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INVESTIGATION ON THE FORMATION OF ETTRINGITE IN THE PRESENCE OF BaO

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ABSTRACT

Two mechanisms of forming ettringite have been proposed: one, through solution reaction; the other, through topochemical reaction. Using XRD and SEM, ettringite were investigated, which formed form very low SO_4^{2-} concentration ($[SO_4^{2-}] \approx 10^{-10}$ M/L). That low SO_4^{2-} concentration was caused by adding soluble BaO. The results show that ettringite can still form when mixing $CaSO_4 \cdot 2H_2O$ with C_3A, CA, $C_{12}A_7$ or $C_4A_3\overline{S}$* respectively. Since the SO_4^{2-} concentration is far below that normally needed to crystallize ettringite ($[SO_4^{2-}] > 10^{-5}$ M/L), it is difficult to explain the formation of these ettringite by the above mentioned two mechanisms. The authors believe that solid-phase reaction mechanism should be the answer.

Introduction

The forming mode of ettringite, which closely correlates with expansion of cement paste, is very vital in cement research. Two main mechanisms as [a] formation through solution reaction (1,2,3) and [b] formation through topochemical reaction (4,5) have been proposed. The former has been confirmed by numerous tests and is accepted by most scholars. It is CaO, Al_2O_3 and SO_4^{2-} that are dissolved into solution first, and then the crystallization of ettringite occurs when the concentration is supersaturated. Having little evidence and supported by few researchers, the

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* Cement nomenclature: C – CaO, A – Al_2O_3, $\overline{S}$ – SO_3

second mechanism hypothesizes that ettringite can be formed directly on the surface of calcium aluminate grains by the reaction between SO_4^{2-} ions in solution and calcium aluminate in solid phase. And only the ettringite formed through topochemical reaction can cause expansion. In this investigation, it yielded a low $[SO_4^{2-}]$ solution ($[SO_4^{2-}] \approx 10^{-10}$ M/L) by incorporating soluble BaO into the $CaO-Al_2O_3-SO_3-H_2O$ system because of the formation of insoluble $BaSO_4$. According to $CaO-Al_2O_3-CaSO_4-H_2O$ equilibrium diagram (6,7), it is impossible to form ettringite from such low SO_4^{2-} concentration. However, the precipitation of ettringite was detected in our experiments. Therefore, we put forward the solid phase reaction mechanism of forming ettringite.

Experimental

1. Materials

Analytical agents BaO and $CaSO_4 \cdot 2H_2O$ were used in the experiment. C_3A, CA, $C_{12}A_7$ and $C_4A_3\bar{S}$ were synthesized using analytical grade reagents in a electric furnace with f-CaO 0.60, 0.13, 0.10 and 0.11 wt% respectively.

2. The Hydration in the $C_3A+CaSO_4 \cdot 2H_2O+H_2O+BaO$ system

The dosage of C_3A, $CaSO_4 \cdot 2H_2O$ and H_2O was determined in terms of the stoichiometric equation $C_3A+3CaSO_4 \cdot 2H_2O+26H_2O=C_3A \cdot 3CaSO_4 \cdot 32H_2O$, and the amount of addition of BaO was calculated to combine all of the SO_4^{2-} from $CaSO_4 \cdot 2H_2O$ to form $BaSO_4$. Therefore, the molar ratio of $C_3A:CaSO_4.2H_2O:H_2O:BaO$ was 1:3:26:3.

The materials were mixed homogeneously with the above molar ratio. An optimum amount of water was added to hydrate the mixture at ambient temperature (25 ± 2 ℃). XRD analysis was performed on the samples hydrated for 2 hours, 1 day and 1.5 days, and SEM analysis on those hydrated for 2 hours. The results are presented in FIG.1 and FIG.2 , respectively. It can be seen from FIG.1 that the diffraction peaks (9.817 5.837 2.784) of ettringite exist in the 2 hour- and the 1 day- hydrated samples, however they vanish in the 1.5 day-hydrated sample. Moreover, it is obvious from the SEM micrograph of 2 hour-hydrated sample, that radiating needles of ettringite seem to be growing from the surface of the solid grains.

3. The Hydration of $CA+C\bar{S}H_2+H_2O+BaO$ System

In accordance with the same calculation regulation as above, the molar ratio of all compounds was $CA:C\bar{S}H_2:H_2O:BaO=3:3:32:3$. The hydration temperature was 25 ± 2 ℃. FIG.3 and FIG.4 respectively present the results of XRD on the 2 hour-, 1 day- and 3 day- samples as well as a SEM micrograph of the 2 hour-hydrated sample. The patterns of XRD show that ettringite formed in the 2 hour- and the 1 day-hydrated samples (9.774 5.625 2.778), but disappeared in the 3 day one. Correspondingly, needles of ettringite formed from the surface of grains (FIG.4).

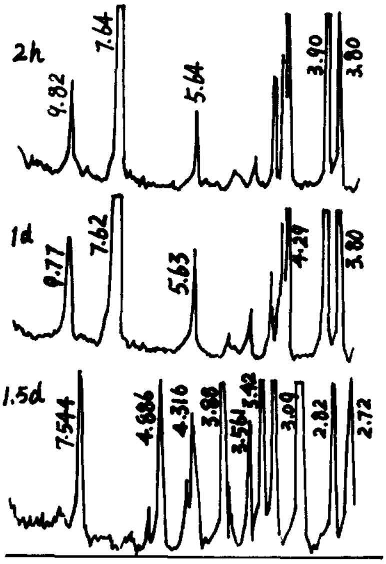

FIG.1

XRD patterns of hydrated $C_3A+C\bar{S}H_2+BaO$ samples

FIG.2

SEM micrograph of hydrated $C_3A+C\bar{S}H_2+BaO$ sample(2h)

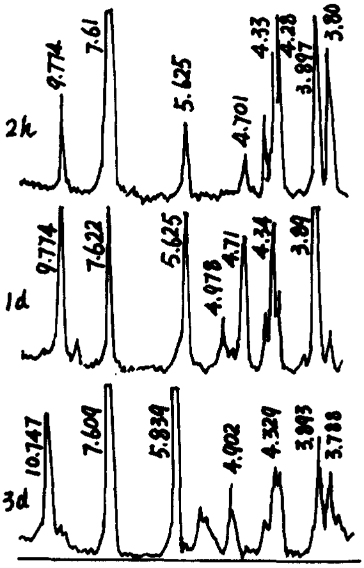

FIG.3

XRD patterns of hydrated $CA+C\bar{S}H_2+BaO$ samples

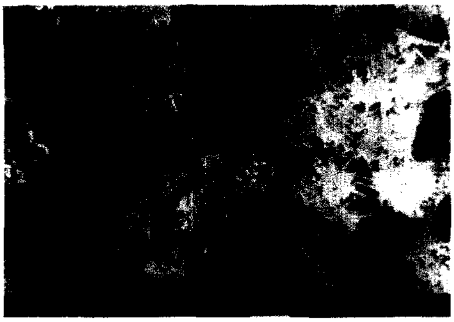

FIG.4

SEM micrograph of hydrated $CA+C\bar{S}H_2+BaO$ sample (2h)

4. The Hydration of $C_{12}A_7$+$C\bar{S}H_2$+BaO System

Reducing half of the amount of BaO, the molar ratio of all constituents was $C_{12}A_7$:$C\bar{S}H_2$:H_2O:BaO=1:12:113:6. The hydration temperature of these mixtures was controlled at 25 ± 2℃. XRD analysis was performed for the 2h-hydrated mixture (FIG.5). Ettringite (9.752 5.625 2.778) was detected in FIG.5.

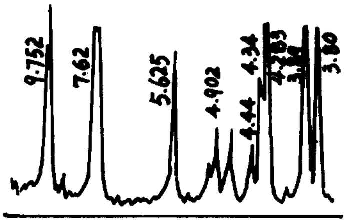

FIG.5
XRD pattern of $C_{12}A_7$+$C\bar{S}H_2$+H_2O +BaO sample hydrated for 2h

5. Hydration of $C_4A_3\bar{S}$+$C\bar{S}H_2$+H_2O+BaO System

This molar ratio of compounds was $C_4A_3\bar{S}$:$C\bar{S}H_2$:H_2O:BaO=1:2:34:3. FIG.6 shows that the diffraction peaks (9.774 5.625 2.772) of ettringite exist in the 2 hour sample and the 1 day one but disappear in the 7 day one. $C_3A{\cdot}CaSO_4{\cdot}12H_2O$ is not detected in all samples.

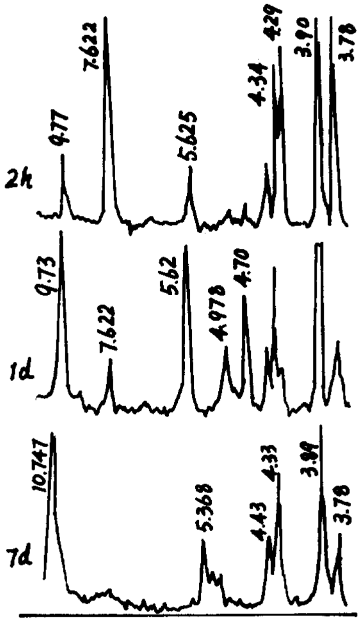

FIG.6
XRD patterns of hydrated mixture at 2h, 1d and 7d

6. Hydration of $C_3A{\cdot}3CaSO_4{\cdot}32H_2O$+BaO and $C_4A_3\bar{S}$+BaO

In order to confirm the low SO_4^{2-} concentration of solution in the presence of BaO, the following tests were carried out:

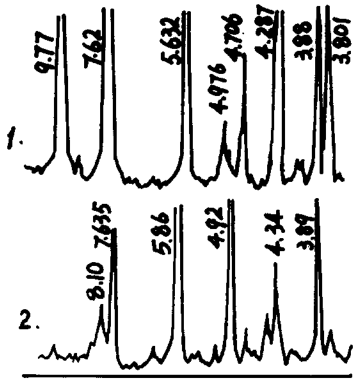

FIG .7

1. XRD pattern of $C_3A+C\bar{S}H_2$ hydrated for 2h
2. XRD pattern of 1d-hydrated sample after adding BaO to No.1

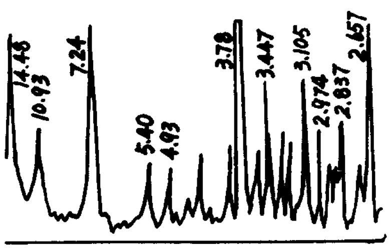

FIG.8

XRD pattern of $C_4A_3\bar{S}$+BaO hydrated for 3 d and 9 d

1) Stability test of ettringite in the presence of BaO

A sample containing ettringite, which was obtained by mixing C_3A and gypsum with 1:3 molar ratio, set 2h at room temperature. A sufficient amounts of BaO was added to the sample, then hydrated one day. The results were presented (FIG.7).

The results show that ettringite vanish after one day. It is obvious that low SO_4^{2-} concentration caused by the addition of BaO makes ettringite decompose progressively.

2) Hydration of $C_4A_3\bar{S}$+BaO

10 g $C_4A_3\bar{S}$ and 1 g BaO were mixed homogeneously and set at 10~27℃ for 3 days and 7 days (FIG.8).

The diffraction peaks of ettringite and monosulpho-aluminate are not observed (FIG.8), which indicates that BaO can seize SO_4^{2-} in $C_4A_3\bar{S}$ when SO_4^{2-} concentration is very low.

Analysis and Discussion

The above experiments show that ettringite gradually transform into hydrated calcium aluminate and $BaSO_4$ crystal in the presence of BaO. Likewise, the hydration products of $C_4A_3\bar{S}$+BaO are hydrated calcium aluminate as well as $BaSO_4$ but no monosulphoaluminate. This leads to the conclusion that very low SO_4^{2-} concentration results in ettringite and monosulpho-aluminate decomposing. According to reference (8) the solubility of BaO (25℃) is 4%, i.e. 2.6×10^{-1} M/L, and Ksp of $BaSO_4$ is 1.1×10^{-10}. It is not difficult to work out the SO_4^{2-} concentration in solution is 4.2×10^{-10} M/L, owing to the combination of Ba^{2+} with SO_4^{2-} to form insoluble crystal $BaSO_4$.

The equilibrium diagram of $CaO-Al_2O_3-CaSO_4-H_2O$ (6,7), shows that ettringite and monosulphoalminate can not be formed if the $[SO_4^{2-}]$ concentration lower than 10^{-5} M/L. But in presence of BaO, SO_4^{2-} concentration in solution is 5 orders of magnitude lower than the minimum $[SO_4^{2-}]$ shown in that diagram. However, under these circumstances, ettringite can still form during the initial stage of hydration. The results can not be interpreted reasonably by the mechanisms of "solution reaction" or "topochemical reaction".

Seen from SEM micrographs, it is clear that needle-shaped ettringite crystals grow from the grains surface, and link the grains together. Consequently, we suppose the ettringite should form through solid reaction, whose mode might be:
(a) First, calcium aluminates dissolve into water, then react with solid-phase $CaSO_4$ and form ettringite on the surface of gypsum.
(b) Once calcium aluminates contact water, hydrated calcium aluminate phase forms rapidly on the surface of grains. These new-form hydrated calcium aluminates, which have high hydration reactivity, react with gypsum to form ettringite by ions diffusing. These ettringite are close to the surface of gypsum.

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