Compatibility analysis of superplastisizers with different types of cements

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Abstract. The article considers the urgent issue of improving the quality and durability of road cement concrete. It is shown that the decrease of the quality of concrete mixtures and concrete is often due to incompatibility between cement and superplasticizer. This can happen if the same superplasticizer is used, but different cements of the same plant. This also happens if superplasticizers of the same type, but of different manufacturers, with the same cement are used. Therefore, it is important to quickly assess the compatibility of cement and superplasticizer at the stage of concrete mix design. The article proposes to evaluate the compatibility by changing the properties of cement paste without superplasticizer and with it. It is shown that compatibility can be established within a few hours. Based on the experiments, it was established which superplasticizers should be used for cements of a certain mineral composition.

1. Introduction
Many scientists have studied the problem of ensuring the durability of heavy concrete. Among the various ways to increase durability, several main ones can be distinguished.

1. Improving the interfacial zone "hardened cement paste - aggregate". To do this, use clean aggregates, without dust, and also process aggregates with water or aqueous solutions of salts [1 – 3].

2. Increasing the density of cement mortars and concrete. For this, four or more fractions of high strength aggregates are used, as well as microfillers and nanoparticles [4 – 8].

3. Increasing the strength of mortars and concrete. Superplasticizers and cements with high activity are used [4, 9 – 12].

4. Creating a backup pore system using air-entraining additives [13 – 15].

There are other ways to increase the durability of concrete, however, in all cases, the main components of concrete, which are all impacts, and which ensure the durability of concrete, are cement and superplasticizer. In construction, especially road construction, the methods described above are not often used, because their application does not always lead to a positive result. Studies over the past two to three decades have shown that the reason of this is the poor compatibility of cements and superplasticizers. With the right choice of cement and superplasticizer, the durability of concrete will be ensured. This choice must be made at the stage of concrete mix design. Therefore, the urgent task of this study is to develop a simple method for assessing the compatibility of cements and superplasticizers. The main objective of this study is a quick assessment of the compatibility of the additive and cement.
2. Status of the issue
In the construction of paved concrete, the replacement of cement or superplasticizer in concrete mixture often leads to serious problems. This is because the construction of roads takes place in different temperature and humidity conditions. For example, in spring and autumn, relative humidity is quite high, and the air temperature is in the range +5...+25 °C. In this case, the use of finely ground cements with superplasticizers based on polycarboxylates or melaminesulphonated formaldehydes gives good results. In the summer, when the air temperature reaches +30...35 °C, it is more efficient to use cements of low dispersion and superplasticizers based on lignosulfonates. The need to ensure the high speed of modern road construction leads to the fact that cements of the same type but different plants are used in production. Also during the construction process, the organization that performs the work can replace one superplasticizer to another. Such a replacement of cement from one plant to cement from another plant, or replacement of a superplasticizer from one manufacturer to a similar but different manufacturer, can lead to negative results. For example, the effectiveness of a superplasticizer can be greatly reduced, which will affect the mobility of concrete mixtures or the strength of concrete. Concrete mixtures may also deteriorate over time. This will lead to a decrease of workability of mixtures, decompaction of concrete and will affect the operational characteristics of the finished concrete pavement. All these changes are caused by one reason, which in science and practice is called "the compatibility of cement and superplasticizer."

The concept of "compatibility" is closely related to the concept of "effectiveness of the additive." Some researchers believe that these two concepts are identical, but this is not so. In the normative documents of Ukraine it is indicated that “the effectiveness of the additive” is the degree of change in the value of the main indicator (or indicators) of the quality of cement composites when the additive is introduced. For example, this may be a decrease of the water-cement ratio or an increase of the slump of the concrete mix cone test.

With the incompatibility of cement and additives, its effectiveness is significantly reduced. Therefore, a decrease in the effectiveness of the additive is a consequence, and the "compatibility of cement and additives" is the reason for this decrease in effectiveness.

There are several definitions of "compatibility." For example, A.V. Usherov-Marshak defines «compatibility» as the ability of an additive to provide the specified properties of concrete mixtures and concrete and to preserve these properties for a certain time. This applies to all composite materials based on cement and superplasticizer.

The main property is the ability of a particular superplasticizer when interacting with a specific cement to provide a certain plasticizing effect, which depends on the chemical basis of the superplasticizer. Most often, three types of superplasticizing additives are used in road concrete technology: modified (sugar-free) lignosulfonates (LS) and their mixtures with other additives; melamine formaldehyde sulfonate (MFS) or naphthalene formaldehyde sulfonate (NFS); polycarboxylates (PC). The most powerful plasticizing effect is PC. MFS or NFS are less effective, and LS are the weakest plasticizers.

A fairly well-known and effective method for assessing the compatibility of cement and superplasticizer is the calorimetric method proposed by A.V. Usherov-Marshak [16, 17]. A special technique was developed and calorimeters were used. A relative disadvantage of the method is the need to have such equipment and specialists who can work on it. In addition, the measurement process itself continues for at least one day. Different sizes of cement particles, changes in test temperature, and fluctuations in the mineral composition of cement can also influence the quality of research.

Therefore, we propose to evaluate the compatibility of cement and additives more simply and quickly - by changing the standard properties of cement paste. There are devices for this in every laboratory. Another goal of this study is an attempt to establish patterns of compatibility of superplasticizers with cements of various mineral composition.

3. Materials and methods of research
For research, we selected cements from the same plant, which have the same clinker, slightly different dispersion, but different slag contents. These are cements: PC II/A-S-400 (CEM II/A-S 32.5 R), PC II/A-S-500 (CEM II/A-S 42.5 N), PC I-500 R-N (CEM I 42.5 R). Cement CEM II/A-S 32.5 R has
a specific surface area of 380 m$^2$/kg. The slag content in the cement is 18%. The specific surface area of the cement CEM II/A-S 42.5 N is 410 m$^2$/kg, and the slag content is 12%. Cement CEM I 42.5 R has a specific surface area of 390 m$^2$/kg, there is no slag in cement.

As superplasticizers that relate to LS, the following additives were used: BV18 from BASF and Sika 2607A from Sika. The following additives were used as superplasticizers such as MFS and NFS: FK 88 from MC Bauchemie, FM 21 from BASF. The effect of superplasticizers like PC was investigated. These are additives Glenium 27 from BASF, Relaxol Super PC from Budindustria (Ukraine), FK 59 from MC Bauchemie, Sika LTP S9 from Sika.

The change in the normal consistency and setting time of the cement paste was investigated. To do this, use the standard test method using a Vicka device.

4. Experimental research
Tests of normal consistency (NC), as well as the beginning of setting (BS) and the end of setting (AS) of the cement paste were conducted.

| №   | Type and amount of additive, % by weight of cement | Normal consistency, % | Setting time | Note                      |
|-----|---------------------------------------------------|-----------------------|--------------|---------------------------|
| 1   | Without additives                                 | 29.0                  | 2 h 40 min   | 3 h 40 min                | water separation       |
| 2   | Muraplast FK 88 – 0.5 %                           | 26.5                  | 3 h 45 min   | 5 h 30 min                | no water separation    |
| 3   | FK 88 – 1.0 %                                     | 25.5                  | 5 h 10 min   | 6 h 50 min                | no water separation    |
| 4   | BASF FM 21 – 0.5 %                                | 26.5                  | 3 h 05 min   | 4 h 25 min                | strong water separation|
| 5   | FM 21 – 1.0 %                                     | 26.25                 | 4 h 20 min   | 6 h 00 min                | strong water separation|
| 6   | BASF BV18 – 0.5 %                                 | 27.5                  | 4 h 30 min   | 6 h 30 min                | no water separation    |
| 7   | BASF BV18 – 1.0 %                                 | 26.5                  | 4 h 00 min   | 5 h 45 min                | no water separation    |
| 8   | Relaxol Super PC – 0.5 %                          | 26.0                  | 1 h 30 min   | 3 h 00 min                | no water separation    |
| 9   | Relaxol Super PC – 1.0 %                          | 24.5                  | 1 h 45 min   | 4 h 00 min                | no water separation    |
| 10  | BASF Glenium 27 – 1.0 %                           | 24.5                  | 4 h 25 min   | 6 h 10 min                | poor water separation  |

Table 1. Properties of cement CEM II/A-S 32.5 R

If we consider the performance of superplasticizers with cement CEM II/A-S 32.5 R, we can see that the use of FK 88 (type MFS) leads to a decrease in NC by 2.5...3.5% (Table 1). At the same time, the beginning of cement setting is extended by 1 h 05 m. With an increase of the amount of this additive to 1.0%, the beginning of setting extended by 2 h 30 m. The end of cement setting is extended by 3 h 10 m respectively. In this case, water cement is not observed on the cement test. This indicates that this additive is very well combined with this cement. However, another additive of the same type FM 21, despite a decrease in NC by 2.5%, slightly lengthens BS and AS. To significantly extend the setting time, it is necessary to increase the consumption of additives. At the same time, the cement paste with this additive shows water separation, which is very dangerous, especially for road mortars and concrete. Water separation can lead to flaking and layer-by-layer destruction of concrete during operation. Therefore, this additive is poorly combined with this cement.

Additive BV18, type LS, has a slightly lower water-lowering effect than superplasticizers type MFS, but it leads to a significant extension of the setting time of the cement paste and does not cause water separation. Therefore, this additive is well combined with CEM II/A-S 32.5 R. PC additives are
also combined in different ways with this cement. Despite a strong decrease in water consumption (3...4.5 %) and the absence of water separation from the cement paste, the addition of Super PC reduces the setting time. This is especially noticeable when the consumption of this additive is 0.5 % by weight of cement. This is dangerous for concrete mixtures and can lead to a quick loss of workability and poor compaction of concrete. Therefore, we can say that the Super PC additive is not compatibility with the CEM II/A-S 32.5 R. Its use requires strict implementation of the concrete mixture transportation modes. Glenium 27 is better combined with this cement. The use of this additive in an amount of 1.0 % contributes to a significant reduction in water consumption and lengthening the setting time of cement paste. However, at the same time, water separation from the cement paste is observed, which is a negative result of the action of the additive and indicates insufficient combination with this cement.

Table 2. Properties of cement CEM II/A-S 42.5 N

| №  | Type and amount of additive, % by weight of cement | Normal consistency, % | Setting time beginning of setting | end of setting |
|----|---------------------------------------------------|-----------------------|----------------------------------|---------------|
| 1  | Without additives                                  | 31,75                 | 3 h 00 min                       | 4 h 00 min    |
| 2  | FK 88 – 0,5 %                                      | 29,0                  | 3 h 15 min                       | 4 h 45 min    |
| 3  | FK 88 – 1,0 %                                      | 28,0                  | 4 h 05 min                       | 6 h 15 min    |
| 4  | FM 21 – 0,5 %                                      | 29,25                 | 3 h 20 min                       | 4 h 15 min    |
| 5  | FM 21 – 1,0 %                                      | 28,25                 | 4 h 00 min                       | 5 h 15 min    |
| 6  | BV18 – 0,5 %                                       | 29,0                  | 4 h 10 min                       | 5 h 20 min    |
| 7  | BV18 – 1,0 %                                       | 28,75                 | 4 h 40 min                       | 5 h 05 min    |
| 8  | Sm 21 – 0,5 %                                      | 29,5                  | 3 h 50 min                       | 5 h 15 min    |
| 9  | Sm 21 – 1,0 %                                      | 28,0                  | 4 h 45 min                       | 6 h 00 min    |
| 10 | Relaxol Super PC – 1,0 %                           | 26,75                 | 0 h 40 min                       | 1 h 20 min    |
| 11 | BASF Glenium 27 – 1,0 %                            | 26,75                 | 2 h 20 min                       | 4 h 05 min    |

A study of the compatibility of additives with cement CEM II/A-S 42.5 N showed that water separation from cement paste with additives of different types was absent in all compositions. At the same time, it is obvious that for higher-quality and more dispersed cement, which is a CEM II/A-S 42.5 N, all superplasticizers of types LS and MFS or NFS are well compatible (Table 2). This is evidenced by a rather large decrease in NC cement test (2.75...3.75) with these additives compared to the cement paste without additives. Such a decrease in water content corresponds to the effectiveness of the additives of these types.

Additives type PC, despite a strong decrease in NC, which is due to their high efficiency, are poorly combined with this cement. The use of these additives, despite their high content in cement paste, not only does not extend the setting time of the cement paste, but even reduces them. Super PC additive is especially poorly compatible with the CEM II/A-S 42,5 N. When it is introduced into the cement paste, its setting time is sharply reduced. Despite this, given the high efficiency of the polycarboxylates and the ability to significantly reduce water consumption, as well as the lack of water separation from cement paste, these additives remain attractive for use in monolithic concrete. However, this requires additional research.

Studies of the compatibility of cement CEM I-42,5 R with additives showed that water separation from the cement paste did not occur. An analysis of the results shows that the additive FM 21, which is of the MFS type, does not combine well with this cement (Table 3). This can be seen from the weak water-lowering effect (reduction of NC is not more than 2 %), which is small for additives of this type. In addition, the introduction of this additive into the cement paste slightly reduces the setting time. The remaining additives combine well with this type of cement. Moreover, the effect of their action is already apparent when the consumption of additives is 0.5 % by weight of cement, which is less than for other types of cement.
Table 3. Properties of cement CEM I 42.5 R

| №  | Type and amount of additive, % by weight of cement | Normal consistency, % | Setting time |  |
|----|-------------------------------------------------|-----------------------|--------------|---|
|    |                                                 |                       | beginning of setting | end of setting |
| 1  | Without additives                               | 30,0                  | 2 h 30 min    | 3 h 50 min    |
| 2  | Fk 59 – 0,5 %                                   | 27,0                  | 4 h 00 min    | 6 h 40 min    |
| 3  | Relaxol Super PC – 0,5 %                        | 27,0                  | 3 h 40 min    | 5 h 10 min    |
| 4  | FM 21 – 0,5 %                                   | 28,0                  | 2 h 30 min    | 3 h 15 min    |
| 5  | Sika LTP S9 – 0,5 %                             | 27,0                  | 4 h 00 min    | more 6 h      |
| 6  | Sika 2607A – 0,5 %                              | 28,0                  | 4 h 30 min    | more 6 h      |

2. Assessment of the water-retaining capacity of cement paste with additives (water separation).

Figure 1. Strong water separation on the surface of cement paste and on glass with the addition of FM 21

Figure 2. Water separation on glass with additive Glenium 27
The initial assessment of the compatibility of cement and superplasticizer additives is conveniently carried out visually. This allows you to most quickly evaluate compatibility. If immediately after compaction of the cement paste in the ring of the Vica device, or after a certain time (from 10...15 minutes to 1 hour), a layer of water appears on the surface of the cement paste in the ring or under the ring (water separation occurs), then the cement is poorly or weakly combined with additive. The water-retaining capacity of this cement paste is low.

For comparison, we take different additives: Fm 21, Fk 88 and Glenium 27 and one type of cement CEM II/A-S 32.5 R. In the case of using the Fm 21 additive, strong water separation can be observed both on the surface of the cement paste sample and on the glass of the device under cement paste (Fig. 1). This indicates a poor water-retaining capacity of the cement paste and the poor compatibility of this additive and this type of cement. In the second case, when using the additive Glenium 27, water separation can be observed only on the glass of the device. It is practically absent on the surface of the cement paste sample (Fig. 2). This indicates a weak compatibility of the additive Glenium 27 and cement. The Fk 88 additive has good compatibility with this cement, as evidenced by the lack of water separation on the glass of the device (Fig. 3).

Conclusions
The analysis of the compatibility of different superplasticizers with cements of different types allows us to draw the following conclusions.

1. Superplasticizers such as MFS and NFS as well as LS type are well combined with cement type CEM II/A-S 32.5 R. PC superplasticizers combine poorly with this cement.
2. Superficialisers such as MFS or NFS, as well as LS type, are well combined with the cement type CEM II/A-S 42.5 N. Polycarboxylate-based superplasticizers are poorly combined with this cement.
3. With cement CEM I-42.5 R, superplasticizers such as PC and LS are well combined. Superplasticizers like MFS and NFS are poorly combined with this cement.
4. With cements containing slag, it is most effective to use superplasticizers such as MFS or NFS, as well as type LS.
5. With cements in which mineral additives, such as slag, are absent, it is most effective to use superplasticizers like PC and LS.
References

[1] Ickovich S M 1983 Aggregates for concrete (Minsk: Higher school)
[2] Vinogradov B N 1979 Effect of aggregates on concrete properties (Moscow: Stroyizdat)
[3] Dobshits L M, Portnov I G, Solomatov V I 1999 Frost resistance of concrete transport structures (Moscow: Stroyizdat)
[4] Sanytsky M, Marushchak U, Olevych Y, Novytskyi Y 2020 Nano-modified Ultra-rapid Hardenin Portland Cement Compositions for High Strength Concretes Lecture Notes in Civil Engineering 47 392-399.
[5] Bazhenov Yu M, Demanova V S, Kalashnikov V I 2006 Modified high-quality concrete (Moscow: Publishing House Association of Construction Universities)
[6] Netesa N I, Kiryash V G 2001 Efficiency of concrete mixtures with rational grain composition Bulletin of the Dnieper State Academy of Civil Engineering and Architecture 5 41-46
[7] Dvorkin L J, Lushkinova N V, Runova R F, Troyan V V 2007 Metakaolin in mortars and concretes (Kiev: KNUBiA publishing house)
[8] Tolmachov S N, Belichenko O A 2014 The use of carbon colloidal nanoparticles in fine-grained cement concrete (Kiev)
[9] Sinajko N P, Likhopud A P, Sopov V P, Tolmachev S N, 2004 The mechanism of action of the additives against a frost Montazhnye i Spetsial'nie Raboty v Stroitel'stve 4 12-16.
[10] Stark I, Whitch B 2004 The durability of concrete (Kiev)
[11] Usherov-Marshak A V 2005 Chemical and mineral additives in concrete (Kharkov: Color)
[12] Batrakov V G 1998 Modified Concretes. Theorium and practice (Moskow)
[13] Shejnin A M, Ekkel S V 2001 Development and implementation of road concrete with high strength and frost resistance Science and technology in the road industry, 3 15-18.
[14] Ekkel S V 2016 Some suggestions to supplement current standards for road concrete Concrete Technology 7-8 50-59
[15] Tolmachov S M, Brazhnik G V, Belichenko O A, Tolmachov D S 2019 The effect of the mobility of the concrete mixture on the air content and frost resistance of concrete.IOI Conf. Series: Materials Science and Engineering 708 012109 doi:10.1088/1757-899X/708/1/012109
[16] Usherov-Marshak A V, Ciak M 2009 Compatibility - the topic of concrete science and the resource of concrete technology Construction Materials 10 12-15.
[17] Usherov-Marshak A V, Kabus A V 2012 Days of modern concrete (Zaporozhye: Publishing House "Budindustriya, LTD") 12-18.