

INFLUENCE OF PRECURING ON HIGH PRESSURE STEAM
HYDRATION OF TRICALCIUM SILICATE IN THE PRESENCE
OF OTHER CONSTITUENTS OF PORTLAND CEMENT

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ABSTRACT

The influence of precuring at room temperature on the autoclave hydration of C_3S in the presence of other constituents of clinker and of gypsum was studied. C_3A , C_4AF and $\beta-C_2S$ hampered the formation of $C_3SH_{1.5}$ and, especially for short precuring times, favored the formation of $\alpha-C_2SH$. Gypsum hampered the formation of both the crystalline hydrated silicates. When the steam treatment took place after a long precuring, C-S-H was the prevailing hydrated silicate formed.

On a étudié l'influence du traitement préliminaire à température ambiante sur l'hydratation en autoclave du C_3S en présence des autres constituants du clinker et de gypse. C_3A , C_4AF and $\beta-C_2S$ ont influencé négativement la formation de $C_3SH_{1.5}$ et, particulièrement pour temps court de traitement préliminaire, ont favorisé la formation de $\alpha-C_2SH$. Le gypse a été nuisible à la formation des deux silicates cristallins hydratés. Quand on a effectué le traitement en autoclave après des long temps de traitement préliminaire, on a vu que le C-S-H était le silicate hydraté le plus abondant.

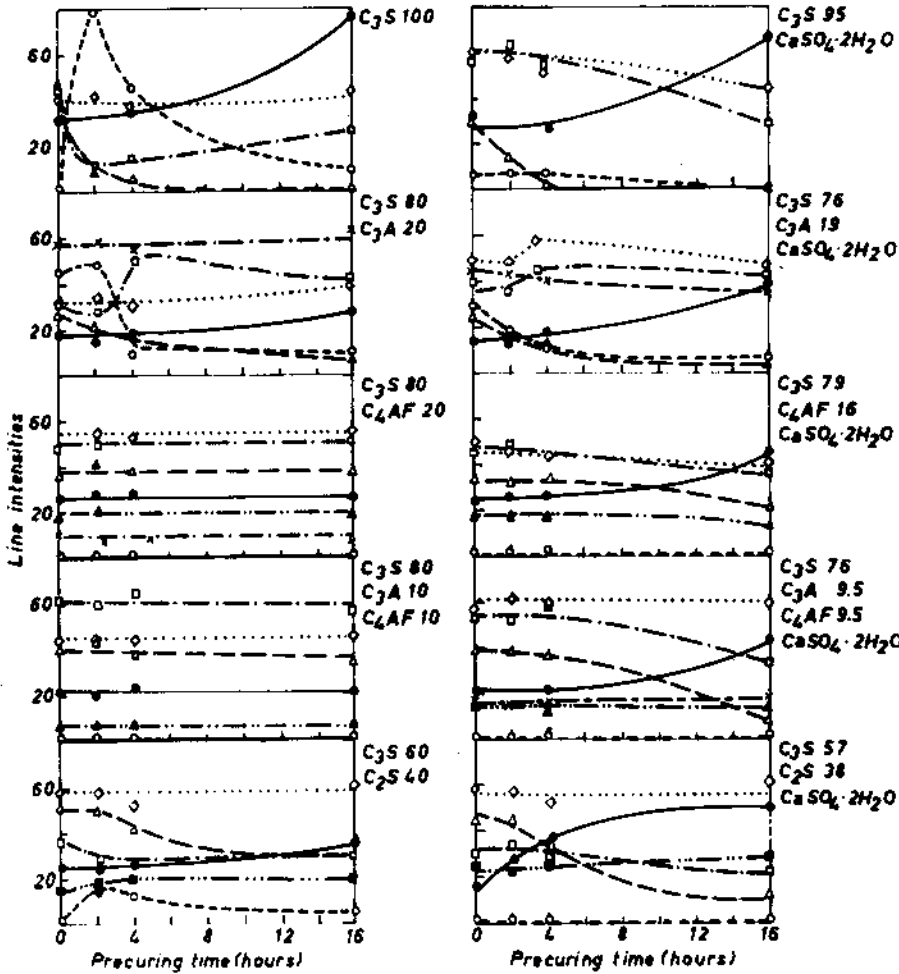


FIG. 1

Intensity of x-ray diffraction peaks in function of the precuring time. Figures after formulas are the percentages of the compounds in the anhydrous mixtures.

Symbols: o ----- C₃SH □ — · — CH
 ◇ ······· C-S-H x — · — · C₃(A,F)H₆
 △ — — — α-C₂SH ■ — ··· B-C₂S
 ● — — — C₃S ▲ — ··· C₄AF

is slightly less than that previously found (4 hours).⁽¹⁾ Recent results⁽⁶⁾ show that the precuring time corresponding to the maximum amount of C₃SH_{1.5} depends on the type of C₃S used (fineness, presence of impurities, differences in structure, etc.). The amount of Ca(OH)₂, on the other hand, has a minimum value at about 2 hours corresponding to the highest content of C₃SH_{1.5}. At long precuring times, for example 16 hours, Ca(OH)₂ increases considerably and this can

FIG. 2

SEM micrograph (x3000) of C_3S autoclaved 5 hours at $190^\circ C$ after a precuring time of 2 hours.



be related to the formation of C-S-H at the expense of the more basic hydrated crystalline silicates $\alpha-C_2SH$ and $C_3SH_{1.5}$. SEM results (Fig. 2) clearly show appreciable amounts of $\alpha-C_2SH$ (as well-formed blocks of rectangular shape, $2 \times 5 \times 10 \mu m$) and $C_3SH_{1.5}$ (as fibrous crystals approximately $10 \mu m$ long and $1 \mu m$ thick).

The addition of gypsum did not cause substantial changes in the amount of hydrated C_3S , but for the same precuring time the amounts of the crystalline hydrated silicates were remarkably reduced and the quantity of the less basic C-S-H and of $Ca(OH)_2$ increased. In the autoclaved specimens, the x-ray diffraction peak (7.56\AA) of gypsum was completely absent, and neither hemihydrate nor anhydrite was detected. Since there is no possibility for the sulphate to combine with the aluminates or the ferrites, the disappearance of gypsum is in this case a direct proof that the SO_4^{-2} ion is incorporated into the hydrated silicates and/or in $Ca(OH)_2$. Furthermore, since in the autoclaved samples after a precuring time of 16 hours both the crystalline hydrated silicates are absent, it can be deduced that the SO_4^{-2} ion is incorporated into the C-S-H gel and/or in $Ca(OH)_2$. This is in agreement with the results obtained by other authors for the solubility of $CaSO_4 \cdot 2H_2O$ in C-S-H and $Ca(OH)_2$ at room temperature. (7-9)

When the C_3S was autoclaved in presence of C_3A , among the products was found the cubic hydrated aluminate, the quantity of which did not vary appreciably with the precuring time. The hydrogarnet formed under similar conditions had the composition $C_3AS_{0.15}H_{5.7}$. (10) By assuming that this is also the composition of the cubic phase detected in this work, from the data of the thermogravimetric analysis it has been calculated that 17.6% of C_3A by weight, with respect to the initial weight of the solid, is present as the hydrogarnet. Since no trace of anhydrous C_3A has been found by x-ray in the autoclaved products, it can be deduced that a fraction of the alumina, equal to about 2-3% expressed

as C_3A , entered into the crystal lattice of the hydrated silicates.

For the same precuring time, the addition of C_3A causes a more rapid hydration of C_3S particularly in the samples precured for a long time (16 hours). A reduction in the quantity of $C_3SH_{1.5}$ was observed.

As the precuring time increases, in the presence of C_3A as well as of gypsum, the amount of $\alpha-C_2SH$ decreases. The maximum amount of $C_3SH_{1.5}$ observed in the case of pure C_3S precured for 2 hours either completely disappeared (gypsum addition) or became hardly detectable (C_3A addition). Also in the samples containing C_3S and C_3A or gypsum, autoclaved after long precuring, C-S-H is the hydrated silicate which predominates among the products obtained.

Autoclave hydration of C_3S in presence of C_3A and gypsum is analogous to that of C_3S mixed with C_3A only. It is worth noting that, at the end of the autoclave treatment, neither the ettringite, nor $C_3A \cdot CaSO_4 \cdot 12H_2O$ and $CaSO_4$ have been found; the last two products should be formed by the decomposition of ettringite at $190^\circ C$.⁽¹⁰⁾ This result shows that the Al^{+3} and SO_4^{-2} ions of the ettringite were incorporated into the hydrated silicates obtained in the autoclave treatment. The TGA data have demonstrated that in the specimens containing C_3S , C_3A and gypsum the percentage of hydrogarnet, expressed as C_3A with respect to the weight of the initial solid, does not vary with the precuring time, being approximately 11-12%. Since also in these samples C_3A is not present at the end of the autoclave treatment, one can deduce that part of the alumina, about 7-8% of C_3A , entered as a solid solution into the lattice of the hydrated silicates obtained in autoclave. This indicates that, when the SO_4^{-2} ions are present, the amount of Al^{+3} entering into the lattice of the autoclaved hydrated silicates is larger than that entering in the absence of the sulphate. The morphology of the product (Fig. 3) appears substantially modified compared to that of the pure C_3S sample. (Fig. 2) The fibrous crystals of $C_3SH_{1.5}$ have almost completely disappeared, while the block-shaped ones of $\alpha-C_2SH$ are still visible. Furthermore spherical particles of about $1 \mu m$ diameter can be seen as well as large aggregates composed of very tiny fibres (about $1 \mu m$ long and $0.1 \mu m$ thick), spherical and irregularly shaped particles, all cemented to each other. Similar changes, although less important, have been observed upon additions of either C_3A or $CaSO_4 \cdot 2H_2O$ separately.

The influence of the addition of C_4AF on the autoclave hydration of C_3S appears rather striking when compared with that of C_3A or gypsum. First, the precuring time does not affect the amount of C_3S hydrated at the end of the steam treatment; second, the nature and the relative amounts of the hydrated products ($\alpha-C_2SH$, $Ca(OH)_2$, $C_3(A,F)_xH_{6-2x}$ and C-S-H) remain unchanged for differ-



FIG. 3

SEM micrograph (x3000) of $C_3S + 5\% CaSO_4 \cdot 2H_2O$ autoclaved 5 hours at $190^\circ C$ after a precuring time of 2 hours.



FIG. 4

SEM micrograph (x3000) of $C_3S + 20\% C_4AF$ autoclaved 5 hours at $190^\circ C$ after a precuring time of 2 hours.

ent precuring times. Moreover, differently from what happens in the case of C_3A which reacts completely during the autoclave treatment, a fraction of the anhydrous C_4AF - approximately the same quantity, independently of the precuring conditions - still remains with the hydrated products. Finally, upon addition of C_4AF to C_3S , $C_3SH_{1.5}$ disappears completely and, for the same precuring time, the amounts of $\alpha-C_2SH$, of $Ca(OH)_2$ and C-S-H increase. Also the morphology of the hydrated products undergoes a drastic change (Fig. 4): the fibrous crystals of $C_3SH_{1.5}$ obviously disappear, and the block-shaped crystals of $\alpha-C_2SH$ are no more visible, although this compound can be detected by the x-ray diffraction and the thermal analysis. The hydrated products appear as irregularly shaped granules of size variable between about 0.5 and 5 μm .

The addition of gypsum to the system $C_3S - C_4AF$ does not result in substantial modifications, except for the fact that a long precuring time (16 hours) causes a reduction of the hydrated C_3S at the end of the autoclave treatment and also in proportion, of $Ca(OH)_2$, $\alpha-C_2SH$ and C-S-H. On the basis of the results previously discussed this effect has to be related to the presence of gypsum rather than to that of C_4AF . Moreover, neither $C_3SH_{1.5}$ nor any form of hydrated

sulphoferrite are found.

The addition of gypsum to the system $C_3S-C_3A-C_4AF$ causes a retardation of the C_3S hydration only in the samples precured for a long time, with the consequent reduction of $\alpha-C_2SH$ and CH . Analogous variations have taken place upon addition of gypsum to the C_3S-C_4AF system.

In the presence of $\beta-C_2S$ the influence of precuring on the autoclave hydration of C_3S remains qualitatively unchanged. Also in this case, as for the pure C_3S , it can be observed that an increase of the precuring time is accompanied by a reduction of the amount of C_3S hydrated at the end of the steam treatment; the quantity of $\alpha-C_2SH$ also decreases, whereas that of $C_3SH_{1.5}$ reaches a maximum value when the precuring time is 2 hours. For the same precuring time, x-ray line intensity of $C_3SH_{1.5}$ present in the autoclaved samples of $C_3S-\beta C_2S$ is about 5 times smaller than that obtained with the C_3S alone, and the difference is larger than one would expect considering the lower initial percentage of C_3S in the $C_3S - \beta C_2S$ system. The XRD results were confirmed by the data obtained by TGA. The percentages of $C_3SH_{1.5}$, determined by TGA were about 53 and 10 respectively in the C_3S alone and $C_3S - \beta C_2S$ mixture. Since the reduction or the disappearance of $C_3SH_{1.5}$ is always associated with the presence of foreign ions, such as SO_4^{-2} , Al^{+3} , Fe^{+3} or even Cl^- ,⁽¹¹⁾ it seems reasonable to attribute the negative effect of $\beta-C_2S$ to the presence of B_2O_3 added as a stabilizer during the preparation of $\beta-C_2S$.⁽³⁾ A similar negative effect brought about by foreign ions in the crystallization process has been noticed in the formation of afwillite by ball mill hydration of C_3S .⁽¹²⁾

For the same precuring time, the amount of $\alpha-C_2SH$ is higher in the presence of $\beta-C_2S$ from which the silicate hydrate is obtained.

The longer the precuring time, the smaller the quantity of $\beta-C_2S$ which is hydrated in the following steam treatment. However, the effect of the precuring time on the percentage of $\beta-C_2S$ hydrated at the end of the autoclave treatment is less marked than that discussed for C_3S .

The addition of gypsum to the $C_3S - \beta C_2S$ system results in general in a reduction of the hydrated products and in particular causes the disappearance of $C_3SH_{1.5}$. In the presence of gypsum, moreover, the negative influence of long precuring on the autoclave hydration of C_3S appears more evident.

Conclusions

The influence of precuring on the autoclave hydration of C_3S is partly modified by the presence of the other components of Portland cement and of gypsum. In the presence of C_3A , $\beta-C_2S$ and gypsum, it is found again that an increase of

the precuring time, particularly beyond 4 hours, is accompanied by a reduction in the quantity of the hydrated C_3S at the end of the subsequent autoclave treatment. In the presence of C_4AF , on the other hand, the precuring time (0-16 hours) does not affect at all the percentage of C_3S reacted during the steam treatment at $190^\circ C$.

The formation of $C_3SH_{1.5}$, which reaches a maximum after a certain precuring time in the samples of pure C_3S or $C_3S-\beta-C_2S$, is in any case hindered by the presence of the other components. In the presence of C_4AF , $C_3SH_{1.5}$ is not formed at all, independently of the precuring time. There are some indications in favour of the hypothesis that the impurities interfere with the formation of the $C_3SH_{1.5}$ crystals.

The formation of $\alpha-C_2SH$, whose quantity increases as the precuring time is reduced, is favoured by the presence of C_3A , C_4AF and obviously $\beta-C_2S$, from which the hydrated silicate is obtained.⁽¹³⁾ Gypsum, on the other hand, hinders the formation of both the hydrated crystalline silicates.

Also when the other constituents are present, C-S-H is the main hydrated silicate or even the only one, if the autoclave treatment occurs after a relatively long precuring time. This seems to confirm the hypothesis^(1,14) that only the freshly prepared C-S-H is an intermediate product liable to be transformed later into the crystalline hydrated silicates; as the precuring becomes relatively long, effect of the aging of the C-S-H is no more negligible and therefore its conversion into the hydrated crystalline silicates is hindered.

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