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THERMAL DECOMPOSITION OF α-DICALCIUM SILICATE HYDRATE*

J. JERNEJČIČ
The Boris Kidrič Institute of Chemistry, 61000 Ljubljana (Yugoslavia)

N. VENE
Institute Jožef Stefan, University of Ljubljana, 61000 Ljubljana (Yugoslavia)

A. ZAJC
Research Institute for Materials and Constructions, 61000 Ljubljana (Yugoslavia)

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ABSTRACT

By hydrothermal treatment in saturated steam at 180°C for 24 h relatively pure α-C_2SH was obtained from lime–quartz mixtures, from β-C_2S, and from γ-C_2S. On heating 100-mg samples at 6°C min^{-1}, the main dehydration of α-C_2SH takes place between 380 and 500°C. In this temperature range, an endotherm at 460–470°C is characteristic for the DTA curve. Both temperature (395–450°C) and intensity of a second endotherm depend on the starting materials used for the synthesis of α-C_2SH. Considerations pertaining to the course of the dehydration show that in various samples the water binding is not equally strong, so that the composition of the samples cannot be directly calculated from the 380–500°C weight loss. On decomposition, α-C_2SH converts into γ-C_2S, during which process the formation of an intermediate phase was confirmed. The disaccord of literature data on thermal decomposition of α-C_2SH is probably due to different preparation of samples examined by various authors. By heating α-C_2SH to 1000°C and by cooling the calcined product to room temperature, β-C_2S can be obtained.

INTRODUCTION

Alpha-dicalcium silicate hydrate was first found by Thorvaldson and Shelton[1] in steam-cured Portland cement mortars at about 150°C. Many investigators have confirmed the possibility of its formation from a wide range of starting materials under hydrothermal conditions at temperatures between 100 and 200°C[2–21]. According to Lea[22] and Taylor[23], α-C_2SH is most reproducibly obtained by hydrothermal treatment of β-C_2S at 140–160°C for about 14 days. The formation of α-C_2SH can be considerably supported by the addition of seed crystals to the starting material[24,25]

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as well as by the presence of excess calcium hydroxide or alkalis[4] in reaction mixtures treated at temperatures up to about 180°C. A higher water/solid ratio, the stirring of the reaction mixture during the hydrothermal treatment, and the use of freshly hydrated lime also favor the formation of α-C_2SH[4]. A synthesis of larger amounts of α-C_2SH from lime and quartz has been reported, its products containing 14–20% of unreacted lime[11]. According to Taylor[23], the formation of α-C_2SH from the lime–silica mixtures occurs through the intermediate formation of an ill-crystallized lime-rich phase. Under favorable conditions, α-C_2SH crystallizes relatively well. Its crystal structure is composed of Ca^{2+}, $(HSiO_4)^{3-}$ and $(OH)^-$ ions making up the constitutional formula $Ca_2(HSiO_4)(OH)$[3]. C/S ratio of α-C_2SH has been suggested as variable[26].

In practice, α-C_2SH may be found in large amounts in Portland cement pastes containing silica in the amount from 0 to 20% of total binder, when they are treated hydrothermally above 100°C. Although strongly crystallized, α-C_2SH is a weak binder[27]. Consequently, the presence of α-C_2SH in autoclaved calcium silicate products lowers their mechanical strength and is therefore generally not desired[10, 13, 16, 28]. On the other hand, α-C_2SH has little tendency to shrink when dried or carbonated and an idea subsists that investigators especially need to examine the C/S mole ratio in the area between 2 and 3 in the range from 100 to 170°C. In this way products marked by useful strength and volume stability characteristics may be obtained. Some investigations in this direction seem to have been performed already[14, 29–31].

According to several authors[3–6, 26, 32, 33], for the DTA curve of α-C_2SH an endotherm at 470–480°C is characteristic, which is sometimes slightly divided[32]. Some authors observed sporadically an additional, less pronounced endotherm at 430°C[4–6]. Similar results but lower temperatures have been reported by other authors (460°C and 410°C[34], 430°C and 350°C[18], respectively).

In the range of these endotherms, the thermogravimetric curve of α-C_2SH shows a sharp loss in weight, which is due to dehydration of this compound. According to Lea[22] and Taylor[23] unoriented β-C_2S is formed at static dehydration in air at about 400–450°C. Garnute and Chromy report similar results[34], whereas according to Butt and his coworkers[4] the decomposition of α-C_2SH at these temperatures proceeds over an X-phase which converts into γ-C_2S at 500°C.

The present work has been carried out on account of the importance of α-C_2SH for the industry of autoclaved calcium silicate building products. It has been supported by various data on the thermal behavior of α-C_2SH.

EXPERIMENTAL

For the synthesis of α-C_2SH four original starting materials were chosen, namely hydrated lime (H.L.), calcined lime (C.L.), quartz flour (Q), and γ-C_2S(I).

γ-C_2S was made by calcining a homogenized mixture of H.L. and Q (molar ratio C/S = 2,0) for several hours at 1450°C. The X-ray analysis revealed that γ-C_2S(I) contained only a few per cent of the β-form. Chemical analyses of these starting

TABLE 1

STARTING MATERIALS ANALYSES (%)

	H.L.	*C.L.*	*Q*	*γ-$C_2S(1)$*
SiO_2	0.04	0.20	99.5	34.3
Al_2O_3	0.09	0.1	0.16	0.28
Fe_2O_3	0.06	0.95	0.04	0.04
CaO	69.5	91.5	0.01	64.5
MgO	0.8	0.8	<0.01	0.3
K_2O	0.02	0.03	[a]	0.17
Na_2O	0.01	0.01	[a]	0.21
SO_3	0.56	0.31	[a]	<0.1
CO_2	2.8	1.06	[a]	[a]
Ignition loss	27.2	4.81	0.25	0.18
Surface area, ($cm^2\ g^{-1}$)	5050	7470[b]	8930	3000

[a] Not determined.

[b] Value for H.L. obtained by hydration of C.L.

TABLE 2

SAMPLE PREPARATION

Sample No.	*Composition of starting mixture (C/S = 2.0; 2% α-C_2SH added)*		*Surface area ($cm^2\ g^{-1}$)*
1	C.L. + Q	from Table 1.	cf. Table 1
2	H.L. + Q	from Table 1.	cf. Table 1
3	β-$C_2S(1)$	made by calcining γ-$C_2S(1)$ for 20 h at 1000°C, 0.5% B_2O_3 added as hot water solution of H_3BO_3.	6300
4	β-$C_2S(2)$	made by calcining Sample 2 for 2 h at 1000°C.	5400
5	β-$C_2S(3)$	made by calcining Sample 1 for 2 h at 1000°C.	7100
6	γ-$C_2S(1)$	from Table 1.	4700
7	γ-$C_2S(2)$	made by calcining Sample 2 for 2 h at 650°C.	6200

materials are shown in Table 1. As can be seen, they were commercial grade, but of appreciable purity.

The preparation of starting mixtures is explained in Table 2. Seven different 500 gram samples of α-C_2SH were synthesized by hydrothermal treatment of these well-homogenized starting mixtures in saturated steam at 180°C for 24 h applying a water/solid ratio of 8,0. After autoclaving, the suspension was filtered by means of suction and the solid product was dried overnight at 150°C.

High-temperature powder patterns were taken on a Guinier-Lenné camera (Enrof-Nonius) at a heating and cooling rate of 2°C min^{-1}, respectively. A high-temperature attachment (Anton Parr, K.G.) was put to a Philips goniometer apparatus in order to follow high-temperature changes isothermally or in shorter periods. In both cases CuKα radiation was used.

Simultaneous DTA–TG–DTG curves were obtained on a Mettler Thermo-

TABLE 3

ANALYTICAL DATA ON SAMPLES

Sample No.	*Chem. analysis*		*X-ray data C_2S (%)*	*Surface area ($cm^2\ g^{-1}$)*
	Free CaO (%)	*CO_2 (%)*		
1	2.42	1.26	0	6500
2	2.80	2.06	0	9000
3	0.15	0.44	3	6300
4	0.30	0.32	1	5400
5	0.15	0.73	1	7100
6	0.15	0.63	6–7	4700
7	0.45	2.63	2	6200

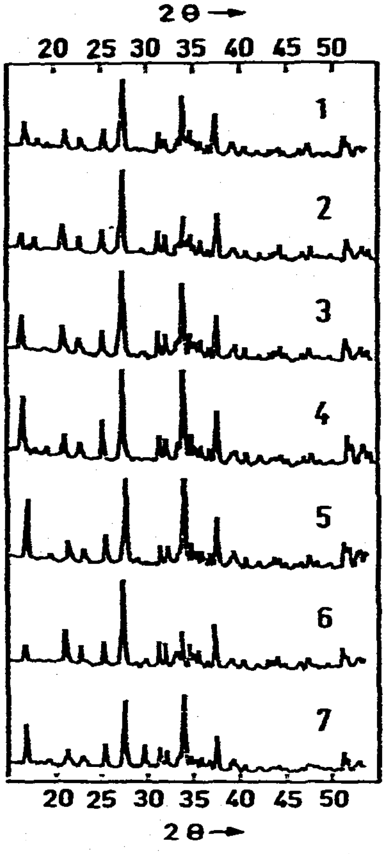


Fig. 1. X-ray diffraction patterns of Samples 1–7.

analyzer. 100-mg samples were heated in dry air at 6°C min^{-1} from room temperature to 950°C. The same quantity of calcined alumina served as reference material.

Further characterization of samples consisted of determinations of the free lime content[35], of the CO_2 content (Westhoff), and of the surface area (Blaine). The content of unreacted β- and γ-C_2S, respectively, was estimated by X-ray diffraction using the method of known additions. Table 3 represents a summary of data on the examined samples; Fig. 1 shows their X-ray diffraction patterns in the range from 15 to 50° 2 θ.

TABLE 4

THERMOANALYTICAL RESULTS

Sample No.	*Weight loss (%) [Temp. range (°C)] [25–380–500–660–760–1000]*					*Total*	*Endotherm height (mm)/ temp. (°C)*		*Peak area 380–500°C (units)*	*Peak area/ weight loss 380–500°C*
							I	*II*		
1	0.55	8.50	1.05	1.05	0.45	11.60	41/430	65/460	308.8	36.33
2	1.15	8.15	1.05	1.50	0.50	12.35	58/450	61/465	286.0	35.09
3	0.50	6.50	1.55	0.30	0.25	9.10	16/405	49/470	254.2	39.11
4	0.15	8.20	0.80	0.45	0.40	10.00	25/400	68/465	340.4	41.51
5	0.25	8.15	0.75	0.50	0.50	10.05	19/400	68/465	311.6	38.16
6	1.30	7.70	0.70	0.65	0.50	10.85	15/400	66/465	306.6	39.82
7	1.15	6.15	0.80	2.25	0.65	11.00	10/400	48/465	222.0	36.10

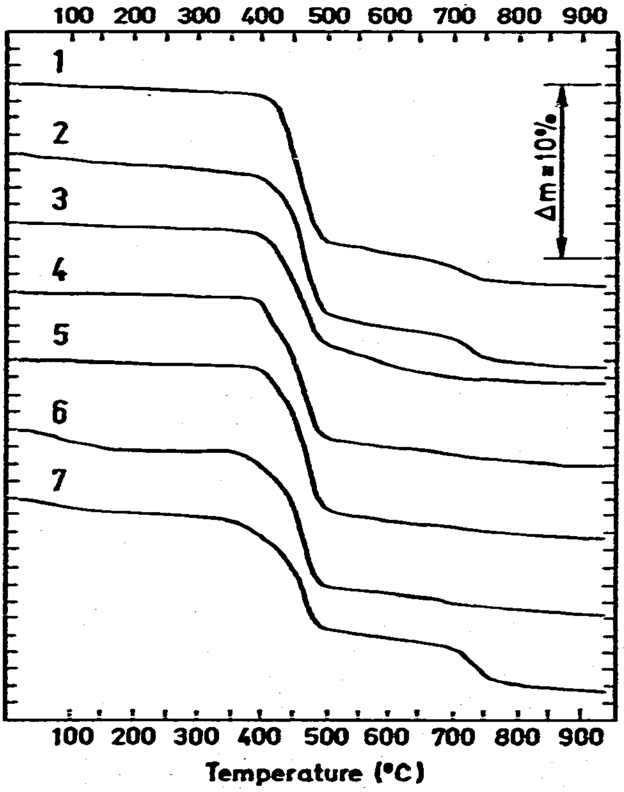


Fig. 2. TG curves of Samples 1–7.

RESULTS AND DISCUSSION

On Figs. 2–4 DTA–TG–DTG curves are shown for samples 1–7. Table 4 represents a summary of quantitative data resulting from these curves.

As can be seen from Fig. 2 and Table 4, the main weight loss of all samples takes place between 380 and 500°C. In the range between 660 and 760°C curves 1, 2 and 7 show an additional well-pronounced weight loss which is proportional to the content of CO_2 in the samples (cf. Table 3).

Figure 3 and Table 4 show that the temperatures of the main endotherm range between 460 and 470°C, whereas the intensities and the temperatures of the smaller endotherm depend on the sample investigated. When α-C_2SH is synthesized from γ-C_2S, the temperature is about 400°C and the endotherm is only poorly expressed (curves 6 and 7). When synthesizing from β-C_2S, the temperature of the endotherm remains almost the same but its intensity becomes stronger (curves 3, 4 and 5). When synthesizing from lime and quartz, the temperature of the endotherm moves to higher values (curves 1 and 2). An additional endotherm (shown on curves 1 and 2) appears at 480°C; it is attributed to the thermal decomposition of calcium hydroxide which is a component of Samples 1 and 2 (cf. Table 3).

From Fig. 4, it follows that the course of DTG curves in the range between 350 and 500°C is quite similar to the course of DTA curves. Consequently, thermal effects can be at least substantially attributed to thermal decomposition. This view can be substantiated by dividing the DTA peak area with the corresponding weight loss (Table 4), where—within the limits of error—satisfactory constant values can be observed.

For further quantitative consideration some helpful stoichiometric calculations can be made use of. Their results are presented in Table 5. Column 2 represents the

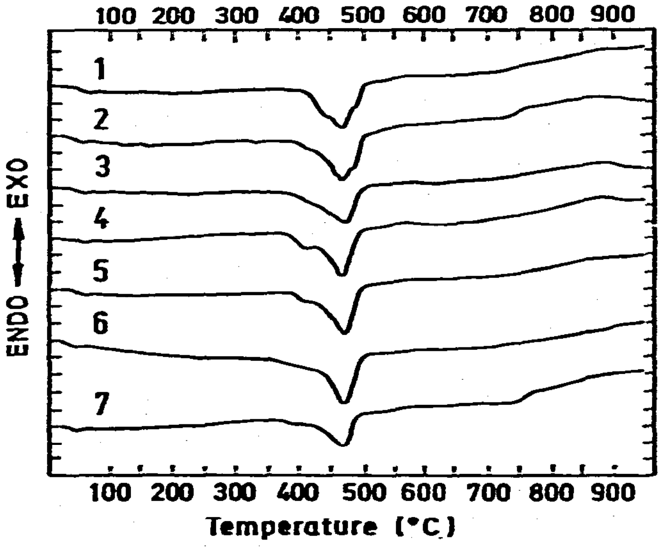


Fig. 3. DTA curves of Samples 1–7.

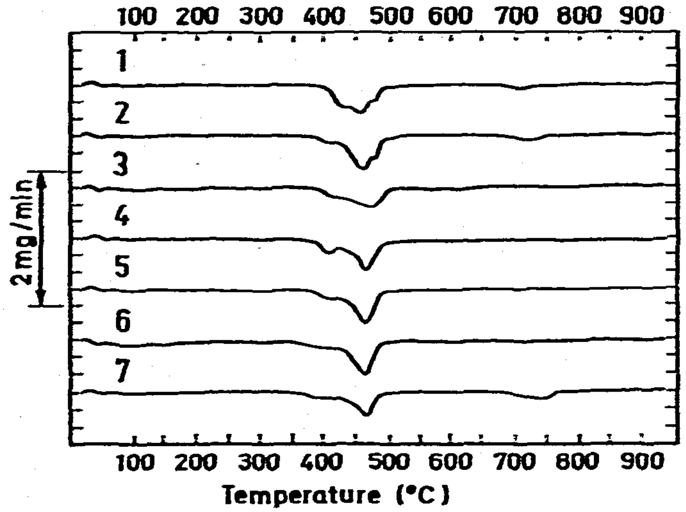


Fig. 4. DTG curves of Samples 1–7.

TABLE 5

IMPORTANT VALUES DERIVED FROM TABLES 3 AND 4

Sample No.	*C_2S as C_2SH_x* (%), exptl.*	*H_2O in C_2SH_x (%), exptl.*	*H_2O in C_2SH (%), calc.*	*Difference 3–4 (%)*	*C_2SH_x content (%), calc.*	*x in C_2SH_x from 2 and 3*	*x in C_2SH_x from 2 and 25–500°C weight loss*
1	84.37	9.56	8.73	0.83	93.93	1.08	0.96
2	82.23	9.39	8.51	0.88	91.62	1.09	0.95
3	87.39	8.61	9.04	−0.43	96.00	0.94	0.71
4	88.04	9.38	9.11	0.27	97.42	1.03	0.89
5	88.07	9.27	9.11	0.16	97.34	1.01	0.88
6	81.90	10.17	8.47	1.70	92.07	1.19	0.90
7	83.79	8.23	8.67	−0.44	92.02	0.94	0.70
1	2	3	4	5	6	7	8

* C/S = 2.0 taken as C/S ratio in calcium silicate hydrate phase.

percentage of C_2S after subtracting its unreacted part, $Ca(OH)_2$ and $CaCO_3$ (derived from Table 3). Column 3 was obtained by subtracting from the total weight loss (Table 4) the CO_2 content and the amount of water bound to the free lime (Table 3). Column 4 indicates the amount of water that should be bound to C_2S (column 2) in order to yield the theoretical composition of α-C_2SH. Column 5 needs no special comment. Column 6 represents the sum of columns 2 and 3, from which also data on the composition of C_2SH_x (column 7) are derived. Column 8 contains the same data as column 7 except that the weight loss from 25 to 500°C (Table 4) was chosen for H_x in C_2SH_x.

TABLE 6

RESULTS OF X-RAY EXAMINATIONS

Sample No.	Phase transitions (°C)		
	Heating		Cooling
1	400	830	520
2	390	870	520
3	400	870	410
4	420	830	540
5	420	860	480
6	410	880	520
7	390	840	540

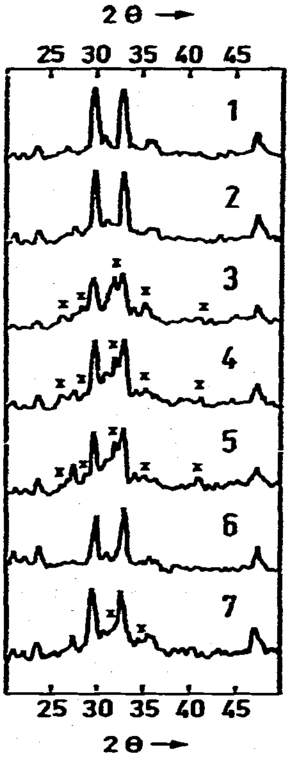


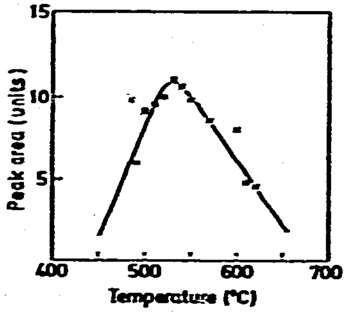
Fig. 5. X-ray diffraction patterns of Samples 1–7 at 500°C.

Table 5 shows that Samples 4 and 5 are the ones that are most close to the theoretical composition of C_2SH; they are also very similar with regard to the course of their thermal decomposition (Table 4). Although Samples 1–3, 6 and 7 are of appreciable purity, their loss of water proceeds somewhat differently (Table 4). This is especially true for Samples 3 and 7, where an extraordinarily low weight loss can be noticed in the range between 380 and 500°C. Obviously, the water binding in different samples is not equally strong. As a consequence of this, even synthetic

TABLE 7

X-RAY DIFFRACTION DATA OF SAMPLES HEATED TO 500 °C

Observed with samples 3, 4, 5 and 7		*Data for β-C_2S from ref. 23*	
d (Å)	*I*	*d (Å)*	*I*
4.67	vw	4.65	w
3.42	w	3.38	w
3.20	vw	3.18	vw
2.82	vs/b	2.794	vs
2.63	ms	2.609	s
2.56	w	2.546	w
2.19	w	2.189	s
2.00	w	1.984	m
1.92	w	1.913	w



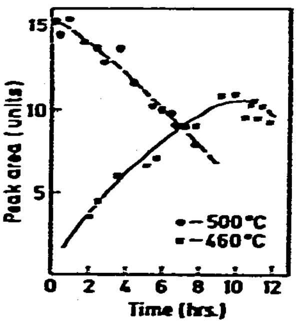


Fig. 6. Areas under the $d = 2.82$ Å reflection in relation to heating temperature for Sample 3.

Fig. 7. Areas under the $d = 2.82$ Å reflection in relation to heating time for Sample 3.

α-C_2SH does not seem to be a perfectly defined substance, a fact which is commonly observed with other synthetic hydrated calcium silicates.

The results of high-temperature X-ray powder diffraction examinations are summarized in Table 6. On heating, the diffraction pattern of α-C_2SH disappears at about 400 °C and weak reflections of γ-C_2S can be observed. On further heating, these reflections become more intense until in the range from 830 to 880 °C the conversion into α'-C_2S (bredigite) occurs. On cooling—at 540 °C or below—α'-C_2S converts into β-C_2S which remains unchanged even after prolonged storage at room temperature. This low-temperature stability of β-C_2S can be attributed to its microcrystallinity on account of relatively low calcining temperature rather than to the stabilizing effect of impurities.

Figure 5 shows diffraction patterns of Samples 1–7 taken on the goniometer apparatus at 500 °C. Besides the reflections of undecomposed α-C_2SH and of γ-C_2S formed, additional reflections denoted as X can be observed on patterns 3, 4, 5 and 7. As can be seen from Table 7, these reflections are very close to some reflections of β-C_2S occurring in this angular range. However, by plotting the area under the reflection X at 31,70° 2 θ ($d = 2{,}82$ Å) versus temperature, Fig. 6 is obtained for Sample 3, and when that area is plotted versus time during the isothermal treatment at 460 and 500°C, respectively, Fig. 7 is acquired. From Figs. 6 and 7 it can be concluded that on prolonged heating the content of the intermediate phase decreases. For these reasons the present authors are not sure that the intermediate phase is actually β-C_2S. As on prolonged heating the reflections of γ-C_2S become more intense, it can just be inferred that γ-C_2S is the final decomposition product of α-C_2SH.

Due to the limited sensitivity of the apparatus it was not possible to state whether or not the formation of the intermediate phase took place during the heating process of Samples 1, 2 and 6. Nevertheless, it can be qualitatively concluded that the amount of the phase formed depends on the starting substances that are used for the preparation of α-C_2SH.

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REFERENCES

1 T. Thorvaldson and G. R. Shelton, *Can. J. Res.*, 1 (1929) 148.
2 A. Aitken and H. F. W. Taylor, *J. Appl. Chem.*, 10 (1960) 7.
3 H. G. Midgley and S. K. Chopra, *Mag. Concr. Res.*, 12 (1960) 20.
4 J. M. Butt, L. M. Raschkowitsch, D. M. Heiker, A. A. Maier and O. I. Goratschewa, *Silikattechnik*, 12 (1961) 281.
5 J. M. Coldrey and M. J. Purton, *J. Appl. Chem.*, 18 (1968) 353.
6 M. J. Purton, *J. Appl. Chem.*, 20 (1970) 293.
7 V. Amicarelli and V. Sabatelli, *Chem. Abst.*, 76 (1972) 64558q.
8 B. V. Imlach and H. F. W. Taylor, *Trans. Br. Ceram. Soc.*, 71 (1972) 81.
9 O. Henning and B. Gerstner, *Wiss. Z. Hochsch. Architekt. Bauw. Weimar*, 19 (1972) 53.
10 B. V. Imlach and H. F. W. Taylor, *Trans. Br. Ceram. Soc.*, 71 (1972) 71.
11 A. Razvadauskas and K. Sasnauskas, *Chem. Abstr.*, 79 (1973) 118015t.
12 R. C. Walker and M. J. Purton, *J. Appl. Chem. Biotechnol.*, 76 (1973) 879.
13 B. Šutej, *Cement (Zagreb)*, 14 (1970) 18.
14 A. Razvadauskas and K. Sasnauskas, *Chem. Abstr.*, 76 (1972) 89573d.
15 A. A. Govorov and N. A. Ovramenko, *Dokl. Akad. Nauk SSSR*, 189 (1969) 1314 *(Khim. Tekhnol.)*.
16 K. K. Kuatbaev, *Chem. Abstr.*, 71 (1969) 15759n.
17 A. Gumulyauskas and G. Pavlyuk, *Chem. Abstr.*, 74 (1971) 34302t.
18 Z. Šauman, *Proc. Symp. Autocl. Calcium Silicate Build. Prod.*, Society of Chemical Industry, London, 1967, p. 101.
19 P. P. Budnikow, L. A. Kroitschuk and B. N. Vinogradow, Preprint of *Symp. Autocl. Calcium Silicate Build. Prod., Hannover 1969*, Paper 10.
20 T. Mitsuda and K. Fukuo, *Mineral. J.*, 6 (1969) 17.
21 T. Mitsuda, *Mineral. J.*, 6 (1970) 143.
22 H. F. W. Taylor, in H. F. W. Taylor (Ed.), *The Chemistry of Cements*, Vol. 1, Academic Press, London, 1964, p. 212.

23 F. M. Lea, *Chemistry of Cement and Concrete*, Arnold, London, 3rd. ed., 1970, p. 198.
24 J. M. Butt and A. A. Maier, *Tr. Mosk. Khim. – Tekhnol. Inst.*, 24, (1957) p. 61.
25 H. Funk, *Z. Anorg. Allg. Chem.*, 297 (1958) 103.
26 G. L. Kalousek, J. S. Loguiduce and V. H. Dodson, *J. Am. Ceram. Soc.*, 37 (1954) 7.
27 ACI Committee 516, in *High Pressure Steam Curing: Modern Practice, and Properties of Autoclaved Products*, ACI-Journal, 1965, p. 869.
28 G. Verbeck and L. E. Copeland, in *Menzel Symposium on High Pressure Steam Curing*, ACI Publication SP-32, Detroit, 1972, p. 1.
29 V. S. Bashkutov, J. M. Butt and V. V. Timashev, *Chem. Abstr.*, 71 (1969) 104844k.
30 A. Balandis, A. Razvadauskas and K. Sasnauskas, *Chem. Abstr.*, 80 (1974) 51771m.
31 A. Gumuliauskas and G. Pavlyuk, *Stroit. Mater.*, (1969), No. 7, p. 29.
32 S. A. Krzheminskij and N. K. Sudin, *preprint of Symp. Autocl. Calcium Silicate Build. Prod., Hannover, 1969*, Paper 40.
33 H. G. Midgley and S. K. Chopra, *Mag. Concr. Res.*, 12 (1960) 76.
34 A. Garmute and S. Chromy, *Silikaty*, (1973) 317.
35 E. E. Pressler, S. Brunauer and D. L. Kantro, *Anal. Chem.*, 28 (1956) 896.