Acceleration and Retardation of Portland Cement Hydration by Additives

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●THE SETTING and hardening of portland cement can be influenced by chemical additives. Several kinds of retarders and accelerators are known. A special committee of the American Concrete Institute summarized the effect of additives upon the properties of concrete (1). The most widely used accelerator is calcium chloride, which almost all commercially manufactured accelerators contain. The variety of retarders is greater; lignosulfonates and their derivatives, carbohydrates, hydroxy-carboxilic acids, dicarboxilic acids, phosphates and borates are generally used.

Reports of basic research on the mechanism of accelerator and retarder action are relatively few contrasted to the vast quantity of. papers dealing with the effect of accelerators and retarders upon the engineering properties of concrete.

The accelerating effect of calcium chloride has been interpreted in several ways. According to the majority of investigators, $CaCl_2$ reacts with the aluminates and ferrites of portland cements, the reaction products being $3\,CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10\,H_2O$ and $3\,CaO \cdot Fe_2O_3 \cdot CaCl_2 \cdot 10\,H_2O$, respectively, but Rosenberg (2), for example, found a composition corresponding to $6\,CaO \cdot 2\,Al_2O_3 \cdot CaCl_2 \cdot X\,H_2O$. This explanation of the effect of calcium chloride has been adopted since the pioneering work of Friedel (3). Other authors (4, 5) stated that calcium chloride reacts with the calcium hydroxide developed during the hydration of calcium silicates. The reaction product has the formula $3\,CaO \cdot CaCl_2 \cdot 12\,H_2O$. All these new formations had acicular crystals; the interwoven structure of these hypotheses stressed that the accelerating effect of calcium chloride is due to the chemical reaction of calcium chloride with the aluminate and/or ferrite phases of cement or with calcium hydroxide formed during hydration while the silicate phases remain unaffected.

It is, however, highly improbable that these processes are really essential in calcium chloride action, because aluminates and ferrites are only a minor part of commercial portland cement and their hydration products not only are small in absolute amount but also have specific surfaces that are negligible in comparison with the hydration products of the silicate phases. According to Powers' theory on the structure of hardened cement paste, the hypothesis of acicular crystals is unsatisfactory to explain the surplus strength caused by calcium chloride. Obviously, the effect of calcium chloride upon the silicate phase of cement must be examined.

In 1959 Lieber and Bleher (6), and in 1960 Kurczyk and Schwiete (7), discovered that the hardening of pure calcium silicates is also accelerated by calcium chloride; the latter investigators found also that the addition of calcium chloride reduces the pH of the cement paste. Vivian (8) wrote of calcium chloride, "Its accelerating action in cement appears to be due (a) to the acceleration of the sulfoaluminate reaction between gypsum and tricalcium aluminate, and (b) to a depression of the pH, which accelerates the rate of hydration of the silicates."

The action of organic materials in retarding setting is not clearly understood (8). Taplin (9) assumed that organic substances retard by adsorption either on the surface of the clinker minerals so as to protect them from attack by water, or on the surface of a coherent coating of hydration products so as to prevent the transport of material to or from the clinker surface.

TABLE 1

COMPOSITION OF CEMENT

Oxide Analysis

Component	Percent
SiO_2	20.57
Al_2O_3	5.35
Fe_2O_3	2.80
CaO	62.11
Free CaO	0.12
MgO	4.36
SO_3	2.42
Insoluble	0.25
Loss on ignition	1.43

Potential Compound Composition

Compound	Percent
C_3S	47.93
C_2S	22.83
C_3A	9.44
C_4AF	8.52

EXPERIMENTAL

Materials

Hungarian-made "Tatabanya"-blend, ASTM Type I cement was used throughout the experiments; its analysis and potential compound composition are given in Table 1. In some cases a 1:1 tricalcium silicate-dicalcium silicate mixture was used, prepared synthetically and ground to normal fineness. If pastes were investigated, distilled water was used as mix water. Reagent grade anhydrous calcium chloride and reagent grade citric acid were used as accelerator and retarder, respectively. Admixtures were added as solutions in distilled water. Quartz gravel having a maximum diameter of 20 mm was used for the experiments with concrete. The concrete was mixed with tap water.

Methods

Thermal investigations were done by the Derivatograph. This instrument records the weight changes, the rate of weight changes and the rate of enthalpy changes as temperature functions of the same sample automatically, thus giving thermo-gravimetric (TG), derivative thermo-gravimetric (DTG) and differential thermal analysis (DTA) curves simultaneously. A detailed description of the instrument is given elsewhere (10). Setting time determination was made by a Swiss automatic Vicat apparatus. This apparatus, manufactured by

TABLE 2

EFFECT OF ADDITIVES ON SETTING TIMES OF NORMAL CONSISTENCY·PASTES

Additive	Time of Addition	Cement		Synthetic Silicate	
		Initial	Final	Initial	Final
Calcium chloride, 2%	at time of mixing	29	85	105	250
	2 min later	25	75	85	195
	4 min later	26	80	89	190
	8 min later	28	80	95	220
Calcium chloride, 1%	at time of mixing	38	103	525	810
	2 min later	32	100	490	750
	4 min later	30	92	485	735
	8 min later	33	109	540	825
No additive	—	134	221	790	>900
Citric acid, 0.05%	at time of mixing	255	645	855	>900
	2 min later	300	735	>900	n.d.
	4 min later	375	>900	>900	n.d.
	8 min later	285	>900	870	n.d.
Citric acid, 0.20%	at time of mixing	840	>900	>900	n.d.
	2 min later	>900	>900	>900	n.d.

Messrs. Amsler, is a self-recording device that will make a test every $2^{1}/_{2}$ to 20 minutes. Setting times reported here were determined with an accuracy of ±5 minutes. Usually pastes of normal consistency made of the cement and of the synthetic silicate binder were examined; heat-on-setting experiments were made on concrete specimens.

Setting Time

The setting times of normal consistency pastes are summarized in Table 2. First and second figures refer to the initial and final set, respectively. After a number of preliminary experiments the amounts of calcium chloride to be used in this work were chosen as 1 and 2 percent; the amounts of citric acid chosen were 0.05 and 0.20 percent. In all cases percentages are given on the cement weight basis. As a further variable, the additive was either dissolved in the entire mixing water and added to the cement at the start, or the bulk of the water was added at the start and the additive, dissolved in the rest of the water, was added after 2, 4, or 8 minutes. This sort of mixing sequence was recommended, in case of retarders, by Bruere (11).

It is seen that calcium chloride has a pronounced accelerating action on both cement and the synthetic silicate binder, while citric acid markedly retards their setting. These tests clearly show that the action of the additive is not limited to the aluminates, because the setting time of a synthetic alumina-free binder (dicalcium silicate + tricalcium silicate mixture) is also influenced by additives.

Thermal Behavior

Figures 1 and 2 give a general view of the Derivatograph tracings for cement and synthetic silicate mixture, respectively. There was no essential difference between the thermal curves of hydrated binders made with or without the addition of admixtures. The curve of the synthetic silicate binder is simpler, but the two diagrams differ only in the low temperature region. Above 400 C only two peaks are seen in both cases: the 500-510 C peak corresponds to the decomposition of calcium hydroxide, the 790-840 C peak to the decomposition of calcium carbonate. This latter compound was formed from the former by partial carbonation due to the air atmoshere. Both thermal
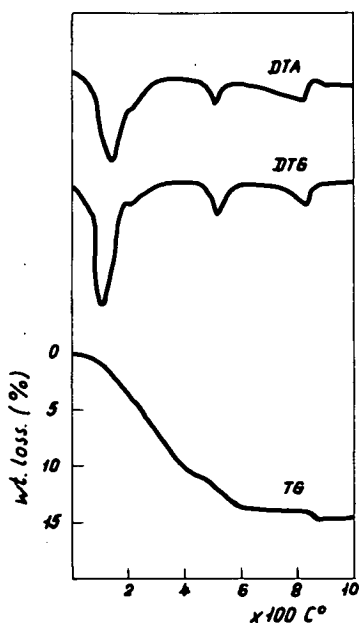

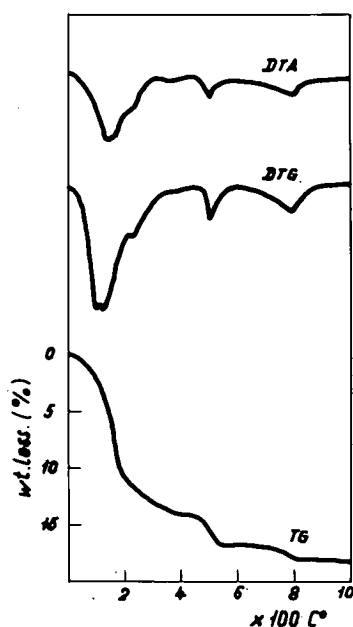Figure 1. Derivatograph tracing for cement.

Figure 2. Derivatograph tracing for synthetic silicate mixture.

peaks are accompanied with weight losses. Considering that the weight loss between 450 and 550 C is due to water and the weight loss between 550 and 900 C is due to carbon dioxide, the amount of CaO formed during hydration can be calculated by multiplying these weight losses by 3.11 and 1.27, respectively. This gives a method of direct quantitative evaluation of the TG diagram in the Derivatograph plots. The curve sections below 400 C are unsuitable for that purpose, because the initial moisture content of samples varies from specimen to specimen in an uncontrollable way. The drying of the specimens by ethanol or acetone was not satisfactory; the lack of high vacuum apparatus made the drying at low temperatures impossible. Therefore only the curve sections above 400 C were evaluated. The figures in Table 3 give the percentages of CaO formed during hydration, as calculated from weight loss curves by the method described. The free CaO content of the portland cement (0.13%) and of the synthetic silicate (0.38%) was always subtracted from the calculated amount.

It can be seen from the table that the addition of calcium chloride increases, while the addition of citric acid decreases, the quantity of calcium oxide formed during hydration. The greatest effect is obtained when the additive is introduced about 3 min after mixing of the paste. The effects of both additives diminish with the age of the paste, and probably vanish completely at later ages.

TABLE 3

EFFECT OF ADDITIVES ON HYDRATION OF CEMENT IN NORMAL CONSISTENCY PASTES

Additive	Time of Addition	Percentage of CaO Formed During Hydration									
		Cement					Synthetic Silicate				
		1	3	9	28	90	1	3	9	28	90
Calcium chloride, 2%	at time of mixing	7.1	7.7	8.2	8.5	8.6	6.7	8.1	9.6	10.8	11.6
	2 min later	7.8	8.0	8.3	8.6	8.8	8.1	8.8	10.5	11.2	11.7
	4 min later	7.9	8.0	8.3	8.6	8.8	8.2	9.0	10.5	11.1	11.7
	8 min later	7.3	7.8	7.9	8.0	8.3	8.0	8.3	10.3	10.0	11.6
Calcium chloride, 1%	at time of mixing	6.7	7.0	8.0	8.3	8.4	6.1	7.6	8.8	10.2	10.7
	2 min later	6.9	7.7	8.1	8.4	8.5	6.9	8.6	9.8	10.5	11.5
	4 min later	7.0	7.7	8.3	8.4	8.5	7.1	8.3	9.9	10.4	11.3
	8 min later	6.5	7.2	8.1	8.0	8.4	6.4	8.0	8.9	10.2	11.0
No additive	—	3.5	6.8	8.0	7.9	8.1	4.0	6.9	7.9	8.5	9.6
Citric acid, 0.05%	at time of mixing	1.2	4.1	7.6	7.8	8.0	2.1	4.8	7.8	8.4	9.4
	2 min later	1.0	3.9	7.6	7.7	8.1	1.1	4.1	7.7	8.4	9.4
	4 min later	0.9	3.0	7.8	7.8	8.0	0.8	4.1	7.7	8.5	9.3
	8 min later	1.1	3.9	7.7	7.7	7.9	0.8	4.3	7.9	8.5	9.4
Citric acid 0.20%	at time of mixing	0.2	0.9	6.3	7.3	7.7	0.1	1.6	6.7	8.4	9.4
	2 min later	0.1	1.0	6.0	7.5	7.9	0.1	1.1	6.5	8.1	9.3

TABLE 4

EFFECT OF ADDITIVES ON INITIAL REACTION IN CONCRETE

Additive	Temperature Increase (deg C)	
	Addition at Time of Mixing	Addition 2 Min Later
Calcium chloride, 2%	16.3	18.3
Calcium chloride, 1%	14.0	16.6
No additive	8.1	—
Citric acid 0.07%	2.0	1.5
Citric acid 0.15%	0.5	0.5

Heat-on-Setting in Concrete Samples

Because of the practical importance, heat-on-setting experiments were made in concrete. For this purpose, concrete cubes of 0.5 m edge length were manufactured in well-insulated molds and the heat evolved during the first 24 hours of setting was measured by the temperature increase. Apparatus and all ingredients of the concrete (cement, mix, water, aggregate) were maintained at 20 C overnight before mixing. Mixing was made by a commercial drum type concrete mixer to plastic consistency, and the mix was transferred to the mold as quickly as possible. The temperature of concrete was measured by a self-recording thermometer. This method, obviously, gives only relative results; the trend, however, is clear from these results. Table 4 gives the temperature increase in Centigrade degrees of the samples.

DISCUSSION

The results provide evidence on a problem stated at the Fourth International Symposium on the Chemistry of Cement (8): "Future work should be directed towards determining, as a first step, whether it is the hydration rate or the nature of the hydration product that modifies behavior."

All results of this study show that the rate of hydration of the silicate phase is changed by the addition of accelerators or retarders. Possibly the additives form an adsorbed layer on the grains of the cement silicates, causing activation or de-activation of the reaction between the silicate phase and water. By the action of calcium chloride the hydration of the silicate phase becomes more rapid, i.e., in the initial period of hardening there is more hydrated calcium silicate produced in pastes containing calcium chloride than in pastes with no additive. This larger amount of hydrated silicate (tobermorite gel) is responsible for the high early strength of calcium chloride-treated cement paste and concrete. The most rapid hydration of the silicate phase yields not only a larger amount of tobermorite gel, but also a larger amount of calcium hydroxide. The surplus of tobermorite gel and calcium hydroxide is very high in the beginning stage of hardening, is later reduced, but a slight surplus remains even after 90 days. This effect is even more marked with the alumina-free synthetic silicate.

The hypothesis described is essential in the interpretation of the calcium chloride effect, but from this point of view only calcium chloride in the dissolved state is active. Part of the calcium chloride, however, becomes insoluble because of the formation of a compound with the aluminates and ferrites of portland cement, and only the remaining amount has an accelerating effect. The insoluble calcium chloroaluminates and chloroferrites have no cementing action (12).

All the considerations described are valid for retarders as well, but with an opposite sign. Thus the retarders de-activate the hydration of calcium silicate; a lower amount of tobermorite gel is formed as compared to the sample with no additive. The formation of insoluble compounds with clinker aluminates occurs in this case too.

Thermal and heat-on-setting experiments are consistent with these considerations. The mechanism described further supports Powers' theory on the structure of hardened portland cement; old hypotheses, which quoted the formation of acicular, interwoven crystals as the explanation of the accelerator effect, were inconsistent with the Powers model.

The effect of mixing sequence, described and interpreted by Bruere (11) in the case of retarders, can be explained through knowledge of the first minute reactions of setting. The first reaction is dissolving of the gypsum of portland cement. The dissolved gypsum then reacts with the aluminates and ferrites of cement, yielding calcium sulfoaluminates and sulfoferrites. If, however, an accelerator or retarder is added dissolved in the mix water, the additive will react with the aluminates, because it is already in dissolved form. After the dissolving of the gypsum, the surface of aluminates and ferrites is already occupied by a slightly soluble compound. The sulfate remains in a dissolved state, but sulfates have no marked effect upon the hydration rate of silicates. If, however, calcium chloride has been added later, the surface of aluminates and ferrites is already occupied by insoluble calcium sulfoaluminates; the chloride remains in solution, which has a very expressed accelerating effect. The same

mechanism can be successfully applied in the case of retarders as well. These considerations explain most of the experimental results, but further examination is necessary to make this oversimplified hypothesis more accurate.

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