Scientifically grounded approach to the prescription of additives for obtaining complex-modified concretes

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Annotation. The results of theoretical and experimental studies on the development of a scientifically grounded method of prescribing plasticizing chemical additives and mineral fillers in the selection of the compositions of complex-modified concretes (CMB) at the design stage are presented. The classification of plasticizing additives according to the degree of decrease in the surface tension of water upon their introduction and the activity of mineral additives according to the indicator of the reduced hydration activity, allowing to obtain highly economical MPC with the required properties.

1. Introduction

At present, concrete has finally established itself as the main building material in world construction practice. This was facilitated by such its main advantages as a wide range of properties, high manufacturability, availability of a raw material base, architectural attractiveness, versatility of application, environmental friendliness and profitability [1].

At the same time, over the past decades, a revolutionary nature of the development of concrete science has been observed, which manifests itself in the emergence of new types of concrete with unique properties, called new generation concretes (BNP).

The new generation concretes include high performance concrete (HPC), a distinctive feature of which is their achievement of maximum performance, strength, density and durability [2]. According to [3], HPC is an engineering material in which one or more of its specific properties are improved through the informed selection of components, design of the composition and maintenance of hardening concrete.

A striking example of new generation composites are modern concretes, realized at the Scientific Research Institute of Concrete and Reinforced Concrete (NIIZhB, Russia) [4]. These materials brilliantly realize the potential functional properties of the components of concrete mixes and concretes. The extremely high capabilities of concrete and reinforced concrete are realized by the authors in the technologies reactive powder concrete (RPC), as well as macrodefect free concrete (MDC) [4].

In France and the USA, the technology of ultra-functional concretes (UHPC) is widely used in construction practice, which are distinguished by high compressive strength (200 MPa) and bending strength (50 MPa) [5, 6].

Self-compacting concrete (SCC) also belongs to the category of BNP. In such concretes, the main technological problem associated with the minimization of material, energy and labor resources while achieving the specified properties of concrete is radically solved [6, 7].

In the domestic practice of concrete science, new generation concretes also include multicomponent high-quality concretes (MVB), developed by a team of authors under the leadership of professor A.I. Adylkhodzhaev [8]. These concretes contain TPP fly ash, JK-08 super plasticizing additive and are distinguished by high strength and performance properties.

As you know, the selection of compositions of traditional concrete without additives is not a big deal, the methods of their calculation are classic and are given in textbooks and teaching aids on
building materials science [9]. A distinctive feature of modified concretes (MB) is the presence in their composition of a plasticizing chemical additive or a finely dispersed mineral filler; the methodology for the purpose of compositions with their use is also reflected in educational and scientific publications [10, 11, 16-17].

As for the complex-modified concretes (CMB), it should be noted that despite the large number of scientific works devoted to this type of concretes, the issue of developing a method for selecting their composition with the appointment of a rational type of mineral fillers in combination with plasticizing chemical additives practically remains unexplored.

The authors of the article for the first time made an attempt to develop a scientifically grounded methodology for the selection of mineral fillers and plasticizing chemical additives for MPC.

2. Research results

According to the proposed method, plasticizing chemical additives are assessed according to the criterion representing the degree of decrease in the surface tension of water upon their introduction.

This approach is based on the ability of the plasticizing additive to reduce the surface tension of water at a certain temperature of the solution. In our opinion, the technological parameters of preparation, the amount of the added filler and the properties of the activated filled binder and concrete significantly depend on the chemical composition, structure and plasticizing ability of the added additive.

For experimental studies, the following types of local and most accessible plasticizing chemical additives and the corresponding dosage limits in percent of the mass of cement (on dry matter) were adopted: technical lignosulfonate (LST) - (0.10-0.25)%, sodium vat liquid -carboxymethyl cellulose (KNZH) - (0.3-0.9)%, waste water caprolactam (SVK) - (0.3-0.9)%, superplasticizer C-3 - (0.3-0.9)% [12, 18-19].

At the first stage of research, the effect of chemical additives on the degree of decrease in the surface tension of water was studied according to the method [11]. As a result of the experiments, isotherms of the surface tension of aqueous solutions of chemical additives were obtained depending on their dosage (Fig. 1), which are a family of falling curves with a pronounced zone of transition from vertical to inclined and horizontal sections.

![Figure 1. Isotherms (at t = 200°C) of the surface tension σ of chemical additives depending on their concentration C in an aqueous solution 1, 2, 3, 4 - chemical additives LST, KNZH, SVK, S-3.](image-url)
This kind of curves in Figure 1 is explained by the fact that, in accordance with the Gibbs equation [13-15], with an increase in the concentration of chemical additives, their content at the interface increases, leading to a decrease in the surface tension of aqueous solutions. Moreover, at low concentrations of chemical additives, the effect of reducing the surface tension of aqueous solutions is more significant than at higher dosages. The characteristic region on the isotherms, related to the transition from the vertical to the horizontal section of the decrease in the value of \( \sigma \), indicates the maximum saturation of the adsorption layer with molecules of chemical additives, which, as was found, corresponds to the region of their rational concentrations.

Thus, the isotherms of changes in surface tension from the concentration of aqueous solutions of chemical additives can be used as the basis for their characteristics in terms of the degree of plasticizing ability and, consequently, according to their surface-active properties - the lower the surface tension isotherm is, the more pronounced the plasticizing ability of the additive. Moreover, the range of rational dosages of chemical additives can be characterized by the relative index of surface tension, which is the ratio of the surface tension at the maximum saturation of the adsorption layer with the molecules of the chemical additive to the surface tension of the solution without the additive. In particular, for the studied additives, the indicator is the following values: LST - 0.90-0.92; CNZh - 0.88-0.90; SVK - 0.78-0.80; C-3 - 0.67-0.70.

The analysis of the obtained values of the relative index of surface tension allows us to propose a classification of chemical additives according to the effect of plasticization, taking into account their surface-active properties, given in Table 1.

| Relative indicators of surface tension, rel. units | Characteristics of the additive by the effect of plasticization |
|---------------------------------------------------|---------------------------------------------------------------|
| \( \bar{\sigma} > 0.95 \)                        | Weak plasticizer                                             |
| \( 0.85 < \bar{\sigma} \leq 0.95 \)              | Medium plasticizer                                           |
| \( 0.75 < \bar{\sigma} \leq 0.85 \)              | Strong plasticizer                                           |
| \( \bar{\sigma} \leq 0.75 \)                     | Superplasticizer                                              |

With regard to the studied chemical additives, the relative surface tension index allows us to arrange the additives studied by us in the following decreasing series according to the effect of plasticization: C-3 > SVK > CNZh ≥ LST, which characterizes a decrease in their plasticizing ability.

The expediency of such a classification of plasticizing chemical additives lies in the fact that their effectiveness is assessed by a specific numerical value of the indicator - a relative indicator of surface tension, an analogue of which can also be used in the scientifically grounded choice of dispersed mineral fillers for cement concretes.

The proposed method for the selection of mineral additives for MPC uses the classification of fillers for cement concretes according to their hydration activity [14-16, 20-21], which makes it possible to most accurately assess the contribution of the surface activity of mineral fillers to the course of the processes occurring in the hydrated system.

As a basis for determining the indicator of the hydration activity of mineral fillers, experimentally obtained graphical dependences of the distribution of adsorption centers \( q \) on their surface are used depending on the acidity constant \( pK_a \), shown in Figure 2 for basalt filler and TPP fly ash.
Figure 2. Distribution of centers of adsorption \( q \) on the surface basalt filler (1) and TPP fly ash (2) depending on from the acidity constant \( pK_a \).

Table 2. Content of adsorption centers on the surface mineral fillers.

| No. | p/p | Mineral filler | Number of Pi-10^3 centers, mg-eq/g, in the ranges of pKa values | Total number of centers, mEq/g |
|-----|-----|----------------|---------------------------------------------------------------|-------------------------------|
|     |     |                | \(-4...0\) | \(0...7\) | \(7...13\) | \(13\) | \(|\geq 13\)| |
| 1   |     | Quartz sand    | 8.04       | 9.11     | 8.75      | 1.88  | 27.78     |
| 2   |     | Sand dune      | 4.12       | 7.08     | 9.95      | 1.07  | 22.22     |
| 3   |     | Gliezh         | 13.22      | 16.47    | 10.08     | 2.87  | 42.64     |
| 4   |     | Basalt         | 23.41      | 22.15    | 11.16     | 1.96  | 58.68     |
| 5   |     | OEP            | 41.18      | 5.48     | 9.34      | 1.14  | 57.14     |
| 6   |     | OMP            | 6.61       | 23.88    | 16.37     | 4.32  | 51.18     |
| 7   |     | Fly ash        | 43.14      | 27.61    | 11.77     | 5.32  | 87.84     |
| 8   |     | CP             | 102.08     | 24.88    | 12.62     | 2.14  | 141.72    |

Notes. 1. Abbreviations: OEP, wastes from electric smelting production; OMP - wastes from copper-smelting production; CP is a zeolite-containing rock. 2. The total number of centers is 

\[ P = P_{kb} + P_{kl} + P_{ol} + P_{ob}. \]

To assess the surface properties of mineral fillers, it seems advisable to use a generalized criterion - an indicator of the reduced hydration activity \( P_{pga} \), calculated by the formula

\[ P_{pga} = P_{kb} + P_{kl} + 0.33P_{ol} - 0.1P_{ob}, \]  

where \( P_{kb}, P_{kl}, P_{ol}, P_{ob} \) – the number of adsorption centers, respectively, in the areas \( 0 \leq pK_a < 7; \ pK_a \geq 13.0; \ -4 < pK_a < 0; \ 7.0 \leq pK_a < 13 \ in \ 10^{-3} \ mg-eq/g. \)

This criterion, which characterizes the acid-base properties of the surface of mineral fillers, makes it possible to scientifically classify mineral fillers according to the degree of their effect on cement systems.
In general, the following classification of mineral fillers is proposed according to the $P_{pga}$ criterion - an indicator of the reduced hydration activity characterizing their potential efficiency in cement systems, assessed by a reduction in cement consumption (Table 3).

**Table 3.** Classification of mineral fillers by indicator the reduced hydration activity of $P_{pga}$.

| Type of mineral filler | Criterion values of $P_{pga}$ | Reducing cement consumption, % |
|------------------------|--------------------------------|--------------------------------|
| Weakly active          | $0 \leq P_{pga} < 10$        | $\leq 10$                      |
| Medium active          | $10 \leq P_{pga} < 25$       | 10-20                          |
| Highly active          | $25 \leq P_{pga} < 50$       | 20-30                          |
| Super active           | $P_{pga} \geq 50$            | 30-50                          |

For the mineral fillers used in the studies, the indicators of the reduced hydration activity of $P_{pga}$ are given in table. four.

**Table 4.** $P_{pga}$ Criterion Values for Mineral Fillers.

| № p/p | Mineral filler | PKa values, rel. units. | Transformed data | $P_{pga}$, rel. units. |
|-------|----------------|-------------------------|------------------|-----------------------|
|       |                | $P_{ol}$ | $P_{kb}$ | $P_{ob}$ | $P_{kl}$ | $0.33P_{ob}$ | $0.1P_{ol}$ |
| 1     | Sand           | 8.04    | 9.11    | 8.75    | 1.88    | 2.65      | 0.87        | 12.77      |
| 2     | Sand dune      | 4.12    | 7.08    | 9.95    | 1.07    | 1.36      | 0.99        | 8.52       |
| 3     | Gliezh         | 13.22   | 16.47   | 10.08   | 2.87    | 4.36      | 1.01        | 22.39      |
| 4     | Basalt         | 23.41   | 22.15   | 11.16   | 1.96    | 7.72      | 1.12        | 30.71      |
| 5     | OEP            | 41.18   | 5.48    | 9.34    | 1.14    | 13.59     | 0.93        | 19.28      |
| 6     | OMP            | 6.61    | 23.88   | 16.37   | 4.32    | 2.18      | 1.64        | 28.74      |
| 7     | Fly ash        | 43.14   | 27.61   | 11.77   | 5.32    | 14.23     | 1.18        | 46.68      |
| 8     | CP             | 102.08  | 24.88   | 12.62   | 2.14    | 33.68     | 1.26        | 59.44      |

Note: OEP - wastes from electric smelting production; OMP - wastes from copper-smelting production; CP - zeolite-containing rock

Comparative analysis given in table. 4 mineral fillers according to the Ppga criterion makes it possible to rank their effectiveness in cement systems and to characterize them according to the degree of activity: sand dune - weakly active; quartz sand, glezh, OEP - medium active; basalt, OMP, fly ash of Angren TPP - highly active and zeolite-containing rock - super active.

The developed classification of mineral fillers according to the proposed criterion for assessing the acid-base properties of the surface of mineral fillers P pga showed a high convergence of the data obtained with the results of previous studies from the standpoint of assessing their effectiveness in the design of various types of cement concretes and mortars, which made it possible to put it in the basis of the developed methodology scientifically a reasonable choice of these additives to obtain rational compositions of MPC [16].

3. Conclusions

The proposed classification of plasticizing additives according to the relative index of surface tension and mineral fillers according to their surface-active properties made it possible to rank such modifiers, respectively, according to the plasticizing effect and activity, which serves as the basis for a scientifically grounded choice of modifiers when obtaining, in particular, highly economical MPCs with the required properties.
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