Наведено результати дослідження реакційних порошкових бетонів, для отримання яких використано в якості дрібного заповнювача суміш річкового піску та техногенного піску, отриманого внаслідок переробки гірських порід, які містять сполуки заліза. Встановлено, що застосування суміші річкового та техногенного піску, який містить сполуки заліза, дозволяє отримати бетон, міцність якого при стиску перевищує міцність бетону аналогічного складу, виготовленого із використанням тільки річкового піску, або тільки техногенного піску

Ключові слова: реакційний порошковий бетон, дрібний заповнювач, сполуки заліза, пластифікатори, міцність бетону

Приведены результаты исследования реакционных порошковых бетонов, для получения которых использована в качестве мелкого заполнителя смесь речного песка и техногенного песка, полученного в результате переработки горных пород, содержащих соединения железа. Установлено, что применение смеси речного и техногенного песка, который содержит соединения железа, позволяет получить бетон, прочность которого при сжатии превышает прочность бетона аналогичного состава, приготовленного с использованием только речного песка или только техногенного песка

Ключевые слова: реакционный порошковый бетон, мелкий заполнитель, соединения железа, пластификаторы, прочность бетона

UDC 691.32
DOI: 10.15587/1729-4061.2017.109977

EFFECT OF THE IRON-CONTAINING FILLER ON THE STRENGTH OF CONCRETE

A. Shishkin
Doctor of Technical Sciences, Professor*
E-mail: 5691180@gmail.com
N. Netesa
Doctor of Technical Sciences, Professor
Department of Build production and geodesy
Dnipropetrovsk National University of
Railway Transport named after academician V. Lazaryan
Lazaryana str., 2, Dnipro, Ukraine, 49010
E-mail: andreynetesa@meta.ua
V. Scherba
PhD*
E-mail: 5691180@gmail.com
*Department of Technology of
building products, materials and structures
Kryvyi Rih National University
V. Matusevicha str., 11, Kryvyi Rih, Ukraine, 50027

1. Introduction

Modern concretes, including reactive powder ones, represent a multicomponent composite system. In its material composition, they contain an aggregate and a microparticle filler, Portland cement, mineral and mineral-organic additives. These additives provide concrete mixtures with a low water requirement and the necessary rheological properties, contribute to their compaction and formation of a solid structure of concrete at its hardening.

In traditional concretes, a fine filler, which is the river sand most often, takes up considerable volume. More sand consumption is required when producing concretes of the new generation – reactive powder concretes whose composition lacks coarse filler.

Given the increasing prices for sand utilized in construction, there is a need to find economical and rational techniques for using local raw materials for the production of concretes, including reactive powder ones. Further aggravating factor that necessitates making such decisions is the ever-growing cost of transporting raw materials to the construction site.

Another issue that hinders wide dissemination of promising technologies is the need to use specialized deflocculators and plasticizers – chemical surface-active substances.

With regard to the polyfunctional effect of modern deflocculants and plasticizers, a relevant task for further improvement and development of concrete technology is the targeted regulation of structurization processes of the cement stone. This is achieved by combining the use of modern deflocculants and plasticizers, as well as technogenic aggregates and fillers for concrete.

2. Literature review and problem statement

At present, the most widespread materials of technogenic origin that have fractional composition, which allows applying them as a fine aggregate of concretes, are the wastes of ore mining and processing enterprises (the so-called “tails” of the iron ore enrichment).

Studies that were conducted in the middle of the twentieth century [1] formed the basis for using “tails” of the iron ore enrichment as a fine aggregate of concretes and for further research in this direction [2–5].

The given papers report results of examining the concretes of different kinds, employing the “tails” of iron ore enrichment as fillers. Thus, in article [2], authors describe results of studies into heavy concretes based on Portland cement during production of which “tails” of the iron ore enrichment were utilized as a fine aggregate. Paper [3] gives results of research into concretes based on a cement- gypsum-pozzolan binder at production of which “tails” of the iron ore enrichment were applied as a fine aggregate. Study

[4] described properties of concretes when using a fine-dispersed part of the "tails" of iron ore enrichment.

Paper [5] shows efficiency of applying "tails" of the iron ore enrichment fillers of cellular concrete. The given work differs in that it addressed the issue of joint use of surface-active substances and "tails" of the iron ore enrichment as fillers of cellular concrete. Article [6] demonstrated effect of different mineral complexes on the properties of cement concrete, however, the mixtures of these complexes were not employed in the studies, at least, there are no data on such studies in the article.

Papers [7, 8] describe research into the influence of a mixture of mineral complexes, as aggregates for concrete, on its properties. The authors, however, did not investigate the application of mineral complexes similar in mineralogical composition to the "tails" of iron ore enrichment.

Regularities for providing a rational grain composition of concrete mixture components in order to improve performance efficiency of using cement in concrete and to enhance its mechanical properties were established in [9]. This made it possible to identify important patterns in applying both superplasticizers and the simplest plasticizers [10] in concrete technology.

Thus, the studies into possibility of replacing traditional river sand with the wastes of iron ore enrichment, reported in papers [1–5], focused on exploring the properties of concretes and mortars, in which, based on the findings obtained in article [1], river sand was fully replaced with the "tails" of iron ore enrichment. In paper [1], authors show results of the studies into coarse-grained concrete in which part of river sand was replaced with the waste of iron ore enrichment. As demonstrated by the results of studies cited in paper [1], increasing the strength of concrete occurs in proportion to the content of waste from the iron ore enrichment in the filler and reaches its maximum at full replacement of river sand with the waste of iron ore enrichment. It should be noted, however, that the given studies were conducted for the coarse-grained concrete, rather than for the fine-grained concrete. Results of the cited studies [1] allowed the authors to make the following conclusions:

1) "tails" of the iron ore enrichment should be "categorized" for using them as a fine aggregate for concrete – to separate from their composition a fraction less than 0.14 mm, which accounts for about 70 % of the "tails";

2) in order to ensure the greatest increase in the durability of concrete, river sand is to be completely replaced with the "tails" of iron ore enrichment.

The degree of elaboration of the properties of concretes, achieved in paper [1], in which "categorized" "tails" of the iron ore enrichment were used as a fine aggregate, made it possible to develop a normative document on their application – DSTU B V.2.7-33-2001 "Construction materials. Quartz-ferruginous sand and fine fraction for using in construction from the wastes of ore mining and processing enterprises of Ukraine. Technical specifications". At the same time, the issue of large-scale application of fine fraction of the "tails" of iron ore enrichment (with a particle size less than 0.14 mm) has not been properly resolved up to now.

Thus, at present there is no practical determination of the joint effect of river sand and mineral complexes, containing iron, including those of technogenic origin, on the properties of fine-grained concretes, as well as of surface-active substances. This necessitates research in this particular direction.

3. The aim and objectives of the study

The aim of present work is to determine a special feature in the formation of strength of fine-grained concrete in the presence of mineral complexes that contain iron in the form of part of a fine aggregate and a filler for concrete and plasticizers of various types.

To achieve the set objective, we solved the following task: to establish features of the influence of a mineral complex that contains iron of technogenic origin, river sand, and plastifiers, including modern superplasticizers, which were jointly introduced to concrete, on the magnitude of concrete strength.

4. Materials and methods for research

4. 1. Materials and equipment used in the experiments

In order to estimate the potential of using "tails" of the iron ore enrichment to create various building materials, the authors studied compositions of the binders prepared by adding activating additives to the "tails" of iron ore enrichment from Kryvyi Rih iron ore basin. We employed as activating additives the Portland cement of grades 500 and 400 (manufactured by Heidelberg Cement Kryvyi Rih), building lime with an activity of 85 %, and soluble glass. To improve workability we used the superplasticizer "FLVICEM" by the Italian company COLMEF, whose recommended consumption is 0.5...1.5 % by cement weight, the superplasticizer of organic origin S-3, the superplasticizer PFS (Poliplast, Russia), and polyol (Ukraine).

The composition of the products of hydration of binders, prepared by adding the activating additives to "tails" of the iron ore enrichment, was examined using the methods of X-ray phase (XPA) and differential thermal (DTA) analyses.

4. 2. Technique for determining property indicators of the samples

The examined compounds were prepared by mixing the estimated amount of components, and then adding water. The samples of working mixtures were made by casting.

The samples were of a cube shape the size of sides 15 cm. After the preparation, the samples hardened under conditions of a climate chamber that maintained a temperature of (20±3) °C at relative humidity (65±5) %.

At the age of 28 days the samples were subjected to compression test. Compression efforts were created by the universal testing machine UMM-100 (made in Russia). A concrete strength was determined as the quotient of dividing the load magnitude that resulted in the destruction of sample by the magnitude of its cross- sectional area.

5. Results of examining indicators of properties of concrete samples

The DTA results have shown (Fig. 1) that the introduction to the "tails" of iron ore enrichment of cement and lime changed qualitatively the nature of components of the system.

X-ray phase analysis (Fig. 2, 3) showed that there remained, in the hardened mixture of "tails" of the iron ore enrichment, cement and lime, the grains of pyrite (d: 0.312; 0.270; 0.242; 1.50 nm) and quartz (d: 3.34; 1.81; 1.54 nm) as a filler, but the new substances were also formed.

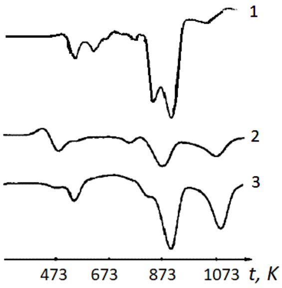

Fig. 1. Results of DTA: 1 – original "tails" of the iron ore enrichment, 2 – "tails" of the iron ore enrichment + 10 % of Portland cement + 10 % of lime, 3 – "tails" of the iron ore enrichment + 10 % of Portland cement + 15 % of lime

Table 1 gives results of testing the samples of concrete with normal curing at the age of 28 days at different consumption of cement. We used as a filler the "tails" of iron ore enrichment whose 90 % of grains are commensurate with the size of cement grains. We also applied the slag Portland cement with an activity of 40 MPa, granite rubble with a maximum dimension of 20 mm, and sand from the river Dnepr with a size modulus of 1.45.

Table 2 gives results of testing the samples of concrete with normal curing at the age of 28 days at different consumption of cement and the addition of the plasticizer PFS.

Fig. 4–9 show nomographs of density, ultrasound velocity and concrete on the consumption of filler and plasticizer at constant water content. Nonograms were derived as a result of statistical processing of the results of conducted experiments and determining mathematical dependences of density magnitudes, ultrasonic velocity and concrete strength on the consumption of filler and plasticizer at constant water content.

Fig. 10 shows dependences of concrete strength on the content of "tails" of iron ore enrichment and a plasticizer – polyol.

Table 1

Compositions and test results of the control samples

No. of composition	Consumption of materials per m^3, kg					Strength, MPa
	C	F	R	S	W	
1	125	375	1200	570	170	19.8
2	250	250	1200	570	170	37.2
3	125	125	1200	820	160	12.9
4	125	–	1200	900	170	9.8
5	250	–	1200	820	170	29.8
6	120	360	1200	520	200	15.3
7	100	380	1200	520	200	13.8
8	75	400	1200	520	200	9.3

Note: C – cement; F – filler; R – rubble; S – sand; W – water

Table 2

Compositions and test results of the control samples of concrete with a variation of filler from the tails of iron ore enrichment, the additive PFS

No. of composition	Consumption of materials per m^3, kg						Strength, MPa
	C	F	R	S	W	PFS, %	
1	125	–	1250	875	150	0.5	5.92
2	250	–	1250	750	130	0.5	25.8
3	375	–	1250	625	115	0.5	47.1
4	500	–	1250	500	130	0.5	61.5
5	125	125	1250	750	130	0.5	18.8
6	125	375	1250	500	120	0.5	20.5
7	250	125	1250	625	115	0.5	41.0
8	250	250	1250	500	120	0.5	43.2
9	375	125	1250	500	130	0.5	53.5

Note: C – cement; F – filler; R – rubble; S – sand; W – water

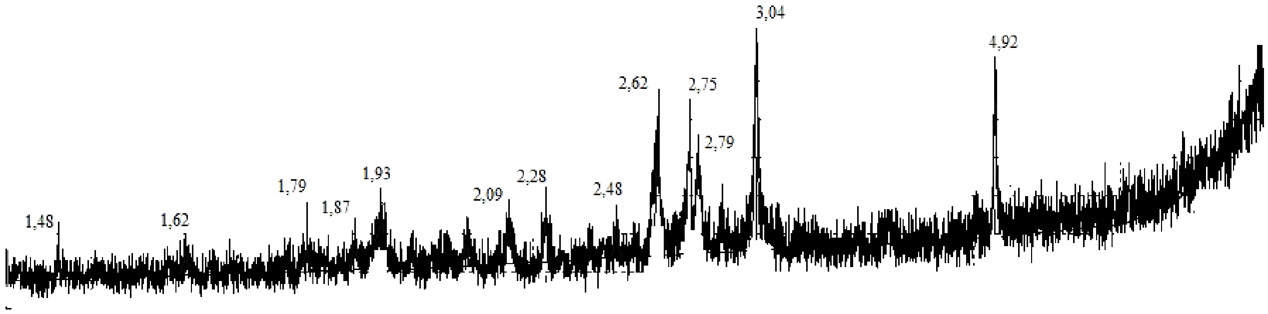

Fig. 2. Results of X-ray phase analysis: the original "tails" of enrichment of iron ores

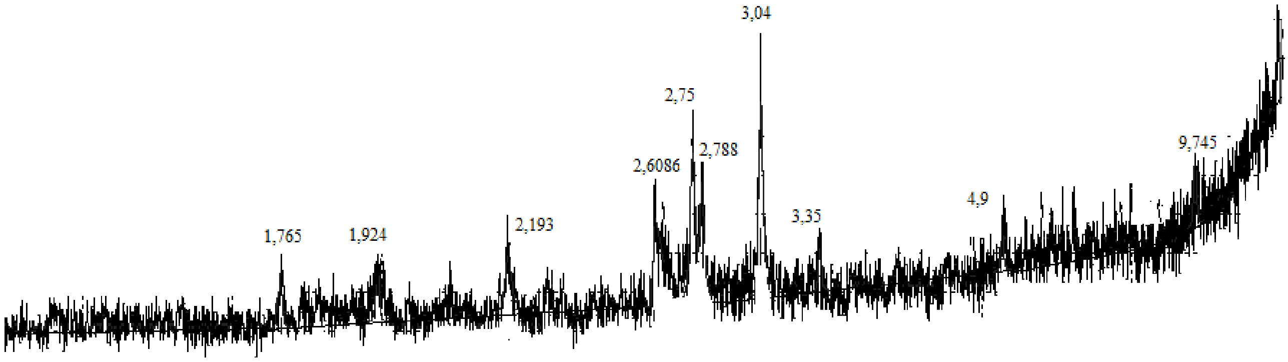

Fig. 3. Results of X-ray phase analysis: the "tails" of enrichment of iron ore + 10 % of Portland cement + 10 % of lime

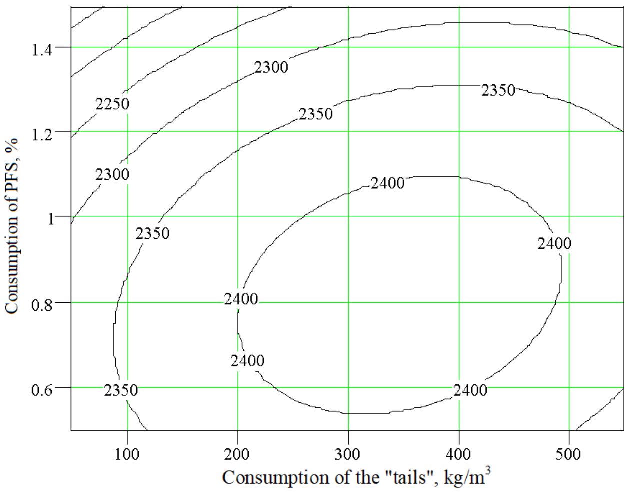

Fig. 4. Dependences of concrete density on the consumption of “tails” of the iron ore enrichment and the plasticizer PFS at a constant water consumption of 125 l/m^3

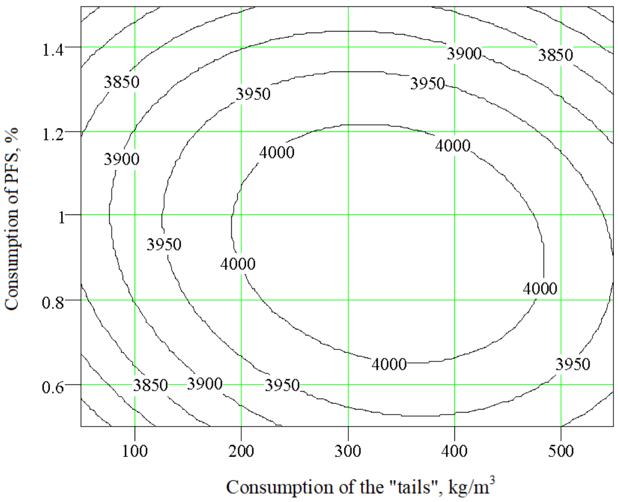

Fig. 7. Dependences of ultrasonic velocity on the consumption of “tails” of the iron ore enrichment and the plasticizer PFS at a constant water consumption of 140 l/m^3

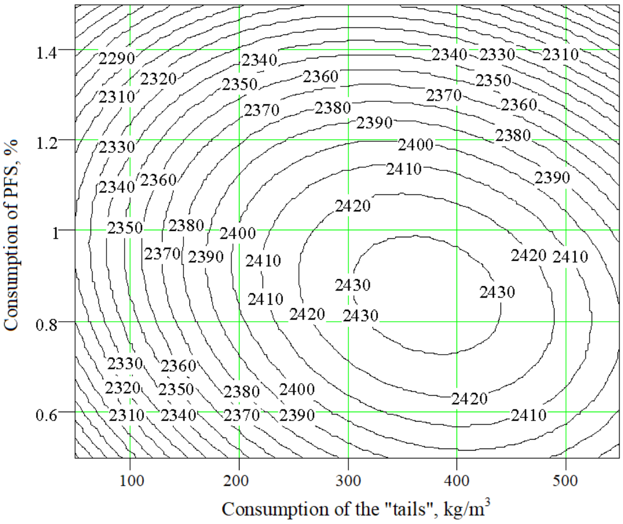

Fig. 5. Dependences of concrete density on the consumption of “tails” of the iron ore enrichment and the plasticizer PFS at a constant water consumption of 140 l/m^3

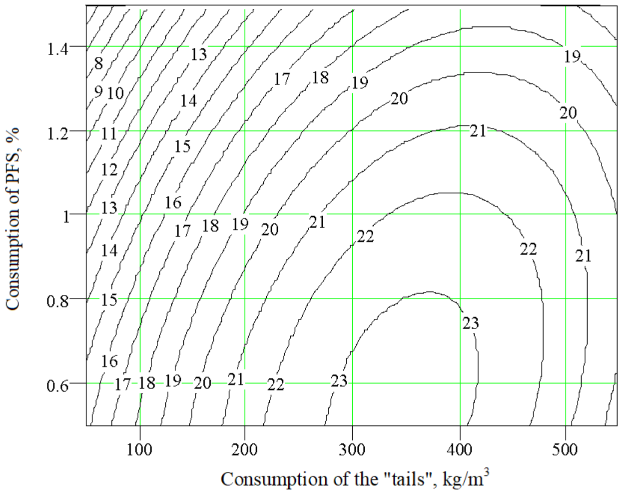

Fig. 8. Dependences of strength on the consumption of “tails” of the iron ore enrichment and the plasticizer PFS at a constant water consumption of 125 l/m^3

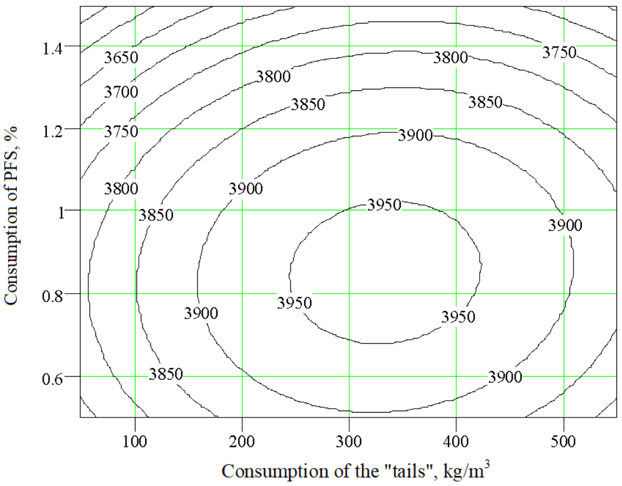

Fig. 6. Dependences of ultrasonic velocity on the consumption of “tails” of the iron ore enrichment and the plasticizer PFS at a constant water consumption of 125 l/m^3

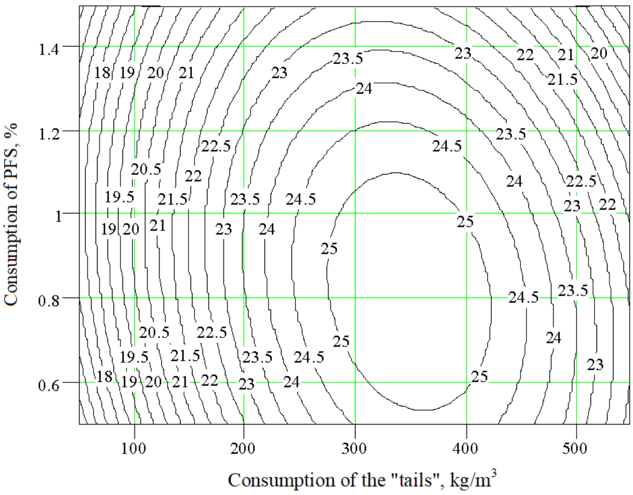

Fig. 9. Dependences of strength on the consumption of “tails” of the iron ore enrichment and the plasticizer PFS at a constant water consumption of 140 l/m^3

6. Discussion of results of examining the properties of compositions that contain "tails" of the iron ore enrichment

The introduction of Portland cement and lime to the "tails" of iron ore enrichment changes the shape of new formations, which is evidenced by the following data. First, the amount of hydrated water in the iron compounds decreased (endothermic effects occur at temperatures of 110, 170, 230 °C, while this effect disappeared at 140 °C), which is obviously related to a decrease in the degree of oxidation of pyrite (loss of mass at endothermic effects with temperatures of 470, 585, 620 °C decreased by 3.1, 6.5, and 42 times, respectively). In this case, the endoeffect shifted from 680 °C to 620 °C. Second, the composition containing a mixture of Portland cement and lime as the activating additive acquired a strength of 9.5 MPa due to the almost complete binding of lime and cement into calcium hydrosilicates (endothermic effects at temperatures of 110, 170, 680–820 °C) and calcium carbonates (endoeffect at a temperature of 860 °C, particularly calcite (d: 0.387; 0.303; 0.250; 0.228 nm). In this case, the endoeffect at a temperature of 550 °C, associated with free calcium hydroxide, did not practically occur along a differential thermogravimetric curve (DTG) curve, while calcium hydroxide is detected on the radiograph (d: 0,492; 0,312; 0,263 nm).

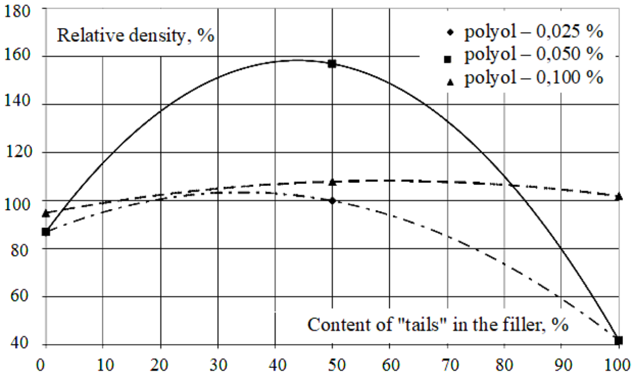

Fig. 10. Influence of the content of "tails" of the iron ore enrichment on the compressive strength of concrete in the presence of polyol

The endothermic effect in a temperature range of 680–820 °C can be assigned to the decomposition of products of the interaction between cement with lime and the components of "tails" of the iron ore enrichment. At the same time, this effect is similar to the effect in slag Portland cement, although the losses of weight in this case are insignificant.

The composition containing the additive of cement with the addition of lime, increased to 15 %, exhibits practically the same endothermic effects.

The DTA results showed that when adding to "tails" of the iron ore enrichment cement and lime, the effects along a DTA curve of the given composition are more pronounced while the losses of weight during effects account for up to 93 % of the total weight losses, while the losses of weight during effects of the composition without lime do not even reach 90 %. Therefore, this composition contains less gel-like constituents. The feature of composition with an increased content of lime is the increased basicity of calcium hydrosilicates (a shift in endoeffect from 110 to 140 °C), as well as the emergence of visible endoeffect at 550 °C, related to calcium hydroxide, with mass losses at 1.5 %, and the corresponding increase in the content of carbonates (930 °C). In addition, the endoeffect significantly increased at 780 °C.

The nest composition represented "tails" of the iron ore enrichment, mixed with liquid glass, which is why the new formations are presented by the products of interaction between iron-containing minerals and sodium silicates. The features of this interaction manifested themselves by a reduction in the losses of weight during endoeffect at 470 °C by almost twice compared to the previous compositions. And, in addition, by increasing weight loss by 1.5–2.0 times compared to the compositions with a cement-lime activation in the third endoeffect. At the same time, the effect temperatures shifted from 680 to 620 °C.

In addition, riebeckite $Na_2 \cdot Fe^{2+} \cdot Fe^{3+} \cdot Si_4O_{11}(OH)_2$ (d: 0.309; 0.253; 0.217; 0.166; 0.131 nm) and chabazite $Na_2 \cdot [Al(Fe) \cdot Si_2O_6]_2 \cdot 6H_2O$ (d: 0.93; 0.435; 0.362; 0.324; 0.293 nm) were formed in this system.

The studies conducted have shown that the "tails" of enrichment of iron ores, when activated by lime or cement, makes it possible to obtain the material with a strength of up to 10 MPa; when activated by sodium silicates – up to 40 MPa; and upon activation by sodium silicates and technogenic glasses – up to 60 MPa. A role of the binder in such materials is performed by the hardening activizers and dispersed components of the "tails". The performed research into new formations during hardening of the compositions of activated "tails" of the iron ore enrichment reveal the possibility of obtaining strong enough materials based on them.

An analysis of experimental results on introducing to the composition of concrete the "tails" of iron ore enrichment as a filler (Table 1), as well as the visual observations, allow us to determine the following regularities. The efficiency of the superplasticizer "FLVICEM", used in the given experiment, with a consumption of 1.5 % by weight of cement, is significantly higher than that of the superplasticizers S3 and PFS, employed in other experiments. However, it was not possible to achieve good workability of the mixture in the compositions without a filler, even applying such an effective super-plasticizer. There was a significant water release in these compositions No. 4, 5 (Table 1).

A similar pattern was observed in composition No. 3, where a filler consumption was 125 kg. It was not possible to compact the samples with these compositions. The efficiency coefficient of using the cement in these compositions, however, remained significantly lower than that in the compositions with the same cement consumption and rational grain composition of components, which was ensured by the introduction of the required quantity of a filler (Table 1).

Compositions with a low consumption of cement and the superplasticizer "FLVICEM" demonstrated a significantly better workability and connectivity than that with S3 and PFS. The strength of concrete, obtained from these compositions, is substantially higher than that from the compositions with the same cement consumption and roughly the same workability but without a super-plasticizer. The same applies to the compositions containing the superplasticizer PFS and to the compositions that are considerably tougher (see composition No. 1, Table 2).

An analysis of the research results shown in Fig. 3–8 allowed us to identify the following regularities.

Both at water consumption 125 and 140 litres per cubic metre, the largest density, ultrasound velocity and concrete strength were determined at consumption of filler 300...400 kg/m^3 and consumption of plasticizer 0.7...1.2 % by weight of cement. These characteristics, however, are slightly better at water consumption 140 l/m^3 of concrete.

Intensity of a decrease in density, ultrasound velocity, strength with a decrease in the consumption of filler 200...50 kg/m^3 and an increase in the consumption of plasticizer 1.2...1.5 % by weight of cement is about the same. Thus, the largest strength is 25 MPa; with a decrease in the consumption of filler in the examined range it is reduced to 18 MPa at constant consumption of plasticizer. And with a decrease in the content of the latter to 0.5 %, or with an increase to 1.5 %, the concrete strength reduces even larger and reaches 16 MPa. With an increase in the content of filler to the limit (550 kg), the strength of concrete also reduces, but less than when it is decreased to 50 kg/m^3 of concrete. The plasticizer consumption in the examined range affects strength less substantially than the content of filler.

A regularity of change in strength at constant water content 125 liters per cubic metre is about the same as that considered in detail earlier at water content 140 l. But the strength of concrete over the entire range of change in the consumption of filler and plasticizer is significantly smaller.

The lowest strength is determined at water content 125 l, filler 50 kg/m^3 of concrete, and plasticizer 1.5 % by weight of cement.

We determined by visual observations that a concrete mixture exhibited the best technological characteristics at filler consumption 300...400 kg/m^3 and consumption of plasticizer 0.7...1.2 % by weight of cement. None of these components could individually enable the same good workability and non-delamination of concrete mix, absence of water release, good and quick filling of forms. The samples made of such mixture have a good smooth surface.

However, as shown by the research results (Fig. 9), in the case of not a complete replacement of river sand with ordinary “tails” of the iron ore enrichment, but rather only some part of it, especially in the presence of polyol, it is possible to achieve a significant increase in the strength of fine-grained concretes. In this case, a technological operation of the so-called “categorization” of “tails” of the iron ore enrichment is excluded, that is, all fractions of “tails” are utilized.

7. Conclusions

The studies we conducted into the impact of technogenic aggregates of fine-grained concrete, which contain iron, together with various kinds of plasticizers, allowed us to establish that such technogenic fillers of concrete interact with minerals and hydration products of Portland cement. This determines mechanical strength of the cement stone and, as a result, the strength of concrete.

The performed research showed the possibility of targeted regulation of the processes of formation of solid structure of fine-grained concretes by a joint application of mineral complex containing iron ions, river sand and surface-active substances that are substantially different in the structure of molecules.

It was proven that there is an optimal ratio between river sand and a mineral complex containing ions of iron, which provides fine-grained concrete with maximum strength.

The effectiveness of using modern superplasticizers in fine-grained concretes significantly increases with a provision of rational grain composition of the concrete mix components, in particular by the introduction of mineral complexes containing iron ions to the compositions.

References

1. Puhal’skiy, G. V. Svoystva betonov na peskah iz othodov gorno-obogatitel’nyh kombinatov [Text] / G. V. Puhal’skiy, G. N. Bondarenko // Beton i zhelezobeton. – 1975. – Issue 5.
2. Bondarenko, S. V. Vykorystannia vidkhodiv hirnycho-zbahachuvalnykh kombinativ ta yikh standartyzatsiya [Text] / S. V. Bondarenko, V. Y. Bolshakov, H. N. Bondarenko // Stroitel’stvo, materialovedenie, mashinostroenie. – 2001. – Issue 12. – P. 215–217.
3. Shishkin, A. A. Osobennosti ispol’zovanie othodov gorno-obogatitel’nyh kombinatov v proizvodstve stroitel’nyh materialov [Text] / A. A. Shishkin, A. A. Shishkina, V. V. Shcherba // Visnyk DNABA. – 2013. – Issue 1 (99). – P. 8–12.
4. Vandolovskyi, A. H. Mitsnisni vlastyvosti osoblyvodribnozernystoho betonu na vidkhodakh hirnycho-zbahachuvalnykh kombinativ u roli zapovniuvacha [Text] / A. H. Vandolovskyi, V. M. Chaika // Zbirnyk naukovykh prats UkrDUZT. – 2016. – Issue 160. – P. 17–24.
5. Prihod’ko, A. P. Yacheistye betony s ispol’zovaniem tekhnogennyh othodov promyshlennosti [Text] / A. P. Prihod’ko, D. O. Malyar // Visnyk PDABA. – 2009. – Issue 4. – P. 5–7.
6. Voglis, N. Limestone, fly ash, slag, and natural pozzolana: a comparative study of their effect on the cement properties [Text] / N. Voglis, S. Tsvilis, G. Kakali // Creating with Concrete: International Conf, 1999: Proc. – Dundee, 1999. – P. 203–210.
7. Erdem, T. K. Use of binary and ternary blends in high strength concrete [Text] / T. K. Erdem, Ö. Kırca // Construction and Building Materials. – 2008. – Vol. 22, Issue 7. – P. 1477–1483. doi: 10.1016/j.conbuildmat.2007.03.026
8. Li, G. Properties of high-volume fly ash concrete incorporating nano-SiO_2 [Text] / G. Li // Cement and Concrete Research. – 2004. – Vol. 34, Issue 6. – P. 1043–1049. doi: 10.1016/j.cemconres.2003.11.013
9. Netesa, N. I. Vliyanie zernovogo sostava komponentov na strukturu, prochnost’ i morozostoykost’ betonov [Text] / N. I. Netesa // Stroitel’stvo, materialovedenie, mashinostroenie. – 2002. – Issue 16. – P. 100–107.
10. Shishkin, A. Low-Shrinkage Alcohol Cement Concrete [Text] / A. Shishkin, A. Shishkina, N. Vatin // Applied Mechanics and Materials. – 2014. – Vol. 633-634. – P. 917–921. doi: 10.4028/www.scientific.net/amm.633-634.917