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Communication

Influence of sodium silicate amount on the setting time and EXO temperature of a complex binder consisting of high-aluminate cement, liquid glass and metallurgical slag

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Abstract

The influence of sodium silicate amount on the setting time and EXO temperature of a complex binder (CB) consisting of high-aluminate cement (HAC), liquid glass and metallurgical slag (MS) has been investigated. Two maximums were observed on exothermal curves during the hydration process of CB, in which sodium silicate quantity was >4%. The first maximum of exothermic temperature occurred due to the reaction proceeding between sodium silicate and the slag. The second maximum of the exothermal effect was observed after the final set in the already hardened CB, and it was accompanied by the hydration of HAC, the degree of which depended on the sodium silicate amount in CB.

Keywords: Calcium aluminate cement; Liquid glass; Hydration

1. Introduction

The use of industrial wastes (i.e., different slags, fly ash, silica fume, etc.) for concrete makes it possible not only to improve major characteristics of cement and concrete but also to solve some environmental problems as well. For example, slag alkaline cements [1], as well as cements with SiO_2 powder [2,3], are widely used. Sometimes, to obtain concrete with the required properties, a combination of binding materials is used, such as Portland cement and aluminate cement [4], aluminate cement, liquid glass and metallurgical slag (MS) [5], etc. Such heterogeneous materials are referred to as complex binders (CB).

In a mix consisting of sodium liquid glass and MS, which is mainly made of dicalcium silicate (γ-C_2S), the latter solidifies liquid glass under normal conditions without removing water from it. Hardening may be expressed by the following reaction [6]:

$$Na_2O \cdot nSiO_2 + 2CaO \cdot SiO_2 + H_2O \rightarrow CaO \cdot mSiO_2aq + SiO_2aq + (Ca, Na_2)O \cdot SiO_2aq \quad (1)$$

In this case, the final products are silicon oxide gel, calcium and sodium–calcium hydrosilicates, generating heat in their formation [7,8]. The setting time of this composition is 20–50 min [9].

Even a small amount of sodium liquid glass (0.03% up to 1%) considerably retards the hydration of aluminate cement [2,10]. It has been determined [11] that the increase of the amount of sodium silicate in liquid glass up to 4% results in the mix of aluminate cement and liquid glass which, at 20 °C, does not set and harden during 28 days when hermetically sealed.

The present investigation is aimed at determining the influence of sodium silicate amount on the setting time and EXO temperature of CB consisting of high-aluminate cement (HAC), liquid glass and MS, which could help to better understand the peculiarities of its hardening process.

2. Experimental

2.1. The materials used

The materials used in the investigation included 3.3 module (SiO_2/Na_2O) sodium liquid glass (its density being changed by diluting with water); HAC produced by Gorka Enterprise, Trzebinia, Poland; MS waste from Cheliabinsk Electrometallurgic Plant, Russia (Table 1). CB, with the ratio of slag-to-HAC being approximately 1:3, has been investigated. The density of the liquid glass ranged from

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Table 1
Properties of HAC and slag

Name of material	HAC	MS
Surface area, m^2/kg	420	250
Bulk density, kg/m^3	1100	990
Chemical composition (wt.%)		
Al_2O_3	70.5	4.33
CaO	28.7	54.3
SiO_2	0.35	29.6
Fe_2O_3	0.1	1.34
TiO_2	0.05	–
MgO	–	6.7
Cr_2O_3	–	1.4

1025 to 1380 kg/m^3, while its amount was taken in such a way that the ratio of water-to-MS + HAC in it would make about 0.3 (Table 2).

2.2. Methods

The internal EXO temperature (exothermic effect temperature) of the binder paste was determined by the Alcoa Industrial Chemicals Europe method [12]. The binder paste was prepared by the mechanical mixing of materials (2 min) and casting them in the moulds under slight vibration (10 s). The cast sample weighed 1.5 kg, and the mould with the binder paste was put into an insulating box. The temperature of the developing exothermic heat was recorded by a T-type thermocouple immersed into a binder paste.

A standard testing technique based on using the Vicat device was applied to determine the setting time of the binder mixtures. The amounts of sodium silicate ($\%Na_2O+\%SiO_2$) in liquid glass were calculated using the empirical formulas [13].

3. Results and discussion

The results of final set of CB are given in Table 3. It can be found that the final setting time of the B1 composition has been determined as being about 13.5 h, while B2–B6 was only 23–32 min. When the sodium silicate amount in the B1 composition is very small (< 1%) the reaction between the latter and MS is probably very weak and does not have a considerable effect on the final setting time of CB. The final setting time of B2–B6 binders is very short, and it can be seen that the larger the amount of sodium silicate (from 4.4% up to 11.4%), the longer is the setting time of a composition.

Table 2
Compositions of CB and density of liquid glass

Number	Composition, wt.%				Liquid glass density, kg/m^3
	MS	HAC	Liquid glass components		
			Sodium silicate	Water	
B1	19.1	57.2	0.7	23.0	1025
B2	18.4	55.6	4.4	21.6	1150
B3	18.2	54.5	5.9	21.4	1200
B4	17.9	53.8	7.4	20.9	1250
B5	17.5	52.5	9.9	20.1	1330
B6	17.2	51.8	11.4	19.6	1380

Table 3
Final setting time of CB, in minutes

Composition number					
B1	B2	B3	B4	B5	B6
810	24	23	27	32	32

The study of an exothermic effect has shown that the temperature curves may vary in two ways, depending on the amount of sodium silicate in the mix. When the latter is very small (B1 composition), the temperature of the specimen rises only by 2 °C (Fig. 1) in the first hours of the hardening and starts rising sharply due to an exothermic reaction, only in 13 h. The maximum of EXO temperature (110 °C) was reached in 15 h, while in pure HAC paste with W/C equal to 0.3, the maximum EXO temperature was reached in about 6 h [14]. It can be seen that in B1 composition, sodium silicate acts as a retarder of HAC hydration.

In B2–B6 compositions, exothermic temperature variations (Fig. 2) are different from that of the B1 composition. Two distinctive stages of temperature variation can be observed in this case. At the first stage, the specimen temperature has risen by 3.5–7 °C due to the reaction proceeding between the sodium silicate and the slag [Eq. (1)]. During the reaction, the temperature reaches its maximum value in 20–60 min, being not changed within the interval of 3.5–5 h. It has been observed that the value of the maximum temperature (as well as the time of binder hardening) depends on the amount of sodium silicate in the binder. The larger the amount of sodium silicate, the higher the maximum exothermic temperature reached at the first stage.

The second stage of the temperature rise begins 4–5 h, when the temperature reaches 44–77 °C. This increase of temperature is caused by the HAC hydration proceeding in a hardened binder. It has been observed that the EXO temperature at the second stage achieves the extremum

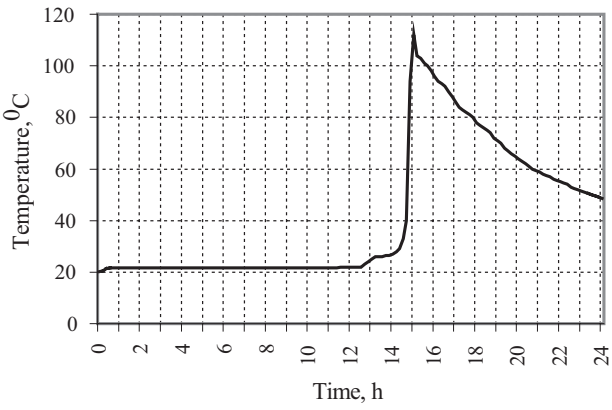

Fig. 1. EXO temperature as a function of time for the B1 binder.

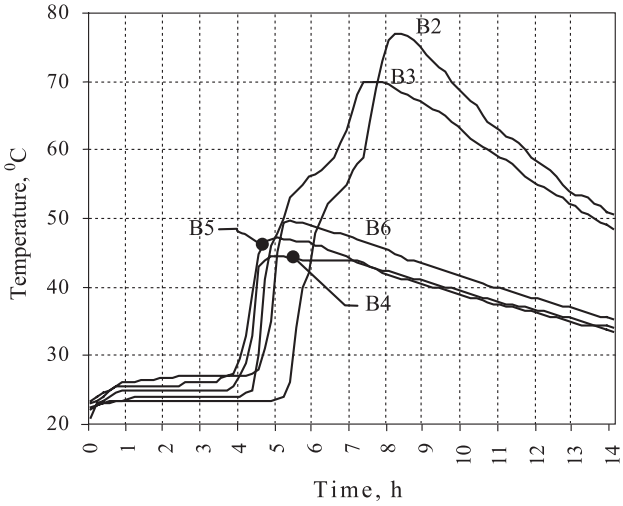

Fig. 2. EXO temperature as a function of time for the B2–B6 binders.

when the density of liquid glass is about 1250–1330 kg/m^3 (sodium silicate amount: 7.4–9.9%). The specific type of CB hardening may be accounted for the particular effect of the slag. During the reaction between sodium silicate and the slag, the latter reduces the amount of sodium silicate in a composition, as well as releases a certain amount of water from the liquid glass. In addition, the silicate gel [Eq. (1)] containing a large amount of water is shrinking and expelling water from its mass when the temperature rises [8]. It is probably because of these processes that the molecules of free water reach the surface of the cement particles, taking part in the hydration proceeding in the hardened binder.

4. Conclusion

A CB consisting of HAC, liquid glass (with the amount of sodium silicate >4%) and MS has two maximums on exothermal curves referring to its hydration. At the first stage of 3–4 h, a reaction of γ-C_2S of the slag with sodium silicate took place, and the exothermal effect was very weak. The second maximum of exothermal effect was observed after the final set in the already hardened CB in 5–7 h, and it was accompanied by the hydration of HAC. The first and the second exothermal effects largely depend on the sodium silicate amount.

References

[1] V.D. Glukhovsky, Concrete in past, present and in future, Proceedings of III-rd Conference on Alkaline Cements, Concrete and its Constructions, Kiev Civil Engineering Institute Publish, Kiev, 1989, pp. 7–14.
[2] B. Sanberg, T. Mosberg, S. Kristiansand, Use of microsilica in binder systems for ultra low cement castables and basic, Adv. Refract. Technol. 4 (1996) 245–258.
[3] J. Larbi, A. Fraay, J. Bijen, The chemistry of the pore fluid of silica fume-blended cement systems, Cem. Concr. Res. 20 (4) (1990) 506–516.
[4] P. Garces, E.G. Alcolel, C.G. Andreu, Hydration characteristics of high aluminate cement/Portland Cement Mixtures, ZKG Int. 11 (1998) 646–649.
[5] S. Goberis, V. Antonovich, R. Maciulaitis, A refractory binder based on liquid glass and aluminate cement, Refract. Ind. Ceram. 43 (5–6) (2002) 188–192.
[6] V. Korneev, V. Danilov, Production and Application of Liquid Glass, Stroiizdat Publish, Leningrad, 1991.
[7] V. Koksharev, A. Urzenko, Heat development in alkali–slag cements, Proceedings of III-rd Conference on Alkaline Cements, Concrete and its Constructions, Kiev Civil Engineering Institute Publish, Kiev, 1989, pp. 229–230.
[8] D. Krizan, B. Zivanovic, Effects of dosage and modulus of water glass on early hydration of alkali–slag cements, Cem. Concr. Res. 32 (2002) 1181–1188.
[9] P. Borsuk, A. Liass, Liquid Self Hardening Mixes, Mashinostroenie Publish, Moscow, 1979.
[10] J. Ding, Y. Fu, J. Beaudoin, Study of hydration mechanisms in the high aluminate cement–sodium silicate system, Cem. Concr. Res. 26 (5) (1996) 799–804.
[11] V. Antonovich, S. Goberis, A. Shpokauskas, The reaction character between aluminous cement and liquid glass, Chem. Technol. 3 (12) (1999) 55–58.
[12] ALCOA calcium aluminate cement test methods brochure, Revision 5, 08/99, Available Through Alcoa Industrial Chemicals Frankfurt.
[13] R.S. Afanasjev, S.D. Tepliakov, Correlation between composition and density of sodium liquid glass, Foundry Ind. 4 (1986) 12–14.
[14] T. Chotard, N. Gimet–Breat, A. Smith, D. Fargeot, J.P. Bonnet, G. Gault, Application of ultrasonic testing to describe the hydration of calcium aluminate cement at the early age, Cem. Concr. Res. 31 (2001) 405–412.