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Influence of Fly Ashes Generated at Burning Hard and Brown Coal in Fluidized Boilers on AAC Phase Composition

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Abstract

Properties of fly ashes coming from the fluidized combustion of brown and hard coal, combined with desulphurization, are totally different as compared to the properties of conventional ashes. The fluidized process runs at about 850°C and calcium carbonate is used as a sorbent. Such an ash, when compared to conventional ashes, contains no glassy phase. It contains a considerable amount of an amorphous phase in the form of dehydrated silty minerals and crystalline phases in the form of quartz, free CaO, $CaCO_3$ and $CaSO_4$ II. The ash coming from fluidal combustion has totally different phases, as compared to conventional ashes. It results in alteration of both the structure and microstructure of autoclaved aerated concrete (AAC). PGS (foamed gas silicate) is an autoclaved aerated concrete manufacturing technology, commonly used in Poland. Its main raw materials comprise siliceous fly ashes from hard coal combustion, burnt lime, natural gypsum and aluminium powder used as a pore generating admixture. From the literature we can see that fly ashes coming from the fluidized brown and hard coal combustion combined with desulphurization can be utilized in AAC production. The main phase components of AAC are C-S-H and tobermorite ($Ca_5[Si_6O_{18}H_2]\cdot 4H_2O$), small amount of C_3A_6, $C_3A\cdot CaSO_4\cdot 12H_2O$ and hydrated calcium aluminosilicate ($C_3AS_xH_{6-2x}$) which contain SiO_2 in their chemical composition.

Due to the increased amount of amorphous dehydrated silty minerals of metakaolin type, it is expected for fly ash from the fluidized combustion to result in a bigger amount of tobermorite ($C_5S_6H_5$) in the fly ash added AAC. Fly ash from fluidized combustion also contains calcite. The presence of calcium carbonate in the mix may result in formation of crystalline calcium carboaluminate ($C_3A\cdot CaCO_3\cdot 11H_2O$) as well as scawtite ($Ca_7[Si_6O_{18}]\cdot(CO_3)\cdot 2H_2O$). It is expected that these phases will improve the properties of the final material. The paper presents the influence of fly ashes generated in burning brown coals in fluidized boilers on AAC phase composition. The investigations were supported by X-ray diffraction (XRD), thermal analysis (DTA, DTG, TG) and scanning electron microscopy (SEM).

Keywords: Fly ashes, Fluidal combustion, Autoclaved aerated concrete, Phase composition

WPŁYW POPIOŁÓW LOTNYCH POWSTAJĄCYCH PRZY SPALANIU WĘGLA KAMIENNEGO I BRUNATNEGO W KOTŁACH FLUIDALNYCH NA SKŁAD FAZOWY AAC

Właściwości popiołów lotnych pochodzących z fluidalnego spalania węgla brunatnego i kamiennego połączonego z odsiarczeniem różnią się całkowicie od właściwości konwencjonalnych popiołów. Proces fluidalny przebiega w ok. 850°C i węglan wapnia wykorzystywany jest jako sorbent. Taki popiół w porównaniu z konwencjonalnym nie zawiera fazy szklistej. Zawiera natomiast znaczne ilości fazy amorficznej w postaci odwodnionych minerałów ilastych oraz fazy krystaliczne w postaci kwarcu, CaO, $CaCO_3$ i $CaSO_4$ II. Popiół ze spalania fluidalnego ma całkowicie różny skład fazowy w porównaniu z popiołem konwencjonalnym. Prowadzi to do zmiany zarówno struktury, jak i mikrostruktury betonu autoklawizowanego napowietrzonego (AAC). PGS (piano-gazo-silikat) oznacza technologię wytwarzania autoklawizowanego betonu napowietrzonego, powszechnie wykorzystywaną w Polsce. Podstawowe surowce tej technologii obejmują popioły lotne krzemianowe ze spalania węgla kamiennego, wapno palone, gips naturalny i proszek aluminiowy, jako dodatek porotwórczy. Dane literaturowe wskazują, że popioły lotne pochodzące ze spalania fluidalnego węgla brunatnego i kamiennego, połączonego z odsiarczeniem, mogą być wykorzystane do produkcji betonu AAC. Główne fazy tego betonu to:. C-S-H, tobermoryt ($Ca_5[Si_6O_{18}H_2]\cdot 4H_2O$), mała ilość C_3A_6, $C_3A\cdot CaSO_4\cdot 12H_2O$ oraz uwodniony glinokrzemian wapnia ($C_3AS_xH_{6-2x}$), który zawiera SiO_2 w swoim składzie.

Z powodu zwiększonej ilości amorficznych odwodnionych minerałów ilastych typu metakaolinu oczekuje się, że popiół lotny ze spalania fluidalnego doprowadzi do zwiększonej ilości tobermorytu ($C_5S_6H_5$) w AAC z dodatkiem tego popiołu. Popiół ze spalania fluidalnego zawiera również kalcyt. Obecność węglanu wapnia w masie może prowadzić do tworzenia krystalicznego węglanoglinianu wapnia ($C_3A\cdot CaCO_3\cdot 11H_2O$), a także scawtytu ($Ca_7[Si_6O_{18}]\cdot(CO_3)\cdot 2H_2O$). Oczekuje się, że fazy te będą poprawiać właściwości finalnego materiału. W artykule pokazano wpływ popiołów lotnych powstałych podczas spalania węgla brunatnego w kotłach fluidalnych na skład fazowy betonu AAC. Wspomniane badania oparto na pomiarach dyfraktometrycznych (XRD), analizie termograwimetrycznej (DTA, DTG, TG) i skaningowej mikroskopii elektonowej (SEM).

Słowa kluczowe: popioły lotne, spalanie fluidalne, beton autoklawizowany napowietrzany, skład fazowy

1. Introduction

Depending on the location in Poland, various production variants of autoclaved aerated concrete can be applied [1]. Traditional siliceous fly ash complies in some technologies, coming from burning coal. The ashes content can reach even 70 % of components.

The fly ashes can be applied as aggregate (naturally crumbled) as well as a part of a binding agent. In these technologies, the binding agent usually consists of fly ashes, lime and gypsum, milled together (in PGS technology). Gypsum can be introduced as large crumbles coming from desulfurization of combustion gases. The level of grinding of used ashes depends on their natural crumbling. As a binding agent, also cement (in UNIPOL technology) can be added. Aluminium is used in each variant of AAC technology in the form of powder or paste. It is worth noticing that AAC technology, especially in the variant utilized ashes, is characterized by low consumption of raw materials and energy when compared with other technologies of building materials production. This results from low density of autoclaved aerated concrete. Finally, AAC production is a waste-free process, friendly for the environment.

In the recent years in Poland the market of conventional fly-ashes has changed considerably due to the increased share of fly ashes coming from fluidized coal combustion combined with desulphurization [2-3].

Literature analysis and the authors own preliminary investigations show that AAC is the technology which can utilize the fly ashes effectively. However, the knowledge of ashes properties is important for technology because they significantly influence AAC phase composition [4-6].

The fluidized coal combustion combined with desulphurization runs at about 850°C and calcium carbonate is used as a sorbent. This is why ash properties are changed radically, as compared to those of conventional ashes (this process runs at 1200-1400°C).

Such an ash contains no glassy phase as compared to conventional ashes. It contains a considerable amount of amorphous phase in the form of dehydrated silty minerals and also crystalline phases in the form of quartz, free CaO, $CaCO_3$ and $CaSO_4$ II. It is the common knowledge that the pozzolana activity of the fluidized ashes is considerably larger than traditional (siliceous) fly ashes. In accordance with this fact one can expect the modification of the structure and microstructure of autoclaved aerated concrete.

The main phase components of autoclaved aerated concrete containing traditional siliceous fly ashes are C-S-H, tobermorite ($Ca_5[Si_6O_{18}H_2]\cdot 4H_2O$, C_3A_6 (in small quantity), $C_3A\cdot CaSO_4\cdot 12H_2O$ and hydrated calcium aluminosilicate ($C_3AS_xH_{6-2x}$) which contains SiO_2 [1, 13].

It can be suppose, that in the case of fluidized ashes in autoclaved aerated concrete new phases, i.e., $C_3A\cdot CaCO_3\cdot 12H_2O$ and scawtite ($Ca_7[Si_6O_{18}]CO_3\cdot 2H_2O$ could appear [14-18]. In the case of the presence of enlarged quantity of $CaSO_4$ II, except of $C_3A\cdot CaSO_4\cdot 12H_2O$, hydroellestadyt ($C_{10}S_3\hat{S}_3H$) can also be observed [19].

The paper presents the influence of fly ashes generated in burning brown coals in fluidized boilers on the AAC phase composition.

2. Experimental procedure

2.1. Characteristics of raw materials

The investigations comprised fly ashes generated in burning brown coals in fluidized boilers, their chemical composition and pozzolana activity, shown in Table 1 and 2.

Table 1. Chemical composition of fly ash from burning brown coal in fluidized boilers.

Property	Content [%]
Loss on ignition	2.60
SiO_2	39.10
Al_2O_3	24.40
Fe_2O_3	4.00
CaO	14.50
CaO_w	3.44
MgO	1.30
Na_2O	1.95
K_2O	1.02
SO_3	4.60
TiO_2	2.50
S^{2-}	0.10
Cl^-	0.02
S	99.53

Table 2. Fly ash pozzolana activity according to ASTM C379-65T.

Property	Characteristic type [%]
$SiO_{2\ solvable}$	20.55
$Al_2O_{3\ solvable}$	10.97
$SiO_{2\ solvable} + Al_2O_{3\ solvable}$	31.52

It follows from chemical analyses of ashes under investigation that the fluidized combustion ash contains a considerable amount of CaO and free calcium and increased content of SO_3 as compared to those of silica ashes.

The tests have indicated that pozzolana activity of fluidized ash is 30 % larger than that shown by silica ash.

2.2. Samples preparation

Siliceous fly ashes in the binding agent composition of investigated samples were fully exchanged with fluidized ashes. Because the fluidized ashes contain free lime and anhydrite, the amount of lime in the binding agent has been reduced from 6 to 12 % (04Pf and 05Pf) and the amount of gypsum was reduced by about 40 % (03Pf) or even gypsum has been eliminated from the mix (02Pf).

Finally, the homogenization of the binding agent composition was carried out in a laboratory grinder.

Except of the binding agent and components specified in Table 3, autoclaved aerated concrete contains also aggregate siliceous fly ashes (naturally crumbled), water, surface active

Table 3. Binding agent composition.

Component	Binding agent composition determination					
	0Pk	01Pf	02Pf	03Pf	04Pf	05Pf
Silica ash	56	-	-	-	-	-
Fluidized ash	-	56	60	57,2	58	65
Lime	36	36	40	38	34	32
Gypsum	8	8	-	4,8	8	8

agent and a porosity creating agent (Al powder). The mentioned composition is called "concrete mixture" in this paper.

3. Results and discussion

3.1. Phase composition of concrete mixture

The phase composition of the AAC in the first step of its production (after finishing the rising process) was determined by using XRD and SEM-EDS analysis. The results are presented in Figs. 1-4.

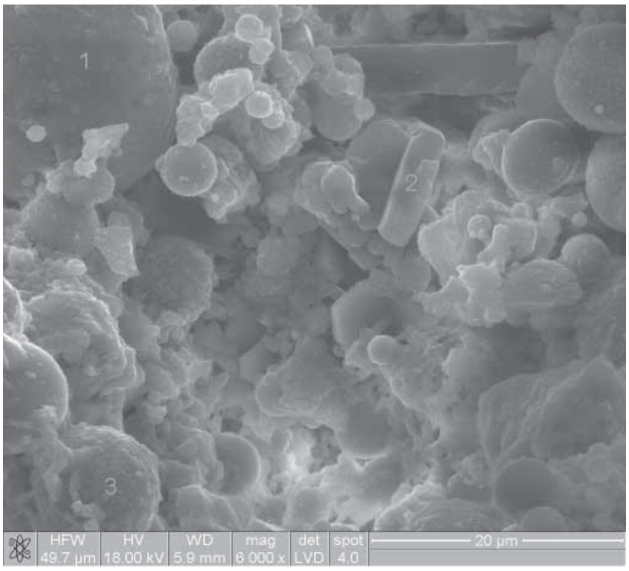

Fig. 1. SEM image of C-S-H phase and unreacted grains of silica ash (0Pk).

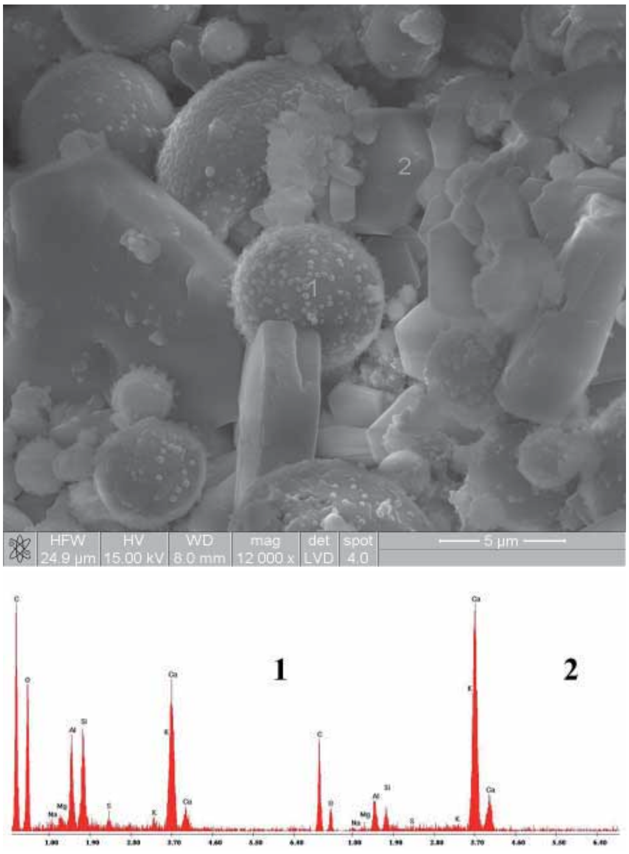

Fig. 2. SEM image and EDS analysis of hydrated calcium aluminosilicate (01Pf).

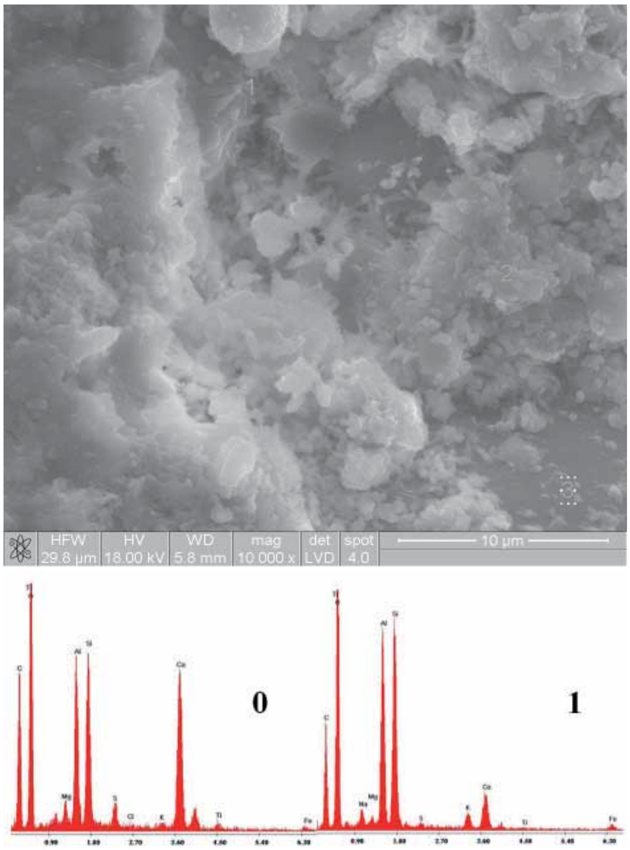

Fig. 3. SEM image and EDS analysis of hydrated calcium aluminosilicate and unreacted grains of silica ash (02Pf).

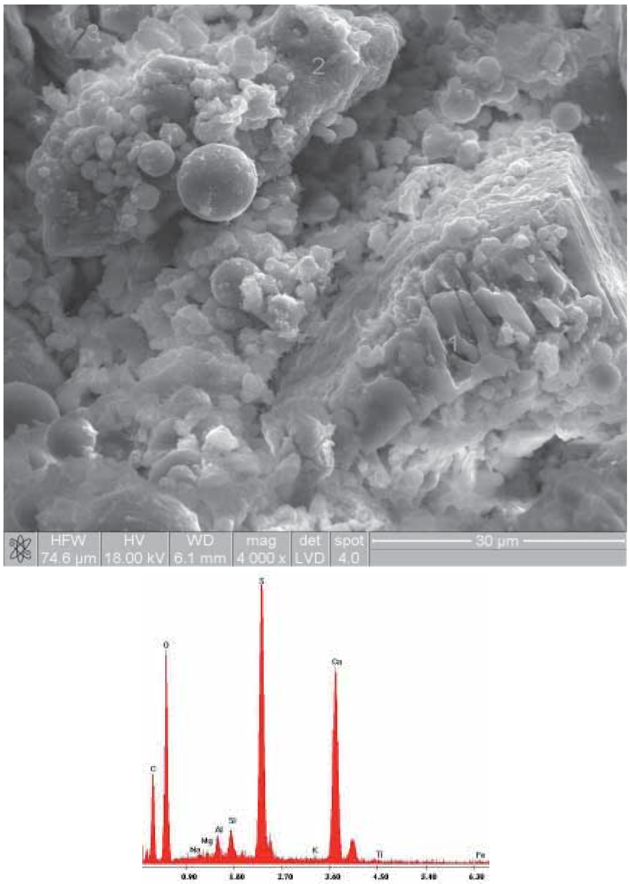

Fig. 4. SEM image and EDS analysis of unreacted gypsum in 05Pf.

The analyses performed for the reference sample of AAC (containing siliceous ash) confirmed that basic hydration products are C-S-H and a small quantity of calcium aluminosilicate. The large unreacted grains of silica ash were also detected.

In the samples containing fluidized ashes, the amount of C-S-H phase and calcium aluminosilicate (Figs. 2-4) grows up with the ash content. In parallel, the content of unreacted gypsum went down. In the sample 02Pf gypsum was not detected. The whole amount of anhydrite present in the fluidized ash has been reacted and monosulfat ($C_3A{\cdot}CaSO_4{\cdot}12H_2O$) has appeared.

3.2. Phase composition and microstructure of AAC

The phase composition tests included microstructure and grain morphology observations (SEM), phase and mineral composition (XRD – X-ray diffraction; thermal analyses: DTA, DTG, TG).

XRD and DTA showed that the basic hydration products were C-S-H and tobermorite. Unreacted gypsum and calcite, which were included in fluidized ashes were also detected (except sample 02Pf). It suggests that the using fluidized ashes in AAC technology leads to a significant reduction or even elimination of gypsum.

The phase composition of AAC was determined by SEM-EDS analysis. The results are presented in Figs. 5-9.

4. Summary

Fluidized ashes influence the phase composition of AAC qualitatively and quantitatively. It was stated that in the first

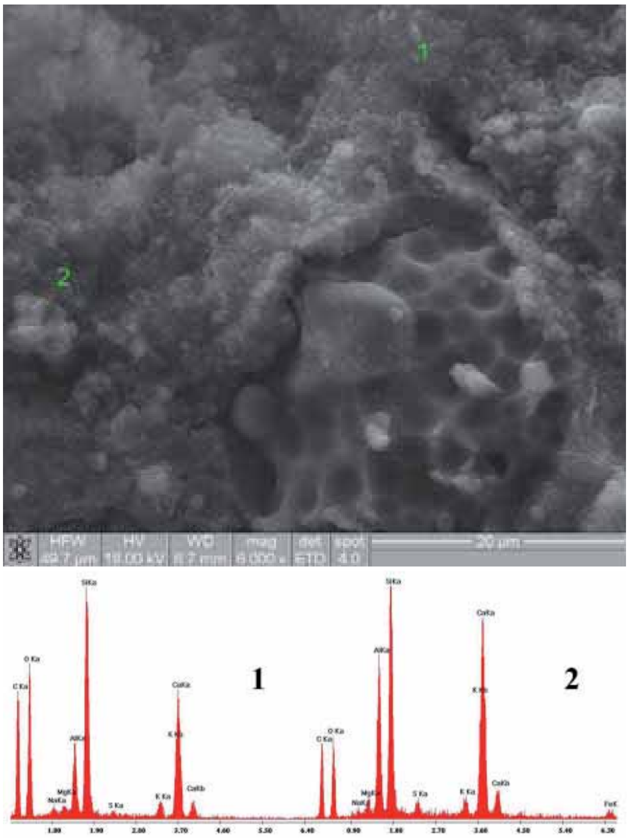

Fig. 5. SEM image and EDS analysis of hydrated calcium aluminosilicate and C-S-H (01Pf).

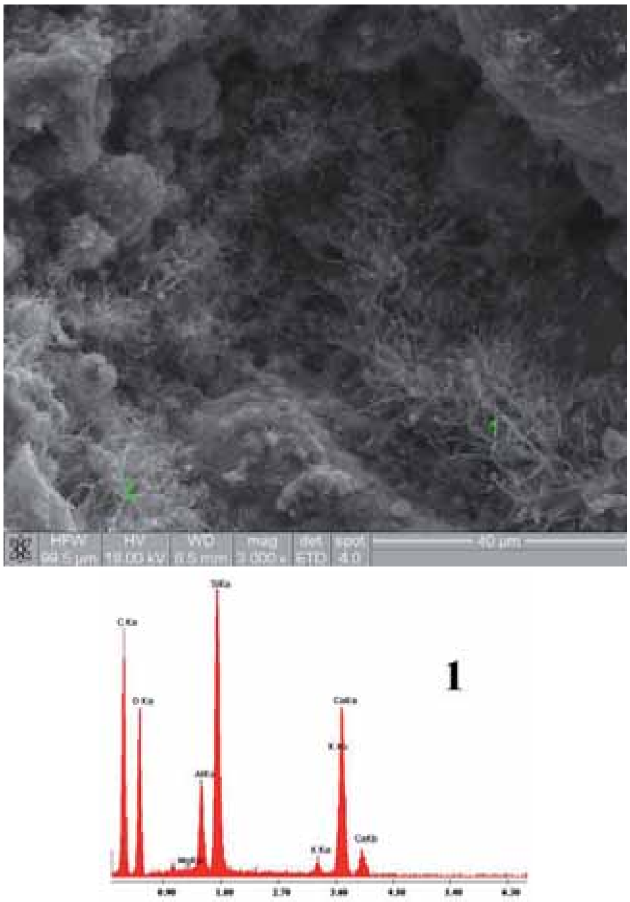

Fig. 6. SEM image and EDS analysis of C-S-H phase (02Pf).

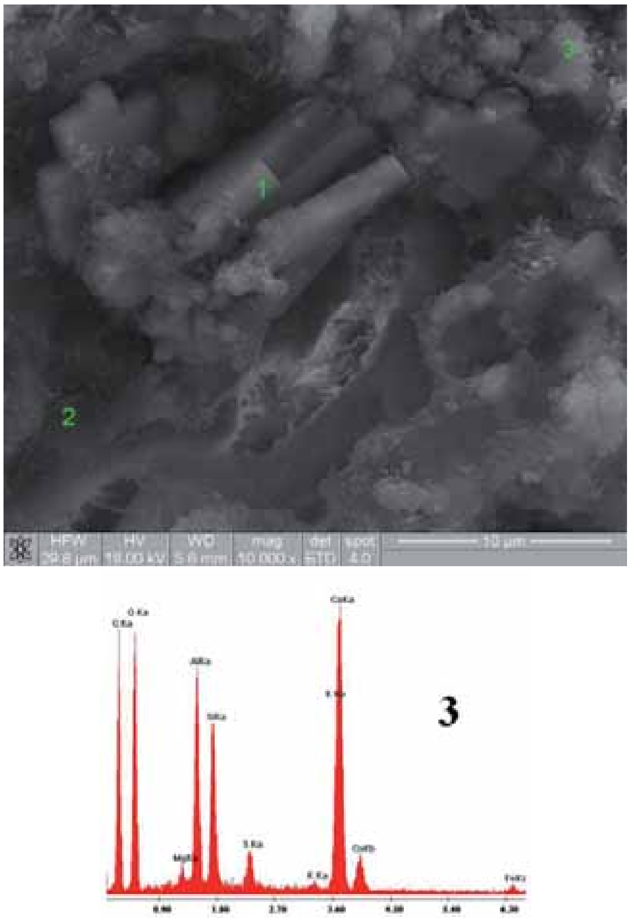

Fig. 7. SEM image and EDS analysis of hydrated calcium aluminosilicate (03Pf).

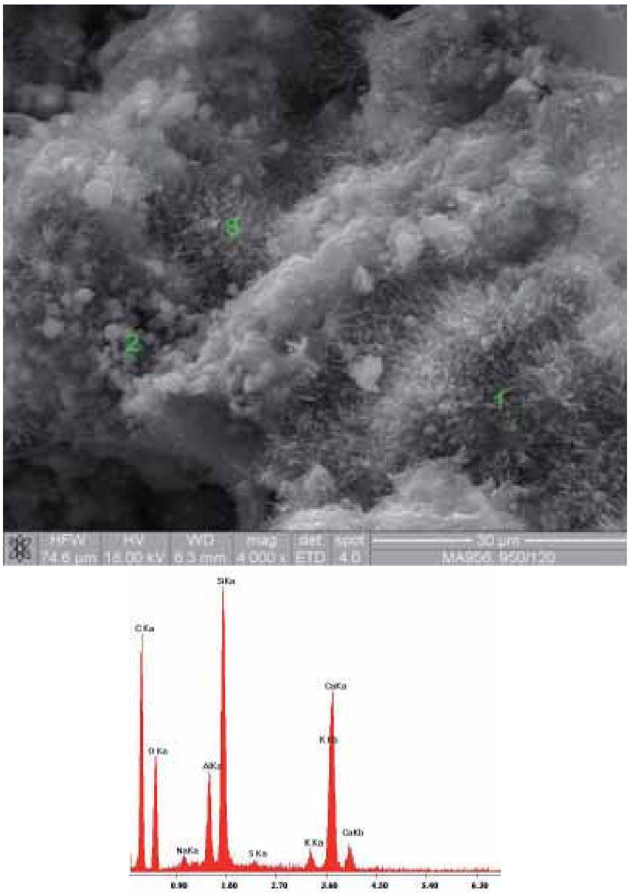

Fig. 8. SEM image and EDS analysis of C-S-H phase containing aluminium ions (04Pf).

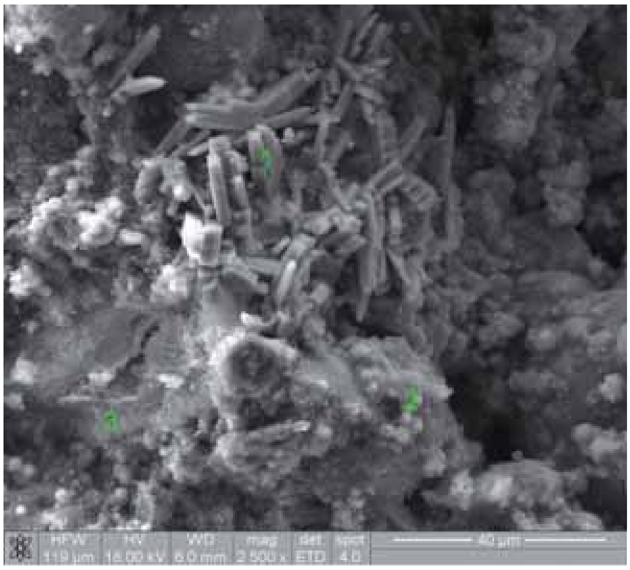

Fig. 9. SEM image of gypsum crystals (05Pf).

period of the autoclaved aerated concrete production the differences concern mainly the amount of C-S-H phase. Its amount rises slightly with the fluidized ashes content.

After the autoclaving process in the autoclaved aerated concrete, the phase composition changes. An increase of C-S-H and tobermorite content is observed. The content of hydrated calcium aluminosilicate in AAC significantly rises. In such a concrete, calcite from fluidized ash can be observed. However, XRD measurements confirm traces of scawtite.

The investigations confirm the possibility of significant reduction or even total elimination of gypsum and partial reduction of lime from the concrete mixture.

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