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INFLUENCE OF FINE-GRINDED GLASS ADDITIVES ON THE INDUCTION AND POST-INDUCTION PERIODS OF PORTLAND CEMENT HARDENING

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Abstract. The investigation results of changes in cement grout observed during the induction and post-induction periods of hardening while adding fine-grinded glass additives are presented. It is assumed that glass introduction decreases pH of the system due to the chemical interaction with alkaline medium of the cement grout. The obtained results are important for the solving of the problem of glass wastes usage in the cement technology.

Keywords: Portland cement, fine-grinded glass, induction period, post-induction period.

1. Introduction

It was established in [1] that the initial, kinetic phase of the chemical reaction between water and cement vigorously proceeds during pre-induction period with great velocity of heat release. Depending on cement phase composition, the period of sharp decrease of heat release velocity fluently turns into the induction period of hardening.

According to the Double'a theory described in [2], the surface of cement grains is *in-situ* membrane allowing to pass Ca^{2+} and OH^- ions and does not allow to pass silica ions. As a result the induction period is characterized by the minimum velocity of heat release and fast growth of Ca^{2+} concentration. The induction period is over after the membrane is broken under osmotic pressure and silica ions transit into the solution forming calcium hydrosilicate (C–S–H phase). Therefore the post-induction period is characterized by the growth of heat release velocity which achieves maximum at the definite moment and then decreases for 40 h.

The above-mentioned process of heat release is connected with cement hydration in the medium with pH = 13–14 [3]. Thus it is assumed that any chemical process proceeding during hydration has to be accompanied by the change of pH level. To check this assumption we developed the special methodic of pH level control during induction and post-induction periods of Portland cement hardening and investigated the influence of alkaline-containing fine-grinded glass, which is irreversible wastes of human vital activity, on the process parameters.

2. Experimental

To measure the pH level we used HANNA H198127 pH-meter with automatic correction by temperature and accuracy of ± 0.1. The pH-meter construction and prepared sample allow to measure pH of cement grout till the end of standard setting. Electrode is completely submerged into the paste and the temperature is fixed near the electrode by digital thermometer mounted into pH-meter frame.

Table 1

Chemical compositions of container glass

Glass	Chemical composition, wt %							
	SiO_2	Al_2O_3	CaO	MgO	Na_2O+K_2O	Fe_2O_3	Cr_2O_3	SO_3
Brown	72.15	1.75	10.00	1.55	13.95	0.25	0.03	0.32
Green	71.80	1.80	10.97	1.00	13.35	0.45	0.25	0.38

Note: Fractional composition of glass is represented in [5].

To determine the parameters of standard setting the automatic variant of Vic device was used – Vicatronic (MATEST).

For the experiments we used CEM I 32.5 R cement (European standard PN-EN 197.1). The chemical compositions of glasses are given in Table 1.

3. Results and Discussion

It is known that at the first stage of hydration the gel-like calcium hydrosilicate [1] is formed, which sticks together cement grains. This phenomenon is called as "false" setting [2]. As a measure of setting the cohesion strength of calcium hydrosilicate (C–S–H) is used. It is determined by rupture work related to the square unit. Thus, while measuring the value of cohesion strength we control the change of system energy state till the end of setting and fix the system pH.

To determine the cohesion strength we developed a special methodology based on the tensile strength measurement of C–S–H-gel formed at the boundary solid body–gel. As a solid body we used polished surface of flat glass with glued sample of cement grout. When the load is increased we determine its maximum value at the rupture of gel layer that corresponds to its tensile strength and cohesion strength of C–S–H-gel. The additional special investigations confirm this fact.

According to the classical dependence of heat release velocity on hydration time, the induction period duration for CEN I 32.5 R cement is 70 min and post-induction period till the moment of heat release stopping – 2720 min [5].

During simultaneous determination of cement grout pH, parameters of standard setting, and cohesion strength we established the effect of fine-grinded glass on the hydration process and Portland cement hardening (Fig. 1).

The results show that within the range of induction period (90–160 min) the pH values are virtually not changed. However, during the post-induction period (160–340 min) the weak tendency to pH decreasing is observed. This fact may be caused by C–S–H phase formation. At the same time there is smooth increase of cohesion strength. The period from 290 to 300 min is of the greatest interest. First of all, it is in the middle of the period of sharp increase of standard setting velocity [6]. Secondly, the decrease of pH level is observed here. Thirdly, twofold increase of cohesion strength velocity is observed from this moment. All these simultaneous phenomena indicate the structural changes in this hardening period. The reason may be $Ca(OH)_2$ crystallization, the increase of gel layer thickness around cement grains and its compacting accompanied by the decrease of liquid phase [2] and changes in C–S–H-gel modification [1].

In the last decade a lot of works dedicated to the problem of fine-grinded powder of glass wastes usage as active additives to Portland cement appeared [7-9]. Taking into account the high content of alkaline oxides in the glass (13–15 wt %) as well as the presence of alkaline medium (pH = 13–14) in which the glass dissolves and transits to the solution by proportions corresponding to the glass chemical composition, we assume that alkaline component of the glass has the essential effect on the hardening of Portland cement. Fig. 2 represents the dependencies of pH, setting time and cohesion strength on the hydration time of cement grout with fine-grinded additives of brown and green glass in the amount of 0.5 wt %. Such amount was chosen because the maximum amount of calcium hydrosilicate is formed during the pre-induction period of cement hardening only at low content of glass (0.5–3 wt %) at the standard water:cement ratio of 0.5 [10].

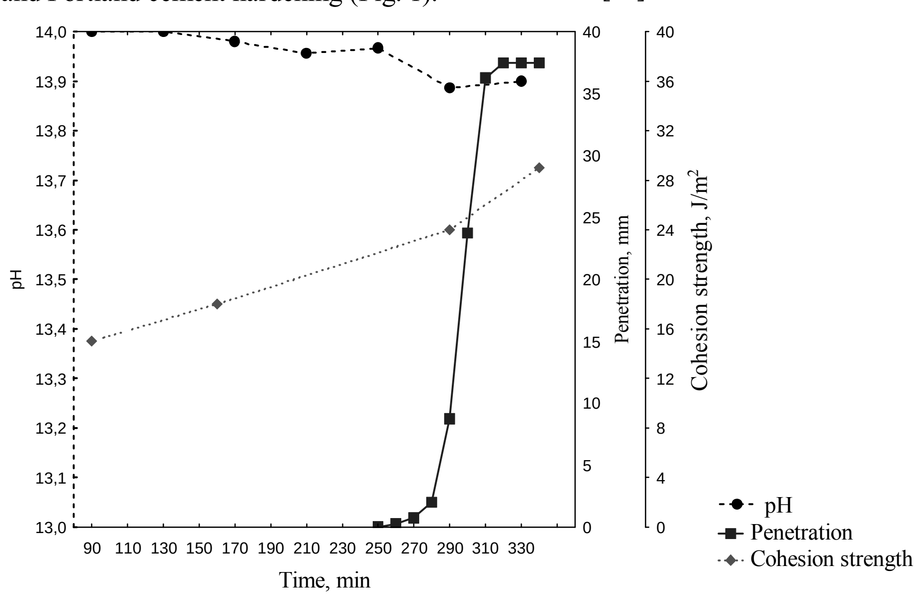
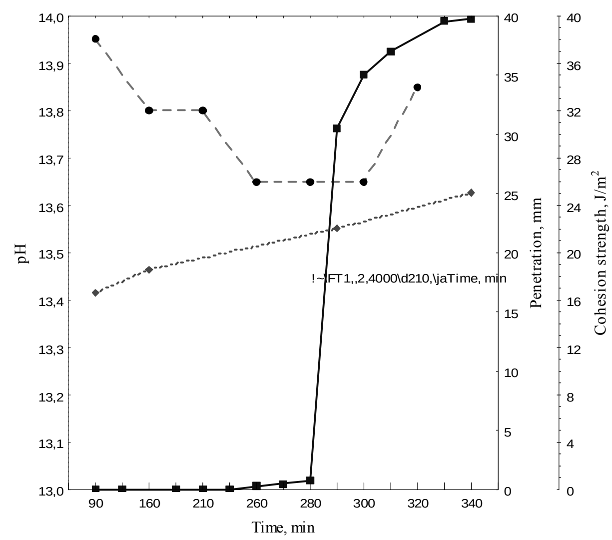
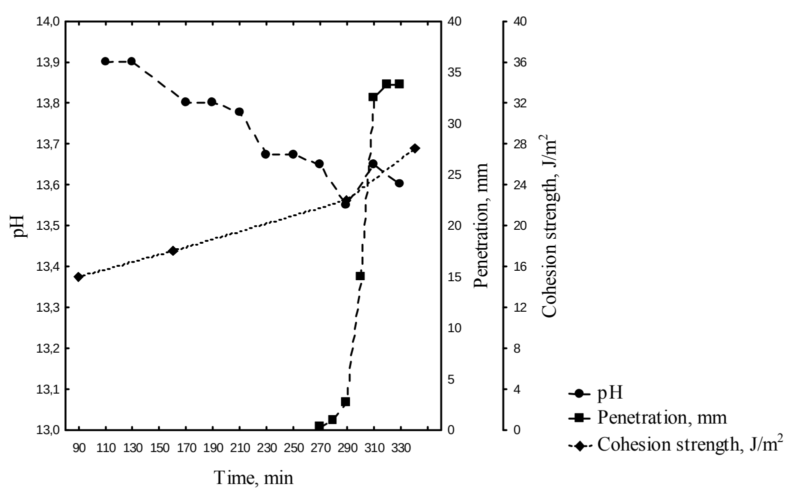


Fig. 1. Dependencies of pH, penetration and cohesion strength of C–S–H-gel on hydration time of cement without glass additives



a)



b)

Fig. 2. Dependencies of pH, penetration and cohesion strength of C–S–H-gel on hydration time with the addition of brown (a) and green (b) glass

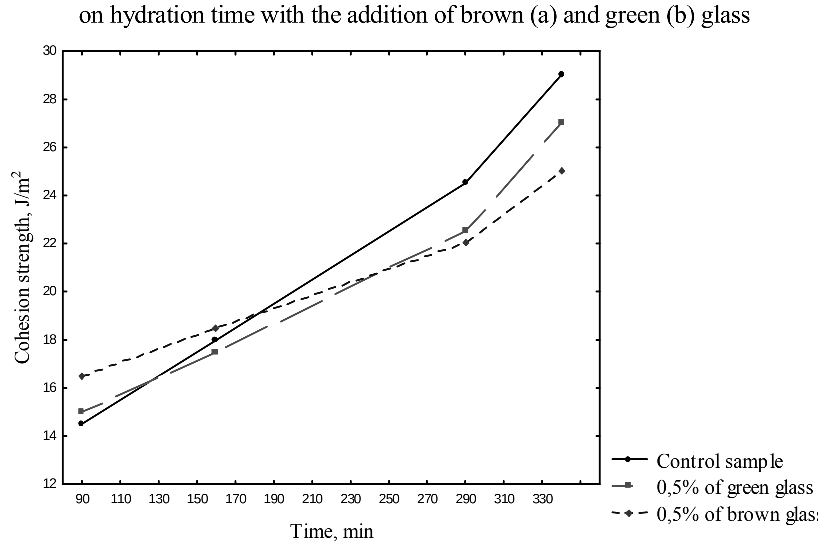


Fig. 3. Dependencies of cohesion strength of C–S–H-gel on hydration time of portland cement

The obtained results show that 0.5 % of fine-grinded glass decrease the pH value of cement grout starting from 90 min. For the control sample the pH decrease is typical starting from 160 min. In accordance with the modern hydration theory the decrease of Ca^{2+} concentration in the post-induction period and pH decrease, correspondingly, is connected with the formation of C–S–H-gel, that promotes the increase of system binding degree. However, the moment of cement setting with brown glass begins after 282 min, with green glass – after 296 min, and control sample – after 288 min. According to the European standard Pn-En 196-3 the determination accuracy should be no more than ± 5 min, therefore the exchange of 0.5 % of cement for the glass practically does not change the parameters of standard setting. We suppose that the decrease in pH of cement grout with glass is caused by the formation of alkaline metals hydrosilicates and is accompanied by the decrease of cohesion strength during the post-induction period (Fig. 3).

Thus, the dynamics of cement hydration process during first 340 min of the hardening may be presented as following. The beginning stage of Portland cement hydration is a kinetic phase of the chemical reaction between clinker and water followed by the formation of calcium hydrosilicate. During this period a sharp increase of cement grout pH is observed. During the induction period the velocity is limited by the formation of *in-situ* membranes over the cement grains from C–S–H-gel and pH of the system is not changed. At the same time during post-induction period the minor decrease of pH is observed connected with the formation of C–S–H-gel. The exchange of cement for fine-grinded glass leads to the pH decrease till the beginning of setting followed by the growth at the final stage of hardening. It should be also noted that the presence of glass decreases the cohesion strength during the post-induction period of hardening compared with the control sample (Fig. 3).

4. Conclusions

The analysis of experimental and literature data allows to suppose that the change of C–S–H-gel energy state before the beginning of setting may be connected with polycondensation and after the beginning of setting – with the change of its modification. Fine-grinded glass, regardless of its chemical composition, leads to the increase of total alkaline content of the system, which is accompanied with the pH decrease due to the formation of alkaline metalsilicates from glass. All the above decreases the cohesion strength of C–S–H-gel and binding degree of the system.

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РОЛЬ ДОДАТКІВ ДРІБНОМЕЛЕНОГО СКЛА В ІНДУКЦІЙНОМУ І ПОСТІНДУКЦІЙНОМУ ПЕРІОДАХ ТВЕРДІННЯ ПОРТЛАНДЦЕМЕНТУ

Анотація. *Приведено результати досліджень змін, які відбуваються в цементному тісті в індукційному та постіндукційному періодах твердіння при введенні додатків дрібномеленого скла. Зроблено припущення, що додаток скла сприяє зниженню pH системи внаслідок хімічної взаємодії з лужним середовищем цементного тіста. Отримані результати важливі для вирішення питання можливості використання скляних відходів в цементній технології.*

Ключові слова: *портландцемент, дрібномелене скло, індукційний та постіндукційний періоди твердіння.*