Plasticizer and Superplasticizer Compatibility with Cement with Synthetic and Natural Air-Entraining Admixtures

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Abstract. When increasing the degree of fluidity of previously aerated cementitious mixtures, there is a problem of maintaining their correct aeration. Most of the available superplasticizers cause a significant increase of the air content of concrete mixtures. The problem of compatibility of superplasticizer and air-entraining admixture increases in case of multicomponent Portland cement, due to different effects of these additives. It comes down to achieving a compatibility of the three variables mentioned in the title of the paper, due to the required air entrainment and consistency of mixture. Achieving compatibility of such a system requires a series of experimental studies that were presented in the paper together with their resulting indications. In case of previously air-entrained concrete that is made with an air-entraining cement, after the addition of new generation SP occurs very large increase in air entrainment. The air-content of mixture according to EN 480-1 may be higher than 13%.

1. Introduction

In order to maintain better durability performance and extended service life in freezing and thawing environments, concrete must consists of a proper air-void system. For this, a suitable amount of entrained air-voids with accurate specific surface and spacing factor should be maintained in concrete. Commonly, limits on volume of air-voids or air content are specified although the role of spacing factor is important. This is since the air content can be determined more effortlessly and immediately than spacing factor [1]. It may happen that the variation in cement’s type, while keeping all other technological and material parameters, may decrease concrete’s frost resistance [2], [3], [4]. This issue is clearly formulated by the opinion of Committee 225 (Guide to the Selection and Use of Hydraulic Cements) and Committee 201 (Guide to Durable Concrete) of American Concrete Institute (ACI). It is stated that: “variations of Portland cements and composite cements, allow to obtain the same level of concrete’s frost resistance, providing the correct proportions of components and correct mixture’s air-entrainment. Crucial, from the point of final air-entrainment effect view apart from the graining, is the type and amount of mineral additives included in cements (blast furnace cement CEM III, pozzolanic cement CEM IV and composite cement CEM V). Mineral additives activate beneficial changes in the structure of paste’s porosity (concrete) resulting in decrease of capillary pores and increase of gel pores. The test results of concrete on cements with mineral additives show that despite enhanced sealing and higher resistance, there are problems with frost resistance of non-air-entrained concretes, even under conditions of moderate frost effect.

One solution to the problem is the creation of possibilities of the use of cement with mineral additives containing in the composition of which air-entraining admixture (AEA): air-entraining multicomponent
Portland cement. The goal of the project supervised by the authors is to establish the innovative technology of the aerating cements production for designing and production of freeze and thaw resistant concrete. Aerating cements technology concludes dosing aerating additives in the grinding or blending process of cement production. Project focuses principally on cements containing large numbers of non-clinker constituents, i.e. Portland-composite cements CEM II (CEM II/B-V, CEM II/B-S), blast furnace cement CEM III (CEM III/A, CEM III/A NA) and composite cements CEM V (CEM V/A, CEM V/B). This choice of aerating cements for implementation by cement industry fits the sustainable development philosophy. However, the results of studies conducted by the authors have shown that the use of new generation superplasticizer with the previously air-entrained concrete mixture causes a problem of maintaining the proper air entrainment. The research results [5], [6], [7] show that the new generation of SPs have side effects manifested by increasing the air content in the mixture (Table 1). The air content in the hardened concrete, which is a side effect of SP, may be higher than 8% [7]. The solution to the present problem is the condition of compatibility of system: innovative air-entraining cement and superplasticizer (SP), due to the presence of the air in the mixture and its consistency.

| Type of SP | Lignosulfonate LS | Naphthalene SNF | Melamine SMF | A new generation of superplasticizers | Aminophosphonates polyoxyethylene AAP |
|------------|-------------------|-----------------|-------------|-----------------------------------|-----------------------------------|
| Air content | ++ | + | 0 | ++ | + |

The present study is an experimental analysis of the impact of the type of plasticizing and superplasticizing admixtures on the air content and consistency of cement based mixtures made with the participation of the air-entraining innovative CEM II/B-V. Unfortunately, fly ash, which contains carbon, can attract and absorb the surfactants in AEAs [8]. Cement based mixture model was adopted as the reference cement mortar model according to EN 480-1. Four types of air-entraining innovative cement were used, diversified manufacturing technology (jointly mixed and ground together), with the participation of two different types of air-entraining admixture: natural and synthetic. The consistency of mortars was changed with different types of plasticizing and superplasticizing admixtures.

2. Experimental

Materials used to prepare mixtures of cement based mortars, which are the subject of the study were: air-entraining innovative CEM II/B-V (Table 2), normalized sand, distilled water and different types of plasticizing and superplasticizing admixtures (Table 3). The content of siliceous fly ash cements V in all cements is 30%. With these materials, standardized cement mortar with w/c = 0.50 was prepared, in accordance with the guidelines of EN 480-1. Reference mortar are also made, i.e. air-entraining and superplasticizing without admixtures.

| Type of cement; method of preparation the cement | Air-entraining admixture | Participation of admixtures, % mass of cement. |
|-----------------------------------------------|---------------------------|-----------------------------------------------|
| CEM II/B-V; cement mixed together             | -                         | -                                             |
| CEM II/B-V; common ground cement              | -                         | -                                             |
| CEM II/B-V; cement mixed together             | synthetic                 | 1.70                                          |
| CEM II/B-V; common mixed cement               | natural                   | 0.12                                          |
| CEM II/B-V; cement ground together            | synthetic                 | 1.70                                          |
| CEM II/B-V; common ground cement              | natural                   | 0.12                                          |
### Table 3. Characteristic of plasticizing and super plasticizing admixtures

| Basic chemical base of SP | Symbol   |
|--------------------------|----------|
| polycarboxylate ether    | PCE1     |
| polycarboxylate ether    | PCE2     |
| polycarboxylate ether    | PCE3     |
| polycarboxylate ether    | PCE4     |
| modified polycarboxylates| PCP2     |
| modified polycarboxylates| PCP1     |
| modified naphthalenes    | N1       |
| substances from the group of polycarboxylates | U1 |
| cross-linked polymers, acrylic | A1 |
| modified amino phosphonates | F1 |
| sulfonated naphthalene-formaldehyde resins | Np1 |
| sulfonated naphthalene-formaldehyde resins | Np2 |
| sulfonated melamine-formaldehyde resins | Mp1 |
| modified lignosulfonates | Lp1      |
| modified lignosulfonates / carbohydrates of natural origin | Lp2 |

### Table 4. The amounts of admixtures used in research; % mass of CEM II/B-V

| Method of preparation the cement | Symbol of cement | Cement mixed together | Common ground cement | Cement mixed together | Common ground cement | Cement mixed together | Common ground cement |
|---------------------------------|------------------|------------------------|----------------------|-----------------------|----------------------|-----------------------|----------------------|
| CEM II/B-V m                    | AEA              | -                      | -                    | synthetic             | synthetic             | natural               | Natural              |
|                                 | PCE1             | 0.44                   | 0.44                 | 0.86                  | 0.81                 | 0.87                  | 1.20                 |
|                                 | PCE2             | 0.45                   | 0.53                 | 2.00                  | 2.00                 | 2.00                  | 2.06                 |
|                                 | PCE3             | 0.46                   | 0.56                 | 1.61                  | 1.47                 | 1.62                  | 1.33                 |
|                                 | PCE4             | 0.44                   | 0.44                 | 3.00                  | 2.66                 | 2.74                  | 2.56                 |
|                                 | PCP2             | 0.46                   | 0.45                 | 1.25                  | 1.45                 | 1.25                  | 0.97                 |
|                                 | PCP1             | 0.44                   | 0.46                 | 1.70                  | 1.65                 | 1.63                  | 1.62                 |
|                                 | N1               | 0.32                   | 0.44                 | 0.62                  | 0.62                 | 0.62                  | 0.44                 |
|                                 | U1               | 0.44                   | 0.44                 | 1.08                  | 0.90                 | 1.00                  | 0.90                 |
|                                 | A1               | 0.46                   | 0.46                 | 1.63                  | 1.02                 | 1.64                  | 1.04                 |
|                                 | F1               | 0.46                   | 0.45                 | 3.08                  | 3.10                 | 3.11                  | 3.05                 |
|                                 | Np1              | 0.96                   | 1.72                 | 2.15                  | 2.19                 | 2.19                  | 2.44                 |
|                                 | Np2              | 0.92                   | 1.80                 | 1.87                  | 2.26                 | 1.90                  | 2.34                 |
|                                 | Mp1              | 1.62                   | 1.69                 | 3.15                  | 3.26                 | 3.45                  | 3.44                 |
|                                 | Lp1              | 1.60                   | 1.72                 | 4.44                  | 4.24                 | 4.08                  | 4.27                 |
|                                 | Lp2              | 1.63                   | 1.64                 | 4.51                  | 4.27                 | 4.71                  | 4.22                 |
In the first step of the test, the goal was to analyse four available AEAs for their air entraining compatibility, the air void system and the air stability. EN 206 for XF classes has specified ranges of air content between 4% and 7%. Commonly, around 4.5% to 6.5% air content is required in concrete for freeze-thaw resistance in Poland. Nonetheless, in mortar, only fine aggregates are used, because of the absence of coarse aggregates the air content in mortar is roughly twice of that in concrete at the same condition. Thus, in the mortar test, air content of about 10-11% was aimed at as the normal condition. After trial and error tests, it was concluded that at a dosage around 0.12% and 1.70 by weight of cement both AEAs could entrain a total air content of around 10-11% (Table 2).

The aim of the second stage of the study was the choice of the type and the quantity of plasticizers and superplasticizers to have air content of mortar approximately similar to that of the reference mortar, i.e. without plasticizing and superplasticizing admixtures. The liquid plasticizing and superplasticizing admixture dosed with the mixing water, in accordance with recommendation of EN 480-1. While plasticizing and superplasticizing admixtures in powder form were dispensed with cement, according to the manufacturer's recommendations. Table 4 summarizes the required amounts of admixtures necessary to liquidate the mortar a comparable degree. In most cases, the greatest degree of fluidity of mortars was obtained which is important, maintaining the stability of the mortar. The consistency of the mortars was determined per EN 1015-3, while the air-content according to EN 1015-7. Ambient temperature during testing mortar was 20°C±1°C. The relative air humidity was about 50%.

3. Results and discussion

Tables 5 -7 show the results of measurements of the air content and flow diameter of mortars. These results show that some of the new generations of superplasticizers significantly increase the volume of air in the previously air-entrained cement based mortar. This is probably perhaps the particles of slag are finer than cement. Replacing cement with SCMs is kind of improving the fineness of the cementitious materials which stabilizes the air bubbles better. The SCM particles usually have higher surface areas than Portland cement grains.

| Type of cement | Air content in mortar, % |
|----------------|--------------------------|
| CEM II/B-V m   | 3.0                      |
| CEM II/B-V w   | 3.0                      |
| CEM II/B-V A m | 10.0                     |
| CEM II/B-V A w | 9.2                      |
| CEM II/B-V D m | 12.0                     |
| CEM II/B-V D w | 9.8                      |

Especially the latest generation admixtures significantly increase air content. It happens that the air content increases three times compared to previously aerated mortar (Figure 2). Surface-active agents can be classified per the type of polar (hydrophobic) group in their molecules: anionic agents, cationic agents, amphoteric agents [9]. There are three groups of AEAs: wood-derived products, vegetables acids, and synthetic detergents. Air entraining agents (AEAs), which can be based on natural resins (for example vinsol) or synthetic surfactants, were added to the concrete mix to enhance the controlled quantity of air in the form of microscopic bubble in cement paste. From the first usage of air-entertainers until now, many various types of air-entertainers have been established. However, disregarding of what kind of air-entertainers, they all have similar properties or functions, that is, all of them are influential surfactants. Research results presented in publication [8] show that the natural admixture aeration is more powerful than synthetic one because the natural admixture participation is much smaller than the synthetic in cement.
Table 6. The diameter flow of mortar with air-entraining cement and plasticizing or superplasticizing admixture

| Type of admixture | CEM II/B-V m | CEM II/B-V w | CEM II/B-V A m | CEM II/B-V A w | CEM II/B-V D m | CEM II/B-V D w |
|-------------------|--------------|--------------|----------------|----------------|----------------|----------------|
| -                 | 11.00        | 11.00        | 15.00          | 15.00          | 15.00          | 15.00          |
| PCE1              | 24.25        | 24.20        | 23.50          | 23.10          | 23.60          | 23.78          |
| PCE2              | 22.50        | 22.95        | 25.50          | 26.00          | 26.00          | 26.70          |
| PCE3              | 26.60        | 25.10        | 23.90          | 24.90          | 26.00          | 26.15          |
| PCE4              | 20.50        | 20.40        | 24.10          | 24.40          | 23.65          | 24.50          |
| PCP2              | 22.50        | 23.00        | 26.00          | 25.15          | 25.00          | 24.60          |
| PCP1              | 20.90        | 19.50        | 27.45          | 27.75          | 27.10          | 26.40          |
| N1                | 20.20        | 21.50        | 22.20          | 22.80          | 23.70          | 24.45          |
| U1                | 20.75        | 19.75        | 22.45          | 22.67          | 24.05          | 25.00          |
| A1                | 20.56        | 19.15        | 25.80          | 25.45          | 25.50          | 26.35          |
| F1                | 19.75        | 19.95        | 26.20          | 26.45          | 25.60          | 24.35          |
| Np1               | 20.50        | 19.85        | 25.70          | 24.45          | 24.45          | 25.30          |
| Np2               | 21.50        | 22.65        | 24.90          | 24.50          | 25.35          | 26.70          |
| Mp1               | 21.30        | 21.45        | 20.50          | 21.25          | 22.70          | 21.60          |
| Lp1               | 21.45        | 20.40        | 20.20          | 20.15          | 20.50          | 21.60          |
| Lp2               | 20.70        | 21.20        | 21.40          | 21.20          | 21.80          | 21.50          |

Table 7. The air content in mortar with air-entraining cement and plasticizing or superplasticizing admixture

| Type of admixture | CEM II/B-V m | CEM II/B-V w | CEM II/B-V A m | CEM II/B-V A w | CEM II/B-V D m | CEM II/B-V D w |
|-------------------|--------------|--------------|----------------|----------------|----------------|----------------|
| -                 | 3.0          | 3.0          | 10.00          | 9.20           | 10.30          | 9.8            |
| PCE1              | 2.4          | 2.3          | 18.70          | 19.50          | 18.90          | 18.6           |
| PCE2              | 4.5          | 4.2          | 22.00          | 22.50          | 20.00          | 21.8           |
| PCE3              | 4.9          | 5.4          | 21.70          | 22.00          | 20.60          | 20.0           |
| PCE4              | 4.3          | 5.8          | 20.60          | 19.80          | 19.50          | 20.0           |
| PCP2              | 5.8          | 5.4          | 21.00          | 21.00          | 20.50          | 21.2           |
| PCP1              | 5.8          | 5.1          | 18.50          | 18.00          | 18.60          | 18.5           |
| N1                | 3.4          | 3.7          | 10.00          | 11.50          | 10.50          | 11.0           |
| U1                | 4.3          | 4.4          | 20.50          | 19.00          | 19.50          | 20.0           |
| A1                | 4.5          | 5.1          | 20.50          | 20.00          | 19.80          | 19.5           |
| F1                | 5.8          | 5.2          | 8.00           | 10.00          | 8.50           | 8.0            |
| Np1               | 4.0          | 3.9          | 11.00          | 10.00          | 11.00          | 11.5           |
| Np2               | 3.5          | 3.9          | 10.50          | 10.00          | 9.70           | 10.2           |
| Mp1               | 3.2          | 3.9          | 11.50          | 10.50          | 9.50           | 10.2           |
| Lp1               | 3.4          | 3.8          | 9.00           | 9.50           | 9.00           | 9.4            |
| Lp2               | 4.5          | 4.0          | 9.20           | 8.00           | 8.50           | 10.0           |

Commercially available air-entraining agents are generally manufactured from chemically complex raw materials, and the final products may consist of blends of these raw materials plus other raw
materials or chemicals, hence, it is challenging to define air-entraining agents chemically except by rather broad classification. Wood-derived products and synthetic detergent, two types of most frequently used air-entraining agents are described here. The aim of using AEAs is to get more balanced and uniform air bubbles with small sizes homogeneously distributed in the cement paste. Synthetic detergents allow for quick production of air bubbles in concrete, these bubbles tend to be coarser than those produced using wood-derived materials. While their primary application has been for foaming agents, some are also used as air-entraining agents.

The results of tests [11] indicated that the different types of high-range water-reducing admixtures influence surface tension, foaming, and stability of air bubbles in a different way. Some types of superplasticizers effect on the surface tension of the liquid phase of the cement paste. The presence of functional groups (oxygen in form of etheric group (-O-), hydroxyl group (-OH) and carboxyl group) produce water surface tension decrease, producing flocculation of associated molecules and increase in moisture of not only grains of cement but also the whole mineral framework [13]. The research [12] results show that the surface tension changed considerably with time depending on the combination of powder and superplasticizer. The change seems to be caused by the sorption, which includes chemical adsorption, physical adsorption and absorption. Among three kinds of sorption, the absorption of superplasticizer by powder obstructs the function of superplasticizer. The tendency was indicated that the absorption could occur in paste according to fluidity test of paste. Many inorganic electrolytes and polar organic materials effect the foaming ability of surfactants. The impact of other chemical admixtures for air entrainment is complex. Generally, most organic chemical admixture can enhance the air entrainment. The test results showed in Figure 1 show that the superplasticizer can reduce the surface tension of water in a similar way as admixture (AEA).

![Surface Tension Comparison](image)

**Figure 1.** Influence of polycarboxylate based superplasticizer (PCP) and air-entraining admixture (AEA) on surface tension of water [7]

Analysis of the results of mortars was made of participation of the innovative, air-entraining multi-component cement (Table 6) indicated that second generation superplasticizers based on modified naphthalene, and then modified phosphoramidate should be used. Comparison of the results from Table 6 demonstrates that the third-generation SPs based on modified naphthalenes provide a good workability of the mortar, no worse than SPs based on a polycarboxylate, polycarboxylate ether, acrylate, or a phosphoramidate. 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 analysed results show that 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, cement mortars contains caused less dosage of SP up to three times. As presented by the research [14], the addition of high range water reducers to air entrained concrete enhances the spacing factor and reduces the specific surface area of the air void system. Yet, present study’s results suggest that the effects of synthetic agents on the air void system
are independent of the effects of high range water reducers. Tests [15] have shown that the pore structure evidently depends on the superplasticizer added to the concrete mix. When superplasticizer, based on a combination of polycarboxylates and viscosity, bonding and hardening regulators, is added to concrete mix, the structure of the achieved concrete is characterized by more beneficial parameters than those characterizing the structure of the concrete made from the concrete mix to which superplasticizer based on polycarboxylic ether was added.

The analysis results shown in Table 5 indicates that, as recommended admixture of the second generation in the case of air-entraining cement admixture based on the naphthalene and melamine can be identified. The results [16] show that melamine and naphthalene-based superplasticizers can form crucial discrepancies in the air content versus the spacing factor relationship. It is concluded that concrete producers must be very careful when using superplasticizers in air-entrained concrete because serious air-void system destabilization can occur without any significant air content variation. In-plant testing is highly recommended to verify the impact of a combination of cement-air-entraining agent-SP, and a general procedure to do was proposed.

4. Conclusions
Within the scope of the research and examined admixtures, it was found that in order to increase the degree of fluidity of previously aerated concrete, made with the participation of innovative air-entraining CEM II/B-V, should be:

- For each air-entraining cement the choice of amount and type of plasticizer or superplasticizer, due to the required aeration and consistency of mixture, can be successfully carried out only on the basis of experimental comparison. The condition of compatibility of entraining and superplasticizing admixtures with cement should be verified, taking into account their mutual influence of both the consistency and the content of the air in the mixture. It is important to verify their interactions and possible consequences for air-entrainment and mortar consistency, as well as concrete.

- The recommended admixtures in the case of the air-entraining CEM II B-V are traditional plasticizers based on the naphthalene and melamine. In case of a significant increase in the degree of liquidity of concrete mixture, first new generation 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 mortars. In certain cases of cement mortars and less dosage of SP, almost three times.

- The third-generation SPs based on modified naphthalenes provide a good workability of the mortar, no worse than SPs based on a polycarboxylate, polycarboxylate ether, acrylate, or a phosphoramidate.

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