

# Effect of Polymorphism of Tricalcium Silicate On Its Reactivity\*

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Early tests on the strength of tricalcium silicate preparations, carried out at the Building Research Station, are summarized and compared with those obtained in a new series of tests. The latter series was intended to bring out any differences in strength which could be ascribed to changes in the structure of the  $C_3S$ . However, chemical effects caused by the fluorine used as a stabilizer were predominant; it is tentatively concluded that effects of structure are small, except possibly for the monoclinic-trigonal change, which may produce low strengths in some circumstances.

•IT FREQUENTLY happens in research that it is just as hard to ask the right question as to find the right answer. In so often asking the right questions T. C. Powers has exerted a positive influence on research on cement; not only has he set out to find the answers himself, but by asking the questions he has encouraged others to make the attempt. In 1956 Powers visited England and lectured at the Institution of Civil Engineers. Among the questions he asked was the following: Given that when tested alone or together with gypsum, the cement compounds hydrate at different rates, do they necessarily do so when present together in the form of cement clinker? Tentative evidence then available suggested no differentiation in the rate of attack; the attempts to explain this anomaly led among many interesting lines of research to new theories concerning the role of diffusion in hydration reactions and to improvements in quantitative X-ray analysis.

The Building Research Station had been working for some years on cements made from waste materials or impure limestone. In particular, close association with a cement works in Africa using a carbonatite limestone had convinced us that the  $C_2S$  in this cement was more reactive than a "pure"  $C_2S$  (i.e., a preparation stabilized in the  $\beta$  form with  $B_2O_3$ ). Nurse (1) had already shown that this was possible. In preparing material for structural studies by Jeffery we had encountered metastable low-temperature inversions in  $C_3S$  (2). We now began to ask whether  $C_3S$  also could vary in its reactivity toward water.

## POLYMORPHISM OF $C_3S$

Before discussing this question, it will be necessary to summarize the latest investigations on the polymorphism of  $C_3S$ . In an investigation of pure  $C_3S$  using high temperature X-ray powder diffraction and DTA, Yannaquis et al. (3) indicated the occurrence of three triclinic polymorphs ( $T_1$ ,  $T_{11}$ ,  $T_{111}$ ), two monoclinic polymorphs ( $M_1$ ,  $M_{11}$ ) and a trigonal polymorph (R). Midgley and Fletcher (4) had reservations about the evidence for the existence of two monoclinic polymorphs but gave additional DTA data confirming the occurrence of three triclinic polymorphs on heating pure  $C_3S$ . Miyabe and Roy (5) thought that three triclinic polymorphs probably occurred, but could detect only one monoclinic and a trigonal polymorph. In a more detailed

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TABLE 1  
STRENGTH OF C<sub>3</sub>S PREPARATIONS  
(psi, tested on 1:3 mortar in 1/2-in. cubes)

Reference	Type of C <sub>3</sub> S	Specific Surface (sq cm/g)	Age (days)		
			1	3	28
(2)	Triclinic T <sub>1</sub> , pure	4000	2800	4300	5500
(8)	Triclinic T <sub>1</sub> , pure	3400	1720	2670	3400
(8)	Triclinic T <sub>1</sub> , pure*	3500	1300	3030	3530
(8)	Triclinic T <sub>11</sub> , C <sub>154</sub> M <sub>2</sub> S <sub>52</sub>	3500	1340	2790	3310
(8)	Monoclinic, C <sub>150</sub> M <sub>5</sub> S <sub>52</sub>	3500	2320	3590	4110
(2)	Monoclinic (Jeffery's alite) C <sub>54</sub> S <sub>16</sub> MA	4000	1800	4300	5100
(8)	Trigonal 2.9 % MnO + 0.7 % F	3400	740	900	1320

\*No gypsum; all others 4 percent gypsum.

TABLE 2  
STRENGTHS OF SOME POLYMORPHS OF C<sub>3</sub>S  
(psi, tested on 1:3 mortar in 1/2-in. cubes)\*

Addition	Structure	Age (days)		
		1	3	28
0.38 % F	T <sub>1</sub>	1700	1920	1900
0.74 % F	T <sub>11</sub>	1070	1470	1790
0.80 % MnO	T <sub>11</sub>	2100	2160	3640

\*Specific surface 3,500 sq cm/g, 4 percent gypsum (1.9 percent SO<sub>3</sub>).

analysis of the data of (3) Regourd (6) suggests that the M<sub>11</sub> structure may in fact be orthorhombic. Woermann et al. (7) reported data on the polymorphic forms of C<sub>3</sub>S stabilized at room temperature by the presence of foreign ions and identified the phases obtained with the T<sub>1</sub>, T<sub>11</sub> and M<sub>1</sub> phases of Yannaquis et al., but could not find the T<sub>111</sub> phase. They confirmed the existence of an R phase, but were uncertain about the M<sub>11</sub> structure. Although the data generally support the occurrence of three triclinic polymorphs, they are not conclusive and it seems possible that the T<sub>111</sub> phase only occurs on heating an extremely pure preparation of C<sub>3</sub>S. The practical distinction between the possible M<sub>11</sub> phase and the R phase is a very fine one and can easily be ascribed to inadequate temperature control in high-temperature experiments and inhomogeneity of the phase in room temperature observations.

In the present paper the interpretation of Woermann is generally accepted and the phases are designated T<sub>1</sub>, T<sub>11</sub>, M<sub>1</sub> and R. (The customary abbreviation of CaO = C, SiO<sub>2</sub> = S, Al<sub>2</sub>O<sub>3</sub> = A, MgO = M is used in this paper; to avoid confusion with M = MgO the M<sub>1</sub> phase will be spoken of as "mono" or "monoclinic.") The trigonal phase occurring in some commercial cement clinkers is clearly the R phase, but it is possible that the trigonal phase reported in this paper as occurring in synthetic preparations containing MnO and CaF<sub>2</sub> is the M<sub>11</sub> phase.

The interpretation as T<sub>1</sub>, T<sub>11</sub>, Mono or R followed from an analysis of the complex reflection obtained on a diffractometer trace in the region of 2θ at about 52 deg, CuKα radiation. The R phase gives a single reflection, Mono a doublet and T a triplet. The relative positions of the 040, 620 and 620 reflections decide the probable structure. Where the reflections are very little different from those of pure triclinic C<sub>3</sub>S quenched to room temperature the structure T<sub>1</sub> is assigned. A definite closing up on the three reflections indicates the T<sub>11</sub> structure.

TABLE 3  
 COMPRESSIVE STRENGTH OF MAGNESIA SERIES  $C_{156-x}M_xS_{52}$ \*

Composition and Structure	Age	Percent SO <sub>3</sub>			
		0	1	2	4
Pure C <sub>3</sub> S	1 day	1785	1707	1400	1184
	3 days	2292	2217	2007	1760
	7 days	2822	2773	2422	2028
	T <sub>1</sub> 28 days	3585	3344	3164	2400
	3 months	4105	4235	3690	3245
x = 1	1 day	1660	1345	1228	1035
	3 days	2182	1840	1699	1408
	7 days	2690	2375	2183	1754
	T <sub>1</sub> 28 days	3794	3468	3031	2423
	3 months	3882	3416	3202	2810
x = 2	1 day	1631	1682	1250	1557
	3 days	2392	2410	2056	1780
	7 days	2998	3280	2698	2308
	T <sub>11</sub> 28 days	3729	3716	2823	2921
	3 months	4310	4039	3340	2838
x = 5	1 day	1485	1414	1079	1115
	3 days	2038	2211	1811	1573
	7 days	2483	2830	2416	2134
	Mono 28 days	3879	3925	3266	2890
	3 months	4633	4582	3844	3497
x = 6	1 day	1371	1449	1126	941
	3 days	1946	1871	1606	1315
	7 days	2390	2410	2230	1804
	Mono 28 days	3552	3402	2810	2437
	3 months	4689	4116	3683	2966

\* Psi, tested on 1:3 mortar in 1/2-in. cubes, 1 day in moist air, then stored in water.

### STRENGTH OF C<sub>3</sub>S PREPARATIONS

Jeffery (2) had already quoted strength results obtained at the Building Research Station on pure C<sub>3</sub>S and alite of his suggested composition. These results were compared with some more recent observations reported by Nurse (8); Table 1 is reproduced from that paper, with the addition of identification of the polymorphism according to the nomenclature of Yannaquis et al. (3).

Welch and Gutt (9) have published a graph showing the drop in strength of C<sub>3</sub>S containing increasing quantities of fluorine. Some C<sub>3</sub>S was formed in the mixes of higher fluorine content, but the two mixes lowest in fluorine were essentially all C<sub>3</sub>S. Their strengths are given in Table 2, together with those of a mix prepared by Gutt, containing added MnO.

At this stage the results of the detailed study of the effect of MgO on C<sub>3</sub>S polymorphism by Midgley and Fletcher (4) became available, and it was decided to design an experiment in the hope of distinguishing between the effects of structural change and chemical composition. Because of possible complications introduced during setting by the formation of complex aluminates, Al<sub>2</sub>O<sub>3</sub> was avoided as a stabilizer; fluorine was included because of the strong effects previously noted (9) and because no other stabilizer had been found to produce a trigonal or near trigonal structure. Because of the observations of Gutt and Welch on clinkers containing fluorine, varying quantities of gypsum were nevertheless added in preparing the experimental cements.

Five preparations were made up in the series  $C_{156-x}M_xS_{52}$  in which x took the values 0, 1, 2, 5, 6. Each of these preparations was also repeated with the addition of CaF<sub>2</sub>

TABLE 4  
 COMPRESSIVE STRENGTH OF MAGNESIA AND  
 FLUORINE SERIES  $C_{156-x}M_xS_{52} + 0.5$  PERCENT  $F^a$

Composition and Structure	Age	Percent $SO_3$				
		0	1	2	4	
$C_3S + 0.5\%$ F	1 day	1011	994	977	765	
	3 days	1619	1505	1453	1106	
	7 days	1990	2102	1930	1490	
	$T_{11}$	28 days	2924	2580	2650	2030
	3 months	—	—	—	—	
x = 1 F = 0.5%	1 day	882	767	688	704	
	3 days	1434	1476	1425	1216	
	7 days	2142	2287	1907	1772	
	$T_{11}$	28 days	3085	2838	2875	2508
	3 months	3410	3028	2908	2850	
x = 2 F = 0.5%	1 day	990	989	867	724	
	3 days	1765	1872	1529	1087	
	7 days	2478	2465	2059	1672	
	$T_{11}$	28 days	3436	3445	2919	2430
	3 months	3639	3493	3093	2761	
x = 5 F = 0.5% Mono	1 day	967	794	754	531	
	3 days	1624	1603	1331	1094	
	7 days	2107	1768	1933	1423	
	$T_{11}$	28 days	3224	3151	3110	2186
	3 months	3621	3408	3102	2633	
x = 6 F = 0.5% Mono	1 day	850	895	832	798	
	3 days	1524	1881	1655	1375	
	7 days	1966	2527	2037	1843	
	$T_{11}$	28 days	2657	3008	2334	2368
	3 months	3152	3334	3625	3198	

<sup>a</sup>Psi, tested on 1:3 mortar in  $\frac{1}{2}$ -in. cubes, 1 day in moist air, then stored in water.

and subtraction of CaO so that 0.5 percent fluorine remained in the mix. The preparations were reacted in the solid state at 1500 C and were carefully checked for completeness of reaction and chemical composition. The average percentage loss of fluorine during heating was 10 percent of the total added. To obtain a preparation as nearly as possible completely in the monoclinic form, the fluorinated compositions with  $x = 5$  and  $x = 6$  had to be water quenched. All others were air quenched. All preparations were then ground with gypsum to give cements containing 0, 1, 2 and 4 percent  $SO_3$ .

The resulting cements were tested for compressive strength by a slightly modified form of Parker's procedure (10). The results are given in Tables 3 and 4. Each result is the mean of the six cubes tested.

#### DISCUSSION AND TENTATIVE CONCLUSIONS

The making of strength tests on  $\frac{1}{2}$ -in. cubes is not as reliable as could be wished, and detailed statistical treatment of the data has not yet been attempted. As a guide, the figure 10.9 percent for the coefficient of variation as obtained by Forrester may be quoted (11). It appears that the effect of adding increasing amounts of gypsum to any of the compositions is to decrease uniformly the strength at all ages. There were no dramatic losses of strength at particular combinations of fluorine and gypsum content as noted by Welch and Gutt (9) on clinker compositions. Other indications at the moment are that in this series the  $T_{11}$  structure may be marginally stronger than the  $T_1$  structure, but as the content of stabilizer increases and the  $M_1$  (monoclinic)

structure takes over, this advantage is lost. In all cases the mixes containing 0.5 per cent fluorine were substantially weaker than the corresponding mixes without, and this effect seems unrelated to structural changes.

Taking all the Building Research Station results together (it is not possible to include other data because of differences in testing technique), and allowing for differences in fineness, gypsum content, etc., the picture at the moment seems to be as follows: leaving aside samples containing fluorine, only one  $T_1$  structure has been tested which was not a pure  $C_3S$ ; it had the lowest strength of the five  $T_1$  structures tested but the result may not be significant. The  $T_{11}$  structures tested fall into two clear groups, with those containing fluorine giving low strengths;  $T_{11}$  structures without fluorine may be marginally stronger than similar  $T_1$  structures. Monoclinic structures give about the same strength as  $T_1$  structures. No trigonal structures were obtained without fluorine; trigonal structures containing fluorine are very much lower in strength, at least at early ages, than  $T_{11}$  structures or monoclinic structures containing fluorine, but they contain more fluorine and the effect of fluorine on strength is very marked.

It seems fairly certain that  $T_1$ - $T_{11}$ -Mono structural changes do not have a strong influence on strength. The effect of the change to trigonal is still in doubt. Fluorine has a specific effect on the strength of  $C_3S$  independent of structural changes, but markedly influenced by the presence of other impurities, and when these are present by gypsum content also.

The indications are that it would be unwise to draw conclusions concerning the effect of structural changes on strength from mixes containing fluorine. Unfortunately we have not succeeded in synthesizing a trigonal  $C_3S$  without fluorine. Thus the only evidence on the trigonal form is the low strength obtained by Gutt on  $C_3S$  containing Mn and F. This does not, however, agree with the observation that the strengths of those commercial cement clinkers which have been found to contain  $C_3S$  in the trigonal form do not differ significantly from the strengths of similar clinkers in which the  $C_3S$  is monoclinic.

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