# Sulfate Attack on Pastes Made with Different $C_3A$ and $C_4AF$ Contents and Stored at 5°C

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*Abstract*—In the present work the internal sulfate attack on pastes made from pure clinker phases was studied. Two binders were produced: (a) a binder with 2% $C_3A$ and 18% $C_4AF$ content; (b) a binder with 10% $C_3A$ and $C_4AF$ content each. Gypsum was used as the sulfate bearing compound, while calcium carbonate added to differentiate the binders produced. The phases formed were identified by XRD analysis. The results showed that ettringite was the deterioration phase detected in the case of the low $C_3A$ content binder. Carbonation occurred in the specimen without calcium carbonate addition, while portlandite was observed in the one containing calcium carbonate. In the case of the high $C_3A$ content binder, traces of thaumasite were detected when calcium carbonate was not incorporated in the binder. A solid solution of thaumasite and ettringite was found when calcium carbonate was added. The amount of $C_3A$ had not fully reacted with sulfates, since its corresponding peaks were detected.

*Keywords*—Tricalcium aluminate, calcium aluminate ferrite, sulfate attack, calcium carbonate, low temperature.

## I. INTRODUCTION

THE results of sulfate attack on cementitious materials are strongly related to the source of sulfate ions, as well as to the deterioration products formed. Sulfate ions may be present in the initial mixture components or may be transferred in the already hardened material from a sulfate-bearing environment. In the first case sulfate attack is considered as *internal*, while in the second as *external* [1]. The reaction of sulfates with CAH and CH leads to the formation of ettringite and gypsum, respectively, known as conventional sulfate attack. These deterioration products lead to expansion and cracking of the material. When sulfates react with CSH, thaumasite may be formed. Additionally, the presence of carbonate ions and excess humidity conditions are necessary for its formation, while low temperatures (<15 °C) are, generally, considered to promote it. Since thaumasite affects the main binding phase of the cement paste its formation may be proved as very detrimental [2]−[6].

Regarding the mechanism of thaumasite formation, it has been proposed that thaumasite can be formed directly from the solution containing all required components. Other considerations claim that ettringite is a precursor of thaumasite or ettringite consists of a template for the initial nucleation of thaumasite. The formation of thaumasite through ettringite results in the formation of a solid solution between the two minerals. [2], [6].

It could be assumed that the presence of reactive alumina is favorable for the formation of thaumasite. Thaumasite has been observed to form in systems in which aluminate phases have already been consumed by the reaction with sulfate ions to form ettringite [7]. Low $C_3A$ cements are used to reduce the effect of conventional sulfate attack. However, thaumasite has been found in cement systems with both high and low $C_3A$ contents [8].

The hydration of $C_4AF$ results in the formation of minerals with a structure similar to those formed from the hydration of $C_3A$ [9]−[11]. In the case of $C_3A$, the hydration is fast in contrast to that of $C_4AF$, which proceeds slower [12]. During hydration, Fe-containing AFm and/or Fe-AFt phases may form, since $Fe^{3+}$ partly exchanges $Al^{3+}$ in the lattice of ettringite and AFm phases [13], [14]. In most cases, the formation of a solid solution with their Al-containing analogous is observed [15]. Monosulfate has been found to form from ettringite more rapidly during $C_4AF$ hydration than that of $C_3A$ [16]. In sulfate environment, $C_4AF$ reacts slowly, but the mechanism of sulfate attack is similar to that of the $C_3A$ phase [10]. The main reaction product of $C_4AF$ with sulfates is the AFt phase, which slows down the hydration progress of $C_4AF$ due to the formation of an AFt-layer on the surface of $C_4AF$ grains [12].

In this paper, the internal sulfate attack on pure clinker phases ($C_3S$, $C_3A$, $C_4AF$) was studied, in the presence or not of carbonate ions derived from calcium carbonate addition.

## II. EXPERIMENTAL

### A. Materials

Pure clinker phases ($C_3S$, $C_3A$ and $C_4AF$) synthesized in laboratory, as well as gypsum ($CaSO_4·H_2O$) and calcium carbonate ($CaCO_3$) were used to produce specimens of four different mixture compositions (Table I).

TABLE I
MIXTURES COMPOSITION (%)

| Code | $C_3S$ | $C_3A$ | $C_4AF$ | Gypsum | Additional gypsum | Additional $CaCO_3$ |
|---|---|---|---|---|---|---|
| A1 | 76.15 | 2.00 | 18.00 | 3.85 | 3.00 | - |
| A2 | 76.15 | 2.00 | 18.00 | 3.85 | 3.00 | 10.00 |
| B1 | 60.88 | 10.00 | 10.00 | 19.12 | 3.00 | - |
| B2 | 60.88 | 10.00 | 10.00 | 19.12 | 3.00 | 10.00 |

The synthesis of $C_3S$ and $C_3A$ was performed in the

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*Institute of Ceramics and Building Materials - Glass and Building Materials Division in Krakow*, while $C_4AF$ was produced in the *Department of Building Materials Technology - AGH University of Science and Technology in Krakow*. The phases produced were mixed in stoichiometrically calculated proportions, so as to obtain: (a) a binder with composition similar to the high sulfate resistant cements (low $C_3A$ content); (b) a binder with a composition similar to that of common cements. In each composition the total $C_3A$ and $C_4AF$ content was 20% w/w. The amount of gypsum used in each mixture, was sufficient to completely react with aluminates to form ettringite. The total amount of $C_3S$, $C_3A$, $C_4AF$ and gypsum consisted 100% of each composition. In addition, a constant amount (3%) of gypsum was added, in order to ensure an excess of sulfates. Furthermore, carbonates were provided to the mixtures, either in the form of $CaCO_3$ (10% w/w) addition or by treatment of mixture with $CO_2$ gas (1% v/v). All mixtures were produced with a water to solid ratio of 0.5.

Specimens (prisms of 10mm×10mm×100mm) were prepared according to the compositions of Table I. The specimens were left in the moulds for 24 h and then placed in sealed plastic containers. The containers were partially filled with distilled water, in order to maintain an atmosphere saturated in water vapor. The specimens were stored for 14 months at 5±1°C. The level of distilled water was maintained by adding fresh water in the containers.

*B. Tests*

XRD analysis was performed on samples obtained from the specimens of each composition, in order to identify the phases formed. A Phillips (nowadays PANalytical) X'Pert Pro X-ray diffractometer, with Cu Ka1 ($\lambda = 1.5406$Å) and a primary curved germanium monochromator (Johansson type) was used. The samples were initially dried for three days (conditions: T = 23°C; P = 500 mbar) and then ground by hand in an agate mortar. After grinding, the material passed through a sieve of 63 μm mesh size.

## III. RESULTS AND DISCUSSION

The relative peak intensities of the phases identified are given in Table II. The XRD patterns relevant to the samples obtained from the specimens of A1 and A2 composition are presented in Figs. 1 and 2, respectively. Figs. 3 and 4 illustrate the XRD patterns for the specimens of B1 and B2 compositions, respectively.

TABLE II
RELATIVE PEAK INTENSITIES OF THE PHASES IDENTIFIED

| Code | E | T | T+E | P | C | Ar | V | G | B | S | A |
|------|-----|---|-----|----|----|----|---|-----|----|----|---|
| A1 | mw | - | - | - | s | - | w | w | m | w | - |
| A2 | mw | - | - | s | m | - | - | mw | w | vw | - |
| B1 | - | t | - | - | s | w | w | vs | vw | - | m |
| B2 | - | - | m | - | vs | - | - | vs | w | - | m |

E = ettringite; T = thaumasite; T+E = thaumasite+ettringite; P = portlandite; C = calcite; Ar = aragonite; V = vaterite; G = gypsum; B = brownmillerite; S = calcium silicate phase; A = tricalcium aluminate.

t = traces; vw = very weak; w = weak; mw = moderately weak; m = moderate; ms = moderately strong; s = strong; vs = very strong.

*A. Specimens with 2/18 Composition (A1 and A2)*

Both samples showed similar peak intensities of gypsum and ettringite. The peaks of both minerals were slightly higher for the specimen A2, which contains $CaCO_3$. Although the specimens were stored at low temperature, no evidence of thaumasite formation was observed. In the specimen of A1 composition no portlandite was detected, while calcite and vaterite were both identified, although no $CaCO_3$ was added in the mixture. This finding indicates that atmospheric carbonation has occurred. The peak intensity of calcite in the specimen of A2 composition is quite lower than that of the A1 one, although $CaCO_3$ was added in A2 mixture. Other calcium carbonate phases were not found in A2 specimen. On the contrary, intensive peak corresponding to portandite was detected in the specimen of A2 composition. The presence of calcite in the mixture affected the amount of portlandite detected in the samples. Brownmillerite was identified in both samples, indicating the form of the existing ferrous phase. The peak intensity of this phase was lower in the specimen prepared with the incorporation of calcium carbonate. It should also be noted that peaks corresponding to calcium silicate phases were identified in A1 and A2 specimens.
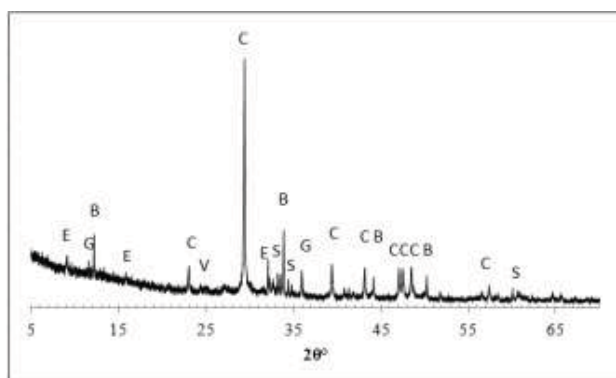


Fig. 1 XRD pattern of the sample obtained from the A1 specimen (E: ettringite; C: calcite; V: vaterite; G: gypsum; B: brownmillerite; S: calcium silicate phase)
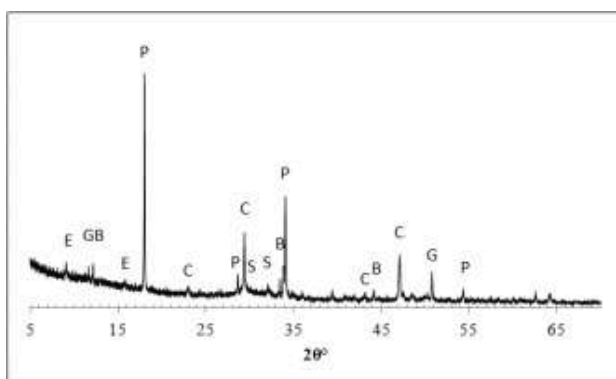


Fig. 2 XRD pattern of the sample obtained from the A2 specimen (E: ettringite; P: portlandite; C: calcite; G: gypsum; B: brownmillerite; S: calcium silicate phase)

*B. Specimens with 10/10 Composition (B1 and B2)*

In B1 specimen, high peak intensities of gypsum were detected, while the presence of tricalcium aluminate was also observed. No ettringite but traces of thaumasite were found in this specimen. As in the case of A1 specimen, no portlandite was identified, however calcite, aragonite and vaterite were detected. This finding shows that carbonation has also occurred in B1 specimen.

In B2 specimen, which contains calcium carbonate, high peaks of gypsum were detected, however being little lower compared to those of B1 specimen. The presence of thaumasite/ettringite indicates that an amount of gypsum was consumed for the formation of their solid solution. The calcite peaks of B2 specimen were higher than those of B1. It should be noted that the presence of calcium carbonate in B2 specimen did not result in the detection of portlandite, as it was the case in A2 specimen. Tricalcium aluminate was identified in B2 specimen; its intensity was quite similar with that of B1 specimen. Brownmillerite was observed in both B1 and B2 specimens. The peak intensities of this mineral are higher for the specimen containing calcium carbonate, which is in contrast with the findings of the A1 and A2 specimens. No evidence of calcium silicate phases was found in both B1 and B2 specimens.
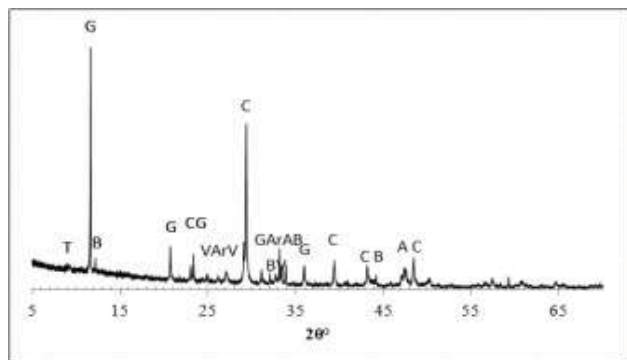


Fig. 3 XRD pattern of the sample obtained from the B1 specimen (T: thaumasite; C: calcite; Ar: aragonite; V: vaterite; G: gypsum; B: brownmillerite; A: tricalcium aluminate)
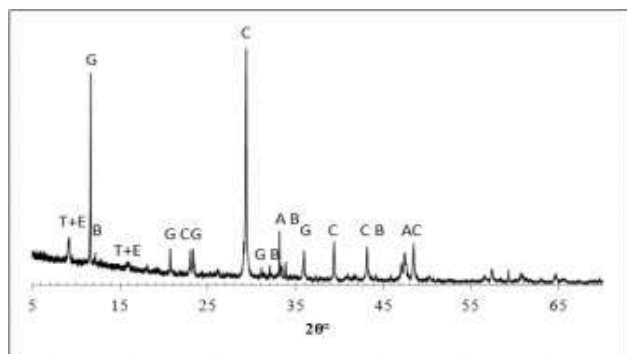


Fig. 4 XRD pattern of the sample obtained from the B2 specimen (T+E: thaumasite + ettringite; C: calcite; G: gypsum; B: brownmillerite; A: tricalcium aluminate)

The XRD analysis results of the specimens with different $C_3A$ and $C_4AF$ contents (compositions A1 and A2) showed that the amount of $C_3A$ contained in them was consumed to form ettringite. The peaks of brownmillerite and gypsum detected in the samples of both compositions indicate that ettringite formation may continue. The presence of calcite and vaterite in A1 specimen was attributed to the carbonation of calcium hydroxide produced due to the hydration process. However, an intensive peak of portlandite was detected in A2 specimen, which was prepared with $CaCO_3$ addition, while the peak of calcite was significantly lower compared to that of A1 specimen. The use of calcium carbonate in cementitious materials results in the formation of calcium aluminate monocarbonate instead of monosulfate [17]. It has been found that this process liberates sulfates which in turn lead to ettringite formation. This reaction requires the consumption of portlandite. However, further addition of calcite results in an increase of the portlandite content. In addition, the formation of ettringite during the early stages of hydration leads to a more dense structure. As a result, atmospheric carbonation is inhibited due to the reduced permeability of the hardened paste and portlandite may remain [18].

In the case of the specimens prepared with the same $C_3A$ and $C_4AF$ contents (compositions B1 and B2) both tricalcium aluminate and brownmillerite peaks were detected. Furthermore, in the sample derived from B1 specimen no evidence of ettringite but traces of thaumasite were found, while gypsum peak intensity was the highest detected. In the case of B1 specimen, it seems that sulfate attack was suppressed. The peaks attributed to calcite, aragonite and vaterite indicate that in B1 specimen carbonation prevailed. When calcium carbonate addition was used (B2 specimen) a solid solution of thaumasite and ettringite and was found, although peaks of tricalcium aluminate and brownmillerite were also detected. The lower peak intensity of gypsum in the sample obtained from B2 specimen, in comparison to that of B1 specimen, confirms that sulfate attack occurred in the form of thaumasite/ettringite solid solution. However, portlandite was not found in B2 specimen, indicating that it was probably consumed for the solid solution formation.

## IV. CONCLUSIONS

The following conclusions can be drawn from the present study. The sulfate attack that occurred on the pastes containing 2% w/w $C_3A$ and 18% w/w $C_4AF$ resulted in ettringite formation. Carbonation took place in the specimen without calcium carbonate addition. High peak intensity of portlandite was observed when calcium carbonate was incorporated in this type of mixture. Calcium silicate phases were identified in the specimens of the low $C_3A$ content composition.

In the case that same contents of $C_3A$ and $C_4AF$ were used (10% w/w each), the attack was rather limited when calcium carbonate was not used in the mixture, while carbonation prevailed. A solid solution of thaumasite and ettringite was found to form when the mixture was provided with carbonate ions as calcium carbonate addition. $C_3A$ had not fully reacted with sulfates since its relevant peaks were detected.

Brownmillerite was identified in the specimens of all four compositions studied.

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