Physicochemical studies of the structure of energy-saving compositions based on slags

Tetyana Kostyuk¹, Varvara Vinnichenko¹, Andrii Plugin², Olga Borziak²,³ and Artem Iefimenko²

¹ Kharkiv National University of Civil Engineering and Architecture, Sumska st. 40, 61002 Kharkiv, Ukraine
² Ukrainian State University of Railway Transport, Feuerbach sq. 7, 61050 Kharkiv, Ukraine
³ Email: borziak@gmail.com

Abstract. Blast furnace slags are subdivided into granular and dump. Granulated slag is widely used in the construction industry to production of Portland cement, Portland slag cement, slag-alkaline cements, and concretes based on these cements. Dump slag is of less use, because it has low activity. The phase composition of granular and waste slag was investigated by methods of physicochemical analysis. The slags contain minerals that are present in Portland cement clinker. Concrete samples were made using granular, waste slag and sand. Unsatisfactory results in compressive and flexural strength were shown by a sample made of only two types of slag. The best strength results were obtained for a composition in which there are three components: granular slag, dump slag (filler) and sodium hydroxide. Electronic images have confirmed the appearance of low-basic calcium silicates, which provide the strength of the cementless composite. The resulting concrete composition is resource-saving, because made from production waste. And it can be called energy-saving, because no energy is expended to obtain components. The ecological feasibility of the production of such concrete is due to the absence of emissions of pollutants into the atmosphere (including carbon dioxide), since the firing of cement clinker is not needed.

1. Introduction
Energy-saving and resource-saving technologies in modern building materials science occupy one of the leading places of scientific research and programs. Cement binders in the production of modern building materials in the construction of buildings and structures are one of the main components of composite materials [1-3]. At the same time, the production process of binders is the most energy-intensive stage of the entire technological process of production of composite materials.

Development of research aimed at finding an alternative replacement of cement materials with production waste is relevant. The relevance is due to the fact that this area is resource-intensive due to the replacement of substances of natural origin with waste. Modern research shows that slag composites are the most effective substitutes for cement binders in concrete [4, 5]. Energy is used for cement production [6], and when cement is replaced by slag, this energy is not used at all, i.e. it is stored.

The aim of the study is to assess the possibility of replacing a traditional cement binder with a composite binder based on slags.
To achieve this goal, a study of the phase composition of slags was carried out; samples of composite materials based on slags were made and their physical and mechanical properties were evaluated.

2. Bibliography analysis
Blast furnace slag is a waste product from pig iron production in a blast furnace. Depending on the cooling rate, slag is divided into granular and dump. Granular slags include substances in an amorphous state and have high chemical and hydraulic activity. Granulated slag is widely used in the construction industry. It is used in the production of Portland cement, Portland slag cement, slag-alkali cements, as well as concretes and products based on these cements. Slag is also widely used in road construction. Crushed granular slag is also widely used as an additive of a mineral binder in the production of dry building and mortar mixtures. Slowly cooled slags - dump - are crystalline substances, most often they show low chemical activity. For this reason, dump slag is of less use. The founder of the scientific direction for the use of blast furnace slag in building materials and products is V.D. Glukhovsky [6].

In recent years, the world has seen a significant increase in the use of slags. One of the reasons for expanding the production of slag concrete is a large supply of thermal energy in the slag. In addition, concretes with aggregate from blast-furnace slag have a number of advantages over traditional concretes. As it was established in [7-9], the surface layer of slags reacts with calcium hydroxide released during the hydrolysis of alite. In this case, an additional amount of calcium hydroxysilicates is formed. Calcium hydroxysilicates create an extremely strong bond between the aggregate and the cementitious matrix. The number of capillary channels in the concrete stone decreases. This leads to a significant increase in the corrosion resistance of concrete in comparison with traditional compositions in most corrosive environments. In addition, due to the specific structure and the absence of microgaps at the interface between the binder and filler, such concretes have good physical and mechanical characteristics. The resulting concrete composition is resource-saving, because made from production waste. And it can be called energy-saving [10], because no energy is expended to obtain components. The ecological feasibility of the production of such concrete is due to the absence of emissions of pollutants into the atmosphere [11, 12], (including carbon dioxide), since the firing of cement clinker is not needed.

3. Materials and methods
Slag produced at the Dnieper Metallurgical Plant was used for experiments: granular and dump. To study the phase composition of slags and composite materials, physical and chemical research methods were used. To determine the quantitative phase ratio in both slag samples, petrographic analysis of samples was performed. The samples were examined in immersion preparations under transmitted light using a MIN-8 microscope at ×100 - 400 magnification. The sample of granular slag had a light gray color, boiled when exposed to 10% HCl with the release of hydrogen sulfide (with a sharp smell of H₂S). X-ray structural studies of the phase composition of slag samples were performed on an X-ray diffractometer DRON-1.5. Filtered (Ni β-filter) Kα 1.2 - radiation of Cu-anode, U = 42 kV, I = 19 mA. Range of scanning angles - 2 Θ = 6 - 100°. Diffraction curves were recorded on the diagram tape of the potentiometer KSP - 4. The speed of the sample - 2°/min, the speed of the diagram tape - 10 mm/min. The JEOL LSM-840 scanning electron microscope was also used for the study.

4. Results of physicochemical research
The bulk of the sample is a colorless transparent isotropic glassy substance with a refractive index N ≈ 1.640 ± 0.005. On the surface of the grains of the glass phase there are films and smears of fine (particle size <0.004 mm) mixture of portlandite Ca(OH)₂ and calcite CaCO₃. The sample of granular slag had a light gray color, boiled when exposed to 10 % HCl with the release of hydrogen sulfide (felt a sharp odor of H₂S).
As impurities in the sample there are dense skeletal growths of gelenite 2CaO·Al₂O₃·SiO₂ and larnite (β - C₂S), oxeremanite 2CaO·MgO·SiO₂, fine aggregates with a predominance of portlandite with impurities of calcite. Calcite is presented in the form of individual crystals and aggregates of complex rhythmic-lobed shape, fine red-brown ferrites and, or calcium aluminoferrites, black non-magnetic grains of graphite.

The sample of slag dump had a gray color, boiled under the influence of 10 % HCl with the release of hydrogen sulfide (a sharp smell of H₂S). Impurities include rectangular crystals of gelenite with a size of 0.015 mm (on the largest side), grains of β - C₂S, small (up to 0.008 mm) crystals of pseudovolastonite α - CaO·SiO₂, growth crystals of belite β - C₂S and gelenite 2CaO·Al₂O₃·SiO₂. The impurities contain grains of rankinite 3CaO·2SiO₂ and, or montmorelonite, or mellite, calcite in the form of individual crystals and aggregates of complex paw-shaped shape up to 0.01-0.02 mm. In the sample there are significantly more fine aggregates of ferrites - calcium aluminoferrites, which usually "cement silicates". There are fine red-brown ferrites and, or calcium aluminoferrites, black non-magnetic grains of graphite, single grains of quartz. In the glass phase, "stars" characteristic of the crystallization of calcium sulfide CaS are visible.

The phase composition of the slag samples of the blast furnace granulated Dnieper Metallurgical Plant is: glass phase 75-85 %, growths of gelenite and laryngitis 3-5 %, β - C₂S 2-3 %, Ochermanite 1-2 %, portlandite 3-5 %, calcite 2-3 %, calcium ferrites and aluminoferrites 1-2 %, black nonmagnetic particles 3-5 %.

The glass phase exists in significant quantities. To obtain the binding properties of the glass phase, the slag must be activated.

X-ray diffraction studies of the phase composition of the slag samples showed that sample 2 (granular slag) has very weak diffraction peaks in the crystalline phases due to the high dispersion of the material. The main phases are the phases of Portland cement clinker - 3CaO·SiO₂ (alite) and 2CaO·SiO₂ (belite): 3.03; 2.84; 2.72; 2.66; 2.29; 2.20Å. Possible content of calcite 3.03 Å. Sample 3 (slag dump) also has weak diffraction peaks. The following phases are observed in the sample: 3CaO·SiO₂ (alite) and 2CaO·SiO₂ (belite): 3.03; 2.68; 2.57; 2.29; 1.97 Å. You can also select the phase of calcite - CaCO₃: 3.86; 3.03; 1.99 Å. The sample contains quartz - SiO₂: 4.23; 3.32; 2.44; 1.824 Å; gelenite - 2CaO·Al₂O₃·SiO₂: 3.70; 3.06; 2.38; 2.09; 2.44; 1.753; 1.508 Å; anorite – CaO·Al₂O₃·2SiO₂: 3.22 Å; iron - Fe: 2.50; 2.04.

The slag was dried to constant weight at a temperature of 100 ºC, cooled in a desiccator and examined on a scanning electron microscope. Electronic images of samples of the microstructure of granular and dump slag (figure 1-2) confirmed that the vitreous phase of granular slag (Figure 1) is fused with silicate splices and aluminane phase petals. In figure 2, the blast furnace slag sample is also represented by a glassy phase. Calcium aluminoferrites (in the upper part of the figure) as well as volostanite crystals, calcite cubes in the form of individual grains (in the lower part of the figure) are observed here.

Electronic images of ground samples of blast furnace granular and blast furnace slag showed that the main part is the vitreous phase. To obtain the binding properties of the slag, it is necessary to break the bonds of the silicate chains and release CaO from the vitreous phase of the slag.

5. Results of physical and mechanical research
A study was conducted to select the composition of heavy fine-grained concrete that does not contain Portland cement. They use a slag activator - sodium hydroxide. Blast furnace slag and quartz sand were used as active filler. Ground granular slag served as a binder. The test results are presented in table 1.
Table 1. The dependence of the strength of samples of slag mixtures on the composition.

| Composition             | Composition of the composite | Compressive strength, MPa  | Tensile strength in bending, MPa |
|-------------------------|------------------------------|-----------------------------|---------------------------------|
|                         |                              | 3 days                      | 28 days                         |
|                         |                              | 3 days                      | 28 days                         |
| 1                       | The slag is granulated + NaOH + sand | 3.0                        | 7.2                             |
| 2                       | The slag is granulated + NaOH + dump slag (as filler) | 3.8                        | 18.0                            |
| 3                       | The slag is granulated + dump slag control | collapsed                  | 13.9                            |

Table 1 shows that the best results in strength showed a sample where sodium hydroxide was used (as an activator), granular slag is a binder, dump blast furnace slag was used as a filler. Figure 3 shows that crystal hydrates are formed similarly to crystal hydrates of cement stone.
Figure 4 shows the microstructure of a sample of cementless composite, where instead of dump blast furnace slag as a filler used quartz sand. The structure is inhomogeneous, to the left of the quartz particle is a half-destroyed shell of slag, there is no connection into a dense monolithic structure of tumors of crystal hydrates. Separate cubes of calcite are visible on the surface of quartz grain, there are accumulations of portlandite and petals of hydroaluminates with felt-like hydrosilicates of calcium.

Figure 5 clearly shows the structure of the control sample, which consists only of ground granular and dump blast furnace slag. At magnification in the picture, Figure 6-7, it is seen that all structural components are combined with tumors of low-basic calcium hydrosilicates, compacted by calcite cubes, Figure 7.

Thus, the results of the study showed that the cementless composite, which consists of blast furnace granulated slag and dump slag, has a compressive strength of 18 MPa.

![Figure 5](image1.png)  
**Figure 5.** Snapshot of the microstructure of the control sample 3.

![Figure 6](image2.png)  
**Figure 6.** Snapshot of the microstructure of the control sample 3 at a magnification of x1000.

![Figure 7](image3.png)  
**Figure 7.** Microstructure of the control sample 3 at a magnification of x3000.
The use of blast furnace granular and dump slag in the production of concrete solves the problem [13-17]:

- conservation of natural and energy resources;
- improving the ecology of the environment (elimination of slag dumps, reduction of gaseous emissions into the atmosphere during cement production);
- solving a number of social problems (organization of additional jobs).

6. Conclusion
During the hardening of the composite, which consists of granular blast furnace slag, dump blast furnace slag and calcium hydroxide, low-basic hydrosilicates of calcium and calcite are formed. These crystal hydrates are insoluble and stable over time, which makes composites competitive with cementitious building materials.

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