Influence of slag substitution on some properties of sand-lime aerated concrete

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The effect of substitution of sand with granulated slag on some properties of sand-lime aerated concrete was investigated. The compressive strength, the hydration kinetics and the nature of the hydration products were studied for samples autoclaved under 8 atm for different periods from 0.5 to 24h. The results indicate that the substitution of slag leads to a marked increase of the compressive strength compared with that of the unsubstituted samples. The extent of hydration, as measured by the chemically combined water, free lime and free silica contents, is enhanced due to the slag substitution. The X-ray diffraction results show that the hydration products are mainly tobermorite-like phases, C_4AH_{13} , C_3AH_6 and CAH₁₀ in the slagcontaining samples. Cement notations are used in the text, e.g. $C = CaO$, $S = SiO₂$, $A = Al₂O₃$ and $H = H₂O$.

1. Introduction

Several investigators have studied the hydrothermal reactions involving granulated slag and quartz activated with lime $[1-4]$ or with Portland cement clinker [5, 6]. When granulated slag powder is mixed with water at room temperature, usually no hydration products are expected to be formed. This is ascribed to the formation of acidic surface films as a small amount of calcium ions is released into the solution. In the presence of lime, reaction occurs removing this film and hydration continues as the lime breaks into the silica framework of the slag. The hydration products usually detected in the granulated slag-lime mixtures are calcium hydrosilicates and calcium hydroaluminates of varying compositions. The phase composition of these hydration products depends upon many factors such as the characteristics and proportions of the starting materials, hydration conditions, reactivity of slag, etc. Under steam curing, the immediate gain of strength in slag-lime-quartz mixtures is ascribed mainly to the hydration of the activated slag and to the reaction between lime and quartz particles. The present investigation deals with the influence of partial substitution of slag for the quartz-sand fraction on the compressive strength, kinetics of hydration and phase compositions in lime-quartz aerated concrete.

2. Experimental details

2.1. Materials

Commercial samples of hydrated lime, quartz-sand and granulated blastfurnace slag were used in this study. The chemical analyses of these materials are as follows:

hydrated lime: CaO, 70.3; SiO_2 , 0.30; Al_2O_3 , 0.70; $Fe₂O₃$, 0.80 and LOI, 27.9%;

Quartz-sand: SiO_2 , 97.5; Al_2O_3 , 0.70; CaO, 0.50; Fe₂O₃, 0.50; SO₃, 0.30 and LOI, 0.12%; and

granulated slag: $SiO₂$, 35.1; $Al₂O₃$, 14.58; CaO, 46.1; Fe₂O₃, 0.56; MgO, 2.17 and SO₃, 0.16. In addition, a BDH grade aluminium powder was used to produce the aeration.

2.2. Preparation of samples

The hydrated lime, sand and slag were separately ground to a Blaine surface area of about 2500 cm g^{-1} . The dry ground materials at the required proportions were thoroughly mixed. Mixtures composed of 70/30/0, 60/30/10 and 40/30/30 of sand/lime/slag, respectively, were prepared and all ratios are expressed on weight basis. The samples were prepared using the method previously described in detail [7]. The autoclaving conditions used were 8 atm for $\frac{1}{2}$, 2, 4, 8, 12, 16, 20 and 24h.

2.3. Methods of investigating the products

Compressive strength measurements were conducted on three dried samples from each individual mix and individual autoclaving period and the average calculated. The load was applied on a direction perpendicular to that of aeration of the samples and at a rate of 0.5 ton in⁻² min⁻¹. The hydration kinetics have been studied from the determination of the chemically combined water; this is considered to be equivalent to the percentage of ignition loss of samples which have been dried at 105° C for 24 h, and after correction for the combined water of free calcium hydroxide. In addition, free lime and free silica contents were also determined using the procedures described by Kondo *et al.* [2]. The hydration products were identified by X-ray diffraction using CuK α radiation at a scanning speed of $1^{\circ} 2\theta$ min⁻¹.

3. Results and discussion

3.1. Compressive strength

The average values of compressive strength of the

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Figure 1 Compressive strength of cellular concrete.

autoclaved products are plotted against the curing period in Fig. 1. The results indicate that the compressive strength increases with the amounts of substituted slag for sand at all autoclaving periods used. For all the mixtures, the strength reaches its maximum after 16h autoclaving and then deteriorates. The samples containing 30% slag show higher strengths than those of 10% slag or of slag-free specimens. The high strength values of the slag-substituted samples are mainly due to the high reactivity of slag as compared to sand. The increase of the slag contents leads to a further increase in the hydraulic reactivity of the mix; this is discussed further in the light of the results of the hydration kinetics and of X-ray investigation.

3.2. Kinetics of hydration

The results of chemically combined water of the products as a function of the autoclaving period are presented in Fig. 2. Examination of this figure indicates that the rate of hydration is rapid during the early stages of autoclaving up to 8 h, after which the rate slows down. The substitution of 10% slag for sand activates early hydration at 0.5 h. This result is due to the higher reactivity of the granulated slag, compared to that of sand, especially during the early stages of hydration. The chemically combined water (W_n) increases from 2.7 to 7.6% after 0.5h autoclaving, and then it becomes nearly parallel to that of slag-free samples. The substitution of additional amounts of slag (30%) enhances the rate of hydration further; the combined water content was found to be 10.5% after 0.5 h autoclaving. On further treatment, the rate of increase of W_n is rapid until 4h and then proceeds at a slower rate.

The free lime contents of the slag-free and slagcontaining specimens are plotted against autoclaving

Figure 2 Chemically combined water of autoclaved cellular concrete.

period in Fig. 3. As hydration proceeds, the results indicate that the free lime contents are completely consumed within the first 12h hydration of the slagfree samples. In the case of slag-substituted samples, this is completed after 8 h only. The presence of slag decreases the time of complete consumption of lime from 12 to 8 h due to the hydraulic reactivity of slag.

The results of free silica shown in Fig. 3 indicate that there is a marked decrease of the free silica contents up to 16h hydrothermal treatment, and then followed by a slower rate of silica consumption. However, samples containing 30% slag show another rapid rate of free silica consumption at longer periods. This is obviously due to the increasing influence of the presence of slag upon the rate and extent of the hydrothermal reactions.

Figure 3 Free silica and free lime contents of autoclaved cellular concrete.

Figure 4 X-ray diffraction traces of autoclaved cellular concrete. (Autoclaving period and slag content are given.)

3.3. X-ray diffraction

X-ray diffraction analysis was performed for the products autoclaved for different periods; only those autoclaved for 2 and 16 h are given in Fig. 4 for the slag-free, together with those containing 30% slag. Investigation of the X-ray results indicates that the presence of 30% slag (traces 2 and 4) leads to the formation of the hydrated calcium aluminates: C_4AH_{13} , C_3AH_6 and CAH_{10} , in addition to the hydrated phases of calcium silicates: tobermorite $(C_5S_6H_5)$, CSH (II). The slag-free samples (traces 1 and 3) show only the presence of calcium silicate hyrate phases. Calcium hydroxide was detected only in the samples hydrated for 2 h and disappeared completely in the 16h samples; its presence is more pronounced in the slag-free samples, which confirms generally the previous results of Fig. 3.

The hydration of slag is commonly accepted to be a topochemical reaction [8], and as shown in Fig. 2, the very early high value of combined water may be ascribed to the formation of a poorly crystallized layer around the slag grains which Regourd [9] called a "pseudomorphic layer". The formation of this layer is associated with an increase in the compressive strength. This early reaction is activated with the lime of the starting mix, and, in fact, lime in this case cannot be considered only as a simple activation catalyst but also as a main reactant, especially in the presence of quartz particles. The subsequent drop in the compressive strength after the maximum has been reached is possibly attributable to the subsequent crystallization of the products in the pseudomorphic layer to yield relatively highly crystalline products. It has been reported that highly crystalline hydration products are believed to be associated usually with strength decline [10].

If the average molar composition of the slag used in

this investigation is taken to be C_6S_4A , then the early hydration reaction may be represented as:

$$
C_6S_4A + 2C + 17H \rightarrow C_4AH_{13} + 4CSH \quad (1)
$$

The formation and subsequent grain growth of these early hydration products lead to the first maximum obtained for the compressive strength. In Equation 1 CSH is used in its broadest sense to denote CSH (II), CSH (I) or tobermorite $(C_5S_6H_5)$. With further autoclaving, further hydrothermal reactions occur between the mix components; the system is depleted of lime but silica is still available to react with C_4AH_{13} according to the following equation:

$$
C_4AH_{13} + S \rightarrow C_3AH_6 + CSH + 6H \qquad (2)
$$

On further hydration, and in the absence of free lime, the reaction with silica continues as follows:

$$
C_3AH_6 + 2S + 6H \rightarrow CAH_{10} + 2 \text{ CSH} \quad (3)
$$

The sequence of events represented by Equations 1 to 3 indicate that the slag might hydrate as a separate phase in the mix. Slag has been supposed to hydrate slowly, but Coale *et al.* [11] showed that slag activated with a very small amount of lime hydrates rather rapidly; this fact has also been pointed out by many investigators [12]. The present results support this point of view and also show that during hydrothermal treatment, the reaction is steadily self-accelerating throughout the test period, to form a series of hydration products. In the present system, the main hydration products are: CSH (I, II or tobermorite), C_4AH_{13} , C_3AH_6 and CAH_{10} which formed in this order as free lime content decreased in the reaction medium.

Formation of the calcium hydroaluminate phases are expected to influence the compressive strength differently according to the individual intrinsic **strengths and to the formed amounts of each phase.** C_4AH_{13} is formed as hexagonal plates which play the **role of crystalline bridges between the unreacted** grains. C_3AH_6 is cubic, while CAH_{10} is reported to be **finely divided, crumpled or rolled foils or hexagonal prisms. It is a matter of fact to assume that the morphology of each of these hydration products, as well as the mode of binding between the products and the unreacted grains, will affect the compressive strength of the products. This fact extends also to cover the influence of the morphology and C/S ratio of the calcium hydrosilicate phases. The maximum and minimum strengths shown in Fig. 1 are believed to be closely associated with the formation, crystal growth and the transformation of the hydration products to other phases according to their sequence of formation.**

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