Thermochimica Acta, 35 (1980) 201—209

APPLICATION OF DIFFERENTIAL THERMOGRAVIMETRY TO THE HYDRATION OF EXPANSIVE CEMENT PASTES

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(Received 8 May 1979)

ABSTRACT

Differential thermogravimetric analysis was used to determine the hydration kinetics of expansive cement and its products at various ages of hydration. Analytical grade reagents, kaolin and Portland cement were used to prepare an expansive cement on the basis of calcium sulphoaluminate. Two mix compositions having the stoichiometric composition of trisulphate and monosulphate were synthesized from pure reagents. Three clinkers were also prepared from kaolin, gypsum and calcium carbonate with different compositions.

The hydration of expansive cement prepared from the stoichiometric composition of trisulphate and Portland cement gives ettringite as the stable phase after seven days of hydration. The presence of more CaO than the stoichiometric composition of trisulphate favours the conversion of some ettringite to the monosulphate hydrate. The hydration of expansive cement prepared from the stoichiometric composition of monosulphate and Portland cement shows the presence of ettringite and the monosulphate phase. Ettringite is formed initially, and then transformed to the monosulphate form.

INTRODUCTION

The differential thermobalance was developed by DeKeyser [1] in 1953 and has been frequently used since in the hydration of Portland cement and its constituents.

The formation of calcium sulphoaluminates is important in expansive cements where the expansion is accompanied by the formation of calcium sulphoaluminate hydrates; these compounds are formed in crack-resistant and chemically-prestressed concrete [2]. Ettringite, $3\ CaO \cdot Al_2O_3 \cdot 3\ CaSO_4 \cdot 32\ H_2O$, is formed in the hardened cement pastes, as a result of the interaction between calcium sulphate and aluminates or ferrites; it changes to the monosulphate hydrate $3\ CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12\ H_2O$ with time [3]. The presence of sufficient amounts of lime and gypsum seems to stabilize the ettringite crystals. In the presence of C_3S and gypsum, the hydration of the sulphoaluminate yields a product with a greater quantity of ettringite than that obtained from the paste without C_3S.

It is not clear whether the low sulphate hydrate or the high sulphate (ettringite) appears immediately after gauging. Green [4] presented an extensive study on the stages of paste hydration of Portland cement and followed the reaction by means of differential thermal analysis. He concluded that the first product of hydration was ettringite, but after the complete consumption of gypsum, the monosulphate hydrate appeared. Chatterji and Jeffery [5] concluded that ettringite was formed, not during the early stages of hydration of Portland cement, but in the later stages of hydration.

Henning et al. [6] concluded that the paste hydration of ignited stoichiometric trisulphate composition yields ettringite after 6 h of hydration. The amount of ettringite increases until the third day of hydration and then remaines constant until the seventh day. The hydration of the stoichiometric composition of the monosulphate yields ettringite and monosulphate hydrate after 6 h, but the main phase is ettringite. As hydration proceeds, the amount of monosulphate hydrate increases while the ettringite decreases. After seven days of hydration, the monosulphate was predominant in the paste with a small amount of ettringite present. In a previous work, El-Didamony et al. [7] showed that the hydration of expansive cement paste made of 20% expansive cement clinker and Portland cement gives ettringite and monosulphate hydrate after 6 h of hydration. As hydration proceeds, the amount of ettringite increases and that of low sulphate decreases. After three days of hydration, monosulphate hydrate disappears completely; the amount of ettringite remains constant even after 28 days of hydration.

In the case of well-crystallized products, one can estimate quantitatively the amount of water liberated in the decomposition of the various hydrates by integration of the differential thermogravimetric curves. In cement hydrates, which are generally very poorly crystallized, differential curves are best used to obtain qualitative data.

The present investigation is therefore based on the application of differential thermogravimetric analysis to the determination of the kinetics of hydration of expansive cement, and its hydration products after 6 h, 1, 3 and 7 days.

EXPERIMENTAL

The materials used were analytical grade reagents: calcium carbonate (0.7 m^2 g^{-1}); gypsum (0.7 m^2 g^{-1}); aluminium oxide (<63 μm); kaolin (Vereinigte Kemmlitzer Kaolin-Werk, Spergau, DDR) and Portland cement 375 (Karsdorf, DDR). Table 1 gives chemical analyses of kaolin and Portland cement.

Anhydrous trisulphate and monosulphate were prepared by calcining stoichiometric proportions of high purity $CaCO_3$, Al_2O_3 and $CaSO_4 \cdot 2\,H_2O$ at 1300°C for one h. Three expansive cement clinkers were also made from $CaCO_3$, $CaSO_4 \cdot 2\,H_2O$ and kaolin according to Nakamora's equations [8]. These clinkers were made with different mole ratios of $CaSO_4$ and CaO relative to one mole of $C_4A_3\overline{S}$ *. In each case the constituents were ground separately in a porcelain ball mill to pass completely through a 200-mesh sieve, then mixed as a slurry with water in the ball mill for one hour and burned as

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* Normal cement notations have been used in this investigation, viz. C = CaO, A = Al_2O_3, S = SO_3, S = SiO_2, F = Fe_2O_3 and H = H_2O.

TABLE 1

Chemical analyses of kaolin and Portland cement

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	$K_2O + Na_2O$	SO_3	I.L.
Kaolin	49.88	33.12	0.67	0.28	0.56	0.90	—	12.42
Portland cement	20.03	6.75	3.11	61.55	3.37	1.40	2.35	1.84

TABLE 2

Chemical analyses of the clinkers

Clinker	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	$K_2O + Na_2O$	m/n [a]
K_1	9.67	7.09	0.19	53.14	0.24	27.27	0.28	8/6
K_2	9.91	7.06	0.17	54.91	0.32	27.12	0.24	8/8
K_3	12.72	8.83	0.35	56.35	0.60	19.18	0.32	2/6

[a] m/n: mole ratio of $CaSO_4$ to CaO relative to one mole of $C_4A_3\bar{S}$.

pellets for one hour at 1250°C. Anhydrous mixes of trisulphate and monosulphate, and the clinkers were ground to pass through a 63-μm sieve. Table 2 gives analyses of the clinkers.

Five different expansive cements were prepared from 10% anhydrous trisulphate or monosulphate, and 15% of each clinker, the balance being provided by Portland cement. The mixes were homogenized for one h in a laboratory ball mill using one ball. Cement and water were mixed at a water/cement ratio of 0.26 using ordinary gauging trowels on a steel plate continuously and vigorously for 4 min. The paste was cast in cylindrical plastic moulds 1″ in diameter and cured for 6 h in a moist cabinet at room temperature 23 ± 1°C. The hardened paste was removed from moulds, wrapped in cotton pads, soaked with distilled water, and transferred to an air-tight contained for further hydration. The progress of hydration was followed by differential thermogravimetric analysis after periods ranging from 6 h to seven days.

After each hydration period, a representative sample of about 10 g was pulverized and placed in a beaker containing 20 ml acetone and 20 ml methanol, then stirred mechanically for one hour. The mixture was filtered through a Gooch crucible, G4, and washed with ether. The solid was then dried at 40—50°C for one hour to complete evaporation of the alcohol. The hardened paste was put into air-tight bottles for thermal analysis. The apparatus used in this work is of the MOM-Budapest type.

RESULTS AND DISCUSSION

Figure 1 shows the derivatograms of expansive cement paste prepared from 10% anhydrous monosulphate ($3\,CaO \cdot Al_2O_3 \cdot CaSO_4$) with Portland

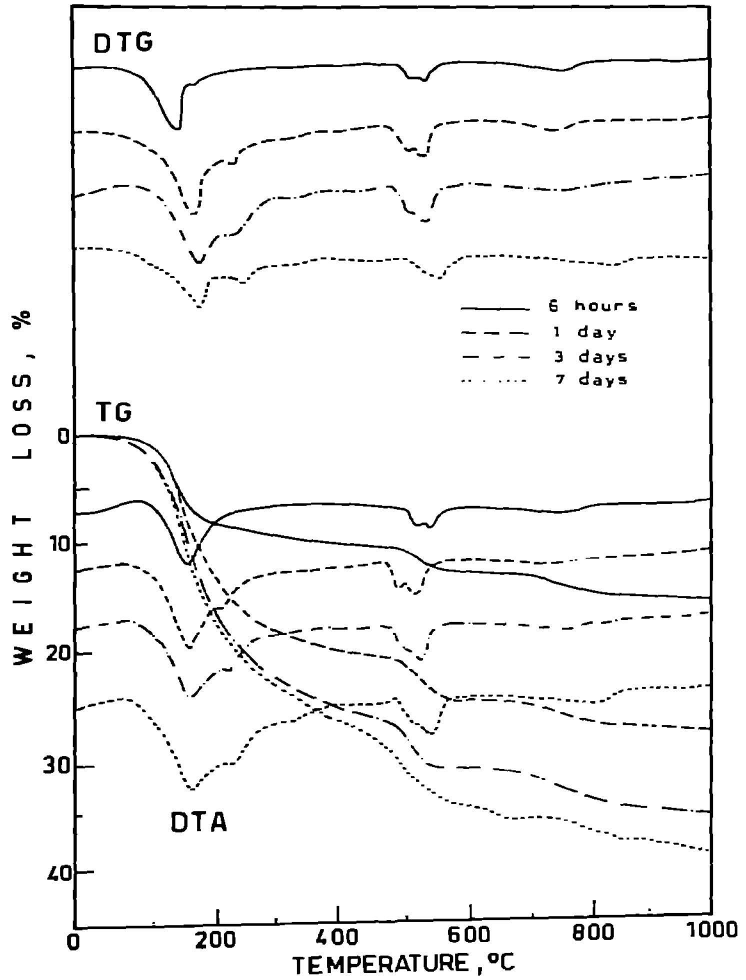

Fig. 1. Derivatograms of samples with 10% anhydrous monosulphate as a function of the age of the paste.

cement as a function of curing time. After 6 h of hydration, the derivatograms show a strong endothermic peak due to dehydration of ettringite at 140° C; the weak endothermic effect observed at 200° C may be attributed to a solid solution of ettringite and monosulphate hydrate. The other endothermic peaks at 490, 520 and 750°C are due to the dehydration of $C_3(A_xF_y)H_{1.5}$ [9,10], $Ca(OH)_2$ and the decomposition of $CaCO_3$, respectively. In the hydration of C_4AF, the hydrated phases formed may be solid solutions containing different amounts of Fe and Al, so that $x + y = 1$. After one day of hydration, new endothermic peaks appear at 200 and 300° C and these are attributed to monosulphate hydrate [6]. As hydration proceeds, samples taken after three and seven days of hydration give derivatograms showing that the trisulphate hydrate is the predominant phase while the monosulphate hydrate is found in small amounts. The endothermic peak at 140° C may be due to the dehydration of ettringite with tobermorite gel [11—13].

Figure 2 shows the derivatograms of hydrated samples of expansive cement made from 15% K_3 with Portland cement; K_3 clinker possesses the stoichiometric composition of the monosulphate. After 6 h of hydration, the derivatogram shows a strong endotherm due to the dehydration of the trisulphate hydrate at about 140°C. The other endothermic peak at 495°C is attributed to the dissociation of $Ca(OH)_2$, which is released during the hydration of calcium silicate. Cement paste hydrated for one day displays $Ca(OH)_2$ and $CaCO_3$; in addition to the peaks of ettringite; two weak endothermic peaks were observed at 200 and 490°C. The first peak may be due to solid solution from the two sulphoaluminate hydrates, and the second is due to the dehydration of $C_3(A_xF_y)H_{1.5}$.

Samples taken after three days of hydration demonstrate the existence of three endothermic peaks at 140, 230 and 300°C. The first is due to ettringite with calcium silicate hydrate but the other two endothermic effects can be considered as due to the monosulphate hydrate [13]. After 7 days of hydration the ettringite phase becomes more dominant.

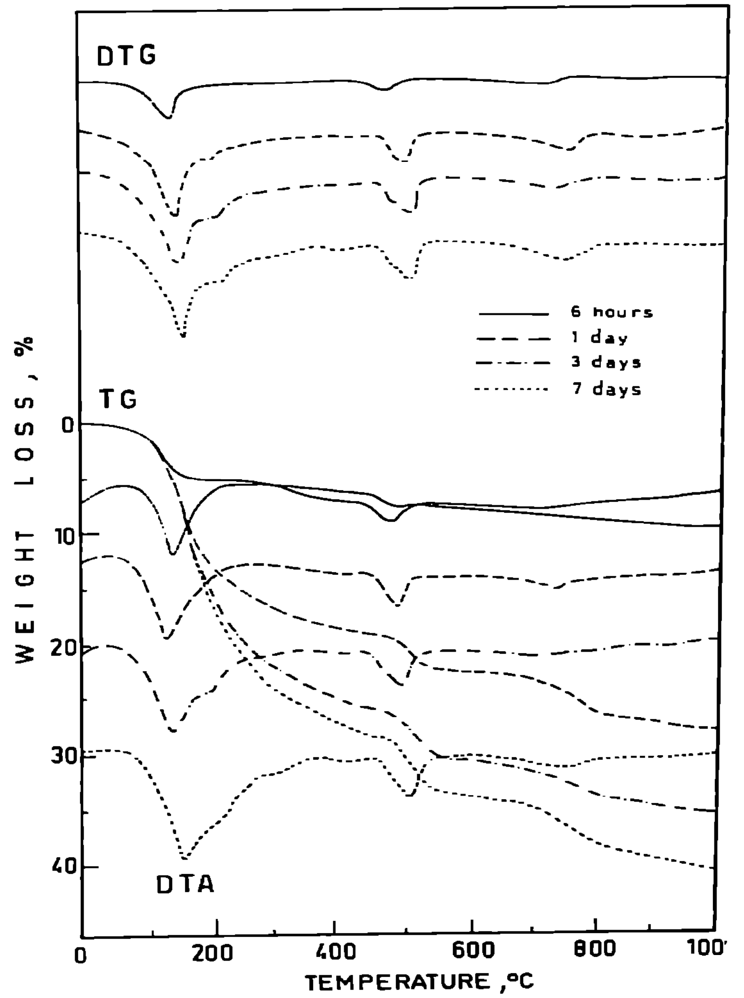

Fig. 2. Derivatograms of samples with 15% K_3 as a function of the age of the paste.

The derivatograms of hydrated samples prepared from 10% anhydrous trisulphate ($3\ CaO \cdot Al_2O_3 \cdot 3\ CaSO_4$) with Portland cement are shown in Fig. 3. After 6 h of hydration, two endothermic peaks in the range of calcium sulphoaluminate hydrate are traced. The first strong peak at 140° C is attributed to the dissociation of ettringite, the other weak effect at 200°.C is assigned to a solid solution from ettringite and monosulphate hydrate. The other endothermic peaks, at 490, 520 and 750°C, are due to dehydration of $C_3(A_xF_y)H_{1.5}$, $Ca(OH)_2$ and $CaCO_3$, respectively.

As hydration proceeds, a strong endothermic peak appears at 150° C after one day, and this corresponds to the decomposition of ettringite with tobermorite gel. By prolonged curing, the amount of ettringite remains constant until the third day of hydration. The presence of $Ca(OH)_2$ stabilizes the formation of ettringite if there is sufficient $CaSO_4$ or in the presence of the stoichiometric composition of trisulphate.

Figure 4 shows the thermograms of expansive cement pastes prepared

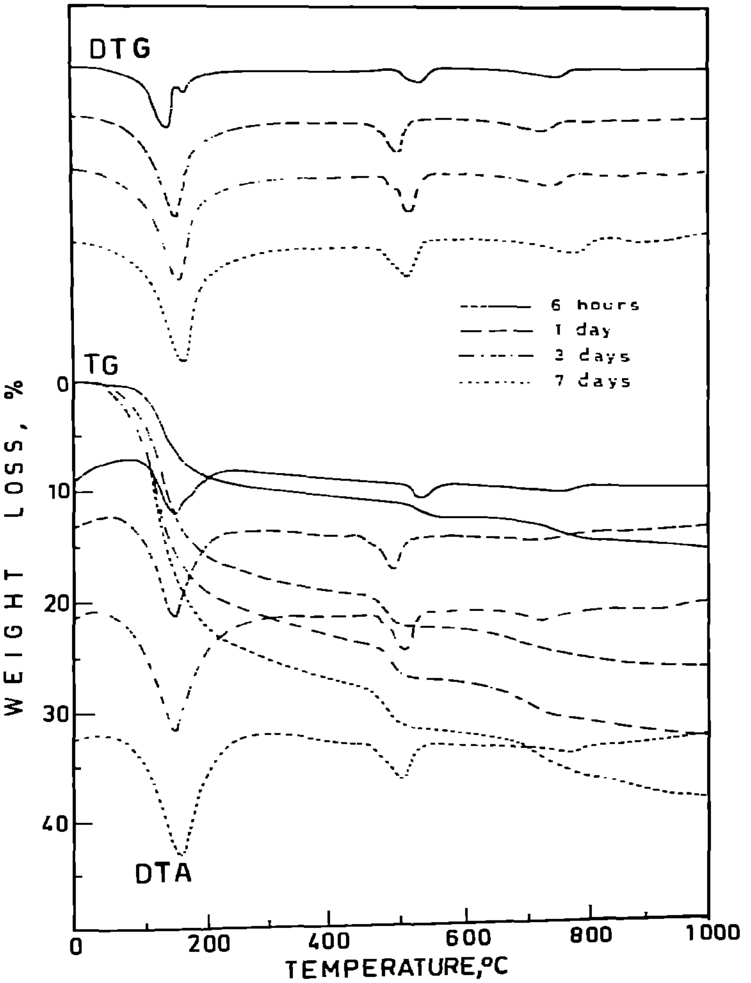

Fig. 3. Derivatograms of samples with 10% anhydrous trisulphate as a function of the age of the paste.

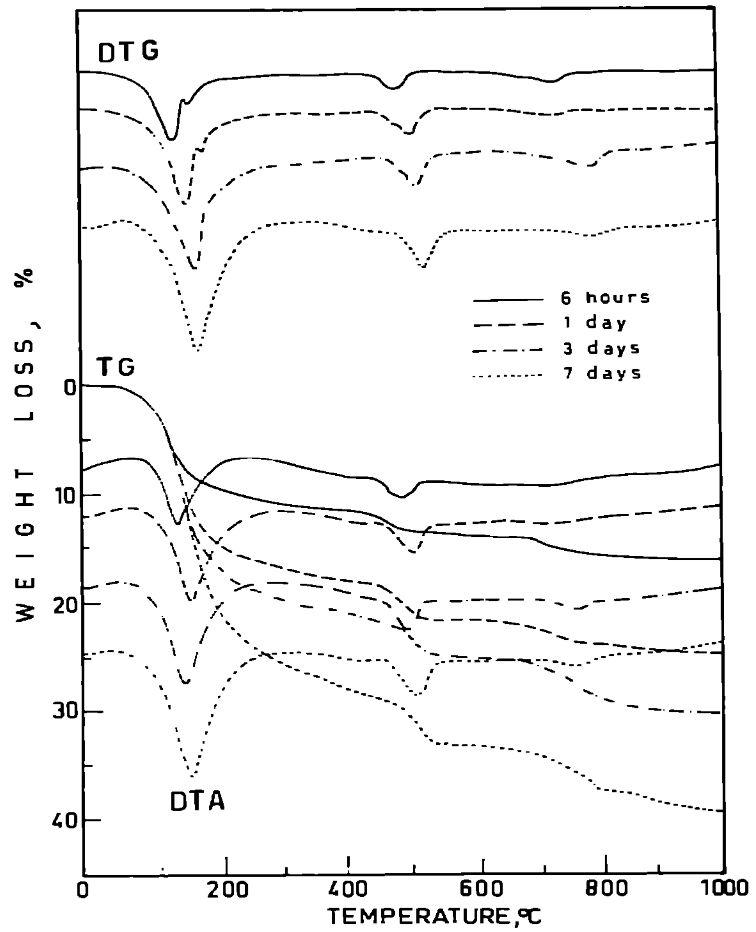

Fig. 4. Derivatograms of samples with 15% K_1 as a function of the age of the paste.

from 15% K_1 with Portland cement; K_1 clinker has the stoichiometric composition of trisulphate. After 6 h of hydration, it shows two endothermic effects at 140 and 185°C. The first is attributed to ettringite and the other is due to a solid solution formed from ettringite and monosulphate hydrate. After one day of hydration, the trisulphate hydrate is the main sulphoaluminate. A very weak peak indicates the presence of the solid solution of the two sulphoaluminate hydrates. The amounts of ettringite, and $Ca(OH)_2$ increase with the increase in hydration time. After seven days of hydration, only ettringite is present, with tobermorite gel and calcium hydroxide.

Thermograms of hydrated samples prepared from K_2 with Portland cement are shown in Fig. 5; K_2 clinker has two moles of CaO more than the stoichiometric composition of trisulphate. After 6 h of hydration, the ettringite is the predominant phase. A weak endothermic peak also appears at 200°C, and this is due to the solid solution of the two sulphoaluminate hydrates. Samples taken after one day have a strong endothermic effect at 150°C and this is attributed to ettringite decomposition. There are also peaks due to $C_3(A_xF_y)H_{1.5}$, $Ca(OH)_2$ and $CaCO_3$. The sample contains negligible monosulphate hydrate.

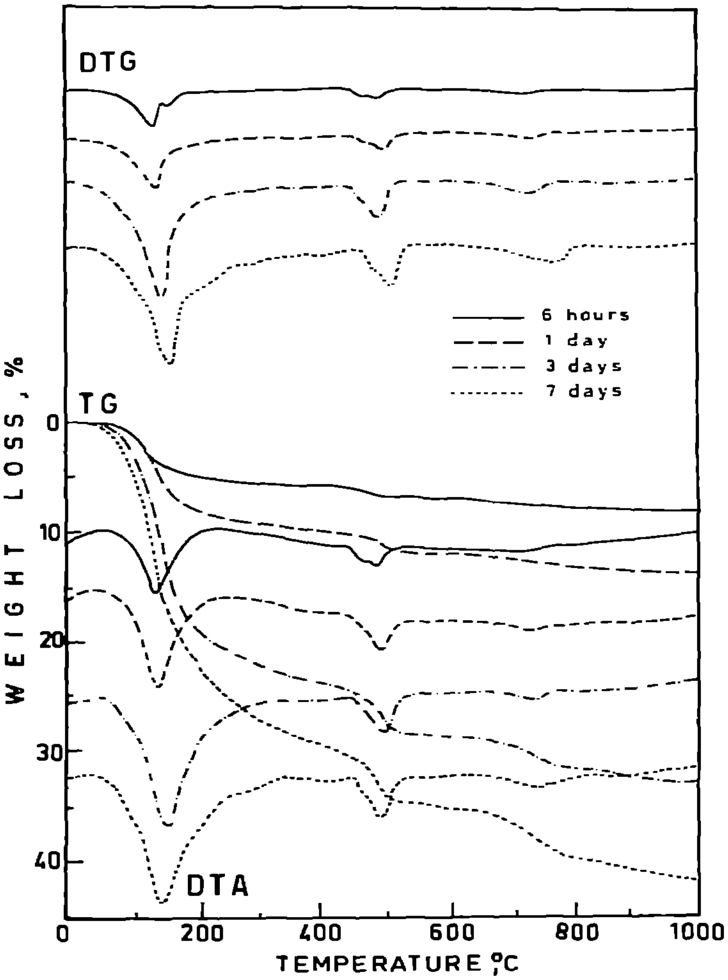

Fig. 5. Derivatograms of samples with 15% K_2 as a function of the age of the paste.

As hydration proceeds the content of ettringite increases, and after seven days some amounts of monosulphate hydrate are also present. This clinker has two moles of CaO more than the stoichiometric composition of trisulphate, which may favour the conversion of ettringite to monosulphate hydrate.

CONCLUSIONS

The following conclusions may be deduced from the above findings:

(1) On hydration of expansive cement made from Portland cement with anhydrous calcium sulphoaluminate, ettringite is formed as the stable phase in the pastes of different composition.

(2) Ettringite is initially formed before monosulphate hydrate, then the solid solution is produced from the two phases and monosulphate appears later.

(3) Anhydrous monosulphate mixed with Portland cement gives ettringite and monosulphate hydrate; the former represents the predominant phase.

(4) The hydration of expansive cement made from anhydrous trisulphate with Portland cement yields only ettringite after 7 days of hydration.

(5) When the expansive cement clinker has more CaO than the stoichiometric composition of trisulphate, monosulphate hydrate and ettringite are formed, the latter being the predominant phase.

(6) In all pastes $Ca(OH)_2$, $C_3(A_xF_y)H_{1.5}$ and $CaCO_3$ were detected among the hydration products.

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