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# HYDROTHERMAL REACTION OF $CaO - SiO_2 - H_2O$ AT 190°C. STUDY OF THE PRIMARY PRODUCT.

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## ABSTRACT

It was confirmed, that at given conditions dominantly originate nearly amorphous CSH[§] phases with molar ratio $CaO/SiO_2$ (further C/S only) fluctuated from 1 to 2. Generally, C/S in the primary product is higher than C/S in the reactants, depends onthis and on the specific surface of $SiO_2$. Study the DTA curves showed, that the thermal effects are clear and simple illustration of the phase composition of the primary product. Value of C/S influences the temperature of the characteristic exopeak of CSH gel on the DTA curve (820-855°C). $\alpha$-$C_2S$ hydrate was detected with the help of the DTA curves and its formation depends next to the specific surface of $SiO_2$ (1) on " degree of crystallinity" of $SiO_2$ too.

## INTRODUCTION

Formation of calcium silicate hydrates takes place in the system $CaO$-$SiO_2$-$H_2O$ at normal temperature and hydrothermal conditions too. C/S, phase composition and structures of these are determined by the composition of the reactants, temperature and pressure at reaction, time of reaction, chemical and mineralogical composition of $SiO_2$ and its specific surface (1-3). Dissolution of CaO and $SiO_2$ is the rate determining step of the reaction in the initial stage (1,3,4). Alteration of the specific surface of $SiO_2$ causes the quantitative alteration of the offer of $SiO_2$ into the solution and into the reaction (1). This explains the formation of primary product in dependence on the specific surface of $SiO_2$ (1,3). Calcium silicate hydrates can be identified by the methods of wet chemical analysis, powder x-ray diffraction, thermal analysis or their combinations (1, 5-7).

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† deceased : 1984 September the 6-th
§ used cement chemistry notation of oxides: C=CaO, $S=SiO_2$, $H=H_2O$

In present work was studied the primary product of the hydrothermal reaction of CaO with $SiO_2$ at 190°C. Especially the effects of C/S, specific surface and "degree of crystallinity" of $SiO_2$ on the phase composition of the primary product and the projection of this on the thermoanalytical curves was studied.

## EXPERIMENTAL

The subject of the experimental study was the system calcium oxide-silicon dioxide-water (water steam) at 190°C. CaO were prepared by 3 hours firing of $CaCO_3$ at 1000°C, $SiO_2$ as β-quartz, silica glass or silica colloidal powder were used. β-quartz and silica glass were separated into two fractions with the grain size (specific surface according the distribution curves of grain size) $\leq$ 5 μm (15 000 cm²/g) , $\leq$ 60 μm (2 000 cm²/g). C/S in reactants was 0.5, 1.0, 1.5, 2.0, water/solidus = 10. Hydrothermal reaction took place 1 - 72 hours, finished was by action of ethylether. Phase composition of the reaction products was estimated form the results of chemical analysis according to method (7), powder diffraction patterns and thermal analysis. The thermoanalytical curves were obtained on a Q 1500 D Derivatograph (MOM, Budapest) in air atmosphere, in the 20 - 1000°C temperature range, heating rate 10 degree/min, weighted amounts 400 mg, sensitivity DTA 250 μV.

## RESULTS AND DISCUSSION

Table 1: Correlation between chemical analysis results and reaction conditions in system CaO - $SiO_2$ - $H_2O$

| C/S in reactants; form and fraction of S | C/S in products(7) |
|---|---|
| 0.5; β-quartz and silica glass 5 μm, 60 μm<br>0.5-2.0; silica colloidal powder | 1.0 |
| 1.0; β-quartz and silica glass 5 μm, 60 μm<br>1.5; " " 5 μm | 1.5 |
| 1.5; " " 60 μm<br>2.0; " " 5 μm, 60 μm<br>0.5-2.0; " " 60 - 90 μm | 2.0 |

Discussed are only results concerning the samples containing CSH gel and α-$C_2S$ hydrate - primary products in studied system, according to (1-4) and our previous finding too.

Results of the chemical analysis give the values for C/S in primary product near to 1.0 1.5 or 2.0 in dependence on C/S in reactants mainly (table 1).Generally, C/S is higher or at least equal to this in reactants, primary product is lima rich, observed (3,4) too. C/S in primary product rises with increasing of the grain size (decreasing the specific surface) of $SiO_2$ too. These results illustrate the connection of the offer of $SiO_2$ into the solution and reaction (dependent on its specific surface, grain size and quantity) with the possibilities of the incorporation of $SiO_2$ into the calcium silicate hydrates (value of C/S in these).

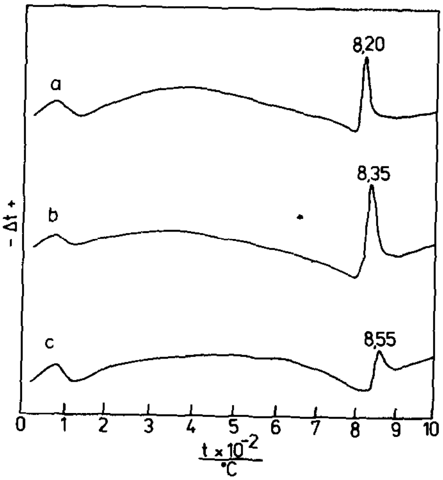


fig. 1: DTA curves of CSH gel
a: C/S ≐ 1, b: C/S ≐ 1.5,
c: C/S ≐ 2

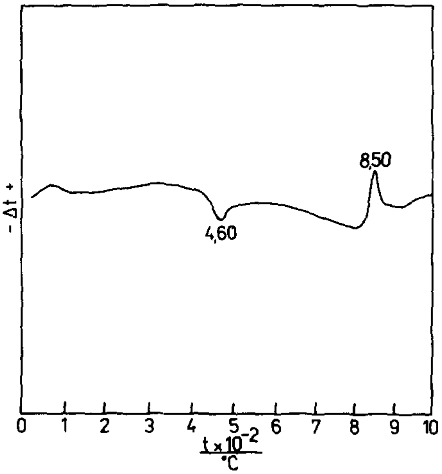


fig. 2: DTA curves of the mixture $\alpha$-$C_2S$hydrate + CSHgel

Generally, on the DTA curves (fig. 1,2) are peaks characteristic for CSH gel (5): endopeak with maximum at 800°C and exopeak with maximum at 820 - 850°C, value of this rises in given temperature interval with increasing of the C/S (fig. 1a - c). DTA curves of reaction products of 60 μm (2000$cm^2$/g) fraction of $SiO_2$ (for β-quartz 5 μm (15000$cm^2$/g) fraction too) and C/S of the reactants equal 1.5 and 2.0 contain the exopeak at 460°C too (fig. 2) - characteristic for $\alpha$-$C_2S$ hydrate (6). $\alpha$-$C_2S$ hydrate originates in studied system in mixture with CSH gel only. Results showed, that the formation of $\alpha$-$C_2S$ hydrate depends next to the influences observed in (1) on "degree of the crystallinity" of $SiO_2$ too: by reaction of $\beta$-quartz originates $\alpha$-$C_2S$ hydrate more frequently than from the cryptocrystalline form - silica glass.

Present results complete the works (1-4) and all these necessitate following interpretation: C/S and the formation of $\alpha$-$C_2S$ hydrate in the primary product are determined by quantity, specific surface and "degree of crystallinity" of $SiO_2$ entering the reaction. Alteration the only of these factors causes the quantitative alteration of the offer of $SiO_2$ into the solution and reaction with CaO. Just this offer is unambiguously responsible (1-4) for the development of the hydrothermal reaction of $SiO_2$ with CaO and for the phase composition of primary product.

## CONCLUSIONS

1. Molar ratio - C/S in primary product is 1 - 2, generally it is higher than this in the reactants.
2. DTA curves are clear and simple illustration of the phase composition of primary product, indicate the presence of $\alpha$-$C_2S$ hydrate and the value of C/S in CSH gel.
3. It was confirmed, primary product of studied reaction contain mainly nearly amorphous CSH gel; $\alpha$-$C_2S$ hydrate is situated in primary product after optimal combination the next factors: C/S in the reactants, specific surface and degree of crystallinity $SiO_2$.

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