The effect of sodium aluminate on the properties of the composite cements

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Abstract. The effect of sodium aluminate activator on properties of the Portland-composite cement (clinker factor 65%) was studied and the results are being discussed. It is shown that the introduction of sodium aluminate (Na[Al(OH)₄]) leads to an increase in the water demand of cement and a decrease in its strength. The results showed that the sodium aluminate and polycarboxylate ether (PCE) admixtures ensure the production of higher strength cements. It has been found that the addition of Na[Al(OH)₄] – PCE significantly increases the compressive strength of cement mortar, particularly at 10–48 h of hydration. XRD and SEM measurements confirm that the hydration of composite cement with the addition of Na[Al(OH)₄] – PCE is greatly accelerated by the way of formation of intense lines ettringite. It has been shown that the introduction of a sodium aluminate into the cement mortars allows to accelerate hardening and increase early strength and using of composite cement will provide improved performance and suitability. The results have shown that alkaline accelerator and polycarboxylate were effective for decrease shrinkage of composite cements.

1. Introduction

Development of innovative building materials is one of the priority tasks of technological and economic development in the construction industry. In recent years, due to the deep specialization of building construction, the market needs for chemical additives have increased, which allow to provide the required level of properties of cement mortars and special-purpose concrete (high-strength, repaired, waterproofing, etc.) [1-3]. Modifiers that regulate the process of hardening of cement systems – accelerators of curing and hardening – should be singled out from various types of chemical functional additives. Traditional effective accelerators of hardening of Portland cement include calcium chloride and alkali metal salts [4, 5]. However, additives containing chlorine ions currently have limited use, as chlorine ion promotes corrosion of the reinforcement [6]. It should be also noted that a number of alkaline accelerators, under certain conditions, can cause the destruction of concrete due to their interaction with the active silica filler [7]. Besides, alkaline hardening accelerators often reduce the final strength of concrete. Therefore, the problem of finding and developing effective hardening accelerators is particularly actual.

Among the hardening accelerators for cements, additives of new generation based on active aluminium oxides can be singled out. The influence of sodium aluminate additive on the properties of
building materials has been investigated by various researchers [8, 9]. These alkaline accelerators are important chemical additives for shotcrete concrete, which allow to shorten curing time from hours to minutes. The mechanism of sodium aluminate action in the cement system is the rapid formation of the hydration product of calcium hydroaluminate (C-A-H), which after some time recrystallizes into ettringite [10, 11]. It was established that concretes made with the addition of 3–5 mass. % sodium aluminate have increased resistance to water. However, there is a decrease in the strength of concretes and mortars. At the same time, the introduction of a sodium aluminate accelerator greatly reduces the water separation in mortars and concrete mixes and prevents corrosion of the reinforcement. The introduction of an increased amount of aluminate component in the composition of cement leads to increase in the water demand of the binder [8, 11]. Such technological features can be used for systems requiring increased W/C ratio in particular in the composition of repair materials, as well as for cement mortars destined for transportation, pouring and pumping. At the same time, such materials should be characterized by water resistance, which allows the frost resistance of concrete and mortars. Therefore, in order to reduce the water consumption of the mixtures and achieve their high fluidity, it is advisable to use polycarboxylate type superplasticizers in combination with alkaline accelerators based on sodium aluminate [12]. On the other hand, the impact of aggressive environment can lead to the rapid destruction of building structures, so it is advisable to develop concretes and repair mortars using composite cements with a high content of mineral additives and fillers [13-15]. It is necessary to study alkaline accelerators based on sodium aluminate to achieve high technological and technical effects in obtaining non-shrinking concretes and mortars with high operational properties for rapid performance of reparation and restoration works.

2. Materials and methods
The Portland-composite cement CEM II/B-M (P-S-L) 32.5 R JSC "Ivano-Frankivsk Cement" (Manufacturer – JSC "Ivano-Frankivsk Cement", Ukraine) was used in experiments. The contents of the main clinker phases were as follows, mass. %: C₃S = 62.92; C₃S = 12.25; C₃A – 7.10; C₄AF – 11.64. Ground granulated blast furnace slag (S) and zeolite tuff (P) were used as SCMs. Limestone powder with 95 mass. % CaCO₃ was used as micro-filler.

According to the data on particle size distribution of the Portland-composite cement used in the experiments, fractions Ø1, Ø5, Ø10 and Ø20 μm constituted 5.14, 19.23 and 30.61%, respectively, and the grain sizes D10, D50 and D90 corresponded to 2.18, 21.0, and 65.3 μm. Fine particles with a size of less than 5 μm determine a specific surface area of the cements used in the experiments, although their contents are less than 20 % by volume. Physical and mechanical properties of the Portland-composite cement used in the study are given in table 1.

| Property                                    | Test results |
|---------------------------------------------|--------------|
| Fineness (specific surface by Blaine), cm²/g | 3920         |
| Water demand, %                            | 29.5         |
| Initial setting time, min                   | 140          |
| Workability (flow value), mm                | 180          |
| Bleeding, %                                 | 21.5         |
| Compressive strength (EN 196-1), MPa, after |              |
| 2 days                                      | 17.2         |
| 7 days                                      | 27.8         |
| 28 days                                     | 36.4         |
| Flexural strength (EN 196-1), MPa, after    |              |
| 2 days                                      | 3.6          |
| 7 days                                      | 6.7          |
| 28 days                                     | 7.2          |

Sodium tetrahydroxoaluminate Na[Al(OH)₄] (SA) (density of 1.34 g/cm³) was used to accelerate the hydration process of cement in the early stages. MasterGlenium ACE 430 (BASF) based on modified polycarboxylic ether (PCE) was used as a superplasticizer.
The grain size of particles was measured by laser granulometry Mastersizer 3000. Hydration processes of the cements were examined by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). Compressive strengths of the cements under study were determined on mortar prisms (40 x 40 x 160 mm) as prescribed in EN 196-1. Workability of fresh mortars (consistency measured on a flow table) was measured as per EN 1015-3. The cement mortar was adjusted to obtain a constant workability of approximately 113...115 mm (flow). The linear shrinkage of the cement mortar was determined using sample prisms 40x40x160 mm.

3. Results of investigation

The effect of sodium aluminate supplementation on the curing time of Portland-composite cement was investigated. It was established that initial setting time is 160 min for CEM II/B-M (P-S-L) 32.5 R, water demand – 29.5%. The initial setting time is accelerated for 50–60 min by the introduction of 1.0–2.0 mass. % alkaline activator SA, with an increase in water demanding of cement paste to 31.6%. Figure 1 shows that the introduction of an alkaline accelerator of hardening SA leads to an increase in binder water demand and a decrease in strength at all hardening times.

![Figure 1. Compressive strengths of the paste based on cement CEM II/B-M (S-P-L) 32.5 R with the additives Na[Al(OH)]₄.](image)

The zeolite-containing Portland-composite cement CEM II/B-M are known to have the increased water demand and, as a result, the lower workability. It is also evident from the results of studies that the introduction of Na[Al(OH)]₄ additive leads to an increase in the water consumption of cement and a decrease in its strength. For this reason, they require superplasticizers to be added. In the current study, the superplasticizer PCE was used. The effect of the PCE taken alone or in combination with Na[Al(OH)]₄ on hydration and hardening processes taking place in the cements under study was studied as well.

Compressive strength of the mortars was determined at the age of 10 and 24 hours, 2, 7 and 28 days. The obtained results are presented in figure 2. The cements under study with 1.5% Na[Al(OH)]₄ by mass (W/C = 0.50, workability of 182 mm (flow)) are characterized by the accelerated early strength gain. The complex additive (1.0 % PCE by mass + 1.5 % Na[Al(OH)]₄ by mass) was found to reduce the W/C value to 0.45 at flow = 180 mm, while at the age of 24 hours the compressive strength was by 3.2 times higher (13.4 MPa), at the age of 2 days – by 2.2 times higher (31.5 MPa), at the age of 7 days – by 1.56 times higher (41.7 MPa), at the standard age of 28 days – by 1.45 times higher (49.8 MPa) (figure 2). The strength of Portland-composite cement with the complex additive is 58.7 MPa after 90 days of hardening. Thus, the Portland-composite cement under study with the complex
additive (PCE + Na[Al(OH)]₄) corresponds to 42.5 Class in strength and is characterized by high early strength (early strength at 2 days ≥ 20.0 MPa, as per EN 197-1 for CEM II/B-M 42.5 R). The flexural strength values were higher, too.

Figure 2. Compressive strengths of the mortars based on CEM II/B-M (S-P-L) 32.5 R with the additives: Na[Al(OH)]₄ and PCE + Na[Al(OH)]₄ (flow = 178...182 mm).

The highest hydration temperature (T = 75 °C) is reached after 700 minutes for Portland-composite cement. The introduction of the aluminum accelerator and the PCE leads to a 300-min acceleration of hydration and a decrease in temperature by 15 °C. The addition of Na[Al(OH)]₄ increases the concentration of Na⁺ in the liquid phase of the Portland-composite cement paste. As a result, the pH of the solution increases from 12.8 to 13.2. According to the XRD, of the lines of ettringite high intensity (d/n=0.973; 0.561 nm) and calcium hydroxide (d/n=0.493; 0.263 nm) are identified on diffractograms of the CEM II/B-M cement paste the Na[Al(OH)]₄ – PCE after 1 day of curing. The ettringite crystals in the “cement-accelerator” system are thin and fibrous (figure 3). This morphology is explained by an increased amount of aluminate due to the addition of an accelerator. It should be noted that intensive reflexes of ettringite have been established during the study of the Ca(OH)₂ – Na[Al(OH)]₄ – CaSO₄·2H₂O system. This formation determines the possibility of obtaining non shrinkage concretes and mortar, as well as the rapid performance of repair and restoration works.

The influence of aluminum-containing additive and polycarboxylate superplasticizer of PCE on the properties of the cement mortar (flow = 113...115 mm) was investigated due to plan of two-factor three-level experiment. The concentration of the sodium aluminate Na[Al(OH)]₄ (X1) was used 0; 1.5; 3.0 mass. %, that of PCE (X2) was 0; 1.0; 2.0 mass. %. Isoparameter lines of influence of Na[Al(OH)]₄ and PCE concentration on the 24 hours compressive strength in cement mortar is shown in Figure 4. From this diagram, the optimal balance between modifier PCE and accelerator Na[Al(OH)]₄ that realize the 24 hours compressive strength 16.7 MPa is Na[Al(OH)]₄ – 1.5 mass. % and PCE – 1.2 mass. %. After 28 and 90 days, the strength of modified cement mortar was 56.2 and 68.9 MPa, respectively.
Figure 3. SEM images of the Portland-composite cement CEM II/B-M (S-P-L) 32.5 R paste with the Na[Al(OH)$_4$] – PCE at an age of 1 day with various magnification.

Figure 4. The isoperimetric lines of the 24 hours compressive strength of the cement mortar.

The effect of alkaline activators of hardening on the linear shrinkage of cement mortar based on CEM II/B-M (P-S-L) 32.5 R was investigated. It is shown (figure 5) that shrinkage for cement mortar based on CEM II/B-M (P-S-L) 32.5 R the after 2 and 20 days are 0.21 and 0.62 mm/m, respectively. The shrinkage is reduced to 0.06 and 0.27 mm/m respectively with the introduction of additives in 1.5 mass % Na[Al(OH)$_4$] and 1.0 mass. % PCE.

The alkaline addition of sodium aluminate reduces water separation in concrete mixtures and mortars and does not cause corrosion of metal reinforcement due to increased pH. Modified concretes and mortars with the alkaline addition of sodium aluminate can be used in carrying out new construction, reconstruction and restoration of existing buildings and structures, sealing of technical openings, plugging of seams, special-purpose working.
4. Conclusion
It is established that introduction of aluminium-containing alkaline activator in the Portland-composite cement CEM II/B-M (P-S-L) 32.5 R leads to the acceleration of curing time, increase in water demand and decrease in strength. The strength of CEM II/B-M with Na[Al(OH)₄] – PCE supplements at an age of 1 day has increased by 3.2 time, at the age of 28 days – by 1.45 times higher. The optimal balance between modifier PCE and sodium aluminate that realize the 1 day, 28 and 90 days compressive strength 16.7, 56.2 and 68.9 MPa are Na[Al(OH)₄] – 1.5 mass. % and PCE – 1.2 mass. %. The linear shrinkage of cement mortar with Na[Al(OH)₄] – PCE supplements at an age of 2 and 90 days have been decreased by 4.5 and 2.2 times, than cement mortar without additives. It is established that sodium aluminate creates the possibility of obtaining mortar for shotcrete, as well as quick performance of repair and restoration works.

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