\text{-}2)$ (30,8%); кварц - SiO_2 (23,4%).

In the phosphorite layer-2 sample the presence of hydrotalcite - $Mg_6Al_2(OH)_{16}{\cdot}CO_3{\cdot}4H_2O$ (0,6%); rutile - TiO_2 (1,3%);

clinoptilolite $((Na,K,Ca,Mg,Al)_6Al_9(Si_{29}Al_9)O_{72}{\cdot}20H_2O)$ (9,0%); fluorapatite $Ca_5(PO_4)_3F$ (38,8%); quartz - SiO_2 (9,9%); monetizes - $CaH_2PO_4{\cdot}H_2O$ (3,7%);

illite - $(K,Na,Ca,H_3O^+)(Al,Fe,Mg)_2(Si_3Al)O_{10}(OH)_2{\cdot}(H_2O,K^+)(x\text{-}2)$ (16,7%); brushes - $CaHPO_4{\cdot}2H_2O$ (0,7%); calcite - $CaCO_3$ (19,5%).

The presence of the following varieties was detected in the sample of the dust fraction: fluorapatite $Ca_5(PO_4)_3F$ (61,4%); rutile - TiO_2 (1,0%); quartz - SiO_2 (5,8%); monetizes - $CaH_2PO_4{\cdot}H_2O$ (13,3%);

illite - $(K,Na,Ca,H_3O^+)(Al,Fe,Mg)_2(Si_3Al)O_{10}(OH)_2\cdot(H_2O,K^+)(x-2)$ (5,4%); calcite - $CaCO_3$ (2,8%); tribasic calcium phosphate -$Ca_3(PO_4)_2$ (1,5%); calcium sulfate sesquihydrate - $CaSO_4 \bullet 0.5H_2O$ (8,8%).

"Exocalcite" is easily separated from phosphate grains, since in terms of chemical activity and structural accessibility during acid decomposition, this carbonate component "exocalcite" has greater potential than "endocalcite", which proceeds according to the reaction equation in the pH range = 6.0-4.2 in the initial stage of acid processing:

$$CaCO_{3(тв)} + M^{II}CO_{3(тв)} + 4H^+_{(р-р)} = Ca^{+2}_{(р-р)} + Mg^{+2}_{(р-р)} + 2CO_{2(газ)} + 2H_2O \quad (1)$$

$M^{II} = Mg^{+2}, Mn^{+2}, Fe^{+2}$

"Endocalcite" is quite strongly interconnected with phosphate components and it is impossible to separate them during washing, flotation and even roasting with sufficient selectivity without chemical intervention, which is possible at higher concentrations of H^+ (H_3O^+) acid reagent (10-20% HNO_3 solution) pH=3.2-2.25, turning carbonate-fluoroapatite into hydrofluoroapatite [6-7].

"Endocalcite" is quite strongly interconnected with phosphate components and it is impossible to separate them during washing, flotation and even roasting with sufficient selectivity without chemical intervention, which is possible at higher concentrations of H^+ (H^3O^+) acid reagent (10-20% HNO_3 solution) pH = 3.2 - 2.25, turning carbonate-fluoroapatite into hydrofluoroapatite:

$$Ca_{10}(PO_4)_6F_2(CO_3)_{1,5(тв)}+9H^+_{(р-р)}\rightarrow Ca_7(HPO_4)_6F_{2(тв)}+3Ca^{+2}_{(р-р)}+CaF_{2(тв)}+ 1,5CO_2+1,5H_2O \quad (2)$$

At the same time, the carbonate and phosphate components in all types of processed samples of low-grade phosphorites are subject to maximum decomposition.

Results. The interaction of nitric acid with samples of low-grade phosphorites occurs through the decomposition of carbonate components (according to equation 1). To prove these statements, we present data from an IR spectral study of one of the samples of low-grade phosphorites - the dust fraction, since similar patterns were also found in the spectra of other phosphorite samples (Fig. 2. IR spectra).

Judging by the spectra, it should be noted that the decarbonization of the phosphorite sample does not proceed until the complete decomposition of the carbonates, as evidenced by the presence of a band in the IR spectrum with frequencies of 1456.26, 1417.68 cm^{-1} $\nu as(CO3)$, 871.82 cm^{-1} (weak), 711.43 cm^{-1} (very weak) bands characteristic of dolomite-calcite (mixed) carbonates in the composition of the nitric acid processed sample (Fig. 2.) [8-9]. Apparently, these carbonates are part of the "endocalcite" forms, deeply penetrating into the internal pores of the crystalline forms of the phosphorite components, to which the particles (H_3O^+) of the acid-decomposing reagent cannot "reach". S:L

Further increase in the amount (up to S:L=1:3) of more concentrated solutions of nitric acid with a decrease in the pH of the liquid phase to 1.88 (10% solution) and 1.75 (20% solution), in addition to the above, promotes the following transformations, accompanied by complete decomposition of carbonate components, incomplete decomposition of fluorapatites and partial decomposition of silicate rocks of phosphorite. The latter is due to the decomposition of CaF_2(s) upon reaching pH < 2.0 and the formation of HF in the reaction medium [10-11].

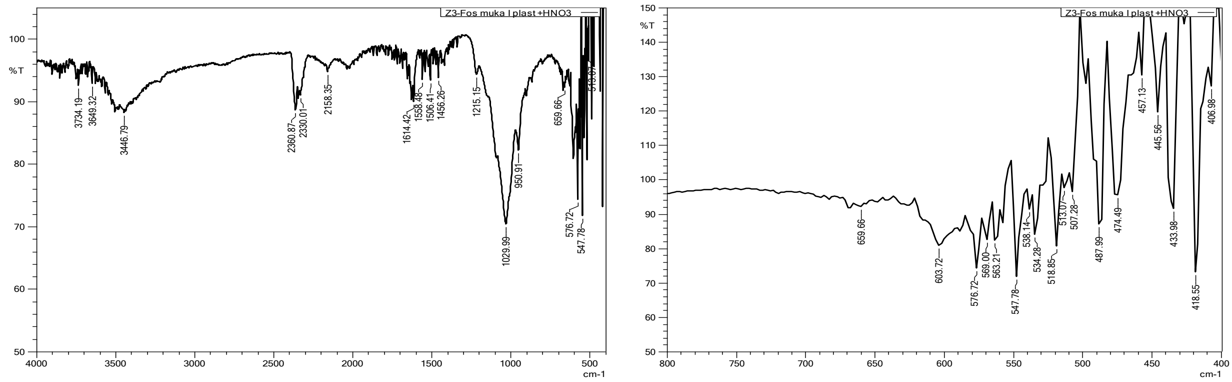
$$Ca_{10}(PO_4)_5F_2(CO_3)_{1,5(тв)}+21H^+_{(р-р)}=2Ca(H_2PO_4)_{2(тв)}+H_3PO_{4(р-р)}+7Ca^{+2}_{(р-)}+CaF_{2(тв)}+1,5CO_2+3H_2O \quad (3)$$

$$Ca_5(PO_4)_3F_{1\,(тв)} + 8H^+_{(р-р)} = Ca(H_2PO_4)_{2(тв)} + H_3PO_{4(р-р)} + 4Ca^{+2}_{(р-р)} + HF_{(р-р)} + 3H_2O \quad (4)$$

$$(K_{0,26}Na_{0,74})AlSi_3O_8 + 24HF = 0,26K^+ + 0,74Na^+ + [AlF_6]^{3-} + 3[SiF_6]^{2-} + 8H_2O + 8H^+ \quad (5)$$

$$(K,Na)(FeAlMg)_2(SiAl)_4O_{10}(OH)_2+18HF \rightarrow K^++Na^++Mg^{2+}+[AlF_6]^{3-}+[FeF_6]^{3-}+[SiF_6]^{2-}+2H_2O \quad (6)$$

Under the influence of nitric acid, silicate and phosphate components also undergo partial decomposition, as evidenced by the data of the IR spectra (Fig. 2), in which a slight decrease in intensity and low-frequency mixing (by 3.8 cm-1) were detected bands mutually overlapped ν_{as} (SiO) and ν(PO) at 1028.06 and a reduction in the number of bands from 9 to 3 in the low frequency region: 601.7, 567.07 and 433.48 cm-1, related to bending vibrations of the O-Si-O, M-Si-O and Si-O-Si bonds in silicate tetrahedra [8-9].



a b

Figure 2. IR spectra of the atomic acid processed sample of the dust fraction: a)400-4000 см$^{-1}$ и b) 400-800 см$^{-1}$

Absorption bands characteristic of phosphate groups, the main component of phosphorite ν_{as}(P=O), ν_{as}(P-O), ν(PO) groups were not detected as separate spectrally identifying bands, which is a consequence of the overlap of these bands with a wide intense band in the range 900-1100 см$^{-1}$. Evidence of the presence of phosphate components is the presence of reflection peaks at 32.09 and 32.14, characteristic of hydrated phosphates in the diffraction patterns in figure. 2. [12].

The resulting suspension after processing was left to settle and mature for 120 minutes, after which it was separated into liquid and solid phases by filtration. The liquid phase was analyzed for the content of dissolved components (Table 1).

The solid phases were dried in air and in an oven at 110 °C for 45 minutes, the compositions were analyzed (Table 2) and used to study the flame retardant properties according to the methods of [13-14]. The results of the chemical analysis of the resulting solutions and solid samples of nitrate processing are reflected in tables 1 and 2.

Table 1. Results of the analysis of liquid phases of pulps obtained by processing low-grade phosphorites with nitric acid solutions of various concentrations Σfire retardant component – (P_2O_5, SiO_2, Al_2O_3, Fe_2O_3)+NO_3^-, %

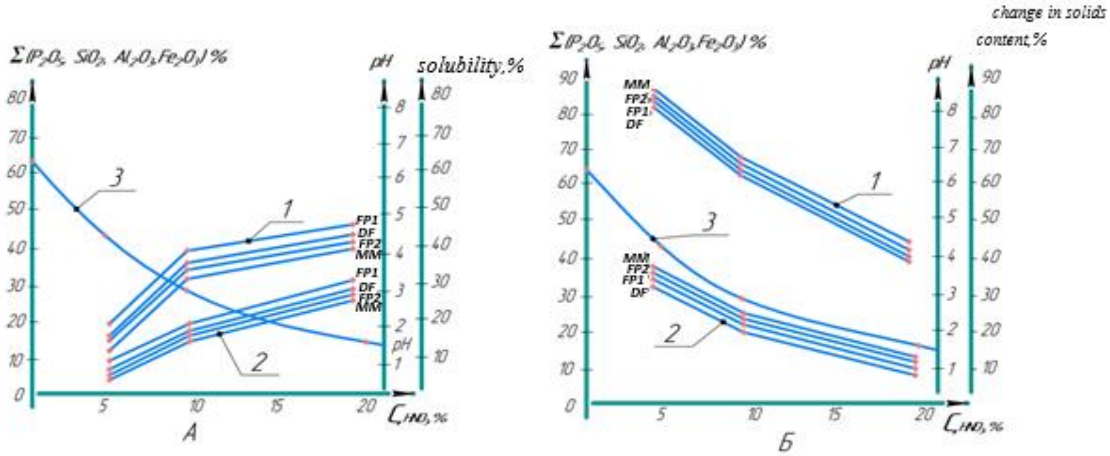
A variety of low-grade components	Contents of main components, %									
	SiO_3^{2-}	**PO_4^{3-}**	**Al^{3+}**	**Fe^{3+}**	**Ca^{2+}**	**Mg^{2+}**	**Na^{+}**	**K^{+}**	**NO_3^{-}**	Dissolve bridge, g / %
A solution obtained by processing with a 5% HNO_3 solution										
Dust fraction (DF)	0,56	3,37	0,57	0,46	8,62	0,89	1,83	0,40	2,38	8,35/ 16,70 Σ_{FRC} = 7,34
Phosphorite from 1 layer (FL1)	0,68	3,42	0,53	0,40	9,02	0,85	1,94	0,39	2,41	8,62/ 17,23 Σ_{FRC} = 7,44
Phosphorite from 2 layer (FL2)	0,63	3,39	0,54	0,48	8,13	0,90	1,87	0,41	2.43	8,18 /16,35 Σ_{FRC} = 7,47
Mineral mass (MM)	0,51	2,79	0,41	0,43	7,53	0,75	1,77	0,38	2,28	7,29 /14,57 Σ_{FRC} = 6,42
A solution obtained by processing with a 10% HNO_3 solution										
Dust fraction (DF)	1,36	7,75	0,88	0,66	18,65	1,36	2,81	0,57	5,73	17,02/ 34,04 Σ_{FRC} =16,06
Phosphorite from 1 layer (FL1)	1,34	7,48	0,90	0,71	17,98	1,39	2,94	0,65	5,68	16,70/ 33,39 Σ_{FRC} = 16,11
Phosphorite from 2 layer (FL2)	1,31	7,60	0,83	0,72	19,06	1,47	2,95	0,64	5,87	17,29/ 34,58 Σ_{FRC} = 16,33
Mineral mass (MM)	1,17	6,67	0,69	0,64	17,70	0,96	2,38	0,46	5.04	15,20 /30,40 Σ_{FRC} = 14,21
A solution obtained by processing with a 20% HNO_3 solution										
Dust fraction (DF)	2,34	10,05	1,13	0,98	23,42	1,74	3,94	0,71	9,81	22,00 /43,99 Σ_{FRC} =24,31
Phosphorite from 1 layer (FL1)	2,38	10,17	1,05	1,04	23,87	1,68	3,81	0,63	10,23	22,32 /44,63 Σ_{FRC} =24,87
Phosphorite from 2 layer (FL2)	2,27	10,34	0,95	0,89	24,12	1,72	3,51	0,66	10,28	22,73/45,46 Σ_{FRC} =24,73
Mineral mass (MM)	1,91	9,03	0,78	0,77	22,02	1,20	2,93	0,47	9,78	19,56/ 39,11 Σ_{FRC} = 22,27

Table 2. Results of analysis of solid phases of pulps obtained processing of low-grade phosphorites with nitric acid solutions of various concentrations Σfire retardant component – (P_2O_5, SiO_2, Al_2O_3, Fe_2O_3,)+CO_2, %

A variety of low-grade components	SiO_2	P_2O_5	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	CO_2	Solid phase, g / %
Solid phase obtained after processing with 5% HNO_3 solution										
Dust fraction (DF)	8,76	12,8	1,81	1,47	35,23	1,31	2,26	0,42	13,23	41,26 / 82,52 Σ_{FRC} = 38,0
Phosphorite from 1 layer (FL1)	7,81	11,32	0,96	0,85	35,78	1,92	2,98	0,38	14,05	41,14 / 82,30 Σ_{FRC} = 35,0
Phosphorite from 2 layer (FL2)	10,61	11,57	1,78	0,58	32,18	0,78	3,72	0,40	12,08	41,70 /83,42 Σ_{FRC} = 36,6
Mineral mass (MM)	10,52	10,15	1,11	0,90	38,32	2,18	1,05	0,20	12,71	42,43/84,87 Σ_{FRC} = 35,4
Solid phase obtained after processing with 10% HNO_3 solution										
Dust fraction (DF)	7,93	8,16	1,68	1,16	23,97	0,82	2,28	0,38	6,43	33,05 / 64,10 Σ_{FRC} = 25,36
Phosphorite from 1 layer (FL1)	7,32	7,15	0,56	0,57	27,01	1,37	1,97	0,21	6,58	32,89/ 65,78 Σ_{FRC} = 22,18
Phosphorite from 2 layer (FL2)	9,67	7,32	0,46	0,24	21,05	0,32	2,54	0,14	6,17	32,53/ 65,05 Σ_{FRC} = 23,87
Mineral mass (MM)	11,73	4,41	0,84	0,62	27,34	1,87	0,43	0,17	7.34	34,40 /68,78 Σ_{FRC} = 24,94
Solid phase obtained after processing with 20% HNO_3 solution										
Dust fraction (DF)	6,75	5,78	1,38	0,84	19,64	0,42	0,17	0,18	2,01	22,00 /43,99 Σ_{FRC} =14,75
Phosphorite from 1 layer (FL1)	6,32	4,38	0,46	0,26	20,71	1,09	1,12	0,19	1,44	22,32 /44,63 Σ_{FRC} =12,86
Phosphorite from 2 layer (FL2)	8,94	4,62	0,32	0,12	16,47	0,62	1,84	0,22	1,08	22,73/45,46 Σ_{FRC} =15,08
Mineral mass (MM)	10,77	2,08	0,74	0,54	3,42	1,60	0,32	0,11	2,04	19,56/39,11 Σ_{FRC} = 16,20

Discussions. The results of the analyzes are presented in tables 1 and 2. A more detailed examination made it possible to note that the total content of the main flame retardant components ΣFRC (P_2O_5,SiO_2,Al_2O_3,Fe_2O_3), extracted into the liquid phase by processing samples of the dust fraction with a 5% solution of nitric acid, phosphorite layer-1, phosphorite layer-2 are 7.34-7.47% and are close to each other, and for a mineral mass sample this figure is 1.163 times lower (6.42%) compared to the above samples of low-grade phosphorites.

An increase in the concentration of HNO_3 to 10% leads to an increase in the total solubility of low-grade phosphorite samples to an average of 34.0% and the content of fire retardant components to 16.25% for three varieties (dust fraction, phosphorite formation-1, phosphorite formation-2) and some underestimation of 14.21 and 30.40% (1.143 times), respectively, extraction for the mineral mass was found.



1- Change in solubility;2 - Changing Σ the flame retardant composition of the liquid phase

3 - Changing the pH of the environment

Б – Dependence of changes in the solid phase content of low-grade phosphorite on $CHNO_3$,%.:

1- Change in solids content; 2 – change in the flame retardant composition in the solid phase;

3 - Changing the pH of the environment

Figure 3. A – Dependence of the solubility of low-grade phosphorites on $CHNO_3$,%

The content of additional nitrogen-containing component (NO_3^- ions) in all obtained liquid phases of processed samples of low-grade phosphorites are very close to each other (5.64-5.87%) and 2.4 times higher compared to those in 5% HNO_3 solutions.

Similar indicators in the liquid phases obtained by processing samples of low-grade phosphorites with a 20% solution of HNO_3 have an average value of 24.04 (ΣFRC) and 43.30% of total solubility, which is 1.48 and 1.274 times more than in the case of a 10% solution of nitric acid. Although in this case there is an increase in the extraction of components into the solution with an increase in the content of the acidic reagent, it should be noted that the specific solubility is lower relative to the increase in concentration, than in the case of an increase in the concentration of HNO3 in the range from 5% to 10% solution (3.24, 3.02 and 2.03, respectively), which may be associated with a change in the rheological characteristics, the hydrodynamic characteristics of the formed pulps and their liquid phases.

A comparison of the data obtained on the extraction of soluble components under the influence of HNO_3 indicates the greatest suitability (acceptability) of a solution of this reagent with a 10-20% concentration for processing the studied samples of low-grade phosphorites in order to obtain fire retardant compositions based on them.

Conclusion. Based on the study, the following conclusions of theoretical and practical significance were presented:

It has been proven by fire tests that composite phosphate fire retardant compositions obtained from solid products of acid processing of low-grade phosphorites exhibit fire retardant effectiveness, exhibiting group II fire protection of wood materials. Samples of the solid phase were used as filler-additives in the composition of fire retardant agents applied to the surface of wood materials, thereby, based on the solid phase, a fire retardant composition for the fire protection of wood materials was obtained. According to the test results, it was found that the wood material lost 12.6% of its mass (the fire retardant effect was 87.4%). Samples treated with all fire retardants become charred and smoke without ignition.

Based on the results of studying the fire retardant effectiveness of solutions obtained by processing with 5 and 10% solutions of nitric acid, it was revealed that there was no sufficient degree of fire protection relative to the established criterion (<25%).

Liquid phases obtained by processing with 20% HNO_3 solutions belong to group II of fire retardant activity to ensure a decrease in the flammability of cellulose materials.

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