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THE HYDRATION OF ALITE IN THE PRESENCE OF CONCRETE ADMIXTURES

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ABSTRACT

The role of three concrete admixtures on the hydration of alite clinker is studied. The effects of the three admixtures are (i) acts as a superplasticizer; (2) acts as a retarder; and (3) acts as an accelerator. The hydration products of alite with and without admixtures, added at different dosages, is examined by DTA and TG methods. The kinetics of hydration were followed by the estimation of free $Ca(OH)_2$ liberated during hydration as well as the chemically-combined water contents of the hydration products. The results reveal that the superplasticizer did not alter the rate of hydration of alite to any considerable extent, though the workability of the paste was greatly increased. The addition of 2–4% retarder delays the hydration of alite by prolongation of the dormant period from 6 h to about 7 days. The chemically-combined water contents suggest that the suitable dosage of this retarding agent is 1.0–2.0%. When 0.15–0.25% accelerator was used, the reaction rate of alite slowed down until the end of the first 24 h and was then enhanced. The chemically-combined water content was found to go parallel with the reaction rate.

INTRODUCTION

The alite is the major constituent of portland cement. When it is brought into contact with water, the following reaction takes place

$$\underset{\text{(alite)}}{2\,(3\,CaO \cdot SiO_2)} + 6\,H_2O \rightarrow \underset{\text{(calcium silicate hydrate)}}{3\,CaO \cdot 2\,SiO_2 \cdot 3\,H_2O} + 3\,Ca(OH)_2$$

The rate of this reaction and the relative amounts of hydration products formed are known to be dependent on several factors, e.g., temperature of hydration, surface area of the starting materials, presence of admixtures and the water/solid ratio. The chemical admixtures are widely used in concrete practice and are classified into water-reducing, retarding, accelerating, water-reducing and retarding, and water-reducing and accelerating agents [1]. A knowledge of the rate of hydration of the alite in the presence of admixtures is an essential step for understanding the role of these concrete admixtures in the hydration, and consequently in the strength development of portland cement.

Due to the low degree of crystallinity of the hydration products of cements at normal temperatures, DTA as well as TG methods appear to be more extensively used than others because of their ability to detect the chemical changes occurring during the hydration [2,3]. DTA has largely been used as a technique to investigate the role of admixtures.

The objective of the present work was to clarify the influence of three different concrete admixtures upon the hydration of alite clinker using DTA and TG techniques. The effects of the three admixtures used are: (1) acts as a superplasticizer; (2) acts as a retarder; and (3) acts as an accelerator. The kinetics of the hydration were followed from 30 min up to 28 days by determining the chemically-combined water and the free $Ca(OH)_2$ contents.

EXPERIMENTAL

The alite clinker stabilized by alumina and magnesia used in the present work is a representative sample of alite provided by A. Klein of the University of California. The alite was prepared in a pilot plant rotary kiln and ground to a surface area of 3500 $cm^2\ g^{-1}$. Its chemical composition is as follows: SiO_2, 25.01; CaO, 70.94; Al_2O_3, 1.07; Fe_2O_3, 0.63; MgO, 1.65; SO_3, 0.20; and ignition loss, 0.50%. Applying the Bogue's equations one can obtain the following alite formula: $182\ CaO \cdot 62\ SiO_2 \cdot 6\ MgO \cdot Al_2O_3$ ($C_{182}S_{62}M_6A$). The phase composition of the alite clinker is as follows: $CaSO_4$, 0.34; free CaO, 1.99; C_4AF, 1.92; and alite, 95.75%.

Three admixtures were used as superplasticizer, retarder and accelerator. The superplasticizer is a sulphonated melamine formaldehyde condensate; the retarder a crude aluminium phosphate; and the accelerator is a solution mixture of inorganic and amine salts and having a chloride content of 11–12%. These admixtures were obtained from Grace Co., Italy. The plasticizer and retarder were dissolved in water at a concentration of 20%. The dosage of each was taken from 0.5 to 4% by weight of the alite clinker. The accelerator dosage ranges from 0.05 to 0.25% by weight of alite. Throughout this study, a W/S ratio of 0.25 was used. Alite was mixed with the appropriate amount of water to which the desired dosage of admixture was pre-added. Mixing was continued for 3 min in a porcelain mortar and the paste was then kept in an atmosphere of 100% R.H. until the time of test. The hydration was followed from 30 min up to 28 days. The hydration was stopped using the technique described elsewhere [4–6].

The kinetics of hydration were studied by DTA and TG techniques using a thermal analyser of the type DT-30 (Shimadzu Co., Japan) at a heating rate of 10°C min^{-1} from ambient up to 1000°C. In the TG analysis, the runs were carried out in a nitrogen atmosphere. The degree of hydration at any given age is defined as the ratio of the chemically-combined water of the paste to the corresponding value at complete hydration; the latter is reported

TABLE 1

Effect of concrete admixtures on the calcium hydroxide and combined water contents of hydrated alite

Curing time	Pure alite		Alite + plasticizer				Alite + retarder				Alite + accelerator			
	Ca(OH) (%)	Wn (%)	2%		4%		2%		4%		0.15%		0.25%	
			$Ca(OH)_2$ (%)	H_2O (%)	$Ca(OH)_2$ (%)	H_2O (%)	$Ca(OH)_2$ (%)	H_2O (%)	$Ca(OH)_2$ (%)	H_2O (%)	$Ca(OH)_2$ (%)	H_2O (%)	$Ca(OH)_2$ (%)	H_2O (%)
30 min	0.78	1.75	0.60	1.65			trace	0.50	trace	0.50				
3 h	1.40	1.85	1.55	2.50			trace	0.50	trace	0.50				
6 h	1.55	2.00	2.33	3.00			trace	0.50	trace	0.50	1.55	1.75	1.55	1.57
24 h	6.22	7.50	5.44	6.75	6.35	8.70	0.30	1.12	0.30	1.12	2.33	3.00	2.33	3.25
3 days	9.30	10.00	9.30	9.74	10.10	9.24	0.70	1.50	0.48	1.25	8.50	11.50	8.55	11.25
7 days	9.33	11.20	9.77	10.50	10.20	10.50	0.77	2.50	0.70	2.50	8.75	15.00	8.70	15.00
28 days	11.16	13.40	11.60	12.30	12.10	12.60	3.1	6.50	3.1	6.60	10.80	17.88	10.75	17.80

to be 21.16 [7]. The chemically-combined water contents as well as the water lost at 480–520°C were calculated from the TG curves. The water lost at 480–520°C was considered to be the combined water of $Ca(OH)_2$; therefore, it was employed in calculating the amounts of this compound.

RESULTS AND DISCUSSION

Table 1 shows the chemically-combined water and the free $Ca(OH)_2$ contents of hydrated alite clinker with and without the concrete admixtures at various dosages and cured to different periods. On using the superplasticizer, the results do not indicate any great difference in the amounts of chemically-combined water as well as $Ca(OH)_2$ between those of alite hydrated without admixture and that hydrated in the presence of 2 or 4%. Since the superplasticizer is an active agent [8], it is adsorbed on the alite particles, giving them a negative charge which leads to repulsion between the particles. In addition, the charges cause the development around each particle of a sheath of oriented water molecules which prevents a close approach of the particles to one another. The particles have, therefore, a great mobility, and water freed from the restraining influence of the flocculated system becomes available to lubricate the mix so that workability is increased. The use of superplasticizers is aimed at obtaining a concrete mix of normal workability but with a considerably higher strength. This goal is attained by the substantial reduction in the water/cement ratio and consequently the total porosity of the mix decreases, therefore, the strength rises.

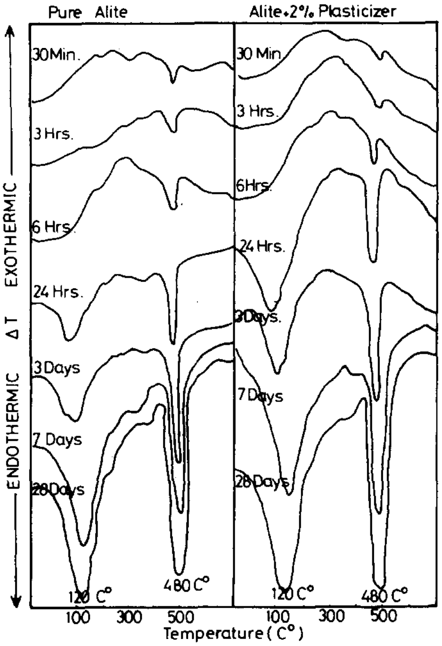
It is seen from the results of Table 1 that a 2% addition of superplasticizer gives 2.33 and 3.0% of $Ca(OH)_2$ and chemically-combined water contents, respectively, compared with 1.55 and 2.0% for pure alite after 6 h of hydration.

Figure 1 illustrates the DTA thermograms of hydrated alite with and without superplasticizer and hydrated from 30 min up to 28 days. The results

TABLE 2

Effect of dosage of retarder and accelerator of alite hydrated for three days

Retarder					
Dosage added (%)	0	0.5	1	2	4
H_2O	10.00	5.75	1.50	1.50	1.25
$Ca(OH)_2$	9.30	3.11	0.77	0.70	0.38
Accelerator					
Dosage added (%)	0	0.05	0.1	0.15	0.25
H_2O	10.00	8.50	9.50	11.50	11.25
$Ca(OH)_2$	9.30	7.77	9.35	8.50	8.55



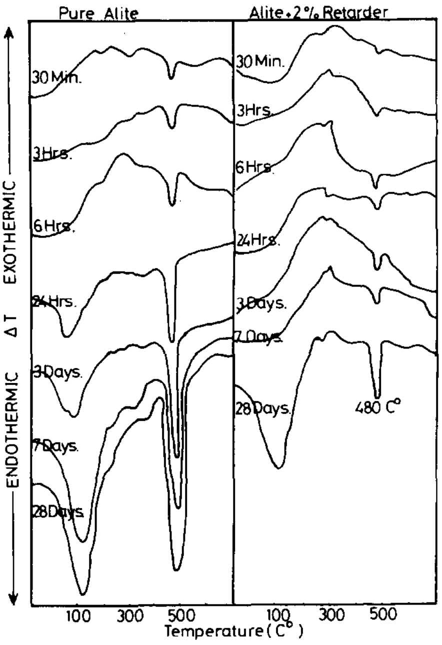


Fig. 1. DTA thermograms of hydrated alite with and without 2% plasticizer.

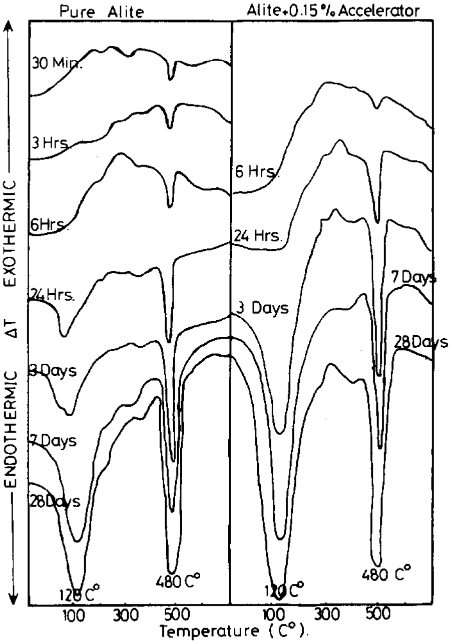
Fig. 2. DTA thermograms of hydrated alite with and without 2% retarder.

show that the endothermic effects of hydrated calcium silicate as well as $Ca(OH)_2$ in the temperature ranges 100–200°C and 48–520°C, respectively, have the same intensity for pure alite and with 2% superplasticizer. It is clear that the presence of plasticizer does not alter the rate of hydration of alite which confirms the results of $Ca(OH)_2$ and chemically-combined water calculated from the TG curves.

The influence of crude aluminium phosphate as a retarder on the hydration of alite is also shown in Table 1. The retarder, either added as 2 or 4%, reduced the rate of hydration dramatically. The chemically-combined water and free $Ca(OH)_2$ contents for the pastes hydrated for 28 days are decreased from 13.4 and 11.16 to 6.50 and 3.10%, respectively, when 2% retarder was used. This retarder lengthens the dormant period from 6 h in the case of pure alite to about 7 days when the retarder was used. The results of chemically-combined water and free $Ca(OH)_2$ for hydrated alite with 2 and 4% retarder are almost the same.

The effect of the retarder dosage on the hydration of alite can be seen in Table 2. It is clear that by using 0.5 and 1.0% retarder, the retardation effect decreases by decreasing the amount of retarder added. To get the required effect of retardation, 1–2% of this admixture is sufficient.

Figure 2 shows the DTA thermograms of hydrated alite without and with



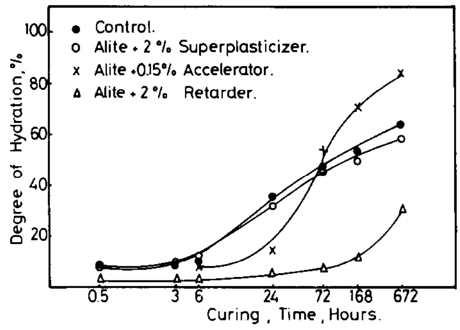


Fig. 3. DTA thermograms of hydrated alite with and without 0.15% accelerator.

Fig. 4. Effect of concrete admixtures on the degree of hydration of alite.

2% retarder as a function of aging time. The retardation is seen from the intensity of the endothermic effects at 100–200°C for calcium silicate hydrate and at 480–520°C for $Ca(OH)_2$.

Table 1 also shows the influence of the accelerator on the hydration of alite as a function of curing time. The reaction rate was slowed down until the end of the first 24 h (dormant period). For longer periods of hydration (3–28 days) the reaction rate was enhanced. The chemically-combined water contents for the 3-day samples were found to be 10.00, 11.50 and 11.25% for the hydration products of alite, alite with 0.15, and with 0.25% accelerator, respectively. The corresponding figures were 13.40, 17.88 and 17.80% after 28 days.

The accelerating action of chloride ions added in the form of $CaCl_2$ was ascribed to the formation of calcium oxychloride hydrate [9,10]. Teoreanu and Muntean [11] found a weak *d*-line in the XRD analysis at 3.28 Å for C_3S pastes hydrated with 2% $CaCl_2$ and ascribed this to the presence of $3\,CaO \cdot CaCl_2 \cdot 12\,H_2O$. The $CaCl_2$ tends to consume the liberated $Ca(OH)_2$ thus forming the complex salt. Therefore, the reaction goes faster in the right direction (or accelerated). It is likely that the effect of accelerator used in this study is, at least, partially similar to that of $CaCl_2$. The analysis of the accelerator shows that it contains 11–12% chloride ions.

Figure 3 illustrates the DTA thermograms of the hydrated alite with and without 0.15% accelerator. It is clear that the rate of hydration increases after 24 h, the extent of the endothermic peak of $Ca(OH)_2$ enhances. On prolonging the hydration for 3 days, the first endothermic effect (100–200°C) also increases. Samples hydrated for 28 days show higher values of the first effect and nearly constant intensity of the $Ca(OH)_2$ peak. A sample hydrated for 24 days gives 11.16 and 10.80% $Ca(OH)_2$ for pure alite and with 0.15% accelerator, respectively. On the other hand, chemically-combined water contents are 13.40 and 17.88%, respectively.

Table 2 also shows the effect of accelerator dosage on the hydration of alite for samples hydrated for only three days. Increasing the amount of added accelerator from 0.15 to 0.25% had no noticeable effect on the rate of hydration of alite. On decreasing the dosage to 0.05 and 0.10%, the amounts of $Ca(OH)_2$ and chemically-combined water contents are decreased. A sample with 0.05% gives lower values than 0.15% whereas 0.10% shows no great difference compared with that of alite alone. Therefore, an amount between 0.10 and 0.15% is considered optimum.

Figure 4 illustrates the degree of hydration of pure alite and with admixtures vs. curing time. The results indicate that the kinetics of hydration of pure alite and with superplasticizer is nearly the same. By using the retarder, the dormant period extends to more than 7 days. On the other hand, the accelerator delays the hydration during the first day of hydration. As the hydration progresses (3–28 days) the rate of hydration is higher than that of the pure alite.

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