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Fig. 1

Figure 1: Fig. 1

Abstract

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ON THE CHANGE IN DISPERSITY DURING THE HYDRATION OF CALCIUM SILICATES β-Ca_2SiO_4 and Ca_3SiO_5

(Presented by Academician P. A. Rebinder, 25 XII 1961)

The dispersity of inorganic binding materials and of the products of their hydration, as has repeatedly been pointed out in the works of P. A. Rebinder and coworkers (1-7) and of other investigators (8,9), is an important factor in structure formation, making it possible to control the rate of hardening processes and, in a number of cases, the properties of the final hardened structures. The most reliable data on the dispersity of the products of complete hydration of cement and of its principal constituents—calcium silicates β-Ca_2SiO_4 and Ca_3SiO_5 (abbreviated C_2S and C_3S)—are given in the works of Brunauer and some other investigators (10,11), but these do not consider the relation between the dispersity of hydrosilicates and the conditions of their formation. We have studied the change in dispersity (S_1) during the hydration process of C_2S and C_3S, in parallel with the kinetics of structure formation, using certain methods for accelerating hydration: increasing the dispersity of the initial silicates, raising the storage temperature of the specimens, and applying disaggregation (6). The characteristics of the C_2S and C_3S used were given by us earlier (12). The study was carried out on concentrated suspensions (pastes) of silicates in mixtures with ground quartz sand ($S_0 = 0.3$ m^2/g by BET), carefully protected from the action of CO_2 in the air. Measurements of S_1 and S_0 were performed on a Khodakov-Sominskii apparatus (13) by low-temperature adsorption of nitrogen. The dispersity of the initial silicates was varied by grinding in a vibratory mill within the limits 0.4-1.2 m^2/g; the concentration of silicates in the pastes was 10 and 20% (by weight of the dry mixture). Drying of the hydrated pastes before determination of S_1, as well as determination of the degree of hydration W, was carried out by a method analogous to that in work (10).

Fig. 1. Kinetics of hydration and structure formation at 20° and W/S = 0.3. *a*—β-C_2S (20% and 80% SiO_2), $S_0 = 0.8$ m^2/g; *b*—C_3S (10% and 90% SiO_2), $S_0 = 0.4$ m^2/g.

Fig. 2

Figure 2: Fig. 2

1—content of bound water in % of the dry residue (W), 2—specific surface of the hydrated mixture (S), 3—plastic strength (P_m).

In Fig. 1 typical curves are compared for the change with time of S_1 of hydrated mixtures (silicates with sand), as well as of W and plastic strength P_m for C_2S (a) and C_3S (b). It is evident that the form of all the kinetic curves is the same —the greatest rate of the process is at the beginning of interaction with water, followed by gradual slowing. The coincidence of the curves $S_1 = f(\tau)$ and $W = f(\tau)$ is noteworthy, indicating proportionality between these quantities. In this connection it is of interest to consider the dependence $S_1 = f(W)$ under various hydration conditions.

The dependence of S_1 of hydrated mixtures on their hydrosilicate content for C_2S and C_3S of different initial dispersities at 20° is shown in Fig. 2a. The amount of hydrosilicate is determined from W', calculated from hydration equations that have received reliable physicochemical substantiation (^{10}). From these works it follows that the hydrosilicate formed during hydration of C_2S and C_3S under conditions of a saturated $Ca(OH)_2$ solution is identical, and its composition is defined as $Ca_3Si_2O_7 \cdot 3H_2O$. During prolonged hydration in our experiments, the interaction of $Ca(OH)_2$, liberated during hydrolysis of the silicates, with the filler becomes noticeable, especially clearly in the case of C_3S and with increasing temperature. In these cases the amount of hydrosilicate is given with a correction for the interaction of $Ca(OH)_2$ with SiO_2. The correction was introduced

Fig. 2. Specific surface area of hydrated mixtures of β-C_2S and C_3S. a—20°, b—preparation of pastes at 20°, storage at 60°. β-C_2S (20%): 1—0.4; 2—0.8, 3 —1.2 m^2/g; C_3S (10%): 4—0.4; 5—0.8, 6—1.2 m^2/g; 7—β-C_2S (10%) after dry grinding to 1.2 m^2/g, disaggregated for 3 min with 50% water.

on the basis of determinations of insoluble SiO_2, with the assumption made that in this reaction the same hydrosilicate is formed as in the direct hydration of anhydrous silicates. The correctness of this assumption is confirmed by the invariably identical rectilinear character of the dependence shown in Fig. 2.

Fig. 2b shows the dependence of S_1 of hydrated C_2S and C_3S (in mixtures with sand) for cases of somewhat modified hydration conditions. Increasing the hydration rate of silicates of different dispersity, initially hydrated at 20°, by further continuous holding at 60°, and also by the use of disaggregation, made it possible in a number of cases to achieve complete hydration in periods of less than 1 month. The limiting content of bound water in the hydrated mixtures was: for C_2S (20%)—4.00%, for C_3S (10%)—2.31%, and the corresponding amounts of hydrosilicate—19.0% and 7.3%. The excess hydrosilicate in the mixtures compared with these values arises through the interaction of $Ca(OH)_2$

Fig. 3. Dependence of the plastic strength of pastes of β-C_2S and C_3S on the hydrosilicate content. Symbols as in Fig. 2.

Figure 3: Fig. 3. Dependence of the plastic strength of pastes of β-C_2S and C_3S on the hydrosilicate content. Symbols as in Fig. 2.

with the filler. In all the investigated cases a single rectilinear dependence was obtained for S_1 of the hydrated mixtures on their total hydrosilicate content. This indicates the constancy of the specific surface area of the hydrosilicate (S_2) throughout the entire hydration process, and also the independence of this characteristic from the nature of the initial silicate (C_3S or C_2S), from S_0, C_3S and C_2S, and from small changes in the hydration conditions used in the na-

experiments. This assertion is also valid with respect to the hydrosilicate formed under these conditions through interaction with the filler.

Calculation of S_2 of the hydrosilicate on the basis of the data obtained gives a value of 50 ± 3 m^2/g, which corresponds to colloidal dispersity. This value is a stable characteristic of the highly basic hydrosilicate formed during the hydration of C_2S and C_3S under these conditions. Obviously, S_2 of $Ca(OH)_2$, which forms simultaneously, may be neglected in comparison with S_2 of the hydrosilicate. The initial mixtures of silicates with filler have negligibly small S_0; therefore the straight lines in Fig. 2 practically pass through the origin. For mixtures containing this hydrosilicate as the only highly dispersed component, as in the cases studied by us, S_1 can serve as a measure of its amount.

The stability of S_2 of the hydrosilicate, and its independence of the nature of the starting silicate and of other factors, makes it possible to assume that the strength of the hardening structures formed in the suspensions under study will likewise not depend on these factors to the extent that structure formation is determined by the dispersity of the hydration products. Fig. 3 shows the dependence of the plastic strength P_m of the investigated hydrated mixtures of C_3S and C_2S (with ground sand) of different initial dispersity on the total hydrosilicate content in these mixtures, which coincides for C_2S and C_3S.

Fig. 3. Dependence of the plastic strength of pastes of β-C_2S and C_3S on the hydrosilicate content. Symbols as in Fig. 2.

Obviously, P_m is, to a first approximation, a function only of the total hydrosilicate content, is the same at equal content for C_2S and C_3S, and does not depend on the initial dispersity of the silicates.

The differences in the binding properties of C_3S and C_2S are reduced mainly to the higher rate of hydration and hardening of the former. It also follows from Fig. 3 that the question of the optimum initial dispersity does not have the significance in the case of calcium silicates that it may have for other binders. The role of increasing the fineness of grinding of the silicates within the limits attainable at the present time is likewise reduced to accelerating their hydration and hardening, whereas the structure-forming properties of the hydrosilicate do not change appreciably. This may be connected with the relatively low fineness of grinding attainable at present. It is generally accepted that, in hardened cement stone, $Ca(OH)_2$, liberated in the process of hydration of calcium silicates, mainly C_3S, takes an active part in the formation of the hardening structure, creating a strong crystallization framework. As our data show, the presence of $Ca(OH)_2$ in the systems investigated does not affect the strength of their dispersed structures.

The regularities found by us are readily explicable from the standpoint of the crystallization theory of hardening. It is known that the dicalcium hydrosilicate formed during hydration of C_2S and C_3S under these conditions has fibrous submicroscopic crystals of the tobermorite-crystal type. The constancy of its S_2 found by us in the hydration process may be regarded as the result of the growth of fibrous crystals of hydrosilicate predominantly in length, without substantial change in cross section. In this case $S_2 = 2/r \cdot \delta = \text{const}$. The radius of the crystal cross section determined from this relation is $r = 0.015\ \mu$, which agrees with data from electron-microscopic observations by various authors ([10,14]).

Assuming that the value of the radius is determined by the concentration of supersaturated silicate solutions, in the medium of which the formation of hydrosilicate crystallization centers occurs, it is in principle possible to calculate the magnitude of the relative supersaturation required for the formation of a nucleus of such a radius. The absence of reliable data on the values of the molecular weight and surface tension of hydrosilicate permits only the observation that, in order of magnitude, this value corresponds to the metastable solubility of calcium silicates found earlier by us ([12]) and independently by Ratinov ([15]).

According to our data, the metastable solubility of C_2S and C_3S is practically identical over a wide range of concentrations of $\mathrm{Ca(OH)}_2$, which also explains the identical S_2 and identical structure-forming properties of hydrosilicates during their hydration and hardening.

The statements found in the literature concerning the topochemical character of the interaction of calcium silicates with water, with the formation of tobermorite-like phases and their subsequent dispersion ([14]), appear to us, with respect to the hydration conditions we investigated, to be erroneous and based on a nonquantitative approach to the consideration of the processes of hydration of binders.

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