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A. PRIBULOVÁ*[#], P. FUTÁŠ*, J. PETRÍK*, M. POKUSOVÁ**, M. BRZEZIŃSKI***, J. JAKUBSKI***

COMPARISON OF CUPOLA FURNACE AND BLAST FURNACE SLAGS WITH RESPECT TO POSSIBILITIES OF THEIR UTILIZATION

Blast furnace and cupola furnace are furnace aggregates used for pig iron and cast iron production. Both furnace aggregates work on very similar principles: they use coke as the fuel, charge goes from the top to down, the gases flow against it, etc. Their construction is very similar (cupola furnace is usually much smaller) and the structures of pig iron and cast iron are very similar too. Small differences between cast iron and pig iron are only in carbon and silicon content. The slags from blast furnace and cupola furnace are very similar in chemical composition, but blast furnace slag has a very widespread use in civil engineering, primarily in road construction, concrete and cement production, and in other industries, but the cupola furnace slag utilization is minimal. The contribution analyzes identical and different properties of both kinds of slags, and attempts to explain the differences in their uses. They are compared by the contribution of the blast furnace slag cooled in water and on air, and cupola furnace slag cooled on air and granulated in water. Their chemical composition, basicity, hydraulicity, melting temperature and surface were compared to explain the differences in their utilization.

Keywords: cupola furnace slag, blast furnace slag, chemical composition, melting temperature, microstructure of slag

1. Introduction

Slag is a by-product generated during the production of pig iron in a blast furnace, as well as during the production of cast iron in a cupola furnace [1]. The blast furnace slag (BFS) is processed and is largely used, primarily in the building industry. Only a certain percentage of the blast furnace slag is stored as waste in dumps. However, cupola furnace slag (CFS) has not yet found as huge utilization in other industries, and represents an environmental burden. It not only pollutes the environment but also requires high storage costs in industrial waste dumps. Therefore, the potential applications of cupola furnace slag should be investigated.

Pig iron and cast iron represent very similar iron alloys that are produced in two different processes and have different purposes; nevertheless, they have identical structures and similar chemical compositions.

The furnace unit most frequently used for melting of pig iron is blast furnace and for cast iron is the cupola furnace. Due to ecological problems associated with the operation of cupola furnaces, cast iron is also melted in electric induction furnaces; however, the energy and costs required for such melting are much higher [2,3].

Both blast and cupola furnaces are shaft furnaces in which a counter-current system is applied. The blast furnace works continuously, where the charging, supplying the air and exhausting the gases are continuous processes. However, the process of discharging the metal melt (pig iron) and the slag is periodical. Unlike blast furnaces, cupola furnaces usually operate in a periodical mode, most frequently 6-12 hours daily.

The blast furnace is a device that is used for the primary smelting of basic raw materials. It is a part of the steel production process via the so-called iron-ore route.

The cupola furnace is a device for the secondary melting and for heating the products of the primary melting and secondary materials. It also facilitates the processing of lower-quality materials. It requires a low investment cost and it is easy to operate.

In both of the furnaces included in this comparison, there is an oxidation and reduction atmosphere. The atmosphere in the blast furnace is mostly a reduction atmosphere, because the production of pig iron in the blast furnace is based on the reduction of iron and its oxides. However, the processes in the cupola furnace run optimally if the largest possible amount of heat is released during the combustion of coke in the hearth. Therefore, the reduction of CO_2, as the combustion product, should be suppressed to the highest possible extent because it creates an endothermic reaction during which the heat is consumed.

In both furnaces, the main fuel component is coke. In the blast furnace, coke also acts as the reducing agent and it forms the furnace skeleton. Thus, coke is irreplaceable in a blast fur-

* TECHNICAL UNIVERSITY OF KOSICE, FACULTY OF MATERIALS, METALLURGY AND RECYCLING, 9 LETNA STR., 042 00 KOSICE, SLOVAKIA
** SLOVAK UNIVERSITY OF TECHNOLOGY IN BRATISLAVA, FACULTY OF MECHANICAL ENGINEERING, 5 VAZOVOVA STR., BRATISLAVA, SLOVAKIA
*** AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF FOUNDRY ENGINEERING, 23 REYMONTA STR., 30-059 KRAKOW, POLAND

[#] Corresponding author: alena.pribulova@ tuke.sk

nace. On the other hand, the production of cast iron in a cupola furnace may also be carried out without coke – it is then called a “cokeless cupola”.

A difference exists in the highest temperatures reached in the furnace that are required for the metallurgical processes. The temperature in the tuyere area of the blast furnace is 2200°C; while in the cupola furnace, the maximum temperature above the tuyere level is 1750-1800°C.

Slag is formed as a by-product in the production of pig iron in a blast furnace, as well as in the production of cast iron in a cupola furnace. BFS and CFS have a number of similar characteristics. Thus, the purpose of the present paper is to compare their basic properties and identify the reason why CFS is not used in a manner similar to BFS.

2. Formation of cupola furnace and blast furnace slag

Slag is formed in a blast furnace gradually and its composition changes during this time. The exact site where the slag formation begins can depend on many factors, e.g. the chemical composition of the charging materials, air temperature, furnace operations, etc.

The formation of slag in a blast furnace begins in the area of the plastic zone at lower temperatures. By melting the tailings from ore materials and dolomitic limestone, the primary slag is formed consisting of easy-to-melt oxides: FeO, MnO, Al_2O_3 and SiO_2. The primary slag settles in the areas with higher temperatures, where it has closer contact with the molten coke. As a result, the iron reductions are terminated and the residual amount of oxides is dissolved. At the highest temperatures, reductions of manganese, silicon and phosphorus also take place. In the area of the tuyeres, the slag absorbs ash from the burning coke and is enriched with FeO and with the oxides of other metals. This slag is referred to as temporary slag, as its properties and its chemical composition are constantly changing. The final slag accumulates in the hearth above the liquid metal level and consists of the oxides of all the elements that are not reduced in the blast furnace, i.e. CaO, Al_2O_3, MgO, or those that are reduced only partially, i.e. MnO, SiO_2, as well as FeO, CaS, FeS and MnS.

BFS is produced in amounts of approximately 230-400 kg per tonne of the produced pig iron. A big difference is the amount of the produced slag. The blast furnace, when compared to the cupola furnace, produces, on average, an amount of slag that is five times larger per 1 tonne of pig iron. This is caused by the fact that the purity of the charging ore materials is significantly lower.

The components for the CFS formation include: impurities from the metal charge (burned silica sand); iron oxides (iron scale); ash from the coke (the coke consists of 10-13.5% ash containing 46% SiO_2, 39% Al_2O_3, 4% CaO and 6% Fe_2O_3); furnace lining (mainly SiO_2); Al_2O_3; oxides of the metals formed during the smelting (especially Si, Mn and Fe); sulphides formed as a result of the passage of sulphur from the coke into the slag; phosphides formed during the smelting; and slagging impurities [2].

The amount of the CFS represents 5-10% of the metal mass, i.e. 40-80 kg per tonne of cast iron.

The slag that is formed spontaneously (without slagging impurities) consists of SiO_2 and Al_2O_3, and the oxides of Fe, Mn, Mg, P and sulphates. Such slag is of a high viscosity and hinders the smelting process. To improve the properties of the slag, slagging impurities are added as they will reduce the melting point of slag. Thus, to ensure the optimal liquidity and the maximum refining abilities of the slag, slagging impurities are typically used.

Table 1 presents the range of chemical compositions found in BFS and CFS.

TABLE 1

The range of chemical composition of BFS and CFS [2]

	Chemical composition, %						
	SiO_2	Al_2O_3	CaO	FeO	MgO	MnO	S
BFS	32-42	7-16	32-45	0.1-1.5	5-15	0.2-1.0	1-2.0
CFS – acid	40-50	5-18	20-40	2-15	0.5-2	—	—
CFS – basic	25-35	10-20	30-50	2-3	15-30	—	—

From a mineralogical point of view, BFS consists mainly of gehlenite and akermanite ($2CaO.Al_2O_3.2SiO_2$-$CaO.MgO.SiO_2$), as well as other mineral components such as monticellite ($CaO.MgO.SiO_2$), merwinite ($3CaO.MgO.SiO_2$), rankinite ($3CaO.SiO_2$), dicalcium silicate $2CaO.SiO_2$, pseudowollastonite $CaO.SiO_2$ and silicate glass.

The mineralogical composition of CFS includes mainly silicates and other complex types of minerals. The minerals that are most frequently contained in cupola furnace slag include wollastonite ($CaO. SiO_2$), fayalite ($2FeO. SiO_2$) and other components that are formed as a result of the SiO_2-Al_2O_3-CaO combinations [4].

In the process of the production of pig iron in the blast furnace, the slag is tapped out of the furnace concurrently with the tapping of the iron, at a temperature of approximately 1540°C. In the slag skimmer, slag is separated from the liquid iron and is poured into slag pans either directly or through channels. The slag may be drained away in channels directly to the granulation plant, into slag pans or into an open pit.

Slag is poured from the cupola furnace through the tap-hole into a pan, where it is left to cool down and then is stored at a waste dump or poured into a water flow, forming a granulate that is also usually dumped. However, the CFS may be processed by applying the same methods as for blast furnace slag.

3. Treating and utilization of blast furnace and cupola furnace slag

BFS is regarded as a valuable secondary material that is suitable for further processing. In the European Union, BFS is most frequently processed by granulation and by air cooling [5]. The rate at which the slag is cooled determines both its structure and its method of further utilisation. Depending on how the melted slag is cooled and how it solidifies, we can distinguish between the following products: granulated slag, air-cooled slag, pelletised slag and expanded slag.

BFS may be used in amounts reaching almost 100%, and the products made of blast furnace slag have a wide range of applications. According to a source, the majority of the products from the blast furnace slag are used for the production of cements (66 %) and for the construction of roads (23%).

Granulated slag contains mainly slag obtained from the glass phase and has latent hydraulic properties, which facilitates its use in the production of cements. Finely-ground granulated BFS is the second most appropriate component (the first one being the silica flight ash) that is added to every cement to reduce the clinker content. Another potential application for BFS is the production of alkali-activated slag concrete, in which the Portland cement clinker is fully replaced with ground granulated blast furnace slag. The hydraulic solidification of the slag is ensured by adding alkaline solutions, e.g. sodium silicate that is added instead of mixing it with water [6].

A mixture of the finely-ground GBFS and the steel slag, together with activators (free lime) for the purpose of hydration, may be applied in thin layers onto roads as a cement replacement. Such roads have a long service life, low costs and a low occurrence of cracks.

By adding BFS gravel to asphalt, the asphalt gains excellent abrasion resistance and provides a non-skid surface. BFS is also applied in the production of roof tiles and in the production of certain types of glass-ceramics. Products made of slag wool represent high-quality insulation materials that are used in the building industry. Alkaline BFS is suitable for the regulation of soil acidity, and in winter it may also be used as road grit.

CFS is not as well-known as blast furnace slag, so the use of this material has not received much attention. Consequently, it usually represents a waste product that burdens the environment.

According to a source [7-9], finely-ground granulated cupola slag may be used as a partial replacement (5-15%) for the ordinary Portland cement in concrete. Singh [10] describes an investigation involving the potential replacement of the natural coarse aggregates in concrete with CFS. A finding of his research was that the optimal replacement amount is 30%, which has a favourable effect on the tensile strength and the compression strength of the concrete. Similar conclusions were also reached by the authors of this article [11]. CFS is also suitable for the production of the insulation wool used for fireproof insulation materials.

Ladomerský et al.[12] shows that CFS contains a certain amount of metal that must be separated prior to the grinding, and this significantly increases the cost. Thus, granulated cupola furnace slag did not prove to perform well as a replacement for natural fillings.

4. Experiments

The blast furnace slag and the cupola furnace slag are very similar, with only small differences. Why then is the blast furnace slag fully used, mainly in the building industry, whereas using the cupola furnace slag is associated with certain problems?

The purpose of the present paper was to identify the differences between the blast furnace and the cupola furnace slag that hinder the application of cupola furnace slag in the fields where blast furnace slag is used.

Experiments were carried out using four different types of slag: two from a blast furnace (granulated – GBFS and air-cooled slag – BFS); and two from a cupola furnace (granulated GCFS and air-cooled slag -CFS). The comparison focused on the chemical composition, basicity, surface structure, microstructure and melting point of each slag type. Fig. 1 shows all four slags used in experiments.

Chemical analyses were made in accredited company Labortest Kosice, Slovakia.

Hydraulicity is a property that is typical for materials used in civil engineering. Because the building industry uses a lot of wastes from metallurgy and from foundry the term “hydraulicity” is very important to know the behaviour of some kinds of metallurgical wastes first of all slags in contact with water.

The chemical composition is a simple and decisive factor in defining slags hydraulicity. Therefore, modules and activity indices were established to assess the hydraulic slags. These indices define the basic or acidic nature of the slag, according to whether they are respectively, above or below unity [13,14]. When the molten slag is swiftly quenched with water in a pond, or cooled with powerful water jets, it forms into a fine, granular, almost fully noncrystalline, glassy form known as granulated slag, having latent hydraulic properties.

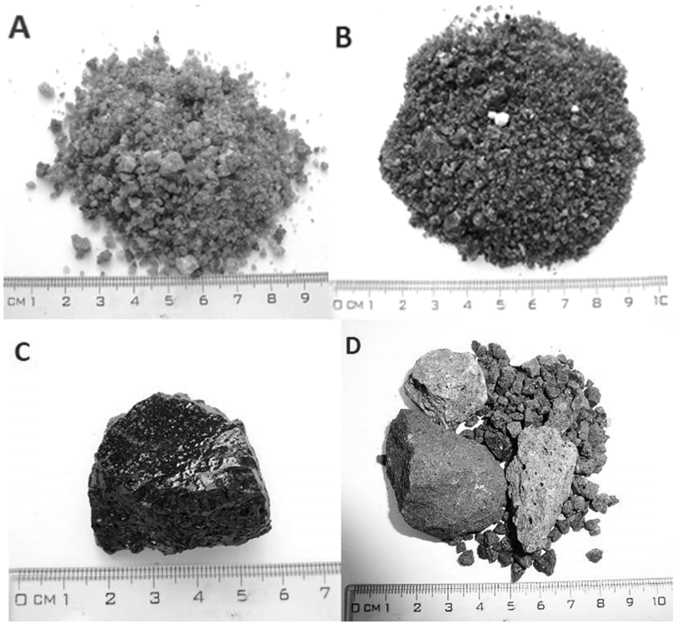

Fig. 1. Slags used in experiment (A-GBFS, B- GCFS, C – CFS, D – BFS)

The reactivity of ground granulated slag is considered to be an important parameter to assess the effectiveness of slag in concrete composites. In order to predict the hydraulic activity of a slag, various hydraulicity formulas have been proposed [15] as summarized in Table 2. However, it has been observed that these formulas do not adequately predict the strength performance expected from a slag, since the hydration reactions taking place are far more complex than indicated by these formulas [14]. From earlier research work, it has been accepted that the reactivity of slag is influenced by the slag properties such as glass content, chemical composition, mineralogical composition, fineness and the type of activation provided.

TABLE 2

Formulas proposed for assesment of hydraulicity of slags [15]

No.	Formula	Requirement for good performance	Preference
1	CaO/SiO_2	1.3-1.4	1
2	$(CaO+MgO)/SiO_2$	>1.4	1
3	$(CaO+MgO)/(SiO_2+Al_2O_3)$	1.0-1.3	1
4	$(CaO+0.56\ Al_2O_3+1.4\ MgO)/SiO_2$	≥1.65	2
5	$(CaO+MgO+Al_2O_3)/SiO_2$	≥1.0	3

From physical properties a melting temperature was obtained. Cylindrical samples of 6 mm diameter and 6 mm high were pressed using the slag powders. High temperature microscope Leitz-Weltzlar was used for measurement of melting temperatures. It consists of next parts: light source, electric laboratory furnace with preparative trolly, microscopy for observation and photography, optical desk, loop galvanometer, camera and halogen fluorescent lamp.

Microscopically enlarged picture of sample that lied in electric laboratory furnace was projected on focusing screen and the photograph was taken. Thermometer scale from galvanometer was projected on the focusing screen too. Determination of melting temperature was according to standard DIN 5173. Melting temperature was reed from the scale when the sample achieved hemispherical shape (original sample shape was cubic).

Microstructure of slags was observed on microscope NEOPHOT 32 and surface of sample together with EDX analyse were made on scanning electron microscopy (TESCAN MIRA 3 FE/EDX – energy dispersive X-ray spectroscopy is the technique in which characteristic X-rays generated from the electron beam-sample interaction are analysed to provide elemental composition of the sample in the form of spectra in elements can be identified. EDX analyse was used for supplement to the chemical analyse.

Results

Chemical composition and basicity of slags used in experiments is given in Table 3.

The comparison of the chemical compositions of the blast furnace and the cupola furnace slags in the above examination indicated that they consist of identical oxides, but the contents of these oxides are different. A more significant difference was observed for the content of SiO_2, which was higher in both types of cupola furnace slag than in the blast furnace slag. Also, there was a difference in the content of CaO, which was contained in higher amounts in the blast furnace slag. The highest content of SiO_2 was observed in the cupola furnace air-cooled slag (51.12%). This was followed by the cupola furnace granulated slag with the SiO_2 content of 45.27%; and then the blast furnace granulated slag that contained 38.71% of SiO_2; while the lowest content of SiO_2 (38.52%) was observed in the blast furnace air-cooled slag. Meanwhile, the highest content of CaO (39.15%) was found in the blast furnace granulated slag. This was followed by the blast furnace air-cooled slag with the CaO content of 36.95%; then the cupola furnace air-cooled slag with the CaO content of 32.64%; and the lowest CaO content (24.08%) that was observed in the cupola furnace granulated slag. The differences in the contents of these two oxides between the blast furnace slag types were minimal, but in the case of the cupola furnace slag types the differences were bigger. A more significant difference was also observed for the content of MgO, which was contained in higher amounts in the blast furnace slag types (granulated 9.8%, artificial metallurgical slag aggregates 6.78%) than in the cupola furnace slag types (air-cooled 1.04%, granulated 5.82%).

TABLE 3

Chemical composition and basicity (B) of slags

	Chemical composition, %							
	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	MnO	S	B
GBFS	38.71	8.42	39.15	0.96	9.8	0.65	0.93	1.26
BFS	38.52	7.28	36.95	0.8	6.78	0.54	0.704	1.14
GCFS	45.27	9.95	24.08	1.12	5.82	0.5	0.14	0.66
CFS	51.12	7.45	32.64	2.01	1.04	1.26	0.218	0.66

Slags hydraulicity is the property that can have a big influence on the application of slags. It is known that blast furnace slag has a very good hydraulicity and it is the most used slag in the cement and concrete production. Theoretical hydraulicities of slags that were calculated by formulas 1-5 from Table 2 are given in Table 4.

TABLE 4

Calculated theoretical hydraulicity of slags used in experiments

Slag	Theoretical hydraulicity calculated by formula (from Table 1)				
	No. 1	No. 2	No. 3	No. 4	No. 5
GBFS	1.0258331	1.278998	1.050499	1.502072	1.496513
BFS	0.9592419	1.135254	0.954803	1.311495	1.324247
CFS	0.6971830	0.717527	0.626259	0.807277	0.863263
GCFS	0.5319195	0.660482	0.54147	0.83499	0.880274
Requirement for good performance	1.3-1.4	>1.4	1.0-1.3	≥1.65	≥1.0

It follows from Table 4 that the best hydraulic properties should have slag GBFS and slag BFS. Slags CFS and GCFS will have very bad hydraulic properties, but it is possibly to expect that slag CFS will have a little bit better hydraulic properties than slag GCFS.

Compressive strength of slags is the measure of hydraulicity. From experiments described in [16] follows that the highest value of compressive strength was achieved in slag from blast furnace – gravel, but after 21 days it started to fall. Compressive strength of granulated blast furnace slag increased very slowly and the highest value reached after 28 days. Compressive strength of granulated cupola furnace slag was very low and cupola furnace slag – gravel rise to 48 hours and that started to fall.

Results observed by measuring of compressive strength accorded to theoretical hydraulicity calculated by formulas.

Granulated blast furnace slag

Fig. 2 shows the sample of the granulated blast furnace slag (magnification 2,5× and magnification 150×). The individual particles had different colours, ranging from light brown to deep brown, and they were shiny and glassy. The chemical composition of the sample is listed in Table 3. The $CaO:SiO_2$ content ratio was 1.01:1.

The slag basicity was 1.26, so this type of slag was classified as moderate alkaline. The sample contained mostly slag from the glass phase. Fig. 3 shows course of melting of sample and melting temperature. The melting point of the sample was 1383°C.

Fig. 4 shows the sample surface, which was of a glassy nature and the results of the EDX analyse. The blast furnace granulated slag had a glassy surface with sharp edges. Blast furnace granulated slag is most frequently used in the building industry as a replacement for sands in the production of cement and concrete.

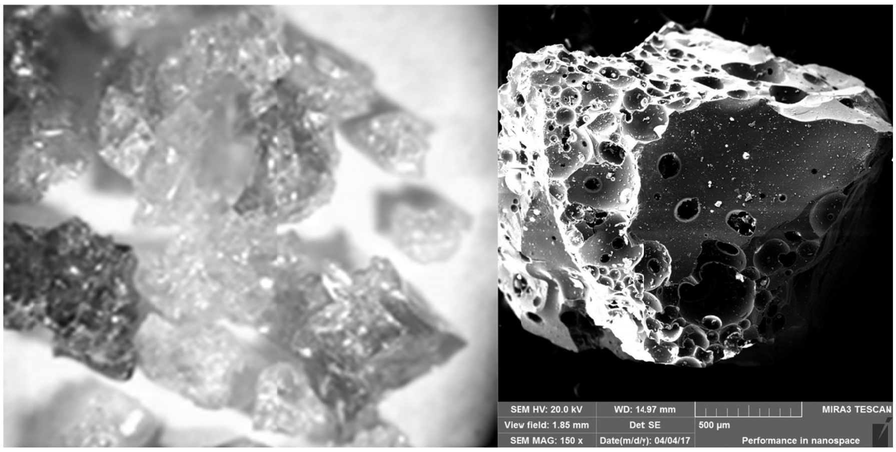

Fig. 2. Granulated blast furnace slag

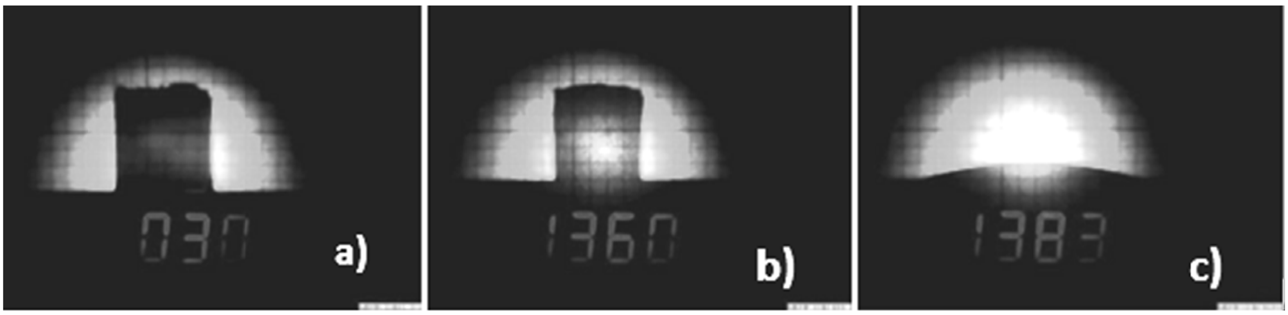

Fig. 3. Course of GBFS sample melting

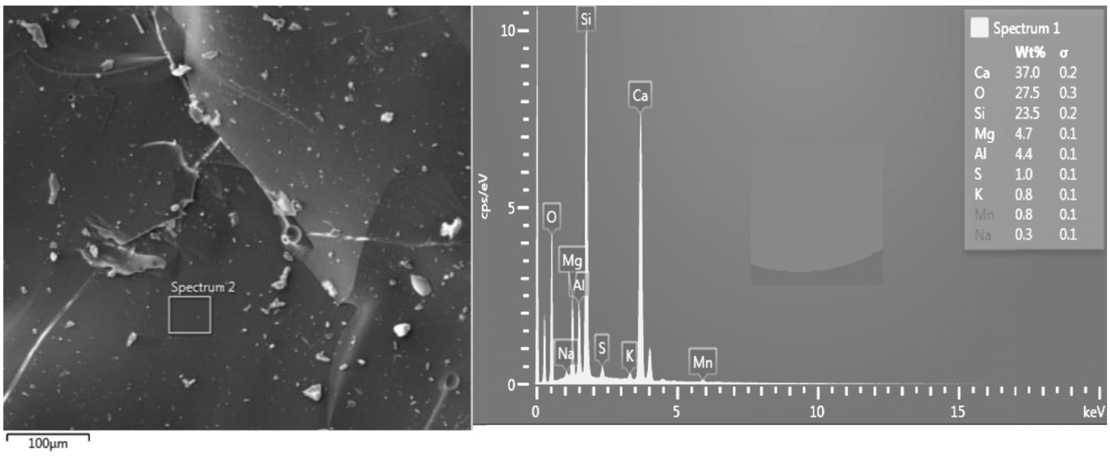

Fig. 4. Surface of granulated blast furnace slag and result of EDX analyse

Granulated Cupola Furnace Slag

Fig. 5 shows the sample of the granulated cupola furnace slag. The slag grains are of a shiny green colour, while the glassy structure is visible at first sight. The chemical composition of GCFS is listed in Table 3. The prevailing component contained in this slag type was SiO_2, and its content in the GCFS was approximately 6% higher than that recorded in the GBFS. However, the CaO content was as much as 15% lower than was found in the GBFS. The alkalinity of the slag was B = 0.66, which makes it an acidic slag.

The results of the EDX analyse and surface of slag are given in Fig. 7. Similarly to the GBFS, the GCFS was also of a glassy nature with sharp edges. Its melting point was 1242°C, Fig. 6. GCFS is not largely used for industrial purposes. It is mostly stored as waste in dumps. In Slovakia, it is used, to a small extent, as a filling material for pipeline laying and for technical recultivation project.

Blast Furnace Air-Cooled Slag

This slag sample was of a matt grey colour and contained a lot of pores, Fig. 8.

The chemical composition of the slag sample is listed in Table 3. In this type of slag, the largest component was SiO_2, representing approximately the same content as was found in the granulated blast furnace slag, but this was 7% lower than in the granulated cupola furnace slag and as much as 13% lower than in the cupola furnace (air-cooled slag). The CaO content was 13% higher than the

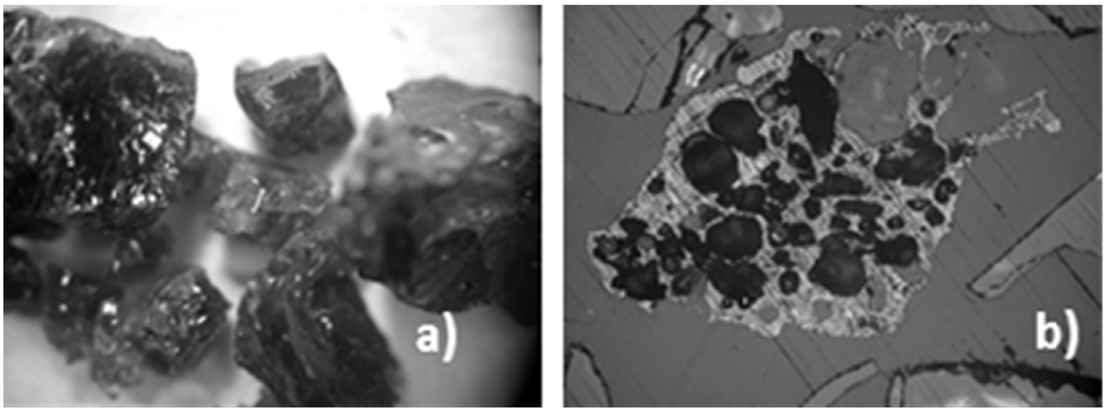

Fig. 5. GCFS (magnification 2.5×) – a and its microsrtucture (100×) – b

Fig. 6. Course of GCFS sample melting

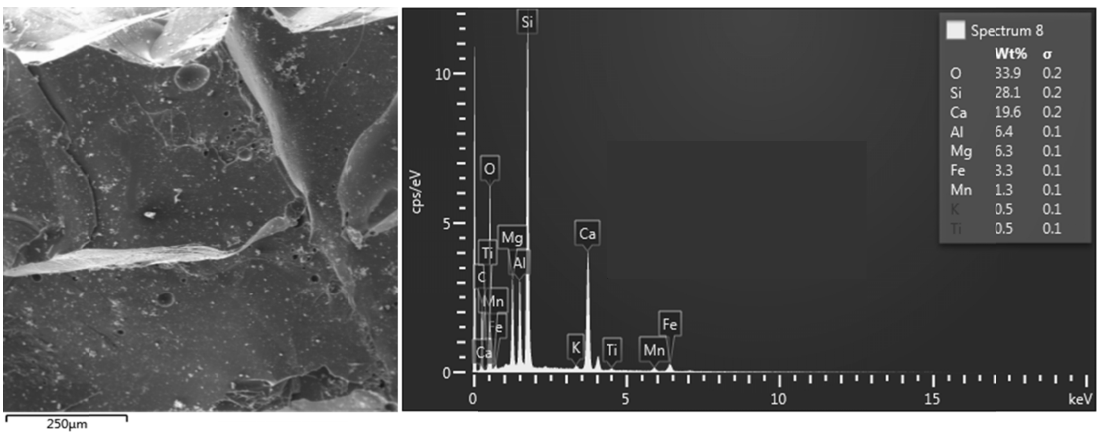

Fig. 7. Surface of GCFS and result of EDX analyse

CaO observed in the granulated blast furnace slag. Its basicity of 1.14 indicated that it was a neutral slag. The melting temperature of the slag was 1309°C, Fig. 9.

Fig. 10 shows the porous surface without a visible glass phase in the sample, as well as the spectrum of the individual elements contained in the sample and their amounts (EDX analyse).

Cupola Furnace Air-Cooled Slag

The sample of the cupola furnace air-cooled slag, Fig. 11, was of a shiny black colour, with visible pores on the surface.

The chemical composition of the sample is listed in Table 3. This type of slag had the highest SiO_2 content; however, out of all four slag types, this one contained the lowest amount of MgO.

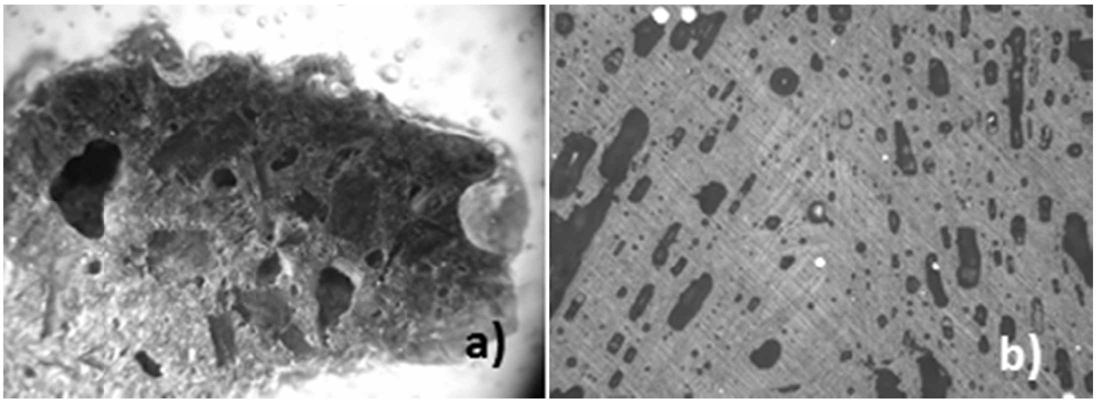

Fig. 8. BFS – air cooled (2.5×) and its microstructure (100×)

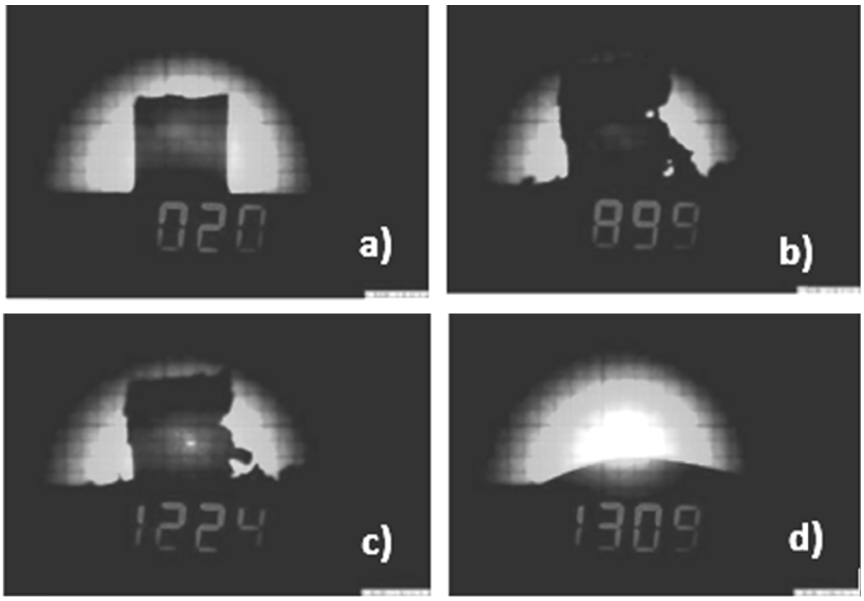

Fig. 9. BFS – course of melting of slag sample

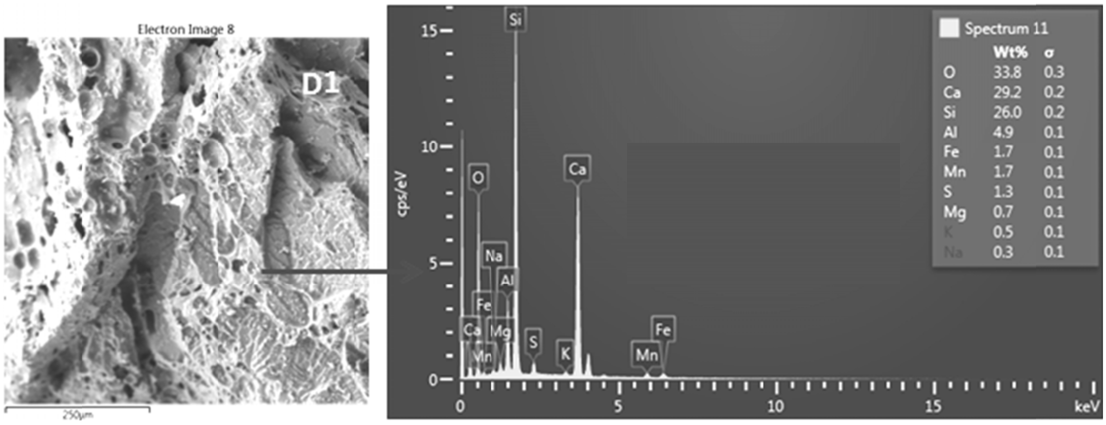

Fig. 10. Surface of blast furnace slag and result of EDX analyse

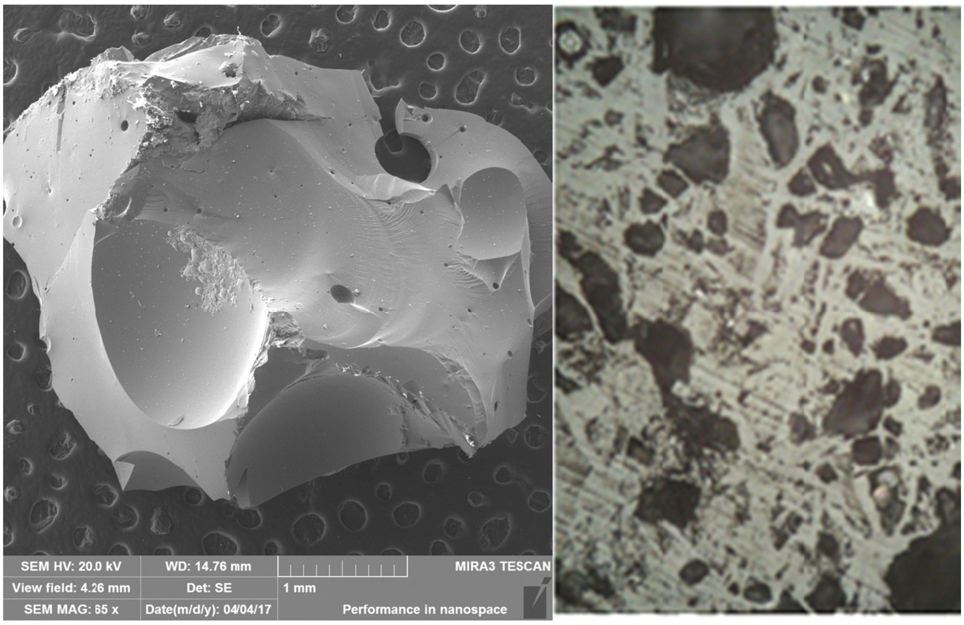

Fig. 11. Sample of CFS (air cooled) and its microstructure

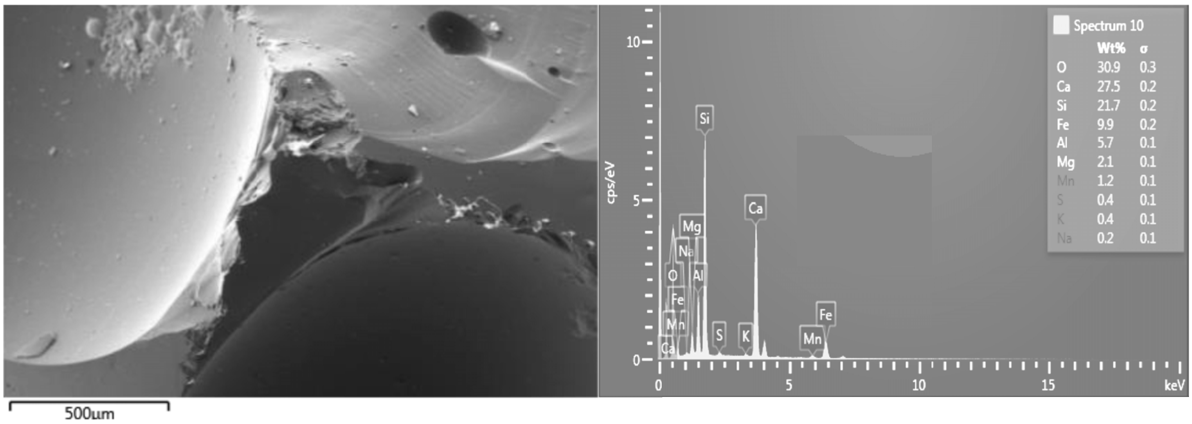

Fig. 12. Surface of cupola furnace air-cooled slag and result of EDX analyse

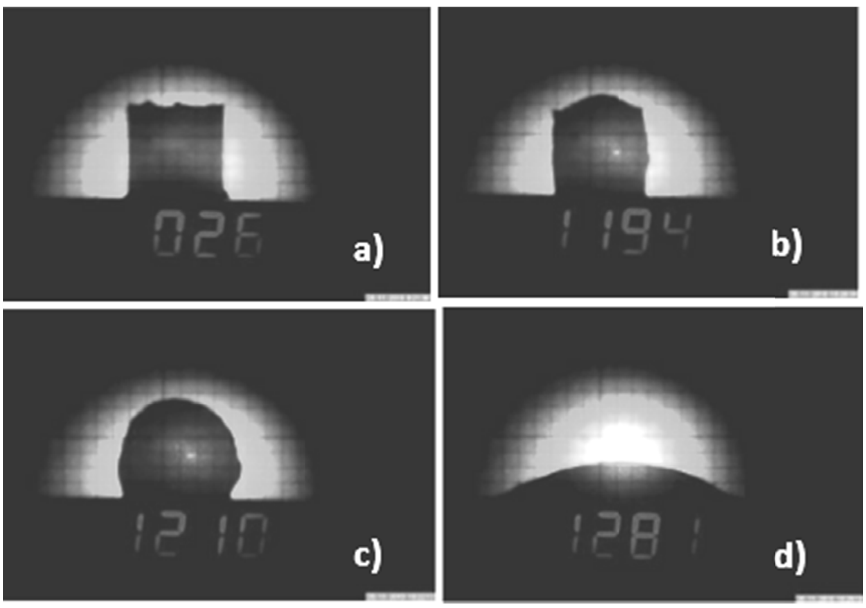

Fig. 13. CFS. – course of melting of slag sample

With a basicity of 0.66, this type of slag belonged to the category of acidic slags. Fig. 12 shows the sample surface which features a noticeable glassy structure and results of EDX analyse. The melting point of the slag sample was 1281°C, Fig. 13. The uses of the cupola furnace air-cooled slag are limited; therefore, it is typically stored as waste in dumps.

5. Conclusion

One of the reasons why cupola furnace slag has not received as much attention as blast furnace slag is the amount of this type of slag produced in smelting processes. For each tonne of cast iron, only 40-80 kg of slag is produced in a cupola furnace. In Slovakia, this represents approximately 2000 tonnes per year, as compared to blast furnace slag which is produced in an amount of over 1 million tonnes annually. Additionally, if we want to find out the reason why cupola furnace slag is not used in various industries as frequently as blast furnace slag, we must first compare their chemical compositions and properties.

The slags of various types were also compared on the basis of their basicity values. According to the basicity values, the blast furnace slag types were categorised as neutral (for the blast furnace artificial metallurgical slag aggregates B = 1.14) and moderately alkaline (for the blast furnace granulated B = 1.26). On the other hand, the cupola furnace slag types belonged to the category of acidic slags (for both samples B = 0.66).

The property that influences the binding properties of slag is its hydraulicity, which can be measured by compressive strength. The highest value of theoretical hydraulicity had the GBFS. The compressive strength of slags were compared. The maximum value was more than 2 MPa for both blast furnace slags and CFS achieved only 0.5 MPa.

An important factor that might affect the utilisation of the slag is its crystalline structure. In the comparison of the blast furnace aggregates, the cupola furnace air-cooled slag was found to have a thicker crystalline structure. Following the smelting process, the cupola slag is poured into a pan in which it cools down, and it is then transported to the dump. To enable its further use, the slag pieces would have to be broken into smaller pieces and the fairly large iron pieces would have to be removed from them, and then the slag would have to be crushed and sorted, which would significantly increase the required costs.

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