

# Alumophosphate binders: Synthesis, phase composition, thermal stability and application in foundry production

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## ABSTRACT

Organic binders currently used in the foundry industry are highly toxic. During the pouring of casting molds, many volatile organic compounds are released, the vast majority of which are environmentally harmful. The development of alumophosphate binders will have a positive impact on the environment. The article gives the results of the study of aluminum phosphate binders, which are the result of the chemical reaction of orthophosphoric acid with powdered aluminosilicates. The subjects of the research are the phase and chemical composition, the dynamics of thermal transformations of the binders, as well as the properties of core mixtures for the production of foundry cores.

It was found experimentally that as a result of the chemical reaction of powdered pyrophyllite  $\text{Al}_2(\text{OH})_2[\text{Si}_4\text{O}_{10}]$  and disten-sillimanite  $\text{Al}_2\text{O}[\text{SiO}_4]$  with orthophosphoric acid after heating to 300 °C, strong and thermally stable binders are formed, which are crystalline and amorphous aluminum orthophosphates. These phases ensure binding of the quartz refractory filler and therefore high strength. Synthesized binders can be used in refractories or core mixtures for foundry production.

X-ray phase and differential thermogravimetric analyzes were used to determine the structure and properties of binders. The compositional planning of the experiment with appropriate data processing was applied to determine the working composition of the mixture for foundry cores.

The structure of aluminum phosphate binders, which were obtained using refractory fillers common in foundry production, was investigated for the first time. The circumstances for the formation of crystalline phases were analyzed for the first time. It was established that as a result of the reaction of orthophosphoric acid and disten-sillimanite, the larger specific amount of aluminum orthophosphate and the smaller amount of residual quartz is formed, compared to the reaction of acid with pyrophyllite. This ensures the higher strength of the core mixture, which is formed from the binders in which orthophosphoric acid and disten-sillimanite are used.

Taking into account the mass ratios for the whole realization of the chemical reaction of the formation of the aluminum phosphate binders, the core mixture on the basis of quartz sand, orthophosphoric acid and disten-sillimanite was developed, which hardens after heating to 300 °C and has a compressive strength of at least 2.0 MPa.

## 1. Introduction

Over the past twenty years, there has been a steady trend towards the replacement of organic binders, including a wide range of synthetic resins (especially those containing phenol, formaldehyde, and furfural), with inorganic materials for the production of foundry cores [1]. Their

advantages in terms of ecology and resource conservation are beyond doubt [2]. However, despite this, the evolution of their commercial use requires continuous technical advances [3].

Core mixtures with inorganic binders are devoid of the main disadvantages of mixtures with phenol-formaldehyde, furan and other types of synthetic resins. For example, they are characterized by minimal

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release of toxic and harmful substances into the environment, as well as the possibility of repeated reuse. The authors [4] draw attention to the need to identify organic and inorganic compounds that are formed as a result of repeated heating-cooling of molding mixtures and are present there in the form of impurities that reduce the complex of their properties. Organic impurities are considered especially harmful. A thorough study [5] shows that for the preparation of core mixtures it is possible to use regenerated sand no more than 20 % by weight, after which the mechanical strength of the rods is significantly reduced. Another relevant problem associated with the use of sand-resin core mixtures is highlighted in the article [6]. In combination with sand-bentonite and sand-clay molding mixtures, sand-resin rods significantly reduce all mechanical and technological properties, and therefore, obviously, the mixtures require a more complex and long-term regeneration process. Researchers [7] emphasize that depending on the type of resin, under the influence of temperature, compounds such as the BTEX group and polycyclic aromatic hydrocarbons can be formed and released. During storage and disposal of the spent mixture, there is a high probability of releasing harmful substances into the environment.

Phosphates occupy the important place between inorganic binders. Though the number of valuable properties, they found use as corrosion-resistant and heat-resistant coatings, heat-resistant concrete, adhesives [8], and components of porous ceramics [9]. In particular, the authors [10] confirm that phosphate binders in the composition of core mixtures have advantages over resin ones not only in terms of ecology, but also in terms of the number of technological indicators.

Historically, it happened that researched in the in the 70s ... 80s of the 20th century, core mixtures with Fe and Mg phosphates could not compete with sand-resin compositions [11]. The reasons are the instability of the chemical composition and properties of both the binders and the powder hardeners required in these technologies, which made it impossible to ensure the stable level of the technological properties of the mixtures.

As an alternative to these materials, compositions based on aluminum phosphates can be considered. Such compositions, which are known today, contain pre-synthesized aluminum phosphate binders at the chemical plant, which is the product of inorganic chemical synthesis. Complex materials based on it are also known, which additionally contain Cr, Mg, B, Fe, Ca, Zn, and sometimes even Na. However, complex binders synthesis technologies are long and multi-operational, they cannot be implemented at foundry enterprises. The shelf life of ready-made binders, as a rule, does not exceed 6 months.

**Statement of the problem.** Aluminosilicate materials are available and widespread, therefore, in the wide range of scientific works, they are considered as raw materials for creating aluminum phosphate binders. For many decades, schemes of their reaction with orthophosphoric acid have been used for the production of refractory products, which are exposed to sintering at temperatures of 900 ... 1300 °C [12]. At the same time, it is noted that the pre-solidification temperature of the developed refractory mixtures is about 300 °C, which is technologically acceptable also for foundry cores.

Obtained by the chemical reaction of orthophosphoric acid with refractories such as fireclay and mullite with the general formula  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , alumina and corundum with the general formula  $\text{Al}_2\text{O}_3$ , kaolinite  $\text{Al}_2(\text{OH})_4[\text{Si}_2\text{O}_5]$  binders have been studied quite fully [12,13]. There are isolated data on pyrophyllite  $\text{Al}_2(\text{OH})_2[\text{Si}_4\text{O}_{10}]$ , which indicate the formation of exclusively amorphous aluminum phosphates, which complicates the study of their structure and properties. Binders are used for the casting of Al-Si alloys, which are promising for the development of highly effective heat-protective [14,15] and functional-gradient [16] coatings. The phase and chemical composition of currently known aluminum phosphate binders has been well studied, which makes it possible to predict their properties and polymorphic changes upon heating.

In our previous studies [17], for the first time, the possibility of obtaining aluminum phosphate binders directly in the composition of

core mixtures during their thermal hardening was considered. Aluminum phosphates with the sufficiently high binding potential were obtained as the result of the chemical reaction of orthophosphoric acid  $\text{H}_3\text{PO}_4$  with powdered industrial products (aluminum-containing slags and sludges [17]), inorganic aluminum salts [18], as well as with aluminosilicate materials [19]. Similar topics are also discussed in articles [20,21]. In order to process production waste and its beneficial use, the authors [21] synthesized the binders from glass manufacturing waste, kaolin clay, and phosphate sludge. During the synthesis of aluminum phosphate, the authors [20] changed aluminum hydroxide with the grout of aluminum nitrate, i.e., as the authors [18] used an inorganic salt. Authors [22] finely dispersed aluminum powder was used in combination with orthophosphoric acid for the synthesis of aluminum phosphates.

In foundry production, disten-sillimanite and chamotte are primarily used as refractory fillers, and corundum and pyrophyllite to the lesser extent. There are currently no data on the chemical and phase structure of aluminum phosphate binders formed from disten-sillimanite and pyrophyllite. There is also no information regarding their thermal stability and the possibility of use in the mixture of foundry cores.

The result of our previous research [19] was established the phase composition of silicon and zirconium phosphates, which are formed after the reaction of powdered quartz and zircon with orthophosphoric acid. The dynamics of changes in the phase composition of these phosphates during heating from 20 to 1000 °C were also established. The study of the reaction of orthophosphoric acid and disten-sillimanite showed that strengthening of mixtures of orthophosphoric acid and kyanite-sillimanite ( $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  or  $\text{Al}_2\text{SiO}_5$  or  $\text{Al}_2\text{O}[\text{SiO}_4]$ ) occurs in the temperature range of 250 ... 300°C. The complete mineralogical structure of powdered kyanite-sillimanite and 85 % orthophosphoric acid  $\text{H}_3\text{PO}_4$ , strengthened at 300 °C, has not been established. Therefore, the phase structure needs to be specified.

According to the article [19], the phase structure of kyanite-sillimanite almost coincides to the phase structure of the sample. Analyzing both distribution and intensities of the peaks on the X-ray diffraction pattern, authors conclude that these binders should be assigned to crystal hydrate forms or amorphous aluminum phosphates. Physical and chemical transformations during heating of this material have not been explained. The DTG graph contains several special effects that raise some scientific questions about the phase transformations in this system. To solve these questions, it was necessary to carry out additional experiments and calculations, which were finally solved and confirmed in this article.

**Statement of research objectives.** The aim of this work is to study the chemical, phase composition and dynamics of thermal transformations of aluminum phosphate binders, which are formed as the result of the reaction of orthophosphoric acid with pyrophyllite and disten-sillimanite, as well as to develop the structure of aluminum phosphate core mixture for foundry production.

Activities.

1. Determine the phase structure of the products of the chemical reaction of orthophosphoric acid and pyrophyllite  $\text{Al}_2(\text{OH})_2[\text{Si}_4\text{O}_{10}]$ .
2. Research the transformation of the specified products during heating from 20 to 1000 °C.
3. Determine the phase structure of the products of the chemical reaction of orthophosphoric acid and disten-sillimanite  $\text{Al}_2\text{O}[\text{SiO}_4]$ .
4. Research the transformation of the specified products during heating from 20 to 1000 °C.
5. To determine the strength of the samples of core mixtures with both studied binders and conduct the comparative analysis.

## 2. Materials and methods

A synchronous thermal analyzer STA 449C Jupiter used for high-temperature transformations were studied by the method of

differential thermogravimetric analysis.

RIGAKU “Ultima IV” diffractometer used to determine the structure and phase composition by X-ray phase analysis.

River quartz sand, which contains 0.8 % of the clay component and has an average particle size of 0.28 mm, was used as the filler in the mixtures.

To determine the compressive strength of core mixtures, cylindrical samples with the diameter and height of 50 mm were made, the strength was determined on the US-700 device. To obtain each experimental value and construct graphical dependences in each experiment, from 4 to 6 standard cylindrical samples were used. Graphical dependences were constructed based on the arithmetic mean values of strength with a confidence probability of 90 %.

Technical orthophosphoric acid in the form of the aqueous grout with the concentration of 85 % and the density of 1670 kg/m<sup>3</sup>, powdered disten-sillimanite  $Al_2O_3/SiO_2$ , and the powdered filler based on pyrophyllite were used for the experiments. Pyrophyllite itself is the natural mineral [23] with the known crystal structure and chemical composition  $Al_2(OH)_2[Si_4O_{10}]$ . The used refractory filler (Korosten, Zhytomyr region, Ukraine) is the natural mixture of different refractories, as determined by phase analysis according to the X-ray diffraction pattern in Fig. 1.

In the studied material, quartz (50 %) and aluminosilicates are distributed in equal amounts, among which pyrophyllite predominates.

### 3. Results and discussion

In experiments of authors [19], it was established that compositions of powdered pyrophyllite and disten-sillimanite with orthophosphoric acid completely solidify after heating to 300 °C. This indicates the formation of binders in these mixtures. In order to establish their composition and structure, X-ray phase analysis was carried out.

The result of the reaction between the material based on pyrophyllite, the composition of which is previously determined (Fig. 1), and orthophosphoric acid was the mixture, the X-ray diffraction pattern of which is shown in Fig. 2.

Pyrophyllite was identified in the sample, as well as lines that two phases may be owned, i.e. quartz and aluminum orthophosphate. These phases have similar crystal characteristics, so it is not possible to determine their mass ratio only on the basis of phase analysis. The amount of pyrophyllite decreased by almost half compared to the data in Fig. 1, so part of it reacted with orthophosphoric acid. There are also no impurity aluminosilicate phases because they have also reacted with the acid.

Silicon phosphates were not detected in the sample. This is explained by the greater activity of the alumina component of pyrophyllite

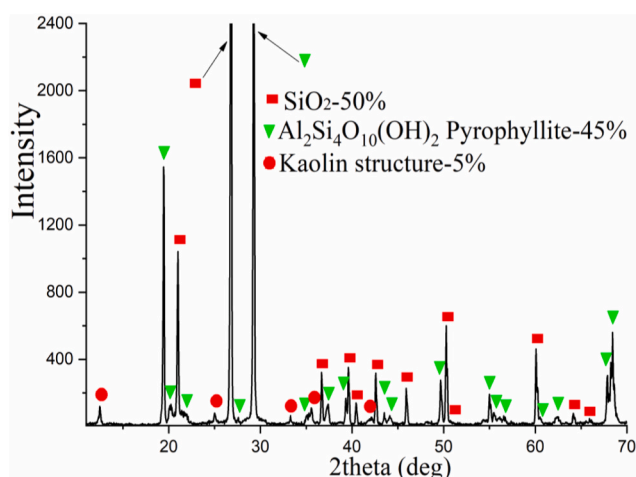


Fig. 1. X-ray diffraction pattern of refractory filler based on pyrophyllite.

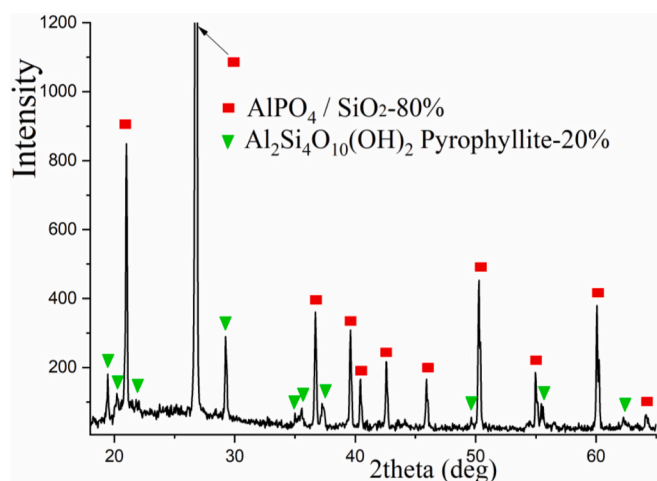


Fig. 2. X-ray diffraction pattern of the mixture of the filler based on pyrophyllite (5 mass units) with orthophosphoric acid (1 mass unit) treated at the temperature of 300 °C.

towards acid, compared to the silica component. Previously, the authors [12,13] based on the results of studies of kaolinite and pyrophyllite mixtures with orthophosphoric acid, indicated that only amorphous products are formed in them. In our study, on the contrary, the character of the X-ray diffraction pattern indicates that amorphous phases are absent or their number is minimal, and all phosphates are in crystalline form.

The chemical transformations that took place in this mixture are described by the following reaction:

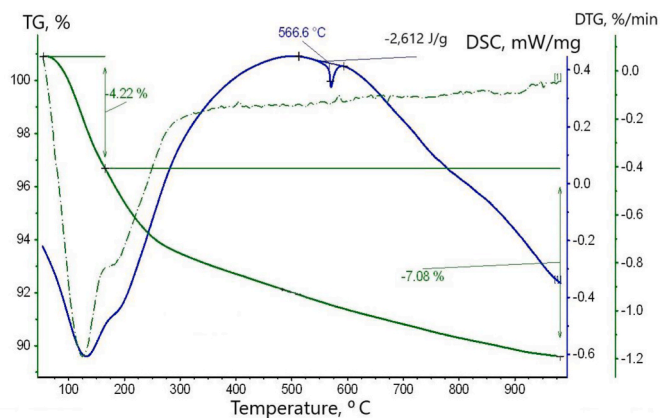


To carry out this reaction, taking into account the molecular mass of all substances, the ratio should be 360 mass units of pure pyrophyllite  $Al_2(OH)_2[Si_4O_{10}]$  per 196 mass units of  $H_3PO_4$  (or 231 mass units of acid, taking into account its concentration of 85 %). In the sample, taking into account the mass ratios of the components, the amount of pyrophyllite in the refractory filler (50 %) and the acid concentration is 1155 mass units of the filler and, accordingly, 580 mass units of pyrophyllite and 231 mass units of acid. In this case, the remaining unreacted pyrophyllite should be  $580 - 360 = 220$  mass units. As the result, reaction (1) produces 244 mass units of aluminum orthophosphate and 240 mass units of quartz.

In the initial sample, the amount of quartz is 50 %, so there are 580 mass units for reaction (1). Adding to this the quartz formed by this reaction, we get 820 mass units. In this case, the calculated composition of the sample are: 820 mass units (or 64 %) of quartz, 244 mass units (or 19 %) of aluminum orthophosphate and 220 mass units (or 17 %) of residual pyrophyllite. The result of the quantitative phase analysis (Fig. 2) is close to the theoretically calculated. The error may be related to impurity aluminosilicate phases revealed by the results on Fig. 1, which are not taken into account in the calculation. As the conclusion, binders in the form of crystalline aluminum orthophosphate were formed in this system. In addition to it, as the result of chemical reaction, residual quartz was released.

Differential thermogravimetric analysis of the sample of filler based on pyrophyllite with orthophosphoric acid and processed at 300 °C, was performed in air at the heating speed of 20 ... 30 K/min. Two endothermic effects were established on the thermal analysis curve (Fig. 3).

The first endothermic effect corresponds to the temperature range of 100 ... 150 °C, while the sample decreases its mass. Taking into account the temperature limits and the relatively significant decrease in mass is taking place, we establish that the removal of free moisture, which the sample absorbed from the atmosphere.

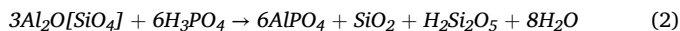


**Fig. 3.** Differential thermogravimetric analysis of the mixture of filler based on pyrophyllite (5 mass units) with orthophosphoric acid (1 mass unit), treated at the temperature of 300 °C.

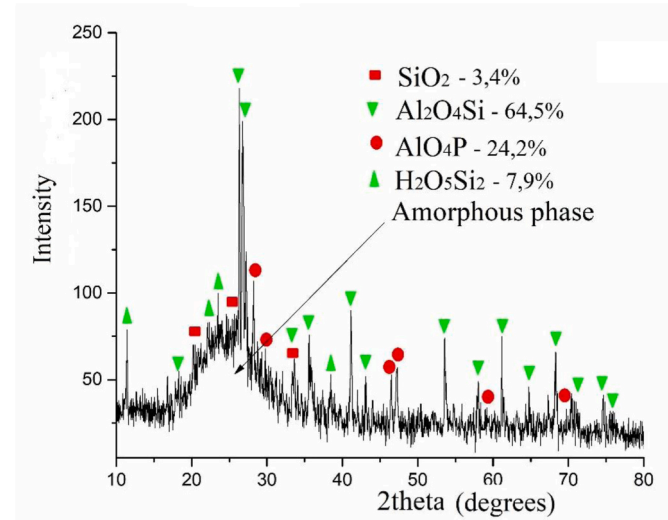
The second endothermic effect with the lower intensity, but without the change in the sample mass, is observed at 566.6 °C. This can be explained by the polymorphic transformation of residual quartz. In turn, aluminum phosphate does not undergo any transformation.

Similar studies were conducted with the sample of disten-sillimanite (7 mass units) with orthophosphoric acid (3 mass units), treated at the temperature of 300 °C. According to preliminary data, the presence of four crystal phases has been established. These are sillimanite (65.4 %), aluminum orthophosphate (17.8 %), quartz (9.8 %) and silicic acid in the form of  $H_2Si_2O_5$  (7.9 %). At the same time, as can be seen from the nature of the X-ray diffraction pattern in Fig. 4, the unidentified part of the sample has an amorphous nature.

The formation of such phases is most probably caused by the following reaction:



According to mass ratios, this reaction is totally carried out under the condition of mixing 486 mass units of disten-sillimanite with 588 mass units of  $H_3PO_4$ . Our sample, considering the acid concentration (85 %) and the mass ratio of the components contained 1372 mass units of disten-sillimanite and 500 mass units of  $H_3PO_4$ . In this case, only 413 mass units of disten-sillimanite could react, and  $1372 - 413 = 959$  mass



**Fig. 4.** X-ray diffraction pattern of the sample of disten-sillimanite (7 mass units) with orthophosphoric acid (3 mass units), treated at the temperature of 300 °C.

units remained. According to reaction (2), 622 mass units of aluminum orthophosphate, 51 mass units of quartz and 117 mass units of silicic acid should be formed. The calculated mass of the sample is 1749 mass units.

However, the unspecified part of the aluminum phosphate is in the amorphous state. To establish it, the data of quantitative phase analysis was used, which gives the relative distribution of crystalline phases. If the amount of residual disten-sillimanite is determined to be 64.5 %, and its calculated amount is 959 mass units, then the total number of crystalline phases is  $\frac{959}{0.645} = 1487$  mass units. Therefore, the amount of amorphous aluminum phosphate is equal to the difference between the calculated mass of the sample and the number of crystalline phases detected in it:  $1749 - 1487 = 262$  mass units. Accordingly, the amount of aluminum phosphate in the crystalline state is  $622 - 262 = 360$  mass units, which is  $\frac{360}{1487} \cdot 100 = 24.2\%$ .

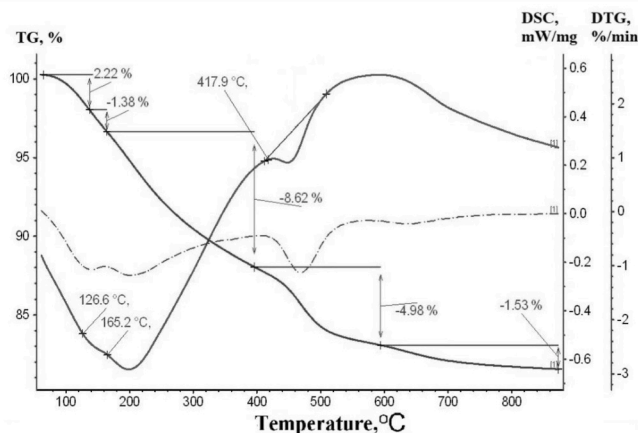
It is known that  $AlPO_4$  and  $SiO_2$  phases have identical X-ray patterns, so it is impossible to establish the quantitative relationship between them based only on the results of phase analysis. At the same time, the total number of these crystalline phases is known:  $17.8 + 9.8 = 27.6\%$ . The calculated amount of crystalline  $AlPO_4$  is 24.2 % and then the calculated amount of quartz is  $27.6 - 24.2 = 3.4\%$ . According to reaction (2), the calculated amount of  $SiO_2$  formed should be  $\frac{51}{1487} \cdot 100 = 3.4\%$ . Calculated amount of silicic acid  $\frac{117}{1487} \cdot 100 = 7.9\%$ . Thus, the calculated data completely coincide with the experimental data. The interpretation of the X-ray diffraction pattern is shown in Fig. 4.

After the final establishment of the phase structure of the formed binders, the peculiarities of the dynamics of its transformations during heating become clear. Fig. 5 shows differential thermogravimetric analysis of the sample of filler based on disten-sillimanite with orthophosphoric acid and processed at 300 °C, was performed in air at the heating rate of 20 ... 30 K/min.

The graph reveals two slightly pronounced endothermic effects at temperatures up to 200 °C. They should be explained by the presence of the hygroscopic phase  $H_2Si_2O_5$  in the sample.

At the temperature of 417.9 °C, the endothermic effect was detected, which was accompanied by the jump-like, but insignificant, decrease in mass. Obviously, this effect is related to the decomposition of the  $H_2Si_2O_5$  phase, as the result of which silica  $SiO_2$  is formed and  $H_2O$  is removed. Notably, the disten-sillimanite reaction yields a small amount of silicic acid in the form of  $H_2Si_2O_5$ . This hydrated silica phase is stable at least until ~400 °C. Its formation is favored by the water released during the acid-base reaction. Upon further heating,  $H_2Si_2O_5$  decomposes, and the liberated silica contributes to the formation of quartz.

General evenness heat dismiss in the range of 200 ... 500 °C is the



**Fig. 5.** Differential thermogravimetric analysis of the mixture of disten-sillimanite (7 mass units) with orthophosphoric acid (3 mass units), treated at the temperature of 300 °C.

result of the passing of aluminum phosphate  $AlPO_4$  from amorphous to crystalline form. Heating above the temperature of 500 °C does not found the thermal effect, that is, aluminum orthophosphate (as well as quartz and disten-sillimanite) remains without change up to 1000 °C. The thermal stability of the system makes it possible to use it as part of foundry cores.

In mixtures of orthophosphoric acid with both refractory aluminosilicates, pyrophyllite and disten-sillimanite, the formation of aluminophosphate binders upon heating was confirmed. To compare their binding capacity, core mixtures of the following composition were prepared: orthophosphoric acid (85 % solution) is 3.0 % by mass, powdered aluminosilicate is 5.0 % by mass, quartz sand is the balance. Samples of the mixtures were drying for 1 h at the temperature of 300 °C.

The results of determining the compressive strength are as follows: the mixture with pyrophyllite is 0.65 MPa, the mixture with disten-sillimanite is 1.55 MPa. This result is explained by the fact that after the reaction of orthophosphoric acid with pyrophyllite, the larger amount of residual quartz is formed. As determined by phase analysis with further calculation, it is 64 %. After the reaction of acid with disten-sillimanite, the total amount of residual phases (quartz and silicic acid) is much smaller. It is about 11 % (Fig. 4). Also, the relatively larger amount of aluminum orthophosphate is formed in the mixture with disten-sillimanite.

Taking into account the obtained theoretical and practical results, the combination of orthophosphoric acid and disten-sillimanite was chosen to create the aluminum phosphate core mixture. For the more complete passage of the chemical reaction (2) formation of binders, the mass ratio of the components must differ from the one used during the previous experiment. Orthophosphoric acid should be in excess relative to disten-sillimanite. In order to achieve such ratio, during the preparation of the mixtures, the acid was pre-mixed with disten-sillimanite. Since the amount of acid was predominant, these pre-prepared compositions were in the form of suspensions.

The influence of the composition of the suspensions on the strength of the core mixture samples is shown in Fig. 6.

On all graphical dependencies shown in Fig. 6, maxima are observed at the amount of 30 % disten-sillimanite (corresponding to 70 % acid) in the suspension. This additionally confirms exclusively the chemical mechanism of the formation of the aluminosilicate binders according to reaction (2), the complete passage of which is ensured by the mass superiority of  $H_3PO_4$  over disten-sillimanite.

Therefore, it was determined that the aluminum phosphate core mixtures should contain 5 ... 6 % of the suspension, which consists of 30 % powdered distensillimanite and 70 % orthophosphoric acid. At the same time, the strength is 2.0 ... 3.0 MPa. The mixture became a patent in Ukraine [24] even before the establishment of the physical and chemical processes of the formation of aluminum phosphate binders and its properties.

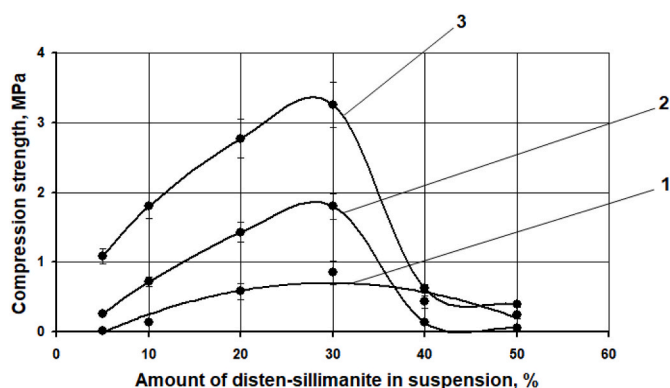


Fig. 6. Strength dependence on the amount of disten-sillimanite in suspension.

A comparative summary of the key experimental differences between the pyrophyllite and disten-sillimanite-based binder systems is presented in Table 1.

#### 4. Conclusions

1. The formation of aluminum phosphate binders in mixtures of orthophosphoric acid with powdered pyrophyllite and disten-sillimanite after their heating to 300 °C was established. Binders are formed as the result of direct chemical reaction of aluminosilicates with acid, and this process can be applied as part of the core mixture.
2. For the first time, the mechanism of reaction of disten-sillimanite with orthophosphoric acid was investigated and it was shown that as the result of chemical reaction between them, in addition to binders (aluminum orthophosphate) and residual  $SiO_2$ , the additional product is formed. This product is the type of silicic acid- $H_2Si_2O_5$ , which is not found in any other mixture of orthophosphoric acid with aluminosilicates.
3. The phase composition of the formed aluminum phosphate binders was studied. It is shown that in the mixture of orthophosphoric acid with pyrophyllite only crystalline phases are formed, namely, aluminum orthophosphate and residual quartz. In the mixture of orthophosphoric acid with disten-sillimanite, aluminum orthophosphate is distributed between crystalline and amorphous states, and its total amount is greater, which provides significantly greater strength of the hardened mixture.
4. It is shown that the formed binders are thermally stable and do not undergo polymorphic transformations during heating up to 1000 °C. Aluminum phosphate binders, formed from orthophosphoric acid and disten-sillimanite, change their amorphous structure to crystalline during heating. These features do not prevent the development of the core mixture based on the studied aluminum phosphates. It was established that the mixture of optimal composition contains 5 ... 6 % suspension (30 % powdered disten-sillimanite and 70 % orthophosphoric acid), the balance is quartz sand. The strength after heating the samples to 300 °C is 2.0 ... 3.0 MPa.

#### CRediT authorship contribution statement

Ivan Petryk: Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation. Rostyslav Liutyi: Writing –

**Table 1**  
Comparison of aluminophosphate binders derived from pyrophyllite vs. disten-sillimanite.

| Aspect  | Pyrophyllite- Based Binder   | Disten-Sillimanite Based Binder   |
|---|--|---|
| Reaction products after curing (300 °C)   | $AlPO_4$ binder (crystalline); significant residual quartz (unreacted silica). No additional phases observed | $AlPO_4$ binder (split between crystalline and amorphous); minor residual quartz plus silicic acid $H_2Si_2O_5$ |
| Residual unreacted content  | High: ~64 % of initial material remains as residual quartz   | Very low: only ~11 % remains  |
| $AlPO_4$ binder yield   | Lower, correspondingly less aluminum phosphate formed (due to the large unreacted fraction)                  | Higher – much greater aluminum phosphate (crystalline and amorphous)  |
| Compressive strength of cores (5 % aluminosilicate, 3 % orthophosphoric acid, cured 300 °C) | 0.65 MPa – relatively low strength, attributed of the small amount of binder and high inert residue content  | 2.0 ... 3.0 MPa – due to the higher binder content and the low inert residue                                    |
| Unique observations   | No unusual phases; all $AlPO_4$ formed is crystalline  | $H_2Si_2O_5$ –by-product forms 4 $AlPO_4$ partially amorphous   |

review & editing, Writing – original draft, Methodology, Investigation, Conceptualization. **Irina Osypenko**: Methodology, Investigation, Conceptualization. **Olexander Myslyvchenko**: Writing – original draft, Resources, Investigation. **Ievgen Byba**: Writing – original draft, Resources, Investigation. **Ivan Lukianenko**: Writing – original draft, Validation, Conceptualization.

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#### Declaration of competing interest

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#### Data availability

No data was used for the research described in the article.

#### References

- [1] F. Czerwinski, M. Mir, W. Kasprzak, Application of cores and binders in metal casting, *Int. J. Cast Metals Res.* 28 (3) (2014) 129–139, <https://doi.org/10.1179/1743133614y.0000000140>.
- [2] F.C. Banganayi, D.K. Nyembwe, H. Polzin, Optimisation of an environmentally friendly foundry inorganic binder core making process for the replacement of an organic binder, *MRS Adv.* 5 (25) (2020) 1323–1330, <https://doi.org/10.1557/adv.2020.225>.
- [3] A. Fortini, M. Merlin, G. Raminella, A comparative analysis on organic and inorganic core binders for a gravity diecasting Al alloy component, *Int. J. Metalcast.* (2021), <https://doi.org/10.1007/s40962-021-00628-1>.
- [4] Robert S. Dungan, B. Reeves James, Near infrared spectroscopic analysis of foundry moulding and core sands, *J. Near Infrared Spectrosc.* 15 (3) (2007) 189–194, <https://doi.org/10.1255/jnirs.729>.
- [5] Bu Yoon Kang, Kyeong Ho Kim, Dae Won Park, Sig Lee Man, Effect of regenerated-foundry sand on the mechanical properties of core, *Mater. Sci. Forum* 922 (May 2018) 149–154. <https://dx.doi.org/10.4028/www.scientific.net/msf.922.149>.
- [6] M. Skrzyński, R. Dańko, J. Kamińska, Reclamation of mixtures of spent sands of inorganic and organic type, *Arch. Foundry Eng.* 13 (4) (2013) 93–96, <https://doi.org/10.2478/afe-2013-0089>.
- [7] M. Holtzer, S. Żymankowska-Kumon, R. Dańko, A. Kmita, Elution of mixed moulding sands with the GEOPOL binder and core sands with the phenolic resin, *Arch. Foundry Eng.* 13 (4) (2013) 53–56, <https://doi.org/10.2478/afe-2013-0081>.
- [8] James Bennett, Anna Nakano, Jinichiro Nakano, Hugh Thomas, Aluminum Phosphate Phase Changes Caused by the Exposure Environment National Energy Technology Laboratory, USDOE, USA; 2 LRST, USA, 2019. <https://www.osti.gov/servlets/purl/1598988>.
- [9] D.D.L. Chung, Review: acid aluminum phosphate for the binding and coating of materials, *J. Mater. Sci.* 38 (13) (2003) 2785–2791, <https://doi.org/10.1023/a:1024446014334>.
- [10] Hui Han, *The exploitation and application of phosphate binders in foundry. Hot Working Technology*, 1990, pp. 40–43.
- [11] S.P. Doroshenko, *Molding Mixtures*, IZMN, Kyiv, 1997, p. 140 [in Ukrainian].
- [12] V. Hopp, A. Masoudi Alavi, D. Hahn, P. Quirnbach, Structure–property functions of inorganic chemical binders for refractories, *Materials* 14 (16) (2021) 4636, <https://doi.org/10.3390/ma14164636>.
- [13] K. Cui, Y. Zhang, T. Fu, J. Wang, X. Zhang, Toughening mechanism of mullite matrix composites: a review, *Coatings* 10 (7) (2020) 672, <https://doi.org/10.3390/coatings10070672>.
- [14] P. Fernández-López, S.A. Alves, J.T. San-Jose, E. Gutierrez-Berasategui, R. Bayón, Plasma electrolytic oxidation (PEO) as a promising technology for the development of high-performance coatings on cast Al-Si alloys: a review, *Coatings* 14 (2024) 217, <https://doi.org/10.3390/coatings14020217>.
- [15] L. Ropyak, T. Shihab, A. Velychkovych, V. Bilinskiy, V. Malinin, M. Romaniv, Optimization of plasma electrolytic oxidation technological parameters of deformed aluminum alloy D16T in flowing electrolyte, *Ceramics* 6 (2023) 146–167, <https://doi.org/10.3390/ceramics6010010>.
- [16] I. Shatskyi, M. Makoviichuk, L. Ropyak, A. Velychkovych, Analytical model of deformation of a functionally graded ceramic coating under local load, *Ceramics* 6 (2023) 1879–1893, <https://doi.org/10.3390/ceramics6030115>.
- [17] R.V. Liutyi, M.V. Tyshkovets, D.V. Liuta, Foundry core mixtures with orthophosphoric acid and different aluminum-containing compounds, *Phys. Chem. Solid State* 21 (1) (2020) 176–184, <https://doi.org/10.15330/pcss.21.1.176-184>.
- [18] R.V. Liutyi, M.V. Tyshkovets, M.M. Yamshinskij, V.Y. Selivorstov, V.G. Ivanov, Synthesis of phosphosulphate substance and properties of its structured mixture with quartz sand, *Nauk. Visn. Nat. Hirn. Univ.* (4) (2022) 59–65, <https://doi.org/10.33271/nvngu/2022-4/059>.
- [19] R. Liutyi, D. Liuta, I. Petryk, Structural construction of binders based on orthophosphoric acid and refractory materials, *Adv. Mater. Sci. Eng.* 2021 (2021) 1–7, <https://doi.org/10.1155/2021/6667769>.
- [20] H. Onoda, R. Sakai, A. Nakahira, I. Tanaka, Synthesis of porous aluminum phosphate bulks by hydrothermal hot pressing process and their analytical characterizations, *Inorg. Mater.* 45 (9) (2009) 1048–1052, <https://doi.org/10.1134/s0020168509090180>.
- [21] S. Moukannaa, A. Aboulayt, R. Hakkou, M. Benzaazoua, K. Ohenoja, A. Palomo, A. Fernández-Jimenez, Fusion of phosphate by-products and glass waste for preparation of alkali-activated binders, *Compos. B Eng.* (2022) 110044, <https://doi.org/10.1016/j.compositesb.2022.110044>.
- [22] I. Petryk, R. Liutyi, A. Kocheshkov, A. Myslyvchenko, D. Liuta, Creation of self-hardening aluminum phosphate binders for manufacturing foundry cores, *Adv. Indust. Manufact. Eng.* (2023) 100114, <https://doi.org/10.1016/j.aime.2023.100114>.
- [23] I.M. Fedorchenko, *Encyclopedia of inorganic materials*, in: Kyiv: The main edition of the Ukrainian Soviet Encyclopedia 1, 1977, p. 840.
- [24] R.V. Liutyi, D.V. Keush, O.A. Anisimova, Method for hardening foundry cores, *Pat. Ukraine* (2015) 99789. Published 25.06.2015. [in Ukrainian].