

Paste Hydration of Beta-Dicalcium Silicate, Tricalcium Silicate, and Alite

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The chemistry of hydration in pastes of β -dicalcium silicate, tricalcium silicate and an alite as functions of water-solids ratio and fineness of the silicate have been investigated at 25 C. The CaO/SiO₂ ratio of the stable tobermorite gel hydration product was found to increase as the water-solids ratio decreased, but was not appreciably influenced by the fineness of the original unhydrated silicate.

Heat of solution data were obtained and heat of hydration values calculated. The effects of surface area, CaO/SiO₂ ratio, and water content were considered in the calculation. The calculated values of the surface energy and the heat of hydration of tobermorite gel were in good agreement with previously obtained values.

Heats of hydration were calculated for hypothetical reactions producing dry tobermorite gel of composition C_{1.5}SH and having a specific surface area of 300 m²/g. The values obtained were 11.6 cal/g C₂S, 81.1 cal/g C₃S, and 77.0 cal/g alite.

•INVESTIGATION of the chemistry of the paste hydration of tricalcium silicate and β -dicalcium silicate provides valuable information contributing to the understanding of the chemistry of hydration of portland cement. Alite and belite, modified forms of tricalcium and dicalcium silicates containing small amounts of impurities, primarily alumina and magnesia (1), are the two major constituents of portland cement.

Earlier investigations have shown that the products of hydration of the pure tricalcium silicate and B₂O₃-stabilized β -dicalcium silicate are calcium hydroxide and a calcium silicate hydrate (2, 3). It was shown, as a first approximation, that the overall hydration reactions may be represented by

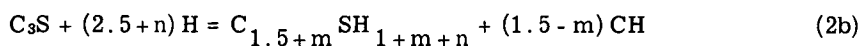
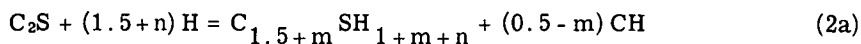


for systems saturated with water. (Cement chemistry abbreviated notation is used throughout this paper: C = CaO, S = SiO₂, H = H₂O, A = Al₂O₃ and M = MgO.) The amount of water in the calcium silicate hydrate depends on its composition, which may differ from that indicated by Eqs. 1a and 1b. The hydrated silicate formed has a high specific surface area, and has been designated tobermorite gel.

The reactions of tricalcium silicate and β -dicalcium silicate with water are exothermic processes, just as is the reaction of portland cement with water. The heat produced, the heat of hydration, is a quantity which has been of especial interest to cement chemists. The subject of heats of hydration of tricalcium and β -dicalcium silicates has been reviewed by Brunauer and Greenberg (4). The values reported by them include contributions due to the chemical reaction which has occurred and to the

surface energy of tobermorite gel. This latter quantity has been determined experimentally (5). The overall heats of hydration are greater than the heats of the chemical reaction for both tricalcium and β -dicalcium silicate because of the contribution from the heat of adsorption of water on the high surface area tobermorite gel.

Recently, investigations have shown that the molar C/S and H/S ratios of tobermorite gel are variable quantities (6, 7). The hydration reaction, expressed in terms of the dried product, may be represented by



It was also shown that in the case of C_2S the C/S ratio of the tobermorite gel decreases with time, passes through a minimum and rises to an approximately constant value at late stages of hydration. In the case of C_3S the C/S ratio drops rapidly at first, then becomes nearly constant. The C/S ratio increases with increasing temperature in the C_2S case, but is independent of temperature in the C_3S case. An inverse relationship was found to exist between specific surface area and C/S ratio of the tobermorite gel. The results were explained by the formation of tobermorite gel sheets having thicknesses of two and three pseudocells. The three-layer sheet has the higher C/S ratio and the lower specific surface area. The molar C/S ratios of the two-layer and three-layer sheets were determined. These values, 1.39 and 1.73, representing m values of -0.11 and +0.23 in the above equations, are limiting C/S ratios for the system under the conditions investigated. All stable tobermorite gel hydration products were considered to be composites of these two compositions (6).

The hydration reaction for tricalcium silicate given above has been found to apply approximately to the hydration of an alite (6) having a composition in the same range as the alites found in portland cements (1).

The variable nature of the paste hydration of the calcium silicates with time and temperature suggests that other factors also affect the reaction. Two quantities which are of primary concern to the cement chemist are water-cement ratio or water-solids ratio and fineness. In the present investigation, the effects of these variables upon stoichiometry have been examined. In addition, heat of solution measurements have been made on a large number of pastes, and heat of hydration calculations have been made which take into account the variable composition of the tobermorite gel hydration product.

EXPERIMENTAL PROCEDURES AND RESULTS

Materials

The preparation of the β - C_2S , alite, and C_3S have been described previously (6, 7). The analyses and computed compound compositions are given in Table 1. Two C_3S analyses are given in Table 1. The first is that of the C_3S previously reported; the second is that of a new preparation. The previously reported compound composition of alite had to be revised for two reasons: redetermination of the analysis, and a different basis for computation. Previously, the alite composition was taken as the sum of C_3S , C_3A , and MgO . More recently the work of Midgley and Fletcher (8) has shown that alite compositions may be represented by the empirical formula $C_{3N-x}M_xS_N$. $C_{4.5}A$. The new alite analysis, and the composition computed on this basis are given in Table 1. The values of N and x for this alite are 47.5 and 0.8, respectively, the composition being then expressed $C_{141.7}M_{0.8}S_{47.5} \cdot C_{4.5}A$. This revision in alite composition and analysis produces no significant effect on previously reported results on alite pastes.

The compounds were ground in porcelain jar mills with flint pebbles. The Blaine surface area (ASTM designation C-204-55) was used as a measure of fineness. For the

TABLE 1
COMPOSITIONS OF UNHYDRATED CALCIUM SILICATES

Component	Material, Percent Ignited Basis			
	Ca ₂ SiO ₄	Ca ₃ SiO ₅		Alite
		Batch 1	Batch 2	
CaO	65.43	73.57	73.87	73.78
SiO ₂	33.56	25.69	26.14	25.07
Al ₂ O ₃	0.12	0.20	0.13	0.88
MgO	0.05	—	—	0.27
B ₂ O ₃	0.47	—	—	—
Total	99.63	99.46	100.14	100.00
C ₃ S or alite	—	98.18	96.77	96.64
C ₂ S	96.43	—	1.81	1.18
C ₃ A	0.32	0.53	0.34	—
CaO (free)	1.45	1.29	1.08	2.18
CaO (dissolved)	1.22	—	—	—
Insol. Res.	0.06	—	—	—
Total	100.00	100.00	100.00	100.00

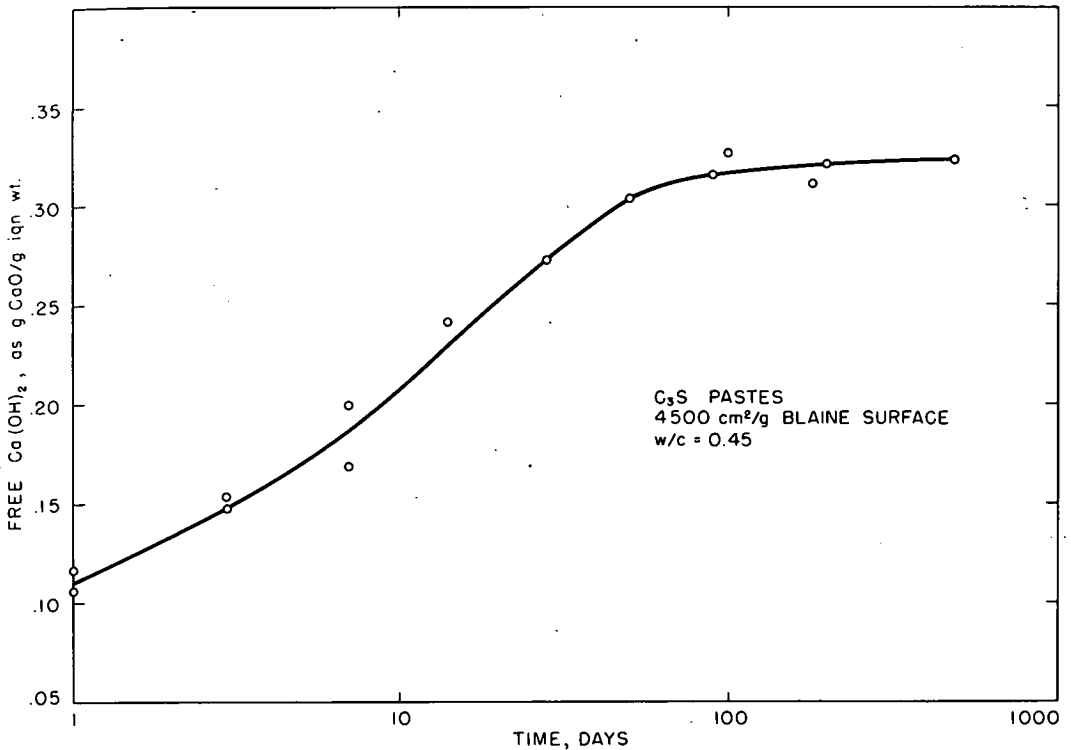


Figure 1. Variation of Ca(OH)₂ contents of C₃S pastes with age of paste (logarithmic time scale).

preparation of the 8000 cm²/g Blaine surface C₂S, an amount of denatured ethanol, 1/2 percent by weight of the C₂S, was added as a grinding aid. Loss on ignition determinations on this finely ground product indicated that about half of the alcohol was lost during grinding. The remainder appeared to be tightly held; it could not be removed by oven heating at 105 C.

All pastes were mixed by the vacuum mixing procedure of Powers et al. (9), and cured continuously moist either in polyethylene test tubes (6) or as 1-in. cubes in sealed jars. After curing, the cubes were crushed in a glovebox containing a CO₂-free atmosphere. The samples were then dried to equilibrium with the vapor pressure of ice at -78.5 C (ca 5 × 10⁻⁴ torr) as described previously (6).

Analysis of Hardened Pastes

Experimental determinations of loss on ignition and CO₂ were made according to the procedures described by Brunauer, Hayes, and Hass (10). The determinations of unhydrated material were made by X-ray quantitative analysis (3). Free Ca(OH)₂ was determined by a modified Franke method (11, and Appendix A). Surface areas were determined by the BET method using water vapor adsorption data (6). Heats of solution were measured with a calorimeter similar to that used by Verbeck and Foster (12) but having certain modifications (13, and Appendix B).

Results

The method of calculation of paste composition was in principle the same as used previously (6, 7). The amount and composition of the tobermorite gel in a paste are obtained as the difference between the total analysis of the original material and the free calcium hydroxide, unhydrated silicate, and minor constituents, such as calcium carbonate. This calculated composition of the tobermorite gel is sensitive to any uncertainty in the free calcium hydroxide determination and the X-ray analysis for unhydrated remainder. It was assumed that these uncertainties, arising primarily from graphical extrapolation in the one case and X-ray intensity ratio measurements in the other, were completely random; consequently, smoothed values were obtained as shown in Figures 1 and 2. The standard deviation of the experimental points from the smooth curve in Figure 1 is of the order of 0.005 g CaO/g ignited weight, which is approximately equal to the standard deviation of the analytical method. The standard deviation for the X-ray data, Figures 2 and 3, corresponds to about 0.01 for degree of hydration.

The results reported in Tables 2, 3 and 4 include smoothed values for free calcium hydroxide and unhydrated silicate contents. Table 2 gives the results for dicalcium silicate pastes. Data are given for pastes made with C₂S of four different finesses: 8000, 4500, 3500, and 2500 cm²/g Blaine surface area. The water-solids ratios used were 0.45, 0.57, and 0.70.

The data for tricalcium silicate pastes are given in Table 3. The finesses used were 4500 and 2500 cm²/g and the water-solids ratios were 0.45, 0.57, 0.70. One paste, made with a water-solids ratio of 0.30, has also been included.

The data for alite pastes are given in Table 4. The fineness used was 4500 cm²/g and the water-solids ratios were 0.45 and 0.70. Some of the pastes, made with 4500 cm²/g material at a water-solids ratio 0.70, although reported previously (6, 7), are included in these tables. The data are slightly changed in some cases by the use of smoothed values, and in the case of alite because of the recalculation of the composition of the alite itself.

The term degree of hydration, as used in the subsequent text, refers to the ratio of the amount of silicate which has been hydrated to the amount which was present initially.

DISCUSSION

Rates and Stoichiometry of Hydration of C₂S, C₃S and Alite

The influence of water-solids ratio on the rate of hydration is best shown by plots of the degree of hydration as a function of time. Such curves for dicalcium silicate are given in Figure 2 for water-solids ratios of 0.45, 0.57, and 0.70, all data being from

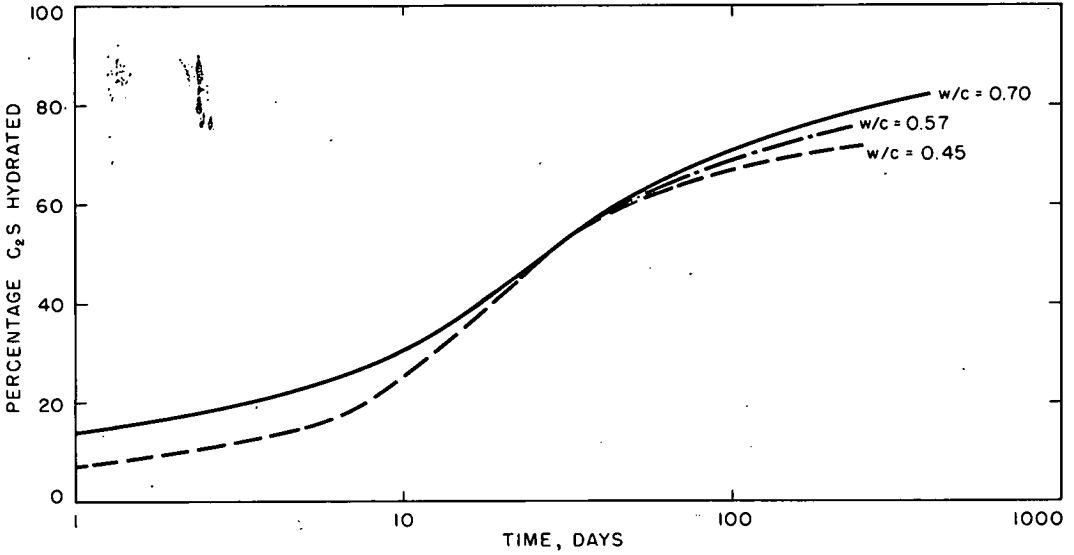


Figure 2. Variation of percentage of C_2S hydrated with age: hydration at 25 C, 4500 cm^2/g C_2S (at early ages, the 0.45 and 0.57 curves are superimposed).

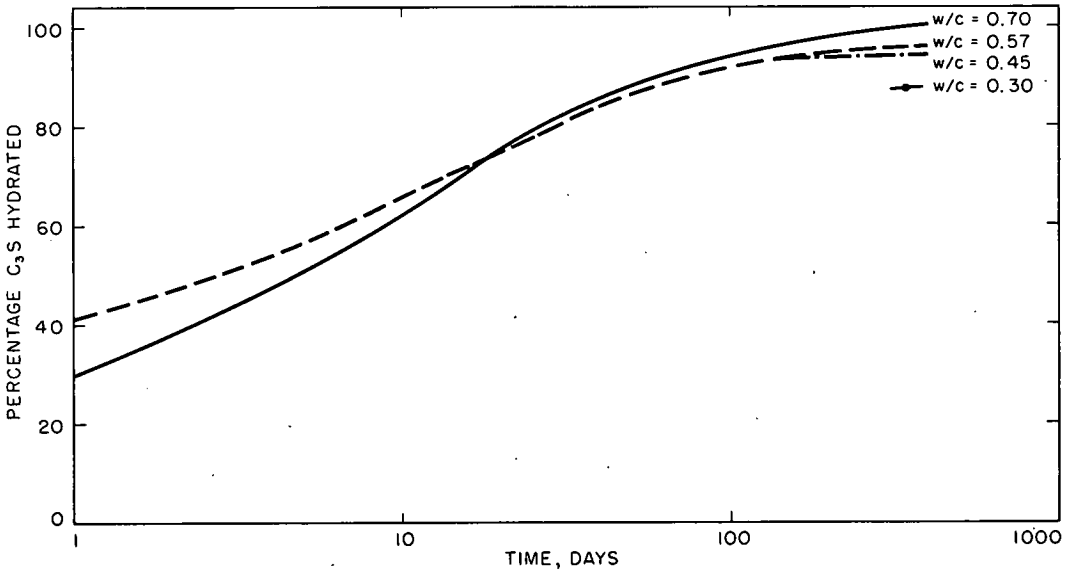


Figure 3. Variation of percentage of C_3S hydrated with age: hydration at 25 C, 4500 cm^2/g C_3S (at all but the latest ages, the 0.45 and 0.57 curves are superimposed).

pastes made with C_2S of a single fineness, 4500 cm^2/g . At early ages, the pastes of $w/c = 0.57$ and 0.45 show the same degree of hydration at any particular time, but at late ages the former show somewhat higher degrees of hydration at a given time. At about 50 days, the degree of hydration is independent of the w/c ratio. Actually, at any given time, the effect of w/c is relatively small, the largest difference amounting to only 7 percent of the C_2S originally present.

TABLE 2
COMPOSITIONS, AREAS, AND HEATS OF SOLUTION OF C₃S PASTES

Age (days)	w/c (g/g)	C ₃ S ^a (g/g (C ₃ S) ₀)	Free Ca(OH) ₂ ^a (g/g (C ₃ S) ₀)	Tobermorite Gel (g/g (C ₃ S) ₀)	Tobermorite Gel Composition		Surface Area of Tobermorite Gel (m ² /g Tob)	Heat of Solution ^b (cal/g (C ₃ S) ₀)
					C/S (moles/mole)	H/S (moles/mole)		
Original Material: 8000 cm ² /g Blaine Surface								
1	0.45	0.854	0.041	0.138	1.61	0.69	317.2	571.8
3	0.45	0.837	0.058	0.149	1.41	1.00	386.4	571.5
7	0.45	0.724	0.069	0.270	1.56	1.14	378.4	571.4
14	0.45	0.527	0.078	0.487	1.72	1.14	312.8	572.0
28	0.45	0.331	0.087	0.706	1.78	1.21	316.4	572.3
90	0.45	0.216	0.098	0.833	1.79	1.25	326.4	572.2
180	0.45	0.180	0.104	0.869	1.78	1.24	310.3	569.8
Original Material: 4500 cm ² /g Blaine Surface								
1	0.45	0.931	0.048	0.049	0.96	0.49	561.7	570.6
2	0.45	0.905	0.057	0.071	1.05	0.59	596.4	572.0
3	0.45	0.881	0.062	0.092	1.14	0.54	413.4	570.3
7	0.45	0.820	0.072	0.152	1.30	0.69	418.2	571.2
9	0.45	0.762	0.076	0.215	1.45	0.79	370.2	571.9
14	0.45	0.676	0.081	0.310	1.57	0.91	345.6	572.1
14	0.45	0.676	0.081	0.308	1.55	1.05	327.1	570.7
28	0.45	0.488	0.090	0.515	1.70	1.00	262.1	570.0
28	0.45	0.488	0.090	0.517	1.70	1.03	327.7	570.6
50	0.45	0.395	0.097	0.626	1.72	1.21	269.8	567.1
90	0.45	0.337	0.101	0.684	1.74	1.14	291.3	569.8
100	0.45	0.328	0.101	0.697	1.74	1.16	290.0	568.1
180	0.45	0.293	0.101	0.736	1.75	1.18	304.3	569.4
200	0.45	0.289	0.102	0.743	1.76	1.18	277.7	568.7
1700	0.45	0.120	0.108	0.940	1.80	1.28	293.5	567.5
2	0.57	0.832	0.070	0.132	1.30	0.18	334.1	571.5
9	0.57	0.716	0.092	0.247	1.42	0.56	317.2	570.6
14	0.57	0.644	0.100	0.323	1.48	0.72	345.5	571.2
28	0.57	0.496	0.113	0.485	1.59	0.92	285.0	570.4
50	0.57	0.390	0.122	0.601	1.63	1.03	271.6	568.2
100	0.57	0.307	0.129	0.693	1.66	1.06	295.0	569.0
200	0.57	0.255	0.131	0.754	1.68	1.12	292.0	568.7
1700	0.57	0.047	0.141	0.992	1.74	1.21	303.0	567.1
1	0.70	0.861	0.050	0.121	1.49	0.39	242.9	569.9
2	0.70	0.829	0.065	0.141	1.39	0.20	247.5	568.3
5	0.70	0.771	0.089	0.181	1.32	0.13	306.8	562.5
8	0.70	0.723	0.095	0.232	1.38	0.35	302.3	563.6
11	0.70	0.679	0.101	0.280	1.43	0.55	336.4	569.0
14	0.70	0.636	0.107	0.328	1.46	0.75	333.0	571.6
18	0.70	0.587	0.112	0.379	1.48	0.83	321.4	570.4
21	0.70	0.549	0.115	0.416	1.52	0.76	314.0	570.6
28	0.70	0.487	0.121	0.481	1.55	0.82	294.2	568.6
41	0.70	0.413	0.130	0.553	1.56	0.83	308.4	568.3
72	0.70	0.327	0.142	0.656	1.60	1.02	275.9	562.4
100	0.70	0.280	0.149	0.700	1.60	0.99	291.8	567.7
200	0.70	0.231	0.162	0.749	1.58	1.05	289.0	566.2
400	0.70	0.179	0.165	0.798	1.58	1.04	302.2	565.5
1700	0.70	0.033	0.174	0.976	1.66	1.14	302.1	567.8
Original Material: 3500 cm ² /g Blaine Surface								
206	0.45	0.324	0.111	0.689	1.70	1.11	310.6	570.4
206	0.57	0.301	0.140	0.697	1.63	1.12	319.0	567.4
50	0.70	0.491	0.133	0.481	1.51	1.05	329.6	567.4
100	0.70	0.339	0.148	0.634	1.57	0.94	305.1	568.9
206	0.70	0.275	0.152	0.711	1.60	1.01	274.4	567.3
Original Material: 2500 cm ² /g Blaine Surface								
7	0.45	0.885	0.046	0.102	1.43	0.88	402.8	570.3
14	0.45	0.767	0.057	0.227	1.64	0.84	292.5	570.7
28	0.45	0.635	0.078	0.355	1.65	0.85	311.9	571.8
90	0.45	0.469	0.097	0.536	1.68	1.09	312.2	569.9
180	0.45	0.384	0.105	0.625	1.70	1.09	299.7	564.9
205	0.45	0.371	0.106	0.641	1.71	1.10	287.5	570.7
205	0.57	0.350	0.134	0.633	1.62	0.96	296.5	569.4
50	0.70	0.523	0.103	0.471	1.61	0.91	268.2	568.6
100	0.70	0.420	0.133	0.554	1.57	0.92	293.0	568.7
205	0.70	0.317	0.150	0.654	1.58	1.08	297.6	568.9

^aValues from smooth curves.

^bCorrected for minor constituent contributions.

Plots of the degree of hydration of C₃S of 4500 cm²/g fineness as functions of time at different water-solids ratios are given in Figure 3. The early age data for the w/c = 0.70 curve were obtained from pastes made with a different C₃S preparation than the rest. The curves for the two other water-solids ratios were obtained from the same C₃S preparation. It is to be noted that at any early age the degree of hydration is the same for w/c = 0.57 and 0.45, whereas at any later age the former gives the higher value. The results obtained for alite were similar to those obtained for these two sets

TABLE 3
COMPOSITIONS, AREAS, AND HEATS OF SOLUTION OF C₃S PASTES

Age (days)	w/c (g/g)	C ₃ S ^a (g/g (C ₃ S) ₀)	Free Ca(OH) ₂ ^a (g/g (C ₃ S) ₀)	Tobermorite Gel (g/g (C ₃ S) ₀)	Tobermorite Gel Composition		Surface Area of Tobermorite Gel (m ² /g Tob)	Heat of Solution ^b (cal/g (C ₃ S) ₀)
					C/S (moles/mole)	H/S (moles/mole)		
Original Material: 4500 cm ² /g Blaine Surface								
480	0.30	0.136	0.296	0.766	1.99	1.49	321.8	
1	0.45	0.580	0.152	0.345	1.97	0.91	296.2	622.8
1	0.45	0.580	0.152	0.343	1.98	0.83	297.6	624.8
3	0.45	0.529	0.202	0.365	1.75	0.96	352.7	618.1
3	0.45	0.529	0.202	0.366	1.75	0.99	360.1	617.9
7	0.45	0.416	0.253	0.458	1.73	1.15	352.4	605.6
7	0.45	0.416	0.253	0.453	1.73	1.04	326.0	608.6
14	0.45	0.291	0.313	0.549	1.69	1.11	348.1	597.7
28	0.45	0.185	0.372	0.620	1.64	1.05	355.1	591.9
50	0.45	0.124	0.413	0.653	1.59	0.99	330.8	585.4
90	0.45	0.086	0.430	0.692	1.60	1.12	373.3	581.5
100	0.45	0.081	0.431	0.692	1.60	1.07	350.5	581.9
180	0.45	0.067	0.437	0.706	1.60	1.08	378.4	580.4
200	0.45	0.065	0.438	0.709	1.60	1.11	342.8	
480	0.45	0.058	0.441	0.724	1.61	1.21	379.3	
1	0.57	0.598	0.166	0.313	1.82	0.79	284.7	622.9
2	0.57	0.544	0.199	0.351	1.74	0.92	334.9	614.8
3	0.57	0.506	0.219	0.376	1.72	0.90	349.1	616.9
4	0.57	0.470	0.229	0.411	1.74	0.99	335.4	613.6
7	0.57	0.395	0.273	0.457	1.68	0.91	330.9	607.8
14	0.57	0.297	0.325	0.529	1.63	1.01	346.4	600.8
50	0.57	0.135	0.429	0.629	1.51	1.01	366.9	584.8
100	0.57	0.083	0.466	0.660	1.48	1.01	384.4	580.8
200	0.57	0.060	0.487	0.674	1.45	1.06	370.2	
365	0.57	0.042	0.497	0.688	1.45	1.05	382.7	
1	0.70	0.700	0.149	0.216	1.63	0.72	352.4	624.8
1.5	0.70	0.654	0.173	0.246	1.59	0.74	367.4	621.0
2	0.70	0.619	0.190	0.269	1.58	0.69	342.4	618.5
4	0.70	0.524	0.230	0.343	1.62	0.78	360.8	612.7
8	0.70	0.420	0.269	0.428	1.65	0.89	344.4	607.6
14	0.70	0.310	0.335	0.496	1.57	0.90	355.2	594.4
21	0.70	0.240	0.386	0.533	1.49	0.91	379.7	585.2
28	0.70	0.195	0.410	0.567	1.48	0.98	357.7	577.4
50	0.70	0.111	0.466	0.599	1.35	0.86	374.0	582.6
72	0.70	0.075	0.472	0.657	1.48	1.07	362.0	565.3
100	0.70	0.052	0.486	0.667	1.47	1.02	354.6	566.9
100	0.70	0.075	0.489	0.633	1.37	0.92	382.3	581.3
200	0.70	0.018	0.506	0.687	1.45	1.03	322.0	560.9
200	0.70	0.038	0.519	0.667	1.39	0.96	358.8	575.5
365	0.70	0.000	0.530	0.697	1.41	0.92	366.9	
400	0.70	0.000	0.532	0.691	1.41	0.87	345.5	577.9
400	0.70	0.000	0.514	0.689	1.42	0.97	332.0	565.3
Original Material: 2500 cm ² /g Blaine Surface								
1	0.45	0.684	0.106	0.264	2.09	0.74	244.7	633.4
3	0.45	0.635	0.147	0.291	1.86	0.92	279.5	624.8
7	0.45	0.542	0.193	0.362	1.79	1.05	324.4	616.7
14	0.45	0.418	0.254	0.450	1.73	0.97	334.7	608.6
28	0.45	0.323	0.331	0.496	1.56	0.96	386.6	601.4
90	0.45	0.179	0.372	0.632	1.65	1.11	352.7	588.3
180	0.45	0.169	0.393	0.619	1.57	1.07	356.7	586.4

^aValues from smooth curves.

^bCorrected for minor constituent contributions.

of C₃S pastes, as Table 4 shows. At corresponding early ages the pastes of w/c = 0.70 and 0.45 gave the same degree of hydration; at corresponding late ages the former gave higher values.

Alite (or the C₃S phase) is the main constituent of normal portland cements, and actually, the hydration behavior of portland cements is similar to that of alite and C₃S. As the results of Verbeck (14) for heats of hydration and the results of Taplin (15) for water of hydration indicate, the degree of hydration of portland cements is nearly independent of the w/c ratio at early ages, but at later ages the pastes with higher w/c show higher values. Verbeck interpreted these results for portland cements (14), and the same explanation can be employed for alite and C₃S. In the first stage of hydration, the rate-determining step is the chemical reaction between C₃S and water molecules. At all w/c ratios used in the present experiments, there is enough water in the system to react with all the accessible C₃S; consequently, the rate is independent of the amount of water in the paste. In the reaction, the tobermorite gel deposits in the water-filled space between the unhydrated grains, and the gel becomes denser as the reaction progresses. Eventually, the gel becomes so dense that the diffusion of molecules through

TABLE 4
 COMPOSITIONS, AREAS, AND HEATS OF SOLUTION OF ALITE PASTES

Age (days)	w/c (g/g)	Alite ^a (g/g (alite) ₀)	Free Ca(OH) ₂ ^a (g/g (alite) ₀)	Tobermorite Gel (g/g (alite) ₀)	C+M S+2A (moles/mole)	H S+2A (moles/mole)	Surface Area of Tobermorite Gel (m ² /g Tob)	Heat of Solution ^b (cal/g (alite) ₀)
Original Material: 4500 cm ² /g Blaine Surface								
1	0.45	0.639	0.205	0.254	1.47	0.92	380.8	636.9
3	0.45	0.489	0.259	0.374	1.60	0.89	344.4	628.2
7	0.45	0.354	0.334	0.470	1.53	1.03	385.2	612.8
14	0.45	0.246	0.394	0.544	1.49	1.06	383.3	600.4
28	0.45	0.143	0.429	0.633	1.54	1.08	385.6	594.8
72	0.45	0.101	0.459	0.658	1.50	1.10	328.1	587.6
90	0.45	0.088	0.466	0.668	1.50	1.09	383.7	586.9
180	0.45	0.060	0.477	0.692	1.51	1.11	382.5	586.8
1	0.70	0.627	0.194	0.275	1.62	0.71	292.9	638.2
2	0.70	0.540	0.238	0.334	1.59	0.83	293.6	629.8
8	0.70	0.345	0.340	0.468	1.51	0.88	336.6	608.4
14	0.70	0.257	0.406	0.519	1.42	0.87	377.9	597.2
21	0.70	0.191	0.450	0.553	1.37	0.92	366.7	593.2
28	0.70	0.138	0.468	0.602	1.40	1.01	347.0	586.4
72	0.70	0.047	0.518	0.669	1.40	1.06	387.3	581.7
100	0.70	0.030	0.528	0.674	1.38	1.00	357.2	581.9
200	0.70	0.000	0.543	0.693	1.39	0.97	337.9	579.1
400	0.70	0.000	0.562	0.685	1.35	0.98	348.8	577.3
800	0.70	0.000	0.575	0.670	1.31	0.92	357.5	579.3

^aValues from smooth curves.^bCorrected for minor constituent contributions.

it to and away from the surface of unhydrated grains becomes the rate-determining step. In this second stage of hydration, the "gel-space ratio" of Powers (16) plays an important role. The concentration of gel in pastes made with low w/c ratios is higher at a given degree of hydration; consequently, the rate is lower.

Tables 2, 3 and 4 show that the calcium hydroxide content of the pastes of the three silicates at a given degree of hydration depends on the w/c ratio. The calcium hydroxide content of a paste determines the C/S ratio of the tobermorite gel and, in fact, the stoichiometry of the reaction. An example of this is given in Figure 4, which represents the variation of the C/S ratio in the gel with degree of hydration for C₂S pastes prepared with w/c = 0.70, 0.57 and 0.45. The C₂S had a specific surface of 4500 cm²/g Blaine.

In an earlier paper (7), the rates and stoichiometry of the hydration of C₂S and C₃S were reported at three different temperatures, 5, 25 and 50 C. Only one fineness (4500 cm²/g) and one w/c ratio (0.70) were used. The results were interpreted in terms of a three-step kinetic mechanism. The first, second, and the beginning of the third step of the hydration process occur in the first stage of hydration just described.

In this early paper (7) it was proposed that as a first step a lime-rich (as compared with the final product) gel coating forms on the surfaces of the unhydrated grains. In the second step thin sheets of gel, one and two molecular layers in thickness, and calcium hydroxide form from the coating. The coating is regenerated by the continuing reaction between the silicate molecules and water. In the third step, the unstable one- and two-layer tobermorite gel sheets convert into stable two- and three-layer sheets. Because the C/S ratio in the gel increases with thickness (6), in the third step of hydration the C/S ratio rises.

In the present investigation no pastes of C₃S and alite were examined which were less than one day old. Because these silicates react with water much faster than C₂S, at one day they are already in the third step of hydration. In this step, they exhibit the same behavior as C₂S. One feature of the results obtained for all three silicates is that the final C/S ratio of the gel increases with decreasing w/c.

The lower the w/c ratio the lower the available volume which the hydration products may occupy. It has been proposed that the pseudocell weight of tobermorite gel is almost constant over the whole composition range discussed (6). If this is true, the formation of a higher lime tobermorite gel from calcium hydroxide and a lower lime tobermorite gel results in a net decrease in volume of the total hydration products.

The lower the water/cement ratio of a cement paste the lower is the porosity and the greater the fraction of total pore volume which occurs as small pores (17). It is expected that pastes of the pure silicates are similarly dependent on water/silicate ratio.

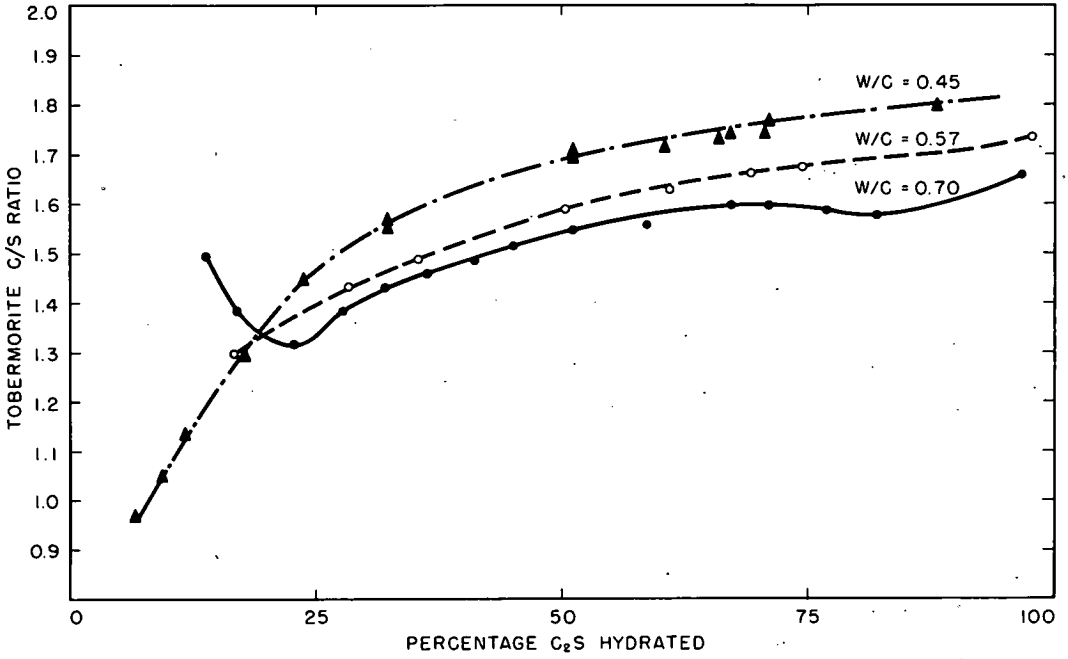


Figure 4. Variation of C/S ratio of tobermorite gel with percentage of C_2S hydrated: hydration at 25 C, $4500 \text{ cm}^2/\text{g } C_2S$.

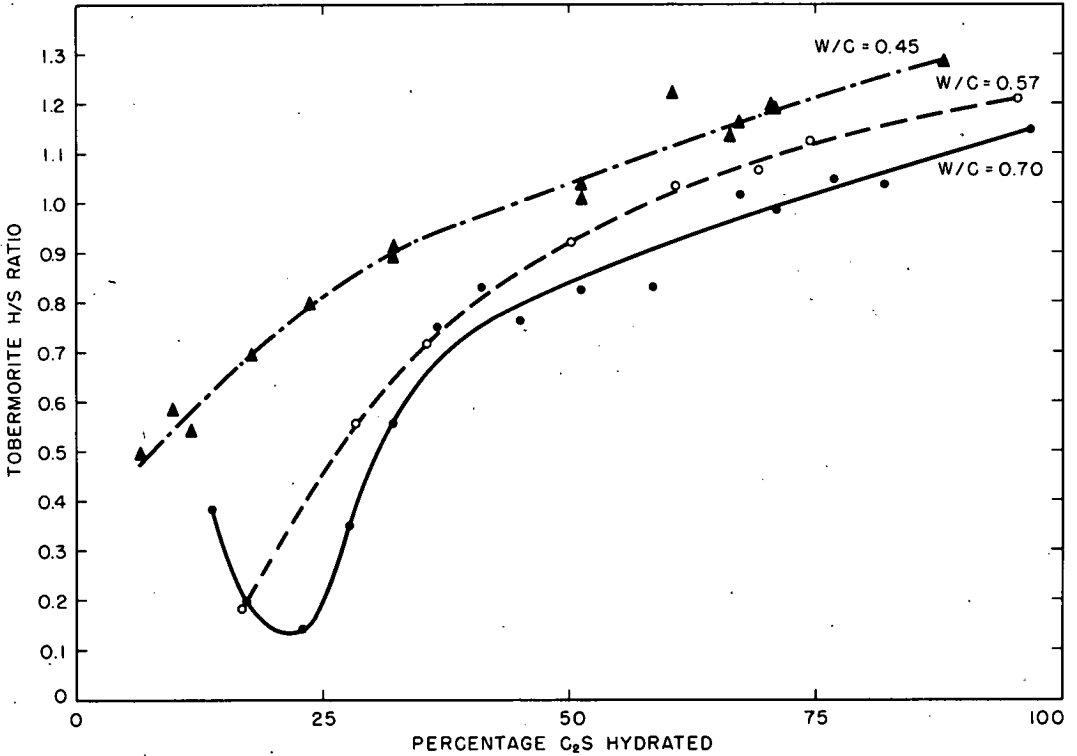


Figure 5. Variation of H/S ratio of tobermorite gel with percentage of C_2S hydrated: hydration at 25 C, $4500 \text{ cm}^2/\text{g } C_2S$.

TABLE 5
HEATS OF SOLUTION OF
UNHYDRATED MATERIALS

Material	Heat of Solution (cal/g)
C ₂ S (B ₂ O ₃ -stabilized)	562.4
C ₂ S (Extrapolated)	572.0
C ₃ S (13)	639.5
C ₃ S (7); (Table 1, Batch 1)	638.1
C ₃ S (Table 1, Batch 2)	641.3
C ₃ S (avg)	639.6
Alite (C ₁₄₆ . 2M ₀ . 8AS ₄₇ . 5)	654.4

It might then be expected that a paste with low porosity could more readily accommodate a tobermorite gel with a high C/S ratio than one with a lower C/S ratio and the concomitant additional calcium hydroxide.

The variation of the H/S ratio of the tobermorite gel with degree of hydration is qualitatively similar to the variation of the C/S ratio; this is illustrated in Figure 5 by the data obtained for C₂S. Brunauer and Greenberg (4) pointed out that the molar H/S ratio for stable tobermorite is less by 0.5 than the C/S ratio. The data in the present paper confirm their conclusion. Thus, the composition of tobermorite gels formed in the third step of hydration can be expressed (for the dried state) by the empirical form C_{1.5+m}SH_{1+m}, where m can be either positive or negative.

The only important effect of increasing the fineness of the calcium silicate is to increase the rate of hydration. The C/S and H/S ratios of the tobermorite gel, naturally, change with the degree of hydration, but the final C/S ratio was found to be independent of the specific surface of the C₂S or C₃S used in the preparation of the pastes.

Thermochemistry of Hydration

The hydration reactions of C₂S, C₃S and alite are not represented quantitatively by the relatively simple Eqs. 1a and 1b, given earlier. A more complicated process occurs. The tobermorite gel formed in the hydration reaction does not have a unique composition, but rather one that depends on time of hydration, temperature of hydration (6, 7) and initial water-solids ratio. The specific surface area of the tobermorite gel, too, depends on these experimental variables.

The data in Tables 2, 3 and 4 indicate the variation from paste to paste in tobermorite gel compositions, in free calcium hydroxide content, in water content of the dried paste, and in specific surface area of the tobermorite gel.

The variation in composition is over a fairly wide range. Previously, the range of variation, expressed in terms of C/S ratio of the tobermorite gel, was thought to be between limiting values 1.39 and 1.73 (6, 7). Also, the specific surface area of the tobermorite gel was thought to be between limiting values 255 and 372 m²/g. The data in Tables 2, 3 and 4 indicate that the range of variation in tobermorite gel composition and in specific surface area is wider than these previously stated limits.

The heats of solution of the pastes are also given in Tables 2, 3 and 4; these, too, show variability. An evaluation of the influence of bound water and surface area on the heat of solution was made in a previous investigation (5). With the information given in Tables 2, 3 and 4, the effect produced by the lime content of the tobermorite gel on the heat of solution may be determined. In the general treatment which follows, the influences of water content and surface area are redetermined, as well. The factors which influence the heat of solution will of course influence the heat of hydration, as this latter quantity is the difference between the heats of solution of the unhydrated and hydrated materials.

The heats of solution of the unhydrated materials used for the hydration studies must be determined before heats of hydration can be obtained. The experimental values obtained for the heats of solution of these materials must be corrected for various impurities. The heat of solution values given in Table 5 are corrected.

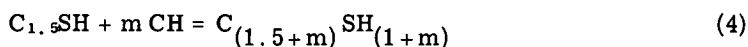
The largest of these corrections is for free CaO. The heat of solution of CaO used for the correction was 861 cal/g (10, 13).

The C₃S batches used in the present investigation all contained small amounts of C₂S. This C₂S was not B₂O₃ stabilized, as was the β-C₂S used for the hydration studies. The heat of solution of C₂S itself depends on stabilizer identity and concentration. Heats of solution of a group of C₂S preparations stabilized with different amounts of B₂O₃ and of another group stabilized with different amounts of alumina and magnesia were determined (18). The values of the heats of solution of each series, in cal/g C₂S, were plotted as functions of stabilizer concentration. These plots were approximately linear, the line for B₂O₃-stabilized material having a negative slope, and that for Al₂O₃-MgO-stabilized material having a positive slope. These lines intersected at a point near zero concentration, and may well intersect at this same value at zero stabilizer concentration if there is a slight curvature in the functions. The value of the heat of solution at the point of intersection, the second C₂S value given in Table 5, was taken to represent the heat of solution of a pure C₂S and was used for the corrections for the small amounts of C₂S in C₃S and alite.

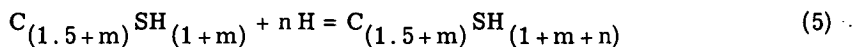
As a first step in obtaining a general expression for the heat of solution of a hydrated paste, it is necessary to express the hydration reaction in a general way that will allow consideration of the differences in composition of the tobermorite gel that is produced. One method of obtaining the desired result is to choose some composition of the tobermorite gel as a "reference" composition, and to consider separately the differences between the reference composition and those compositions actually produced. For the present work C_{1.5}SH was taken as the reference composition. In the case of C₃S; the hydration to form the reference gel is represented by



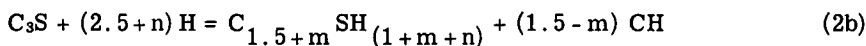
Differences in C/S ratio between the actual and reference gels can be considered as reactions of the reference gel with calcium hydroxide:



Differences in the water content between the actual and reference dried gels can be represented by reactions between the product in Eq. 4 and water:



The "overall" reaction is the sum of these three reactions:



The quantities *m* (moles CH/mole C₃S) and *n* (moles H/mole C₃S) in the above expressions may be either positive or negative. Analogous reactions may be written for C₂S and alite.

This scheme is not to be interpreted as a mechanism. It is not a sequence of events, but merely three components of a single process, as far as the present investigation is concerned.

TABLE 6
LEAST SQUARES RESULTS—HEAT OF SOLUTION CALCULATIONS

Parameter	Least Squares Estimate	Previous Determination
H (C ₂ S)	2277.4 ± 22.7 cal/g Ca(OH) ₂	
H (C ₃ S)	1100.4 ± 11.8 cal/g Ca(OH) ₂	
H (Alite)	1148.8 ± 36.1 cal/g Ca(OH) ₂	
Y	-47.0 ± 14.5 cal/g Ca(OH) ₂	
h	-425 ± 110 cal/g H ₂ O	-421 cal/g H ₂ O
ε _s	0.107 ± 0.032 cal/m ²	0.092 cal/g H ₂ O

The next step in obtaining the general expression for the heat of solution of a paste is to consider this heat as the sum of several components. These are: the heat of solution of reference state products formed according to Eq. 3 (in the case of C₃S), the heats of reaction of these products according to Eqs. 4 and 5, the heat of solution of any remaining unhydrated material, and the total surface energy of the hydration products.

The last step in obtaining a general expression for the heat of solution of a paste is to fit the experimental data by the method of least squares to an equation expressing the heat of solution as the sum of the several terms given in the preceding paragraph. The mathematical derivation of the general heat of solution equation is given in Appendix C. The experimental data fitted to this equation were obtained from 70 C₂S pastes, 58 C₃S pastes, and 27 alite pastes. Some of these data were obtained from pastes hydrated at 5 and 50 C at 0.70 w/c. The composition data for the 5 and 50 C pastes were reported previously (6, 7). The heats of solution of all pastes used in the calculations were corrected for the contributions of the Ca(OH)₂ formed from the free CaO in the original silicates.

The general expression obtained for the heat of solution of a hydrated paste is

$$H_i = w_u H_u + w_c H + b Y + w_x h + A \epsilon_s \quad (6)$$

where the experimentally determined quantities are:

- H_i = the corrected heat of solution of the paste, in calories per "gram of original silicate";*
- H_u = the corrected heat of solution of the unhydrated silicate, in calories per gram of original silicate;
- w_u = the amount of unhydrated silicate remaining in the paste, in grams per gram of original silicate;
- w_c = the amount of calcium hydroxide that would be formed according to Eq. 3 (in the case of C₃S), in grams per gram of original silicate;
- b = the amount of calcium hydroxide that has reacted according to Eq. 4, in grams per gram of original silicate;
- w_x = the amount of water that has reacted according to Eq. 5, in grams per gram of original silicate;
- A = the surface area of the hydration products, in m²/g original silicate;

and the parameters which were estimated with the method of least squares are:

- H = the heat of solution of the reference hydration products that would be formed according to Eq. 3, in calories per gram of calcium hydroxide produced in that reaction;

*The term "gram of original silicate" is the weight of the initial anhydrous sample corrected for impurities in all definitions.

TABLE 7
HEATS OF HYDRATION

Original Material	Tobermorite Gel			Heat of Hydration (cal/g Silicate)
	C/S Ratio (moles/mole)	H/S Ratio (moles/mole)	Specific Surface Area (m ² /g Tob)	
C ₂ S	1.5	1.0	300	11.6
C ₃ S	1.5	1.0	300	81.1
Alite	1.5	1.0	300	77.0
C ₂ S	1.39	0.89	372	4.0
C ₃ S	1.39	0.89	372	75.3
C ₂ S	1.72	1.22	255	23.0
C ₃ S	1.72	1.22	255	89.7

Y = the heat of reaction of Eq. 4, in calories per gram of calcium hydroxide involved in that reaction;

h = the heat of reaction of Eq. 5, in calories per gram of water involved in that reaction;

ϵ_s = the surface energy of tobermorite gel, in cal/m².

The results of the calculation are given in Table 6.

The heat liberated in the hydration of a paste, H_s , is given by

$$H_s = H_u - H_1 \quad (7)$$

where H_s is given in calories per gram of original silicate. Combining Eqs. 6 and 7 gives

$$H_s = (1 - w_u) H_u - (w_c H + b Y + w_x h + A \epsilon_s) \quad (8)$$

The quantity $(1 - w_u)$ is the amount of calcium silicate that has reacted, in grams per gram of original unhydrated material, and therefore is a measure of the degree of hydration, α . Eq. 8 may therefore be written

$$H_s = \alpha H_u - (w_c H + b Y + w_x h + A \epsilon_s) \quad (9)$$

The heats liberated by complete hydration of C₂S, C₃S and alite to form C_{1.5}SH with surface area 300 m²/g were calculated from Eq. 9 by using the values of the parameters H and ϵ_s given in Table 6. The heat of hydration values thus obtained are the first group of data given in Table 7. These values are of interest because they may be compared with previously reported values.

Brunauer and Greenberg (4) reported heat of hydration values for C₂S and C₃S based on earlier unpublished work by the present authors. These earlier values, 7.9 cal/g C₂S and 77.2 cal/g C₃S, are to be compared with the values 11.6 cal/g C₂S and 81.1 cal/g C₃S given in Table 7. The discrepancies, 3.7 and 3.9 cal/g silicate, respectively, are surprisingly small in view of refinements incorporated into the present investigation.

A comparison of the C_3S and alite results in Table 7 shows that the presence of alumina and magnesia has a significant influence on the heat of hydration. Even though the heat of solution of the alite used is considerably higher than that of C_3S , its heat of hydration is lower. This means that the tobermorite gel produced by this alite has a higher heat content than that produced by C_3S , probably because it contains Al_2O_3 and MgO in solid solution.

The heat of reaction of Eq. 4 corresponds to the value of Y obtained for Eq. 6. This value, -47.0 ± 14.5 cal/g calcium hydroxide indicates that Eq. 4 represents an endothermic process. The higher the C/S ratio of the tobermorite gel formed, the higher the heat of hydration. Thus, since a decrease in initial water/solid ratio of the paste tends to increase the C/S ratio of the tobermorite gel, there will be a corresponding increase in heat of hydration.

The heat of reaction of Eq. 5 corresponds to the value of h obtained for Eq. 6. This value, -425 ± 110 cal/g water, is in good agreement with a previously obtained result, -421 cal/g water (5).

The surface energy of tobermorite gel obtained in the present calculation is 0.107 ± 0.032 cal/m², or 450 ergs/cm², as compared with 386 ergs/cm² reported previously (5). A value of 418 ergs/cm² was reported for a tobermorite-like hydrate which forms as the precursor of afwillite in the ball-mill hydration of C_3S (19).

The results obtained here provide information which can be used to correct the observed heats of hydration of C_3S , C_2S and alite to values corresponding to a single reference state, no matter what the conditions of hydration are, so long as tobermorite gel is the calcium silicate hydrate formed. These corrected heats of hydration will be useful in investigations into the kinetics of hydration of C_2S , C_3S and alite.

Heats of hydration have been calculated for the "limiting" C/S ratio and specific surface area values discussed previously (6, 7). The calculated results are the last two groups of data given in Table 7. The values obtained illustrate the variation in heat of hydration for C_2S and C_3S that may occur over the range of reaction conditions that have been examined so far.

SUMMARY

The chemistry of hydration of C_2S , C_3S and alite has been examined for pastes hydrated under different experimental conditions. A decrease in water-cement ratio results in an increase in the C/S ratio of the tobermorite gel formed.

The higher the fineness of the original silicate, the greater the rate of hydration; no influence on the chemistry of the reaction can be attributed to fineness. The heats of hydration of C_2S , C_3S and alite have been related to the variation in C/S ratio of the tobermorite gel, as well as to the variation in H/S ratio and to the surface area of the hydration products.

Heats of hydration were evaluated for hydration to a reference tobermorite composition $C_1.5SH$. The chemical heats of hydration of C_2S , C_3S and alite for this case are 11.6, 81.1 and 77.0 cal/g original silicate, respectively.

Heats of reaction of $Ca(OH)_2$ and H_2O with the reference composition tobermorite were calculated. These are -47.0 cal/g $Ca(OH)_2$ and -425 cal/g H_2O , respectively. The surface energy of tobermorite was redetermined. A value of 450 ergs/cm² was obtained.

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Appendix A

MODIFIED FRANKE METHOD FOR THE DETERMINATION OF FREE $\text{Ca}(\text{OH})_2$

A modification of the Franke free $\text{Ca}(\text{OH})_2$ determination called the TVM, or time variation method, is described elsewhere (11). This procedure involves extractions for different periods of time and extrapolation of the data to zero extraction time. Certain refinements in the procedure were made. These revisions do not result in values different from those obtained previously, but they lead to an increase in the precision of the individual determinations. The standard deviation of the results of the present method is 0.005 g CaO per g ignited weight. In the revised method, the individual sample size used was 0.2 g, instead of 0.1 g, and the solvent was a 3 to 10 mixture of acetoacetic ester and isobutyl alcohol, a ratio double that previously used. The ester was vacuum distilled from technical grade material. Prior to extraction, 0.25 ml of a solution of 1 g NaOH in 100 ml denatured ethanol were added to the contents of the extraction flask. The alkali served to catalyze the conversion of the ester to the enol form, thereby shortening the required extraction times. Extractions were carried out for four different times; a blank determination was also made for each set. The blank correction included the contribution from the added alkali. Before titration, eight drops of a solution of 0.1 g methylene blue in 100 ml isobutyl alcohol were added, as a color mask, along with the thymol blue indicator. The color change observed at the end point, light green to dark blue, is more distinct than the yellow to reddish brown change observed without the masking agent.

Appendix B

HEAT-OF-SOLUTION CALORIMETER

Some modifications to the heat-of-solution calorimeter devised by Verbeck and Foster (12) have been described in another work (13). Further modifications have since been made. The calibrated Beckmann thermometer was replaced by a 20-junction copper-constantan thermopile. The reference thermopile was rigidly mounted on the calorimeter head by means of a bakelite extension arm. When the assembled calorimeter was placed in its constant-temperature water bath, the reference thermopile was immersed in water in a separate vacuum-wall flask which itself was immersed in the same water bath as the calorimeter. The output of the thermopile measured the difference in temperature between the calorimeter and the bath. The thermopile output was opposed by the output of a Leeds and Northrup K3 potentiometer. The difference signal was amplified by a Leeds and Northrup DC microvolt amplifier and recorded by a Speedomax type G recorder.

The thermopile output was approximately 800 microvolts per degree. An output of 10 millivolts from the DC amplifier which resulted in full scale deflection of the recorder pen corresponded to a 100-microvolt input to the amplifier. The sensitivity of the recorded signal was approximately 0.00125 deg per scale division (100 divisions full scale). These modifications resulted in a decrease in the time required to make each calorimetric determination. The standard deviation of the results obtained in the calorimeter is 0.75 cal/g sample.

Appendix C

DERIVATION OF EQUATION 6

In addition to the symbols defined in the text, the following symbols are used here:

H_c = the heat of solution of calcium hydroxide in calories per gram;

H_T = the heat of solution of tobermorite gel of composition $C_{1.5}SH$ or $(C, M)_{1.5} \cdot (S, 2A) \cdot H$ in calories per gram; and

K = the gravimetric factor referring $Ca(OH)_2$ to $C_{1.5}SH$ in accordance with reactions such as Eq. 3.

For C_2S and C_3S , respectively, the heat liberated by reaction according to Eq. 3, ΔH_3^o , may be expressed as

$$\Delta H_3^o = H_u^o + 1.5 H_H^o - H_T^o - 0.5 H_c^o \quad (C-1a)$$

$$\Delta H_3^o = H_u^o + 2.5 H_H^o - H_T^o - 1.5 H_c^o \quad (C-1b)$$

where

H_u^o = the molar heat of solution of C_2S or C_3S ;

H_H^o = the molar heat of solution (or dilution) of water;

H_T^o = the molar heat of solution of tobermorite gel of composition $C_{1.5}SH$; and

H_c^o = the molar heat of solution of calcium hydroxide.

The second term on the right side of Eqs. C-1a and C-1b is negligible.

The heat liberated by reaction according to Eq. 4, ΔH_4^o , may be expressed as

$$\Delta H_4^o = H_T^o + m H_c^o - H_T^{\prime o} \quad (C-2)$$

where $H_T^{\prime o}$ is the molar heat of solution of tobermorite gel of composition $C_{1.5+m}SH_{1+m}$.

The heat liberated by reaction according to Eq. 5, ΔH_5^o , may be expressed as

$$\Delta H_5^o = H_T^{\prime\prime o} + n H_H^o - H_T^{\prime\prime o} \quad (C-3)$$

where $H_T^{\prime\prime o}$ is the molar heat of solution of tobermorite gel of composition

$C_{1.5+m}SH_{1+m+n}$. The second term on the right side of Eq. C-3 is negligible.

The overall heat of hydration, ΔH_2^o , corresponding to the reactions expressed by Eqs. 2a and 2b, is given by the sum of Eqs. C-1, C-2 and C-3

$$\Delta H_2^o = \Delta H_3^o + \Delta H_4^o + \Delta H_5^o \quad (C-4)$$

Combining Eqs. C-1a and C-1b with Eq. C-4 gives

$$\Delta H_{2a}^o = H_u^o - (H_T^o + 0.5 H_c^o + \Delta H_4^o + \Delta H_5^o) \quad (C-5a)$$

$$\Delta H_{2b}^o = H_u^o - (H_T^o + 1.5 H_c^o + \Delta H_4^o + \Delta H_5^o) \quad (C-5b)$$

The parts of Eqs. C-5a and C-5b in parentheses represent the total molar heats of solution of the hydration products per mole of original silicate of Eqs. 2a and 2b, H_1° ,

$$H_1^{\circ} = H_T^{\circ} + 0.5 H_C^{\circ} + \Delta H_4^{\circ} + \Delta H_5^{\circ} \quad (\text{C-6a})$$

$$H_1^{\circ} = H_T^{\circ} + 1.5 H_C^{\circ} + \Delta H_4^{\circ} + \Delta H_5^{\circ} \quad (\text{C-6b})$$

According to Eq. 3, each gram of silicate hydrated produces w_T grams of $C_{1.5}SH$ and w_c grams of calcium hydroxide, where the quantities w_T and w_c are given by

$$w_T = \frac{M_T}{M_{C_2S}} \text{ or } \frac{M_T}{M_{C_3S}} \quad (\text{C-7})$$

and

$$w_c = \frac{0.5 M_c}{M_{C_2S}} \text{ or } \frac{1.5 M_c}{M_{C_3S}} \quad (\text{C-8})$$

where M_T , M_c , and M_{C_2S} and M_{C_3S} are the molecular weights of $C_{1.5}SH$, $Ca(OH)_2$, C_2S and C_3S .

When the heat of solution of the hydration products, Eqs. C-6a and C-6b, is expressed in calories per gram of original silicates, H_1' , the equations become

$$H_1' = w_T H_T + w_c H_c + \Delta H_4 + \Delta H_5 \quad (\text{C-9})$$

where ΔH_4 and ΔH_5 are the heats of Eqs. 4 and 5 in calories per gram of original silicate.

Dividing Eq. C-8 by Eq. C-7 gives

$$\frac{w_c}{w_T} = \frac{0.5 M_c}{M_T} \text{ or } \frac{1.5 M_c}{M_T} \quad (\text{C-10})$$

Thus, in general

$$w_c = K w_T \quad (\text{C-11})$$

The C_2S preparation used in the present investigation contained a small amount of excess CaO dissolved in it, as was described previously (8). This dissolved CaO was assumed to hydrate at the same rate as the C_2S . For calculation purposes, with z moles of dissolved CaO per mole of C_2S , the composition of the C_2S may be represented by $C_{2+z}S$. The reaction products in Eq. 3a become $C_{1.5}SH + (0.5 + z)CH$. The constant K in Eq. C-11 is given by $(0.5 + z)M_c/M_T$ for this C_2S preparation. Combining Eq. C-11 with Eq. C-9 gives

$$H_1' = w_c \left(H_c + \frac{H_T}{K} \right) + \Delta H_4 + \Delta H_5 \quad (\text{C-12})$$

This last step was necessary in order to set up an equation for H_i' containing only independently measurable quantities, thus avoiding a redundancy which would prevent least squares solution for the parameters.

The terms ΔH_4 and ΔH_5 can be written as

$$\Delta H_4 = bY \quad (C-13)$$

$$\Delta H_5 = w_x h \quad (C-14)$$

Combining Eqs. C-13 and C-14 with Eq. C-12 gives

$$H_i' = w_c \left(H_c + \frac{H_T}{K} \right) + bY + w_x h \quad (C-15)$$

Eq. C-15 is an expression for the heat of solution of a hypothetical fully hydrated paste having negligible surface area. In fact, however, many of the pastes investigated were only partly hydrated, and the tobermorite gel hydration product in all pastes investigated had high surface area.

The observed heats of solution include contributions from unhydrated silicate and surface energy

$$H_i = w_u H_u + A\epsilon_s + H_i' \quad (C-16)$$

Combining Eq. C-16 with Eq. C-15 gives

$$H_i = w_u H_u + w_c \left(H_c + \frac{H_T}{K} \right) + bY + w_x h + A\epsilon_s \quad (C-17)$$

Eq. C-17 may be rewritten in the form

$$H_i - w_u H_u = w_c \left(H_c + \frac{H_T}{K} \right) + bY + w_x h + A\epsilon_s \quad (C-18)$$

The quantity $(H_c + H_T/K)$ may be represented by H , in which case Eq. C-18 becomes

$$H_i - w_u H_u = w_c H + bY + w_x h + A\epsilon_s \quad (6)$$

which is the form of the heat of solution equation discussed in the text.