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Contribution to the knowledge of melamine superplasticizer effect on some characteristics of concrete after long periods of hardening

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Abstract

The influence of melamine superplasticizer on some characteristics of concrete was determined. Volume density, compressive strength after 28 days and 360 days, water absorption, and frost resistance after 200 days of freezing and thawing were tested. The content of bound water in cement hydration products was determined. It was found that there was a decrease in the strength of concrete with superplasticizer after longer periods in relation to the strength of this concrete after 28 days. This was accompanied by an increase in the bound water content.

Keywords: Concrete; Admixture; Long-term performance; Hydration products; Microstructure

"It was predicted that the most recent technological developments in concrete technology rely on enhanced admixture efficiency rather than on improvement in cement manufacturing" [1]. Cement admixture compatibility problems are becoming more frequent, especially in the field of superplasticizers [1,2].

Superplasticizer efficiency depends on properties of both the cement and the admixture. In case of cement properties, phase composition (especially C_3A content) [3] and, according to some authors [4,5], free lime content, alkali content, form of calcium sulfate (dihydrate, bassanite, anhydrite), and specific surface of cement are important. Taking into account the properties of a superplasticizer, the following factors are of great importance: its chemical structure, molecular weight of polymer, amount of admixture, and the method of its addition (at the beginning of mixing, portion by portion, or at the end of mixing).

Different superplasticizers may behave differently with different cements because of probable synergistic effects that may contribute to compatibility or incompatibility of cement admixture [1].

Superplasticizers are widely used as effective admixtures for improving the workability of the mix or reducing the water content in concrete, which should lead to higher compressive strength and improved durability. SMF-type superplasticizers consist of salts of sulfonated melamine formaldehyde polymers with large molecular weights, which are most effective with molecular weight of about 30,000. The literature points to three basic physicochemical phenomena that influence the fluidifying effect of superplasticizers. These are dispersion, adsorption, and intermolecular repulsion zeta potential [3,6,7]. It has not been conclusively determined whether superplasticizers are adsorbed on the surface on the cement grains or on the hydration products as well, particularly on the surface of the hydrated phase of aluminates and sulfates [6]. Not always are a higher (in absolute value) zeta potential and what follows a more effective dispersing action tied to greater adsorption of superplasticizers on the surface of cement grains. This results from various forms of calcium sulfate in the cement: dihydrate, bassanite, or anhydrite [3].

According to the most recent studies, "the exact way in which superplasticizers modify interparticle forces in cement suspensions, whether it is by electrostatic, steric or entropic effects or a combination of these is still a debated matter" [8].

There are little data from tests of the microstructure of cement composities with superplasticizers. The available literature reports that using superplasticizers makes the cement paste denser [3,9,10].

Changes in the morphology and size of cement hydration products affected by superplasticizers apply mainly to ettringite crystals [6]. In place of the thicker needle-like crystals, smaller and shorter crystals are formed, which measure about one tenth of those obtained in the absence of the super-

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plasticizer and in smaller amounts. Those observations are confirmed by other authors [10] indicating a cube-like shape of the ettringite crystals modified by superplasticizers. According to some studies [11], ettringite crystals are more distinct and thicker in configurations with the superplasticizer.

The size of portlandite crystals decreases with the addition of admixture, and their form changes from block-like to thin plate.

The effectiveness of superplasticizers in terms of fluidizing, water reduction, workability retention, segregation, and bleeding with reference to the properties of concrete mixes and by strength characteristics at the early stages of hardening (after 1, 3, or 7 days) and after 28 days concerning hardened concretes is obvious from the point of view of concrete technology. Moreover, the effects of admixtures on hardened concrete characteristics, such as water absorption, frost resistance, resistance to sulfate attack, and chloride penetration, which in a sense are durability indicators, are important.

In the literature we find relatively few well-documented data on the changes of strength and structural characteristics of concrete with superplasticizers, cured under different conditions of temperature and humidity for longer than 28 days.

To evaluate the influence of superplastcizers on concrete, complex tests of physicomechanical and structural characteristics of concrete were used. These include determining the compressive strength, water absorption, frost resistance, and volume density of concrete, as well as determining the bound water content in hydration products and hydrolysis product and the content of calcium hydroxide. The characteristics of concrete after 28 days are a reference point for comparing their changes after longer periods of concrete hardening [12].

1. Experimental

1.1. Materials

Ordinary Portland cement with a low amount of C_3A and a total of 350 kg/m^3, natural aggregate and melamine superplasticizer (SMF) in the amount of 2.2% by cement weight were used. Properties of the cement are given in Table 1.

Table 1
Characteristics of cement used

Characteristic	Result of test
Phase composition (%)	
C_3S	58.75
C_3A	3.94
SO_3	2.42
Other properties (%)	
Ignition loss	0.37
Insoluble parts	0.45
SiO_2	21.18
Al_2O_3	3.56
Fe_2O_3	4.80
CaO	64.91
MgO	0.71
Alkalies as Na_2O	0.50
Blaine specific surface (m^2/kg)	300

1.2. Range and methods

The test were carried out to reduce the water-to-cement ratio, which was 0.43 in concrete without the admixture and 0.35 in the series with superplasticizer. The consistency of concrete mixes was 7–8.5s according to VeBe. The amount of mix water for the series with superplasticizer decreased by 18%. The tests were conducted on cubes a = 10 cm. The terms and hardening conditions of concretes were as follows: 28 days in standard conditions, 360 days in air-dry conditions, 360 days in water, and 200 cycles of freezing and thawing (freezing in air and thawing in water according to Polish Standard PN-88/B-06280 [13]). The content of bound water in cement hydration products [silicates, aluminates, and calcium aluminate sulfates (HI)] and cement hydrolysis products [calcium hydroxide (HII)] were determined in the concrete using differential thermal analysis (derivative thermogravimetry [DTG], differential thermal analysis [DTA], and thermogravimetry [TG]). The microstructure of the concretes was examined qualitatively using scanning electron microscopy (SEM). Specially prepared, fresh surfaces of concrete fractures were observed at magnifications ranging from 20 to 10,000×. Qualitative X-ray analysis was conducted on selected samples.

2. Results and discussion

The results of tests of physicomechanical and structural characteristics of concretes are given in Tables 2 and 3, respectively.

Figs. 1–4 show the microstructure and morphology of some concrete samples examined by SEM.

To evaluate the influence of superplasticizer on the physicomechanical and structural characteristics of concrete, the changes of values in the concrete both without and with superplasticizer were examined.

Table 2
Physicomechanical characteristics of concretes without and with SMF superplasticizer

	Result of concrete test	
Characteristic of concrete	Without superplasticizer	With SMF superplasticizer
Volume density (kg/m^3) after		
28 days in standard conditions	2350	2380
360 days in air-dry conditions	2409	2385
360 days in water	2392	2403
200 freeze-thaw cycles	2381	2409
Compressive strength (MPa) after		
28 days in standard conditions	34.9	43.7
360 days in air-dry conditions	35.5	35.0
360 days in water	38.5	33.0
200 freeze-thaw cycles	31.3	31.1
Water absorption (%)	4.6	3.4
Frost-resistance drop (%) in compressive strength	18.5	7.7

Table 3
Structural characteristics of concretes without and with SMF superplasticizer

Characteristic of concrete	Result of concrete test	
	Without superplasticizer	With SMF superplasticizer
Bound water content (kg/m^3) in products of hydration (HI) and hydrolysis (HII), after		
28 days in standard conditions		
HI	49.4	45.2
HII	9.4	7.1
360 days in air-dry conditions		
HI	67.5	57.2
HII	9.6	7.2
360 days in water		
HI	69.4	50.5
HII	12.0	7.2
200 freeze-thaw cycles		
HI	64.3	55.4
HII	9.5	7.2
Calcium hydroxide content (kg/m^3) after		
28 days in standard conditions	37.6	28.6
360 days in air-dry conditions	38.5	28.6
360 days in water	50.2	28.8
200 freeze-thaw cycles	38.1	28.9

The volume density of concrete without the admixture is contained within 2350 to 2409 kg/m^3. In the case of concrete with superplasticizer, the volume density is within the range from 2380 to 2409 kg/m^3.

The water absorption of concrete with admixture is lower by 26% compared to concrete without the superplasticizer.

Frost resistance expressed by the drop of compressive strength of samples after 200 cycles with respect to strength of control samples kept in water is 18.5% for the series of concrete without admixture; for concrete with superplasticizer it is much lower at 7.7%. It must be noted that in these samples there were no macroscopic signs of damage or loss of mass. At the same time, the bound water content (HI) in concrete samples without admixture clearly decreases (by 7.3%) with its increased content (by 9.7%) in the samples with the superplasticizer.

Other characteristics of the concretes change depending on the hardening conditions. In concrete without admixture the values of the tested strength and structural characteristics support the data. The greatest compressive strength, bound water content, and calcium hydroxide are found in concrete maturing 360 days in water. Lesser values are found in concrete matured in air-dry conditions for 360 days, and the smallest in concrete after 28 days. Freeze-thaw cycles lead to a drop of strength of 10.3% with respect to strength at 28 days, a significant increase in bound water content in hydration products (HI), and a slight increase in a hydrolysis products (HII). Concrete with superplasticizer shows the maximal compressive strength after 28 days of curing in standard conditions with a minimal for this series bound water content in cement hydration products (HI). After 360 days of air-dry hardening, strength drops by 20%, whereas bound water in hydration products (HI) increases by 26.5% with an unchanged calcium hydroxide content.

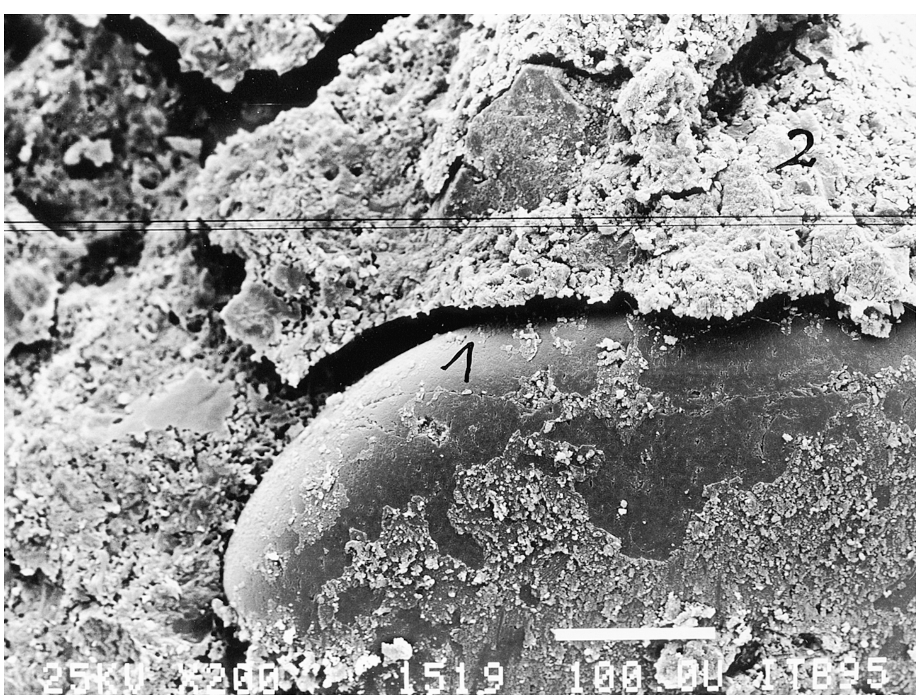

Fig. 1. SEM image of concrete without SMF superplasticizer at age 28 days (magnification 200×). 1, aggregate; 2, cement paste.

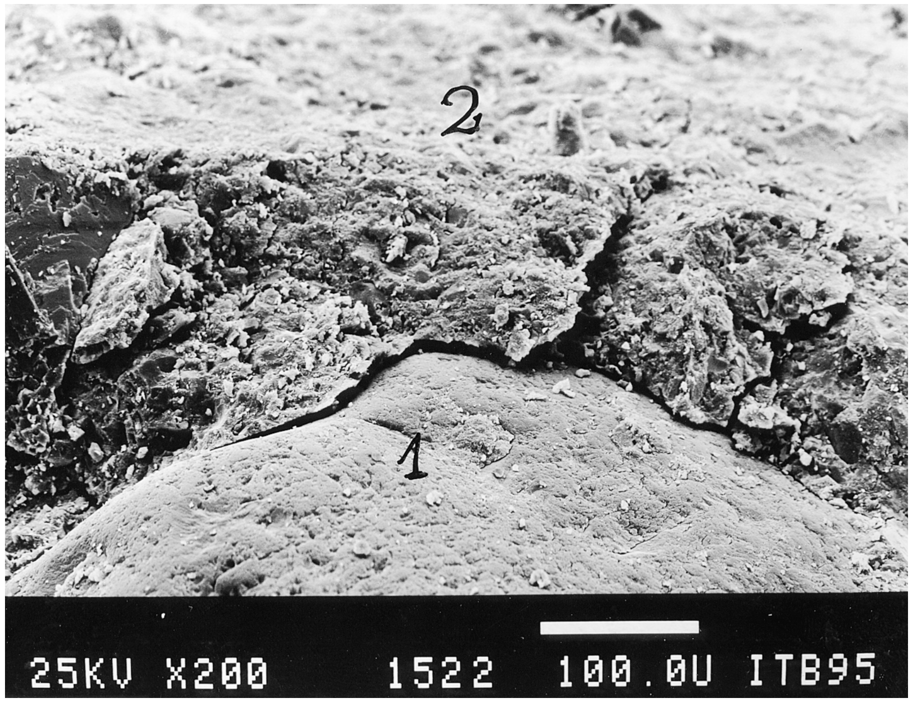

Fig. 2. SEM image of concrete with SMF superplasticizer at age 28 days (magnification 200×). 1, aggregate; 2, cement paste.

The same concrete after 360 days of curing in water is characterized by an even greater drop of strength at 25%, and an increase in the bound water content (HI) by 12% with a constant calcium hydroxide content. The greatest drop in strength of 29% in this concrete was found after 200 cycles of freezing and thawing. At the same time there is an increase in the content of bound water (HI) by 23% and unchanged calcium hydroxide content.

To compare the degree of cement hydration in both concrete series we used the bound water content in hydration

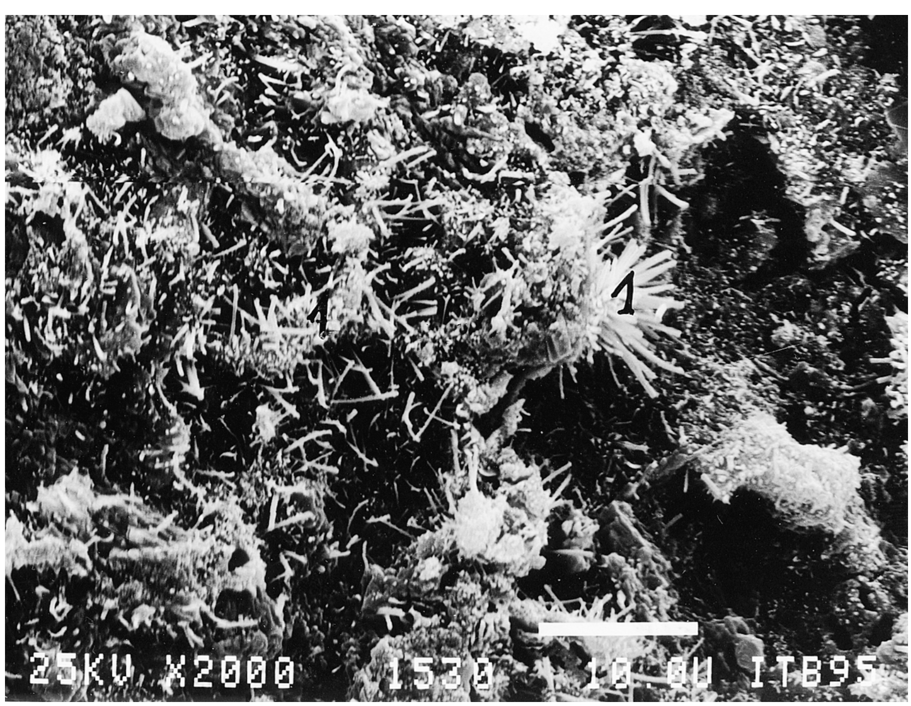

Fig. 3. SEM image of concrete with SMF superplasticizer at age 28 days (magnification 2000×). 1, ettringite.

Fig. 4. SEM image of concrete with SMF superplasticizer, 200 cycles of freezing and thawing (magnification 2000×). 1, ettringite; 2, hydrated calcium aluminates.

products (HI) and hydrolysis products (HII). According to Yilmaz and Glasser [11], the $Ca(OH)_2$ content after longer periods of hardening is a reliable indicator of the degree of cement hydration. The ratio of the bound water content in hydration products (HI), i.e., in hydrated aluminate sulfates, aluminates, and calcium silicates, to the bound water content in hydrolysis products (HII), that is, in calcium hydroxide, may indirectly characterize the changes taking place in both series of concrete. In the concrete without admixture, the ratio of bound water in hydration products to water found in hydrolysis products ranges from 5.3 to 7. Maximal strength in this series of concrete is found in samples with an HI-to-HII (HI/HII) ratio = 5.8. Samples with the least strength in this series have an HI/HII ratio = 6.8. In concrete with superplasticizer the HI/HII ratio ranges from 6.4 to 7.9. Maximal strength is found in samples with HI/HII = 6.4, minimal 7.7.

From the data presented we see that, in samples with superplasticizer after longer periods of hardening, changes take place in the bound water content in hydration products (HI) with small hydration of the remnants of unhydrated cement. This is shown by both the increase in the bound water content in hydration products HI and the constant $Ca(OH)_2$ content. In the series without admixture, on the basis of calcium hydroxide content the extent of hydration of cement is much greater.

Examination of the microstructure on fresh surfaces of fracture of 28-day-old concrete shows that the structure of concrete with superplasticizer is more compact than concrete without admixture. It should be stressed that in the concrete with superplasticizer there are numerous clusters of ettringite. After 360 days of maturing in air-dry conditions, the concrete continues to show a more compact structure than the concrete without the admixture. The hydrated silicates CSH-type have indistinct, as if washed out, contours. In the sample of concrete without superplastcizer, CSH has the structure of crumpled foil; only in some places does it have a fibrous structure. In both types of concrete there are small ettringite crystals. In the sample of concrete with superplasticizer, after 360 days in water there are signs of washing out of paste and small cracks. Numerous, unhydrated cement grains have surface etchings. CSH with indistinct contours, similar to those appearing after 360 days in air-dry conditions, are found.

The ettringite crystals are clearly shorter than those observed in concrete after 28 days. Worth noting is the abundant crystallization of ettringite, in single form and in clusters, apparent only in deep pores. After 200 cycles of freezing and thawing, in the concrete with admixture we find microcracks passing not only through the pores, but also between them. In these microcracks we find ettringite crystals and large table-like crystals, most probably hydrated calcium aluminates. Ettringite crystals also are found in the entire cement paste. In the sample without superplasticizer, the surface of the paste shows signs of carbonation. The microcracks pass mainly through air pores. There are many ettringite crystals in them, but in the paste mass there are much fewer of them than in the concrete with admixture. X-ray analysis of the paste separated from concrete with superplasticizer showed the presence of three diagnostic reflexes of ettringite in all the samples examined (d = 0.973, 0.561, and 0.388 nm). The most distinct is the d = 0.388 nm reflex. Its intensity is greatest in the concrete with superplasticizer, maturing in air-dry conditions, and it is smallest in concrete after 200 cycles of freezing and thawing. In the concrete without admixture there is only one diagnostic reflex for ettringite (d = 0.388 nm), whose intensity also is lowest in concrete after 200 cycles of freezing and thawing and slightly lower than in concrete with admixture. On the basis of SEM observations, we found that the microstructure of concrete with superplasticizer is more compact. By X-ray analysis the most ettringite is found in the sample of concrete with superplasticizer after 360 days of hardening in air-dry conditions.

Results of tests on the amount of ettringite, found to be the lowest in the concrete with SMF superplasticizer after 200 cycles of freezing and thawing, are contradictory to the view held by Stark and Ludwig [14], although they examined concrete without superplasticizers. Their investigations showed a significant increase in the quantity of ettringite during exposure to freeze-thaw cycles. Those large quantities of newly formed ettringite in cracks and coarse pore are attributed to the conversion of the monosulfate into ettringite during the frost treatment and the carbonation of the monosulfate leading to the formation of gypsum, which then can form ettringite. The main cause of the transformation is the change in thermodynamic stability conditions at lower temperatures [14].

Stark and Ludwig [15] pointed out that C_3A content is not a decisive factor affecting resistance to freeze-thaw, particularly of ordinary concrete, but the quantity of monosulfate before freeze-thaw treatment and its composition (derived from C_3A or C_4AF) have a greater influence. This was confirmed by Kurdowski and Małolepszy [16]. According to their investigations, C_3A content does not influence the frost resistance of cement-based systems.

3. Conclusions

1. The influence of superplasticizer is expressed by an increase in the compressive strength after 28 days, lowering of water absorption, and improvement in frost resistance compared to concrete without admixture.
2. The influence of superplasticizer after 360 days of hardening in air-dry conditions and in water is expressed by a significant lowering of the compressive strength compared to the same concrete after 28 days.
3. The greatest drop in strength with respect to 28-day concrete with superplasticizer is found after 200 cycles of freezing and thawing.
4. The decreases of strength of concrete with superplasticizer most probably are tied to the changes taking place in cement hydration products. This is shown by the significant increase in the amount of bound water in these products in concrete after 360 days of hardening and after 200 cycles of freezing and thawing, with an almost constant calcium hydroxide content.
5. In evaluating the effectiveness of the superplasticizer it is not enough to measure the strength after 28 days, but also after longer periods of hardening.

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