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# Influence of polymer superplasticizers on the properties of autoclaved aerated concrete

ABSTRACT: Second generation superplasticizers based on polycarboxylates were investigated in terms of their influence on the properties of autoclaved aerated concrete (ACC). The macromolecules of the plasticizers contained polycarboxy and polyether segments, and free carboxylic groups gaining solubility of the plasticizer in water. Water solutions of the plasticizers of concentration of 30 wt% were applied as admixtures to concrete. Concrete samples were based on gypsum, calcium oxide and fly ash as binder and an aggregate. The concrete was produced by foam-gas-silicate (FGS) technique.

Fresh mixtures both containing and not containing superplasticizers were autoclaved, and the hardened samples were characterized. The samples containing superplasticizer in amounts enabling to reduce water quantity to 20% showed density about 10% higher, and compressive strength about 20% higher comparing to the samples without plasticizers. Phase analysis did not show any differences between the concrete samples containing or not containing the admixtures. All samples contained tobermorite, hydrogranates, and C-S-H phase.

KEY WORDS: autoclaved aerated concrete, superplasticizers, polycarboxylates

1. Introduction

Autoclaved aerated concrete (ACC) is a lightweight building material with a fast growing production and usage in both hot and cold weather countries [1,4,5,9]. It is produced by molding and hydrothermal processing of various raw materials containing mainly quartz, Portland cement and/or lime with traces of aluminum powder. The concrete mix generates hydrogen gas by the following chemical reaction between fine aluminum powder and calcium hydroxide:

$$2Al + 3Ca(OH)_2 + 6H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O + 3H_2$$
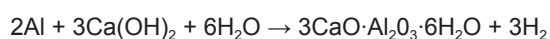
After the molding period concrete is subjected to autoclaving process under steam pressure. This process is associated with the formation of tobermorite as the main binding phase. The final product is highly porous, lightweight, with low bulk density and low thermal conductivity. Comparing to classic concrete it also shows lower shrinkage and higher heat resistance [2,6,7]. However it shows relatively low compressive strength. ACC is usually used for construction of outer walls.

If ACC is produced as a structural material it requires high-pressure steam-curing, i.e. autoclaving. If curing of a cement-based material takes place at ambient temperature and pressure, only the binder reacts to hold the aggregates together. However, when curing takes place at higher temperature and higher pressure in saturated steam, silica reacts with calcium hydroxide, creating a micro-crystalline structure with a much lower specific surface than that obtained in normal curing conditions [8].

Applying mineral additions as fly ash for the aggregate filler in aerated concrete has many ecological and economic benefits.

The residues are very fine and do not require additional grinding as aggregate usually does. It is also claimed that ACC made with fly ash have better thermal insulation and strength properties compared to ACC made from quartz sand [3]. Most likely, this is a result of fly ash ability to react with calcium hydroxide in the presence of moisture and to create calcium silicate hydrate that has cementitious properties [10].

In our work we focused on the influence of superplasticizers on the properties of ACC. Superplasticizers are principally referred as high-range water reducers in concrete. Reduction of the amount of water in the mix is crucial for decreasing capillary porosity of the hardened cementitious materials. The second important function of a superplasticizer is to maintain a specific workability of the fresh concrete for a particular period of time, even at low water/binder ratio. By chemical nature superplasticizers are water-soluble polymers and comprise sulfonated and carboxylated macromolecules. We focused on the last generation superplasticizers, i.e., carboxylated polymer containing ether linkages.

2. Materials and methods

Concrete samples were produced by foam-gas-silicate (FGS) technique. They were based on gypsum, calcium oxide and selected fly ash as a binder and an aggregate. Fly ash has the following chemical composition (% wt.): SiO_2 – 53.6; Al_2O_3 – 23.3; Fe_2O_3 – 5,4; CaO – 4.1; CaO_{free} – 1.0; MgO – 2.5; SO_3 – 1.0; $Na_2O + K_2O$ – 2.5, and loss on ignition (C) – 4.3, other (TiO_2, P_2O_3) – 2.3. Other properties of the fly ash are as follows: Blaine surface area – 3950 cm^2/g, density – 2.20 g/cm^3, water demand – 41.3%.

Superplasticizers based on polycarboxylate ethers (ascribed as D1, D2 and D3) were applied as the admixtures. They were purchased from BASF. According to FTIR spectra and GPC analysis all three admixtures were chemically identical, but differed by molecular weight and polydispersity factor. They consisted of two main fractions of polymer molecules differing by the molecular weight. M_w of D1 was determined by GPC as ~1000 Da for fraction I and ~3500 Da for fraction II. D2 was characterized as 800 Da (fraction I) and 3300 Da (fraction II), and D3 – 900 and 4600 Da, respectively. In D1, however, higher molecular weight fraction was dominating, in D2 amounts of the two fractions were comparable, and in D3 lower molecular weight molecules were in higher quantities. The admixtures showed also different thermal behavior. They were water soluble, and 30 %wt solutions were applied for concrete mix preparation. As a porogen aluminum powder with a contact surface of 6000 cm^2/g was applied.

The research was done on a binder-aggregate composition containing 48.6% of binder and 51.4 % of the aggregate. The binder consisted of 37% of calcium hydroxide, 10% of gypsum, and 53% of fly ash.

Compositions were prepared in the following way: appropriate amounts of the binder and aggregate were placed in a mixer and stirred for 1 min. Then water with the temperature of about 60°C was added and the stirring was continued for 3 min. A superplasticizer was always dissolved in water prior to concrete mixture preparation. Next, suspension of aluminum powder in a surfactant was added and stirred for additional 1 min. The composition was poured into a steel mold (100x100x100 mm) preheated to 50°C. The mold was kept in the temperature of 50°C until evolution of

hydrogen was finished, and then autoclaved for 8 hours at the temperature of 180°C, and pressure of 1.2 MPa.. The compositions of the mix together with the determined appropriate amounts of water are given in Table 1. Properties of the compositions are in Table 2.

Water demand and setting times of the mixtures were determined according to the standard PN-EN 19 -3:2005. Bulk density of the obtained concrete was determined according to the standard PN-EN 678:1998. Compressive strength was determined according to the standard PN-EN 699:2008. X-ray diffraction (XRD) analyses were performed using Philips X'Pert apparatus (Cu K$_\alpha$). Scanning electron microscopy (SEM) was performed using FEI Nova Nano SEM 30. FTIR spectra were recorded with Digilab FT spectrometer using KBr pellet technique.

3. Results and disscussion

3.1. Water demand end setting time

Low water/binder ratio is an important issue in concrete technology because the excess of water always leaves capillary porosity in the hardened concrete. In our work the main reason of introducing superplasticizers into concrete mix was to reduce the amount of water. In Table 3 water demand for different concrete mixtures is shown. In all cases significant water reduction was observed comparing to the parent sample not containing a superplasticizer. Namely, the water reduction for D1 is 29%, D2 - 31%, and D3 - 30%. The water demand dropped from 43% to 30-31%. It can be stated then, that the investigated admixtures are high-range water reducers.

Table 1. Composition of the investigated aerated concrete.

Amounts [kg/m^3]		D0		D1-0.7		D2-1.0	
BINDER	Calcium oxide		119		119		119
	Gypsum	321	32	321	32	321	32
	Fly ash		170		170		170
FLY ASH (aggregate)		339		339		339	
WATER		365		290		294	
SUPERPLASTICIZER		-		2.25		3.2	
ALUMINUM POWDER		0.42		0.42		0.42	
Ratio							
w/b		1.14		0.90		0.92	
w/b+a		0.55		0.44		0.45	

Table 2. Comparison of the properties of fresh concrete mixtures without (D0) and with superplasticizers (D1-0.7, D2-1.0).

Sample	Amounts of admixtures*	Components ratio		Water reducing [%]	Density of mixtures [kg/m^3]
		Water/ binder	Water/ (binder+aggregate)		
D0	–	1.14	0.55	–	1698
D1-0.7	0.7 %	0.90	0.44	21	1740
D2-1.0	1.0 %	0.92	0.45	19.5	1705

* Percentage of the admixture was calculated in relation to the amount of dry binder.

Setting times of the concrete samples with and without superplasticizer are shown in Fig. 1. The results show that the admixtures D1 and D2 are accelerating the hardening process, and can be classified as type E (HRWR and accelerating), while D3 is type G (HRWR and retarding). Noticeably different is, however, the beginning of the curing process, which starts 25 min earlier in case of D1, and only 5 min in case of D2. Total curing time of samples containing D1 is 20 min, while 15 min when D2 has been applied. D3 acts a retardant of curing process. It starts 5 min later and is completed 10 min later comparing to D0 sample. It can be concluded than, that lower molecular weight polymer causes the delay in the hardening process.

3.2. Density and compressive strength

Final properties of the hardened samples were examined. The obtained results are

Table 3. Water demand and water/concrete ratio in the investigated samples.

Sample	Amounts of admixtures* [%wt]	Water demand [%]	Ratios	
			w/b	w/b+a
D0	-	43	1.01	0.43
D1-1.05	1.05	31	0.72	0.31
D2-1.74	1.74	30	0.70	0.30
D3-2.50	2.50	31	0.71	0.31

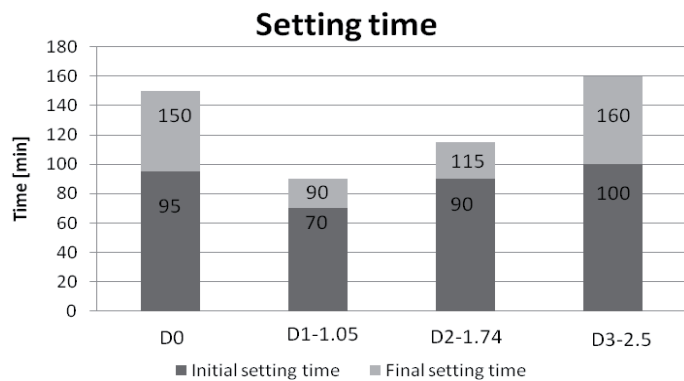* Percentage of admixture was calculated in relation to the amount of dry binder.

Setting time

Fig. 1. Setting times of concrete mixtures.

presented in Table 4. Density of the samples containing D1 and D2 is about 10% higher than that of D0. It might be the evidence on the negative influence of the superplasticizers on the pores formation, as the difference between density of D0 and the samples containing superplasticizers is quite large. At the same time, there is almost no difference between D1 and D2.

Simultaneously, compressive strength of the samples modified with superplasticizers is higher than this of D0. The difference is significant and the increase is ~20%. It can be easily explained
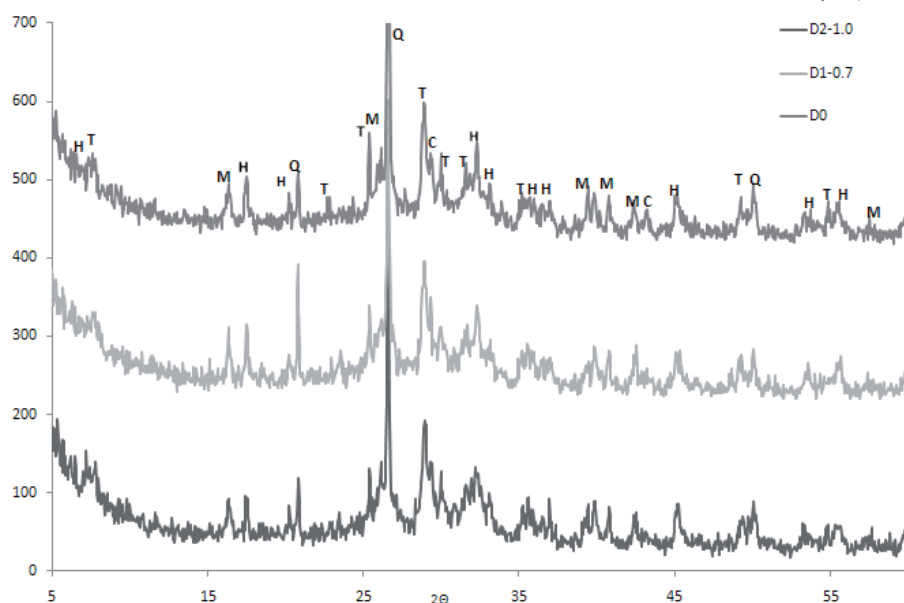
Fig 2. X-ray diffraction patterns of the concrete samples. The following designations are used in the diagrams stands for: H-hydrogranates, T-tobermorite; M-mullite, Q-quartz; C-calcite.

Table 4. Properties of cured samples.

Sample	Density [kg/m³]	Compressive strength [MPa]
D0	538 ± 7	3.88±0.07
D1-0.7	599 ± 9	4.72±0.43
D2-1.0	590 ± 8	4.70±0.23

with the decrease of w/b ratio, and the difference in porosity of the samples.

On the other hand, the difference between superplasticizers, like molecular weight and polydispersity factor, does not play any role in changing the final mechanical properties of the final ACC. Compressive strength of both samples is almost identical.

3.3. X-ray diffraction and sem analysis

X-ray diffraction patterns of the hardened concrete samples are shown in Fig. 2. The XRD patterns can be used to identify crystalline phases and their concentrations. In case of hardened concrete
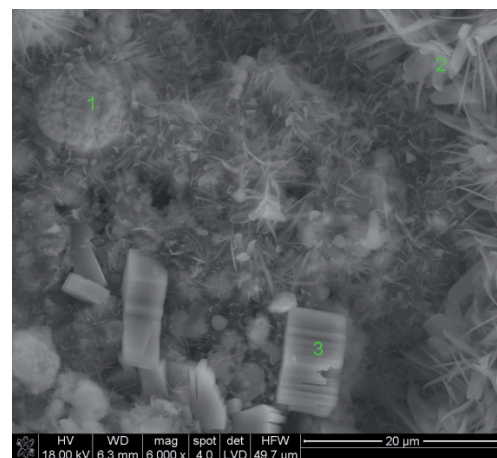
Fig. 3. SEM image of the hardened concrete samples D0. Marks 1, 2, and 3 refer to fly ash, tobermorite, and gypsum, respectively (confirmed with EDS analysis).

the hydration process can be explained and the hydration products identified. The type, amount and distribution of hydrated products which have significant influence on strength, durability and dimensional stability of the hardened concrete can be assumed on the basis of X-ray diffraction pattern, SEM and EDS analysis of the final product.

X-ray spectra of all samples are almost identical. In all tobermorite phase is present (see also SEM images in Figs. 2, 3 and 4). This calcium silicate hydrate gel (C-S-H) usually makes up 50–60% of the solids of hydrated binding material. The presence of tobermorite phase in concrete is crucial for the correct shrinkage of the sample on drying, since water trapped between the surfaces of planes of C-S-H structure is lost only on very extensive drying.
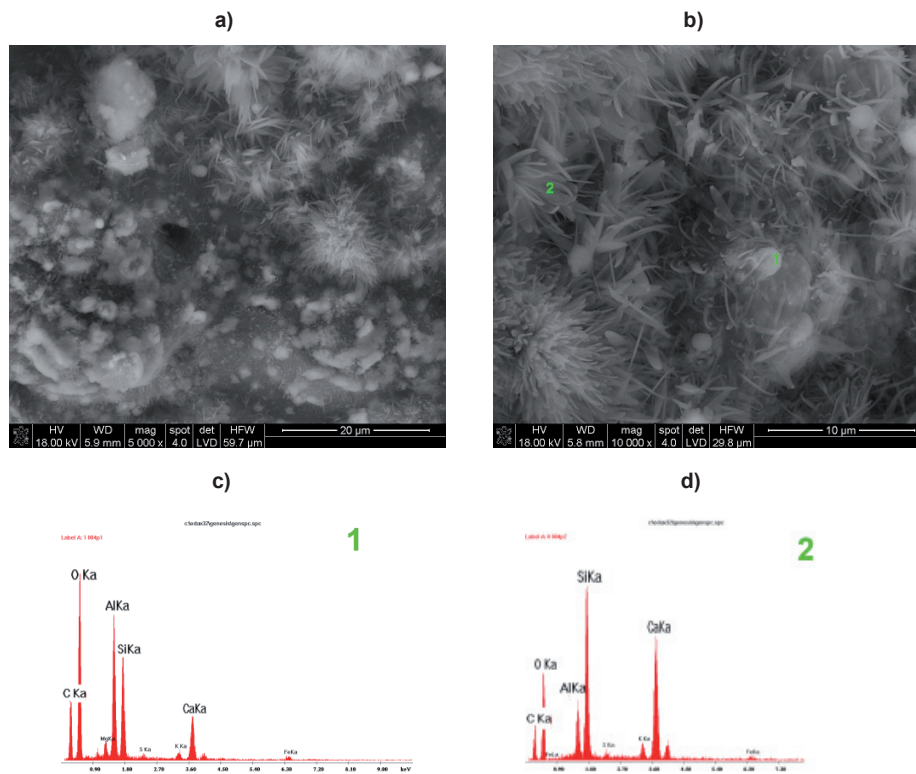
Fig. 4. a) SEM image of sample D1-0.7, b) SEM image of sample D1-0.7 – closer view on tobermorite phase, c) EDS analysis of 1 – fly ash; c) EDS analysis of 2 – tobermorite.
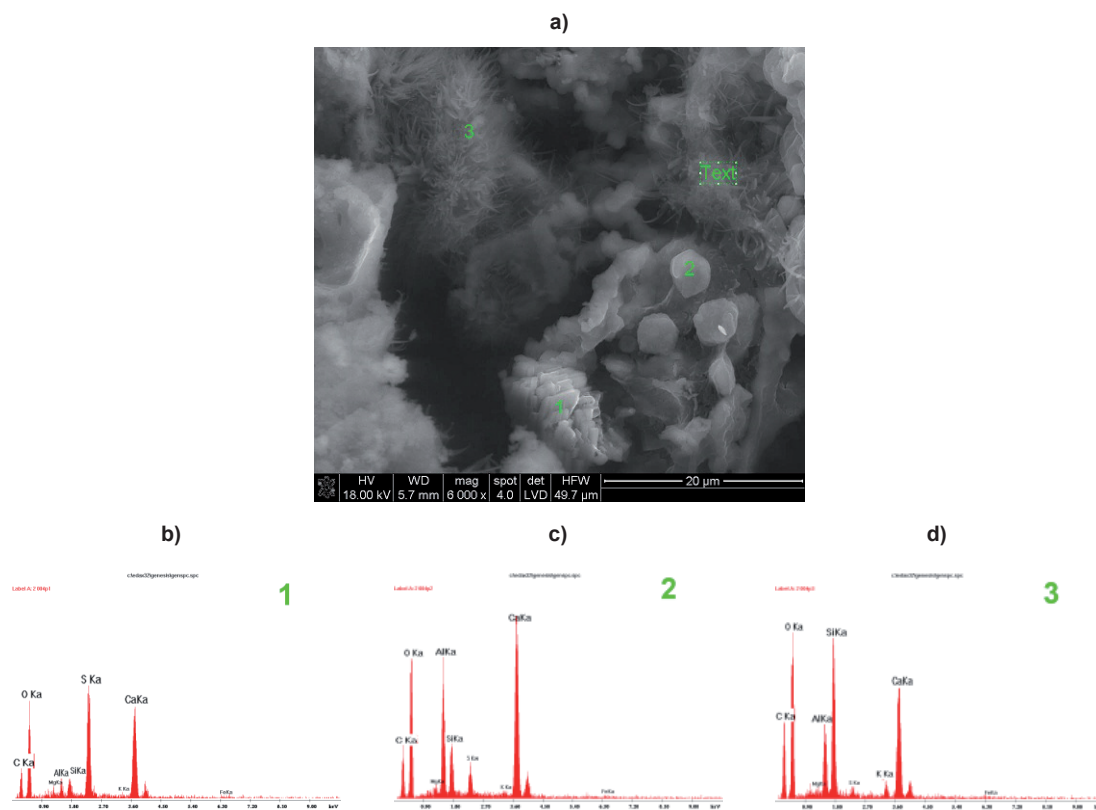

Fig. 5. a) SEM photos of the sample D2-1.0, b) EDS analysis of 1 – gypsum, c) EDS analysis of 2 – tobermorite; d) EDS analysis of 3 – hydrogranate.

Presence of hydrogranate is also clearly visible in all cases. Hydrogranate is typical for cellular concrete based on fly ash. Formation of this phase is beneficial for correct shrinkage and strength of concrete. Quartzite and mullite phases are visible in the diffraction patterns, and they are also characteristic of fly ash.

Electron scanning microscopy and EDS analysis shows that morphology of the samples is similar. In the samples three or four main phases can be distinguished, C-S-H and crystalline tobermorite with the average dimensions of crystals ~5 μm, spherical fly ash,

gypsum crystals, and hydrogranates. It remains in a good agreement with X-ray diffraction patterns. The dominant phase in the XRD patterns is quartz, which is characteristic to fly ash.

No separation of the polymer admixture is observed. However the bulky structure marked as 4 in Fig. 5a is very characteristic for linear polymers with flexible chains. Differently from D0 and D1 the D2 sample shows a lot of voids in the structure. Spherical particles of fly ash are also clearly visible.

4. Conclusions

It can be concluded that the examined superplasticizers based on polycarboxylate ethers can act both as accelerating and retarding agents for workability of ACC. Their influence depends on the molecular weight and polydispersity of the polymer, i.e., short-chain polymers increase setting time.

The applied admixtures are high-range water reducers. The samples containing superplasticizer in amounts enabling to reduce water quantity to 20% showed density about 10% higher, and compressive strength about 20% higher comparing to the samples without plasticizers. The superplasticizers do not influence hydrogen evolution, however, increase of density of the final ACC was observed as compared to ACC without a superplasticizer. The ACC obtained with the use of superplasticizers show higher mechanical strength, specifically the compressive strength.

No significant changes were observed in the properties of the final ACC depending on the kind of superplasticizer.

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