

CHEMICAL PROCESSES IN KAOLIN SINTERED WITH NaH₂PO₄

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Abstract

The results of experiments on application of NaH₂PO₄ as a binding agent for ceramic kaolin samples were presented. The experiments were carried out at temperatures of 973, 1073 and 1173 K and NiO and CoO additives were used as tempering agents. The parameters of the obtained samples with NaH₂PO₄ were compared with the samples compressed with water only. The materials of 3–4 times higher bending strength, lower water absorption as well decreased open porosity were prepared during these experiments. The binding function of the NaH₂PO₄ additive relies on creation of some compounds in reaction between the products of its condensation and products of kaolin decomposition. Finally a ceramic material of prospective properties was created.

Keywords: dehydroxylation, kaolin, NaH₂PO₄, sintering

Introduction

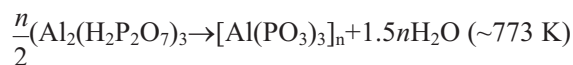
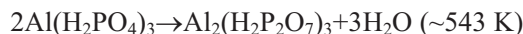
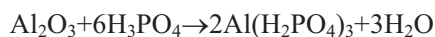
An intense development in the use of phosphates as ceramic binders for various ceramic materials is observed since 1950s. In particular it concerns refractory materials [1], guniting masses and adhesive refractory coatings considerably improving useful properties of refractory materials [2]. Phosphate binders are also used for manufacture of products based on silicon carbide and carbides of other elements, as well as on metal nitrides [3]. Phosphate binders are also used for impregnation of carbon and graphite materials. In addition to the increase of mechanical strength the use of phosphate provides a protection of such materials against air oxidation at elevated temperatures.

Phosphate binders as well as H₃PO₄ are used in building materials industry for manufacturing ceramic tiles and other building materials at relatively low temperature [4]. Phosphate binders are also used in production of dentist's cement [5].

First papers on phosphate binders were published in the USA by W. D. Kingery [6, 7]. The hardening and binding processes of phosphate binders includes polycondensation and formation of inorganic polymers. In systems containing aluminium oxide this is bound by the phosphate anions formed in the condensation processes. In

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compositions containing aluminium oxide and orthophosphoric the following reactions can be expected:



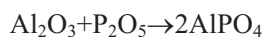
A complete neutralisation of monoaluminium phosphate by Al₂O₃ or Al(OH)₃ can result in a formation of orthophosphate:



At temperatures within 700–1000°C AlPO₄ is formed in the decomposition reaction:



The P₂O₅ formed in this reaction can react with the oxides present in the refractory mixture:



or



Although many papers on the reactions of phosphate binders with various compounds have been published, most of them describes aluminium phosphates stabilised with chromium phosphates. Very few of these papers have been devoted to the application of NaH₂PO₄ as a substitute of phosphoric(V) acid used for obtaining products not exposed to higher temperatures, such as ceramic tiles. The main goal of our work was to prepare ceramic materials based on ‘Sedlec’ kaolin with application of NaH₂PO₄ as a ceramic binder of good physical parameters.

The pH of NaH₂PO₄ solutions is about 4 and this fact facilitates considerably the use of this binder for the manufacture of ceramic products in comparison with phosphoric(V) acid or aluminium polyphosphates.

Experimental

Materials and sample preparation

The experiments were carried out using standard procedures applied in the technology of ceramics for preparation of ceramic products. The thermal analyses of the samples were performed with the use of OD-102 Derivatograph produced by MOM, Hungary. The samples were heated up to 1273 K at the rate of 10° min in air.

The phase analyses of the starting materials and of the products of calcinations at specified temperatures were carried out using a HZG-4 diffractometer (Carl Zeiss Jena).

The studies were performed using 'Sedlec' kaolin of the following chemical composition: SiO₂ – 46.08%, Al₂O₃ – 37.28%, K₂O – 0.89%, Fe₂O₃ – 0.88%, CaO – 0.78%, MgO – 0.69%, TiO₃ – 0.30% and NaH₂PO₄·H₂O (p.p.a. produced by POCh Gliwice, Poland).

Kaolin was mixed with 10 parts by mass of a 2.5 M aqueous solution of NaH₂PO₄. The obtained slurry was homogenised by rubbing 5 times through a sieve of 2 mm mesh and then rectangular prism plates of 30×10×9 mm were prepared by pressing in a die at 25 MPa. The plates were dried for 24 h at 378 K and then sintered in a Carbolite CWF1200 furnace for 1 h at 973, 1073 or 1173 K with a temperature increase rate of 200 K h⁻¹.

Methods

In order to find how the addition of NaH₂PO₄ affects the properties of the plates prepared from the Sedlec kaolin analogous plates were prepared with addition of 10 parts of distilled water only and were then fired together with the plates with NaH₂PO₄. Determination of water absorption (*N*) and bending strength index (*W*_{zg}) were performed on the sintered samples. The bending strength was measured by the three-point method on a mechanical press WPM ZDM 5/91 (Germany) at the stylus speed of 3 mm min⁻¹ and the final result was calculated from the following formula:

$$W_{zg} = \frac{3Pl}{2bh^2}$$

where *P* – sample-breaking force/MPa, *l* – distance between supports/1.5 cm, *b* – sample width/cm and *h* – sample height/cm.

Besides, the effect of addition of some metal oxides on the essential parameters of the kaolin plates was studied. The oxides selected as the test additives were NiO (pure, prod. by POCh) and CoO (pure, prod. by POCh) used in amount of 1, 2 or 3% by mass of kaolin. The oxide was mixed with kaolin, then 10 parts of 2.5 M aqueous solution of NaH₂PO₄ was added, and the further procedure was identical as in the case of plates without the oxide additives.

Results and discussion

The influence of temperature and NiO and CoO additives on the essential parameters of the prepared plates is shown in Figs 1 and 2. As can easily be seen, both the water absorption and the bending strength are much different in the plates containing NaH₂PO₄ and in those prepared with water alone. The bending strength of the sintered plates prepared with the use of NaH₂PO₄ is 3–4 times as high as that without this additive. For example, the control samples containing no NaH₂PO₄, sintered for 1 h at 973 K, exhibited the bending strength index of 2.57 MPa, whereas the analogous plates prepared with the use of NaH₂PO₄ had as much as 10.76 MPa. Different relations were observed

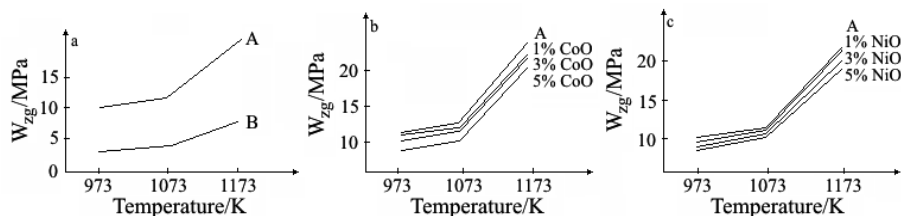


Fig. 1 Influence of sintering temperature on bending strength of Sedlec kaolin plates prepared with the use of NaH₂PO₄ (A), water alone (B), or those of (A) supplemented with NiO or CoO (C)

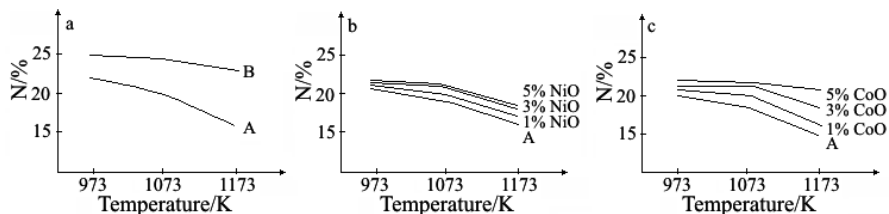


Fig. 2 Influence of sintering temperature on water absorption of Sedlec kaolin plates prepared with addition of NaH₂PO₄ (A), of water alone (B), or with addition of NiO or CoO to (A) (C)

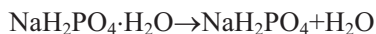
in the case of water absorption, which was about 24% in the samples containing no NaH₂PO₄, fired for 1 h at 1173 K, and only 15.5% in the analogous samples prepared with the use of the additive.

The figures show also, that the effect of NiO and CoO additions is small in the temperature range studied. They act merely as tempering agents, giving a small increase of water absorption and decrease of bending strength, the action being the more easily seen, the more oxygen is included in the samples.

In order to elucidate the way the NaH₂PO₄ additive binds kaolin a complex thermal analysis was performed for NaH₂PO₄·H₂O – Fig. 3a, Sedlec kaolin – Fig. 3b, and equimolar mixture of the two components – Fig. 3c.

The behaviour of NaH₂PO₄·H₂O exposed to heating can be divided into several steps, corresponding to definite chemical processes:

- dehydration of the compound, connected with an endothermic effect on the DTA curve, proceeding at temperatures up to 453 K, with a maximum on the DTA curve at 433 K, and with general mass loss conforming to the equation:



- endothermic condensation, proceeding with a maximum rate at 493 K, conforming to the equation:



- further condensation step with a maximum at 593 K, resulting in formation of metaphosphate(V):

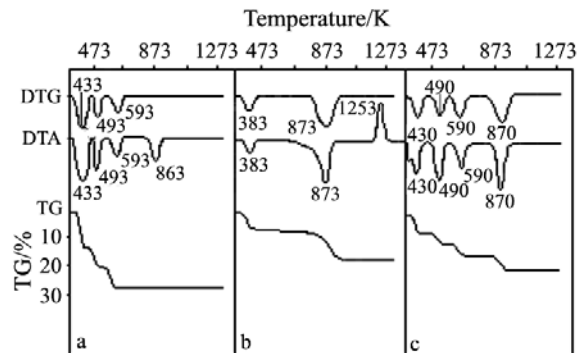
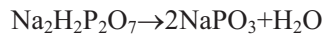


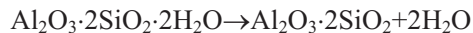
Fig. 3 Thermogravimetric curves of: A – NaH₂PO₄·H₂O, B – kaolinite ‘Sedlec’, C – equimolar mixture of NaH₂PO₄·H₂O and kaolinite



The phase analysis proved that the compounds formed at each stage of the experiments were identical with the standards of the PDF data base: NaH₂PO₄·H₂O – 11-0651; NaH₂PO₄ – 84-0112; NaH₂P₂O₇ – 02-0751; NaPO₃ – amorphous phase.

The formed metaphosphate(V) melts at 863 K. The performed phase analysis confirmed the course of decomposition according to the above equations.

The thermogravimetric curves shown in Fig. 3b demonstrate that the ‘Sedlec’ kaolin loses water at temperatures up to 300 K, then it decomposes giving the endothermic effect with a maximum reaction rate at 873 K and the mass loss corresponding to the loss of water. The process may roughly be described in terms of dehydroxylation of kaolinite, which is the main component of kaolin:



Finally, the exothermic effect typical of kaolin, often referred to as the ‘kaolinite effect’ [8–13], is observed at 1253 K.

The thermogravimetric curves presented in Fig. 3c, representing the compounds mixture allow to distinguish the effects due to individual reactions. In the temperature range up to 623 K they comprise transformations of NaH₂PO₄·H₂O, its dehydration overlapping the dehydration of kaolin, and two successive condensation reactions ending by the formation of NaPO₃.

The independent nature of the decomposition was confirmed by the phase analysis of the products obtained by firing the mixture at temperatures of 423, 523 and 623 K.

The phase analysis of the annealing products demonstrated the presence of identical compounds as for annealing of pure components of the mixture.

The losses in mass are in agreement with the content of NaH₂PO₄·H₂O in the mixture. Only at higher temperatures the decomposition of kaolinite is accompanied by a reaction with polymeric NaPO₃, which is the final product of the NaH₂PO₄ decomposition and to formation of other compounds with a participation of other components of the mixture. It is seen from Fig. 3b that temperature of dehydroxylation of kaolinite

equals 873 K. Figure 3c (for mixture of compounds) suggests that the temperature of dehydroxylation of this kaolin is 870 K, thus for the mixture this temperature is lower than in absence of NaH₂PO₄. The mixtures sintered at 823, 873 and 1073 K contain, in addition to the products of kaolinite decomposition, the compounds formed in the reaction with metaphosphate such as: Na₇(AlP₂O₇)₄PO₄, NaAlP₂O₇, AlPO₄. Other compounds, solid solutions such as Na_xAl_{1-x}PO₄, Na₃AlP₈O₂₃, Na₃Al(PO₄)₂, and Na₃Al₂(PO₄)₃, can also be formed in the system [14].

Conclusions

The presented results of investigation of the influence of NaH₂PO₄ as a binder for 'Sedlec' kaolin based ceramic materials show its advantageous impact on the parameters of these materials when sintered at temperatures of 973, 1073 and 1173 K. The reference samples which were pressed with water addition only had water absorption of 21–23%, open porosity of 37–38% and bending strength of 2–8 MPa while the levels of these parameters for the samples modified with NaH₂PO₄ were 15–21%, 30–38% and 10–24 MPa, respectively. Thus the materials of 3–4 times higher strength, lower open porosity and water absorption were prepared during the course of our studies. Simultaneously a negligible influence of NiO and CoO additives on basic properties of the sintered kaolin samples was observed. These oxides behaved as typical tempering agents.

The effect of the applied NaH₂PO₄ additive relied on formation of polymeric NaPO₃ which reacted with kaolin and created a series of compounds leading to compact ceramic material of advantageous properties.

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