

A STUDY OF REACTIONS BETWEEN THE $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}(\text{A})$ PHASE AND β -QUARTZ IN THE COURSE OF THE AUTOCLAVE PROCESS

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Hydrothermal treatment of the main Portland cement minerals $3\text{CaO} \cdot \text{SiO}_2$ and β - $2\text{CaO} \cdot \text{SiO}_2$ at above 120 — 130 °C produces $\text{C}_2\text{SH}(\text{A})$ as the main hydrosilicate phase, apart from $\text{Ca}(\text{OH})_2$ liberated by the reaction. Under hydrothermal conditions $\text{C}_2\text{SH}(\text{A})$ reacts fairly readily with β -quartz since already a 2-hour reaction at 175 °C (9 atm. g) yields $\text{CSH}(\text{I})$ as the main hydrosilicate phase of the system in question. In the subsequent process stage the above phase is partially transformed to 11 \AA tobermorite ($5\text{CaO} \cdot 6\text{SiO}_2 \cdot 5\text{H}_2\text{O}$). After a 72-hour reaction, $\text{C}_2\text{SH}(\text{A})$ could no longer be identified in the system.

INTRODUCTION

Hydration of $3\text{CaO} \cdot \text{SiO}_2$ or β - $2 \text{XaO} \cdot \text{SiO}_2$ at temperatures above 110 to 130 °C under corresponding pressure yields the $\text{C}_2\text{SH}(\text{A})$ phase also known as C_2S α -hydrate. Heller and Taylor [1] have shown that 52-day hydration of β - C_2S at 130 °C produces $\text{CSH}(\text{I})$ as the main phase, together with a small amount of $\text{Ca}(\text{OH})_2$. A 14-day reaction at 180 °C resulted in a mixture of α - and β -hydrates. Funk [2], [3], [4] showed that the $\text{C}_2\text{SH}(\text{A})$ phase is formed by the hydration of β - C_2S at temperatures from 100 °C upwards, probably from the metastable component of the $\text{CSH}(\text{II})$ type or possibly from CSH gel. The formation and conversion of those phases to $\text{C}_2\text{SH}(\text{A})$, apart from the formation of C_3S -hydrate (TSH), is similar in the case of $3\text{CaO} \cdot \text{SiO}_2$, as shown by Buckle and Taylor [5] and others [6]—[9].

Šauman [10]—[12] found that hydration of both C_3S and β - C_2S at 175 °C/9 atm.g. yielded $\text{C}_2\text{SH}(\text{A})$ beside $\text{Ca}(\text{OH})_2$ and C_3S -hydrate (in the case of C_3S); during this process no metastable components such as $\text{CSH}(\text{II})$ and possibly CSH gel were found. At the same time no transformation of $\text{C}_2\text{SH}(\text{A})$ to $\text{C}_2\text{SH}(\text{B})$ could be proved as could have been expected. This can be explained by the fact that the mixes were in the form of paste and not suspensions, in order to make the results applicable for practical technical purposes.

It can thus be assumed that the main hydrosilicate phase which is formed by the hydration of C_3S or β - C_2S at 175 °C/9 atm.g. is $\text{C}_2\text{SH}(\text{A})$, so that in mixtures of those components with quartz under the above hydrothermal conditions quartz reacts simultaneously with both $\text{Ca}(\text{OH})_2$ and $\text{C}_2\text{SH}(\text{A})$, and phases of the tobermorite group are formed.

In view of the fact that the reaction of β -quartz with α -hydrate has not yet been investigated in greater detail, this represents the main subject matter of the experimental part of the present study.

EXPERIMENTAL

Starting materials

A sample of $C_2SH(A)$ was prepared by hydrating β - C_2S in the form of suspension for a period of 72 hours at 175 °C. The calcium hydroxide liberated by the belite hydration process was removed by extraction using a mixture of ethyl acetoacetate with isobutyl alcohol. The other starting component was β -quartz (moisture-0.02 %, ignition loss-0.14 %, SiO_2 -99.73 %, Al_2O_3 -0.01 %, Fe_2O_3 -0.03 %, TiO_2 -0.01 %, CaO -0.04 %, MgO -0.05 %, K_2O -0.03 %, Na_2O -0.03 %). Specific surface (Blaine): 3.100 $cm^2 \cdot g^{-1}$.

A mixture of quartz and $C_2SH(A)$ was prepared in a 1 : 1 weight ratio; cubes (approx. $10 \times 10 \times 10$ mm) made of paste (addition of approx. 26–30 % boiled distilled water) were placed in a special holder located in small pressure vessels above the water level. The actual hydrothermal process was selected in such a way that the isothermal holding periods at 175 °C/9 atm.g. were 2, 4, 8, 16, 24 and 72 hours.

After spontaneous cooling of the pressure vessels, the reaction product was dried for 8 hours at 105 °C in nitrogen.

Methods employed

The main method utilized in the identification of components was microstructural X-ray diffraction analysis (X-ray diffractograph "Mikro 111"). The sample was first homogenized with an addition of 10 % $Mg(OH)_2$ employed as internal standard. DTA (Derivatograph, Orion) was also used together with transmission electron microscopy (Tesla). The techniques have been described in greater detail in a previous paper [13].

RESULTS AND THEIR DISCUSSION

Already after a 2-hour reaction the mixture quartz— C_2HS α -hydrate exhibits a relatively large amount of the hydrosilicate tobermoritic phase, since in the X-ray diffraction diagram the 3.09 Å interference shows a considerably intensity. Apart from this there are the 2.98 and 2.82 Å lines (the latter diffraction belongs also to α -hydrate). The remaining interferences correspond either to unreacted β -quartz or to α -hydrate (Fig. 1).

If the reaction period is prolonged to 4 hours, the intensity of the 3.09 Å line is substantially increased, with a simultaneous reduction of the ~ 3.28 Å interference intensity which belongs to α -hydrate. After 8-hour hydration there occurs an already considerably lower increment in the intensity of the 3.09 Å line. In the course of the 16 hour hydrothermal process one can observe another increment of the hydrosilicate content with a simultaneous decrease in the content of α -hydrate. The 2.83 Å line corresponds to both α -hydrate

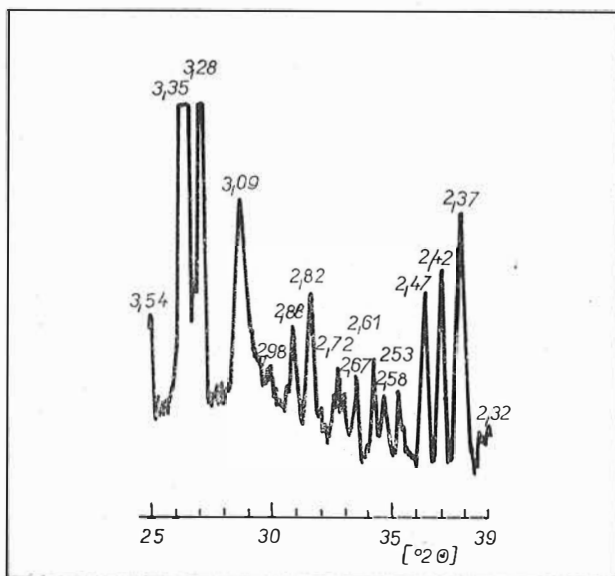


Fig. 1. X-ray diffraction diagram of a mixture of $C_2SH(A)$ with β -quartz (1 : 1); 2 hours/175 °C.

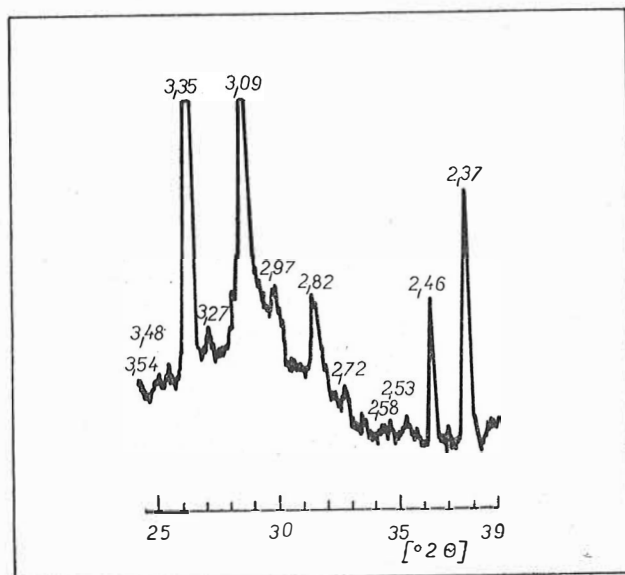


Fig. 2. X-ray diffraction diagram of a mixture of $C_2SH(A)$ with β -quartz (1 : 1), 24 hours/175 °C.

and the tobermoritic phase. After 24-hour hydration the reaction mixture already contains a very small quantity of C_2S α -hydrate, since the most intensive line of this component in the X-ray diffraction diagram is of low intensity. The α -hydrate content is lower than 5 % (Fig. 2).

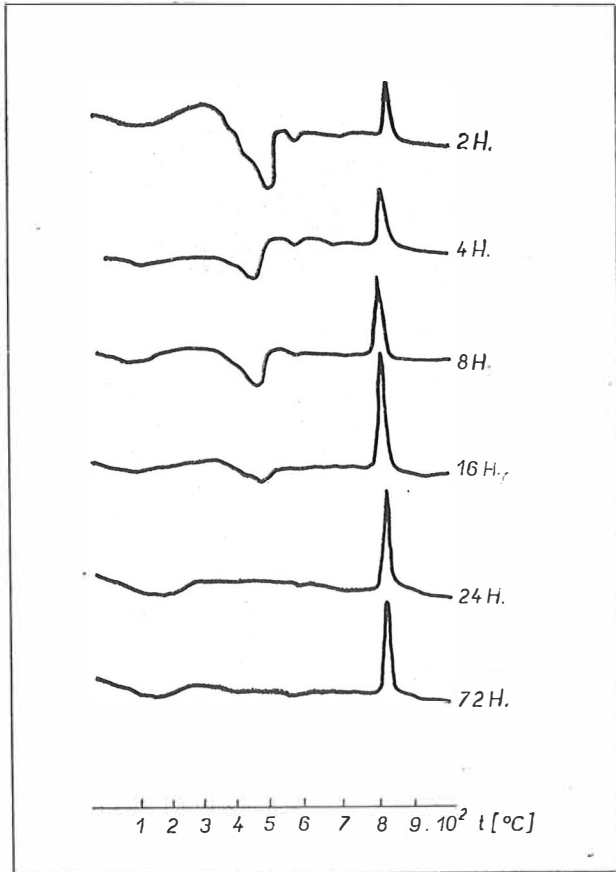


Fig. 3. The course of reactions between $C_2SH(A)$ -phase and β -quartz (1 : 1) followed by DTA.

After 72-hour reaction the sample contains practically only the tobermoritic phase, besides unreacted quartz. Other components which could possibly be present do not attain the limit content which is essential for their identification with the aid of the X-ray method employed.

The samples were also subjected to differential thermal analysis.

After 2-hour reaction there appears a very pronounced doubled endothermic peak caused by the decomposition of C_2S α -hydrate. The very slight deflection

of the differential curve is caused by the transformation of quartz from β - to α -modification (575 °C). A steep exothermic peak which probably indicates the presence of CSH(I) can be observed in the 800—900 °C temperature range.

The mixture of C₂S α -hydrate with quartz, hydrated for 4 hours, exhibits an already lower α -hydrate content, as can be seen from the area of the above mentioned endothermic peak with two exothermic ones. The exothermic peak between 800—900 °C is, however, still higher; analogical is the thermal analysis of the reaction product that has been treated hydrothermally for a period of 8 hours.

The sample hydrated for 16 hours already contains a very small quantity of α -hydrate only, since the area of the relevant double peak is indeed minimal. The height the exothermic peak reaches its maximum when compared with the DTA diagrams of the other samples.

The DTA curve of the sample that has been hydrated for 24 hours no longer displays the α -hydrate peak; only a slight inflection of the curve due to the change in SiO₂ modification can be observed. The result of DTA after 72-hour reaction (Fig. 3) is analogical.

Differences in morphology between C₂S α -hydrate and the tobermoritic phase allow also electron microscopy to be employed in the investigation of the reaction products.

Already after a 2-hour reaction the electron micrograph shows small, irregular leaves which belong to α -hydrate and also larger typical leaves and plates of the tobermoritic phase (Fig. 4).

After a 24-hour reaction there appear small leaves which look like needles at low magnification (α -hydrate), and larger leaves and plates of the tobermoritic component (Fig. 5).

Evaluation of the reaction course

From the measured values of the integral intensity of the individual lines there was determined the dependence of the relative content of the tobermoritic phase or C₂SH(A) on the time of reaction.

In the enclosed diagram (Fig. 6) the reaction time is plotted along the abscissa in hours after reaching the temperature of 175 °C and along the ordinate the line intensity ratio $\frac{I_{3.09 \text{ \AA}}}{I_{2.36 \text{ \AA}}}$ for plotting the increment of the tobermoritic component (on the left-hand side of the diagram) and the percent content of the soluble SiO₂-form together with the line intensity ratio $\frac{I_{3.27 \text{ \AA}}}{I_{2.36 \text{ \AA}}}$ for the determination of C₂SH(A) relative content on the right-hand side.

A generally uniform increase in the content of the tobermoritic component with the length of hydration process can be observed. In the case of the relative content of C₂S α -hydrate there takes place a rapid decrease of this component in the first reaction period (2, 4, 8 and 16 hours, respectively); however, in the further time stages the reduction of its content is very small.

The curve which represents the content of soluble SiO₂ becomes steeper between the 8—16-hour reaction period (maximum quantity of soluble SiO₂).

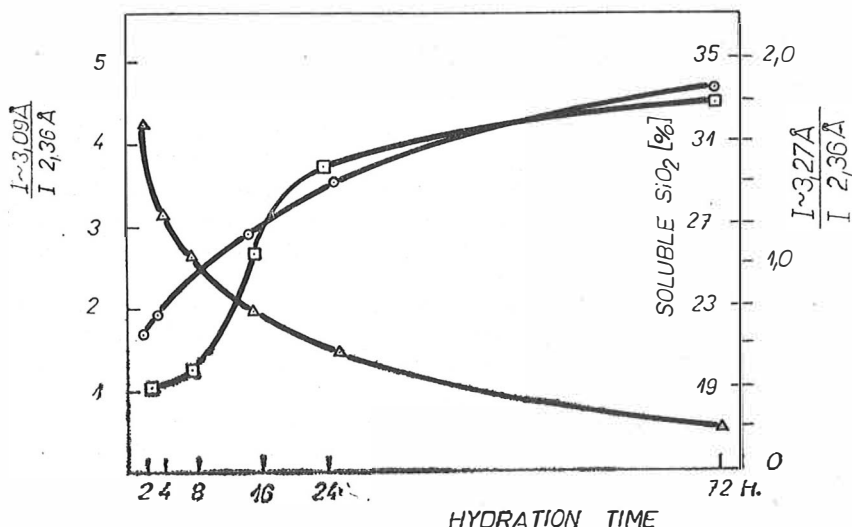


Fig. 6. Graphical representation of the reaction mechanism;

Δ $\frac{I_{3.27\text{Å}}}{I_{2.36\text{Å}}}$; ○ $\frac{I_{3.09\text{Å}}}{I_{2.36\text{Å}}}$; ◻ soluble form of SiO₂.

CONCLUSION

The reaction between the C₂SH(A) phase and β-quartz at 1 : 1 weight ratio was investigated at 175 °C/9 atm.g. for isothermal holding periods from 2 to 72 hours. It was found that the reaction proceeds at relatively high rate, since already within 2 hours of the hydrothermal process at the above temperature a hydrosilicate component of the tobermoritic group is formed, apparently CSH(I), which is indicated above all by the steep exothermic peak after 800 °C. The contents of the main hydrosilicate component—CSH(I)—increase in proportion to the lengthened period of the hydrothermal process. The maximum content of this phase was noted after the 16-hour reaction. In the further course of time this phase is apparently transformed to 11 Å-tobermorite. The formation of gyrolite (2CaO · 3 SiO₂ · 2H₂O) or xonotlite (5CaO · 5SiO₂ · H₂O) could not be positively identified.

The content of the C₂SH(A) phase is reduced as the reaction period proceeds; after the 72 hour reaction, if still present at all, its quantity is insignificant.

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STUDIUM REAKCÍ MEZI FÁZÍ C₂SH(A) A β-KŘEMENEM
 V PRŮBĚHU AUTOKLÁVOVÁNÍ

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Zkoumána reakce mezi fází C₂SH(A) a β-křemenem ve váhovém poměru 1 : 1 při teplotě 175 °C/8 atp. od 2 do 72hodinové izotermní prodlevy. Zjištěno, že reakce probíhá poměrně značnou rychlostí, neboť již po 2 hodinách hydrotermálního pochodu při uvedené teplotě vznikají hydrosilikátové složky tobermoritické skupiny, zřejmě CSH(I), čemuž nasvědčuje především prudký exotermní efekt na křivce DTA po teplotě 800 °C. Úměrně s prodlužující se dobou hydrotermálního procesu vzrůstá obsah hlavní hydrosilikátové složky — CSH(I). Maximální množství této fáze je obsaženo po 16hodinové reakci. V dalším časovém sledu nastává zřejmě jeho přeměna v 11 Å-tobermorit. Tvorba gyrolitu (2CaO . 3SiO₂ . 2H₂O) nebo xonotlitu (5 CaO . 5 SiO₂ . H₂O) nebyla jednoznačně prokázána.

Obsah fáze C₂SH(A) s postupující dobou reakce se snižuje, po 72hodinové reakci, pokud je ještě přítomná, je její množství nepatrné.

- Obr. 1. Rentgenový difrakční záznam směsi C₂SH(A) s β-křemenem (1 : 1), 2 h/175 °C.
 Obr. 2. Rentgenový difrakční záznam směsi C₂SH(A) s β-křemenem (1 : 1); 24 h/175 °C.
 Obr. 3. Časový průběh reakcí mezi C₂SH(A) a β-křemenem (1 : 1), sledovaný DTA.
 Obr. 4. Elektronogram směsi C₂SH(A) s β-křemenem (1 : 1), 2 h/175 °C.
 Obr. 5. Elektronogram směsi C₂SH(A) s β-křemenem (1 : 1), 24 h/175 °C.
 Obr. 6. Grafické znázornění reakčního mechanismu;

$$\Delta \frac{I_{3,27 \text{ \AA}}}{I_{3,36 \text{ \AA}}}; \quad \circ \frac{I_{3,09 \text{ \AA}}}{I_{2,36 \text{ \AA}}}; \quad \square \text{ rozp. forma SiO}_2.$$

ИССЛЕДОВАНИЕ РЕАКЦИЙ МЕЖДУ ФАЗЕЙ C₂SH(A)
 И β-КВАРЦОМ В ТЕЧЕНИЕ ОБРАБОТКИ В АВТОКЛАВЕ

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Исследовалась реакция между фазей C₂SH(A) и β-кварцом с весовым отношением 1 : 1 при температуре 175 °C/8 атп от 2 до 72-часовой изотермической выдержки. Было установлено, что реакция протекает с относительно большой скоростью, так как уже после двух часов гидротермического процесса при приведенной температуре образуются гидросиликатные компоненты тоберморитической группы, вероятно CSH(I), свидетельством чего является прежде всего резкий экзотермический эффект на кривой DTA, появляющийся после температуры 800 °C. Пропорционально с увеличивающимся временем гидротермического процесса увеличивается содержание основного гидротермического компонента — CSH(I). Максимальное количество приведенной фазы

имеется после 16-часовой реакции. В дальнейшей последовательности во времени наступает со всей правдоподобностью его превращение в 11 Å-тоберморит. Образование гиролита ($2\text{CaO} \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) или ксопотишта ($5\text{CaO} \cdot 5\text{SiO}_2 \cdot \text{H}_2\text{O}$) не удалось однозначно доказать. Содержание фазы $\text{C}_2\text{SH(A)}$ с последовательным временем реакции понижается, после 72-часовой реакции (если она еще имеется) ее количество весьма незначительно.

Рис. 1. Рентгеновская дифракционная запись смеси $\text{C}_2\text{SH(A)}$ с β -кварцом (1 : 1); выдержка 2 часа, температура 175 °C.

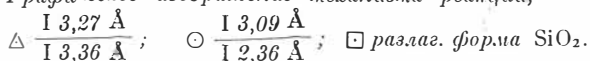
Рис. 2. Рентгеновская дифракционная запись смеси $\text{C}_2\text{SH(A)}$ с β -кварцом (1 : 1); выдержка 24 часа, температура 175 °C.

Рис. 3. Временная характеристика реакций между $\text{C}_2\text{SH(A)}$ и β -кварцом (1 : 1); исследуемый ДТА.

Рис. 4. Электронограмма смеси $\text{C}_2\text{SH(A)}$ с β -кварцом (1 : 1); выдержка 2 часа, температура 175 °C.

Рис. 5. Электронограмма смеси $\text{C}_2\text{SH(A)}$ с β -кварцом (1 : 1); выдержка 24 часа, температура 175 °C.

Рис. 6. Графическое изображение механизма реакции;



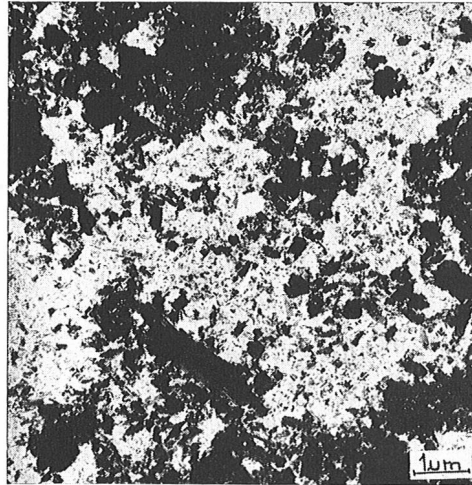


Fig. 4. Electron micrograph of a mixture of C₂SH(A) with β-quartz (1 : 1); 2 hours/175 °C.

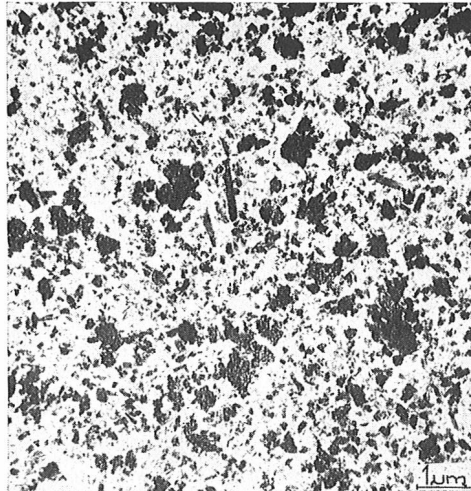


Fig. 5. Electron micrograph of a mixture of C₂SH(A) with β-quartz (1 : 1); 24 hours/175 °C.