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# Chemical, Physical, Morphological and Structural Characterization of Blast Furnace Sludge

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Blast furnace sludge (BFS) is a hazardous metallurgical waste generated in the ironmaking process [1]. Extraction of Fe from ores and its conversion into alloys is the most important metallurgical process [2]. Besides Fe and C other elements are also introduced into the blast furnace. Zn especially forms a problem: during the metallurgical process it evaporates because of high temperatures in the furnace and subsequently condenses on the walls of the furnace at lower temperatures and it damages the installation and the fireproof coating of the furnace. To ensure proper working of the furnace, the input Zn concentration should not exceed an average value of 120 g/ton of pig iron. Consequently, the ores are carefully selected, and the quality of the additives is checked. Part of the evaporated Zn leaves the blast furnace with the effluent gas and condenses on the dust particles, the concentration of Zn being highest on the finest dust particles. Between 8 and 12 kg of dust is produced per ton of pig iron. This dust is normally removed in the air pollution control system. Large particles (> 50 μm) are removed from the flue gas in a dust bag and a cyclone and can directly be recovered in the blast furnace after sintering because the Zn content is in general low (< 0.1% Zn). Smaller particles are washed out in a wet scrubber and generate sludge [2]. The sludge is allowed to settle in a pond, where it is stored until a suitable processing technique is available. Typically, blast furnace sludges (dry solid) contain 21 – 32 % of Fe, 15 – 35 % of C, 1.0 – 3.2 % of Zn, and 0.3 – 1.2 % of Pb [3, 4]. In Europe alone, the steel industry produces yearly about 500 000 tons of blast furnace sludge (dry solid). Due to the high C and Fe content of the sludge, it can be considered worthwhile to recycle the sludge in the furnace. The dry sludge, however, has an average Zn content of a few percent, which limits its direct recoverability because of the mentioned limitations on the Zn input of the blast furnace.

Due to the presence of these elements it becomes very important to know how these elements are combined before studying new technologies for BFS processing. The aim of this work was to carry out a chemical, physical, morphological and structural characterization of the BFS. The investigation was carried out by using granulometry analysis, chemical analysis, scanning electron microscopy (SEM) with EDX, X-ray diffraction (XRD) and Mössbauer spectroscopy to completely characterize the BFS sample. Moreover, the use of several characterization techniques is important because the findings about the existence of Zn phases are of great importance to its recycling as raw material.

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A sample of blast furnace sludge from U. S. Steel Košice s.r.o. was used in this investigation. BFS is slightly alkaline, in our case with a pH range of 9 – 10 this is partially caused by the presence of carbonates. The granulometric distribution analysis and SEM analysis (Fig. 1) of the BFS showed that the sample has a heterogeneous distribution of particle size, where 70 – 75 % have the size between 0.90 and 30.00 μm. It is known that the non-ferrous metals are more concentrated in the fine fraction of the waste [5].

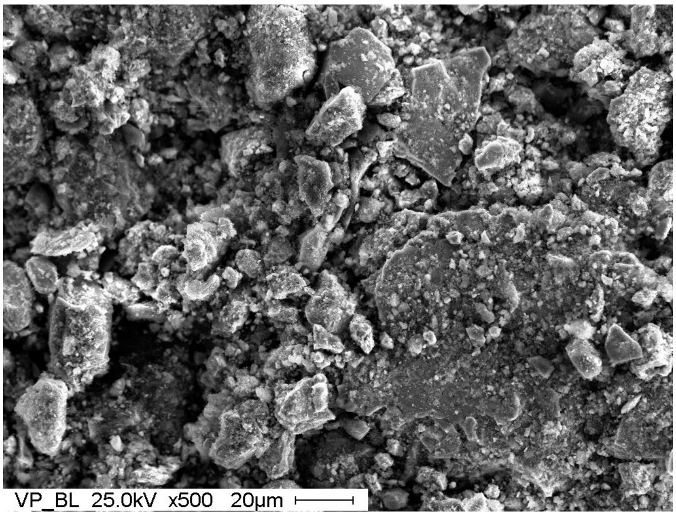


**Fig. 1** Scanning electron micrograph of BFS particles.

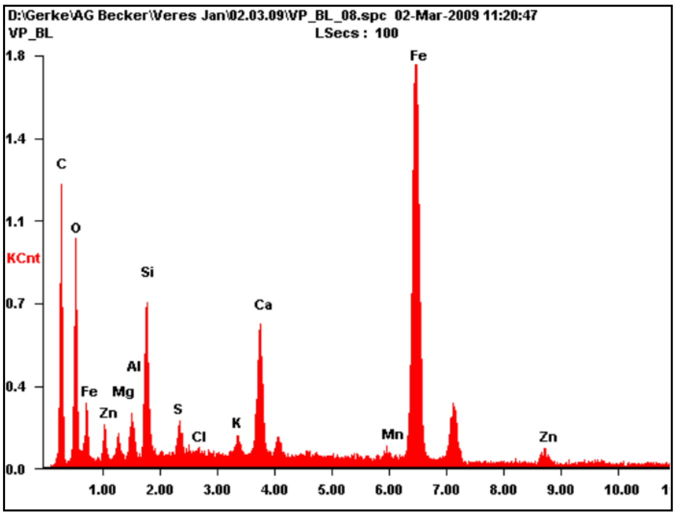


**Figure 2** EDX analysis of the BFS sample.

The results of the chemical analysis of the BFS sample are presented in Fig. 2. The BFS is dominated by Fe and C as indicated by mean concentrations of > 100 g/kg. Both elements are used in abundance during the blast furnace operation in the form of metallurgical coke and iron ores. Ca, Mg, Al, Zn, Pb are the minority elements in the blast furnace sludge. However, the concentration of the elements is different in each blast furnace sludge; it depends on the charge and on the process of treatment.

To identify the phases presented in the BFS sample XRD analysis was used. Fig. 3 shows the XRD pattern of the BFS sample. It was revealed that four major phases (hematite, magnetite, calcite and quartz) are present in the sample.


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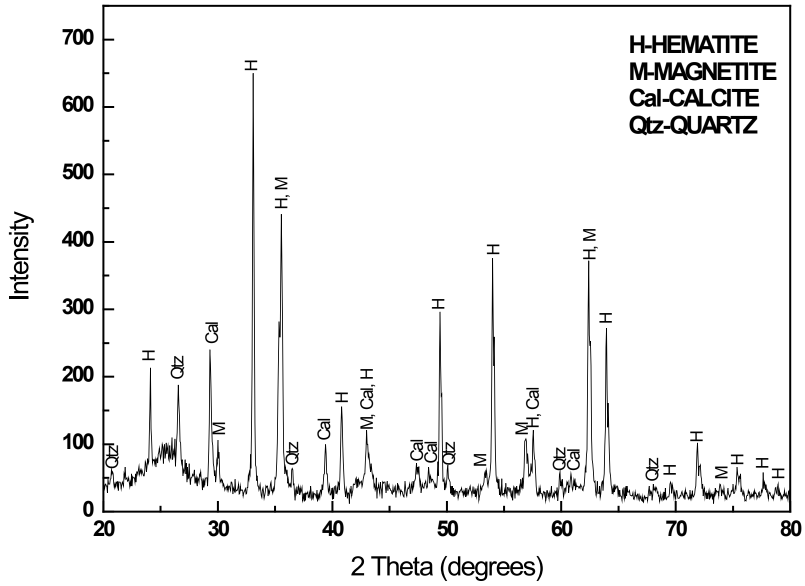


**Fig. 3** X-ray diffraction pattern of the BFS sample.

Iron ores are the source of hematite and magnetite phases. Quartz originates mainly from ash containing coke, but also from flux and iron ores [1]. Calcite is originated from limestone which is an additional material added to the blast furnace to produce blast furnace slag. An increased background (between 20 and 30° 2$\theta$) in the XRD pattern indicates the presence of amorphous compounds. These compounds are mostly composed of coke. Additionally, less crystalline oxides of Fe, Al, Zn, Pb, and other metals could also be present in this fraction. The presence of Zn-containing minerals, due to their low amount, could however hardly be detected. To identify the Fe-containing phases in the sample, $^{57}$Fe Mössbauer spectroscopy was employed.

The Mössbauer spectrum for BFS is displayed in Fig. 4. Hyperfine parameters (isomer shift, *IS*, quadrupole splitting, *QS*, and hyperfine magnetic field, *H*, obtained from the fit of Mössbauer spectrum are presented in Table 1. It was found that the main Fe-containing phases in the BFS sample are $\alpha$-$Fe_2O_3$, $Fe_3O_4$, and $ZnFe_2O_4$. The Mössbauer parameters obtained for these compounds are in agreement with those reported in the literature [6].

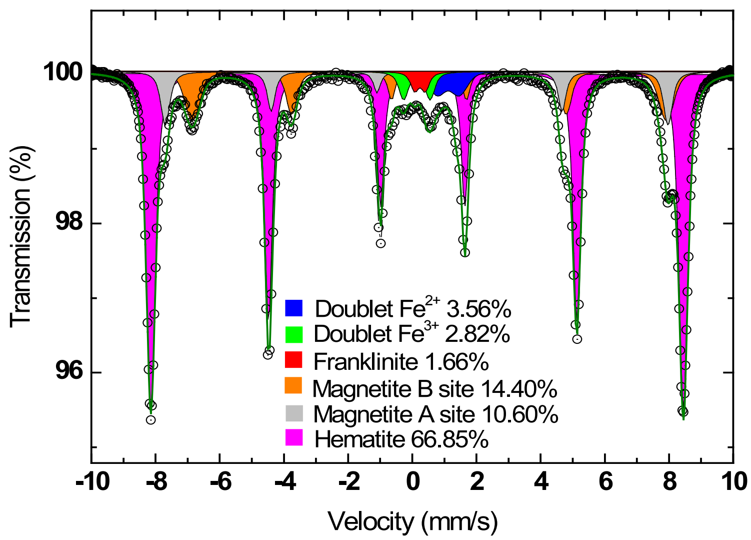


**Fig. 4** Mössbauer spectrum of BFS.


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**Table 1.** Mössbauer parameters derived from the fit of the room-temperature Mössbauer spectrum of BFS

| Sample | Phase | *IS* (mm/s) | *QS* (mm/s) | *H* (T) |
|---|---|---|---|---|
| BFS | $Fe_2O_3$ | 0.23 | 0.44 | 51.46 |
| | $Fe_3O_4$ A site | 0.13 | 0.43 | 48.57 |
| | $Fe_3O_4$ B site | 0.52 | 1.09 | 45.81 |
| | $ZnFe_2O_4$ | 0.24 | 0.33 | – |
| | Doublet $Fe^{2+}$ | 1.11 | 0.70 | – |
| | Doublet $Fe^{3+}$ | 0.14 | 0.83 | – |

Recovery and separation of metals, especially zinc, from blast furnace sludge is a practical idea in iron-making industries. The fact that it is not possible to recycle this sludge directly or to reject it as landfill makes it necessary to consider the proposed process to obtain a non-hazardous residue, which can be stored without problem or can be used in agglomeration units. The characterization of a solid metallurgical waste using various experimental techniques increases the reliability in the results and also gives more conditions to decide about the best possible recycling method.

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**References**

[1] T. Mansfeldt, R. Dohrmann, Environ. Sci. Technol. 38 (2004) 5977.
[2] P. van Herck P., C. Vandeasteele, R. Swennen, R. Mortier, Environ. Sci. Technol. 34 (2000) 3802.
[3] B. Das, S. Prakash, P. S. R. Reddy, V. N. Misra, Conservation and Recycling 50 (2007) 40.
[4] P. Dvořák, J. Jandová, Waste forum 22 (2002).
[5] G. M. S. J Machado, F. A. Brehm, C. A. M. Moraes, C. A. dos Santos, A. C. F. Vilela, J. B. M. da Cunha, J. Hazard. Mater. 136 (2006) 953.
[6] V. Šepelák, S. Wißmann, K.-D. Becker, J. Mater. Sci. 33 (1998) 2845.

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