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## Durability of autoclaved aerated concrete produced from fluidized fly ash

**ABSTRACT:** The properties of autoclaved aerated concrete (AAC) formed with the utilization of modified raw materials - new generation of fly ash from coal power plants (fluidized fly ash) were studied. The fluidized fly ash is a mixture of bed material and fly ash in the ratio 2:1. The high content of CaSO<sub>4</sub>, CaO and clay minerals (illit, diaspore) has been proved during the chemical and phase composition investigations. The fluidized fly ash was used as 0%, 30% and 100 % component of the raw mixture respectively. The AAC produced commercially (with fly ash from classical combustion) was used as reference material. The results of long-range experiments, aimed at the durability characteristics within the three years tests, are comprehensively discussed. The strength of samples decreases with the addition of fluidized fly ash, the lowest values are exhibited by samples with 100 % fluidized fly ash content in the raw mixture. The X-ray analysis, TG and DTA, IR spectroscopy, electron microscopy and EDX spectroscopy have been employed. Both phase analysis and strength data show the higher tendency of samples with fluidized fly ash towards the thaumasite formation, being the result of partial conversion of hydraulic C-S-H and tobermorite-like phases to nonbinding thaumasite. However, the expansion of tested samples resulted from the formation of thaumasite, as well as gypsum and ettringite in AAC, does not imply the deterioration on such a scale as observed in the concretes. The difference is due to the porosity and pore structure in AAC, developed as a result of air drying. These data contribute also to the discussion of topics of thaumasite formation vs. thaumasite sulfate attack. The results represent a basis of the proposals of modified production of AAC.

**KEY WORDS:** fluidized fly ash, autoclaved aerated concrete, durability, phase composition

### 1. Introduction

The production of ash-based autoclaved aerated concretes (AAC), as compared to the sand-based AAC, utilizes and valorizes the important amounts of wastes, with the positive environmental effect. The nowadays technologies are based upon the classic fly ash. However, due to the technological changes in the coal power plants, the utilization of new generation of fly ash as a modified raw material [Balkovic S. & co-w., 2010] must be taken into account. These ecologically related changes of raw mix composition and a potential of the use of a new generation of fly ash formed in coal power plants – fluidized fly ash, in the production of the ash-based autoclaved aerated concretes (AAC) are a challenge for both R&D institutions and industry.

SiO<sub>2</sub> and CaO, constituting 50 to 60 % of the total mass are the dominant components of fluidized fly ash. The other ones are SO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> (tens of %), Fe<sub>2</sub>O<sub>3</sub>, MgO, K<sub>2</sub>O (of %), TiO<sub>2</sub> and Na<sub>2</sub>O (tenths of %), MnO and sulfides (traces). The content of free CaO in this fly ash varies broadly and may reach the level as high as 30 %. CO<sub>2</sub> is present as a primary CaCO<sub>3</sub> (usually several %), its content differs for various types and regimes of combustion in particular power plants. Due to the low combustion temperature – around 850°C, the amount of glass phase in fluidized fly ash is low.

The use of this fly ash for the production of AAC should be verified by experimental production. In such a way the addition of fluidized fly ash can be optimized so that the technology will be economically and commercially acceptable and will exert minimal (if any) negative consequence upon the strength and the other physico-mechanical properties of AAC [Balkovic S. & co-w., 2010, Mróz R. et al., 2007]. This is focused on the mix design and verification of modified AAC in the region of Slovakia, Czech Republic and Poland. The results are discussed also from the point of view of thaumasite formation.

### 2. Experimental procedures and methods

Standardized samples (cubes of dimensions 10x10x10 cm) have been prepared from the AAC raw mixtures, one half of the cubes have been stored at relative humidity of 80 % (over water) whilst the second portion have been tested on the effect of drying, the experiments were carried out at room temperature (20 ± 2°C). The tests on physico-mechanical and phase changes, as described and discussed below, have been done on parallel series of samples in monthly periods of exposures. The constant level of 6 to

8 % humidity has been achieved by tested AAC samples already after 3 months (see Fig. 1).

A similar drying condition occurs in the building constructions. Mathematical and graphical evaluations of the strength values show the strength decrease during AAC drying (see Fig. 2). Fragments of samples after the mechanical testing were ground and homogenized. The phase composition was identified by XRD (digital STOE diffractometer, CoK $\alpha$  radiation). Simultaneously, the thermal analysis (sdt 2960 – T.A. Instruments), electron microscopy (Zeiss EVO 40 SEM) and EDX microanalysis (Bruker axs) was done. The presence of solid solution of ettringite – thaumasite, as indicated on the DTA curves, has been found in wet stored samples also by means of IR spectroscopy (MAGNA 750 of Nicolet, method of KBr discs).

The scope of raw compositions tested by the procedures and methods during the experimental production of novel AAC, together with sample codes, is as follows: A – AAC stored in dry environment, B – AAC stored in the environment of increased relative humidity; I – 100 % bed fly ash, II – 70 % bed fly ash, 30 % fluidized fly ash, III – 100 % fluidized fly ash. (The designation A, B, I, II and III respectively, are used throughout the text and in figures captions to indicate the relations between the individual compositions and several details and parameters of samples.

### 3. Results and discussion

#### 3.1. Physico-mechanical properties

The reference AAC produced from the mix being the 100 % bed fly ash has approx. 7,5 % of humidity, the AAC produced from the mix with 30 % fluidized fly ash has 7 % of humidity and that AAC produced from the mix with 100 % of fluidized fly ash shows the lowest 6 % humidity, all data are valid for one year exposures. During the spring (humid) season during the 2nd year the humidity temporarily increased (from the reported values to around 10,5 % for dry-stored samples, and from around 30 – 35 % to the level of 40 – 45 % for wet-stored samples) and subsequently it lowered down to the former level. Thus, the ability of AAC to undergo reversible drying and wetting has been proved in both dry and wet storage. The samples of AAC from the mix with 100 % fluidized fly ash exhibit the lowest sensitivity.

The strength of AAC during the dry storage depends also upon the percentage of fly ash in the raw mix; the compressive strength

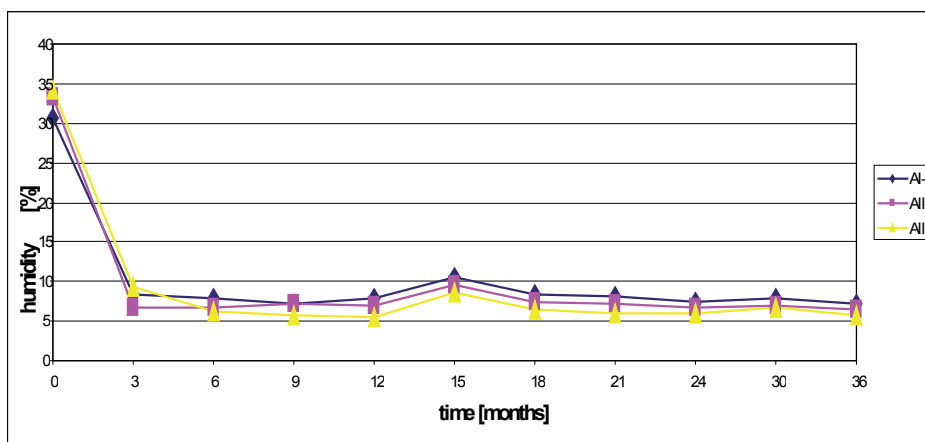


Fig. 1. The course of drying of AAC samples during the dry storage

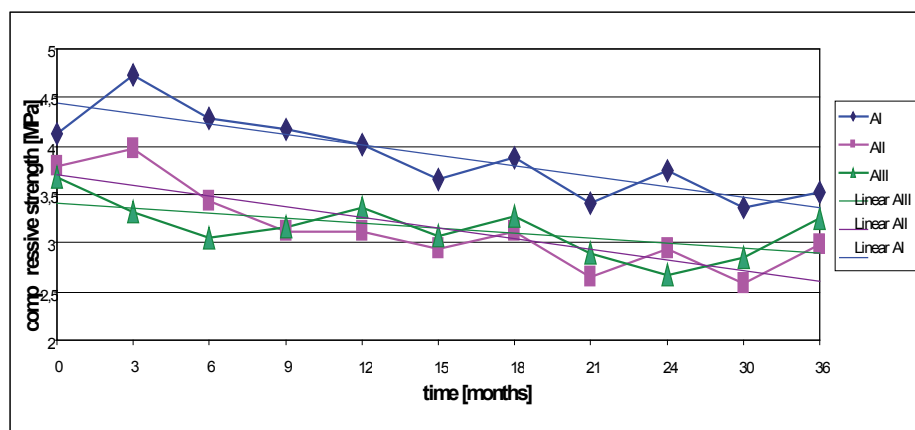


Fig. 2. The values of strength of AAC samples during the dry storage

decreases within one year from 4,2 MPa to 3,7 MPa for bed fly ash based AAC, from 3,8 MPa to 3,0 MPa for AAC made from fly ash with 30 % of fluidized fly ash, and from 3,7 MPa to 2,7 MPa for fluidized fly ash based AAC respectively. The strength of reference AAC (free of the fluidized fly ash) stored in the wet conditions very slightly increases, with strength growth of approx. 0.1 MPa. Opposite, the strength of AAC samples produced with fluidized fly ash, added as 30 % to 100 %, slightly decreases by about 0.2 MPa. The reason should be as follows: the filling of pores by the external water inhibits the effect of CO<sub>2</sub> – both the lower degree of carbonation and the lower strength decrease take place than in the case of dry storage. The strength decrease may be basically the consequence of re-crystallization and carbonation during the elimination of post - autoclaved moisture in the CO<sub>2</sub> containing atmosphere [Matsushita F. et al., 2000]. The suggested phase changes and reactions, as well as the contents of products thus formed were investigated in more details by differential thermal analysis, X-ray diffraction, SEM & EDX and IR spectroscopy as it is reported in the next chapters.

#### 3.2. Differential Thermal Analysis

The DTA curves (Fig. 3) exhibit the evacuation of surface- and hydrate- water (at 60 and 105°C), decomposition of thaumasite (at 130°C), decomposition of C-S-H phase (at approx. 290°C, that

is the temperature typical for the partial Si – Al substitution in this phase), decomposition of hydrogarnet (at 330 °C), as well as portlandite and gypsum (between 370 – 400°C). The curves show also that the complete consumption of CaO does not occur. Endotherms between 530 – 650°C represent the carbonated microcrystalline C-S-H and vaterite, while these at 750 – 780°C prove the presence of crystalline calcite which is thermally more stable. Exotherms at 420°C and 900°C, respectively, indicate the final decomposition of portlandite, gypsum, carbonated microcrystalline C-S-H phase and modifications of CaCO<sub>3</sub>.

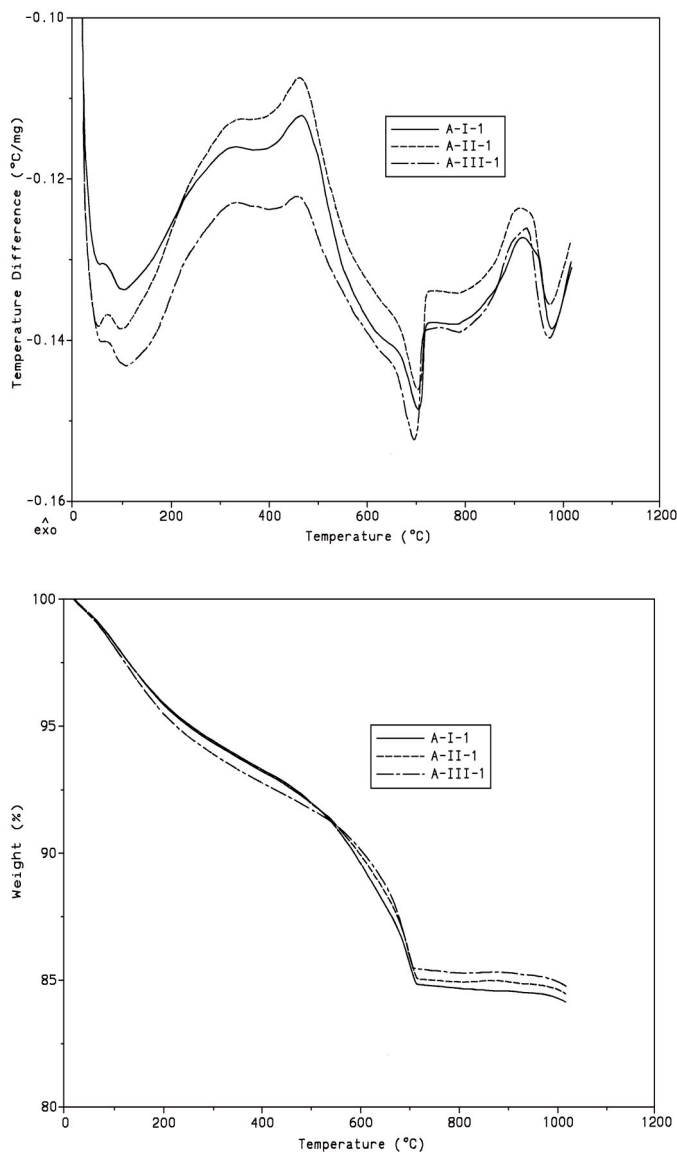


Fig. 3. DTA-TG curves of AAC samples dry stored for 24 months

The thermogravimetric (TG) curves, shown also in Fig. 3, up to the temperature of 600°C give that mass loss accompanying the decompositions of individual phases cannot be unambiguously distinguished. It suggests that the samples are in a thermodynamic nonequilibrium. However, the DTA peaks correspond to the temperature intervals of decomposition of individual phases and the relevant sequences of TG traces are indicative as the quantities of phases decomposed, i. e. thaumasite [Drabik M. et al., 2006] are concerned. The samples of AAC undergo continuous crystallization, carbonation and/or re-crystallization of hydrates. This process

is more pronounced in the samples kept in wet environment and the outline of its mechanism has been proposed, basing on the additional data, below.

### 3.3. XRD phase composition

The XRD data basically confirm the increased content of gypsum and the presence of ettringite and thaumasite. Detailed studies show no qualitative phase changes/differences after 36 month period in the samples cured in either dry or wet environment. The small differences of diffraction intensities are only due to the improved crystallinity as the result of higher degree of crystallization of individual hydrated/carbonated phases. This effect is more pronounced for the samples stored in the wet environment. The presence of portlandite is found also on the DTA curves. The results suggest that the incidental appearance of portlandite is due to the sulfate attack when a sufficient amount of liquid phase is available in the pore space.

Sulfate corrosion of binding phase in AAC is a complex process starting by the dissolution of sulfates and followed by the attack upon the binding components (AFm phases, hydrogarnet, Al-containing phases and portlandite) [Skalny J., Marchand J., Odler I. 2002]. When portlandite is completely exhausted, after around 12 months, the more acidic environment of pore solution and the atmospheric carbon dioxide cause the partial degradation of C-S-H phase and the formation of solid solution of thaumasite-ettringite takes place. This process is accompanied by the liberation of CaO to the pore solution. This is more pronounced for the AAC cured in the wet environment and with the source of sufficient amount of CO<sub>2</sub>.

### 3.4. SEM & EDX

The CSH phase, ettringite and thaumasite are the predominant crystalline new phase seen by SEM and analyzed by EDX. The frequency of appearance and positioning of individual phases in the AAC samples is detailed in Figs. 4 and 5. The data fully support the results of both thermal analysis and X-ray phase analysis. The needle-like crystals are the solid solution of ettringite and thaumasite as characterized by EDX. The crystals of thaumasite are found in all samples of AAC produced with the fluidized fly ash. Their habitus does not change with the increased duration of storage. Anyway, the wet storage conditions, promoting the carbonation of samples, lead to the increase of the dimensions due to crystallization and formation of carbonates, including cubic calcite. EDX spectra of samples of AAC stored either in dry or in wet environment differ, as the time of storage is concerned (up to 36 months) only slightly. Chiefly, the better crystallizations of new formations of Mg, Fe – hydrogarnet and Na, K in C-S-H phase is found as a consequence of prolonged storage (36 vs. 12 month).

The expansion and large deterioration of the construction materials due the thaumasite sulfate attack have been reported by some authors [Skalny J., Marchand J. & Odler I. 2002]. Our results show that this phenomenon in AAC does not occur on such a scale as the deterioration usually observed in the concretes. There is practically no thaumasite sulfate attack and this is the consequence of the

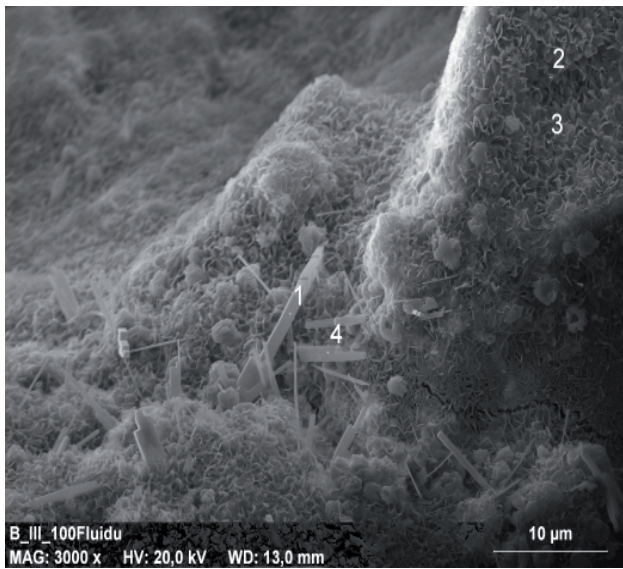


Fig. 4. SEM, AIII, dry stored for 36 months.

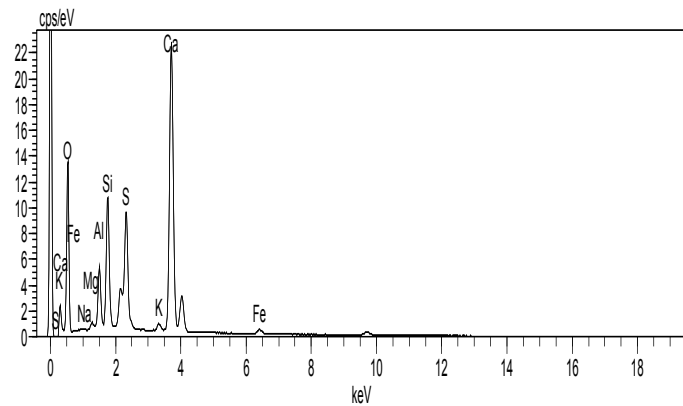


Fig. 5. EDX spectrum, AIII, dry stored for 36 months. Needle-like crystals: positions 1 & 4 showing the solid solution ettringite – thaumasite (EXD of point 4 cf. in Fig. 4), positions 2 & 3 represent the C-S-H and tobermorite-like structure.

sufficient and accessible pore space in AAC. The pores in AAC produced from the modified raw mixes are filled by thaumasite during curing.

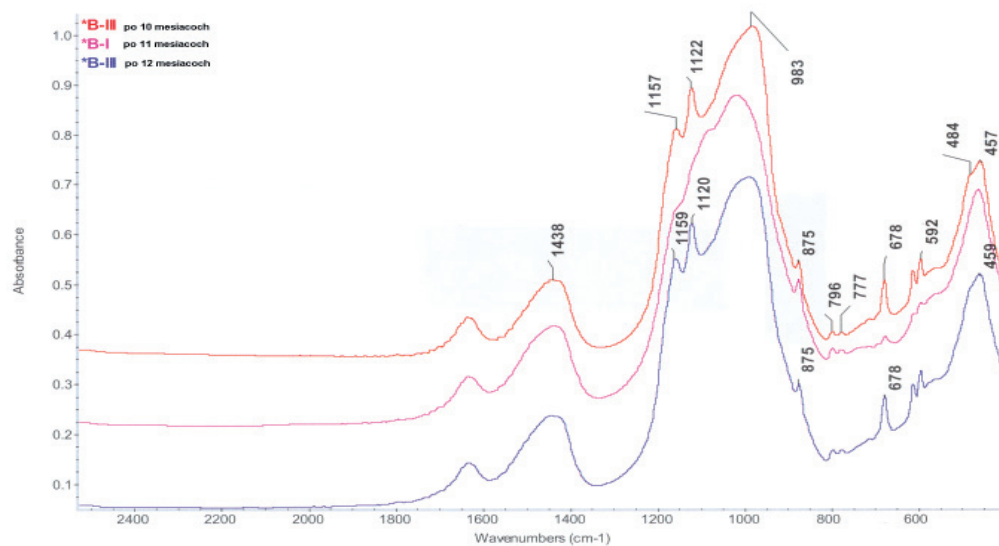


Fig. 6 IR spectrum of AAC samples wet stored for 10, 11 and 12 months

### 3.5. IR spectroscopy

IR spectra (Fig. 6) have been analysed with the goal to explain the changes found in the DTA studies and to get more straightforward insight about the series of thaumasite-*ettringite* solid solutions. The samples from the wet storage have been used; here the most pronounced differences appear between those from 10th and 12th month of storage. The sample after 10 months of storage is composed of thaumasite-*ettringite* solid solution, and the IR spectrum exhibits a band at  $1438\text{ cm}^{-1}$  – characteristic for carbonates and the broad band at around  $1100\text{ cm}^{-1}$  – characteristic for S-O bonds of sulfates, both present in thaumasite [Barnet, S.J. et al., 2002]. In the latest one the two sub-bands – at  $1158$  and  $1122\text{ cm}^{-1}$  can be distinguished and they reflect the internal changes in thaumasite. These subbands disappear from the spectra after 11 months of storage; it means that the process of re-crystallization is hampered. The effect appears again after 22 – 24 months and, to lesser extend, after the final 3rd year storage, also. In the remaining parts of the IR spectra there are the most intensif bands at  $980$  and  $450\text{ cm}^{-1}$ , these are typical of the tetrahedral coordination of  $\text{SiO}_4$  in C-S-H [Bensted J., Varma S. P., 1974.]. Bands of low intensities at around  $875\text{ cm}^{-1}$  are typical of C-O bonds in  $\text{CO}_3^{2-}$  ions and reveal the partial carbonation – formation of calcite [Bensted J., Varma S. P., 1974.].

### 3.6. The key remarks on the technological and environmental relevancy of the topic and results

The production of ash-based autoclaved aerated concretes (AAC), as compared to the sand-based AAC, utilizes and valorizes the important amounts of wastes, with the positive environmental effect. The nowadays technologies are based upon the classic fly ash. Due to the technological changes in coal power plants, the utilization of new generation fly ash as the modified raw material became a topical challenge. The results of long-range experiments, aimed at the durability of final product, reflect the need to optimize the addition of fluidized fly ash so that it will be economically and commercially acceptable and will exert minimal (if any) negative consequence upon the strength and the other physico-mechanical properties of AAC.

The tests performed and the discussion of results are focused on the change of raw mix composition and on the potential use of new generation fly ash separated in coal power plants - fluidized fly ash, in the production of the ash-based autoclaved aerated concretes (AAC). The results of three years tests allow to present a comprehensive analysis of the topic. The strength of samples decreases with the addition of fluidized fly ash; the lowest values are exhibited by the

samples with 100 % fluidized fly ash content in the raw mixture. The data relating to the chemical and phase composition display the high contents of CaSO<sub>4</sub>, CaO and clay minerals (illit, diaspor). Both phase analysis and strength measurements show the higher tendency of samples with fluidized fly ash towards thaumasite formation, as a result of partial conversion of hydraulic C-S-H and tobermorite-like phases to nonbinding thaumasite. However, the expansion connected with the formation of thaumasite, as well as gypsum and ettringite in AAC does not exert the scope of deterioration seen in the other concretes; the difference is due to the sufficient and accessible pore space in AAC. These results form a significant contribution to the updating of discussions of cement chemists and technologists as the aspects of thaumasite formation vs. thaumasite sulfate attack are concerned. This knowledge and the practical experience allow for the modification of AAC production in the region of Slovakia, Czech Republic and Poland.

#### 4. Conclusions

- The strength of dry stored AAC decreases with the duration of storage, the wet storage does not lower the strength. The key contributions towards the observed effect of duration upon the strength represent the carbonation of C-S-H phase and accompanying phase changes.
- The Fe, Mg- hydrogarnet, ettringite – thaumasite solid solution, C-S-H and tobermorite-like phases are the crystalline components formed in AAC. The increased ratio of carbonated component (thaumasite) in ettringite – thaumasite solid solution after 36 months of storage has been found.
- The solid solution of ettringite and thaumasite occur as crystals of sticky habitus; they are typically present in each AAC sample produced with the use of fluidized fly ash. The expansion, usually reported due to the thaumasite sulfate attack, does not contribute to the deterioration in AAC as in concrete, because the thaumasite is located in the abundant pore space.
- The amount of fluidized fly ash additive should be further optimized – particularly lowered to, or below 25%; accounting for the economic, technological and environmental aspects of such a modified production of AAC.

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