

HYDROTHERMAL REACTIONS IN THE SYSTEM $3\text{CaO} \cdot \text{SiO}_2 - \text{CaSO}_4 \cdot 2\text{H}_2\text{O} - \text{H}_2\text{O}$

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The DHA method was used to investigate the sequence of reactions taking place in aqueous suspensions of mixtures of tricalcium silicate and gypsum, at heating rates of 1 to 10° C min⁻¹. The first product to form is crystalline hydroxyllelladite $\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3(\text{OH})_2$, and after the calcium sulphate has been spent, calcium hydrosilicate $\text{C}_3\text{SH}_{1.5}$ is produced. Extrapolation to zero heating rate shows that hydroxyllelladite can already form at a temperature of 95° C, and $\text{C}_3\text{SH}_{1.5}$ at temperatures higher than 160° C. The size of hydroxyllelladite crystals is larger by an order of quantity than that of $\text{C}_3\text{SH}_{1.5}$ crystals, and this is probably the cause of decreasing mechanical strength with increasing proportion of hydroxyllelladite in the reaction product.

INTRODUCTION

Djabarov and Slatanov [1] showed that in autoclave production of calcium silicate building materials, the presence of gypsum in the initial mix results in a decrease in strength of the final product. The same conclusion was reached by Takemoto and Kato [2] in their study of autoclaved materials based on Portland cement, where they convincingly proved the loss in strength to be due to the presence of a crystalline phase having the composition $\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3(\text{OH})_2$, which arises in the reaction mixture under hydrothermal conditions, and occurs in nature as the mineral hydroxyllelladite (further on HX).

The presence of this phase in autoclaved (high-pressure cured) materials based on quartz and lime was also proved by Šauman and Vavřín [3] who investigated the conditions for its formation and showed, that at a gypsum content in the initial mixture lower than 10 wt. %, the HX is only an intermediate product which eventually decomposes, forming tobermorite and anhydrite.

The present study is concerned with utilizing the DHA method in establishing the sequence of reactions taking place in suspensions of C_3S and $\text{C}\bar{\text{S}}\text{H}_2^1$ during their heating up. The method has the main advantage of allowing the course of the hydrothermal reactions to be examined continuously, i.e. without using interruption of the process by instantaneous cooling down [4, 5], as was done by the earlier authors.

EXPERIMENTAL

Materials

Tricalcium silicate (further on C_3S) was prepared from CaO and SiO_2 of AR purity. The triclinic

¹Use is made of the symbols C... CaO , S... SiO_2 , $\bar{\text{S}}...$ SO_3 and H... H_2O

modification was identified by X-ray analysis. Gypsum – $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (further on $\text{C}\bar{\text{S}}\text{H}_2$). Precipitated gypsum of AR purity was used. Hemihydrate $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ (further on $\text{C}\bar{\text{S}}\text{H}_{0.5}$) was prepared by dehydrating gypsum in an autoclave.

Method

Differential hydrothermal analysis (DHA) – the apparatus and method were already described in earlier studies [4, 5]. The mixtures of C_3S and $\text{C}\bar{\text{S}}\text{H}_2$ or $\text{C}\bar{\text{S}}\text{H}_{0.5}$ were put into the DHA sample holder and saturated with water directly before starting the analysis. Graphite was used as the reference sample.

Results

The sequence of reactions taking place on heating an aqueous suspension of 25% $\text{C}\bar{\text{S}}\text{H}_2$ and 75% C_3S at a water ratio of 0.4 is shown by the DHA curve in Fig. 1.

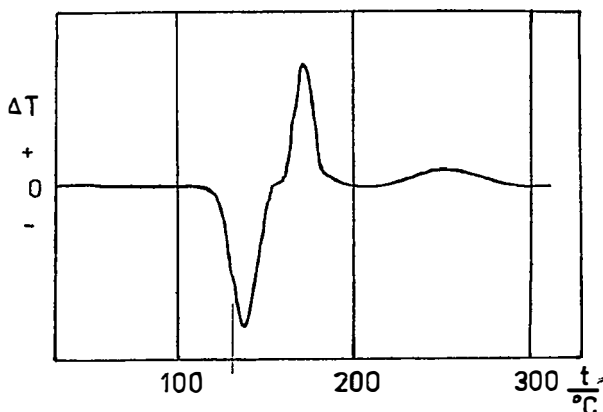


Fig. 1. DHA curve of aqueous suspension of C_3S + 25 wt. % $\text{C}\bar{\text{S}}\text{H}_2$.

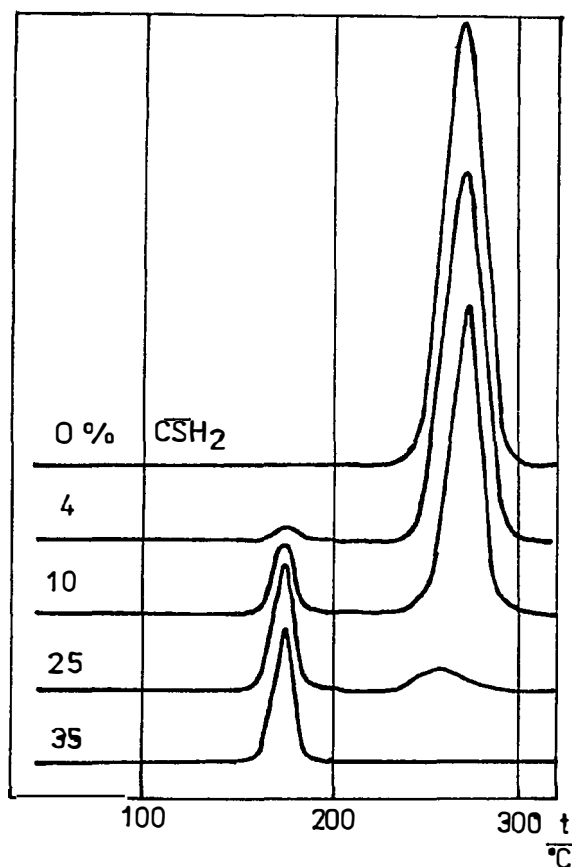
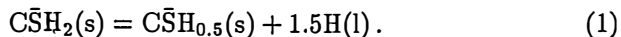
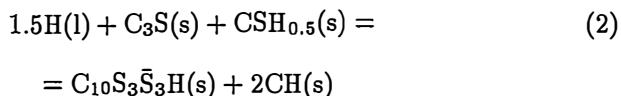


Fig. 2. DTA curves of aqueous suspensions of C_3S + $CSH_{0.5}$ mixtures.

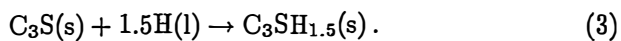
The first endothermal peak represents the reaction



The exothermal peak at 180°C is due to the reaction



and the last exothermal peak (240°C) is caused by the reaction



The products of these reactions, obtained by the abrupt cooling method [4, 5] were identified by X-ray analysis and DTA. The $C_3SH_{1.5}$ phase is formed as a metastable product. The effect of the phase composition on the sequence of the reactions is demonstrated by Fig. 2 (The gypsum was replaced by hemihydrate, thus eliminating the endothermal peak of reaction (1)).

The dependence of the composition of product on the composition of the initial mixture follows from the plot of the height of HX (180°C) and $C_3SH_{1.5}$

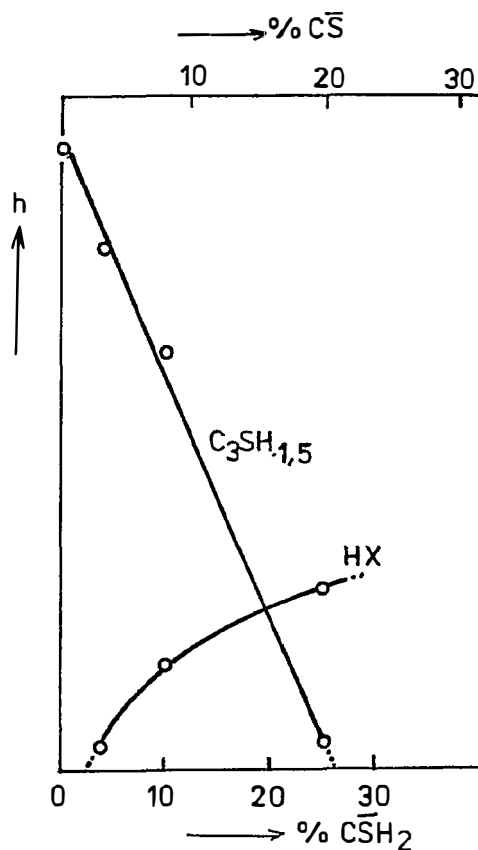


Fig. 3. Relationship between peak height (h) in diagram 2 and the gypsum content in the initial mixture.

(240°C) peaks vs. the $CSH_{0.5}$ content in the initial mixture (cf. Fig. 3).

The peak onset temperature, indicating the formation of HX, is 170°C at a heating rate of 10°C min⁻¹. However, it decreases with decreasing heating rate, as demonstrated by Fig. 4. The dependence is non-linear, but its extrapolation to zero heating rate indicates that HX can form as low as at 95°C. The actual temperature at which HX is capable of existing, is probably still lower.

Fig. 3 shows that in a mixture containing 25% CSH_2 , all of the C_3S was combined to form HX. Theoretically, according to equation (2) the C_3S should disappear completely from a mixture containing 25.3% CSH_2 . At a CSH_2 content higher than 25.3%, the hydrothermal reaction product contains only HX, anhydrite and portlandite, as has been proved by diffraction analysis. The lath-shape and the medium size of the HX crystals is shown in Fig. 5.

DISCUSSION OF THE RESULTS

According to the phase diagram which was established by Takemoto and Kato [2] for the temperature of 235°C (Fig. 6), only HX and portlandite should be

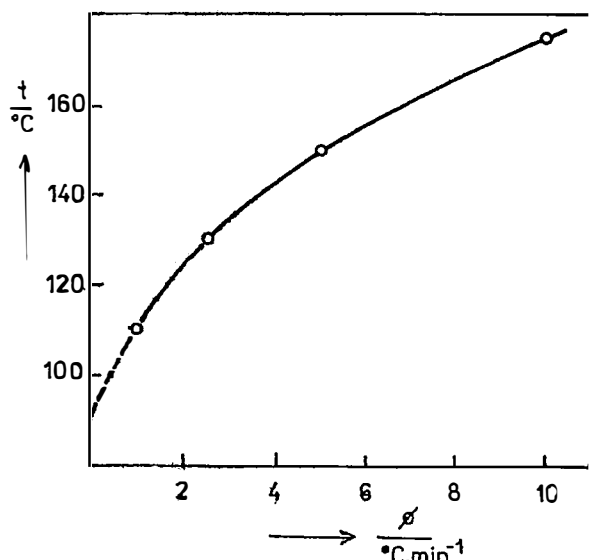


Fig. 4. Relationship between HX peak height and the rate of heating ϕ

present in a mixture with the ratio $\text{C}\bar{\text{S}} : \text{C}_3\text{S} = 0.20$ (i.e. 25.3% $\text{C}\bar{\text{S}}\text{H}_2 + 74.7\% \text{C}_3\text{S}$) at 235°C. Fig. 3 indicates that reaction (2) was almost quantitative, i.e. proceeded until both initial components were spent.

In mixtures containing a lower amount of $\text{C}\bar{\text{S}}\text{H}_2$, the phase diagram indicates formation of hillebrandite (C_2SH). In fact, however, the phase formed, described by Buckle [6], has the composition $\text{C}_3\text{SH}_{1.5}$ and according to some authors should be stable up to more than 270°C. The dependence of the onset of the peak on the heating rate (Fig. 7) indicates that the $\text{C}_3\text{SH}_{1.5}$ phase may form as low as at 150°C.

Figs. 1 and 2 show that HX is formed preferentially by reaction (2) from C_3S . As the size of its crystals is larger by at least one order of magnitude than that of the primary particles of $\text{C}_3\text{SH}_{1.5}$ (Fig. 8), one can see the reason why the final products exhibit a decrease of strength proportional to the content of HX, or in other words the content of $\text{C}\bar{\text{S}}\text{H}_2$ in the initial mixture. No explanation has so far been provided for the increase in strength at low gypsum contents (up to 3%), observed by Takemoto and Kato [2]. The cause may probably be found in the fact that the authors studied materials based on Portland clinker, and not pure C_3S .

It should be noted that HX is formed even in cases when the SO_4^{2-} ions have been introduced into the initial mixture by some substance other than gypsum, for example FeSO_4 , as demonstrated by Fig. 9.

The preferential formation of HX prior to that of calcium hydrosilicates during the heating of lime and quartz mixtures is indicated to by the results of investigations by Šauman and Vavřín [3]. These authors

studied mixtures in which the $\text{CaO}:\text{SiO}_2$ ratio was lower than unity in order to get into the composition region where tobermorite is stable at the given temperature (190°C). This composition belongs to the region where HX is not a stable phase, as can be readily seen in the diagram in Fig. 6. However, it may form in the initial stage of the reaction, where only a small proportion of quartz has reacted and the CaO/SiO_2 ratio in the reaction zone fits the existence region of HX. Eventually, of course, attainment of the state of equilibrium will bring about disappearance of the reactions of HX with quartz with simultaneous formation of anhydrite.

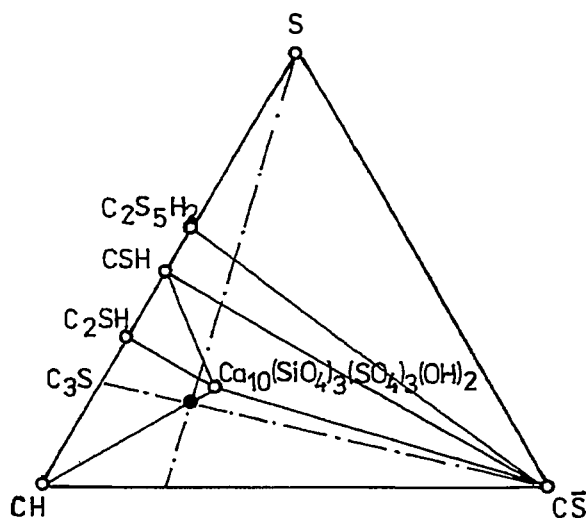


Fig. 6. Isothermal section through the system $\text{CaO}-\text{SiO}_2-\text{CaSO}_4-\text{H}_2\text{O}$ at 235°C.

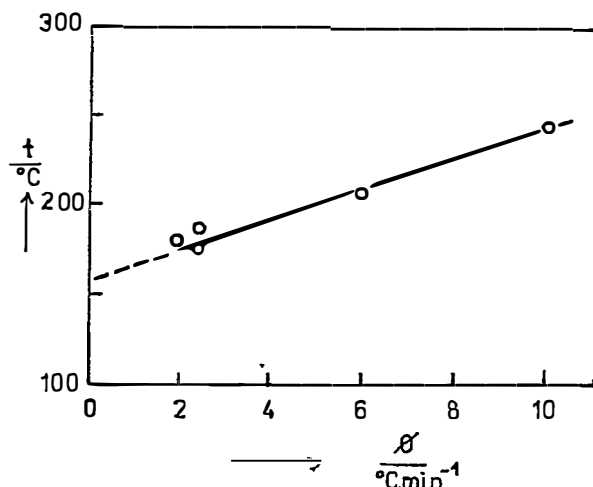


Fig. 7. Relationship between the height of peak of $\text{C}_3\text{SH}_{1.5}$ and the heating rate ϕ .

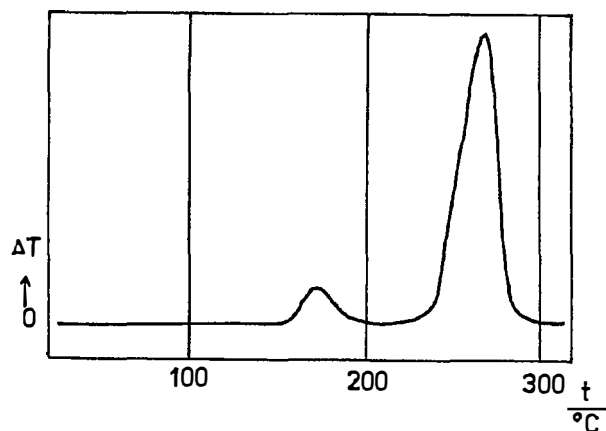


Fig. 9. DHA curve of C_3S mixture with 5% $FeSO_4$.

CONCLUSION

Heating up of an aqueous suspension of tricalcium silicate and gypsum leads to the formation of the hydroxyllelladite from the temperature of 95°C upwards. Once the gypsum has been spent and at temperatures in excess of 160°C, the remaining tricalcium silicate is converted to hydrated calcium silicate having the composition $C_3SH_{1.5}$.

The decrease of mechanical strength, associated with increasing content of hydroxyllelladite in the reaction product, which has been described by several authors, can probably be best explained to result from the difference in particle size of hydroxyllelladite and hydrated calcium silicate (amounting to at least one order of magnitude) which forms under the given conditions.

References

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HYDROTERMÁLNÍ REAKCE V SYSTÉMU $3CaO \cdot SiO_2 - CaSO_4 \cdot 2H_2O - H_2O$

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Metodou DHA byl vyšetřen sled reakcí probíhajících ve vodných suspenzích směsí tricalcium silikátu a sádrovce při rychlosti ohřevu 1 až 10°C/min. Jako první produkt vzniká krystalický hydroxyllelladit $Ca_{10}(SiO_4)_3(SO_4)_3(OH)_2$ a po vyčerpání síranu vápenatého se tvoří hydrosilikát vápenatý $C_3SH_{1.5}$. Z extrapolace na nulovou rychlost ohřevu vyplývá, že hydroxyllelladit může vznikat již při teplotě 95°C a $C_3SH_{1.5}$ při teplotě vyšší než 160°C. Krystaly hydroxyllelladitu jsou řádově větší než krystaly $C_3SH_{1.5}$, což je pravděpodobnou příčinou poklesu mechanické pevnosti s rostoucím podílem hydroxyllelladitu v reakčním produktu.

Obr. 1. Křivky DHA vodné suspenze směsí $C_3S + 25\% CSH_2$.

Obr. 2. Křivky DHA vodných suspenzí směsí $C_3S + CSH_{0.5}$.

Obr. 3. Závislost výšky peaků (h) v diagramu 2 na podílu $CaSO_4$ ve výchozí směsi.

Obr. 4. Závislost výšky peaku HX na rychlosti ohřevu ϕ .

Obr. 5. Krystaly hydroxyllelladitu. Snímek SEM.

Obr. 6. Izotermní řez systémem $CaO-SiO_2-CaSO_4-H_2O$ při 235°C.

Obr. 7. Závislost výšky peaku $C_3SH_{1.5}$ na rychlosti ohřevu ϕ .

Obr. 8. Krystaly $C_3SH_{1.5}$. Snímek SEM.

Obr. 9. Křivka DHA směsi C_3S s příměsí 5% $FeSO_4$.

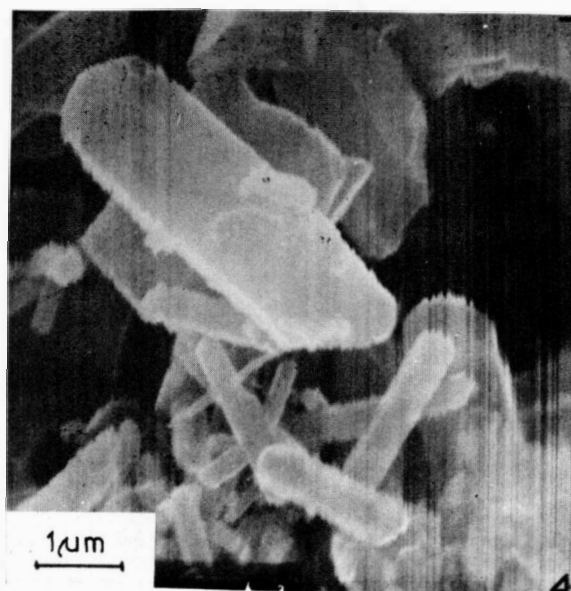


Fig. 5. Crystals of hydroxyllellestadite. SEM micrograph.

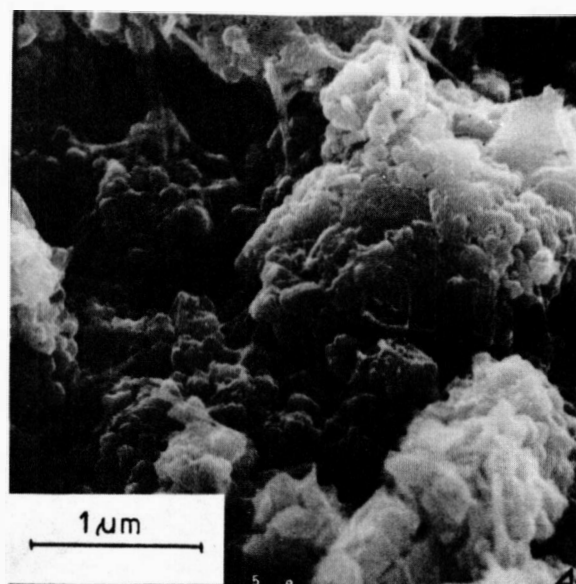


Fig. 8. Crystals of C₃SH_{1.5}. SEM micrograph.