www.czasopisma.pan.pl PAN POLSKA AKADEMIA NAUK www.journals.pan.pl

GOSPODARKA SUROWCAMI MINERALNYMI – MINERAL RESOURCES MANAGEMENT

2022 Volume 38 Issue 4 Pages 153–172

DOI: 10.24425/gsm.2022.143625

IWONA JONCZY[1], BARTŁOMIEJ GRZESIK[2], ANDRZEJ NORBERT WIECZOREK[3],
ANNA GERLE[4], PAWEŁ NUCKOWSKI[5], MARCIN STASZUK[5]

Characteristics of the phase and chemical composition of blast furnace slag in terms of the possibility of its economic use

Introduction

The reuse of smelter slags to produce materials for use in road construction is an increasingly popular form of waste recovery. However, the development of urbanization and shrinking deposits of natural resources force the search for new, alternative sources of raw materials, inter alia, for the production of road aggregate. As a result, companies producing road construction materials, concrete, and various types of aggregates are increasingly

✉ Corresponding Author: Iwona Jonczy; e-mail: iwona.jonczy@polsl.pl

[1] Silesian University of Technology, Faculty of Mining, Safety Engineering and Industrial Automation, Gliwice, Poland; ORCID iD: 0000-0003-2635-8484; e-mail: iwona.jonczy@polsl.pl

[2] Silesian University of Technology, Faculty of Civil Engineering, Gliwice, Poland

[3] Silesian University of Technology, Faculty of Mining, Safety Engineering and Industrial Automation, Gliwice, Poland

[4] Łukasiewicz Research Network, Institute of Ceramics and Building Materials, Refractory Materials Division in Gliwice, Poland

[5] Silesian University of Technology, Faculty of Mechanical Engineering, Gliwice, Poland

© 2022. The Author(s). This is an open-access article distributed under the terms of the Creative Commons Attribution-ShareAlike International License (CC BY-SA 4.0, http://creativecommons.org/licenses/by-sa/4.0/), which permits use, distribution, and reproduction in any medium, provided that the Article is properly cited.

www.czasopisma.pan.pl PAN POLSKA AKADEMIA NAUK www.journals.pan.pl

turning to artificial aggregates. These are defined as aggregates of mineral origin, obtained from material produced as a result of an industrial process involving thermal treatment or other modifications. A significant part of this group are aggregates produced on the basis of metallurgical slags, especially steel slags and blast furnace slags (Shi 2004; Reddy et al. 2006; Sofilić et al. 2010; Václavík et al. 2012).

This article focuses on blast furnace slags, which are a by-product of the blast furnace process during the smelting of iron ore into pig iron. In practice, blast furnace slags are widely used in the construction industry and road building, as a basis for the production of, for example, cements, road binders, and slag bricks. They are also used in the production of concrete floors, mortars, and plasters (Sheikibrahim et al. 2018; Zulu et al. 2019). Blast furnace slag is increasingly used as a valuable material in the production of hydraulic binders, especially of cement that improves the mechanical properties of concretes (Kefeng 1998; Lizarazo-Marriaga et al. 2011; Zhu et al. 2012; Arora et al. 2016). A wide application of slags is described by Joulazadeh and Joulazadeh (Joulazadeh and Joulazadeh 2010), who point out that, apart from the above-mentioned applications, slags, due to the presence of iron droplets in their composition, can be a secondary source for the recovery of this metal. The favorable physical and mechanical properties of slags, apart from aspects of economics, are undoubtedly an asset when deciding to use them instead of natural raw materials. In addition to the above, there is also the ecological aspect because by using waste materials, the environmental interference that occurs during the opencast mining of natural aggregates is reduced, it is necessary from the viewpoint of sustainable development (Yuksel 2018). Moreover, this means waste utilization through secondary management (Patra and Mukherjee 2017; Senani et al. 2018). Parron-Rubio et al. (Parron-Rubio et al. 2019) demonstrate that substituting cement with slag has two distinct benefits; it minimizes the amount of waste, and secondly, it reduces the consumption of cement and therefore contributes to the reduction of CO_2 emissions needed for its production. Blast furnace slag can make up to even 90% of cement mixtures (Çelik and Nalbantoglu 2013; Öner and Akyuz 2007; Khatib et al. 2005).

The goal of the study was to determine the mineralogical and chemical characteristics of blast furnace slags.

1. Characteristics of blast furnace slags – literature review

Blast furnace slag is a by-product of pig iron smelting in a blast furnace at a temperature of 1400 to 1600°C. The furnace charge in the blast furnace process consists of iron ore, coke, and fluxes (limestone, dolomite). Fluxes are used to lower the melting temperature of the ore, but most importantly to facilitate the separation of metal from the ore by combining with barren rock, resulting in a by-product of molten slag on the surface of the pig iron. After separation from the pig iron, the slag is subjected to a granulation process by means of rapid cooling with water or air. Generally, blast furnace slag can be divided into four types depending on the cooling method: air-cooled blast furnace slag; expanded or foamed slag; palletized slag and granulated blast furnace slag (Cabrera-Madrid et al. 2016; Górażdże Group 2022; Construction Portal 2022). The rapid cooling of the slag aims to develop its appropriate microstructure. It prevents the formation of bigger crystals, resulting in a granular material that comprises almost 95% of the compound of the alumina-silicate of non-crystalline calcium (Cabrera-Madrid et al. 2016). This structure of slag, the main component of which is glass, influences the appropriate level of slag activity, making this material a valuable component of cement. The chemical composition of blast furnace slags is dominated by CaO (30–45%), SiO_2 (30–48%), Al_2O_3 (15–25%), Fe_2O_3 (0.5–2%), and other oxides in lower quantities (Shetty 2013). Václavík et al. (Václavík et al. 2012) also point to the possibility of small amounts of sulphides, especially of CaS, MnS, and FeS, in the chemical composition of blast furnace slags. Pulverised blast furnace slag is slightly alkaline and presents a solution pH that is within the range of 8 to 10; however, slag leachate can exceed a value of 11, which may be disadvantageous due to the possibility of corrosion in elements (e.g. aluminum) which come into contact with the slag (Wang 2010).

The way slag is cooled affects its hydraulic properties, for example, air-cooled slag does not present the same hydraulic properties as water-cooled slag. When it is slowly cooled with air, its compounds can reach a greater degree of crystallization, which would result in a material with low reactive activity. The type of slag used as cementing material is the blast furnace granulated material; accelerated cooling of melted slag by applying water on its surface results in the formation of vitreous material characterized by a certain degree of activation (Malhotra and Mehta 1996). Granulated slag is most frequently crushed and used as aggregate in concrete composition or as road aggregate (Giergiczny 2019). Such slag has good hydraulic properties, and when properly granulated and activated, it exhibits binding properties, i.e. when combined with water, it binds and hardens in the same way as Portland cement does. The hydration process of cement in the presence of granulated blast furnace slag is more complex than the same process for clinker phases, but the reaction products are always the same and are hydrated calcium silicates and aluminosilicates. According to Singh et al. (Singh et al. 2015), the use of granulated blast furnace slag as an aggregate in concrete by the replacement of natural aggregates is a very good idea because its impact strength is considerably higher than that of natural aggregate.

2. Methods

Laboratory research included:
- analysis of chemical composition (XRF),
- X-ray spectral microanalysis,
- scanning microscopy,
- identification of phases by means of x-ray diffraction (XRD).

In order to determine the chemical composition of the slag by means of X-ray fluorescence (XRF), the magnetic parts were first separated from the slag; the sample was then ground to a grain size below 63 μm using a tungsten carbide lined mill and dried; the ignition loss was determined at 1,025°C. The sample, roasted to a constant weight, was melted with a mixture of lithium tetraborate, lithium metaborate, and lithium bromide (66.67, 32.83, and 0.5%) of flux purity for XRF (from Spex). The weight ratio of the sample to flux was 1:9. Samples for analysis were prepared by melting to destroy their mineralogical and granular structure. The samples prepared in this way were measured using a PANalytical MagiX PW2424 spectrometer calibrated with the JRRM 121-135, JRRM 201-210, JRRM 301-310 series of certified reference materials, from the Technical Association of Refractories, Japan. Magnetic parts separated from the slag sample at 0.46% h were dissolved in aqua regia and the Fe content of the resulting solution was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Shimadzu ICPE 9800 plasma excitation emission spectrometer.

The sulphur content of the slag was determined using a Leco SC 144 DR sulphur and carbon analyzer with a resistance furnace. The sample, with the addition of vanadium pentoxide, was burned in an oxygen stream at 1350°C. The SO_2 content of the resulting gas was determined by infrared absorption measurement.

X-ray spectral microanalysis was performed using an X-ray microanalyzer type JXA 8230 from JEOL. Analyses were conducted using metallographic specimens dusted with a thin layer of carbon to transfer the electric charge. Surface X-ray distributions of the elements were performed using energy-dispersive spectroscopy (EDS). Local quantitative analyses of selected grains were conducted using wave dispersive spectroscopy at a voltage of 15 kV and a beam current of 30 nA.

Microscopic observations were carried out with a scanning electron microscope (SEM) using secondary electron detection SE at an accelerating voltage of 20 kV and at a magnification of 60–1000×. The qualitative analysis of the chemical composition in the micro areas of the material studied was performed by energy dispersive X-ray spectroscopy (EDS) at an accelerating voltage of 20 kV. Prior to testing, the samples were sprayed with a thin layer of gold to ensure electrical charge dissipation during the test.

Phase composition studies were performed in a Panalytical X'Pert PRO MPD X-ray diffractometer equipped with a cobalt anode X-ray tube (λKα = 0.179 nm) and a PIXcel 3D detector. Diffractograms were recorded in Bragg-Brentano geometry in the 15–100° 2Theta angle range with a step of 0.026° and a counting time of 80 seconds per step. X-ray qualitative phase analysis was performed using HighScore Plus software (v. 3.0e) and the dedicated PAN-ICSD inorganic crystal structure database. The glass content was determined by the XRD method using an internal standard which was added to the sample. Standard quantitative analysis was then performed. Due to the presence of glass, the standard content was overestimated, which made it possible to determine the amount of glass.

3. Results

The tests were conducted using granulated blast furnace slag obtained from the current production of one of the Polish metallurgical plants operating on the basis of the blast furnace process (Figure 1).

Macroscopically, the slag was characterised by a white colour, a fine-grained structure, and a loose texture. Observation of the slag grains using scanning electron microscopy indicated that their surface was not homogeneous and fine crystallites of silicate phases could be observed, with crystallization stopped by the rapid cooling of the slag.

When observing the surface of the slag grains using scanning electron microscopy, fine crystallites could be distinguished, surrounded by a microcrystalline mass (Figure 2).

Fig. 1. Granulated blast furnace slag

Rys. 1. Żużel wielkopiecowy granulowany

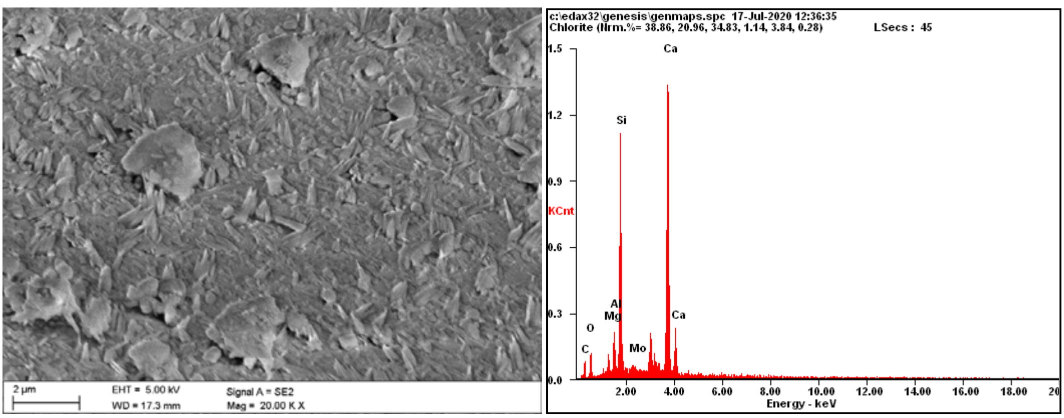

Fig. 2. Surface of blast furnace slag grain in an SEM image along with EDS analysis

Rys. 2. Powierzchnia ziarna żużla wielkopiecowego w obrazie SEM wraz z analizą EDS

More detailed information on the components of the tested slag and their chemical composition was provided by X-ray spectral microanalysis (Figure 3 and 4; Table 1).

On the presented micrograph (Figure 3) it can be clearly seen that the predominant component of the slag is glass (points 002–004 according to Figure 1), which was formed as a result of its rapid cooling. In the chemical composition of the glass, Ca (33.51–33.67%) is the most abundant, accompanied by the presence of Si (18.48–18.64%), Al (4.35–4.39%),

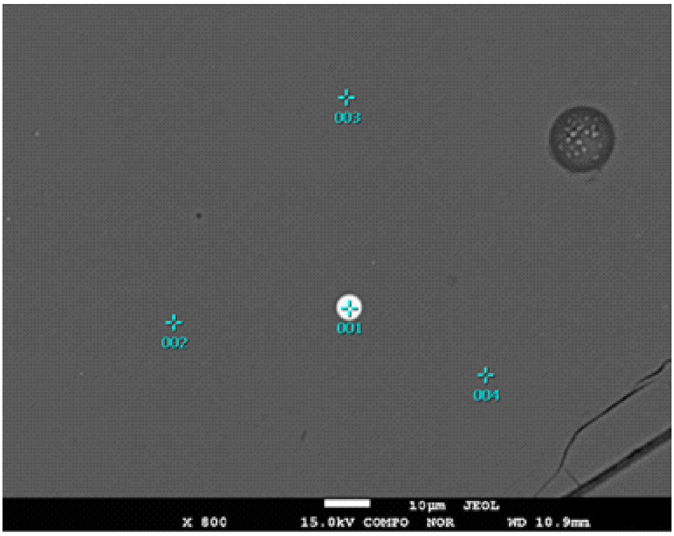

Fig. 3. Micrograph of blast furnace slag; glass (points 002–004) with metallic precipitate (point 001); X-ray spectral microanalysis

Rys. 3. Mikrofotografia żużla wielkopiecowego; szkliwo (punkty 002–004) z wytrąceniem metalicznym (punkt 001); rentgenowska analiza spektralna w mikroobszarach

Table 1. Chemical composition of glass and metallic precipitate according to Figure 3

Tabela 1. Skład chemiczny szkliwa oraz wytrącenia metalicznego według rysunku 3

Point no.	Elemental content (% by weight)													
	O	Al	Si	Mg	Ca	Fe	Mn	Ti	V	Ni	Cr	Zn	Pb	S
001	0.14	0.00	0.06	0.00	1.02	94.50	0.08	0.00	0.07	0.00	0.01	0.09	0.02	0.02
002	38.54	4.35	18.48	3.51	33.61	0.06	0.12	0.20	0.00	0.00	0.00	0.05	0.80	0.80
003	38.79	4.39	18.64	3.45	33.51	0.03	0.06	0.20	0.03	0.03	0.02	0.03	0.84	0.84
004	38.67	4.35	18.61	3.52	33.67	0.06	0.07	0.16	0.01	0.01	0.01	0.01	0.82	0.82

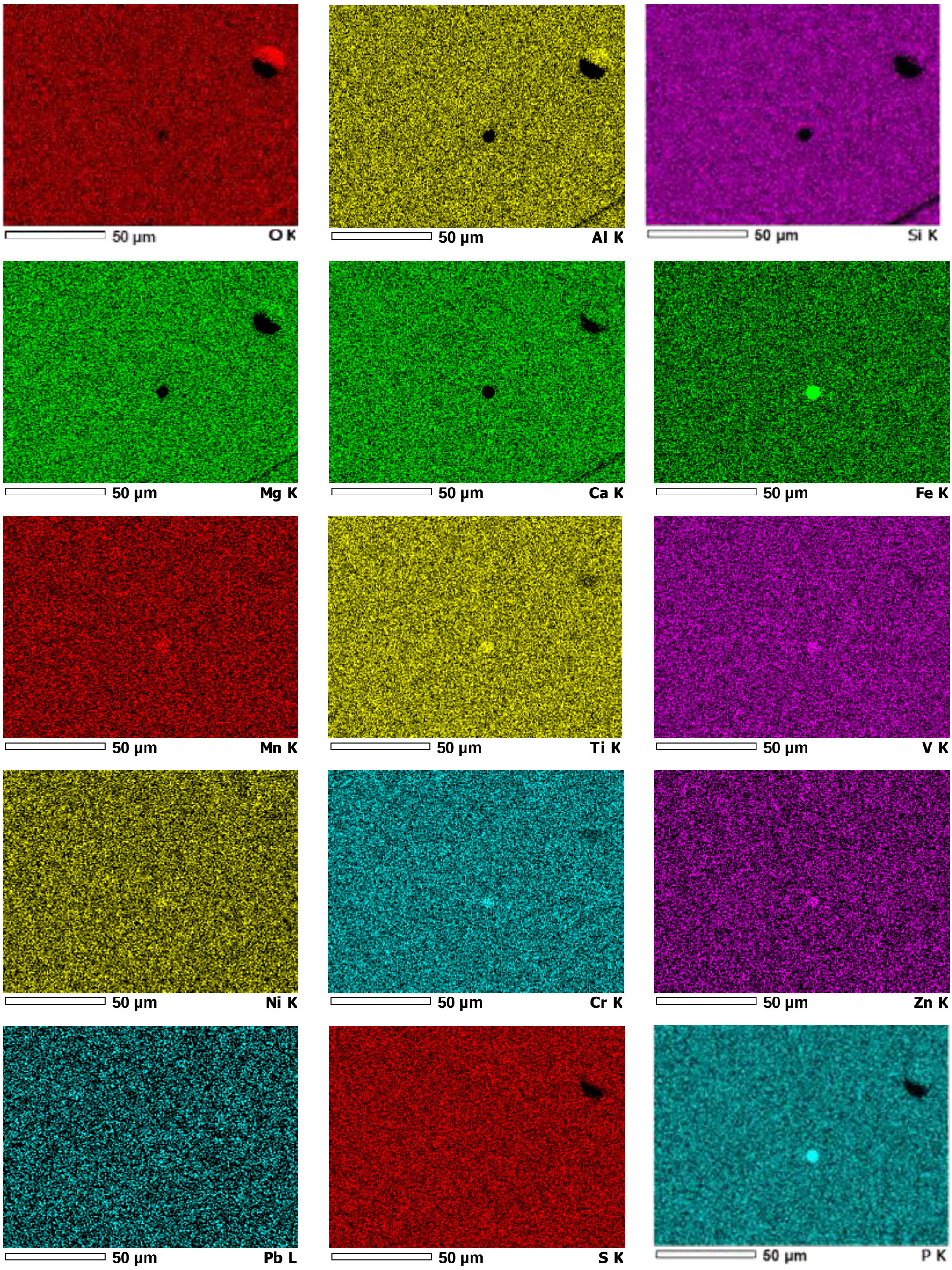

Fig. 4. Surface distribution of elements according to Figure 3; X-ray spectral microanalysis

Rys. 4. Rozkład powierzchniowy pierwiastków według rysunku 3; rentgenowska analiza spektralna w mikroobszarach and Mg (3.45-3.52%). Other elements such as S and P are also dispersed in the glass, along with heavy metals: Fe, Mn, Ti, V, Ni, Cr, Zn, Pb. The precipitate occurring in the vicinity of the glass (point 001 according to Fig. 3) is a metal drop consisting of almost 95% metallic iron accompanied by P at the amount of 3.91% and admixtures of other elements, including heavy metals: Zn (0.11%), Pb (0.09%), Mn (0.08%), V (0.07%). The presence of oxygen in the metallic precipitate indicates a progressive oxidation process.

Apart from the above-mentioned microstructure, which is typical for blast furnace slags and their components, periclase and dicalcium silicate precipitate was observed in some places on the grain surface (Figure 5 and 6, Table 2 and 3).

Periclase forms precipitate of various shapes. The most common are oval or spherical forms, though in the studied slag, also skeletal forms of accumulations were observed (Figure 6). The chemical composition of periclase showed admixtures of other elements, such as heavy metals, including Cr.

Dicalcium silicates are present as crystallites forming skeletal structures, which indicates that their crystallization was stopped by the rapid cooling of the slag. Dicalcium silicates also contain Ti, Mn, V, Zn and Mg.

In order to verify the obtained results, additional tests were performed by means of XRD analysis which confirmed that the predominant component of the blast furnace slag is glass for which an extensive effect was marked on the X-ray diffraction patterns between

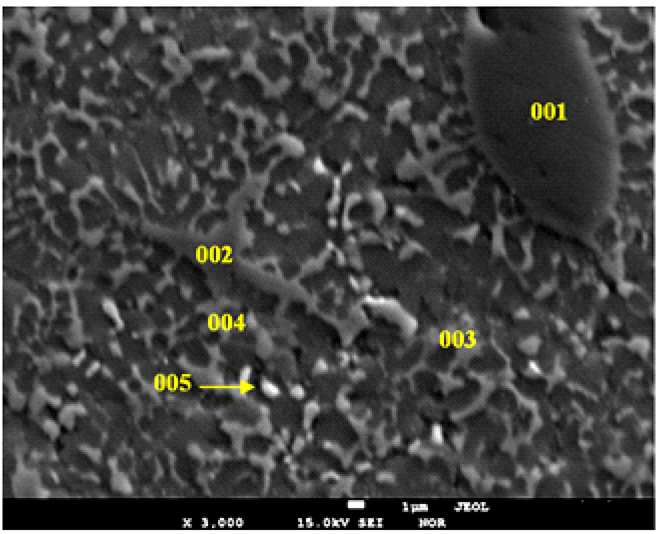

Fig. 5. Micrograph of blast furnace slag; quantitative analyzes made of the selected points: glass (points 002–004) with metallic precipitate (point 001); X-ray spectral microanalysis

Rys. 5. Mikrofotografia żużla wielkopiecowego; analizy ilościowe wykonane z zaznaczonych punktów: szkliwo (punkty 002–004) z wytrąceniem metalicznym (punkt 001); rentgenowska analiza spektralna w mikroobszarach

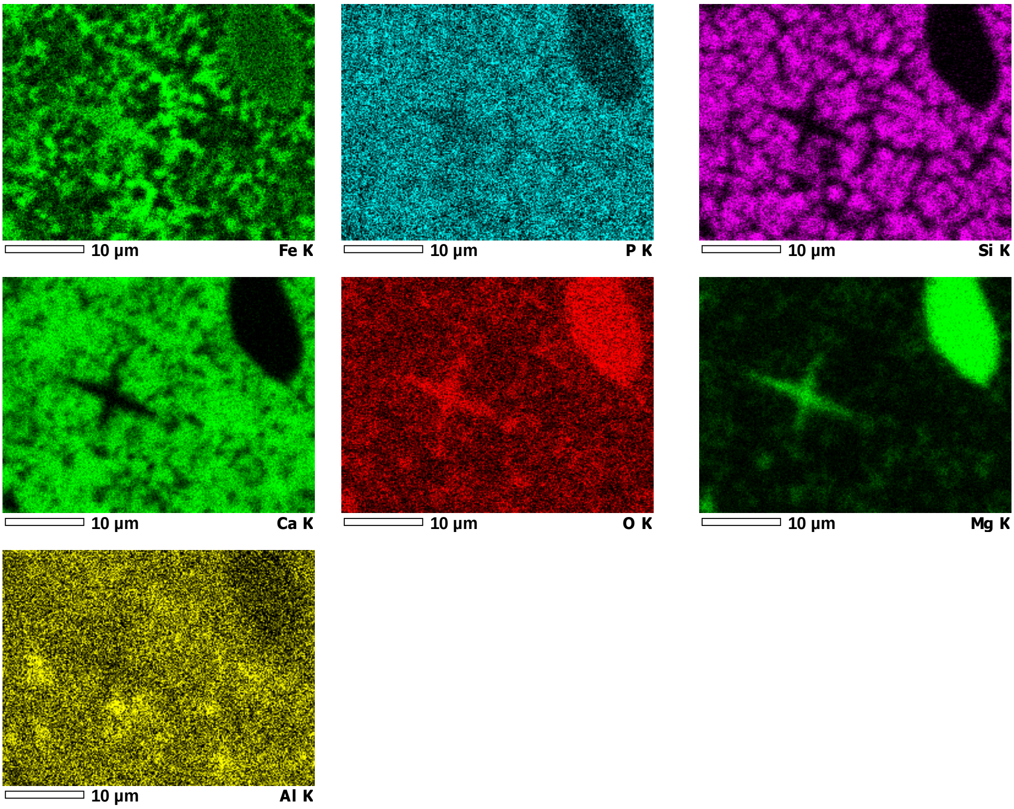

Fig. 6. Surface distribution of elements according to Figure 5; X-ray spectral microanalysis

Rys. 6. Rozkład powierzchniowy pierwiastków według rysunku 5;
rentgenowska analiza spektralna w mikroobszarach

Table 2. Chemical composition of slag compounds, according to Figure 5

Tabela 2. Skład chemiczny składników żużla, według rysunku 5

Point no.	Elemental content (% by weight)													
	O	Al	Si	Mg	Ca	Fe	Mn	Ti	V	Cr	Zn	Pb	S	P
001	35.00	0.06	0.00	46.87	1.60	13.34	2.86	0.00	0.00	0.26	0.01	0.00	0.00	0.00
002	33.11	0.04	0.79	32.92	3.31	26.51	2.78	0.00	0.01	0.43	0.00	0.01	0.00	0.07
003	35.74	0.49	12.76	0.20	45.76	2.97	0.12	0.43	0.10	0.03	0.09	0.00	0.02	1.30
004	33.73	0.46	11.09	0.95	43.37	7.96	0.92	0.29	0.06	0.04	0.03	0.00	0.00	1.13
005	11.63	0.41	5.85	0.07	22.25	58.46	0.37	0.29	0.03	0.01	0.00	0.10	0.05	0.48

Table 3. Chemical composition slag compounds in terms of oxides, according to Figure 5

Tabela 3. Struktura składników żużla w przeliczeniu na tlenki, według rysunku 5

Point no.	Oxide content (% by weight)											
	Al_2O_3	SiO_2	MgO	CaO	FeO	MnO	TiO_2	Cr_2O_3	V_2O_5	SO_3	ZnO	P_2O_5
001	–	–	88.02	1.54	8.41	1.84	–	0.20	–	–	–	–
002	0.10	1.92	72.15	3.70	19.51	2.08		0.38	–	–	–	0.15
003	1.23	34.68	0.47	56.95	2.44	0.11	0.54	–	0.13	–	0.05	3.40
004	1.18	30.67	2.35	54.90	6.65	0.77	0.37	–	0.07	–	–	3.03

1, 2 – periclase.
3 – dicalcium silicate ($Ca_{1.70}$ $Fe_{0.06}$ $Ti_{0.01}$ $Mn_{0.003}$ $Mg_{0.002}$ $V_{0.002}$ $Zn_{0.001}$) [($Si_{0.97}$ $P_{0.08}$ $Al_{0.04}$)O_4].
4 – dicalcium silicate ($Ca_{1.69}$ $Fe_{0.16}$ $Mg_{0.10}$ $Mn_{0.02}$ $Ti_{0.008}$ $V_{0.001}$) [($Si_{0.88}$ $P_{0.07}$$Al_{0.04}$)$O_4$].
5 – precipitation of metallic iron with oxide phase.

0 and 40° 2Theta, as also metallic iron (ICSD: 98-018-5745) and periclase MgO (ICSD: 98-015-7524); in addition, the presence of quartz SiO_2 was found (98-004-1474, 98-020-0729, 98-017-1573) (Figure 7).

The characterization of the analyzed blast furnace slag was complemented with the determination of its chemical composition. Table 4 presents the results of the analysis of the chemical composition of the slag.

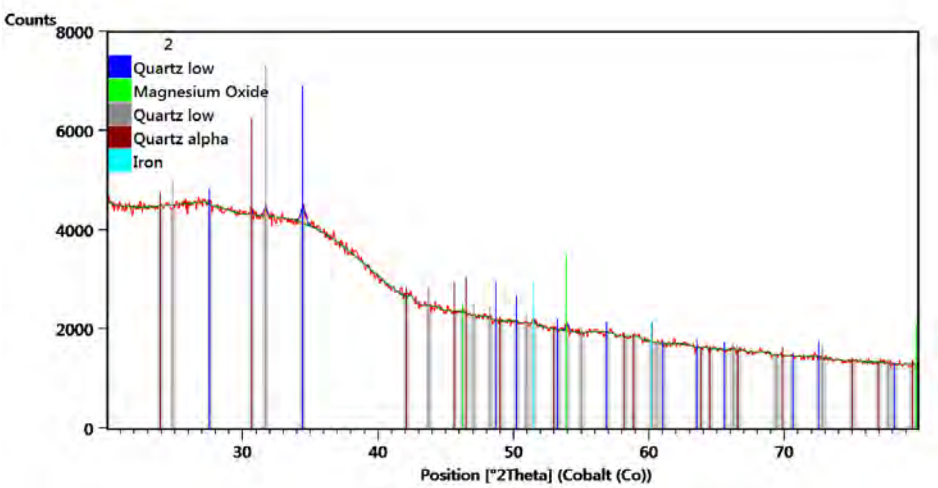

Fig. 7. X-ray diffraction pattern of blast furnace slag

Rys. 7. Dyfraktogram żużla wielkopiecowego

Table 4. Chemical composition of blast furnace slag (%)

Tabela 4. Skład chemiczny żużla wielkopiecowego [%]

Component	Blast furnace slag
L.O.I. 1025°C.	0.70 ± 0.07
SiO_2	38.32 ± 0.96
Al_2O_3	7.35 ± 0.37
Fe_{total} converted to Fe_2O_3*	0.42 ± 0.21*
TiO_2	0.27 ± 0.14
MnO	0.12 ± 0.06
CaO	44.54 ± 1.11
MgO	5.48 ± 0.27
Na_2O	0.36 ± 0.18
K_2O	0.32 ± 0.16
P_2O_5	0.01 ± 0.00
Cr_2O_3	0.06 ± 0.03
Fe from magnetic share (Fe from magnetic share converted to Fe_2O_3)	0.25 ± 0.06 (0.36 ± 0.08)
S total (S total converted to SO_3)	0.79 ± 0.14 (1.98 ± 0.35)
In addition to the quantified components, qualitative analysis revealed the presence of trace contents:	Sr

Values indicated by ± are expanded uncertainty for k = 2, p = 95%.
* 0.42 % Fe_2O_3 is the iron remaining in the non-magnetic share of the sample determined by XRF.

The obtained results demonstrated that the chemical composition of slag is dominated by two oxides: CaO and SiO_2. In slag, the CaO content is 44.54% and the SiO_2 content reaches 38.32%. Along with other components, both materials contain Al_2O_3: 7.35% in slag, MgO (5.48%), and sulphur with content converted to SO_3 amounting to 1.98% in slag.

The total iron content converted to Fe_2O_3 in the slag is 0.42%, which is the residue in the non-magnetic components. Magnetic components (see Research Methodology) were separated from the slag prior to XRF analysis and accounted for 0.25%, where Fe converted to Fe_2O_3 accounted for 0.36%.

The content of other components determined by mass spectrometry is shown in Table 5.

www.czasopisma.pan.pl PAN POLSKA AKADEMIA NAUK www.journals.pan.pl

Table 5. Chemical composition of blast furnace slag, continued

Tabela 5. Skład chemiczny żużla wielkopiecowego, cd.

Element	Content (mg/kg)
As	1.5
Ba	189
Cd	0.3
Ce	9.4
Co	1.1
Nb	138
Ni	12
Pb	8
Se	1
Sr	227
V	718
W	67.7
Y	7.4
Zn	11.1
Zr	110

4. Evaluation of the possibilities of the economic use of the studied slag in the context of mineralogical and chemical analyses

4.1. Use in road engineering

Due to its good mechanical properties, blast furnace slags are artificial aggregates that are especially valued in road engineering. The process of forming blast furnace slag as a by product of the metallurgical industry and, thus, its complex composition are the reason why this material must meet specific chemical requirements to be used safely in the construction industry. The results obtained and presented in the article enable the evaluation of the usefulness of the slag as an aggregate for unbound and bound mixtures of materials used in road building, in reference to national environmental laws stipulated in the Resolution of the Minister of Environment of 1 September 2016 on the method of conducting the assessment of soil surface pollution (Dz.U. 2016 poz. 1395) and technical requirements WT-4 (GDDKiA 2010a) and WT-5 (GDDKiA 2010b), which are PN-EN 13242:2010 standard application documents. In terms of acceptable heavy metal content, the slag meets the environmental requirements set in the regulation of the minister (Dz.U. 2016 poz. 1395) for materials used 0.25 m and more below the ground level on the land intended for public roads, as shown in Table 6.

Table 6. The content of heavy metals found in the slag in relation to the requirements of the Minister of the Environment (Dz.U. 2016 poz. 1395)

Tabela 6. Zawartość metali ciężkich stwierdzonych w żużlu w odniesieniu do wymagań Ministra Środowiska (Dz.U. 2016 poz. 1395)

Element	Content [mg/kg] (in relation to the table 5)	Limit values [mg/kg]
As	1.5	100
Ba	189	3,000
Cr	0	800
Cd	0.3	20
Co	1.1	300
Cu	0	1,000
Hg	0	50
Mo	0	200
Ni	12	500
Pb	8	1,000
Sn	0	300
Zn	11.1	3,000

In the context of using the material for unbound road layers according to WT-4 (GDDKiA 2010a), the key parameter is the total sulphur content, the element which, due to its reactivity, is not a desired component of aggregates. The PN-EN 13242:2010 standard specifies a maximum sulphur content of. 2% by weight for the blast furnace slag. The obtained results show a sulphur content of 0.79% by weight, which is similar to typical content values for natural aggregates.

The chemical composition of the blast furnace slag plays a more important role in the case of mixtures bound with hydraulic binders, according to Wt-5 requirements (GDDKiA 2010b). In these mixtures, slag is a binder the hydraulic activity of which is determined according to the PN-EN 14227-2:2013-10 standard, i.e. by means of a CA product where C is the CaO content and A is the Al_2O_3 content. The higher the CA product, the more reactive the slag. The presence of the selected slag components that are important due to their usefulness as binders according to WT-5 (GDDKiA 2010b) is shown in Table 7.

Table 7. The share of selected slag components important for suitability as a hydraulic binder

Tabela 7. Udział wybranych składników żużla istotnych z uwagi przydatność jako spoiwa

Mineral component	Content (%) (in relation to Table 4)	Requirements (%) (GDDKiA 2010b)
SiO_2	38.32	27–41
Al_2O_3	7.35	7–20
CaO	44.54	30–50
MgO	5.48	< 20

According to PN-EN 14227-2:2013-10 standard, there are three categories identified in terms of activity, depending on CA product (Table 8).

Table 8. Categories of CA product

Tabela 8. Kategorie według iloczynu CA

CA product	Category
> 550	CA1
425–550	CA2
< 425	CA3

According to Table 8, CA = 327 for the studied slag, which means that it is in the CA3 category. It should be mentioned that the hydraulic activity of granulated blast furnace slag is a function of chemical composition, activators (including quick lime, hydrated lime, gypsum, air-cooled steel slag or other similar products containing lime and/or sulphate) and fine contents. An increase in fine content can increase the reactivity of slag considered to be relatively un-reactive because of its chemical composition.

4.2. Use in the cement industry

Due to their potential hydraulic activity, slags were used in the cement industry in Germany in as early as 1865 (Matthes et al. 2018). Granulated blast furnace slag is an additive with hidden hydraulic properties. It means that when activated, it binds and hardens in both water and air. It also gives products hydraulic characteristics (Janic and Gołaszewska 2018). At present, the chemical requirements for slag used in concrete, mortar and slurry are set in the standard PN-EN 15167-1:2007. The results obtained in terms of these requirements are presented in Table 9.

Table 9. Test results in relation to the characteristic values of chemical requirements

Tabela 9. Wyniki badań w odniesieniu do charakterystycznych wartości wymagań

Property	Result	Requirements (%)
Magnesium oxide (MgO)	5.48	≤ 18.0
Sulfide (S^{2-})	0.0	≤ 2.0
Sulfate (SO_3)	1.98	≤ 2.5
Loss on ignition, corrected for oxidation (LOI)	0.70	≤ 3.0
Chloride (Cl^-)	trace	≤ 0.1
Moisture content	0.0	≤ 1.0

According to PN-EN 197-1:2012 standard, blast furnace slag is a valuable cement component if it contains at least two-thirds by mass of glassy slag and possesses hydraulic properties when suitably activated. The high content of the glassy phase plays an important role in blast furnace slag used as the main ingredient of cement because the slag glass reacts much more intensively with water than crystalline compounds (Giergiczny 2015). Dicalcium silicate and periclase present in the tested slag also hydrate. Due to this fact, it is considered that granulated blast furnace slag should consist of at least two-thirds by mass of sum of CaO, MgO and SiO_2. The remainder is Al_2O_3 together with small amounts of other compounds. The ratio by mass (CaO + MgO)/SiO_2 should exceed 1.0. The relevant characteristics of the slag are presented in Table 10.

Table 10. Characteristics of the slag in terms of suitability as a cement component

Tabela 10. Charakterystyka żużla pod względem przydatności w roli dodatku do cementu

Property	Result	Requirements
Content of glassy slag	≥ 80%	≥ 67%
CaO + MgO + SiO_2	88.34	≥ 67%
CaO + MgO/SiO_2	1.3	≥ 1.0

Discussion of research results

Blast furnace slag is a byproduct from the manufacture of melted steel in blast furnaces, which consists mainly of silicates and calcium aluminosilicates (Cabrera-Madrid et al. 2016), which is also shown in the performed studies. It can be concluded that the dominant component of the studied blast furnace slag is glass, which can amount to up to 80%, which, as the research confirms, is typical for polish blast furnace slag (Giergiczny and Góralna 2008). In its vicinity, there are metallic precipitate and crystallites of periclase, dicalcium silicates and quartz. In blast furnace slags, solid solutions of gelenite and akermanite as small amounts of monticellite and merwinite may also occur (Dąbrowski and Małolepszy 2010).

The chemical composition of the slag is dominated by two compounds – CaO (44.54%) and SiO_2 (38.32%) – but also includes Al_2O_3 (7.35%) and MgO (5.48%) whereas the content of other components does not exceed 1%, which also refers to the particles of key importance during the economic use of slag, that is, sulfur and heavy metals. The presented chemical composition of slag is typical for this type of waste material, similar results can be found in Giergiczny's publication (Giergiczny 2015), in which it was stated that the blast furnace slag usually contains 30–50% of CaO, 28–40% of SiO_2, 6–24% of Al_2O_3 and 1–18% of MgO. The same data of the chemical composition of blast furnace slats is confirmed by Shetty (Shetty 2013) and Cabrera-Madrid et al. (Cabrera-Madrid et al. 2016).

With regard to the use of the slag in the construction industry, one can conclude that it meets the environmental and technical requirements regarding unbound and hydraulically bound mixtures. In the case of the latter, in terms of its chemical composition, the slag meets the hydraulic activity category CA3. It also meets chemical requirements for using it as a valuable addition to mortars and concretes, and it is useful in the production of CEM II Portland-composite cement, CEM III blast furnace cement and CEM V composite cements.

The tests of slag intended for use in construction mainly involve the exclusion of its unsoundness related to chemical activity. According to the PN-EN 1744-1 + A1: 2013-05 standard, the most important factors are the presence of potentially expansive free lime, dicalcium silicate disintegration (γ-Ca_2 [SiO_4]) and iron disintegration (iron sulphide or metal iron). Comprehensive slag tests according to the methodology presented in the article allow the widest possible recognition of the suitability of the slag both as aggregate for unbound and bound road layers that must meet environmental requirements, as well as the active ingredient of cements that meets the requirements of the PN-EN 197-1:2012 standard. Although blast furnace slag has the widest range of applications, the methods used are also applicable in assessing the suitability of steel, copper, zinc and nickel slags.

REFERENCES

Arora et al. 2016 – Arora, A., Sant, G. and Neithalath, N. 2016. Ternary blends containing slag and interground/blended limestone: hydration, strength and pore structure. *Construction and Building Materials* 102, pp. 113–124.

Cabrera-Madrid et al. 2016 – Cabrera-Madrid, J.A., Escalante-García, J.I., Castro-Borges, P. 2016. Compressive strength of concretes with blast furnace slag. Re-visited state-of-the-art. *Journal of the Latin-American Association of Quality Control, Pathology and Recovery of Construction* 6(1), pp. 64–83.

Çelik, E. and Nalbantoglu, Z. 2013. Effects of ground granulated blast furnace slag (GGBS) on the swelling properties of lime-stabilized sulfate-bearing soils. *Eng. Geol.* 163, pp. 20–25.

Construction Portal 2022. Characteristics of blast furnace slag [Online:] https://www.portal-budowlany24.pl/budowa/charakterystyka-zuzla-wielkopiecowego [Accessed: 2022-05-04] (*in Polish*).

Dąbrowski, M. and Małolepszy, J. 2010. Properties of concrete with slag-limestone cement (*Właściwości betonu z cementów zuzlowo-wapiennych*). *Drogi i Mosty* 4, pp. 5–28 (*in Polish*).

GDDKiA 2010a. WT-4 2010. Unbound mixtures for national roads. Technical Requirements. General Directorate of National Roads and Motorways (*in Polish*).

GDDKiA 2010b. WT-5 2010. Mixtures bound with a hydraulic binder for national roads. Technical Requirements. General Directorate of National Roads and Motorways (*in Polish*).

Giergiczny, Z. 2015. Contemporary slag cements in construction (*Współczesne cementy żużlowe w budownictwie*). *XVI Scientific and Technical Conference: Rheology in concrete technology*, pp. 139–153 (*in Polish*).

Giergiczny, Z. 2019. Fly ash and slag. *Cement and Concrete Research* 124, pp. 1–15.

Giergiczny, E. and Góralna K. 2008. Ground granulated blast furnace slag - additive for type II concrete (*Mielony granulowany żużel wielkopiecowy – dodatek do betonu typu II*). *Budownictwo, Technologie, Architektura* 1, pp. 56–59 (*in Polish*).

Gomes, J.F.P. and Pinto, C.G. 2006. Leaching of heavy metals from steelmaking slag. *Revista de Metalurgia* 42(6), pp. 409–416.

Górażdże Group 2022. Granulated blast furnace slag as a component of cement and road binders [Online:] https://www.gorazdze.pl/pl/granulowany-zuzel-wielkopiecowy-skladnikiem-cementu-i-spoiw-drogowych [Accessed: 2022-05-04] (*in Polish*).

Taylor, H.F.W. 1997. *Cement Chemistry*. Londyn: Academic Press.

Janic, A. and Gołaszewska M. 2018. The influence of physico-chemical properties of ground granulated blast furnace slag on the shaping of the activity index. *Zeszyty Naukowe Politechniki Częstochowskiej* 24, pp. 139–147.

Jonczy, I. 2014. Diversification of phase composition of metallurgical wastes after the production of cast iron and cast steel. *Archives of Metallurgy and Materials* 59(2), pp. 481–485.

Joulazadeh, M.H. and Joulazadeh, F. 2010. Slag; value added steel industry byproducts. *Archives of Metallurgy and Materials* 55(4), pp. 1137–1145.

Kefeng, T. 1998. Strengthening effects of finely ground fly ash, granulated blast furnace slag, and their combination. *Cement and Concrete Research* 28(12), pp. 1819–1825.

Khatib et al. 2005 – Khatib, J., Hibbert, J. and Khatib, J. 2005. Selected engineering properties of concrete incorporating slag and metakaolin. *Constr. Build. Mater.* 19, pp. 460–472.

Kongsat et al. 2021 – Kongsat, P., Sinthupinyo, S., O'Rear, E.A. and Pongprayoon, T. 2021. Effect of Morphologically Controlled Hematite Nanoparticles on the Properties of Fly Ash Blended Cement. *Nanomaterials* 11(4) [Online:] https://www.ncbi.nlm.nih.gov/pmc/articles/PMC8070749/ [Accessed: 2022-05-04].

Lizarazo-Marriagaa et al. 2011 – Lizarazo-Marriagaa, J., Claisseb, P. and Ganjian, E. 2011. Effect of steel slag and Portland Cement in the rate of hydration and strength of blast furnace slag pastes. *Journal of Materials in Civil Engineering* 23(2), pp. 153–160.

Malhotra, V.M. and Mehta, P.K. 1996. *Pozzolanic and cementitious materials*. UK: Advances in Concrete Technology, pp. 102.

Matthes et al. 2018 – Matthes W., Vollpracht A., Villagrán Y., Kamali-Bernard S., Hooton D., Gruyaert E., Soutsos M. and De Belie N. 2018. Ground granulated blast-furnace slag. RILEM State-of-the-Art Reports, pp. 1–53, DOI: 10.1007/978-3-319-70606-1_1.

Öner, A. and Akyuz, pp. 2007. An experimental study on optimum usage of GGBS for the compressive strength of concrete. *Cem. Concr. Compos*. 29, pp. 505–514, DOI: 10.1016/j.cemconcomp.2007.01.001.

Parron-Rubio et al. 2019 – Parron-Rubio, M.E., Perez-Garcia, F., Gonzalez-Herrera, A., Oliveira, M.J. and Rubio-Cintas, M.D. 2019. Slag Substitution as a Cementing Material in Concrete: Mechanical, Physical and Environmental Properties. *Materials* 12, pp. 1–15, DOI: 10.3390/ma12182845.

Patra, R.K. and Mukherjee, B.B. 2017. Properties of concrete incorporating granulated blast furnace slag as fine aggregate. *Advances in Concrete Construction* 5(5), pp. 437–450, DOI: 10.12989/acc.2017.5.5.437.

PN-EN 13242:2010 Aggregates for unbound and hydraulically bound materials for use in civil engineering work and road construction. European Committee for Standardisation: Bruxelles, Belgium, 2010.

PN-EN 14227-2:2013-10 Hydraulically bound mixtures – Specifications – Part 2: Slag bound granular mixtures. European Committee for Standardisation: Bruxelles, Belgium, 2013.

PN-EN 15167-1:2007 Ground granulated blast furnace slag for use in concrete, mortar and grout – Part 1: Definitions, specifications and conformity criteria. European Committee for Standardisation: Bruxelles, Belgium, 2007.

PN-EN 1744-1 + A1:2013-05 Tests for chemical properties of aggregates – Part 1: Chemical analysis. European Committee for Standardisation: Bruxelles, Belgium, 2013.

PN-EN 197-1:2012 Cement – Part 1: Composition, specifications and conformity criteria for common cements. European Committee for Standardisation: Bruxelles, Belgium, 2012.

Reddy et al. 2006 – Reddy, A.S., Pradhan, R.K. and Chandra, pp. 2006. Utilization of Basic Oxygen Furnace (BOF) slag in the production of a hydraulic cement binder. *International Journal of Mineral Processing* 79(2), pp. 98–105.

Regulation of the Minister of the Environment of 1 September 2016 on the method of conducting pollution assessment the surface of the earth (*Rozporządzenie Ministra Środowiska z dnia 1 września 2016 r. w sprawie sposobu prowadzenia oceny zanieczyszczenia powierzchni ziemi*) (Dz.U. 2016 poz. 1395) (*in Polish*).

Senani et al. 2018 – Senani, M., Ferhoune, N., Guettala, A. and Aguiar, J.B. 2018. Eco-concrete with incorporation of blast furnace slag as natural aggregates replacement. *Science and Technology of Materials* 30, pp. 144–150.

Sheikibrahim et al. 2018 – Sheikibrahim, K., Sathish, S., Mohammed Fahad, A.S., Sathish Sharma, A., Karthika, H. and Shanmuganathan, N. 2018. Ground Granulated Blast Furnace Slag (GGBS or GGBFS) and Fly ash in Concrete. *Int. Res. J. Eng. Technol.* 5, pp. 266–270.

Shetty, M.S. 2013. *Concrete technology – Theory and practice*. India: S. Chand, pp. 201.

Shi, C. 2004. Steel slag – its production, processing, characteristics, and cementitious properties. *Journal of Materials in Civil Engineering* 16(3), pp. 230–236, DOI: 10.1061/(ASCE)0899-1561(2004)16:3(230).

Sofilić et al. 2010 – Sofilić, T., Merle, V., Rastovčan-Mioč, A., Ćosić, M. and Sofilić, U. 2010. Steel slag instead natural aggregate in asphalt mixture. *Archives of Metallurgy and Materials* 55(3), pp. 657–668.

Václavík et al. 2012 – Václavík, V., Vojtech, D., Dvorský, T. and Daxner, J. 2012. The use of blast furnace slag. *METABK* 51(4), pp. 461–464.

Vidhya, R.D.K. 2015. An Experimental Investigation on Strength Characteristic of High Density Concrete Incorporating Hematite. *Int. J. Innov. Res. Sci. Technol.* 2(6) [Google Scholar].

Wang et al. 2010 – Wang, L.K., Hung, Y.T. and Shammas, N.K. 2010. *Handbook of Advanced Industrial and Hazardous Wastes Treatment*. E. U.: CRC Press Taylor & Francis Group, pp. 170.

Yuksel I. 2018. Blast-furnace slag. Waste and Supplementary Cementitious Materials in Concentrate. Characterisation, Properties and Applications. Woodhead Publishing Series in Civil and Structural Engineering, pp. 361–415.

Zhu et al. 2012 – Zhu, Y., Yang, Y. and Yao Y. 2012. Use of slag to improve mechanical properties of engineered cementitious composites (ECCs) with high volumes of fly ash. *Construction and Building Materials* 36, pp. 1076–1081, DOI: 10.1016/j.conbuildmat.2012.04.031.

Zulu et al. 2019 – Zulu, B.A., Miyazawa, S. and Nito, N. 2019. Properties of blast-furnace slag cement concrete subjected to accelerated curing. *Infrastructures* 4, pp. 1–13, DOI: 10.3390/infrastructures4040069.

CHARACTERISTICS OF THE PHASE AND CHEMICAL COMPOSITION OF BLAST FURNACE SLAG IN TERMS OF THE POSSIBILITY OF ITS ECONOMIC USE

Keywords

blast furnace slag, phase composition, glass

Abstract

This article presents the results of studies into the phase and chemical composition of blast furnace slag in the context of its reuse. In practice, blast furnace slags are widely used in the construction industry and road building as a basis for the production of, for example, cements, road binders and slag bricks. They are also used in the production of concrete floors, mortars, and plasters. Blast furnace slag is mainly used as a valuable material in the production of hydraulic binders, especially cement that improves the mechanical properties of concretes.

The favorable physical and mechanical properties of slags, apart from economic aspects, are undoubtedly an asset when deciding to use them instead of natural raw materials. In addition to the above, there is also the ecological aspect, since by using waste materials, the environmental interference that occurs during the opencast mining of natural aggregates is reduced. Specifically, this means waste utilization through secondary management.

However, it should be kept in mind that it is a material which quite easily and quickly responds to environmental changes triggered by external factors; therefore, along with the determination of its physical and mechanical properties, its phase and chemical composition must be also checked.

The studies showed that the predominant component of the blast furnace slag is glass which can amount up to 80%. In its vicinity, metallic precipitate as well as crystallites of periclase, dicalcium silicates and quartz can be found. With regard to the chemical composition of the slag, it was concluded that it meets the environmental and technical requirements regarding unbound and hydraulically bound mixtures. In case of the latter, in terms of its chemical composition, the slag meets the hydraulic activity category CA3. It also meets the chemical requirements for using it as a valuable addition to mortars and concretes, and it is useful in the production of CEM II Portland-composite cement, CEM III blast-furnace cement and CEM V composite cements. The blast furnace slag is a valuable raw material for cement production. Cement CEM III/C contains 81–95% of blast furnace slag in accordance with EN 197-1:2012. In 2019, the Polish cement industry used 1,939,387.7 tons of slag.

CHARAKTERYSTYKA SKŁADU FAZOWEGO I CHEMICZNEGO ŻUŻLA WIELKOPIECOWEGO W ASPEKCIE MOŻLIWOŚCI JEGO GOSPODARCZEGO WYKORZYSTANIA

Słowa kluczowe

żużel wielkopiecowy, skład fazowy, szkliwo

Streszczenie

W artykule przedstawiono wyniki badań składu fazowego i chemicznego żużla wielkopiecowego w aspekcie możliwości jego wtórnego wykorzystania. W praktyce żużle wielkopiecowe znajdują dość szerokie zastosowanie w przemyśle budowlanym oraz w drogownictwie, m.in. na ich bazie produkowane są cementy, spoiwa drogowe oraz cegły żużlowe; stosowane są również przy wykonywaniu posadzek betonowych, do produkcji zapraw murarskich i tynkarskich. Wiodącą rolą żużla wielkopiecowego staje się jego wykorzystanie jako cennego surowca w produkcji spoiw hydraulicznych, zwłaszcza cementu poprawiającego właściwości mechaniczne betonów.

Korzystne właściwości fizykomechaniczne żużli, obok aspektów ekonomicznych, stanowią niewątpliwie atut przy podejmowaniu decyzji o ich wykorzystaniu zamiast surowców naturalnych. Do tego dochodzi jeszcze aspekt ekologiczny, gdyż wykorzystując materiały odpadowe, ogranicza się ingerencję w środowisko, jaka ma miejsce podczas odkrywkowej eksploatacji kruszyw naturalnych, ponadto prowadzona jest utylizacja odpadów poprzez ich wtórne zagospodarowanie.

Należy jednak zwrócić uwagę, że jest to materiał, który dość łatwo i szybko reaguje na zachodzące w środowisku zmiany wywołane czynnikami zewnętrznymi, dlatego obok oznaczeń właściwości fizykomechanicznych żużla niezbędna jest kontrola jego składu fazowego i chemicznego.

Przeprowadzone badania wykazały, że w badanym żużlu wielkopiecowym dominującym składnikiem jest szkliwo, którego udział można szacować na około 80%, w jego otoczeniu występują wytrącenia metaliczne żelaza, a także krystality peryklazu, krzemianów dwuwapniowych oraz kwarcu. Biorąc pod uwagę skład chemiczny żużla, stwierdzono, że spełnia on wymagania środowiskowe oraz wymagania techniczne dotyczące drogowych niezwiązanych i związanych hydraulicznie mieszanek. W przypadku tych ostatnich pod względem składu chemicznego żużel spełnia kategorię aktywności hydraulicznej CA3. Spełnia także wymagania chemiczne dotyczące stosowania go jako wartościowego dodatku do zapraw i betonów oraz jest przydatny do produkcji cementów portlandzkich żużlowych CEM II, cementów hutniczych CEM III oraz cementów wieloskładnikowych CEM V. Żużel wielkopiecowy jest cennym surowcem do produkcji cementu. Cement CEM III/C zawiera 81–95% żużla wielkopiecowego zgodnie z normą EN 197-1:2012. W 2019 roku polski przemysł cementowy zużył 1 939 387,7 ton żużla.