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REACTION OF CALCIUM SILICATES WITH SILICA DURING HYDROTHERMAL HARDENING

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REACTION OF CALCIUM SILICATES WITH SILICA DURING HYDROTHERMAL HARDENING

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One method of intensifying hardening of cement materials is autoclave treatment. During this treatment it is possible to add to the cement significant amounts of ground quartz sand without lowering the strength of the article. However, the reactions of sand with cement have been insufficiently studied; therefore, selection of the optimum mineralogical composition of the cement and autoclaving regime for the preparation of articles of high strength cannot be satisfactorily made.

TABLE 1

Results of the Chemical Analysis of the Raw Mixtures and the Autoclaved Samples (in %)

Samples with tricalcium silicate								Samples with dicalcium silicate (β-form)					
8 tech. atm., 8 hours				16 tech. atm., 8 hours				8 tech. atm., 8 hrs			16 tech. atm., 8 hrs.		
Content of crystalline silica in the raw mixture	Content in autoclaved samples			Content of crystalline silica in the raw mixture	Content in autoclaved samples			Content of crystalline silica in the raw material	Content in autoclaved samples		Content of crystalline silica in the raw mixture	Content in autoclaved samples	
	Free SiO_2	Free CaO	Loss on ignition		Free SiO_2	Free CaO	Loss on ignition		Free SiO_2	Loss on ignition		Free SiO_2	Loss on ignition
0	—	13.38	12.74	0	—	13.65	12.19	0	—	3.18	0	—	6.92
5.28	3.98	11.86	12.27	5.24	3.83	12.52	11.95	5.11	3.15	4.58	5.00	2.98	6.38
10.17	7.91	10.37	12.15	10.01	7.19	10.90	11.91	10.09	6.20	4.35	10.11	4.22	7.49
20.17	16.02	8.93	10.77	20.37	14.34	9.12	10.78	20.16	13.70	5.06	—	—	—
29.91	22.75	6.03	9.27	29.71	20.60	3.81	8.80	29.90	21.93	5.44	30.11	19.07	7.28
40.00	31.85	3.63	7.81	39.93	25.30	0.62	7.75	39.84	30.00	4.75	39.82	26.43	6.86
49.94	39.13	0.76	5.84	49.81	31.60	0.05	5.16	49.99	39.81	4.72	49.63	39.31	5.84
72.47	58.23	—	5.00	69.56	54.35	—	6.85	70.00	61.77	1.13	—	—	—
89.79	82.9	—	2.44	90.00	32.35	—	2.16	90.00	85.90	0.69	—	—	—

In recent years, Kalousek [1, 2], by means of x-ray and thermal analysis, succeeded in identifying two new phases in hardened porland cement containing sand. According to his data, the first of these – the α-hydrate of dicalcium silicate – decreases the strength of the articles, and the second – a hydrosilicate with a basicity of 0.9 – increases strength.

Below are presented the results of an investigation of the reactions of crystalline silica with the basic minerals of portland cement clinkers, di- and tricalcium silicates.

The calcium silicates (with impurities of the order of 3%) used in the experiments were synthesized by means of repeated calcinations, and the finely ground quartz sand was treated, after grinding, with hydrochloric acid. The samples, 1.41 × 1.41 × 1.41 cm cubes, were prepared from soft paste. After a day in the molds, the samples were removed and placed in the autoclave where they were soaked for 8 hours at 8 or 16 technical atmospheres. The strength was determined 12 hours after the end of the soaking. The data are presented in Figure 1.

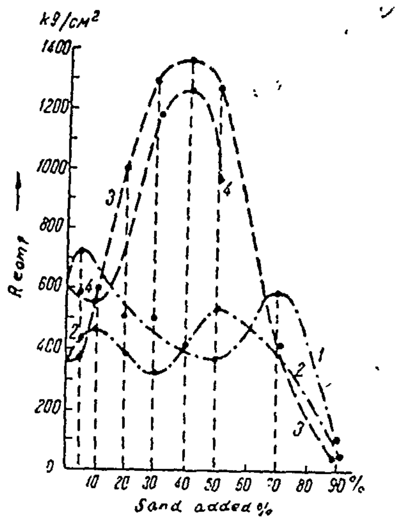

Figure 1. Strength of samples of mixtures of calcium silicates with sand after hydrothermal treatment. 1) samples of $3CaO \cdot SiO_2$ with sand, soaked 8 hours at 8 technical atm.; 2) the same soaked 8 hours at 16 tech. atm.; 3) samples of β-$2CaO \cdot SiO_2$ with sand, soaked 8 hours at 8 tech. atm.; 4) the same soaked 8 hours at 16 tech. atm.

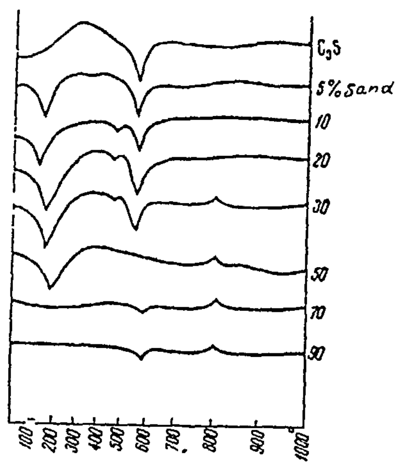

Figure 2. Differential thermal analysis curves of samples of tricalcium silicate (C_3S) and added sand. Samples soaked 8 hours at 16 technical atmospheres.

The differential thermal analysis curves are presented in Figures 2 and 3. All curves were recorded at a constant rate of temperature rise (20° per minute). The endothermic effect at 450° corresponds to the α-hydrate of dicalcium silicate; the exothermic effect at about 800° corresponds to the hydrosilicate with a basicity of 0.9 (according to the data of Kalousek). The endothermic effects at 550 and 575° relate, respectively, to the dehydration of calcium hydroxide and a polymorphic transformation of quartz.

On the basis of these data and the analytical data (Table 1), the mechanism of the reaction of clinker minerals — silicates — with sand during hydrothermal treatment is as follows.

Tricalcium silicate. Hydration of pure tricalcium silicate (without added sand) at temperatures up to 200° always leads to the formation of the α-hydrate of dicalcium silicate [3, 4]. In samples with sand, the coexistance of the following compounds (besides unreacted sand) is possible: undecomposed tricalcium silicate, calcium hydroxide, the α-hydrate of dicalcium silicate, and the hydrosilicate with a basicity of 0.9. From the results of the chemical analysis (Table 1) it is possible to calculate the content of these compounds in the samples. Graphs corresponding to such calculations (for one regime) are presented in

Figure 4. Note that the content of these compounds were calculated on the basis of calcium silicates, not of the hydrosilicates.

As seen from a comparison of Figures 1 and 4, the minimum strength of the sample corresponds to the maximum content of the α-hydrate, and maximum strength corresponds to the maximum content of the slightly basic silicate. The increase in strength with small additions of sand can be associated with an acceleration of the hydrolysis of tricalcium silicate.

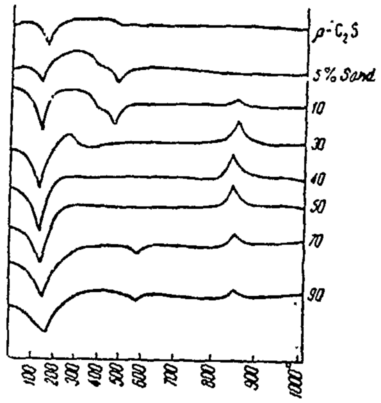

Figure 3. Differential thermal analysis curves of samples of dicalcium silicate (β-C_2S) with sand additions. Samples soaked 8 hours at 16 technical atmospheres.

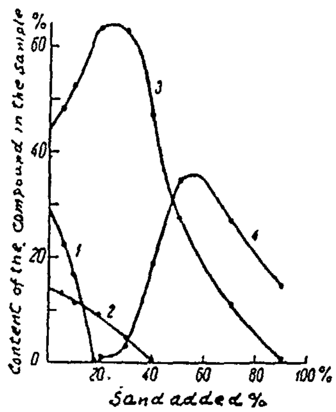

Figure 4. Composition of cements in samples of tricalcium silicate with added sand, soaked 8 hours at 16 tech. atm. (in weight % of the total sample).
1) undecomposed tricalcium silicate; 2) free calcium hydroxide; 3) α-hydrate of dicalcium silicate; 4) hydrosilicate with a basicity of 0.9.

Dicalcium silicate (β - modification). Hydration of this compound under the conditions of the experiment can lead to the formation of several hydrates of dicalcium silicate [4]. It is not possible to calculate the amount of each of them and also of the unreacted starting material. However, it is possible to calculate the total amount of compounds with a basicity of 2, both hydrated and unhydrated, and also the hydrosilicate with a basicity of 0.9. The results of the calculations (for samples autoclaved 8 hours at 8 tech. atm.) are presented in Table 2.

From a comparison of these data with Figure 1, it is seen that maximum strength corresponds to maximum content of slightly basic hydrosilicate. The decrease in strength with small additions of sand is associated with the formation of large amounts of α-hydrate (Figure 3).

Thus maximum strength of the samples prepared from each of the clinker materials – silicates – corresponds to the maximum content in these samples of calcium hydrosilicate with a basicity of 0.9; the latter, in turn, depends on the amount of crystalline silica added.

The optimum amount of this addition depends on the type of silicate, on the autoclaving regime, and, evidently, on fineness of grinding of both the silicate and the sand.

TABLE 2
Content of Dicalcium Silicates (total) and Silicate with a Basicity of 0.9 in Samples of β-$2CaO \cdot SiO_2$ (in %)

Crystalline silica in the original material	Dicalcium silicates in the autoclaved mixtures	Slightly basic silicate (hydrosilicate) in the autoclaved mixtures
0	96.82	0
5.11	86.40	5.85
10.09	77.70	11.74
20.16	62.90	18.35
29.90	51.10	21.50
39.84	32.15	27.20
49.99	27.90	27.57
70.00	12.90	24.20
90.00	2.44	11.95

It is interesting to note that an increase in pressure, that is, an increase in temperature, lowered the possible maximum strength of the samples and, moreover, decreased the optimum amount of sand. In our experiments, the possible maximum strength of the samples of β-$2CaO \cdot SiO_2$ with sand were higher than the strengths of the samples of $3CaO \cdot SiO_2$ with sand by a factor of approximately 2.5. It is also pointed out that the strength of the samples of pure β-$2CaO \cdot SiO_2$ was lower than that of the samples of pure $3CaO \cdot SiO_2$ when the hydrothermal treatment was carried out at 8 tech. atm., and higher when the treatment was at 16 tech. atm.

It should be stressed that it was established in this work that both the dicalcium and the tricalcium silicates become bonded to the sand during autoclaving. The strength of the samples of β-dicalcium silicate and sand (optimum composition) were higher than the strength of the samples of tricalcium silicate and sand.

Although the results obtained on the clinker materials cannot be transferred directly to sandy Portland cements, they do confirm that, by changing the dosage of sand and the autoclaving regime, it is possible to obtain concrete and ferroconcrete articles from belite clinkers with the addition of sand which are not inferior to articles made from cement from alite clinkers.

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