Stabilization of metallurgical slug from arc steel-making furnaces

A N Bodyakov, K V Meshkova and G S Dukhovny

Belgorod State Technological University named after V.G. Shukhov, Kostyukov St., 46, Belgorod, 308012, Russia

E-mail: savaa72@mail.ru

Abstract. At the present time the deficit of stone construction materials for transport construction points to the need for improving the range of used materials. The experience of motorway construction in economically advanced countries shows that the deficit of materials and construction costs can be significantly reduced through extensive use of industrial wastes. One promising avenue of researches is the use of metallurgical production wastes. Main methods on the prevention of slag decomposition by its stabilization are considered. The principle of increasing the stability of stone slag materials by adding a stabilizer to the steel-making slag composition during slag removal from the arc steel-making furnace, ensuring slag stabilization and prevention of the silicate decomposition after cooling, is established. Processes of the slag structure formation during its stabilization are studied. Processes of crystallisation and change of structure of dicalcium silicate are shown. The decomposition of steel-making slag can be prevented by adding a chemical stabilizer into its composition. It is established that a stabilizing agent shall consist of metallurgical production wastes that allows to fully stabilize slag and keep high-temperature modifications of belite in it when cooled. The possibility of obtaining crushed slag with a stable structure achieved by a chemical stabilization of melted slag is shown.

1. Introduction

One of the primary reasons constraining the pace of motorway construction in the Russian Federation is a severe shortage of main road construction materials, including crushed stone. According to the general assessment [1, 2], steel and foundry industries in Russia collected in heaps more than 300 million tons of steel-making slags. As per the directive of European Commission and European Parliament on wastes and by-products, steel-making slag is classified as a nonwaste by-product [3]. Despite of a sufficient number of available slagheap recycling schemes, no solutions on the recycling of so-called self-disintegrating slag of the iron and steel Industry have been found to date. Self-slaking slags from arc steel-making furnaces (ASF) cannot be recycled with the use of schemes implemented in the industry, as they quickly turn into fine powder during solidification and cooling processes.

The reason of metallurgical slag decomposition is the polymorphic transformation of dicalcium silicate (C2S, belite) which is a part of its composition. There are five polymorphic forms of C2S at room temperature [3]. Due to a big difference in the lattice structure, transformation of \( \beta \)-C2S into \( \gamma \)-C2S is accompanied by the increase in volume by approximately 12% resulting in slag slaking.
To stabilize high-temperature modifications of belite and prevent its polymorphic transformation into a low-temperature modification, either quenching or addition of stabilizers is required. The general requirement to stabilizers is a similar size of ionic radii and charges of a stabilizing element and ions of dicalcium silicate\(^4 - 6\). While embedding into the structure of dicalcium silicate, they deform the belite lattice preventing the rotation of silicon–oxygen tetrahedrons and their transformation into low-temperature polymorphic modifications. \(^7, 8\)

Therefore, the purpose of this work is to study the influence of stabilizer addition to the structure and properties of steel-making slags. New technical solutions on recycling of melted slags allow to exclude removal of metallurgical slags to heaps and ensure their large-capacity use in various industries\(^9, 10\).

2. Materials and methods

To study physical, chemical and processing behaviour, samples of ASF slag obtained with the use of dry recycling process and slag cooled by a hydraulic method with the use of current process were taken. The chemical composition of selected samples is given in Table 1. There are no significant differences in the composition of slag cooled hydraulically or by air. The main difference may be in the defect rate of particles of slag cooled hydraulically or by air.

![Table 1. Chemical composition of slag and stabilizer.](image)

| Name                      | Content of oxides (%) |
|---------------------------|-----------------------|
|                          | CaO  | SiO\(_2\) | Fe\(_2\)O\(_3\) | MgO  | Al\(_2\)O\(_3\) | MnO  | Cr\(_2\)O\(_3\) | P\(_2\)O\(_5\) | ZnO | SO\(_3\) | K\(_2\)O | Na\(_2\)O |
| Air-cooled slag           | 39.73 | 30.04 | 17.39 | 8.67 | 2.39 | 0.82 | 0.25 | 0.17 | 0.16 | 0.05 | 0.04 | 0.14 |
| Hydraulically cooled slag  | 34.30 | 29.21 | 22.12 | 9.71 | 3.17 | 0.67 | 0.13 | 0.18 | 0.22 | 0.15 | 0.08 | 0.15 |
| Stabilizer                | 10.87 | 6.51 | 54.64 | 4.35 | 0.48 | 2.33 | 0.35 | –   | 3.85 | 1.16 | 6.19 | 8.05 |

Stabilizer chemical composition is given in Table 1. To stabilize slag, the weight of added portion of stabilizer granules was accepted as equal to 0–7 % of the slag weight in increments of 1 %. The portion was added into melted slag in the form of a paper envelope (to imitate a paper bag), affixed to the end of a 1.5-meter rod. The chemical composition of used raw and synthesized materials was determined with the help of an x-ray fluorescence spectrometer of ARL 9900 WorkStation series with integrated diffraction system. The scanning electron microscopy (SEM) was carried out to study the structure and composition of synthesized stone materials. Studies were carried out using the high-resolution scanning electron microscope TESCAN MIRA 3 LMU. The strength grade of crushed slag (crushability) was determined by the degree of destruction of grains in the water-saturated condition during the cylinder crushing test (GOST 32817-2014). Crushing strength grade was determined by weight loss of the crushed stone sample resulting from the impact of shock loads from steel balls and abrasion forces in the abrasion testing machine (GOST 32819-2014). Micro-Devaluation I abrasion grade was determined by weight loss of the crushed stone sample, resulting from abrasion of material grains in the presence of steel balls and water (GOST 32816-2014). Resistance of crushed slag grain structure to disintegration was determined by weight loss of the sample after storage in distilled water within 30 days and further three-time steam curing (GOST 32858-2014). The freeze resistance grade was evaluated by exposing slag samples to alternating cycles of freezing in the water-saturated condition and thawing in water (GOST 32863-2014). A stabilized part of slag was estimated visually. To estimate the percentage output of the stabilized fraction, sifting of unstabilized part through a sieve with a mesh width of 0.63 mm was carried out. The calculation of disintegrated fraction was evaluated by the weight of sieved substance.
3. Results and discussion

The crystal structure of slag in the initial state is uneven and zonal which is conditioned by a regular distribution of additives and inclusions (Fig. 1). Separate polycrystals of monticellite in the form of grains grow freely until contact with each other. Thickness of these crystals does not exceed 400 nm. Magnesioferrite is represented by isometric rounded crystals forming compact aggregates. Photomicrographs of slag clearly show merwinite crystals with a rounded shape, larnite crystals resemble merwinit crystals.

![Image of photomicrographs](image)

**Fig. 1.** Photomicrographs of initial slag after decomposition.

Addition of 1 % of stabilizer granules into melted slag ensures stabilization of 46.2 % of slag (Table 1). Addition of granulas in the proportion from 2 to 4 % of the weight of recycled slag results in the stabilization of more than 90 % of slag. The maximum percentage of stable fraction (100 %) can be observed in case of addition of 5 % of a stabilizer. Increase in the weight of a stabilizer over 5 % is accompanied by a partial decomposition of cooled slag (3.6–5.1 %) due to decrease of solubility of the added stabilizer as a result of temperature reduction in the crucible.

**Table 2.** Results of selection of the stabilizer portion weight.

| Stabilizer portion weight (% of slag weight) | Slag fully decomposed | Slag partially decomposed. There are unstabilized inclusions 53.8 % of weight | Slag didn't decompose. There are unstabilized inclusions 6.6 % of weight | Slag didn't decompose. There are unstabilized inclusions 4.7 % of weight | Slag didn't decompose. Separate pieces have cracks 1.5 % of weight | Slag didn't decompose during cooling (3.6 % of weight). A stabilizer didn't dissolve completely 96.4 % stabilized | Slag partially decomposed during cooling (5.1 % of weight) A stabilizer didn't dissolve completely 94.9 % stabilized |
|-----------------------------------------------|-----------------------|-------------------------------------------------------------------|-------------------------------------------------------------------|-------------------------------------------------------------------|-------------------------------------------------------------------|-------------------------------------------------------------------|-------------------------------------------------------------------|
| 0.0                                           |                       |                                                                   |                                                                   |                                                                   |                                                                   |                                                                   |                                                                   |
| 1.0                                           |                       |                                                                   |                                                                   |                                                                   |                                                                   |                                                                   |                                                                   |
| 2.0                                           |                       |                                                                   |                                                                   |                                                                   |                                                                   |                                                                   |                                                                   |
| 3.0                                           |                       |                                                                   |                                                                   |                                                                   |                                                                   |                                                                   |                                                                   |
| 4.0                                           |                       |                                                                   |                                                                   |                                                                   |                                                                   |                                                                   |                                                                   |
| 5.0                                           |                       |                                                                   |                                                                   |                                                                   |                                                                   |                                                                   |                                                                   |
| 6.0                                           |                       |                                                                   |                                                                   |                                                                   |                                                                   |                                                                   |                                                                   |
| 7.0                                           |                       |                                                                   |                                                                   |                                                                   |                                                                   |                                                                   |                                                                   |

Fig. 2 and 3 show the slag microstructure stabilized with 2 % and 5 % of stabilizer granules respectively. Petrographic studies of stabilized slag samples have shown that it has a tight porous structure of rounded pores up to bubbles of different shape, perceptible to the eye. The slag microstructure resem-
bles a porphyroclastic structure: respectively idiomorphic, bigger crystals of minerals are immersed into less decrystallized, cryptomeric mass of the same minerals. Individual specimens demonstrated a specific orientation of crystals, although variously oriented, deeply intertwined and alternating individuals and aggregates prevail (Fig. 2, 3).

Fig. 2. Photomicrographs of slag specimens and cleavages stabilized with 2 % of an additive.

Fig. 3. Photomicrographs of slag specimens and cleavages stabilized with 5 % of an additive.

Two phases are clearly seen in the microstructure of stabilized samples: siliceous belite crystals (matrix) with inclusions of calcium ferrites (2CaO·Fe₂O₃). Calcium ferrites form a three-dimensional grid in the matrix, evenly distributing throughout the sample volume. The three-dimensional grid in slag with 2 % of a stabilizer is formed by thin films. Increase of a stabilizer content up to 5 % leads to the formation of disperse particles of calcium ferrite with bigger volume ratio and more even distribution in the matrix volume.
Physical and mechanical properties of the obtained stone material are given in Table 3. It is worth mentioning that increase in the amount of added stabilizer does not affect strength properties of ready products but rises the output percentage.

Table 3. Slag physical and mechanical properties.

| Indicator name                  | Unstabilized slag | Stabilized slag |
|--------------------------------|-------------------|-----------------|
| Strength grade                  | M300              | M1000           |
| Micro-Devaluation abrasion      | Below the minimum | MD2             |
| Abrasion grade in the abrasion  | Below the minimum | I2              |
| testing machine                 | permissible value |                 |
| Freeze resistance grade         | Below the minimum | F50             |
| Structure stability             | Below the minimum | US1             |
|                                | permissible value |                 |

Physical and mechanical properties of broken slag not exposed to stabilization do not comply with minimum permissible requirements of the standard, such material cannot be used in the road construction. As per results of laboratory tests of samples, stabilized slag corresponds to strength grade in the water-saturated condition M1000, micro-Devaluation abrasion indicator MD2, abrasion grade in the abrasion testing machine I2, freeze resistance grade F50 and structure stability US1. Physical and mechanical properties of the obtained stone material allow to use it as base courses and surfacings in road structural layers.

4. Summary
Studies have shown that even distribution of a stabilizer in the volume of recycled liquid ASF slag ensures stabilization of high-temperature forms of dicalcium silicate (excluding silicate decomposition) during and after cooling. Addition of 5% of a stabilizer to melted slag is the best solution. When adding a stabilizer in lower volume, an incomplete stabilization of liquid melt composition occurs, resulting in partial or full slag decomposition when cooled. Addition of a stabilizer in bigger volume results in incomplete dissolution and recovery of stabilizing components by melted slag. Slag stabilization is ensured by calcium ferrites formed when using a stabilizing substance close by its composition to recycled slag. The obtained stone material can be classified by its properties as crushed stone which can be used for construction and reconstruction of motorways as base courses and surfacings. Stabilization of melted slag will prevent formation of fine dust from γ-decomposition of dicalcium silicate which will lead to reduction of the negative impact of decomposition products on the environment.

5. References
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**Acknowledgments**

This work was realized in the framework of the Program of flagship university development on the base of the Belgorod State Technological University named after V G Shukhov, using equipment of High Technology Center at BSTU named after V G Shukhov.