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# STATE-OF-THE-ART AND ANALYSIS OF CHARACTERISTICS, PROPERTIES, SIGNIFICANCE, AND APPLICATION PROSPECTS OF METALLURGICAL SLAGS

The review article is concerned with the modern state, analysis of characteristics, properties, significance, and prospects of the slags' application, which are wastes of ferrous and non-ferrous metallurgy. The material considers the structure of steelmaking slags, characteristics of steel slags, separation of slags by composition, as well as the world and Kazakhstan experiences of processing them, using environmental safety assessment. The article reviews and studies the methods of slag application in road construction, agriculture, casting technologies, manufacture of Portland cement, clay bricks, green concrete, *etc*. The article summarizes the practical experience of many scientists' research in the fields of metallurgical slag applications. The scientific novelty consists in the study of both the world and Kazakhstan experiences in the using metallurgical production slags based on practical data of researchers around the world with the identification of positive and negative properties of various slags under certain conditions. This topic will be of interest of scientists and researchers in the field of metallurgy and materials science. As found based on the obtained data, the extraction of metal from slag significantly reduces the cost; slag is recyclable after recovery of useful metals from it; reduction of slag dumps makes it possible to improve the ecological situation, as well as to free valuable land areas. The issues of identifying the peculiarities of mining and metallurgical industries' development and fundamentally new directions'

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elaboration, as well as unconventional ways of existing production technologies' improvement require further study.

**Keywords:** converter slag, blast furnace slag, ferroalloy slag, useful metals, production wastes, waste processing, recycling.

## 1. Introduction

Metallurgy is one of the national economy leading branches, which provides the rest of the country with all the necessary raw materials. Metallurgical slag is a by-product, in other words, concomitant waste in metal production. After depletion of metal, namely purification of multicomponent compound of metals and non-metals from valuable metal residues and their compounds, slag is sent to dump.

Metal slags are products of high-temperature treatment. These are silicate type wastes having a multicomponent structure. For a long time, slags were simply disposed, not presenting much interest. Everything changed in the second half of the 20th century. It was from this moment that metallurgy waste began to be actively used in construction, agricultural sector, in the laying of roads and many other areas [1].

Slags are produced in very large quantities in the smelting process, and huge waste sources need to be recycled. With the rapid growth of industrialization, the number of lands available for waste disposal is decreasing, that causes increasing of its costs. The effect of global warming and the natural resource are common environmental problems now. In addition, the land is filled with waste; side materials have led to significant pollution of air, water and soils, as well as adversely affect person, his life and health [2].

Metallurgical industry processes and reduces the volume of slag in order to ensure environmental protection. In addition, slags are potential source of valuable metals and an attractive alternative of primary raw materials processing (non-renewable resources — minerals), that allows to reduce the extraction of raw materials and reduce the area of slag dumps, in order to minimize environmental pollution, preserve and expand the country's raw material base.

The composition of slag plays an important role in its disposal. The most cost-effective method for reducing metallurgical dumps is its further processing. However, some industries still dispute the efficiency of recycling large amounts of slag produced. This important issue is being addressed now in several ways:

• due to the extraction of metal not from ore, but from slag, the cost of final products is significantly reduced;

• slag is recyclable after extraction of useful metals from it;

• the benefit of processing slag dumps lies in improving of ecological situation at a large radius from the dumping zone;

• reduction of slag dumps allows freeing valuable land areas [3].

Slag was first used in road construction in the Roman era, when slag crushed stone from the processing of raw iron was used in the construction of the roadway. The first modern roads in the construction of which slag was used were built in England in 1813, and after that, the use of slag quickly spread to the American continent. The use of slag in road construction there was recorded first in 1830. Already 15 years later, after good experience confirming the use of this material in road construction, slag began to be used in railway construction [4]. More mass use of slag in various activities began in the middle of 19th century with the discovery of hidden hydraulic properties of granular blast furnace slag. Since then, slag-casting blocks have been widely used in Europe and America for road pavements. Europe started using steel slag for phosphorus fertilizers as early as 1880. Due to its chemical composition, containing calcium oxide (CaO), iron oxide (FeO), silicon oxide ($SiO_2$), magnesium oxide (MgO) and manganese oxide (MnO), steel slag can be used in metallurgical plants for sintering and converter processes [5, 6], as well as for wastewater treatment due to its porous structure and alkalinity [7, 8].

Currently the authors have formulated the basic concepts of waste-free and low-waste technologies, main tasks and directions of their development were outlined, in particular, features of development in mining and metallurgical industries in the development of fundamentally new directions, non-traditional methods and improvement of existing production technologies were revealed [9, 10].

## *2. Structural Analysis, Separation by Composition and Usage of Steelmaking Slags*

Metallurgical slags are divided by types of smelted metal into blast furnace, converter, electric steel smelting, ferroalloy and cupola. They can be combined into two groups: slags of primary metallurgical processes, *i.e.*, blast furnace and ferroalloy slags, and slags of secondary processes — steelmaking cupola [1].

*Blast furnace slags* are obtained during sintering of charge ore part. The outlet of blast furnace slag, its composition and properties depend on chemical and mineralogical composition of iron ores waste rock, ash, coke, sulphur content in the charge, nature of reduction process and the thermal state of the furnace, as well as on the type of smelted iron.

*Steelmaking slags* are formed because of cast iron and scrap impurities oxidation, melting of lime, bauxite, melting spar, iron and manganese ores, as well as dissolution and destruction of the furnace lining.

*Ferroalloy and cupola slags* are the result of processes of reducing elements from oxides that are part of ore or concentrate. The reducing

*Fig. 1*. Decaying (*a*) and non-decaying (*b*) slag rocks [11]

agents are C, Si, and Al. The amount and properties of slag depend on process technology, type and quality of raw material used, grade of the alloy to be produced, lining composition of the melting units and melt receptacles.

According to its composition, slags of ferrous metallurgy after cooling are divided into decaying (Fig. 1, *a*) and non-decaying (Fig. 1, *b*) rocks. The second group takes the form of rocky formations. It is customary to divide second category according to its mineral composition:

• silicate — breaking down into fine powdered particles during recycling;

• lime — crushed into crumbs of different sizes;

• manganese — dissolving in a moist environment;

• glandular — susceptible to cracking under the influence of moisture.

Slags that do not decay under the influence of the external environment are used as the basis for the production of crushed stone and other types of building stones. Depending on the treatment method, they are cooled and crushed by a semi-dry method in special drums or subjected to a “wet” action using strong water jet. In this case, the material is immediately grounded in the process of blast furnace leaving and then it is blown for drying and final cooling.

Granular slags, — wastes of ferrous metals smelted in blast furnace, — are the most accessible for further processing. They are source of crushed stone — cheaper than natural stone. This finished product is used:

• for road construction, as filling;

• in the production of reinforced concrete products;

• in agriculture, as a drainage for soil;

• in the manufacture of concrete, as aggregate.

Slags from production of ferroalloys and steel are added to cement in the form of powdered impurities. This composition acquires increased chemical resistance. In combination with Portland cement clinker, physical properties of the material can be further improved. Granular slags

*Fig. 2*. Moulding of molten slag [12]

mixed with liquid glass or soda are used for making concrete mixtures capable of hardening at lower temperatures [11]. At the same time, different finished products, such as paving tiles, curbstone, interior flooring, can be obtained during the process of slag casting. In addition, this method allows creating pipes and fittings to them, elevation finishes. Production costs are significantly reduced, and in terms of its characteristics, finished material is not inferior to traditional analogues made of metal or reinforced concrete. Casting is carried out by forming of molten slag (Fig. 2). The technology of production of double-layer metal-slag pipes, branches of slag plates and other products has been developed. Pipes are intended for pneumatic-hydraulic transportation of abrasive materials — crushed stone, sand, ores, concrete, *etc*. [12].

Mineral wool can be obtained from viscous blast furnace, steelmaking, and cupola raw materials. For this liquid-heated composition is sent to exhaust machines to form fibres. The boards obtained by this way can be very rigid or rather soft, have an elastic or dense structure. Due to synthetic polymers and bitumen binders, they retain their properties for a long time.

As a result of the extensive research conducted by authors, it was found out that the main consumer of slags is a cement industry using up to 75% of their volume for production of hydraulic additives for production of Portland cements, blast furnace slag cement, and slag-alkaline cements of high classes. Many cement plants are located directly near metallurgical plants. This allows using slags in the production of high-quality cements efficiently. Wastes from non-ferrous metallurgy enterprises are also widely used. Slags and sludge of nonferrous metallurgy mineral waste have received some usage. Studies of physicochemical, physicomechanical and technological properties of the slags formed in mining and metallurgical plants as a result of non-ferrous metal ores processing have shown that slags obtained during the processing of copper nickel ores are suitable for the production of building materials. Their wear and acid resistance significantly exceed the same characteristics of blast furnace slags. Granular slags of these industries are good raw material for preparing of autoclave hardening binders [13]. However, at present, the share of slag processing at nonferrous metallurgy enterprises remains at a low level. Most of them are dumped or thrown into the waste dumps. In natural form, these granular slags can be used as fine aggregates in concrete.

Waste products are not used to insulate surfaces exposed to precipitation, or concrete screeds are applied over the backfill to protect against waterlogging. It has been proven that wet slag loses the properties of an insulator [12].

The main difference between the nonferrous and ferrous metallurgy slags are as follows. The non-ferrous metallurgy slags are characterized by a high content of iron oxides, reduced composition of magnesium and calcium oxides. The properties of non-ferrous metallurgy slags depend on their chemical composition and differ from ferrous metallurgy slags in their high specific gravity, variety and additional content of valuable rare metals. If during the smelting of ferrous metals the output of slags per 1 ton of metal is 0.1–0.7 tons, then in non-ferrous metallurgy for the production of 1 ton of metal it is obtained 100–200 tons of slags [14].

According to the World Steel Association [15], global steel production increased from 2 million tons in 1950 to 18.69 million tons in 2019. China produces the largest amount of steel (53%), followed by the European Union (8.5%), India (6.0%), and Japan (5.3%) [16]. Due to the consumption of large quantities of raw materials and energy steel industry also produces a large number of various by-products and types of waste as a result of complex manufacturing processes such as raw material handling, iron smelting, steel smelting and rolling. It was produced 27.68 million tons of slag in 2019, including 16.56 million tons of blast furnace slag and 11.12 million tons of steelmaking slag from these by-products [17].

## 3. Description and Worldwide Results of the Slag Research

Method of carbothermal reduction was investigated as one of steel slag processing methods, which makes possible to process valuable metals from steelmaking slag and use the residual slag in the glass and ceramic industries. Scientists Ferreira and Pasetto [14] have confirmed that steel slag can be effectively used as an aggregate for roads and hydroelectric power plants construction due to its beneficial physical and mechanical properties, including hardness, wear resistance, adhesion, roughness and toughness. The authors have studied that grains with the size of sand are formed in the production of granulated slag.

Due to its composition, this material has excellent hydraulic properties; and in the presence of an appropriate activator (such as calcium hydroxide) will behave similarly to Portland cement. Foamed slag is more porous and has a lower volume than air-cooled slag [18]. The current amount of ferrous slag from the Sisak and Split smelters located in Croatian landfills is estimated at about 1.8 million tons. The large amount of this material lying in landfills and its potential prompted Croatian researchers to investigate the possibilities of various uses of slag in construction or replacement of traditional materials, primarily as an aggregate in concrete mixes. Steel slag contains a significant proportion of free calcium and magnesium oxides [19], which are responsible for the greatest shortage of this material and its limited used in road construction. As steel slag is very voluminous, its volume can be changed by as much as 10% (free calcium and magnesium oxides hydrate under the influence of moisture, causing large volume changes) [7]. Aeration of slag under atmospheric conditions is considered one of the most suitable methods for eliminating of this unfavourable property. Weathering period varies depending on the method of application and the type of slag, *i.e.* the amount of free oxides of calcium and magnesium. Therefore, sometimes only a few months of aeration in atmospheric conditions or accidental irrigation with water are required [8].

According to Belgian and Dutch national standards, one year of weathering is sufficient for the use of slag in road construction, while German scientists have known that it is necessary to weather the slag for as long as 18 months before using. These large volume changes limit the use of steel slag in hard pavement [20], however, in asphalt mixes, they can be controlled or even used to improve the properties of embedded material on curbs or unpaved parking lots. The presence of more than 1% free calcium oxide causes another disadvantageous property of the steel slag, namely the appearance of a white powder as a precipitate. Free CaO from the filtrate binds to water, forming calcium hydroxide Ca(OH), which in atmospheric conditions reacts with carbon to form calcium carbonate (CaCO) [21]. It settles as a white powder and can cause obstructions in drainage systems and water retention. These obstacles are especially dangerous in the event of freezing, which causes great damage to the road surface structures. However, this, unlike expansion, cannot be prevented by weathering of slag. Among other characteristics of steel slag, two more should be distinguished — a large bulk density of steel slag and specific gravity of 1600–1920 kg/m. The grains of this material are pointed, with a rough surface, and this is especially suitable for use in asphalt mixtures due to the increased adhesion between the road surface and the wheels. A large angle of internal friction (40–45°) contributes to a high stability of materials and a value of up to 300% [22]. On the other hand, in the works of Shen [23], it was proved that the presence of free CaO increases the resistance to cleaning, adhesion between the aggregate grains and the binder, thereby increasing the durability of the road surface. The very nature of the slag as a by-product of the steelmaking process contributes to the increase in adhesion because it does not contain clay. Confirmation of the advantages of using slags in asphalt mixes was obtained as a result of studies carried out at McMaster University [24], which showed that the modulus of elasticity of asphalt mixes with steel slag is 20–80% higher than that of mixes with standard aggregate at a temperature of 29 °C.

The author of Emery's works [25] claims that the Poisson's ratios of these mixtures are lower than standard, which, in turn, additionally indicates a higher stability in use and resistance to the occurrence of plastic deformations [26]. This makes it possible to design pavement structures with a reduced thickness of asphalt concrete mixtures up to as much as 37 mm.

Due to this, one of these mixtures' disadvantages can be compensated — the bulk density is 15–25% higher, which contributes to an increase in the cost of fresh asphalt concrete mixtures transportation. The disadvantages also include an increased need for a binder due to granular sharp edges and rough surface. Steel slag can be used as an aggregate in both hot and cold asphalt mixes. The only limitation indicated for this use is the amount of slag aggregate. More precisely, mixtures with 100% steel slag as filler proved to be resistant to cracking at large distances and high bulk of the mixtures due to sharp edges and regular grain shape [27]. In particular, it is indicated in the works of scientists Ahmedzade and Sengoz [28] that in such mixtures there may be an increased need for a binder in the process of production and removal of bituminous binder during the disposal of the road surface. For this reason, it is recommended to use the slag only as a substitute for smaller or larger aggregate grains when applied to wear-prone asphalt layers. Asphalt mixes are more resistant to friction when they contain 30% slag and that 75% slag replacement of limestone aggregate has significantly improved the mechanical properties of the asphalt concrete. The above study also included electrical conductivity testing, which confirmed that the slag was the aggregate with the best performance. Electrical conduction can be useful during the usage of special winter maintenance techniques (for instance, runways servicing).

Studies by Sue *et al.* [26] showed that the restoration of a rigid pavement with a new layer of asphalt concrete from mastic, in which slag is used as an aggregate, leads to a slow expansion of the built-in layer (in 7 days, only 1%). At the same time, the adhesion bond between the aggregate grains and binder is extremely good, which leads to increased resistance of the coating against wear, tear, deformation at high temperatures and cracking at low temperatures.

For example, in the Lipetsk region of Russia, there are no deposits of durable stone materials and road organizations mainly use imported road construction materials. At the same time Novolipetsk Metallurgical Plant (NLMK) is located in the region where millions tons of slag, including converter slag, are produced annually as by-products. Local scientists carried out studies to determine the degree of slag decomposition, which does not adversely affect the structural and mechanical properties of asphalt concrete, and allows expanding the range of road construction materials, improving the environmental situation, and reducing dumps area and cost of road construction. Converter slag of the oxygen-converter shop No. 2 of NLMK was determined like an object of study, which presents black-brown material with a dense, less often porous structure, with a high density.

One of the characteristics of slag materials is their activity. Studies have been carried out [29] on the influence of the age of the slag from the moment of its arrival on the hydraulic activity. For this purpose, the slag material was ground in a ball mill to the fineness of grinding the mineral powder. Cylindrical specimens were prepared from the obtained slag flour with a sealing load of 10 MPa and water to slag ratio of 0.16. After fabrication, the samples were kept in air for 7 days, and then placed in a humid environment and the compressive strength was determined. The results of testing the activity of slag materials depending on the age of the slag from which the slag flour is made, and on the holding time of the samples in humid conditions are presented in Table 1.

An analysis of the results presented in Table 2 indicates that the converter slag is classified as inactive slag, since the compressive strength at 30 days is less than 6 MPa. With increasing storage term of samples of slag flour in wet conditions, its strength increases, especially intensively after 30 days [29].

*Table 1.* **Influence of slag age on its hydraulic activity [30]**

| The age of the slag from which the slag flour is produced, days | Compressive strength, MPa, samples stored in humid conditions, days | | | | |
|---|---|---|---|---|---|
| | 7 | 28 | 60 | 120 | 360 |
| 20 | 1.23 | 2 | 9.05 | 8.05 | 14.5 |
| 30 | 1.48 | 1.96 | 8.08 | 9.2 | 15 |
| 60 | 1.7 | 2.3 | 9.6 | 10.11 | 17 |
| 90 | 1.7 | 2.2 | 9.9 | 10 | 17.6 |
| 120 | 1.58 | 2.2 | 9 | 9.3 | 16.5 |
| 180 | 1.5 | 2 | 8.8 | 9.1 | 17 |
| 270 | 1.44 | 2 | 8.7 | 8.8 | 17.5 |
| 320 | 1.33 | 1.9 | 9.2 | 9.4 | 18.9 |
| 360 | 1.28 | 1.6 | 7.5 | — | — |

It was turned out that with an increase in the shelf life of slag flour samples in humid conditions its strength increases, especially intensively after 30 days. The age of converter slag at the time of its grinding into slag flour also has a significant effect on tensile strength. The maximum tensile strength is observed for samples of all test ages, prepared from converter slag, the age of which at the time of grinding into slag flour is 60–90 days. This is due to such factors as carbonization of free lime, hydrolysis and hydration of slag minerals [30].

*Table 2.* **Influence of converter slag samples age on decomposition degree and on the physical and mechanical properties of asphalt concrete [29]**

| Age of samples, days | Average density, g/cm$^3$ | Water saturation, % volume | Swelling, % of volume | Tensile strengths in compression, MPa, at temperature, °C | | Coefficients: water resistance/ long water resistance |
|---|---|---|---|---|---|---|
| | | | | 20 | 50 | |
| slag age 1 month, decay **5.3%** | | | | | | |
| 2 | 3.19 | 0.68 | 0.70 | 4.1 | 1.0 | 0.98/1.15 |
| 28 | 3.14 | 1.51 | 0.46 | 4.7 | 1.8 | 0.94/1.17 |
| 90 | 3.17 | 0.98 | 0.91 | 4.3 | 1.8 | 0.98/1.13 |
| after steaming in an autoclave | | | | | | |
| 2 | samples collapsed | | | | | |
| slag age 2 month, decay **2.4%** | | | | | | |
| 2 | 2.85 | 3.81 | 0.72 | 5.2 | 2.1 | 0.98/0.86 |
| 28 | 2.83 | 3.88 | 0.19 | 6.4 | 1.8 | 0.81/0.83 |
| 60 | 2.83 | 4.18 | 0.58 | 6.6 | 2.2 | 0.82/0.98 |
| 90 | 2.85 | 4.70 | 0.34 | 7.1 | 2.1 | 0.83/0.75 |
| steaming in an autoclave | | | | | | |
| 2 | 2.71 | 6.05 | 0.00 | 1.7 | 0.6 | 1.11/1.05 |
| slag age 4 month, decay **1.7%** | | | | | | |
| 2 | 2.80 | 5.49 | 0.09 | 4.2 | 2.1 | 0.97/0.98 |
| 28 | 2.87 | 4.06 | 0.07 | 4.3 | 2.2 | 0.93/0.91 |
| 60 | 2.96 | 3.03 | 0.00 | 5.5 | 1.5 | 0.85/1.02 |
| 90 | 2.81 | 5.87 | 1.76 | 5.0 | 1.1 | 0.77/1.08 |
| 180 | 2.82 | 4.13 | 0.89 | 4.8 | 1.2 | 0.91/0.91 |
| after steaming in an autoclave | | | | | | |
| 2 | 2.75 | 7.63 | 0.70 | 2.6 | 0.9 | 0.88/0.97 |
| slag age 7 month, decay **1.27%** | | | | | | |
| 2 | 2.68 | 3.17 | 0.00 | 6.1 | 2.8 | 0.9/1.15 |
| 28 | 2.66 | 3.57 | 0.32 | 6.0 | 3.0 | 1.07/1.15 |
| 60 | 2.67 | 3.66 | 0.94 | 7.2 | 2.5 | 1.11/1.11 |
| 90 | 2.69 | 1.74 | 0.00 | 10.9 | 2.6 | 0.86/1.05 |
| 180 | 2.67 | 2.99 | 0.00 | 8.1 | 2.6 | 0.85/0.75 |
| after steaming in an autoclave | | | | | | |
| 2 | 2.58 | 7.58 | 0.00 | 5.6 | 1.5 | 1.07/1.10 |

Silicate decomposition of slag occurs during the transition of dicalcium silicate from the β-form to the γ-form, which causes an increase in the volume of substance and creates high internal pressures - pieces of slag are cracking, and some of them are disintegrated into flour. Ferrous decomposition occurs after the slag has been wetted with water, when iron sulphide transforms into iron hydroxide and pieces of slag are cracking under the action of internal pressures. Lime decomposition occurs when the minerals of converter slag interact with water. The decay time is long, since it occurs in the places where the inclusions of free lime and metal come into contact with atmospheric moisture. During the heat treatment of the slag for 6 hours, according to GOST 3344, all types of decomposition occur [31].

The influence of decomposition degree on the mechanical properties (crushability, abrasion and frost resistance) of converter slag with a fraction of 5–10 mm was studied in different periods of aging of the slag under natural conditions [32]. The stability of the physical and mechanical properties of asphalt concrete mixtures based on converter slag depends on decomposition degree. The greatest decomposition of converter slag is observed in the initial period from the moment of its arrival. With an increase in the shelf life, the decay rate decreases. To clarify the degree of decomposition at which the converter slag can be used, samples were made from slag held in air for various periods. After each aging period of the degree of slag, decomposition in an autoclave was established, samples were moulded, and the properties of asphalt concrete at the age of 2 days and after steaming in an autoclave were determined. In addition, the physical and mechanical properties were studied after exposure to air for 28, 60, 90, and 180 days. This research technique made it possible to judge the change in the properties of asphalt concrete on converter slag, depending on the degree of decomposition [33]. Table 2 presents data of converter slag samples age influence on decomposition degree and on the physical and mechanical properties of asphalt concrete.

For a more detailed study of the structural and mechanical properties of asphalt concrete based on converter slags with an unstable crystal structure, samples were formed from asphalt concrete mixtures with different slag aging (1, 2, 4, and 7 months) and tested at the age of 2, 28, 60, 90, and 180 days from the date of manufacture. Analysis of the data showed that samples of asphalt concrete mixtures with a slag decomposition rate of 5.3% have a fairly high compressive strength at temperatures of 20 and 50 °C, low water saturation, high coefficient of water resistance and long-term water resistance. A certain increase in tensile strength over time, especially at a temperature of 50 °C, is explained by hydration processes and the interaction of functional groups of bitumen with calcium and magnesium oxides of converter slag [34, 35]. A bituminous membrane on the surface of the slag material prevents moisture

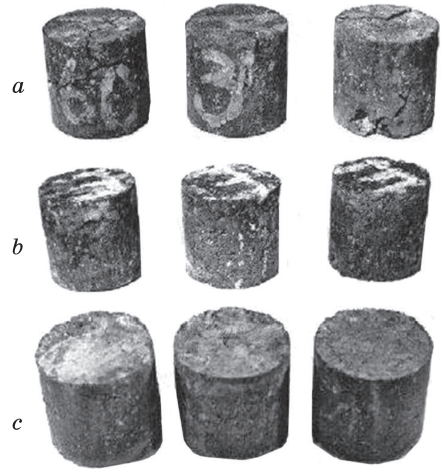


*Fig. 3.* Condition of asphalt concrete after 180 days of water saturation with the degree of decomposition of converter slag 5.4% (*a*), 1.7% (*b*), and 1.27% (*c*) [29]

penetration, and therefore, during a long time storing in air, asphalt does not show visible damage. However, steaming in an autoclave, asphalt concrete samples are destroyed.

Cracks, chips and slag decomposition products appear on them. With a decrease of decomposition degree to 2.4%, asphalt concrete samples withstand autoclaving, but the values of compressive strength dropped sharply below the required standard. This indicates unstable structure of slag asphalt concrete and the possibility of its destruction during the operation of asphalt concrete pavements. With the degree of converter slag decomposition of 1.27%, asphalt concrete retains stable properties when exposed to air samples and after autoclaving. After steaming in an autoclave, the samples do not change shape and no cracks or chips are observed on them. Studies have shown that such a degree of decomposition occurs approximately not earlier than after 7–8 months of storage of converter slag in air with intensive irrigation. Figure 3 shows 3 samples with varying degrees of converter slag decomposition with 5.4% (*a*), 1.7% (*b*), 1.27% (*c*) after 180 days of water saturation.

Thus, it follows from the above that converter slag with a decomposition rate no more than 1.2–1.3% is suitable for the production of asphalt concrete. Insufficient corrosion resistance of asphalt leads to premature deterioration of the pavement. Asphalt concrete is intensively destroyed by prolonged exposure of water and alternating freezing-thawing [29]. Since the converter slag has an unstable structure, prolonged exposure of water should accelerate these processes. The study of long-term exposure of water was carried out with slag with varying degrees of decomposition and duration of saturation with water during 2, 28, 90, and 180 days [35]. As a rule, with an increasing of samples storage time in water, the water saturation increases. This is due to the partial decompression of the samples during saturation with water and creation of pore reserves during slag decomposition, which were previously inaccessible for water migration. With an increase in the duration of water saturation with a slag decomposition rate of 1.7% or more, the compressive strength decreases, but remains above the standard requirements. However, on the sample with a slag decomposition degree of

5.4%, cracks and chips are observed after 180 days. Swelling is observed on samples made from slag with a decomposition rate of 1.7%, and these phenomena are not observed on samples made of slag with a decomposition rate of 1.27%. The results of work [34] lead to the conclusions following below.

(i) Converter slag with a decomposition rate less than 1.27% can be used in road construction for asphalt concrete pavements creation. Asphalt concrete has high heat, water and frost resistance.

(ii) The possibility of using converter slag will expand the range of local building materials, which will lead to decreasing of road construction cost.

(iii) The use of converter slag will significantly improve the ecological situation, reducing the area occupied by the dumps [30].

Authors of Ref. [27] described the use of slag obtained from the production of stainless steel as an aggregate in cement-base levels in the construction of plateau warehouse in Belgium. Changes in the volume of the manufactured material by 2.3% were observed after 7 days and its compressive strength reached 7 MPa that confirms the effectiveness of this material using. The same authors presented another example of slag using, which is a waste product from stainless steel production in rigid road structures for coiled concrete pavements built on a suburban road. However, some problems were observed due to the reaction of free calcium oxides and water, fractures and swelling of the road surface appeared. The problem of hydration of free oxides can be solved by the correct choice of the particle size distribution of the slag, as described in Ref. [26]. Research results have shown that fine-grained slag (0–4 mm) has great expansion properties, comparing with coarse slag. This fact is an advantage, provided that slag is used as a binder, the proportion of which, in comparison with the filler is low; in this case, the expandability of the slag is lost in the total mass of the mixture.

The authors also studied the use of metallurgical slag in the production of building materials. For example, as found in Ref. [36], the total Fe content and the leaching potential of heavy elements such as As, Cr, and V are key factors influencing the use of steel slag in cement production. One of the alternative options for such an application of non-ferrous metallurgy slags is the manufacture of Portland cement. The use of non-ferrous metallurgy slags as a replacement for Portland cement is often limited in the literature to low volume (<30%) replacement, since high volume replacement often results in low strength. However, for lead–zinc slag in $60 \div 40$ ratio with Portland cement, the compressive strength of 90 MPa reaches 85% of the reference value of Portland cement [37], and indicates that in some cases it is possible to replace Portland cement in large volumes. Moreover, previous work on blended cement composed of 70% Portland cement and 30% non-ferrous slag has shown that the compressive strength after 90 days is higher than the reference. Therefore, replacing a large volume, up to 70% of Portland cement with slag from non-ferrous metallurgy is more effective. In addition, the authors of this article familiarized themselves with the studies [38] of nonferrous metallurgy slag hydrated mixtures phase composition with Portland cement, since the higher iron content in these systems compared to classical Portland cement systems can affect the hydration products. In the experiment water-cooled slag of non-ferrous metallurgy was used [39], chemical composition and set of phases of which were analysed by the method of x-ray fluorescence. The slag was ground to a specific surface area of $4500\pm200$ cm$^2$/g, determined by the Blaine permeability method and mixed with cement CEM I 52.5N in the ratios $30\div70$, $50\div50$, and $70\div30$%. After 28 days, the hydration was stopped by solvent exchange with isopropanol and diethyl ether, followed by drying under low vacuum at room temperature. Then the phase assembly was investigated using x-ray and thermogravimetric analysis (TGA), which was carried out at a flow of $N_2$ equal to 100 ml/min with a heating rate of 10 °C/min. The TGA results showed that the amount of CH decreases as the slag content increases. This was expected due to the lower Portland cement content and lower CH production, as well as the pozzolanic reactions. Mixing PC with slag of 30, 50, and 70% did not give any clear new phases in comparison with pure PC at 28 days. However, the formation of x-ray amorphous phases and an increase in iron inclusion with an increase in the slag content in these phases cannot be ruled out. The slag increased the compressive strength in the late stage, while the strength at 28 days still reached 47 MPa when replacing the PC by 50%. Since the initial strength was low, slag/PC blended cements can be a suitable alternative to PC for applications where low initial strength is acceptable, provided that durability aspects are not affected [39].

One of the most effective ways to improve the properties of the cementing agent was discovered and described in Ref. [22]. Slag of electric arc furnace was melted and cooled under the water stream; it resulted in the significant changes in the composition and structure of the slag. The results of laboratory tests showed that this procedure increased the hardness of the pozzolan by 4 times. Authors of Ref. [40] investigated an environmentally friendly building material, so-called "green concrete", using slag as a partial or complete replacement for concrete constituents such as cement, fine or coarse aggregate. Concrete in which waste slag is used as at least one of its components in the production process does not have a negative impact on the environment. To obtain environmentally friendly concrete, cement is first replaced with granular blast furnace slag, coarse aggregate is replaced with recycled aggregate, and water is replaced with recycled water. Cement production generates an average global $CO_2$ emission of 0.81 kg per kg of cement produced by calcining of raw materials and burning fuels. In order to reduce the environmental hazard, alternative raw materials will be used, which will allow to reduce greenhouse gas emissions [41]. In the experiment, cement was replaced by slag from the ferrous metallurgy GGBFS by 60%, 70%, and 80% by weight, while the replacement of recycled aggregate and circulating water was 100%. Given the recent challenges of global warming, the need for environmentally friendly materials is a revolutionary requirement. Based on the experiments, the authors made the following conclusions:

• the compressive strength of green concrete decreases when replacing 60% by 13.51%, when replacing 70% by 32.6%, when replacing 80% by 42.6% compared to ordinary concrete;

• the tensile strength of green concrete decreases: when replacing 60% of the mass by 7.9%, replacing 70% by 18.9%, replacing 80% by 25.9% compared to ordinary concrete;

• the flexural strength of green concrete when replacing 60% decreases by 6.6%, replacing 70% by 17.3%, replacing 80% by 23.10% compared to ordinary concrete.

Thus, the researchers concluded that replacing 60% of the mass of ordinary concrete with slags from ferrous metallurgy is acceptable for use as an alternative to ordinary concrete, since the change in strength is minimal [42].

No less effective and promising is the experience of using metallurgical waste in the form of blast furnace slags and dust from flue gas filters of an electric arc furnace for brick production [43, 44]. Both wastes have been tested in full-scale trials [45], resulting in clay bricks with performance characteristics comparable to those of commercial products [46]. Steel slags have only been studied for their potential use in cementitious [45] or innovative ceramic materials [44]. The purpose of this study was to evaluate the feasibility of steel slag processing in the production of clay bricks through laboratory and industrial testing. Slag from conventional steel processing was selected as it represents the best prospect for reuse, since, firstly, it is the most common residue formed in metallurgical plants, and secondly, it does not contain a large amount of potentially hazardous elements, such as chromium, nickel or molybdenum [47]. The experiment was based on slag samples from three steel plants, as well as three clay mixtures from brick plants located next to the steel plants. Technological behaviour was assessed by simulating the brick making process in laboratory conditions and full-scale tests at an industrial plant, including milling (<1 mm), vacuum extrusion, drying and firing. The effect of slag on drying behaviour is more or less the same for all the studied clays. In particular, the increase in the percentage of slag affected [48]:

• significant reduction in drying shrinkage;

• reduction of mechanical resistance;

• clear decrease in hygroscopicity;

• there is a slight tendency towards increased sensitivity to drying and an increase in the shrinkage phase with loss of weight.

The processing of steel slag into clay brick has been made possible through laboratory tests, confirmed by full-scale industrial tests [49]. During extrusion, the ductility remained more or less constant with increasing slag content, while the amount of water decreased slightly. After firing, moderate changes in brick properties are observed: the presence of slag mainly contributes to an increase in porosity. The main limitation is the decrease in mechanical strength, which, however, is negligible when adding a slag of 2–3 wt.% [50]. This detrimental effect on both adobe and fired bricks appears with relation to the fact that slag particles act as major defects in the microstructure, concentrating stresses during mechanical testing [51]. The presence of slag does not significantly affect flowering and soluble salts. Roasting, apparently, ensures that the slag practically becomes inert and there are no signs of the formation of hexavalent chromium, which has pronounced general toxic, carcinogenic and mutagenic properties [49].

In work [52], a practical technological scheme for Al-containing slag processing was proposed with the aim of its further use as a secondary refractory dusting material (SRDM), determining positive influence of SRDM on the quality of refractory ceramic moulds for casting investment. Its use contributes to a nine-fold increase in the strength of refractory ceramic moulds compared to a mould made of quartz sand and an increase in gas permeability by 15 and 33% compared to moulds made of fused aluminium oxide and quartz sand. The SRDM application for the formation of the ceramic coating determines the formation of aluminium hydroxide micelles with a negative charge on a contact diffuse layer. The interaction of oppositely charged micelles $Al(OH)_3$ and $SiO_2$ promotes close interaction of particles of the secondary refractory dusting material with each other. The models were made by pressing a model suspension composition by introducing refractory dust-like filler into the finished binder. The theoretical substantiation of the ceramic mould layers using SRDM formation makes it possible to explain the decrease in roughness characteristics on the surface of alloy castings by investment.

There are studies [53] showing that the complex processing of aluminium salt slags makes it possible to use processed products as additives in non-stick paints, refractory concrete compositions for lining smelting furnaces, *etc*. The products of processing of aluminium salt slag can also serve as additives to the main sand mixtures [21].

Authors of Ref. [54] point out that the biggest problem with internal slag recycling in steel mills is the enrichment of P and S. In addition, the amount of free CaO and MgO is an important factor that should be considered when using steel slag in construction, as it affects volume stability. On the other hand, the content of free CaO and MgO in steel slag makes it possible to reuse it for capturing and storing carbon dioxide [54, 55].

Foreign studies have shown that components of steel slag that are useful for stimulating plant growth, such as Si, Ca, Mg, P, and Fe can be reused for fertilization and soil improvement. Article [55] cites soil and river surveys around steel mills and nearby warehouses for over 36 years, reporting that toxic slag tends to seep into groundwater and nearby rivers, thereby harming the environment.

In Kazakhstan, blast furnace slags are most often used in the cement industry. Also in this industry the use of ferroalloy, steelmaking, nonferrous metallurgy slags is wide spread. The work [56] describes a production that provides a high chemical resistance of cement, which can be used even in aggressive environments. It is obtained by joint grinding of metallurgical slag, gypsum and lime. Slags are also used as active additives to Portland cement clinker or instead of clay. Depending on the proportions taken, it can be obtained ordinary cement or cement with increased resistance. Slag-alkali cements are obtained by joint grinding of granular slags, caustic or soda ash and water glass. Such hydraulic binders are water-, bio-, heat-, corrosion resistant and high-strength. Concretes made with their addition withstand the effects of oil products, weak acids and harden at low temperatures.

Slag crushed stone is widely used in construction, which successfully replaces natural. It is obtained by crushing dump slag or casting using a special technology. It is tested for resistance to degradation before usage. The material is abrasion resistant, withstands high and low seasonal temperatures. It is used as filler for various types of concrete. For heavy concrete products, dump or cast crushed stone serves as a large filler, and granular slag — for small ones [57].

In work [58], crushed stone from slag pumice is intended for light products, which is obtained by swelling with the use of mineral gas formers with rapid cooling of the slag mass. Then it is crushed into fractional crushed stone. This material has found wide application in road construction as a reliable and at the same time cheap material. It is used for the preparation of substrates, as well as in the production of slag binders for road surfaces, preparation of asphalt concrete. The authors of Ref. [58] cite the following technology: slag casting is used to obtain tiles and stones for paving sidewalks, making curbs, floor coverings for interiors, pipes, facade slabs and other products. In many respects, they are not inferior to their reinforced concrete and steel counterparts. They are obtained by pouring molten metallurgical slags into moulds supplied directly from blast furnaces. Such a production process is very economical — no additional resources are required to melt raw materials, transport and store them. The manufacturing technology is simple, the casting of such items is more economically profitable than the manufacture of artificial stone, and the mechanical properties are not much different from their analogues [56].

In addition, excellent materials are obtained from metallurgical slags — slagositalls. They consist of a glassy amorphous mass and the smallest glass crystals of different types and colours. Properties depend on the feedstock and manufacturing technology. The process takes place in a glass furnace. Metallurgical slags, sand and other additives are used as raw materials. Slagositalls are distinguished by high strength, close to cast iron and steel, but at the same time, they are 3 times lighter. These materials are easy to process and they are in great demand in construction. They are well-drilled, polished, cut. Slagositalls are widely used for the manufacture of durable products and as finishing materials: pipes, bearings, optical instruments, electrical insulators, grinding parts of mechanisms, chemical equipment, facing plates for facades and interior walls, floor coverings, windowsills, roofs, balconies, *etc*.

No less popular material that is made from metallurgical slag is slag wool, which is used for the production of heat-insulating products. About 80% of mineral wool is obtained from blast-furnace slags. Slags of non-ferrous metallurgy and cupola slags are also used for these aims. Raw materials with optimal viscosity are selected for the production of mineral fibres by the drawing method. Slag melt is obtained in bath or cupola furnaces, which is then processed into fibre. Cotton wool can be made of 3 types: for plates of increased rigidity, for semi-dry pressing of products, for hot pressing. Based on mineral wool, various products, such as plates, cylinders can be obtained, where bitumen, emulsions and synthetic polymers are used as binders [49].

Cinder block structures consist of screenings, cement and water. Currently, all buildings with their use are sound- and heat-proof. The main advantage of the cinder block implementation is its low cost and the availability of its constituent components. Prices for this material are lower than for brick, foam concrete, *etc*. [57].

## 4. Conclusions

World and domestic experience shows that the use of many types of secondary material resources is technically feasible and economically profitable. The recovery of raw materials from waste in the industrially developed countries of the world is a matter of national importance, which made it possible to solve the economic and technological problems associated with waste processing [2].

Increased attention to the use of secondary material resources is explained, on the one hand, by the depletion of mineral reserves, and, on the other, by the direct economic benefit from the use of additional raw materials. For the Kazakhstan metallurgy, the problem of waste is of particular relevance due to the high level of their specific generation per unit of metal products: 1.5–3.0 times higher than in developed countries. This determines high resource and energy intensity of domestic metallurgical enterprises and environmental pollution in the regions where they are located. In addition, the development of ferrous metallurgy in the second half of the XX century showed that metallurgical enterprises have abundant opportunities for the processing of various types of waste produced by humanity: from automobile scrap metal to household waste.

It is generally accepted that fabricated mineral raw materials are a competitive, promising, constantly replenished mineral resource. Wide involvement in the processing of secondary resources of the metallurgical industry will ensure saving of material and technical resources, development of waste processing industry and reduction of environmental pollution [3].

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## СУЧАСНИЙ СТАН І АНАЛІЗ ХАРАКТЕРИСТИК, ВЛАСТИВОСТЕЙ, ЗНАЧИМОСТИ ТА ПЕРСПЕКТИВ ЗАСТОСУВАННЯ МЕТАЛУРҐІЙНИХ ЖУЖЕЛІВ

Оглядова стаття стосується сучасного стану, аналізи характеристик, властивостей, значущости та перспектив застосування жужелів, що є відходами чорної та кольорової металурґії. У матеріялі розглядаються будова жужелів від виробництва сталі, характеристики жужелів чорної металурґії, поділ жужелів за складом, а також світовий і казахстанський досвіди з пероблення із застосуванням екологічної оцінки безпеки. У статті оглядаються та вивчаються методи застосування жужелю у дорожньому будівництві, сільському господарстві, технологіях лиття, у виготовленні портландцементу, глиняної цегли, зеленого бетону тощо. Стаття узагальнює практичний досвід досліджень багатьох учених у галузях застосування металурґійних шлаків. Наукова новизна полягає у вивченні як світового, так і казахстанського досвіду застосування жужелів металурґійного виробництва на підставі практичних даних дослідників усього світу з виявленням позитивних і неґативних властивостей різних жужелів за певних умов. Розглядувана тема буде цікавою науковцям і дослідникам у галузі металурґії та матеріялознавства. На підставі одержаних даних було виявлено, що вилучення металу із жужелю значно понижує собівартість; шлак піддається утилізації після вилучення з нього корисних металів; скорочення жужільних відвалів дає змогу поліпшити екологічну ситуацію, а також звільнити цінні земельні площі. Питання виявлення особливостей розвитку гірничо-металурґійних виробництв і розроблення принципово нових напрямів, нетрадиційних способів удосконалення наявних технологій виробництва потребує подальшого вивчення.

**Ключові слова:** жужіль конвертерний, жужіль доменний, жужіль феростопний, корисні метали, відходи виробництва, перероблення відходів, рециклінґ.