New Binder Materials from Industrial Waste of the Ural Region

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Abstract

In the scientific article the results of development and research of technological and physico-mechanical characteristics of new type slag-alkaline binder on the basis of ground granulated blast furnace slag production company “Mechel-materials” and waste in ceramic production. A review of existing research on the subject. It is revealed that the increase in content and decrease in silicate module of liquid glass accelerates the processes of structure formation during solidification and slag cement increases the compressive strength and Flexural strength. Optimized the composition of the new type of binding agent. The proposed processing methods and established the validity of the beginning of industrial production of slag cement on the basis of wastes of the Ural region.

Keywords: ground granulated slag, Portland cement, slag-alkaline stone, liquid glass, silica module, compressive strength, cementless hydraulic binder

1. Introduction

The construction materials industry has a significant impact on the environment, which is defined by enormous volumes of production of materials for construction and significant energy costs. For example, in the production of Portland cement consumes up to 5% of world energy production. Today, the production volume of cement for reinforced concrete structures and products is closer to 3 billion tons [1, 2]. Due to the huge volume of production of concrete mixtures, the application of resource-saving technologies recycling waste is very important. Currently, to improve the environmental situation are wide-spread energy-saving technologies, in which raw materials it is possible to use industrial waste or products of their processing, in terms of industrial production makes a significant economic and resource effects.

The use of metallurgical slag as fine and coarse aggregates for heavy concrete is studied and implemented in industrial production in many countries. In the building materials industry is the most promising way of reducing the energy intensity of production is to replace Portland cement chemically bonded to binders alkaline activation,
which further gives environmental benefits. Economic efficiency of production is also high due to the lack of necessary capital investments in production equipment development, energy-intensive manufacturing operations.

Commercial production of slag cement began in Germany in 1865, and since 1880 more intensively slag cement used throughout Europe, including for the construction of the Paris Metro. European leaders in the production of this cement are the United Kingdom and the Netherlands, in Europe and Asia this type of binder is a priority means of reducing impact on the environment [1–7, 11]. In the USSR and in Russia research of the special slag binders was done by V. D. Glukhovskiy, P. V. Krivenko, E. K. Pushkareva, R. F. Runova, A. V. Artamonova, K. M. Voronin, E. V. Korneev, S. I. Pavlenko, L. I. Ryabokon, S. V. Bednyagin etc. [8–10].

2. Material and Theoretical Bases of Research

Slag cement is the hydraulic binder of high strength, consisting of fine ground slag with a predominance in the composition of \( \text{CaO}, \text{SiO}_2, \text{Al}_2\text{O}_3 \) (the total content of up to 95%) and alkaline activator curing (baking soda, liquid glass, etc) [4]. Upon receipt of slag cement granulated slag – blast, electrotermometria, aluminum potassium and non-ferrous metallurgy (smelting). The necessary conditions of the possibility of using slag is the presence of glassy phases that interact with the alkali in the process of hardening and high specific surface area of at least 300 m\(^2\)/kg.

With increasing content in the slag of small particles increases the rate of hardening and strength of the binder by increasing the number of defects in the structures and formations on the surface, with a large reserve of excess surface energy. As the alkaline component is most often used caustic and soda ash, potash, soluble sodium silicate, and alkaline industrial wastes, which allows obtaining significant amounts of slag binders. The optimum content of alkaline compounds in the binder is 2-5% by weight of the slag.

Compared with calcium compounds to the high activity of compounds of alkali metals allows to obtain rapid hardening, high-strength binders. The presence of alkalis intensificare destruction and hydrolytic dissolution of slag glass, formation of alkaline hydroalumination and creating an environment that promotes education and high resistance low-basic calcium hydrosilicates. Poor solubility of tumors, the stability of the structure in time determines the durability of slag-alkaline stone.

When using slag cement in concrete production, the resulting structure of cement stone is much less capillary pores than that of concrete with ordinary Portland cement. The difference between this binder of Portland cement is in high specifications of water resistance and frost resistance, as well as in low rates of shrinkage and creep.
<table>
<thead>
<tr>
<th>Material</th>
<th>Content (%)</th>
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<tbody>
<tr>
<td>SiO₂</td>
<td>35.7</td>
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<tr>
<td>CaO</td>
<td>40.1</td>
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<tr>
<td>MgO</td>
<td>5.5</td>
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<tr>
<td>Al₂O₃</td>
<td>14.4</td>
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<tr>
<td>Fe₂O₃</td>
<td>0.9</td>
</tr>
<tr>
<td>MnO</td>
<td>1.2</td>
</tr>
<tr>
<td>SO₂</td>
<td>1.5</td>
</tr>
<tr>
<td>Slag</td>
<td></td>
</tr>
<tr>
<td>Waste ceramic production</td>
<td></td>
</tr>
<tr>
<td>Slag</td>
<td></td>
</tr>
</tbody>
</table>

**Table 1**: Chemical composition of ground granulated blast furnace slag and ceramic waste production.

The Institute of new materials and technologies of Ural Federal University named after first President of Russia B. N. Yeltsin developed slag cement, consisting of 97% of industrial wastes of the Ural region. The mineral component of ground granulated blast furnace slag, the waste of a local steel production company “Mechel-materials”. The faculty of the Department “Materials in construction” and the Department “Chemical technology of ceramics and refractories” working for many years on the scientific direction of the waste of the industrial enterprises of the Urals for the production of new efficient building materials [9, 10].

Ground-granulated blast furnace slag is a man-made waste arising from smelting iron ore, which is produced by rapid water cooling of the slag melt. Production of ground slag was made possible with the installation of “Mechel-materials” modern grinding equipment — vertical roller mill with simultaneous drying of the Austrian company Loesche. Grinding of material takes place under high pressure using a roll rolling on the table, and the removal of material using a centrifugal separator, which allows to obtain a product with high specific surface 450 m²/kg. Crushed in a centrifugal-impact mill slag has particles of isometric shape with depreciable surface that increases the activity of slag.

The main mass of granulated blast furnace slag is a glassy phase containing in an amount of from 66,6% to 95%. In slags crystallized minerals two calcium silicate, mellilite, terfeit (see table 1).

Module basicity is the characteristic activity of metallurgical slags and their stability in limestone dissolution is determined by the ratio of the content in the slag oxides to the acid according to the formula:

\[
M_o = \frac{CaO + MgO}{SiO_2 + Al_2O_3}
\]  

where CaO, MgO – content in the slag relevant oxides, SiO₂, Al₂O₃ – content in the slag of appropriate acidic oxides.

For slag module basicity greater than one may apply all the alkaline compounds, or mixtures thereof. The module basicity of the studied ground granulated blast furnace slag 0.96, so the slag refers to the acidic lime and are not susceptible to decay.
The alkaline activator liquid glass, made of semi-industrial method with varying quality characteristics (siliceous module from 1.3 to 1.7, a density of 1500 kg/m$^3$) from waste ceramic production in Sverdlovsk region (see table 1). The dry matter content of liquid glass 35%.

Physical characteristics of ground granulated blast furnace slag are given in table 2. Obtaining liquid glass by the developed technology lies in a few simple technological operations:

- obtaining a powdery mixture of waste with 30% NaOH solution;
- low temperature treatment (90-95°C) with constant stirring for 4-6 hours;
- cooling the mineral water glass.

Properties of slag cement are controlled by changing concentration of components and depend on the type, mineral composition and specific surface of the slag, the type and concentration of the alkaline component. Water-binding ratio and the type of activator affects the strength of the slag cement. In the course of laboratory experiments that studied the effect of characteristics and the ratio of ingredients on rheological, structural and strength characteristics of slag cement:

- The dependence of the rate of structure formation from the silica module of liquid glass;
- Influence of density and concentration of liquid glass on the rheological properties of cement paste;
- Liquid glass silicate with different modules, the impact of the liquid glass content on the compressive strength of the hardened slag composite (see Figure 1).

The experiments are installed:
Compressive strength, MPa

![Diagram showing the dependence of compressive strength on the content of liquid glass silicate with different modules.]

**Figure 1**: The dependence of the strength characteristics of slag cement from the content of liquid glass silicate with different modules.

- Microscopic and rheological studies revealed that the increase in content and decrease in silicate module of liquid glass accelerates the processes of structure formation during solidification slag cement;
- the increase in the content of liquid glass in the range from 2 to 20% increases the compressive strength and Flexural strength slag cement up to 380% with other conditions constant;
- the optimum ratio of slag and liquid glass with silica modulus of 1.3 is 1:4, which allows to obtain a hydraulic binder with a compression strength of 86 MPa after curing for 28 days in air-humid conditions.

### 3. Summary

The Institute of new materials and technologies of Ural Federal University named after first President of Russia B. N. Yeltsin in the research laboratory of the Department “Materials in construction” of the conducted research and the obtained slag cement – an alternative to Portland cement. In the course of the experimental tests within the research studied the influence of properties and ratio on the quality characteristics of the new material and optimized its composition.

The result is a high strength cement-free hydraulic binder (slag cement) consisting of 97% of industrial wastes of the Ural region. Currently, the study of the properties of this
material based on metallurgical wastes continues. Preliminary economic calculations of material costs and the results of laboratory tests indicate the practical possibility and economic feasibility of industrial production of slag cement.

The use of technogenic raw materials in the production of artificial composite material will partially improve the environmental situation by means of the secondary use of waste, reduction of volumes of extraction of mineral raw materials and reduce emissions of fine mineral dust into the air of industrial areas in urbanized areas.

References


