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Effect of Barium Hydrosilicates on the Early Hydration Rate of Portland Cement

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Abstract—We have studied the effect of a barium hydrosilicate-based modifier on the phase composition of Portland cement hydration products. The results demonstrate that the addition of a modifier containing barium hydrosilicates, silicic acid, and calcium carbonate makes it possible to reduce the nucleation rate of crystals of new phases during the induction period of the hydration process, increase alite ($3CaO \cdot SiO_2$) hydration, and reduce the rate of aluminate phase ($3CaO \cdot Al_2O_3$) hydration. The use of such a modifier increases the degree of cement hydration and the amount of calcium hydrosilicates and reduces the amount of forming portlandite and ettringite, thereby improving the mechanical properties and durability of the set cement.

Keywords: barium hydrosilicates, early hydration of Portland cement, isothermal calorimetry, phase composition

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INTRODUCTION

As shown by Satyukov and Grishina [1], the technical and economic efficiency of radiation-protective materials can be improved by adding a modifier produced by precipitating sodium hydrosilicates with a barium chloride solution and consisting primarily of barium hydrosilicates with the composition $BaO \cdot SiO_2 \cdot 6H_2O$ (BSH) and small amounts of silicic acid and barium carbonate [2]. The improved efficiency of the radiation-protective materials prepared using BSH is due to the presence of barium atoms and chemically bound water, as well as to the ability of the modifier to control structure formation processes and the properties of the set Portland cement [3, 4]. There is solid experimental evidence that the use of BSH makes it possible to reduce the attenuation coefficient for gamma-rays and improve the mechanical performance of set cement [3, 4]. Unfortunately, the mechanism behind the effect of BSH on the Portland cement hydration process and the composition of the hydration products has not yet been studied in sufficient detail. This entails difficulties in the use of barium hydrosilicates in formulations of building composites.

The purpose of this work was to investigate the processes involved in early Portland cement hydration (during the first 72 h after mixing with water) in the presence of micron-sized BSH particles and determine the composition of the Portland cement hydration products. Materials containing Portland cement and mineral additives (in particular, BSH) are termed "composite binders" [5].

EXPERIMENTAL

To produce a specialty composite binder, BSH particles with an average diameter $d_{av} \sim 6$ μm and true density of 3014 ± 100 kg/m^3 were added to TsEM I 42,5 B Portland cement (RF State Standard GOST 31108-2003; manufactured by OAO Mordovtsement). The compositions of the composite binders are indicated in Table 1. The amount of the precipitant for the synthesis of barium hydrosilicates was calculated with allowance for the stoichiometric coefficients in the equations of the chemical reactions involved [6]. BSH was synthesized via low-temperature precipitation from sodium hydrosilicates with the composition $Na_2O \cdot 3SiO_2 \cdot 4.5H_2O$ and concentration $\omega(Na_2O \cdot 3SiO_2 \cdot 4.5H_2O) = 11\%$ and an aqueous $BaCl_2$ solution with concentration $\omega(BaCl_2) = 17.86\%$. The barium hydrosilicate synthesis procedure was described in greater detail elsewhere [4]. A mixture of the Portland cement and barium hydrosilicates was ground in a Fritsch Pulverisette 7 ball mill for 5 min at a grinding vial rotation rate of 500 rpm.

One effective way of achieving the above purpose is by studying the kinetics of heat release from the binders during mixing with water and the behavior of their phase composition during hydration.

Table 1. Compositions of the composite binders

Composition	Portland cement, wt %	BSH, wt %
1 (control)	100	–
2	83.3	16.7*
3	71.4	28.6*
4	83.3	16.7**

* The amount of the precipitant ($BaCl_2$) is 100% of the stoichiometric amount.
** The amount of the precipitant ($BaCl_2$) is 70% of the stoichiometric amount.

Heat release during hydration was analyzed using a TAMAir eight-channel microcalorimeter over a period of 72 h in adiabatic mode. The samples were mixed with water at a water-to-cement (W/C) ratio of 0.5, stirred for 1 min, and placed in holders for subsequent analysis [7, 8].

The evolution of the phase composition during hydration was followed using X-ray powder diffraction. Samples were taken 12, 17, and 72 h after mixing the composite binder with water. To interrupt the hydration process, water was removed using acetone [9]. The samples were ground in an agate mortar with acetone (2 mL) and then dried to constant weight in a desiccator.

X-ray diffraction patterns were collected on an ARL X'tra powder diffractometer in the angular range $2\theta = 4°$ to $60°$ in step scan mode (scan step of 0.02°) with a counting time of 1 s per data point.

RESULTS AND DISCUSSION

Analysis of the kinetic curves of the heat flux in Fig. 1 indicates that the addition of BSH has a significant effect on the heat release kinetics: it shifts the induction period, increases the heat release due to alite hydration, and shifts it to earlier stages (Table 2). Since the addition of BSH increases the released heat and shifts the C_3S hydration onset to earlier stages, the heat release during C_3A hydration does not reach its maximum before the C_3S hydration onset, which significantly differentiates the heat release curves of the modified binders from those for Portland cement hydration. There are also differences in the induction period (Table 2): the addition of the modifier considerably retards the onset of the induction period (by 26–65 min) and increases the induction time (by 132–207 min).

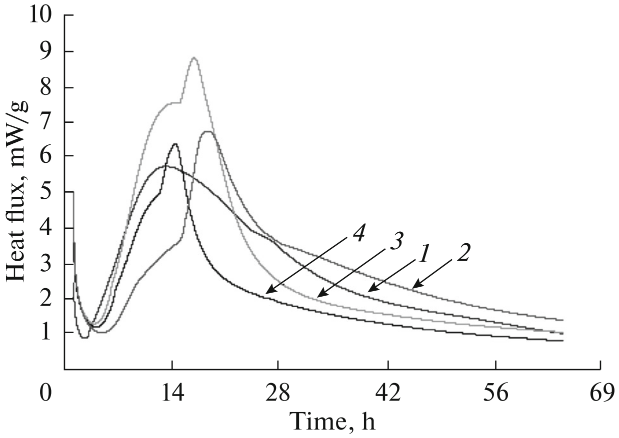

Fig. 1. Heat flux kinetics during the hydration of the composite binder. The curves are numbered as the compositions in Tables 1 and 2.

According to Pashchenko et al. [10], there are two groups of hypotheses that explain the origin of the induction period and the retardation of Portland cement hydration, which in fact reflect the sequence of the processes that take place during the induction period rather than distinctive features of its mechanism. One group of hypotheses suggest that the induction period is due to nucleation retardation or the formation of secondary hydration products. Some researchers believe that such a hydrate is calcium hydroxide (hypothesis 1), while others propose calcium hydrosilicates (CSH gel) (hypothesis 2) [10]. The other group of hypotheses consider various distinctive features of reaction products: the products formed in the initial stage of hardening act as a barrier that prevents further hydration, and the induction period terminates when the barrier disappears as a result of aging processes (hypothesis 3) or osmotic disruption (hypothesis 4) [10]. Thus, on the addition of BSH, there is no nucleation during the induction period because of the blocking of the surface of the Portland cement particles. The silicic acid in the BSH modifier can depolymerize in the alkaline medium of the cement paste to form sol. Silicic acid sol is capable of reacting with calcium hydroxide to form CSH gel [11–14]. This accounts for the shift of the induction period and the change in the induction time.

The silicic acid content of the BSH modifier depends on the amount of the precipitant used in the synthesis [2] and the modifier content of the composite binder (Table 1): increasing the silicic acid content of the additive increases the onset time of the induction period. The nature and amount of the BSH modifier have an insignificant effect on the duration of the induction period. This fact attests to a decrease in nucleation rate in the cement paste in the presence of the BSH modifier and an increase in surface blocking duration. The maximum heat release during C_3A hydration is observed later in comparison with the control composition, but the hydration rate of C_3A is higher (except for composition *4*). The rate of this process is determined by the composition of the modifier: with increasing silicic acid content, the maximum heat release rate decreases and the heat flux for composition *4* is lower than the control value (composition *1*).

Table 2. Heat released at different hydration times of the composite binder/cement in the composite binder

Composition	Q, J/g		
	12 h	17 h	72 h
1 (control)	50.16	88.05	252.30
2	49.98/60.00	100.23/120.32	241.85/290.34
3	49.19/68.89	93.46/130.90	222.15/331.13
4	24.05/28.87	51.26/61.54	244.00/292.92

It follows from Fig. 1 that the addition of barium hydrosilicates considerably increases the rate of C_3S hydration. In particular, the heat released in 12, 17, and 72 h after mixing exceeds that for the control composition. At the same time, the hydration rate of composition *4* in the initial stage of the process is slower than that of the control composition, which is consistent with the data in Table 2 and can be interpreted as evidence for lower early strength of the synthetic cement [15].

Analysis of the data in Table 2 demonstrates that the addition of BSH increases the heat released during cement hydration by a factor of 1.3–1.5, which points to an increase in the amount of hydrated C_3S in the composition binder relative to Portland cement.

The amount of hydration products can be increased in several ways, by displacing chemical equilibrium toward the formation of hydration products, in particular, by removing the products from the reaction zone. C_3S hydration is known to follow the scheme [5]

$$3CaO \cdot SiO_2 + (3 - x)H_2O$$
$$\rightarrow (3 - x)Ca(OH)_2 + xCaO \cdot ySiO_2 \cdot mH_2O.$$

Therefore, the degree of C_3S hydration can be increased by removing the forming calcium hydrosilicates and portlandite. It follows from the composition of the modifier [2] that BSH is similar to $xCaO \cdot ySiO_2 \cdot mH_2O$. Therefore, there is the possibility of epitaxy of the forming $xCaO \cdot ySiO_2 \cdot mH_2O$ on the large surface of BSH as a substrate [2]. This may lead to the removal of the hydration product (calcium hydrosilicates) from the reaction zone. The concentration of calcium hydroxide can be reduced by combining it with silicic acid to give calcium hydrosilicates. To verify this hypothesis, we examined the evolution of the phase

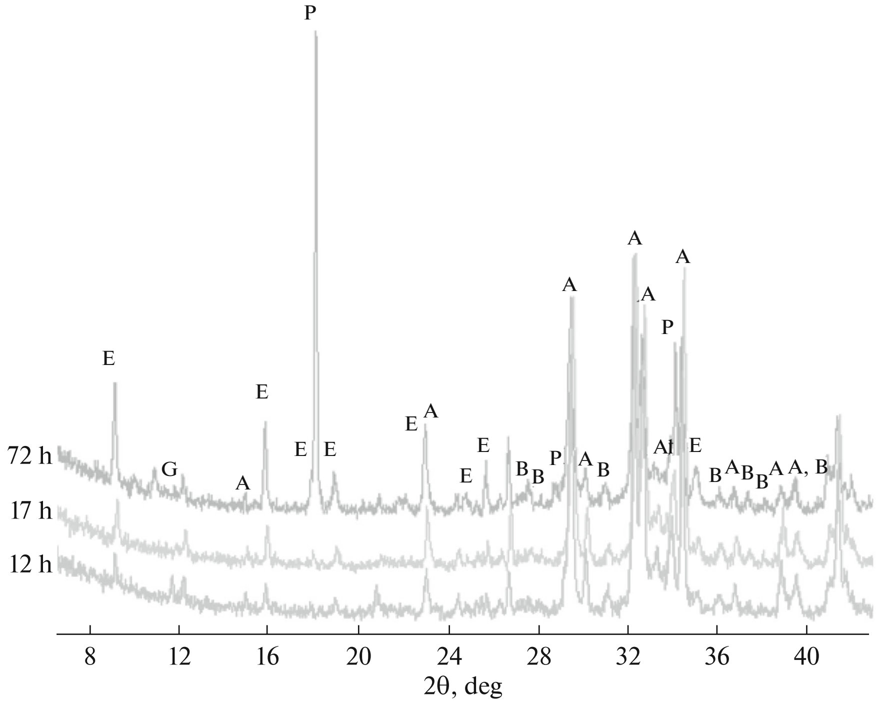

Fig. 2. X-ray diffraction patterns of composition *1*: E = ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$; P = portlandite, $Ca(OH)_2$; G = gypsum dihydrate, $CaSO_4 \cdot 2H_2O$; A = C_3S; B = β-C_2S; Al = C_3A.

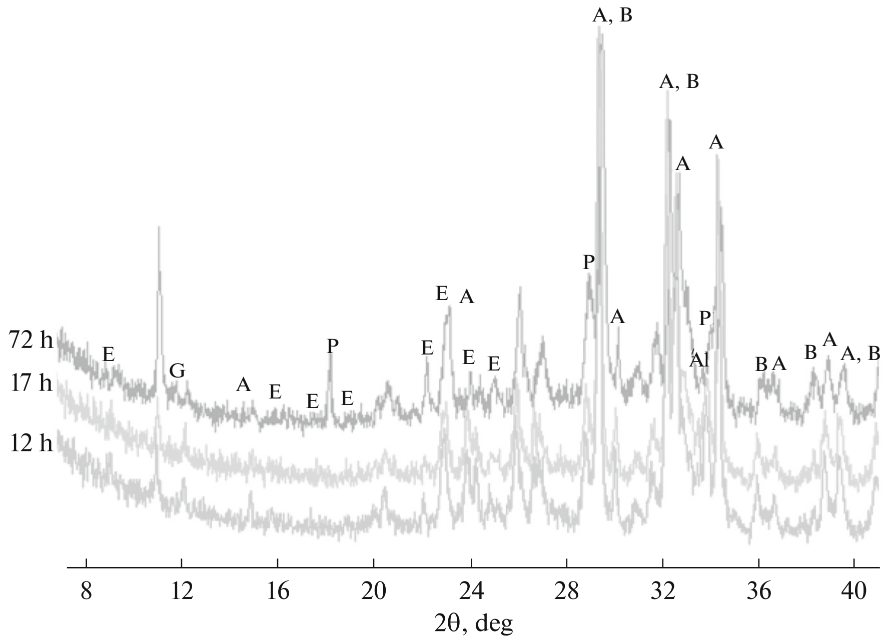

Fig. 3. X-ray diffraction patterns of composition *3*; the same notation of the peaks as in Fig. 2.

composition of the composite binder in the initial stage of hydration (Figs. 2, 3).

Analysis of Figs. 2 and 3 indicates that the amount of portlandite in the synthetic cement based on the composite binder is substantially lower. Note that, after 17 h, the concentration of portlandite is sufficient to detect it in the control composition, whereas it cannot be identified in the modified composition, which suggests that it is chemically combined, because the alite concentration in the composite binder (with allowance for its content) is lower than that in the control composition.

In addition, the X-ray diffraction patterns in Figs. 2 and 3 contain unidentified reflections corresponding to interplanar spacings $d = 8.052$, 3.864, 4.026, 3.419, 3.060, and 2.104 Å, which may be due to the formation of compounds containing both calcium and barium atoms. Moreover, the intensity of the reflections from ettringite is substantially lower, which can be interpreted as evidence for the formation of calcium and barium hydrosulfoaluminates. An increased ettringite content of set cement in the latter stages of hardening is known to cause cracking of the concrete and reduce its strength [16]. Calcium hydroxide has a similar effect [16]. Ettringite formation is only possible in a highly alkaline medium, that is, in the presence of $Ca(OH)_2$ [17]. If the system contains a sufficient amount of amorphous silica, ettringite formation is suppressed for lack of calcium hydroxide, which is necessary for the reaction to reach completion. Under the conditions of this study, there is the possibility of the formation of a low-sulfate form of calcium hydrosulfoaluminate, which has no adverse effect on the strength of the set cement [18]. This should significantly imp[rove the physicomechanical properties and durability of synthetic cement based on the composite binder.

CONCLUSIONS

The present experimental data on early hydration processes in the composite binders studied here demonstrate that the induction period in the binders begins later than that in Portland cement because of the blocking of calcium hydrosilicate nuclei. Increasing the silicic acid concentration reduces the hydration rate of C_3A. The hydration rate of C_3S increases markedly, and the hydration time decreases. This is caused by the removal of the reaction products from the reaction zone.

Determination of the phase composition of the synthetic cement by X-ray diffraction pattern demonstrates a decrease in the amount of forming portlandite and ettringite in the reaction products and the formation of new, unidentified compounds. The amount of C_3S in the synthetic cement is lower than that in set cement.

Thus, we have identified key features of the processes involved in early Portland cement hydration in the presence of BSH of various compositions and determined the phase composition of the reaction products.

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