

CALCIUM ORTHOPHOSPHATES HYDRATES: FORMATION, STABILITY AND INFLUENCE ON STANDARD PROPERTIES OF PORTLAND CEMENT

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Preparation of phosphogypsum to produce the binders requires a much higher input than preparation of natural gypsum stone. This makes it uncompetitive material. The investigations presented therein are meant to reduce this input by looking for the ways of rendering impurities harmless. Soluble acid orthophosphates are the main harmful impurity of phosphogypsum. The studies show that dry insoluble calcium orthophosphates hydrates (1.09 % and 2.18 % P_2O_5 in gypsum) have little effect on W/C, setting times and soundness of Portland cement pastes. Insoluble calcium orthophosphates hydrates $\{CaHPO_4 \cdot 2H_2O, Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$ and $Ca_9(HPO_4)(PO_4)_3(OH) \cdot 4H_2O\}$ formed in acidic medium (pH = 4.2 - 5.9) have been destroyed in alkaline medium and reduce standard compressive strength of cement up to 28 %. Calcium orthophosphates hydrates of hydroxyapatite group are stable in alkaline medium, while in dry state they reduce the standard compressive strength of cement until 10 %, but their suspensions prolong setting times of Portland cement as soluble orthophosphates – 2 - 3 times. Alkalis in cement increase pH of paste, but do not change the process of formation of calcium orthophosphates hydrates of hydroxyapatite group: it takes place through an intermediate phase - $CaHPO_4 \cdot 2H_2O$, whose transformation into apatite lasts for 2 - 3 months.

INTRODUCTION

Phosphogypsum is a by-product of the phosphoric acid industry and consists of 65 - 70 % gypsum, 25 - 30 % water and 5 - 10 % impurities, i.e. phosphoric acid and its salts, hydrofluoric acid and its compounds, R_2O_3 (Al_2O_3 + Fe_2O_3), quartz, apatite, alkali, organic matter, and others. The P_2O_5 and F impurities are found in three different forms: on the surface of gypsum crystals as water soluble compounds (H_3PO_4 , $Ca(H_2PO_4)_2 \cdot H_2O$, H_2SiF_6), substituted in the lattice of gypsum crystals (effectively solid solutions of $CaHPO_4 \cdot 2H_2O$, $SrSO_4$ or Na_2SiF_6) and as insoluble compounds, i.e. apatite and quartz. These impurities, particularly hydrofluoric acid and its salts, contaminate an environment [1-4].

A successful utilization of phosphogypsum in the production of building materials is impeded by the acidic impurities found in its composition that considerably worsens the properties of the products [5-8]. Actually, in all technologies applied for the processing of phosphogypsum into the gypsum binder wet processing is used for the elimination or neutralization of impurities. In such cases the great amount of water must be eliminated by evaporation [9, 10]. Soluble orthophosphates $\{H_3PO_4$ and $Ca(H_2PO_4)_2 \cdot H_2O\}$ had maximum influence on the fall of compressive strength and elongation setting time

of plaster of Paris. $CaHPO_4 \cdot 2H_2O$ had small influence, but with the present of $Ca(OH)_2$ it had great influence on the plaster properties [11-15].

The most impurities in phosphogypsum can be found in the particle size fractions above 160 μm and below 25 μm . There are more than few plants (those of "Onoda" in Japan, "Giulini chemic GmbH", "Knauf" in Germany, etc.) where the impurities are eliminated by washing phosphogypsum with water or separating of coarse and very fine particles. Up to 4 m^3 of water is necessary for 1 ton of phosphogypsum [9, 16].

Untreated phosphogypsum can be used for trass cement but it does not fit for regulation of setting times of Portland cement [17]. Untreated phosphogypsum can be used to regulate Portland cement setting times only adding phosphogypsum into raw mixture prepared for burning the clinker. The addition of phosphogypsum to the cement raw mixture shows that the burning temperature decreases and therefore improves the production process of clinker. The addition of 10 % phosphogypsum permits a complete clinkerization at low burning temperature (1200°C), instead of 1470°C, which increases the cement factory efficiency by 25 % and extends the service life of furnace fire brick [18]. The phosphogypsum admixtures are also eliminated by using a combined method when phosphogypsum is washed with a smaller amount of

water, and the rest of the acid admixtures are neutralized by adding the following additives: $\text{Ca}(\text{OH})_2$, CaCO_3 , K_2CO_3 , KOH , Portland cement, NH_4OH , fly ash and other industrial wastes [19-26].

Phosphoric acid residues are eliminated by washing phosphogypsum with water, but soluble calcium phosphate is decomposed into less soluble calcium phosphate $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and phosphoric acid. $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ solubility is very low, so the further washing with dividing it into calcium orthophosphates hydrates of hydroxyapatite group and H_3PO_4 solution is not carried out in practice due to enormous water demand [27-29]. So, the amount of insoluble calcium phosphates increases slightly in the course of washing. It is recommended to dissolve the accumulating insoluble calcium phosphates in citric acid solution [30]. Input needed to carry out the above washing procedures and evaporation of phosphogypsum moisture are far higher than the natural gypsum stone processing costs. This makes phosphogypsum uncompetitive and low-used material. Preparation of phosphogypsum neutralizing unwashed phosphogypsum in suspension of lime according to the method [31, 32] also requires gross expenditure associated with the accurate determination of impurities and precise execution of the neutralization process. The overall use of phosphogypsum in the world does not reach 15 % [3, 4].

On the other hand, soluble phosphates are one of phosphate cements components. These cements have been explored in detail within the last two decades and are widely used in dentistry and surgery [33-36]. Hydration processes taking place in phosphate cements are close to the hydration processes occurring in alkaline cements [37, 38]. Reaction of lime with soluble phosphates gives a rise to the formation of mixture of various insoluble calcium phosphates [1, 2]. It was stated [31-33] that the primary product of this reaction was colloidal X-ray amorphous calcium orthophosphate. Its formation place in respect of lime particles determines the course and duration of the formation of calcium orthophosphates hydrates of hydroxyapatite group [31, 32]. New compounds have been discovered at executing the phosphate cements research, and they are: $\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$, $\text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH}) \cdot 4\text{H}_2\text{O}$, $\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-(0 < x < 1)} \cdot 3-4,5\text{H}_2\text{O}$ – calcium-deficient hydroxyapatite and tetracalcium orthophosphate [39-41]. Pure calcium orthophosphates of the required composition are produced using the solution $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{HPO}_4$. Formation and stability of calcium orthophosphates in neutral medium is actual in medicine (pH 6 - 8), which is characteristic for human body [42-50]. In the course of Portland cement hydration there forms the alkaline medium (pH 12 - 13). Formation and stability of calcium orthophosphate has not been examined under these conditions.

The purpose of this study is to investigate formation processes of calcium orthophosphates hydrates, their stability in alkaline medium and to determine their influence on standard properties of Portland cement.

EXPERIMENTAL

Materials

Portland cement CEM I 42.5R of JSC “Akmenes cementas”, Lithuania. Composition, %, and standard properties of the cement: C_3S - 63.3, C_2S - 8.2, C_3A - 4.2, C_4AF - 12.7, lime - 0.8, MgO - 3.8, $\text{Na}_2\text{O}_{\text{ekv}}$ - 0.8, quartz - 0.6, calcite - 2.2, SO_3 - 2.9; W/C = 0.28, setting times, min: initial - 170, finish - 230, compressive strength, N/mm^2 : after 2 days - 23, after 28 days - 51, soundness - 2 mm.

Clinker granules was of the same cement.

Orthophosphoric acid, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and CaCO_3 have been used quality “analytical grade”.

CaO has been produced while burning the “C” (clean) CaO at the temperature of 900°C for 2 h.

Cement testing materials - according EN 196-1 and EN 196-2.

Equipments

The following equipment has been used in the testing:

- a magnetic mixer MM;
- mechanical mixer with ≤ 3000 rad/s;
- 200 ml and 5 l glass reactors;
- an universal-purpose ionometer I-130;
- X-ray powder diffraction (XRD) data were collected with a DRON-6 X-ray diffractometer with Bragg-Brentano geometry using $\text{Cu K}\alpha$ radiation, operating with the voltage of 30 kV and emission current of 20 mA;
- Portland cement testing equipment - according EN 196-1 EN 196-2 and EN 196-3.

Methods

Insoluble calcium orthophosphates hydrates $\{\text{Ca}_4(\text{PO}_4)_2(\text{OH})_2 \cdot x\text{H}_2\text{O}$ ($\text{CaO}/\text{P}_2\text{O}_5 = \text{C}/\text{P} = 4$), $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \cdot m\text{H}_2\text{O}$ ($\text{C}/\text{P} = 3.33$), $\text{Ca}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ ($\text{C}/\text{P} = 3.0$), $\text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH}) \cdot 4\text{H}_2\text{O}$ ($\text{C}/\text{P} = 2.84$), $\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$ ($\text{C}/\text{P} = 2.67$), $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ($\text{C}/\text{P} = 2$)} were synthesized from CaO and H_3PO_4 solution according to the method [31, 32]: stoichiometric amount of CaO was mixed in distilled water for 3 - 10 min., stoichiometric amount of H_3PO_4 solution was dripped into the prepared mixed suspension of lime with maintaining alkaline pH medium during 25 - 30 min. When the suspension thickens, mixing intensity was increased in order to prevent the hard particles settle on the bottom of the reactor. Upon dripping, the suspension was filtered off after 10 min of additional mixing and dried at 40°C temperature. Dry material was sieved through sieve 0.08 mm.

At determining standard properties of Portland cement according to EN 196-1 and EN 196-3, the part of cement has been replaced with orthophosphates (1.09 % and 2.18 % P₂O₅ in gypsum). The maximum amount of soluble orthophosphates that has been determined in phosphogypsum of Kedainiai chemical factory was 1.09 % water soluble P₂O₅. As a precautionary measure, in research there has been used and two times higher amount of phosphates - 2.18 %.

At determining the influence of calcium orthophosphates suspensions, they were synthesized in the amount of water, required to prepare the cement paste, and Portland cement was poured into the prepared suspension.

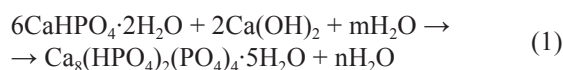
pH kinetics in orthophosphates-cement pastes was determined when placed in hermetically sealed dishes. Before carrying out the measurements, pastes were mixed for 2 - 5 s with a glass rod, medium pH was measured and the dishes again were closed hermetically. The temperature during the experimental period (140 days) in the laboratory ranged between 15 - 23°C. Clinker granules of the cement prior to the experiment were grinded and sieved through a sieve of 0.08 mm.

RESULTS AND DISCUSION

Synthesis of insoluble calcium orthophosphates hydrates in stirred suspensions

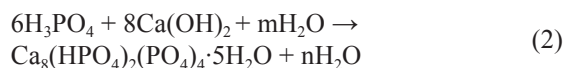
New calcium orthophosphate compounds have been discovered in the last two decades [33-35]: tetracalcium phosphate, octacalcium orthophosphates and calcium deficit orthophosphates {Ca₈(PO₄)₄, Ca₈(HPO₄)₂(PO₄)₄, Ca₉(HPO₄)(PO₄)₃(OH)}. Formation of its hydrates {Ca₈(HPO₄)₂(PO₄)₄·5H₂O, Ca₉(HPO₄)(PO₄)₃(OH)·4H₂O} from H₃PO₄ solution and Ca(OH)₂ suspension is alike to formation of calcium orthophosphates hydrates of hydroxyapatite group [31, 32]: the first phase of the reaction is X-ray amorphous colloidal calcium orthophosphate hydrate. Location of this material in respect of lime particles determines the course and duration of end product formation. When stoichiometric amounts of the materials are suddenly mixed, the initial colloidal calcium orthophosphate hydrate forms close to the lime particles surface, thus not allowing their free dissolving. The medium pH stabilizes at 4 (Figure 1).

In this medium all phosphates are bound to CaHPO₄·2H₂O crystals, lime particles surface breaks loose, the particles start to dissolve freely and pH medium suddenly increases. Then interaction of CaHPO₄·2H₂O with solving limes takes place until the end-product forms (curve 1 in Figure 2 and Equation 1):



Reaction of solution H₃PO₄ with CaCO₃ suspension even at stoichiometric components ratio CaO/P₂O₅ = C/P = 4 takes place in acidic medium (curve 3 in Figure 1) and reaction products are CaHPO₄·2H₂O and residue of CaCO₃ (curve 2 in Figure 2).

When the dissolved lime flow during the reaction exceeds the flow of the dissolved orthophosphate (medium pH until full dissolution of lime particles maintains as alkaline, which is achieved by dripping solution H₃PO₄ into suspension of lime), colloidal calcium orthophosphate hydrate is formed far from the lime surface without preventing the particles from free dissolution and formation of final substance (curves 4 and 5 in Figure 3, curve 2 in Figure 4 and Equation 2):



In the first case the reaction lasts 7-8 h, while in the second case - about 20 min.

All insoluble calcium orthophosphates hydrates were synthesized by dripping H₃PO₄ solution into the stirred suspension of lime with monitoring and recording of pH kinetics. (25.85, 51.69, 68.75, 73.40, 77.54, 86.32) g of CaO was poured into a glass reactor with 4 l of distilled water and mixed 3 - 10 min. 100 ml solution of H₃PO₄ (ρ = 1445 kg/l, 90.33 g H₃PO₄) was prepared and feeded in the suspension of lime within 25 - 30 min. Upon the infusion, the suspension was filtered off and dried after 10 min of additional mixing. Stoichiometry of the reactants (molar ratio CaO/P₂O₅ = C/P) were:

- 1) C/P = 4.0, Ca₄(PO₄)₂(OH)₂·xH₂O,
- 2) C/P = 3.33, Ca₁₀(PO₄)₆(OH)₂·mH₂O,
- 3) C/P = 3.0, Ca₃(PO₄)₂·nH₂O,

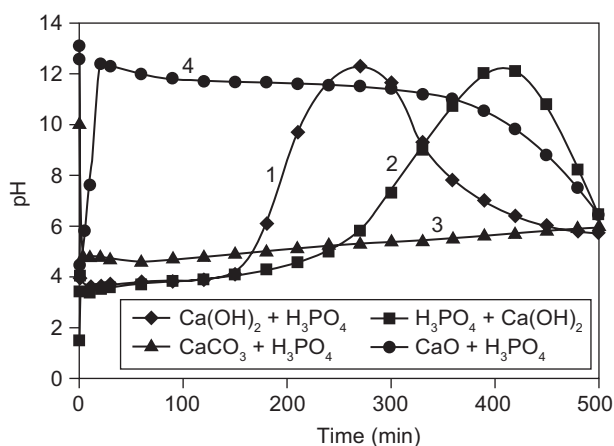


Figure 1. pH kinetics in suspensions (stoichiometric components CaO/P₂O₅ = C/P = 2.67 calculated for formation of Ca₈(HPO₄)₂(PO₄)₄·5H₂O) by suddenly pouring of 18 % H₃PO₄ solution into 8 % Ca(OH)₂ and CaO suspensions (curves 1 and 4, respectively) or CaO into 18 % H₃PO₄ solution (curve 2). Curve 3 - pouring of 18 % H₃PO₄ solution into 12 % CaCO₃ suspension (C/P = 4).

- 4) $C/P = 2.84$, $\text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH})\cdot 4\text{H}_2\text{O}$,
- 5) $C/P = 2.67$, $\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4\cdot 5\text{H}_2\text{O}$,
- 6) $C/P = 2.0$, $\text{CaHPO}_4\cdot 2\text{H}_2\text{O}$,
- 7) $C/P = 1.5$,
- 8) $C/P = 1.0$, $\text{Ca}(\text{H}_2\text{PO}_4)_2\cdot \text{H}_2\text{O}$

The curves of pH kinetics during synthesis and XRD patterns of the products are presented in Figures 3 and 4.

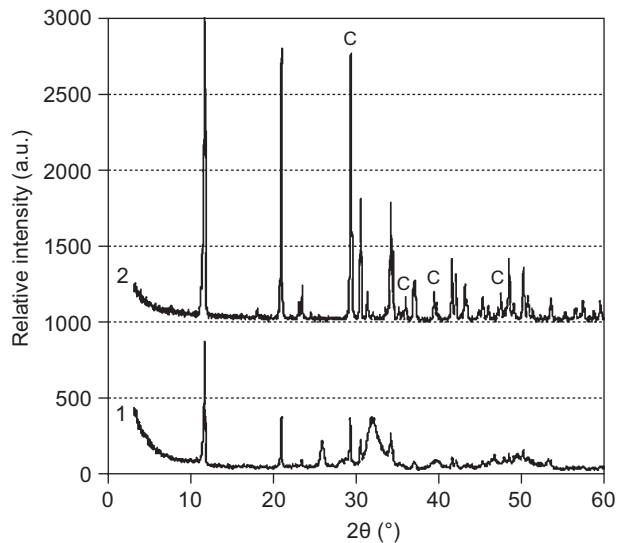


Figure 2. XRD patterns of the reaction products of H_3PO_4 with lime ($C/P = 2.67$) after mixing 450 min. (curve 1 - $\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4\cdot 5\text{H}_2\text{O}$) and H_3PO_4 with CaCO_3 ($C/P = 4$) (curve 2 - $\text{CaHPO}_4\cdot 2\text{H}_2\text{O}$), C - CaCO_3 .

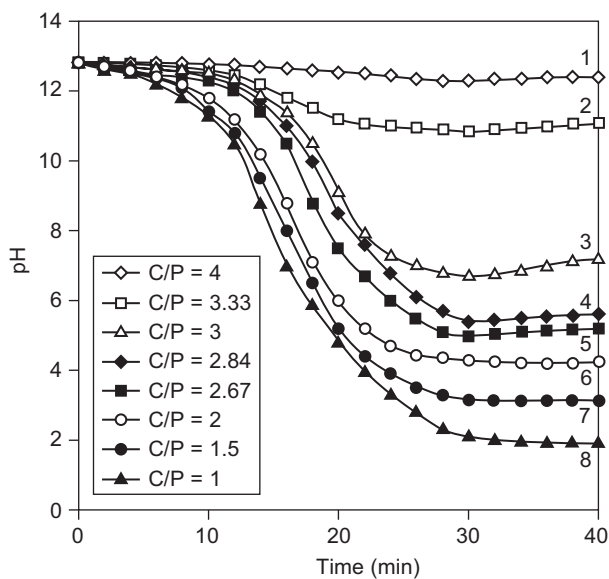


Figure 3. pH kinetics of suspensions (materials stoichiometry $C/P = 1 - 4$) by dripping H_3PO_4 solution into the stirred lime suspension for 25 - 30 min. and going on stirring for another 10 min.

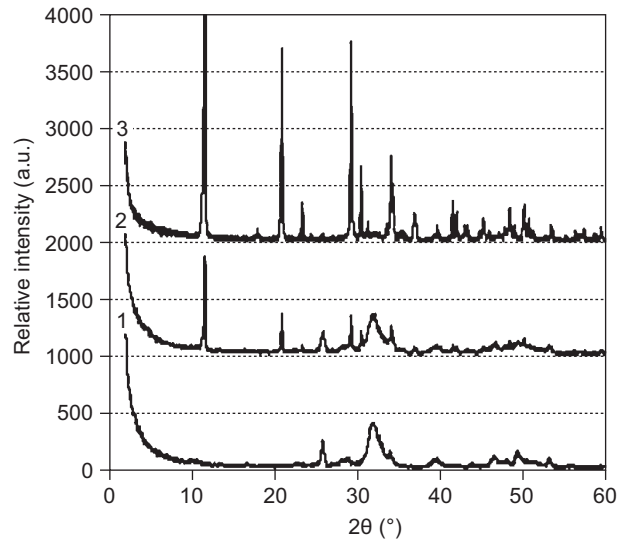


Figure 4. XRD patterns of the synthesised insoluble calcium orthophosphates hydrates: 1 - $\text{Ca}_4(\text{PO}_4)_2(\text{OH})_2\cdot x\text{H}_2\text{O}$, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2\cdot m\text{H}_2\text{O}$ and $\text{Ca}_3(\text{PO}_4)_2\cdot n\text{H}_2\text{O}$, 2 - $\text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH})\cdot 4\text{H}_2\text{O}$ and $\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4\cdot 5\text{H}_2\text{O}$, 3 - $\text{CaHPO}_4\cdot 2\text{H}_2\text{O}$.

Properties of insoluble synthesized calcium orthophosphate hydrates

XRD patterns (curve 1 in Figure 4) and properties of $\text{Ca}_4(\text{PO}_4)_2(\text{OH})_2\cdot x\text{H}_2\text{O}$ (molar ratio $\text{CaO}/\text{P}_2\text{O}_5 = C/P = 4.0$, $\text{pH} \leq 12.2$), $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2\cdot m\text{H}_2\text{O}$ ($C/P = 3.33$, $\text{pH} = 10.8-11.2$) and $\text{Ca}_3(\text{PO}_4)_2\cdot n\text{H}_2\text{O}$ ($C/P = 3.0$, $\text{pH} = 6.5 - 7$) are similar. They all are nano-crystalline, colloidal and difficult to filter materials. According to XRD patterns they all are attributed to calcium orthophosphates hydrates of hydroxyapatite group.

XRD patterns (curve 2 in Figure 2) of $\text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH})\cdot 4\text{H}_2\text{O}$ ($C/P = 2.84$, $\text{pH} = 5.5 - 6$) and $\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4\cdot 5\text{H}_2\text{O}$ ($C/P = 2.67$, $\text{pH} = 5 - 5.4$) are similar to XRD patterns of calcium orthophosphates hydrates of hydroxyapatite group, only with $\text{CaHPO}_4\cdot 2\text{H}_2\text{O}$ crystals addition. They are also colloidal and difficult to filter materials.

$\text{CaHPO}_4\cdot 2\text{H}_2\text{O}$ ($C/P = 2.0$, $\text{pH} = 4 - 4.5$) is well-crystallized (curve 3 in Figure 4) and easily filter material.

All filtered calcium orthophosphate hydrates with $C/P = 1.5 - 4$ were dried at 40°C temperature, grinded, sieved through sieve 0.08 mm and added to the cement (1.09 % and 2.18 % P_2O_5 in gypsum).

Influence of orthophosphates on standard properties of Portland cement

The water portion needed to determine influence of orthophosphates on the properties of cement CEM I 42.5R was replaced with aqueous solution H_3PO_4 , while the part of cement was replaced with $\text{Ca}(\text{H}_2\text{PO}_4)_2\cdot \text{H}_2\text{O}$

and the synthesized, desiccated and sieved insoluble calcium orthophosphate hydrates, by adding 1.09 % and 2.18 % of P_2O_5 as to calculate the proper ratio for gypsum. The tests showed that orthophosphate compounds had small influence on W/C and soundness of cement pastes. Soluble orthophosphates (H_3PO_4 , $Ca(H_2PO_4)_2 \cdot H_2O$) prolong the setting times of cement 2 - 3 times (Figure 5).

This coincides with the test results and recommendations thereof not to use acid phosphogypsum for the purpose of managing setting times of Portland cement [17,18]. The desiccated insoluble calcium orthophosphate hydrates (C/P = 2 - 4) have small influence on setting times of Portland cement paste.

To determine the influence of drying-out, insoluble calcium phosphates were synthesized in water amount

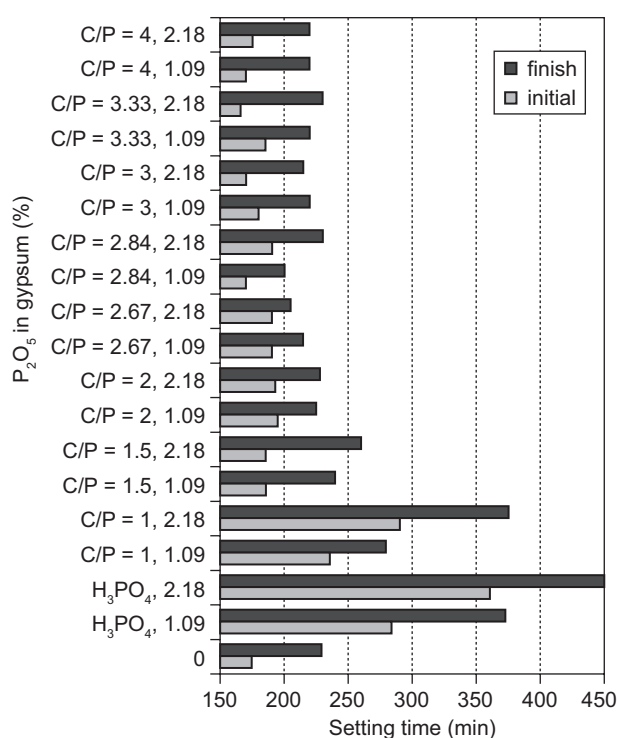


Figure 5. Influence of H_3PO_4 , $Ca(H_2PO_4)_2 \cdot H_2O$ and desiccated synthesized calcium orthophosphates hydrates (1.09 % and 2.18 % P_2O_5 in gypsum) on setting time of Portland cement CEM I 42.5R paste.

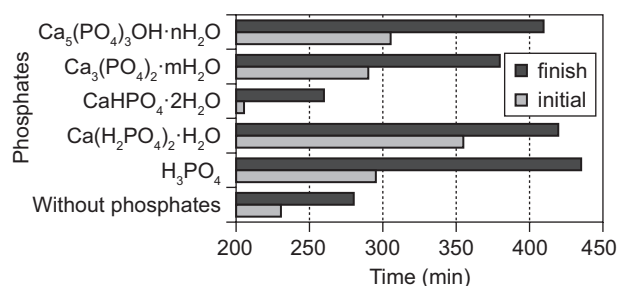


Figure 6. Influence of H_3PO_4 , $Ca(H_2PO_4)_2 \cdot H_2O$ and insoluble calcium phosphates hydrates suspensions (2.18 % P_2O_5 in gypsum) on setting time of CEM I 42.5R paste.

required to prepare the cement paste, and cement was poured into the prepared suspension. Cement paste setting times with soluble orthophosphates and synthesized insoluble calcium orthophosphate hydrates suspensions are presented in Figure 6.

The results show that only $CaHPO_4 \cdot 2H_2O$ suspension does not have any influence on the setting, but other insoluble calcium orthophosphates hydrates suspensions prolong setting times as soluble phosphates – about 2 - 3 time. This is explained by the fact that $CaHPO_4 \cdot 2H_2O$ are crystals while the latter are poorly crystallized colloids, which settle on the surface of cement particles thus not allowing hydration of this surface. These investigations show that insoluble calcium orthophosphates hydrates of hydroxyapatite group in cement must to be in dry state.

Influence of aqueous solution H_3PO_4 , dry $Ca(H_2PO_4)_2 \cdot H_2O$ and desiccated calcium orthophosphates hydrates on standard compressive strength of CEM I 42.5R is presented in Figure 7.

Soluble orthophosphates $\{H_3PO_4$ and $Ca(H_2PO_4)_2 \cdot H_2O\}$ considerably prolong hydration of cement. As a result, upon 2 days cement stone will have lower strength, but after 28 days of curing it has decreases slightly. Here we see the participation of phosphates, as a phosphate binder, in formation of cement stone. Standard compressive strength of cement has mostly decreased at adding calcium orthophosphate, on the XRD patterns thereof there are crystals $CaHPO_4 \cdot 2H_2O$ (C/P = 1.5 - 2.67). Desiccated calcium orthophosphates hydrates of hydroxyapatite group are stable in alkaline

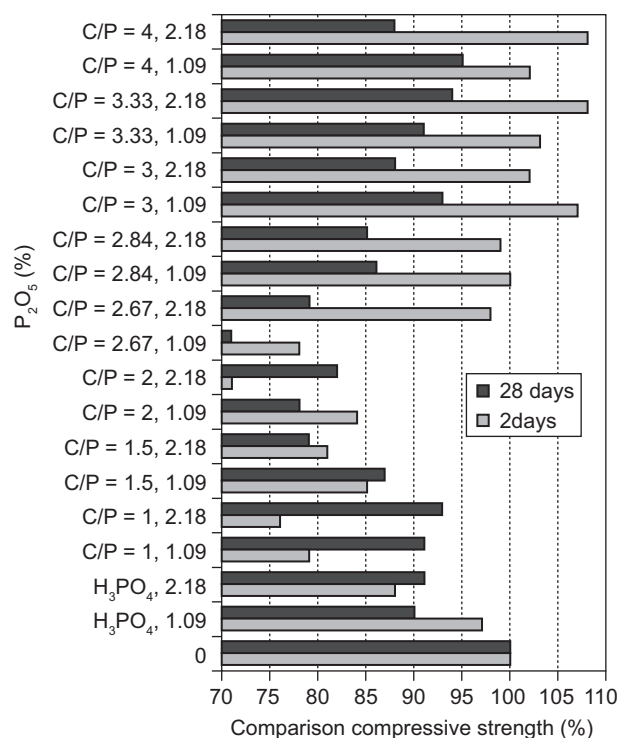


Figure 7. Influence of H_3PO_4 and dry calcium orthophosphates hydrates (1.09 % and 2.18 % P_2O_5 in gypsum) on standard compressive strength of CEM I 42.5R after 2 and 28 days of curing.

cement medium, do not change standard compressive strength of cement after 2 days of curing and reduce it up to 10 % after 28 days of curing. The results of testing the setting times and standard compressive strength of cement paste show that dried calcium orthophosphates hydrates of hydroxyapatite group have the least influence on these indices.

Formation and stability of calcium orthophosphates hydrates in the Portland cement pastes without stirring

Formation and stability of calcium orthophosphates in cement pastes were investigated according to the above methods measuring „ H_3PO_4 - H_2O -clinkers“ paste pH kinetics and considering XRD patterns of the hydrated products. Portland cement was replaced with clinker of the same cement due to identity of $CaHPO_4 \cdot 2H_2O$ and $CaSO_4 \cdot 2H_2O$ XRD patterns. The obtained data are presented in Figures 8 and 9.

Curves 2-8 in Figure 8 show that in the pastes with 6 - 20 g of clinker, medium pH stabilizes for a while at 8 - 9. Curve 3 in Figure 9 shows that under these conditions the by-product is formed, which is $CaHPO_4 \cdot 2H_2O$ crystals, i.e. colloidal x-ray amorphous calcium phosphate formed in the beginning of the reaction shields clinker particles, thus stopping their hydration. Time of shielding decreases from 40 days up to a few days with increasing amount of clinker in paste from 10 up to 20 g (curves 4-8 in Figure 8). The formed $CaHPO_4 \cdot 2H_2O$ crystals free clinker grain surface and can hydrate freely. This is demonstrated by sudden paste pH increase due to Portlandite, evolving during cement hydration, which reacts with $CaHPO_4 \cdot 2H_2O$ thus forming calcium orthophosphates hydrates of hydroxyapatite group

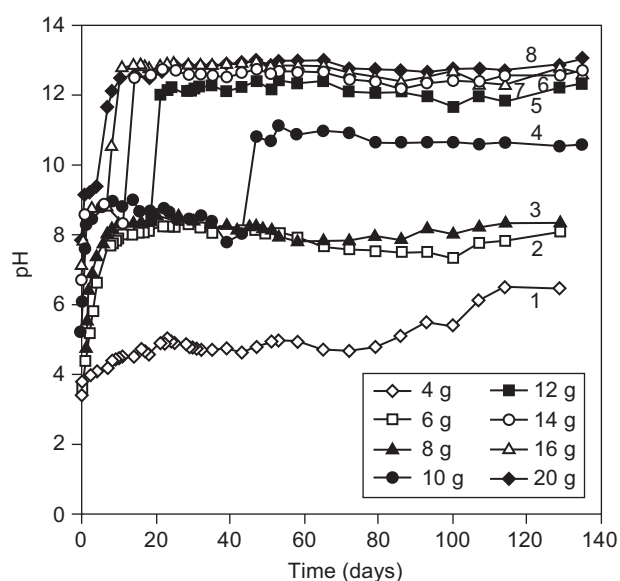


Figure 8. pH kinetics in the non-stirred pastes: H_3PO_4 (3.46 g P_2O_5) + 40 ml H_2O + (4, 6, 8, 10, 12, 14, 16, 20) g of Portland cement clinker.

(curve 4 in Figure 9.) or their mixtures with the excess of Portlandite (curve 5 in Figure 9). In the pastes with lime, such shielding occurs at pH = 4 - 4.5. Increase in medium pH of cement pastes is associated with the alkali in cement clinkers, which increase medium pH but do not change the course of formation of calcium orthophosphates hydrates of hydroxyapatite group: their formation takes place through the intermediate phase - $CaHPO_4 \cdot 2H_2O$.

The amount of portlandite evolving in the pastes with 4 - 8 g of cement is sufficient for binding soluble phosphates (3.46 g P_2O_5) only into $CaHPO_4 \cdot 2H_2O$ (curves 1, 2 in Figure 9.). SiO_2 gel is formed in the upper part of these pastes within the very first hours, i.e. H_3PO_4 solution destroys calcium silicates.

With the purpose of determining the duration of intermediate phase – transformation of $CaHPO_4 \cdot 2H_2O$ into calcium orthophosphates hydrates of hydroxyapatite group in the non-stirred Portland cement pulps, it was mixed with CEM I 42.5R. To achieve this aim, 5 g of $CaHPO_4 \cdot 2H_2O$ were mixed with (0.5, 1, 1.5, 2, 2.5, 3) g of CEM I 42.5 R and 40 ml of water. Medium pH was determined for the pulps stored in hermetically sealed dishes (Figure 10), and after 140 days of hydration - XRD patterns of desiccated products (Figure 11).

Curves 4, 5, 6 in Figure 10 shows that $CaHPO_4 \cdot 2H_2O$ is bound to calcium orthophosphates hydrates of hydroxyapatite group within 2 - 3 months: there stabilizes the characteristic medium pH = 9 - 12. This is confirmed by characteristic curves of XRD patterns (curves 2 and 3 in Figure 11). If the quantity of cement is smaller, $CaHPO_4 \cdot 2H_2O$ is bound into octa calcium phosphate within a month (curve 2 in Figure 10 and curve 1 in Figure 11).

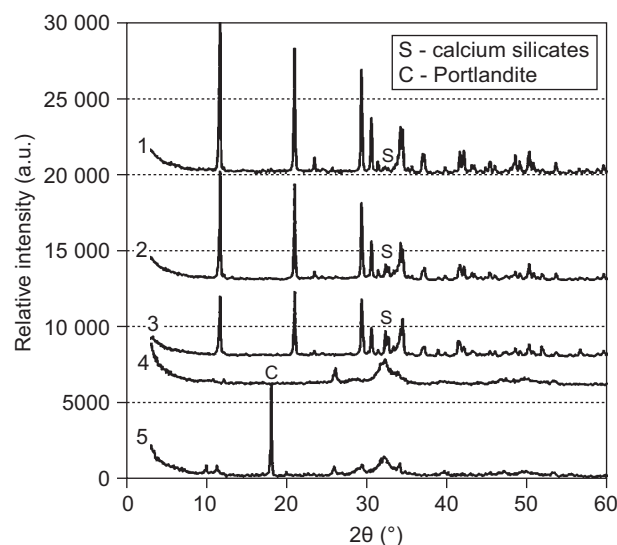


Figure 9. XRD patterns of the clinker reaction products of pastes from 40 ml of H_3PO_4 solution (3.46 g P_2O_5) with (4, 8, 10, 20) g of clinker after 140 days of hydration: curves 1, 2, 4 and 5 accordingly, curve 3 – H_3PO_4 solution with 12 g of clinker after 6 days of hydration.

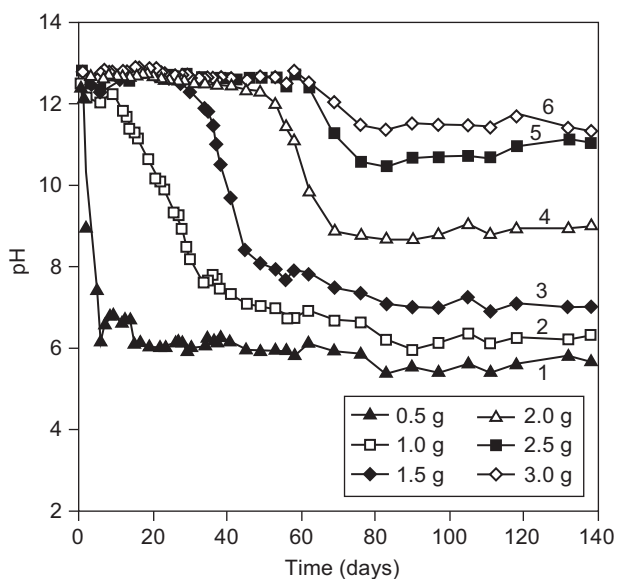


Figure 10. Kinetics pH of the pulps: 5 g $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ + (0.5, 1, 1.5, 2, 2.5, 3) g of CEM I 42.5 R + 40 ml H_2O .

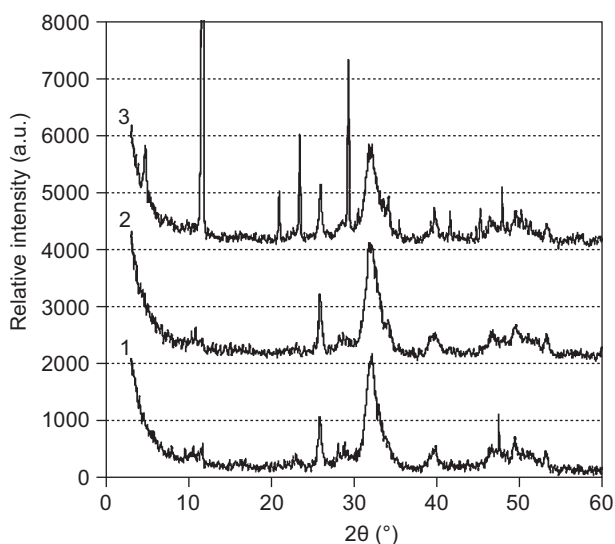


Figure 11. XRD patterns of reaction products of pulps from 5 g $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ + (1, 2, 3) g CEM I 42.5 R (curves 1, 2, 3 respectively) after 140 days hydration: 1 - $\text{Ca}_8(\text{HPO}_4)_4(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$; 2 - $\text{Ca}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$; 3 - $\text{Ca}_{10}(\text{PO}_4)_6 \cdot m\text{H}_2\text{O}$.

The said investigations allow to explain some results of the above tests. Mixture of soluble phosphate (H_3PO_4 or $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) nearly does not change the standard compressive strength of Portland cement after 28 days of curing, although the setting times increase 2 - 3 times. This is associated with the formation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ crystals and their participation in making of cement stone frame at the initial stage of cement curing stage. As curves in Figure 10 show, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ crystals disintegrate in alkaline cement medium within 2 - 3 months, i.e. one can predict that the formed cement stone frame will break down in the course of further cement hydration, so the cement strength will not only increase but, what is more,

can decrease. When $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ crystals are mixed into cement paste, their breaking down starts right from the very beginning due to the created alkaline medium. The cement stone strength decreases as these crystals break down.

CONCLUSIONS

All dry insoluble (molar ratio $\text{CaO}/\text{P}_2\text{O}_5 = 2 - 4$) calcium orthophosphates hydrates (1.09 % and 2.18 % P_2O_5 in gypsum) have little effect on W/C, soundness and setting times of Portland cement CEM I 42.5R paste.

Dry insoluble calcium orthophosphates hydrates $\{\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}, \text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$ and $\text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH}) \cdot 4\text{H}_2\text{O}\}$ which are formed in an acid medium (pH 4.2 - 5.9) have been destroyed in an alkaline medium of cement paste and reduce the standard compressive strength of cement up to 28 %.

Insoluble calcium orthophosphates hydrates of hydroxyapatite group are stable in alkaline medium. Their suspensions prolong setting times of Portland cement paste as soluble phosphates – 2 - 3 times. In dry state they reduce the standard compressive strength of cement up to 10 %.

Alkalis being in Portland cement increase pH of cement-soluble phosphate paste, but do not change the course of formation of insoluble calcium orthophosphates hydrates of hydroxyapatite group: it takes place through an intermediate phase - $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, whose transformation into apatite last for 2-3 months.

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