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THE EFFECT OF STORING CONDITIONS ON PHYSICAL PROPERTIES OF PHOSPHATE-BONDED INVESTMENT MATERIAL AND THE STUDY OF CHANGES IN POWDERY COMPOSITION OWING TO MOISTURE

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Abstract

Changes in the powdery composition and physical characteristics of phosphate-bonded investment material on exposure to 90% relative humidity as well as storing conditions and suitable packing material were investigated by means of thermogravimetry (TG), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The setting agents ($NH_4H_2PO_4$ and MgO) reacted due to moisture. They were converted into $MgNH_4PO_4\cdot6H_2O$. The quantity of $NH_4H_2PO_4$ decreased as the exposure time was prolonged. $NH_4H_2PO_4$ was not detected in the mixture of $NH_4H_2PO_4$ and MgO, which was exposed to moisture for 51 days. The quantity of $NH_4H_2PO_4$ in the powder seems to be related to the initial setting time and setting expansion. The quantity of $MgNH_4PO_4\cdot 6H_2O$ in the powder may contribute to the extreme delay of the setting reaction. Changes in powdery composition of setting agents due to moisture are similar to the reaction of setting the of $NH_4H_2PO_4$ - MgO mixture.

Introduction

The phosphate-bonded investments consist essentially of two main groups of ingredients, fillers and binders. The fillers are usually quartz and cristobalite, and they play a very small role in the chemistry of the investments during setting. The binders are essentially basic MgO and acidic $NH_4H_2PO_4$. The setting reactions and further thermal reactions are the results of the initial interaction between MgO and $NH_4H_2PO_4$ [1].

Dedicated to the memory of Prof. dr. Jože Šiftar

Unsuitable storage conditions and unsuitable packing materials are also the reasons for poor quality of phosphate investment. Owing to the humidity physical properties of phosphate investment change, especially setting characteristics. Miyaji [2,3] reported that phosphate investment on exposure to 100% relative humidity exhibited a progressive increase in the setting rate when mixed with colloidal silica solution and a decrease in the strength of the set investment.

This study investigates the changes in the powdery composition of phosphate-bonded investment material owing to moisture by means of thermogravimetry (TG), differential scanning calorimetry (DSC) and X-ray diffraction (XRD) and in the physical characteristics by measuring the fluidity, initial setting time, linear setting expansion and thermal expansion. The purpose of this study was to explain the deterioration process of one experimental investment material on exposure to (90±5)% relative humidity and to investigate storing conditions and suitable packing material.

Experimental

The powder of the experimental phosphate-bonded investment material used in this study was a mixture of cristobalite, fine-, medium- and coarse-grained quartz (80%), MgO and $NH_4H_2PO_4$ (20%). The median grain sizes of the SiO_2-components were 3 μm for the cristobalite, 10 μm for the fine-grained, 20 μm for medium-grained, and 160 μm for coarse-grained quartz. The MgO had grain sizes from 0 to 50 μm with a median grain size of 10 μm. The median grain size of ammoniumdihydrogenphosphate was 25 μm, approximately 75 wt% of the powder had grain size below 60 μm.

Samples were prepared by using MgO and $NH_4H_2PO_4$ alone, and also in combination with fillers. Water and colloidal silica suspension were used as mixing liquids.

The composition of the experimental investment powder was identical in all cases (20% cristobalite, 15% quartz-fine, 35% quartz-medium, 10% quartz-coarse, 10% MgO, 10% $NH_4H_2PO_4$) and was prepared by mixing all ingredients in laboratory mixer for 60 minutes.

A part of prepared investment was analysed immediately and packed in three-layered (polypropylene-PE, aluminium-Al, polyethylene-PE) bags and was exposed to (50±5)% relative humidity (stored in a desiccator above saturated aqueous solution of $Mg(NO_3)_2 \cdot 6H_2O$) at temperature 22-24°C [4]. The results in this case were used as control and plotted at day 0.

In order to investigate the storing conditions and to find out suitable packing material of phosphate investment, the following packing materials were chosen:

- unpacked investment
- investment packed in polyethylene-PE bags
- investment packed in three-layered bags.

In all cases the material was exposed to (90±5)% relative humidity atmosphere (stored in a desiccator above saturated aqueous solution of K_2SO_4 at room temperature) and was taken to analyse after 10, 23 and 30 days of exposure. before the representative sample was taken the exposed material was carefully mixed with each other.

Because it was anticipated that the setting agents will react with moisture, the mixed powder of $NH_4H_2PO_4$ and MgO at a weight ratio of 1:1 was prepared by mixing ingredients in laboratory mixer for 30 minutes and was exposed to (90±5)% relative humidity (stored in a desiccator above saturated aqueous solution of K_2SO_4 at room temperature). The representative samples were taken to analyse after 1, 2, 5, 6, 7, 9, 15, 19, 21, 22, 23, 27, 28, 29, 30, 51 days of exposure.

In order to confirm the formation of product in the phosphate-bonded investment owing to moisture, the mixed powder of $NH_4H_2PO_4$ and MgO at a weight ratio of 1:1 was prepared and mixed with water, and the product formed was analysed. The amount of the water corresponded to a liquid/powder ratio of 22,5 ml / 20 g, which yielded fluidity of investment material suitable for specification requirements (ISO 9694/1996) and for laboratory practice.

The collected powder was used in the TG/ DSC measurements (TG 951 and DSC 910 modules of TA 2000 instrument, TA Instruments, Castle Point, DE, USA) and X-ray diffraction (PW 1710, Phillips, Almelo, The Netherlands). In the TG and DSC measurement 10-30 mg of sample was heated from the room temperature to 300°C at a heating rate of 10°C/min in the flow of He (50 ml/min). X-ray diffraction measurements were carried out at 40 kV and 30 mA by means of CuK α.

The physical characteristics of investment material samples were determined according to International standard ISO 9694/1996 [5]. The powder was mixed by hand with a colloidal silica solution at a liquid/powder ratio of 0,225 (ml/g) for 15 s followed by 45 s vacuum mixing at room temperature (23±2)°C.

Fluidity was determined by filling a cylindrical ring mould (35 mm in diameter by 50 mm long) positioned on a glass plate, with investment slurry immediately after mixing. After 135 s from the start of mixing, the ring was lifted vertically from the plate allowing the mix to slump on the plate. As soon as the mixed investment had set, the average diameters of the set investment base were determined.

Initial setting time measurements were performed by Vicat needle apparatus. The setting time was recorded as the time from the start of mixing until the needle first failed to penetrated the investment to within 5 mm of the mould bottom.

The room-temperature linear setting expansion of investment was measured over a two hour period in extensometer, which was fitted with a dial gauge. One end of the trough was blocked with an immovable end pieces.

Linear thermal expansions at 900°C were determined on cylindrical samples (8 mm in diameter by 50 mm long) with a horizontal dilatometer at a heating rate of 5°C/min.

Results

Figure 1 shows the weight loss of the unpacked phosphate-bonded investment powder exposed to (90±5)% relative humidity atmosphere due to heating up to 300°C. The weight loss occurred in two stages in the lower temperature range (<180°C). DTG_{max} were determined: first stage 82°C (10 days); 87°C (23 days); 89°C (30 days); second stage 122°C (10 days); 126°C (23 days); 135°C (30 days). The total weight loss increased in proportion to days of exposure. Weight loss corresponded to two endothermic peaks detected in the DSC curves (figure 2). The area of higher-temperature peak was larger than that of lower-temperature one. The area increased with prolonged exposure time.

(Pictures availaible in printed version only!)

Temperature (°C)

Figure 1. TG curves of unpacked phosphate-bonded investment material exposed to 90% relative humidity atmosphere for 0 day, control (– · –), 10 days (——), 23 days (– – –) and 30 days (········).

(Pictures availaible in printed version only!)

Temperature (°C)

Figure 2. DSC curves of unpacked phosphate-bonded investment material exposed to 90% relative humidity atmosphere for 0 day, control (– · –), 10 days (——), 23 days (– – –) and 30 days (········).

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Temperature (°C)

Figure 3. TG curves of phosphate-bonded investment material packed in PE bags and exposed to 90% relative humidity atmosphere for 0 day, control (– · –), 10 days (——), 23 days (– – –) and 30 days (········).

(Pictures availaible in printed version only!)

Temperature (°C)

Figure 4. DSC curves of phosphate-bonded investment material packed in PE bags and exposed to 90% relative humidity atmosphere for 0 day, control (– · –), 10 days (——), 23 days (– – –) and 30 days (········).

(Pictures availaible in printed version only!)

Temperature (°C)

Figure 5. TG curves of phosphate-bonded investment material packed in three-layered bags and exposed to 90% relative humidity atmosphere for 0 day, control (– · –), 10 days (——), 23 days (– – –) and 30 days (········).

(Pictures availaible in printed version only!)

Temperature (°C)

Figure 6. DSC curves of phosphate-bonded investment material packed in three-layered bags and exposed to 90% relative humidity atmosphere for 0 day, control (– · –), 10 days (——), 23 days (– – –) and 30 days (········).

The TG curves of investment material powder packed in PE bags and exposed to (90±5)% relative humidity atmosphere are shown in figure 3. Weight loss occurred in two stages in the lower temperature range (<180°C) and was similar to that of unpacked investment material. Two-stage weight loss was accompanied by two endothermic peaks in DSC curves (figure 4).

Figures 5 and 6 present TG and DSC curves for samples of investment material which was packed in three-layered bags and exposed to (90±5)% relative humidity. There is obviously little variation in these curves. The weight loss in the lower temperature range (<180°C) was very low (cca. 0.1%).

Table 1. Effect of storing conditions and packing material on fluidity of investment material.

Exposure time (days)	Packed in three-layered bags 90% rel. humidity	Packed in PE bags 90% rel. humidity	Unpacked 90% rel. humidity
0	112 mm (45ml/200g)	112 mm (45ml/200g)	112 mm (45ml/200g)
10	110 mm (45ml/200g)	110 mm (45ml/200g)	109 mm (67ml/200g)
23	111 mm (45ml/200g)	107 mm (45ml/200g)	110 mm (82ml/200g)
30	110 mm (45ml/200g)	105 mm (45ml/200g)	111 mm (90ml/200g)

Table 1 shows that the fluidity of investment material packed in three-layered and PE bags remained the same at a given liquid/powder ratio (0.225 ml/g). Because the exposure of unpacked investment reduced the fluidity of the freshly mixed slurry at a given liquid/powder ratio, the fluidity suitable for laboratory practice could be obtained only by increasing the liquid/powder ratio. As the exposure was prolonged, the liquid/powder ratio increased from 0.225 ml/g at day 0 to 0.45 ml/g at 30 days of exposure to (90±5)% relative humidity.

Table 2 shows that the setting time remained the same for investment material packed in three-layered bags, decreased for investment material packed in PE bags, but increased after 10 days and could not be measured after 30 days of exposure to (90±5)% relative humidity atmosphere for unpacked investment material.

Table 2. Effect of storing conditions and packing material on initial setting time of investment material.

Exposure time (days)	Packed in three-layered bags 90% rel. humidity	Packed in PE bags 90% rel. humidity	Unpacked 90% rel. humidity
0	11.25 min	11.25 min	11.25 min
10	10.75 min	8.00 min	22 min
23	11.00 min	6.75 min	45 min
30	10.75 min	6.50 min	/

Table 3 shows that the setting expansion of samples packed in three-layered bags remained the same as the exposure to (90±5)% relative humidity was prolonged. The setting expansion of investment material packed in PE bags decreased from 1.58% at day 0 to 0.16% at 30 days. There was no expansion of unpacked investment exposed to (90±5)% relative humidity for 10 days.

Table 3. Effect of storing conditions and packing material on linear setting expansion of investment material.

Exposure time (days)	Packed in three-layered bags 90% rel. humidity	Packed in PE bags 90% rel. humidity	Unpacked 90% rel. humidity
0	1.58%	1.58%	1.58%
10	1.60%	0.46%	0.00%
23	1.50%	0.21%	0.00%
30	1.52%	0.16%	0.00%

The results of linear thermal expansion measurements are shown in table 4. Thermal expansion at 900°C was about 1.2% in every case with the exception of unpacked investment where the value decreased from 1.24% at day 0 to 0.98% at 30 days of exposure.

Table 4. Effect of storing conditions and packing material on linear thermal expansion of investment material.

Exposure time (days)	Packed in three-layered bags 90% rel. humidity	Packed in PE bags 90% rel. humidity	Unpacked 90% rel. humidity
0	1.24%	1.24%	1.24%
10	1.23%	1.18%	1.12%
23	1.23%	1.25%	1.09%
30	1.25%	1.22%	0.98%

(Pictures availaible in printed version only!)

Time (days)

Figure 7. Variation in weight loss of the mixed powder ($NH_4H_2PO_4$ and MgO) on exposure to 90% relative humidity atmosphere.

Figure 7 shows the weight loss increase due to heating the mixed powder of $NH_4H_2PO_4$ and MgO at a weight ratio of 1:1 from room temperature to 180°C in relation to the time of exposure to (90±5)% relative humidity. The weight loss was very small on day 0 (control), steeply increased to 30% at 19 days, and then gradually increased to 36.1% at 51 days of exposure.

Using the experimental mixed powder of $NH_4H_2PO_4$ and MgO TG and DTG curves are given in figure 8. As shown in graph 1, corresponding to the control sample, single weight loss was detected at about 200°C, and the weight loss in the lower temperature range (<180°C) was not detected. Two-stage weight loss in the lower temperature range was detected at 1 day of exposure; the temperatures of DTG_{max} were 76°C and 118°C. The weight loss at lower temperature was 1.9%, and 1.7% at higher temperature. As the exposure time was prolonged the weight loss in the lower temperature range (<180°C) also increased, the second stage of weight loss merged with first stage and moved to higher temperature, but the weight loss at about 200°C gradually decreased. After 51 days of exposure only single weight loss at 125°C was detected.

(Pictures availaible in printed version only!)

Temperature (°C) Temperature (°C)

Figure 8. TG and DTG curves of the mixed powder ($NH_4H_2PO_4$ and MgO) exposed to 90% relative humidity atmosphere for 0 day (graph 1), 1 day (graph 2), 2 days (graph 3), 5 days (graph 4), 7 days (graph 5), 15 days (graph 6), 30 days (graph 7), 51 days (graph 8).

The sample of the mixed powder of $NH_4H_2PO_4$ and MgO (weight ratio 1:1) exposed for 51 days was investigated also by x-ray diffraction (figure 9). In the range of diffraction angles (2θ = 5 - 85°) the peaks of $MgNH_4PO_4 \cdot 6H_2O$ and MgO were detected but the peaks of $NH_4H_2PO_4$ were not.

(Pictures availaible in printed version only!)

2θ (degree)

Figure 9. X- ray diffraction pattern of the mixed powder of $NH_4H_2PO_4$ and MgO (weight ratio 1:1) exposed to 90% relative humidity atmosphere for 51 days.

(Pictures availaible in printed version only!)

Temperature (°C)

Figure 10. TG and DTG curves of product formed by the reaction of the mixed powder $NH_4H_2PO_4$ / MgO = 1 (weight ratio) with water.

Figure 10 shows TG and DTG curves of the product of reaction of the mixed powder $NH_4H_2PO_4$ / MgO = 1 (weight ratio) with water. TG and DTG curves are similar to that observed at mixed powder ($NH_4H_2PO_4$/MgO=1) exposed to (90±5)%

relative humidity for 51 days (figure 8, graph 8). The weight loss due to heating from 25 to 175°C was 22.7% and the weight loss at about 200°C was also detected.

Figure 11 shows x-ray diffraction spectra of product of the reaction of mixed powder $NH_4H_2PO_4/MgO=1$ (weight ratio) with water. The principal XRD lines proved that the major reaction product was $MgNH_4PO_4 \cdot 6H_2O$. A trace of unreacted $NH_4H_2PO_4$ was present along with some MgO.

(Pictures availaible in printed version only!)

2θ (degree)

Figure 11. X-ray diffraction pattern of the product formed by the reaction of the mixed powder of $NH_4H_2PO_4$ and MgO (weight ratio 1:1) with water.

Discussion

Phosphate-bonded investment material absorbed water from the moist atmosphere. Owing to the humidity, the investment material powder contained physically adsorbed and chemically combined water. Both weight losses (DTG_{max} = 80-90°C and DTG_{max} = 120-135°C) of investment material powder from TG curves (figures 1 and 3) corresponded to endothermic peaks in DSC curves (figures 2 and 4) and resulted from the expulsion of water. In DSC curves the areas of the peaks corresponded to quantity of the heat change, and these areas increased as the exposure time was prolonged.

As compared with the result for the control sample the weight loss of the sample of unpacked investment material exposed to moisture increased in the lower temperature range (<180°C), but decreased at about 200°C. The results obtained in the case of the mixed powder ($NH_4H_2PO_4/MgO=1$) exposed to 90% relative humidity atmosphere for

51 days (figure 8, graph 8) were similar to the one detected in the case of unpacked phosphate-bonded investment material. It is evident that setting agents in the investment material adsorbed water and reacted with it.

Bamford and Tipper [6] reported that the $NH_4H_2PO_4$ decomposed at about 200°C resulting in polymetaphosphate $(NH_4PO_3)_n$. It is presumed that the weight loss and endothermic peak that appeared at about 200°C corresponded to the thermal decomposition of $NH_4H_2PO_4$. As the exposure time was prolonged the quantity of $NH_4H_2PO_4$ in the investment material decreased. $NH_4H_2PO_4$ reacted with MgO present and together with water they formed product with chemically combined water.

The weight loss of mixed powder ($NH_4H_2PO_4$/MgO=1) exposed to moisture for 51 days due to heating from room temperature to 180°C was 36.1% (figure 7). That is similar to theoretical weight loss (37.4%) corresponding to the formation of an intermediate hydrate $MgNH_4PO_4 \cdot H_2O$ from $MgNH_4PO_4 \cdot 6H_2O$ at about 100°C [7]. This reaction is as follows:

$$MgNH_4PO_4 \cdot 6H_2O \longrightarrow MgNH_4PO_4 \cdot H_2O + 5\,H_2O.$$

The formation of $MgNH_4PO_4 \cdot 6H_2O$ was confirmed by x-ray diffraction of mixed powder ($NH_4H_2PO_4$/MgO=1) exposed to moisture 51 days (figure 9). The same products formed by mixing the powder of $NH_4H_2PO_4$ and MgO at a weight ratio of 1:1 with water. The peaks of $MgNH_4PO_4 \cdot 6H_2O$, but also the peaks of unreacted MgO and $NH_4H_2PO_4$ were detected (figures 11).

According to Allan and Asgar [8], at room temperature during the mixing of the phosphate-bonded investment the following reaction occurs:

$$2\,NH_4H_2PO_4 + 2\,MgO + 6\,H_2O \longrightarrow MgNH_4PO_4 \cdot 6H_2O + NH_4H_2PO_{4(\mathrm{unreactive})} + \\ + MgO_{\,(\mathrm{excess})} + H_2O.$$

This setting reaction seems to be similar to the process of the deterioration of the setting agents.

As the exposure time was prolonged the initial setting time of phosphate investment increased, and after 30 days of exposure it was impossible to measure it. If the quantity of $NH_4H_2PO_4$ in the investment is small, the formation of phosphate bond is expected to be slow, and the setting expansion of the investment is expected to decrease. Because the quantity of $MgNH_4PO_4 \cdot 6H_2O$ tended to be larger after 30 days of exposure this may contribute to the delay of setting.

The powdery composition and physical properties changed significantly in the case of unpacked investment material, but the changes were also detected in investment packed in PE bags. It is evident that PE bags are permeable to moisture and therefore unsuitable as a packing material for phosphate-bonded investment material.

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Povzetek

Študirali smo spremembe v sestavi in fizikalnih lastnostih (fluidnost,začetek strjevanja, linearna vezivna in termična ekspanzija) fosfatne vložne mase izpostavljene vlagi. Posredno smo želeli ugotoviti tudi primerne pogoje za shranjevanje vložne mase in izbrati ustrezno vrsto embalaže. Študij je potekal ob uporabi različnih instrumentalnih metod kemijske analize (termogravimetrična analiza - TG,

diferencialna dinamična kalorimetrija - DSC, rentgenska difrakcija - XRD), katerih rezultati se lepo dopolnjujejo. Rezultati kažejo, da je v vložni masi vezivo tisto, ki adsorbira vlago iz atmosfere in kemijsko reagira z njo. $NH_4H_2PO_4$ skupaj z MgO in vodo daje produkt, ki vsebuje kristalno vezano vodo, to je $MgNH_4PO_4*6H_2O$. Izguba mase, ki jo detektiramo na TG krivuljah in dvojni endotermni minimum na DSC krivuljah v nizkotemperaturnem območju (<180°C), sta povezana z izhajanjem fizikalno adsorbirane in kemijsko vezane vode. Nastanek produkta $MgNH_4PO_4*6H_2O$ smo potrdili tudi z rentgensko difrakcijo. Z daljšanjem časa izpostavitve vlagi pada količina $NH_4H_2PO_4$ vvložni masi, kar pa ima za posledico slabše fizikalne lastnosti, zlasti vezivne in sicer podaljšanje časa strjevanja in ekstremen padec vezivne ekspanzije vložne mase. Spremembe v sestavi prahu fosfatne vložne mase, kot posledica izpostavljenosti vlagi, so zelo podobne vezivnim reakcijam v procesu strjevanja vložne mase.