Heavy-weight concrete with the use of by-products of chemical process industry and metallurgy

Yu Sokolova\textsuperscript{1}, E A Stepanova\textsuperscript{2}, M V Akulova\textsuperscript{2}, T E Slizneva\textsuperscript{2} and V S Polyakov\textsuperscript{2}
\textsuperscript{1}Moscow State University of Civil Engineering, Yaroslavskoye shosse, 26, Moscow, 129337, Russia
\textsuperscript{2}Ivanovo State Polytechnic University, Sheremetyevsky prospekt, 21, Ivanovo, 153000, Russia

Abstract. The present research comprises the complex approach to inclusion of industrial by-products as the recoverable cost saving raw materials. It also enables to tackle the number of issues related to elimination of man-caused impact on ecological system arising when physical and mechanical properties of concrete are being enhanced. In the course of investigation, there has been developed the complex chemical additive on the base of caprolaktam oligomers that, being a sustainable component, remain behind extraction water filtering. The characteristics of powder acid electric furnace slag of foundry operation have been determined. The authors have stated the impact of additives on the properties of heavy-weight concrete.

1. Introduction
Heavy-weight concrete is regarded as the major modern structural material, due to its universal and non-competitive application in civil engineering and other types of construction [1].

There exist various methods of enhancing the quality of concrete. Introduction of chemical additives of various purposes into the concrete mix is regarded as an effective scientifically validated and approved method [2, 3, 4].

Nowadays, a great variety of additives, both foreign and home-produced, is presented on the market. Foreign-produced modifiers are traditionally more expensive, i.e. their use is not economically viable. While improving particular properties of concrete, the major part of home-produced compositions has no significant impact on other properties [5]. Therefore, complex additives consisting of two or more components that affect rheological, physical-chemical properties and structure of concrete are the most sought after [3].

Due to the great demand and efficiency of complex additives, the development of innovative, cost-efficient and affordable multifunctional modifiers, as well as the recycling of raw materials, industrial by-products, is of paramount importance [6].

Among the great variety of natural and synthetic additives, organic substances, including oligomers, water-soluble and water-disperse polymers, ethers of fatty acids, the products of condensation of naphthalene sulphonic acid and formaldehyde and others are very popular [7]. Man-induced by-products of chemical process industry are considered as a valuable source of organic substances. In particular, the methods of utilizing industrial by-products and polymerization of caprolaktam as the components of chemical additives for concrete are well known. Along with that, these by-products have not been thoroughly studied; therefore, the research in this sphere could be of great interest [8, 9, 10].

The type of industrial by-products of caprolaktam and its derivatives depends on the manufacturing method. Polyamide-6 (PA-6) is regarded as one of the main materials produced by hydrolytic polymerization of caprolaktam [8]. When manufacturing PA-6, caprolaktam and oligomers are at the
equilibrium with a polymer. Low-molecular weight compounds (LMC) in the composition of PA-6 aggravate the polymer treatment processing into articles.

The water extraction method of LMC-removal is the most popular and wide spread in industry. Bead polymer is treated by hot water at 90-120°C in the apparatus-extractor [8]. Formed extraction waters are filtered, and the pure LMC, caprolaktam oligomers, are left. Presently, only alkaline wastes of caprolaktam process (AWCP) are applied as the components of chemical additives for concretes [5, 10]. However, these wastes are extremely toxic. Caprolaktam oligomers, left after extraction, are sustainable, green and easy-to-use.

In the present paper, there was developed the innovative efficient chemical additive on the base of extracted oligomer wastes of caprolaktam process. It has plasticizing and water-reducing effect on concrete mix, increases concrete mix cohesion, enhances operational characteristics of heavy weight concrete.

The present study allows solving the important issue of recycling industrial wastes of metallurgy as the main source of man-made raw materials [11]. Blast-furnace slags as well as open-hearth furnace and converter steelmaking slags are widely used in manufacturing of concrete and slag-concrete articles, cement production and road construction works [12]. Steelmaking in electric steel furnaces was not widely spread before, thus, a number of research works is dedicated to the possible use of blast-furnace slags [9, 11, 12, 13, 14]. However, there is a current tendency towards transition to the improved melting method: from open-hearth and converter ones to electric-furnace steelmaking [6].

The main sources of electric-furnace slags of foundry operation are the enterprises specializing in melting extra high quality steel made of scrap steel for various spheres of mechanical engineering. The principal process task in this case is extraction of extra carbon and admixtures from scrap in order to produce steel of the designed grade [9]. Due to high equipment productiveness in steelmaking and ever increasing accumulation of electric-furnace slags, the issue of their recycling is gaining momentum [12].

Thus, the analysis of the global issues and literature sources has shown that application of by-products of chemical process industry and metallurgy is perspective for development of highly efficient heavy weight concretes and their modifying components.

2. Materials and methods
For manufacturing concrete mixes, there have been used Portland cement CEM I 42.5H, produced by “Oskolcement” Plc, Stary Oskol; enriched coarse sand for 1st class construction works produced by “Chromtsovsky quarry” Ltd, Ivanovo region; gravel graded 5-20 mm, manufactured by “Chromtsovsky quarry” Ltd, Ivanovo region; and pure water pH=7.31.

As a recyclable man-made raw material, there have been used the slag of foundry operation, produced by “Mechanical Engineering Complex CRANEX” Plc, Ivanovo, and the chemical additive on the base of caprolaktam oligomers with the provisional name “X”.

In the paper, the authors have determined the properties of the initial materials, cement stone, heavy weight stone under the corresponding standards and by means of up-to-date research methods [15].

3. Results and discussion
3.1 The study of electric-furnace slag
Electric-furnace slag in the banks is a solid material of dark color with the particles size of 5-25 mm. For the research purposes, slag preparation included its milling. Milling has been carried out on the three-step impactor, with rotation velocity 3000 revolution per minute, until the slag particles reach the average size of 0.201 mm. Particle-size distribution of slag powder is presented in the table 1, the fig. 1.
Table 1. Particle-size distribution of milled slag, produced by “Mechanical Engineering Complex CRANEX” Plc

| Sieve number | Average particle size | Sieve residue, g | Sieve residue percentage, % |
|---------------|-----------------------|------------------|-----------------------------|
| 0.315         | 0.36                  | 54.56            | 27.86                       |
| 0.14          | 0.2275                | 51.6             | 26.36                       |
| 0.08          | 0.11                  | 49.46            | 25.26                       |
| 0.071         | 0.0755                | 21.4             | 10.92                       |
| 0.063         | 0.067                 | 4.16             | 2.12                        |
| 0.045         | 0.054                 | 10.82            | 5.52                        |
| 0               | 0.0225                | 3.84             | 1.96                        |
| ∑              | 195.84                | 100              |                             |

Figure 1. Degree of dispersion of milled slag produced by “Mechanical Engineering Complex CRANEX” Plc

In order to determine elemental composition, the analysis of obtained powder has been implemented on the scanning electronic microscope SEMVEGA 3 TASCAN (table 2).

Table 2. Elemental composition of milled slag produced by “Mechanical Engineering Complex CRANEX” Plc

| Element | Weight, % |
|---------|-----------|
| O       | 37.18-41.09 |
| C       | 14.33-17.07 |
| Fe      | 15.98-19.54 |
| Si      | 14.57-16.08 |
| Mn      | 6.66-12.76  |
| Cr      | 0.56-1.13  |
| Al      | 0.82-0.84  |
| Ca      | 0.21-0.38  |
| Ni      | 0-0.31     |
| Cu      | 0-0.3      |
| Na      | 0-0.26     |
| Ti      | 0-0.23     |
| ∑       | 100.00     |
Slag elements are presented mostly in the form of oxides. According to the data of analysis, slag contains about 14-17% of carbon (C). Carbon is formed in such amount because steel resmelting in electric furnace is carried out by carbon prods. We could suggest that carbon is present in the form of iron carbides Fe₂C, Fe₄C₃. It is quite logical to assume that carbides enhance slag strength affecting also the strength of modified concrete. The carbon content in concrete also increases its thermal fastness, which is considered a very important property [16].

As slag contains a small amount of CaO, it may be concluded that it has low hydraulic properties. According to the analysis data of dispersion degree of electric-furnace slag, the powder contains fine particles, including those under 0.045 mm that gives a plausible evidence of possible inclusion of nanoscale particles (up to 2%).

Fine fraction powder of slag could react with the mixing water forming hydraulic formations of cement stone [17].

Nanoscale particles of carbon and other substances modify the contact zone between a cement matrix and a filler hereby increasing density due to the change of porous space and forming the structure of concrete with improved physical and mechanical properties [16].

Total varied dispersion degree of slag also has a positive impact on the density of particle structure of concrete composite [16].

3.2. Development of chemical additive
In the present study, the authors have developed a chemical additive on the base of caprolaktam oligomers remaining after filtering extraction waters, with the provisional name “X”. In order to obtain modified concrete, the additive with density of 1150kg/m³ has been obtained on the base of oligomer wastes of caprolaktam (OWCL). The developed additive will have a multifunctional effect: lowering the content of hard-to-get components, plasticizing and water reduction of concrete mix consequently, the initial inhibition of concrete hardening facilitating the formation of more refined structure, acceleration of concrete hardening on later stages [5, 10].

3.3. The study of the impact of slag and chemical additive on the composite properties
In order to determine the properties of heavyweight concrete as well as their alteration induced by the components introduction, the reference composition has been used. The materials consumption (cement – C, sand – S, gravel – G, water – W) per one cubic meter of concrete, grade B40 and the main characteristics are given in the table 3.

| Name title | Mix workability | Materials consumption, kg |
|------------|-----------------|---------------------------|
| Reference  | P3              | Cement (C) Sand (S) Gravel (G) Water (W) |
|            |                 | 356 680 1150 192           |

In order to research the influence of slag produced by “Mechanical Engineering Complex CRANEX” Plc and the complex additive “X” on the properties of heavy weight concrete, there have been elaborated the cubic specimens of the reference composition with the various slag content and introduction of oligomer additive.

In the experimental compositions, the partial substitution of a binder by slag has been done in the amount of 2%, 5%, 10% and 15% of the cement weight. The oligomers were added for 0.3% of a binder’s weight.

When water was introduced, its consumption was corrected to maintain the concrete mix grade corresponding to its workability.

The materials consumption per one cubic meter of the investigated compositions is presented in the table 4.
Table 4. Concrete compositions per one cubic meter

| Specimen number | Additive name   | Materials consumption, kg |  
|-----------------|-----------------|----------------------------|
|                 |                 | Cement | Sand | Gravel | Water | Slag | «Х» |
| 1               | Reference       | 356    | 680  | 1150   | 192   | -    | -   |
| 2               | 2% Slag         | 348.88 | 680  | 1150   | 192   | 7.12 | -   |
| 3               | 5% Slag         | 338.2  | 680  | 1150   | 192   | 17.8 | -   |
| 4               | 10% Slag        | 320.4  | 680  | 1150   | 192   | 35.6 | -   |
| 5               | 15% Slag        | 302.6  | 680  | 1150   | 192   | 53.4 | -   |
| 6               | 0% Slag with «Х»| 356    | 680  | 1150   | 189   | -    | 1.068|
| 7               | 2% Slag with «Х»| 348.88 | 680  | 1150   | 183   | 7.12 | 1.068|
| 8               | 5% Slag with «Х»| 338.2  | 680  | 1150   | 182   | 17.8 | 1.068|
| 9               | 10% Slag with «Х»| 320.4  | 680  | 1150   | 182   | 35.6 | 1.068|
| 10              | 15% Slag with «Х»| 302.6  | 680  | 1150   | 185   | 53.4 | 1.068|

When the components (slag and additives) are introduced into the concrete composition, there has been determined their impact on water requirement of concrete mix; the authors have measures strength, water absorption and abrasiveness of concrete.

3.4. Determining water absorption of concrete mix
To determine the influence of introduced components on water consumption when retaining workability of concrete mix, the authors have obtained the following experimental data presented in the table 5.

Table 5. Water absorption of concrete mix of the studied compositions

| Specimen number | Additive name | Water consumption per one cubic meter of concrete mix | Water/Cement Ratio |
|-----------------|---------------|------------------------------------------------------|--------------------|
| 1               | Reference     | 192                                                  | 0.54               |
| 2               | 2% Slag       | 192                                                  | 0.54               |
| 3               | 5% Slag       | 192                                                  | 0.54               |
| 4               | 10% Slag      | 192                                                  | 0.54               |
| 5               | 15% Slag      | 192                                                  | 0.54               |
| 6               | 0% Slag with «Х»| 189                                                  | 0.53               |
| 7               | 2% Slag with «Х»| 183                                                  | 0.51               |
| 8               | 5% Slag with «Х»| 182                                                  | 0.51               |
| 9               | 10% Slag with «Х»| 182                                                  | 0.51               |
| 10              | 15% Slag with «Х»| 185                                                  | 0.52               |

The analysis of experimental data has proven the stability of water consumption at slag’s introduction and its lowering when the additive is introduced or the joint introduction of slag and the additive takes place. This results in the lowering of water-cement ratio and thus, serves as a plausible evidence of plasticizing properties of the additive.

3.5. Determination of strength properties of concrete, its water consumption and abrasiveness
The concrete specimens’ compressive strength has been determined in compliance with the All-Union Standard GOST 10180-2012. The cubical specimens with dimension 100x100mm have been tested
after hardening under standard conditions at 28-days. The test results have accumulated in the table 6 and presented at the figure 2.

From the data presents in the table 6 and the figure 2 it is clear that strength of the specimens is varied insignificantly. When slag is added, the specimens’ stringy is lowered, but at introduction of slag with the additive “X” the strength is increased if compared with the specimens with slag’s use.

When 5% slag and 0.3% additive is introduced, the parameters of strength in relation to the reference specimen is remained unchanged, however, this solution enables to apply man-induced wastes in manufacturing of concrete and the concrete’s components.

Water consumption has been determined in compliance with the All-Union Standard GOST 12730.3-78 and the GOST 12730.0-78. The specimens have been cleaned before testing and dried till they reach the permanent weight. The results are presented in the table 6 and the figure 3.

The tests results demonstrate the lowering of water consumption when slag and additives are introduced into the concrete composition. This confirms the formation of more refined and dense structure of cement-concrete composite. This effect builds forecasts of enhancing freeze-thaw durability of concrete and other performance properties.

The abrasiveness tests have been done in compliance with the GOST 13087-2018; for the tests, the so-called “Abrasive Disc” and the concrete specimens – cubes with the rib of 70 mm – have been used. The tests results are presented in the table 6 and the figure 4.

| Specimen number | Additive name | Compression strength, MPa | Water consumption by weight, % | Abrasiveness, g/cm² |
|-----------------|---------------|---------------------------|--------------------------------|---------------------|
| 1               | 0% Slag       | 51.68                     | 6.27                           | 0.46                |
| 2               | 2% Slag       | 46.39                     | 6.17                           | 0.42                |
| 3               | 5% Slag       | 45.52                     | 6.06                           | 0.38                |
| 4               | 10% Slag      | 43.38                     | 6.05                           | 0.35                |
| 5               | 15% Slag      | 38.24                     | 6.1                            | 0.37                |
| 6               | 0% Slag with «X» | 49.64                     | 6.2                            | 0.44                |
| 7               | 2% Slag with «X» | 47.42                     | 6.1                            | 0.39                |
| 8               | 5% Slag with «X» | 49.32                     | 6.0                            | 0.34                |
| 9               | 10% Slag with «X» | 42.43                     | 6.02                           | 0.33                |
| 10              | 15% Slag with «X» | 39.32                     | 6.05                           | 0.35                |

**Table 6.** Physical-mechanical and physical properties of concrete

![Figure 2. The dependency of ultimate compressive strength on the additive’s type](image-url)
3.6. Electronic scanning microscopy

In order to determine the influence of acid slag of foundry process and the complex additive on the base of caprolaktam oligomers on the structure and the properties of cement composite, the specimens of reference compositions have been made and the analysis has been carried out by the method of electronic scanning microscopy (table 5).
Table 5. Reference compositions of specimens

| Specimen number | Composition |
|-----------------|-------------|
| 1m              | Cement+Water, Water/Cement ratio=0.54 |
| 2m              | Cement+Slag(5%)+Water, Water/Cement ratio=0.54 |
| 3m              | Cement+Slag(5%)+X (0.3%)+Water, Water/Cement ratio=0.54 |

The specific peculiarities of specimen’s surface for the cement stone of the reference composition have been investigated by the appliance SEMVEGA 3TASCAN. The obtained images of the specimens’ surfaces with the resolution of 5 mcm are presented on the figures 5-7.

Figure 5. The specimen of cement composite 1m

Figure 6. The specimen of cement composite 2m

Figure 7. The specimen of cement composite 3m

The substances formed during the cement-water interaction are close to the minerals in their crystalline composition. The study of the additives’ influence on their structure is understudied. It represents a certain interest as one of the methods of formation process of coagulation-crystallization structures on the base of hydraulic binders.

When slag or slag with additive “X” is introduced, the structure and morphology of cement stone’s specimens are changed.
The images of the reference specimen’s surfaces (figure 5) and the specimen with slag 2m (figure 6) have some differences mainly due to the fact that in the reference specimen, the crystallites of needle-like shape are shown more clearly whereas for the specimen 2, they are spread disorderly at some degree in amorphized structures. Fixation of amorphized gel-like structures is clearly observed for the specimen 3m (with the additive “X”) (figure 7). This effect could be explained by the modifying action of the additive “X”.

It is well known that the smaller the particles size, the better the substance’s microcrystalline structure and the higher the material’s property. The figures 6 and 7 clearly exhibit that the researched slag and the additive facilitate the particles bonding and forming the large aggregates. The particles size remains unchanged, but the packing density is increased. On the assumption of this, the authors can draw a conclusion that the use of these materials has a positive impact on the properties of cement composites.

4. Conclusions
In the paper, the possibility of application of metallurgy man-induced wastes (acid electric furnace slag of foundry process) as the fillers has been stated. Along with that, they could replace the most expensive concrete component – a cement binder.

The innovative complex additive on the base of oligomer caprolaktam by-products has been developed. The by-products have been extricated after the stage of granulated Poliamide-6 extraction.

The authors have carried out the investigation of the influence of slag and the additive on physical and mechanical properties and the structure of cement composite. The interrelations between structural characteristics of cement stone, the concrete property and the composition of the researched objects have been established.

It was stated by the experimental research that the additive on the base of oligomer caprolaktam wastes is an effective modifier for heavyweight concretes.

The most rational concrete composition allowing the use of man-induced recyclable by-products is the mixture of traditional components with 5% of the researched slag and the additive “X” for 0.3% of the binder weight.

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