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HYDRATION AND STRENGTH CHARACTERISTICS OF SYNTHETIC Al-, Mg- AND Fe ALITES

by G. Mascolo and V.S. Ramachandran

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Hydration and strength characteristics of synthetic Al-, Mg- and Fe alites (*).

G. MASCOLO ⁽¹⁾ V. S. RAMACHANDRAN ⁽²⁾

Alites containing different amounts of Al, Mg or Fe were hydrated up to 30 days and their kinetics of hydration and compressive strengths were determined. At the same degree of hydration Fe-alites showed greatest strength. There was evidence that the nature of C—S—H formed in different alites is not the same.

INTRODUCTION

The silicate-based phases, tricalcium silicate ($3\text{CaO} \cdot \text{SiO}_2$, abbreviated to C_3S) ⁽³⁾ and dicalcium silicate ($2\text{CaO} \cdot \text{SiO}_2$, abbreviated to C_2S) together constituting about 70-80 % of Portland cement much influence many of the properties of concrete. In commercial Portland cements however, these silicates are solid solutions containing a minor amount of oxides. Solid solutions of tricalcium silicate and dicalcium silicate are known respectively as alite and belite.

The major phase in Portland cement being alite, much more attention has been directed to its study than to other clinker minerals. In recent years some synthetically prepared alites have been examined with a view to investigating the possibility of producing an alite with higher reactivity and strength than the

normal alite. The hydraulic properties of alite depend on the chemical nature of the addition, its amount and the heat treatment accorded during their preparation ([1]-[7]). In spite of some work on alites controversy still exists on many aspects and no general agreement exists on the relationship between the reactivity and mechanical properties of various types of alites. In this paper alites containing different amounts of Al, Mg and Fe were prepared of same particle size and hydrated to different periods. Attempts have been made to understand the mechanical behaviour in terms of the kinetics of hydration.

EXPERIMENTAL

Pure $3\text{CaO} \cdot \text{SiO}_2$ was prepared by heating a stoichiometric mixture of CaCO_3 and SiO_2 (Reagent grade C. ERBA). Tricalcium silicate solid solutions (alites) were prepared by calcining a mixture of $\text{Al}(\text{OH})_3$, $(\text{MgCO}_3)_4$, $\text{Mg}(\text{OH})_2$, $5\text{H}_2\text{O}$ or Fe_2O_3 with stoichiometric proportions of CaCO_3 and SiO_2 . Each sample was ground in a ball mill to a Blaine fineness of $5,040 \pm 40 \text{ cm}^2/\text{g}$. The chemical composition and crystallographic forms of the samples are described in Table I.

(*) Work carried out in Naples. Supported by National Research Council of Italy (C.N.R.).

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(3) In cement chemistry $\text{C}=\text{CaO}$, $\text{S}=\text{SiO}_2$, $\text{H}=\text{H}_2\text{O}$.

TABLE I
CHEMICAL COMPOSITION AND CRYSTALLOGRAPHIC FORMS OF ALITES

Sample No.	Chemical analysis (weight per cent)						Crystallographic form
	SiO_2	CaO	Free CaO	MgO	Al_2O_3	Fe_2O_3	
1	26.07	73.47	0.33	—	—	—	T_1
2	26.08	73.17	0.27	0.45	—	—	T_1
3	25.02	71.90	0.12	1.00	—	—	T_{11}
4	25.64	72.25	0.19	2.01	—	—	T_{11}
5	25.98	73.57	0.15	—	0.32	—	M_1
6	25.68	73.00	0.11	—	0.90	—	T_1
7	25.91	73.51	0.50	—	—	0.80	T_{11}
8	26.35	72.50	0.24	—	—	1.08	T_{11}

Each sample was hydrated at 25°C to different periods viz 1, 2, 3, 5, 7, 14 and 30 days at a water/solid ratio of 0.5.

The degree of hydration at any particular period was obtained using the DTA method proposed by Ramachandran [8] and further extended by Mascolo [9]. The technique proposed by Ramachandran consists in heating a constant amount of the hydrated material ground to pass through 100 mesh sieve at a constant rate in a sensitive DTA apparatus. In the first heating cycle to 1 000°C thermal effects due to crystallization, decarbonation, dehydration of calcium silicate hydrate and recrystallisation of β -wollastonite occur. On cooling and reheating all the irreversible effects are annulled and crystalline transitions due to $3\text{CaO} \cdot \text{SiO}_2$ are registered which can be directly related to the amount of unhydrated material.

The kinetics of the hydration of alites was also followed by a conduction calorimeter containing 6 chambers. The technique enabled determination of the rate of heat development as a function of time. The sensitivity of the calorimeter was 20 mV/W.

Compressive strength of alites hydrated to different periods was obtained on mortars containing 5% quartz. The water/solid ratio was adjusted to 0.5. Each value of compressive strength was the average of 3 values determined using cubes of dimensions $4 \times 4 \times 4$ cm [10].

RESULTS AND DISCUSSION

Conduction calorimetric curves were used to determine the rate of heat development and the total amount of heat developed in 1 day. The latter was compared with the percentage hydration at 1 day (fig. 1). There seems to be a reasonable linear relationship between the extent of hydration and heat evolved. It is also apparent that all alites do not hydrate to the same extent in one day (fig. 2). In the first day samples containing 0.45% and 1.00% MgO and sample with 0.90% Al_2O_3 hydrate to the greatest degree and samples with 2.01% MgO and 0.80% and 1.08% Fe_2O_3 hydrate to the least degree. However between 1 and 7 days, samples with Fe_2O_3 show greatest increase in the rate of hydration. Some variance is also obvious in the initial rate of hydration or reactivity. Calorimetric curves indicate that in the first 3-4 hours, the period after the induction period, the rate of heat development of alites is in the decreasing order: Pure C_3S , 2.01% MgO, 0.80% Fe_2O_3 , 0.32% Al_2O_3 , 0.90% Al_2O_3 , > 0.45% MgO, 1.00% MgO > 1.08% Fe_2O_3 , whereas the total heat developed in the first 24 hours is in the order 0.90% Al_2O_3 > 0.32% Al_2O_3 , 1.00% MgO, 0.45% MgO > C_3S , 2.01% MgO, 0.80% Fe_2O_3 , 1.08% Fe_2O_3 . These results indicate that though some samples hydrate fast initially hydration slows down subsequently within a day. The converse is true for some other samples. The exception is sample containing 1.08% Fe_2O_3 which hydrates slowly in the beginning and remains so even at 1 day. In the very initial period most alites hydrate slower than pure C_3S but after a few hours alites hydrate much

faster and subsequently the total degree of hydration between samples becomes less significant. The dislocations or strains or distortions in the lattice seem to affect the nucleation and diffusion processes.

The study shows that the rate of reaction is not directly correlatable with the crystallographic form of the alite or with the type of ion in the lattice. At 1 day however, the monoclinic form hydrates slower than other crystallographic forms which is not in accordance with the results of Yamaguchi *et al.* [11].

Figure 2 shows the degree of hydration of alites at different times. Generally at 1 day these results are comparable to those by conduction calorimetry. The differences in the degree of hydration gradually narrow down at 30 days, only sample 2 (0.45% MgO alite) showing some deviation from others. The curves show that even with alites containing the same element in solid solution reactivity in terms of degree of hydration differs, especially at early times.

Figure 3 illustrates the relationship between the degree of hydration and the compressive strength of alites. In the figure curves *a*, *b*, and *c* represent an average curve for Fe, Al- and Mg-alites respectively in the hydration range between about 30% and 85%. In addition curves for pure triclinic $3\text{CaO} \cdot \text{SiO}_2$ are drawn to show the relative strength development in alites with respect to tricalcium silicate. It is interesting to note that to a good approximation, at about the same degree of hydration, the compressive strength depends on the type of the element in the solid solution. It appears that a solid solution containing any particular element produces similar hydrated product as far as compressive strength is concerned. Al-alites follow more or less the same trend as pure C_3S but the Mg-alites show some deviation after 50% hydration, giving poorer strengths than the pure C_3S . Of all alites, Fe-alites exhibit greatest deviation with respect to pure C_3S , giving much higher strengths at any degree of hydration. Also at any degree of hydration Fe-alites show greater strengths than other alites. The highest strengths in Fe-alites may be related to their slow rate of hydration in the first 24 hours. Retarding admixtures in cements are also known to increase the 28-day compressive strength compared to the cement containing no retarder. It is possible that slow rate of hydration produces C—S—H products that can be accommodated in the system without producing many strains or microcracks. In addition possibly better or greater number of interlocking bonds are formed. Sersale found evidence of more compactness in electron micrographs of hydrated Fe-alites [1]. It is possible that the products may also be different with respect to crystallinity and chemical composition.

That the type of C—S—H formed is not the same in all alites can be seen from the temperature at which recrystallization to β -wollastonite occurs in different samples (fig. 4). The temperature at which the thermal peak occurs is in the decreasing order Al-alites > Fe-alites > Mg-alites. The differences in the temperature of crystallization may be attributed to differences in crystallinity and to varying CaO/SiO_2 ratio of the C—S—H product [12].

Fig. 1. — Heats of hydration of alites compared to the degree of hydration at 1 day.

Fig. 2. — Kinetics of hydration of alites.

Fig. 3. — Compressive strengths of alites in terms of the degree of hydration.

Fig. 4. — Temperatures of the exothermal peaks due to β -wollastonite formation in hydrated alites.

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RÉSUMÉ

L'hydratation et les caractéristiques de résistance des alites synthétiques d'Al, de Mg et de Fe. — Des alites contenant différentes quantités d'Al, de Mg ou de Fe sont hydratées pendant une période allant jusqu'à 30 jours et on en détermine la cinétique d'hydra-

tation et la résistance à la compression. Les courbes calorimétriques de conduction indiquent que, malgré l'hydratation initiale rapide de quelques échantillons, celle-ci ralentit ensuite en moins d'une journée. L'étude montre également que la vitesse de la réaction ne se corrèle pas directement avec la forme cristallographique de l'alite ou avec le genre d'ion dans le réseau. Il y a quelques corrélation entre la résistance à la compression et le genre d'élément dans la solution solide. Parmi les alites mises à l'étude, les alites de Fe deviennent le plus du C_3S et leur résistance est plus élevée que celle des autres alites quel que soit le degré d'hydratation. La température à laquelle se produit la cristallisation en β -wollastonite varie d'une alite à l'autre, ce qui indique que le genre de $C-S-H$ formé n'est pas le même dans toutes les alites.

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