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COMPATIBILITY OF SUPERPLASTICIZER WITH INNOVATIVE AIR-ENTRAINING MULTICOMPONENT PORTLAND CEMENT CEM II/B-S

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ABSTRACT

This paper presents the results of a study on the stability of the air-entrainment of innovative air-entraining multi-component CEM II/B-S with different types of air-entraining admixture. Plasticizers and superplasticizers compatible with air-entraining cement CEM II/B-S were evaluated in terms of stability of air entrainment and ability to maintain consistency for one hour in mortar according PN-EN 480-1. In the next stage of the research the influence of the most compatible SPs on air-entrainment and the consistency of fresh concrete according to PN-EN 480-1 were investigated. The research results indicated that in case of a significant increase in the degree of liquidity of the air-entrained mortar or concrete with innovative, air-entraining multi-component cement CEM II/B-S, plasticizers or superplasticizers based on modified naphthalene, and then modified phosphoramidate should be used. The new generation superplasticizers based on polycarboxylate, polycarboxylic ether and acrylate cause a significant increase in the air-content of the air-entrained mortar and concrete.

Keywords

air-entraining cement, ground granulated blast furnace slag, air-entraining admixture, superplasticizer, concrete

INTRODUCTION

The results of a number of different studies carried on by the authors have shown that the use of new generation superplasticizer (SP) with the previously air-entrained concrete mixture causes a problem of maintaining the required air-entrainment. The research results (Mosquet 2003) [1], (Sakai et al. 2006) [2], (Szwabowski and Łaźniewska-Piekarczyk 2008) [3] show that the new generation of SPs have side effects manifested by an increase in air content in mixtures (Kqlaots et al. 2004) [4]. The air content in the hardened concrete, which is a side effect of SP, may be higher than 8%. Therefore the solution to the present problem is the verification of system compatibility of system: innovative aerated cement and superplasticizer (SP). Compatibility is assessed due to the volume of the air in the mixture and its consistency.

Condition of the system compatibility must be verified is not for any admixture for cement separately, but together, to determine the impact of their interactions with each other and cement. This can be accomplished only through experimentation, by selecting the type and quantity of the air-entraining admixture (AEA) for the type of cement, because of the required air-entrainment. Then the SP should be selected due to the maintenance of the air entrainment and to obtain the required stability and consistency, also over time.

The aim of the study is verification of the impact of the type of plasticizing and superplasticizing admixtures on the air content and consistency of cement based mortar acc. PN-EN 480-1 made with the air-entraining innovative CEM/II B-S incorporating natural or synthetic air-entraining admixture. The plasticizers and superplasticizers compatible with innovative air-entraining cement were evaluated in terms of stability of air entrainment and consistency of mortar for one hour. Then the influence of the most compatible SPs on air-entrainment and consistency of fresh concrete acc. PN-EN 480-1 was investigated.

EXPERIMENTAL PROCEDURE

Materials used to prepare mixtures of cement based mortars comprise CEM II/B-S, air-entraining innovative CEM II/B-S (450 g) with natural or synthetic AEA, normalized sand (1350 g), distilled water (225 g), and different types of plasticizing and superplasticizing admixtures. The content of ground granulated blast furnace slag in all cements was 30%. With these materials, standardized cement mortar with w/c = 0.50 was prepared, in accordance with PN-EN 480-1 [5] recommendations.

Table 1. The type and amounts of admixtures used in the research; % mass of CEM II/B-S

| Basic chemical base of SP | Symbol | % mass of cement |
|--|--------|------------------|
| polycarboxylate ether | PCE-1 | 0.870 |
| polycarboxylate ether | PCE-4 | 2.740 |
| modified polycarboxylates | PCP-1 | 1.250 |
| modified polycarboxylates | PCP-2 | 1.630 |
| modified naphthalenes | MN | 0.620 |
| cross-linked polymers, acrylic | CLAP | 1.640 |
| modified amino phosphonates | AAP | 3.110 |
| sulfonated naphthalene-formaldehyde resins | SNF-1 | 2.190 |
| sulfonated naphthalene-formaldehyde resins | SNF-1 | 1.900 |
| sulfonated melamine formaldehyde | SMF | 3.450 |
| modified lignosulfonates | MLG-1 | 4.080 |
| modified lignosulfonates/carbohydrates of natural origin | MLG-2 | 4.710 |

Table 1 summarizes the required amounts of admixtures necessary to obtain flowability of mortars at a comparable level. The properties of admixtures used are given in Tables 2 and 3. The most compatible plasticizers and superplasticizing admixtures (that are listed in Table 1) were evaluated in terms of stability of air entrainment and consistency of mortar for one hour.

The consistency of the mortars was determined according to PN-EN 1015-3 [6], while the air-content was determined according to PN-EN 1015-7 [7]. The consistency of fresh concrete was investigated according to PN-EN 12350-2 [8].

| Technical data | PCE-1 | PCE-4 | PCP-2 | PCP-1 | CLAP | AAP |
|------------------------------------|---------------|---------------|---------------|-------------|---------------|---------------|
| Form | Liquid | Liquid | Liquid | Liquid | Liquid | Liquid |
| Density (at 20°C), | 1.06 | 1.08 | 1.06 | 1.04 | 1.07 | 1.06 |
| kg/dm ³ | ± 0.02 | ± 0.02 | ± 0.02 | ± 0.02 | ±0.02 | ± 0.01 |
| pH (at 20°C): | 6.0 ± 1.0 | 4.5 ± 1.0 | 7.5 ± 1.0 | 6.5 ± 1 | 6.0 ± 1.0 | 4.0 ± 0.5 |
| Chloride content Cl ⁻ , | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| % of mass | ≥ 0.1 | ≥ 0.1 | ≥ 0.1 | ≥ 0.1 | ≥ 0.1 | ≥ 0.1 |
| Alkali Content | < 0.6 | < 0.8 | < 1.5 | < 1.0 | < 3.0 | < 3.0 |
| Na ₂ O, % of mass | ≥ 0.0 | ≥ 0.8 | ≥ 1.5 | ≥ 1.0 | ≥ 3.0 | ≥ 3.0 |
| Type of admixture | F and E | G | G | G | F and E | G |
| acc. ASTM C494 | 1 and L | IG L | J |) | 1 and L | 0 |
| Type of admixture | SP | SP | SP | SP | SP | SP |
| acc. PN-EN 934-2 | 51 | 51 | 51 | 51 | 51 | 51 |
| Conventional dry | 37.0 | 36.0 | 36.0 | 37.0 | 35.0 | 31.0 |
| material content, % | ± 1.5 | ± 1.7 | ± 1.6 | ± 1.5 | ± 1.7 | ± 1.5 |

Table 2. Properties of the PCE, PCP, CLAP and AAP based admixtures

Table 3. Properties of the MN, SNF, SMF and MGL based admixtures

| Technical data | MN | SNF-1 | SNF-2 | SMF | MLG-1 | MLG-2 |
|--|--------|-----------------|---------------|----------------|--|-----------------|
| Form | Powder | Liquid | Liquid | Liquid | Liquid | Liquid |
| Density (at 20°C), kg/dm ³ | 0.60 | 1.17 ± 0.03 | 1.19 | 1.13 ± 0.03 | 1.13 ± 0.03 | 1.17 ± 0.02 |
| pH (at 20°C): | 5.0 | 6.5 | 6.0 | 7.0 | 10.0 ±1.0 | 4.5 ± 1.0 |
| Chloride content Cl ⁻ % of mass | ≤ 0.1 | ≤ 0.1 | ≤ 0.1 | ≤ 0.1 | ≤ 0.1 | ≤ 0.1 |
| Alkali Content Na ₂ O, % of mass | ≤ 3.0 | ≤ 4.5 | ≤ 4.5 | ≤ 5.0 | ≤ 6.5 | ≤ 0.8 |
| Type of admixture acc. ASTM C494 | F | D and F | A and F | A and F | A | A |
| Type of admixture acc. PN-EN 934-2 | SP | P and SP | P and SP | P and SP | P | P |
| Conventional dry material content, % | 100.0 | 34.5 ±1.7 | 30.0 ± 1.5 | 28.0 ± 1.6 | $\begin{array}{c} 27.0 \\ \pm 1.4 \end{array}$ | 36.0 ± 1.8 |

The influence of superplasticizers on the air-entrainment and consistency of fresh concrete acc. PN-EN 480-1 with air-entraining cement CEM II B-S with synthetic AEA and w/c=0.50 was tested. In this stage of the research the two most compatible superplasticizers, and for comparison one incompatible SP. were used (Table 1). The influence of w/c ratio (0.45 and 0.55) on the air-entrainment of fresh concrete with air-entraining CEM II/B-S was investigated too. The variation in w/c values corresponds to the indication of PN-EN 206-1 [9], as the minimum recommended values for the XF1-XF4 class of aggressiveness of the environment. The air-content of fresh concrete was investigated according to PN-EN 12350-7 [10].

| Components | w/c=0.45 | w/c=0.50 | w/c=0.55 |
|---------------------------|----------|----------|----------|
| Water | 167.64 | 175.00 | 181.45 |
| Air-entraining CEM II/B-S | 372.36 | 350.00 | 329.82 |
| Sand 0-2 mm | 522.55 | 522.00 | 522.55 |
| Crushed gravel 2-8 mm | 521.00 | 511.90 | 512.00 |
| Crushed gravel 8-16 mm | 853.09 | 853.10 | 853.00 |

Table 4. The mix proportions, kg/m³

TEST RESULTS AND DISCUSSION

Figs 1 and 2 show the results of the measurements of air-content and consistency of mortars. These results show that some of the new generation superplasticizers significantly increase the volume of air and consistency of previously air-entrained cement based mortar, regardless of the type of AEA. The latest generation of admixtures significantly increase the air content. The superplasticizers based on polycarboxylate, polycarboxylic ether and acrylate cause a significant increase in the air-content of the air-entrained mortars, in certain cases of cement mortars up to two times. Replacing cement with SCMs is a way of improving the fineness of cementitious materials, which better stabilizes air bubbles (Yang 2012) [11]. The SCM particles usually have higher surface areas than Portland cement grains.

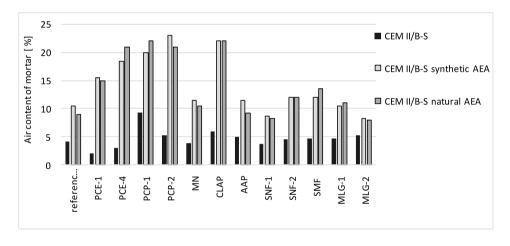


Fig. 1. The comparison of the air-content of the air-entrained mortar with w/c=0.50 and with different types of plasticizers and superplasticizers.

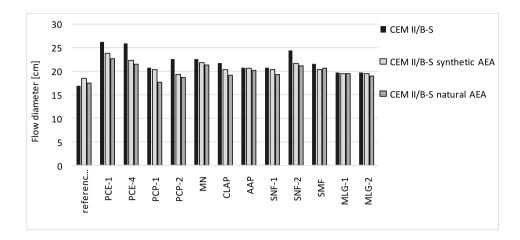


Fig. 2. The comparison of flow diameter of the air-entrained mortar with w/c=0.50 and with different types of plasticizers and superplasticizers.

Analysis of the results in Figs 1 and 2 indicate that the superplasticizers based on modified naphthalene, and then modified phosphoramidate should be used in the case of mixture made with the innovative, air-entraining multi-component cement CEM II/B-S. The action of admixtures mentioned in the second order involves only the steric dispersion - and so the natural, blockade of polymer without using deflocculating electrostatic phenomena. This results in compatibility with cements that have extremely different properties and compositions, including air-entraining cements.

The analysis of the results shown in Figs 3 and 4 indicates, that the admixture based on naphthalene, melamine and lignosulphonates may be recommended for air-entraining cement. The results of measurements of stability of air-entrainment and maintenance of the mortar consistency in relation to the different types of plasticizers or superplasticizers are presented in Fig.3. Research results show that all types of investigated admixtures, selected on the basis of an earlier stage of research, provide stability of the air bubbles in mortars with air-entraining CEM II/B-S.

Admixtures based on modified naphthalene (MN) and lignosulfonates (MGL) stabilize the air-entrainment the best (Fig. 3). Admixtures based on aminophosphonates (AAP) and naphthalene (SNF) reduce the flow of mortar over the time the least. Moreover, in the case of air-entrained mortars with traditional naphthalene (SNF) there is an increase in workability over time. The results (Saucier et al. 1990) [13] show that melamine and naphthalene-based superplasticizers can form crucial discrepancies in the air content versus the spacing factor relationship.

The comparison of the results from Fig. 4 demonstrates that SPs based on modified naphthalenes (MN) provide good workability of the mortar, no worse than SPs on the basis of polycarboxylate, polycarboxylate ether, acrylate, or phosphoramidate.

Some serious advances have been made in process, production, and application of lignosulphonate based admixtures. There is a broad range of lignosulphonates available and their performance in concrete differs from basic water reduction and strong retardation to a high range of water reduction (Reknes 2004) [14], (Jun 2008) [15]. With the progress of a new modified lignosulphonate superplasticizer, it is possible to produce self-compacting concrete with such an admixture (Reknes 2004) [14], (Jun 2008) [15]. With modified lignosulphonate superplasticizers entering the market, its primary performance, including workability,

retardation and strength, have been researched. However, there is not enough information available in the literature on the effect of these freshly developed modified lignosulphonate superplasticizers on cement hydration, workability retention and pore structure, in comparison to other types of superplasticizers such as naphthalene and polycarboxylate based admixtures and to those of traditional lignosulphonate water reducing admixtures.

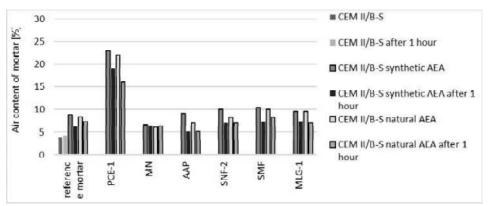


Fig. 3. The comparison of the air-content of the air-entrained mortar with w/c=0.50 and with different types of plasticizers and superplasticizers after 5 and 60 min.

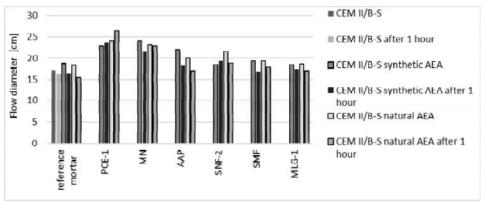
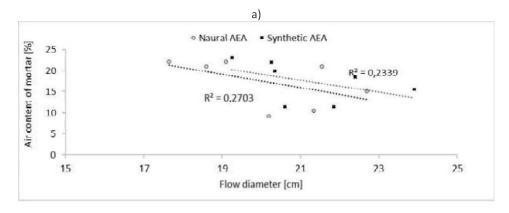


Fig. 4. The comparison of flow diameter of the air-entrained mortar with w/c=0.50 and with different types of plasticizers and superplasticizers after 5 and 60 min.

Research results summarized in Fig. 5 show the relationship between the consistency and air content of the air-entrained and then superplasticized or plasticized mortar. The research results suggest that the relationship between air-content and consistency of superplasticized mortar is not strong, because it depends on the type of superplasticizers. In the case of plasticizers this relationship is somewhat stronger.



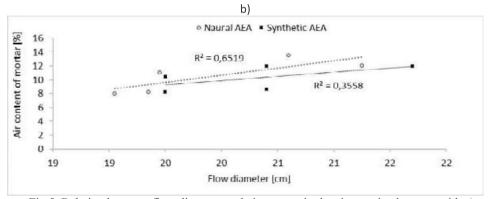
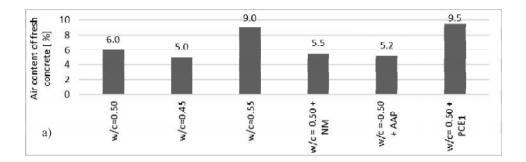


Fig 5. Relation between flow diameter and air content in the air-entrained mortar with a) superplasticizers and b) plasticizers (acc. Tables 2 and 3).

Fig 6 presents the influence of w/c ratio and superplasticizer type on the air-content and consistency of fresh concrete. Generally, the more water in a volume of concrete, the more air bubbles are formed. The foaming property of surfactants can be affected by the impurities present in the host solution. Inorganic electrolytes are most effective with ionic surfactants and polar organic additives can affect all types of surfactant (Du and Folliard 2005) [17].

The research results presented in Fig. 6 indicate that in case of the necessity to improve the workability of concrete, NM or AAP-based superplasticizers should be used. PCE-based superplasticizer creates too much air-entrainment of concrete (Fig. 6a). Nevertheless, it is impossible to speculate the effects of admixtures interactions with surfactants on the air entrainment. The compatibility of the admixtures should be experimentally tested, if the effects of such combinations are unknown in advance. Most organic chemical admixtures, such as superplasticizer can enhance the air entrainment since it can slightly reduce the absorbed AEA molecules on the solid surface by competing with them (Baekmark et al., 1994) [16].

Moreover, some superplasticizers may have the air-entraining potential themselves. However, the addition of straight calcium chloride may tend to limit the number of entrained air due to the precipitation of surfactants in the solution by creation of insoluble salts (Mosquet 2003) [1], (Rudnicki 2004) [18], (Lianxiang and Folliard 2005) [17].



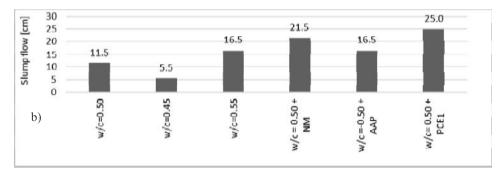


Fig 6. The influence of w/c ratio and type of superplasticizer on a) air-content and b) consistency of the fresh concrete with air-entraining CEM II/B-S.

Yet, today there are many types of AEAs, like wood-derived acid salts AEA, vegetable oil acids AEA and synthetic detergents AEA, which may react with chemical admixtures. This creates some difficulty for the study of the impact of chemical admixtures on the air entrainment (Kobayashi et al. 1981) [19]. The compatibility of admixtures should be experimentally tested if the effects of such combinations are unknown in advance. Compatibility of plasticizers or superplasticizers should be checked in relation to the reference mortar or concrete with air-entraining CEM II/B-S.

CONCLUSIONS

Within the scope of the research it was found that:

- The compatibility of admixtures SP and the AEA and cement can be checked only when
 they occur together during preparation of mortar or concrete. Checking each individual
 admixture does not take into account their interaction. The effects of plasticizer or
 superplasticizer action should be compared to reference mortar with air-entraining CEM
 II/B-S.
- Tested superplasticizers based on polycarboxylate, polycarboxylic ether and acrylate cause a significant increase in the air-content of the air-entrained mortars and concrete. In the case of innovative, air-entraining multi-component cement CEM II/B-S, superplasticizers based on modified naphthalene, and then modified phosphoramidate may be used, because they allow keep the proper air entrainment of mortar or concrete. Moreover, these superplasticizers provide good workability of the mortar, no worse than

- SPs on the basis of a polycarboxylate, polycarboxylate ether, acrylate, or a phosphoramidate.
- In terms of the research and tested admixtures it has been shown that the admixtures based on modified naphthalene and lignosulfonate are the most effective in stabilizing the air-content of air-entrained mortars. Nevertheless, admixtures based on aminophosphonates and naphthalene reduce the flow of mortar, the least over time. Moreover, in case of the air-entrained mortar with naphthalene there is an increase in workability over time.

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