THE INFLUENCE OF ORTHOPHOSPHATES ON THE PROPERTIES OF PORTLAND CEMENT

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The article continues the research of input reduction of phosphogypsum preparation for the production of building materials. Desiccated apatite (2.18 % P_2O_5 in gypsum) makes the least changes in the properties of Portland cement: it prolongs the cement setting times and reduces the compressive strength about 10 %. The apatite formation in the pastes of soluble orthophosphate-cement occurs during the formation of X-ray amorphous colloidal calcium orthophosphate hydrate, which prolongs cement setting time 2 - 3 times; next crystallization of $CaHPO_4 \cdot 2H_2O$ is involved in the formation of cement stone; therefore, it does not affect the strength of CEM I 42.5R Portland cement after 28 days of curing; however, due to the decomposition of these crystals in the alkaline medium during the further hydration of cement and formation of apatite, the strength is reduced to 20 % after 2 months. Destruction additive of insoluble calcium orthophosphate hydrates (molar ratio $CaO/P_2O_5 = 2 - 3$) by lime and formation of apatite beginning after mixing cement with water and continue about 30 days; it reduces the strength of Portland cement to 27 % after 28 days of curing. After 3 months of cement hydration, the strength of Portland cement with a maximum (2.18 % P_2O_5 in gypsum) amount of additive of various orthophosphates level off and remains about 10 % less than control. Adding the apatite suspension to the cement of temperature 80 - 110°C increase the setting times up to 30 % and reduce the strength to 5 - 8 % as compared with the additive of desiccated apatite.

INTRODUCTION

Phosphogypsum is a by-product of the chemical reaction of sulfuric acid with phosphate rocks (apatite or phosphorite) to produce the phosphoric acid needed for fertilizer production. Phosphogypsum consists of 65 - 70 % calcium sulphate, 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, unreacted phosphate rock, alkali, organic matter, strontium and lanthanides (mostly cerium) sulphates and others. Depending on the production process of orthophosphoric acid, calcium sulphate in phosphogypsum can be in $CaSO_4 \cdot 2H_2O$, $CaSO_4 \cdot 0.5H_2O$ or $CaSO_4$ forms [1, 2]. The P_2O_5 and F impurities of phosphogypsum 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. Hydrofluoric acid and its salts contaminate an environment [3, 4]. 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

and Portland cement [3-6]. $CaHPO_4 \cdot 2H_2O$ had small influence, but with the present of $Ca(OH)_2$ it had great influence on the plaster properties [7-11]. In some places, the phosphate deposits are contaminated with radioactive materials; therefore, phosphogypsum may be radioactive [4]. Phosphogypsum in hemihydrate form, formed in Kola Peninsula and other non-radioactive deposits of apatite could become a competitive feedstock for a natural gypsum stone, if the input spent for impurity decontamination and desiccation of phisphogypsum would not exceed the preparation costs of gypsum stone. This way, the prepared phosphogypsum could primarily be used in the regulation of setting times of Portland cement [3, 4].

Untreated phosphogypsum can be used for trass cement but it does not fit for regulation of setting times of Portland cement [12]. 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 [13-15].

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 and separating of coarse and very fine particles. Up to 4 m^3 of water is necessary for 1 ton of phosphogypsum [3, 4, 16-19]. Phosphoric acid residues are eliminated by washing phosphogypsum with water, but soluble calcium phosphate is decomposed into less soluble calcium phosphate $CaHPO_4 \cdot 2H_2O$ and phosphoric acid. $CaHPO_4 \cdot 2H_2O$ 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 [2, 3]. Formed by washing calcium orthophosphate hydrate sequence: $CaHPO_4 \cdot 2H_2O \rightarrow$ $\rightarrow Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2 \cdot mH_2O$ [2]. 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 [23]. 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: $Ca(OH)_2$, $CaCO_3$, K_2CO_3, KOH, Portland cement, NH_4OH, fly ash and other industrial wastes [24-31]. 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 [1-5]. The humidity of phosphogypsum does not affect the costs if the production of gypsum binder is performed by processing the pulp of raw materials in autoclave [3]. The overall use of phosphogypsum in the world does not reach 15 % [3, 4].

Preparation of phosphogypsum neutralizing unwashed phosphogypsum in suspension of lime according to the method [32, 33] also requires gross expenditure associated with the accurate determination of impurities and precise execution of the neutralization process. The calcium orthophosphates hydrates of hydroxyapatite group, formed during the neutralisation, aggravates filtration of phosphogypsum pulp; therefore, more humidity remains in phosphogypsum cake, which increase the costs, necessary for the evaporation of humidity [35].

The formation and stability of calcium orthophosphates hydrates in the alkaline medium, as well as the influence on standard properties of Portland cement are examined [36]. It was found that dry calcium orthophosphates hydrates of hydroxyapatite group have the least influence on standard properties of Portland cement. The formation of $Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$, $Ca_9(HPO_4)$ $(PO_4)_5(OH) \cdot 4H_2O$, $Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}$ $(OH)_{2-(0<x<1)} \cdot$

$\cdot 3$-$4,5H_2O$, $Ca_3(PO_4)_2 \cdot nH_2O$ and calcium orthophosphates hydrates of hydroxyapatite group in the pastes of "Portland cement-soluble orthophosphate" occurs during the intermediate phase - $CaHPO_4 \cdot 2H_2O$. The transition of intermediate phase - $CaHPO_4 \cdot 2H_2O$ to calcium orthophosphates hydrates of hydroxyapatite group in the cement pastes lasts approximately 2 months [36].

The stability of hardened cement stone with other orthophosphate additives during the long-term hydration remains unexplored. A lot of energy is consumed in order to dry out the humidity of phosphogypsum; therefore, an opportunity to take advantage of the warmth of cement, emitting during its milling, is relevant to dry out the neutralized phosphogypsum.

The aim of this work is to investigate the stability of orthophosphates in cement paste during the long-term hydration and to determine the influence of milling temperature on the properties of Portland cement with the additive of apatite suspension.

EXPERIMENTAL

Materials

Portland cements CEM I 42.5R and CEM II/ A-L 42.5R of JSC "Akmenes cementas", Lithuania. Mineralogy, %, and standard properties of CEM I 42.5 R/CEM II/A-L 42.5R: C_3S – 63.3/53.2, C_2S – 8.2/8.3, C_3A – 4.2/4.0, C_4AF – 12.7/10.5, lime – 0.8/0.95, MgO – 3.8/3.4, $Na_2O_{ekv.}$ – 0.8/0.6, quartz – 0.6/1.0, calcite – 2.2/14.2, SO_3 – 2.9/2.7; W/C = 0.28/0.28, setting times, min.: initial – 170/180, finish – 230/260, compressive strength, N/mm^2: after 2 days – 23/22, after 28 days – 51/48, soundness – 2/1 mm.

Orthophosphoric acid and $Ca(H_2PO_4)_2 \cdot H_2O$ 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:
- mechanical mixer with ≤ 3000 rad/s;
- 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 Cu Kα 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.
- 5 l ceramic mill with ceramic balls;
- 50 l thermostat with 30 - 300 °C temperature.

Methods

Insoluble calcium orthophosphates hydrates {$Ca_4(PO_4)_2(OH)_2 \cdot xH_2O$ (molar ratio $CaO/P_2O_5 = C/P = 4$), $Ca_{10}(PO_4)_6(OH)_2 \cdot mH_2O$ ($C/P = 3.33$), $Ca_3(PO_4)_2 \cdot nH_2O$ ($C/P = 3.0$), $Ca_9(HPO_4)(PO_4)_5(OH) \cdot 4H_2O$ ($C/P = 2.84$), $Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$ ($C/P = 2.67$), $CaHPO_4 \cdot 2H_2O$ ($C/P = 2$)} were synthesized from CaO and H_3PO_4 solution according to the method [42]. In brief, 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 (medium pH until full dissolution of lime particles maintains as alkaline) during $25 - 30$ min. 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 and strength after 56 and 84 days hydration of Portland cement according to EN 196-1 and EN 196-3, the part of cement has been replaced with orthophosphates (2.18 % P_2O_5 in gypsum).

pH kinetics in orthophosphates-cement and orthophosphate-lime pastes (10 g insoluble calcium orthophosphate hydrate + 40 ml H_2O) 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.

In order to determine the influence of cement temperature, the cylinder of ceramic mill with ceramic balls was kept in the thermostat at the suitable temperature for 3 hours. Later 1.6 kg cement was filled into it and the cylinder was kept at the thermostat for half an hour. After the cylinder was removed from thermostat, the additive was filled into the cement, the cylinder was closed and the content was milled for 5 minutes. The prepared cement was removed from the cylinder and cooled down. Then its properties have been determined according to EN 196-1 and EN 196-3 standards. Phosphate cements properties are examined in detail

RESULTS AND DISCUSION

The previous investigations [36] showed that in the alkaline medium, the formation of stable calcium orthophosphates hydrates of hydroxyapatite group in the paste of $CaHPO_4 \cdot 2H_2O$-CEM I 42.5R continues for about 2 months. This has led to the prediction that after the standard time of curing (28 days), during the further hydration, the formed framework of cement stone will be destroyed; therefore, the cement strength will not increase, but rather decrease. In order to check this prediction, test samples have been formed with

orthophosphates additive (2.18 % P_2O_5 in gypsum) and the kinetics of their strength have been determined: after 28, 56 and 84 days of curing. Test results are provided in Figure 1.

The results provided in Figure 1 confirms the following prediction [36]. The apatite formation in the pastes of soluble orthophosphate-lime and soluble orthophosphate-cement occurs during the formation of X-ray amorphous colloidal calcium orthophosphate hydrate, which formation on the surface of cement and lime particles, slows down the hydration and prolongs cement setting time 2-3 times [32, 33, 36]; next crystallization of $CaHPO_4 \cdot 2H_2O$ is involved in the formation of cement stone, therefore, it does not affect the strength of CEM I 42.5R Portland cement after 28 days of curing (properties of phosphate cement are examined in detail [37-53]); however, due to the decomposition of these crystals in the alkaline medium during the further hydration of cement and formation of apatite, the strength is reduced to 20 % after 56 days. After 84 days of hydration, the strength of Portland cement with various orthophosphates level off and remains about 10 % less than the cement strength without these additives.
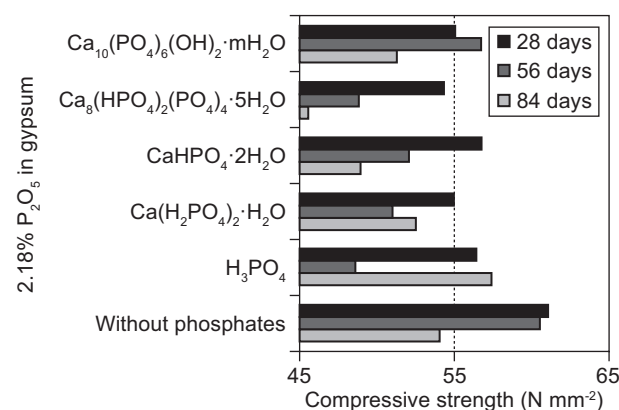

Figure 1. Compressive strength of CEM I 42.5R with orthophosphates (2.18 % P_2O_5 in gypsum) after 28, 56 and 84 days of curing.
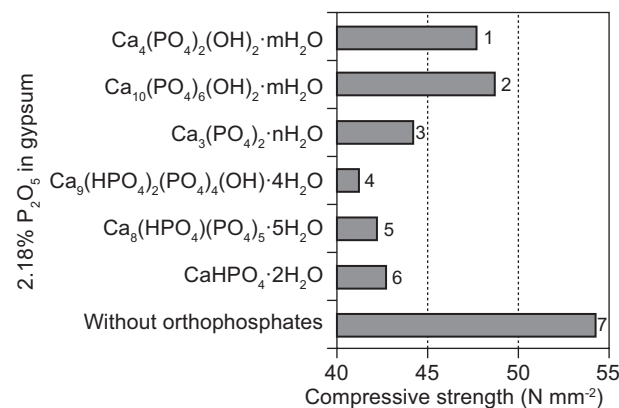

Figure 2. Influence of insoluble calcium orthophosphates hydrates (2.18 % P_2O_5 in gypsum) on standard compressive strength of Portland cement CEM I 42.5R.

The decrease of cement strength with insoluble calcium orthophosphates hydrates, formed in the acid medium ($CaHPO_4 \cdot 2H_2O$, $Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$ and $Ca_9(HPO_4)(PO_4)_5(OH) \cdot 4H_2O$), is obvious after 28 days of curing (see Figure 2).

Some uncertainties occur with $Ca_3(PO_4)_2 \cdot nH_2O$: the medium formation of this compound is slightly acidic (pH = 6.2 − 6.5), XRD patterns of $Ca_3(PO_4)_2 \times nH_2O$ is similar to the XRD patterns of calcium orthophosphates hydrates of hydroxyapatite group; however, its influence on the hardening of cement is different: $Ca_3(PO_4)_2 \times nH_2O$ decrease the strength of cement more than an apatite (columns 3 and 2, accordingly, in Figure 2). During the examination of causes of the decrease of cement strength

and the stability of insoluble orthophosphates hydrates during the long-term hydration, the kinetics of pH variation of non-mixable suspensions $Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$, $Ca_9(HPO_4)(PO_4)_5(OH) \cdot 4H_2O$ and $Ca_3(PO_4)_2 \cdot nH_2O$ with lime and cement. The stoichiometry of lime has been calculated for the formation of more basic calcium orthophosphates (see Figures 3, 4 and 5).

The curves of Figures 3-5 show that pH of medium in the suspensions stabilises after 20 − 25 days, i.e. in this period $Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$, $Ca_9(HPO_4)(PO_4)_5(OH) \cdot 4H_2O$, and $Ca_3(PO_4)_2 \cdot nH_2O$ bind the lime, transferring to calcium orthophosphates hydrates having higher basicity, destroying the structure of cement stone and reducing its strength after 28 days of curing. During the time of further hydration (up to 140 days), pH of medium does not change or slightly increase. It shows that the formation process of calcium orthophosphates hydrates in cement or lime paste has ended.

The attempts to take advantage of the warmth of cement, emitting during its milling in the mills, in order to dry out the calcium orthophosphates hydrates of hydroxyapatite group has failed. The apatite (2.18 % P_2O_5 in gypsum) suspension was filled in the cylinder of the mill with the heated cement that was heated to the necessary temperature. The water content in it was equal to the water content with 5 % of phosphogypsum with 25 % of humidity. After 5 minutes of milling, the cement is removed and cooled down. Then its properties are determined. Test results provided in Figure 6 are related to the influence of cement temperature on the setting times of cement with the paste of apatite, as well as compressive strength after 28 days of curing.

As can be seen from the results, apatite makes the least changes in the properties of Portland cement when it gets to the mill in the dried state. The humidity in apatite prolongs the setting times of cement up to 30 % and slightly decreases the strength (about 3 − 7 %) when
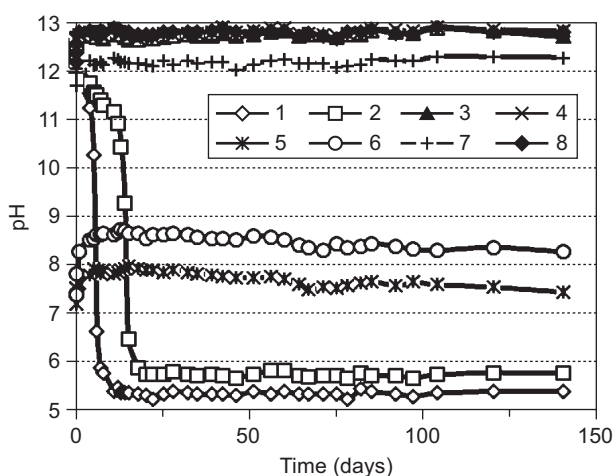

Figure 3. pH kinetics in the pastes of $Ca_8(HPO_4)_2(PO_4)_2 \cdot 5H_2O$ with lime (curves 1-4) and with CEM I 42.5R (curves 5-8). Stoichiometric components calculated for formation: $Ca_9(HPO_4)(PO_4)_4(OH) \cdot 4H_2O$ – curves 1 and 5, $Ca_3(PO_4)_2 \cdot nH_2O$ – curves 2 and 6, $Ca_{10}(PO_4)_6(OH)_2 \cdot mH_2O$ – curves 3 and 7, $Ca_4(PO_4)_2(OH)_2 \cdot xH_2O$ – curves 4 and 8.
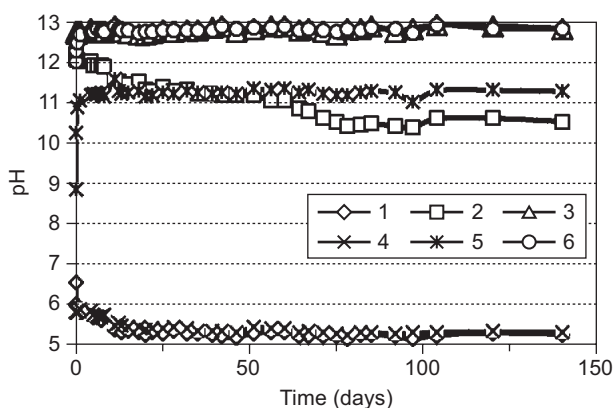
Figure 4. pH kinetics in the pastes of $Ca_9(HPO_4)(PO_4)_5(OH) \cdot 4H_2O$ with lime (curves 1-3) and with CEM I 42.5R (curves 4-6). Stoichiometric components calculated for formation: $Ca_3(PO_4)_2 \cdot nH_2O$ – curves 1 and 3, $Ca_{10}(PO_4)_6(OH)_2 \cdot mH_2O$ – curves 2 and 5, $Ca_4(PO_4)_2(OH)_2 \cdot xH_2O$ – curves 3 and 6.
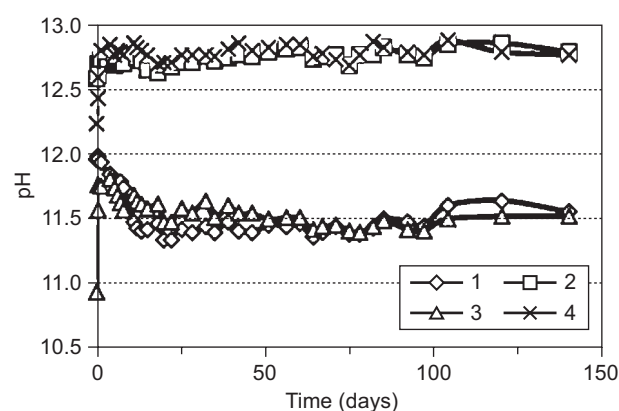
Figure 5. pH kinetics in the pastes of $Ca_9(HPO_4)(PO_4)_5(OH) \cdot 4H_2O$ with lime (curves 1-3) and with CEM I 42.5R (curves 4-6). Stoichiometric components calculated for formation: $Ca_3(PO_4)_2 \cdot nH_2O$ – curves 1 and 3, $Ca_{10}(PO_4)_6(OH)_2 \cdot mH_2O$ – curves 2 and 5, $Ca_4(PO_4)_2(OH)_2 \cdot xH_2O$ – curves 3 and 6.

the temperature in cement rises up to 110°C. When the temperature rises up to 120°C, the change in cement properties is related not only with the influence of apatite suspension, but also with gypsum dehydration [54].

The performed tests allow to select the most appropriate neutralizer and to determine the most appropriate processes. After the determination that non-mixable paste of soluble orthophosphates-lime or soluble orthophosphates-cement contains the lowest content of harmful compounds - the formation of apatite takes place during the intermediate phase - $CaHPO_4 \cdot 2H_2O$, it is advisable to use limestone for the formation of this
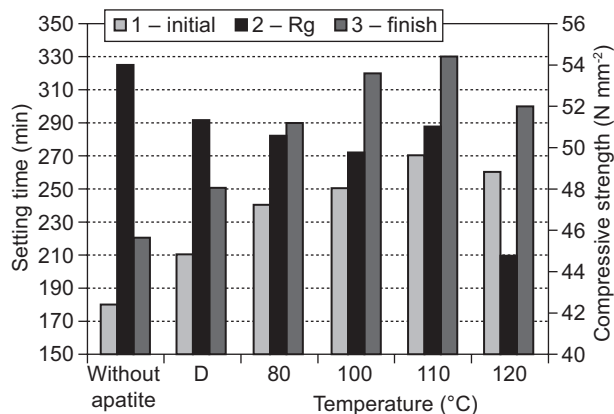

Figure 6. Influence temperature of cement on setting times (columns 1 and 2) and compressive strength after 28 days hydration (column 3) of Portland cement CEM I 42.5R with apatite suspension (2.18 % P_2O_5 in gypsum). D – desiccated apatite.
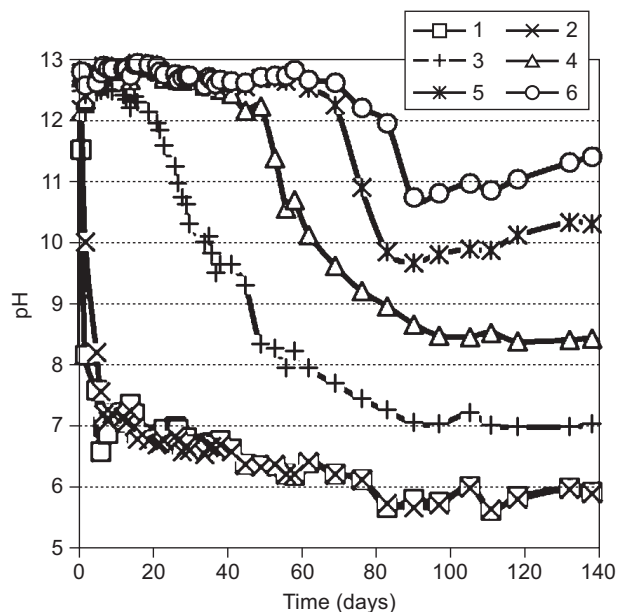

Figure 7. pH kinetics in the non-stirred suspensions: 5 g $CaHPO_4 \cdot 2H_2O$ + (0.5, 1, 1.5, 2, 2.5 and 3) g CEM II/AL 42.5 R + 40 ml H_2O (curves 1, 2, 3, 4, 5 and 6, accordingly).

compound. In order to neutralize the orthophosphate impurities in phosphogypsum it is rational to use Portland cement with limestone additive - CEM II/AL 42.5 (see Figure 7).

In this case, the pH in the soluble mixture of orthophosphate-cement remains alkaline. The costs of Portland cement CEM II/AL 42.5 R in the transfer of soluble orthophosphates of phosphogypsum to apatite in the mixture of phosphogypsum-cement would contain about 4 % in 1 % of soluble P_2O_5. Since the amount of soluble orthophosphate additives in phosphogypsum may slightly vary and the amount of neutralizer would be added according to the maximum amount of phosphates, then the amount of unused neutralizer in the prepared phosphogypsum may also slightly vary. The residues of non-reactive cement would be harmless. Such mixes must be densified, the cavities between the particles in the phosphogypsum-cement briquette should be filled with water [35] and maintained for approximately 2 − 3 months. Later they would be dried and supplied to the cement mills. At a maximum quantity of soluble orthophosphates (2.18 % P_2O_5 in gypsum), the usage of prepared phosphogypsum for the production of Portland cement would prolong its setting times and reduce the standard strength to 10 %.

CONCLUSIONS

Desiccated apatite (2.18 % P_2O_5 in gypsum) makes the least changes in the properties of Portland cement: it prolongs the cement setting times and reduces the compressive strength about 10 %.

The apatite formation in the pastes of soluble orthophosphate-cement occurs during the formation of X-ray amorphous colloidal calcium orthophosphate hydrate on the surface of cement particles, which prolongs cement setting time 2 − 3 times; next crystallization of $CaHPO_4 \cdot 2H_2O$ is involved in the formation of cement stone; therefore, it does not affect the strength of CEM I 42.5R Portland cement after 28 days of curing; however, due to the decomposition of these crystals in the alkaline medium during the further hydration of cement, the strength is reduced to 20 % after 2 months. Destruction of insoluble calcium orthophosphate hydrates (molar ratio $CaO/P_2O_5 = 2 − 3$) by lime and conversion to apatite bigining after mixing cement with water and continue about 30 days; it reduces the strength of Portland cement to 27 % after 28 days of curing.

After 3 months of hydration, the strength of Portland cement with a maximum (2.18 % P_2O_5 in gypsum) amount of additive of various orthophosphates level off and remains about 10 % less than control.

Adding the apatite suspension to the cement of temperature 80 − 110°C increase the setting times up to 30 % and reduce the strength to 5 - 8 % as compared with the additive of desiccated apatite.

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