Zinc recovery from iron and steel making wastes by conventional and microwave assisted leaching

Ján Vereš[1], Štefan Jakabský[1] and Michal Lovás[1]

Significant quantities of sludge and dust are generated as a waste material or byproduct every day from iron and steel industries. Nowadays The occurrence and recovery of metallurgical wastes from steelmaking and iron making processes is a great problem, mainly due to the big amount and environmental pollution of these wastes by heavy metals. The future technology of fine-grain metallurgical wastes treatment is mainly the thing of ecological and financial limits. This work explains the removal of zinc from blast furnace sludge by hydrometallurgical process. The aim of this work was to carry out a chemical, physical, structural, and morphological characterization of these waste materials and subsequently to find out the best suitable method for the hydrometallurgical treatment. The experimental work includes full plant experiments. Extraction conditions such as the effect of microwave power, leaching agent, acid concentration, S/L ratio and extraction time on the zinc removal efficiency were evaluated. The main goal is to set the best conditions to transfer zinc into the solution while the iron should to remain in the solid phase.

Key words: blast furnace sludge, extraction, microwave assisted leaching, zinc recovery

Introduction

Industrial development has led to the generation of more and more industrial waste during production processes. Blast furnace sludge (BFS) is one of the hazardous metallurgical wastes generated in the iron industry (Mansfeldt T. et al., 2004). Extraction of Fe from its ores and its conversion into alloys is the most important metallurgical process (Coudurier L. et al., 1985, van Herck P. et al., 2000). 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 the very high temperatures in the furnace and subsequently condenses on the walls of the furnace at lower temperature. The condensed Zn prevents the descending of the furnace load (the mixture of the iron ores, additives, and cokes). This leads to a sudden falling of the load, which generates large amounts of dust and may even damage 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.t^{-1} 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/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 (van Herck P. et al., 2000). Typically, blast furnace sludge (dry solid) contain 21-32 % of Fe, 15-35 % of C, 1.0-3.2 % of Zn, and 0.3-1.2 % of Pb (Das B. et al., 2007, Dvořák P. et al., 2002). In Europe alone, the steel industry produces yearly about 500 000 ton 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. At steel factories after the removal by the wet scrubber, the fine dust is allowed to settle in a pond, where it is stored until a suitable processing technique is available. Leaching of Zn and Pb may cause contamination of groundwater; moreover, government regulations no longer tolerate long term storage of waste on industrial areas. Several possible treatment processes for the recycling and recovery of blast furnace sludge are under investigation, e.g., pyrometallurgical processes (Asadi Zeydabadi B. et al., 1997, Das B. et al., 2007). The construction of prototypes for these processes is however very expensive, working costs are high and only large quantities of sludge with a relatively high Zn concentration can be processed economically. The fine particle fraction of the sludge as obtained at U.S.Steel Košice s.r.o. has a Zn content of only a few percent (0.7 %). Hydrometallurgy is therefore, in our opinion, a more suitable alternative, offering the advantage that it can be used for small quantities of sludge with a low Zn concentration. This paper describes a hydrometallurgical process by using a microwave furnace to remove the Zn from sludge in order to recycle the Fe and C in the blast furnace and to recover the Zn.

[1] Ing. Ján Vereš, Ing. Štefan Jakabský PhD., RNDr. Michal Lovás PhD., Institute of Geotechnics of the Slovak Academy of Sciences, Watsonova 45, 043 53 Košice, Slovak Republic, veres@saske.sk

Experimental

Materials and methods

A BFS sample from Steelmaking Company U.S.Steel Košice s.r.o. was used in this investigation. At first the sample was characterized: the total composition was determined. The investigation was carried out by using chemical analysis, granulometry analysis, scanning electron microscopy (SEM) with EDX, X-ray diffraction (XRD) and Mössbauer spectroscopy to completely characterize the BFS sample.

The granulometric analysis of BFS was evaluated on Helos/LA Sympatec (Germany). The chemical characterization of BFS was focused in the determination of majority elements as Fe, Zn and Ca. The analysis was executed by using atomic absorption spectroscopy (AAS) Varian Spectr AA-30 (Australia).

Mineralogical composition of samples was determined by XRD using a Philips PW1820 Automatic Powder Difractometer with Cu Kα radiation. Powder samples were measured on the range of 20-80°2θ with a scan step 0.05° and fixed counting time of 2s for each step. The pattern was analyzed by using the Powder Cell software and the PDF database was used for the phase identification. Mössbauer spectroscopy measurements were carried out with a ^{57}Co/Rh γ-ray source (Germany) at the room temperature. The velocity scale was calibrated relative to ^{57}Fe in Rh. Recoil spectral analysis software was used for the quantitative evaluation of the Mössbauer spectra. Scanning electron microscopy (SEM) with energy-dispersive X-ray (EDX) was executed to get additional knowledge of the BFS particle structure, morphology and chemical composition.

Leaching studies to determine optimum operational conditions such as efficiency, solid-liquid (S/L) ratio, leaching reagents, reaction time, in the reactor with volume of 300 ml were performed. In all experiment 10 – 20 g of BFS sample were used depending on the S/L ratio. Using conventional method the samples were leached with sulphuric acid at temperature between 20 °C and 50 °C. The leaching reactor was dipped in a water bath and was covered to keep an S/L ratio constant. Mechanical stirrer with a constant stirring speed 350 rpm was used to mix the sample with a leaching agent. In case of microwave assisted leaching a microwave oven Whirlpool AVM 434 with a power range from 90 to 160 W at frequency of 2.45 GHz was used. A schematic diagram of the microwave-leach system is presented on Fig. 1. About 5ml solution was removed at convenient time intervals, filtered and analyzed for zinc by atomic absorption spectroscopy.
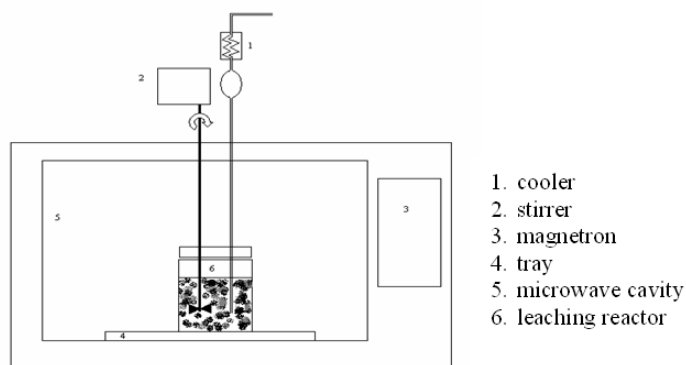

1. cooler
2. stirrer
3. magnetron
4. tray
5. microwave cavity
6. leaching reactor

Fig 1. Schematic diagram of the microwave leaching system.

During the microwave leaching process a mechanical stirrer was used to mix the BFS sample with a leaching agent, with a stirring speed 350 rpm. After the acquired leaching time the temperature of the solution was measured immediately with a manual non-contact thermometer Raytek-Raynger MX4.

In all the experiments, the zinc concentration and dissolution percent was determined by AAS. The effects of parameters on zinc dissolution were studied. Results of these experiments are described in the following sections.

Results and discussions

Blast furnace sludge is slightly alkaline, in our case with a pH range 9.88 that is partially caused by the presence of carbonates. The granulometric distribution analysis of the BFS sample is shown in Fig. 2. It presents a heterogeneous distribution of particle size and contains two major size fractions: a fine grained portion (1–10 μm) and a coarser part (10–100 μm), where 90 % of particles is below 50 μm. As also known that the metals are more concentrated in the fine fraction of the waste (Machado G.M.S.J. et al., 2006), but mesh analysis was unsuccessful to separate fractions from the sludge, which could contain markedly different

amount of zinc as the average composition. Due to the samples for extraction were taken from all content of the blast furnace sludge.
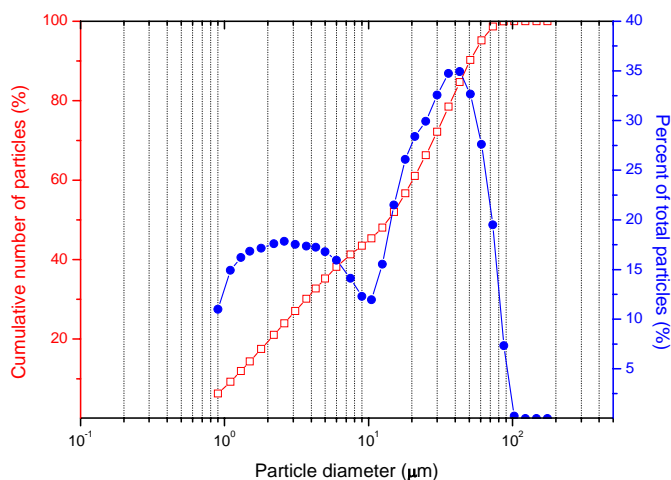

Fig. 2. Granulometric distribution of BFS.

The chemical analysis of the BFS sample was carried out and the elements were determined by AAS. The chemical composition is shown in Tab. 1. The blast furnace sludge is dominated by Fe and C as indicated by mean concentrations of >100 g.kg^{-1} (Tab. 1). Both elements are used in abundance during the blast furnace operation in the form of metallurgical coke and iron ores. The air, which is blown through the blast furnace from the bottom to the top, carries over coke and iron ore particles into the top gas. Thus with its high C and Fe concentrations, landfilled blast furnace sludge clearly reflects the process of pig iron production. Silicium, Ca, Mg, Al, Zn, Pb are the minority elements in blast furnace sludge. However the concentration of the elements is different in each blast furnace sludge, it depends on a charge and on the process of treatment.

Tab. 1. Chemical composition of blast furnace sludge.

Component	Fe	C	SiO$_2$	CaO	MgO	Al$_2$O$_3$	Zn	Pb	Loss of ignition
[volume %]	41.44	18.54	7.02	4.28	1.87	1.74	0.77	0.06	21.91

Scanning electron microscopy (SEM) with energy-dispersive X-ray (EDX) was executed to get additional knowledge of the BFS particle structure, morphology and chemical surface composition. The SEM picture with EDX spectra are showed on Fig. 3 and 4.
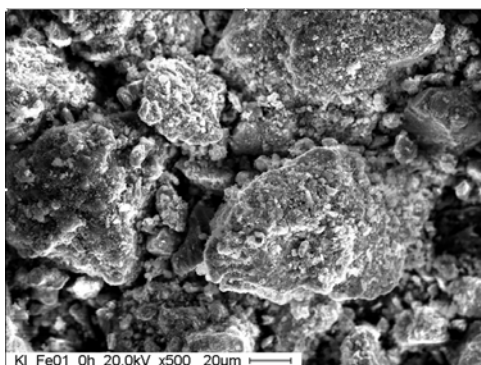

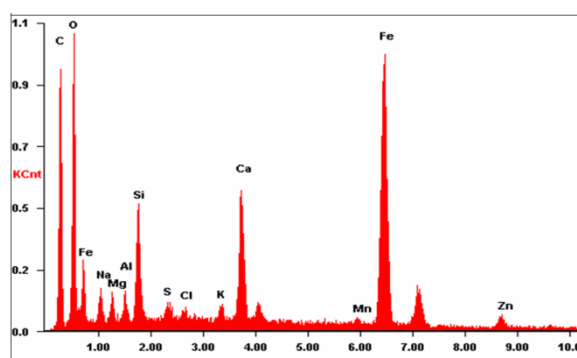*Fig. 3. Scanning electron micrograph of BFS particles.*

Fig. 4. EDX analysis of BFS sample.

To identify the phases presented in the BFS sample the X-ray analysis was used. Figure 5 shows the X-ray diffraction pattern of the BFS sample. XRD analysis of the BFS sample as it can be seen are presented with 4 major phases as hematite, magnetite, calcite and quartz.
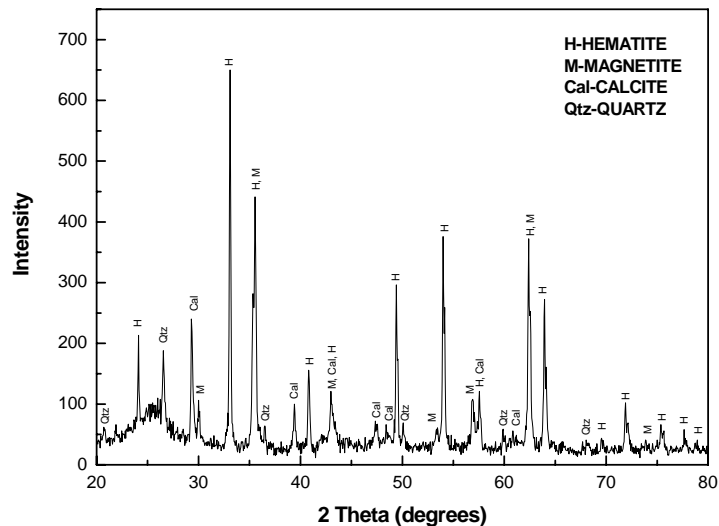
Fig. 5. X-ray diffraction (XRD) pattern of BFS sample.

Iron ores are the source of hematite and magnetite phases. Quartz originates mainly from ash containing coke, but also from flux and iron ores (Mansfeldt T. et al., 2004). Calcite is originated from limestone which is additional material added to the blast furnace to produce blast furnace slag. The main substances were identified, however there are amorphous compounds. These compounds are mostly composed of coke. Additionally, less crystalline oxides of Fe, Al, Zn, Pb, and other metals could be present in this fraction. The presence of Zn minerals, due to their low amount could however hardly be detected. To identify the Zn-Fe phase the Mössbauer spectroscopy was used.

The Mössbauer spectrum for BFS is displayed in Fig. 6. The isomer shift (IS) and the quadrupole splitting (QS) obtained from best fitted Mössbauer spectrum line are presented in Tab. 2.
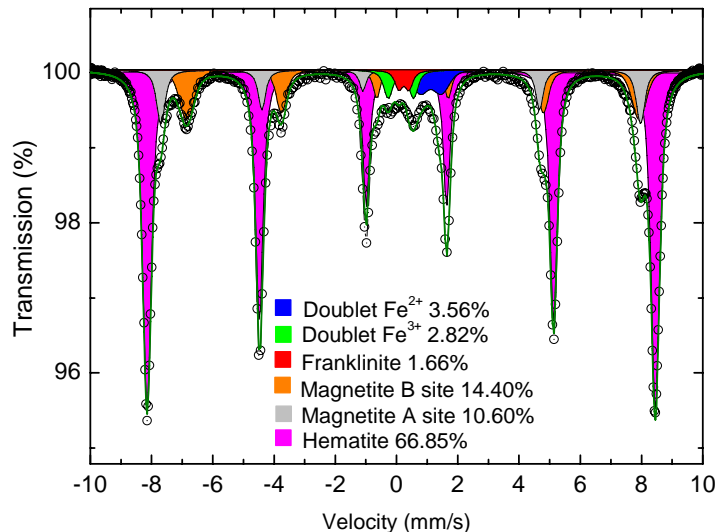

Fig. 6. Mössbauer spectrum of BFS.

The Mössbauer parameters obtained for $ZnFe_2O_4$, Fe_3O_4 and Fe_2O_3 in the blast furnace sludge are in agreement with those reported in the literature (Šepelák V. et al., 1998).

As it was mentioned before, zinc in BFS is present as $ZnFe_2O_4$ (franklinite) and less amount in the form of zinc oxide ZnO (zincite). Iron is present, except of franklinite, mostly as magnetite, Fe_3O_4 and hematite, Fe_2O_3. The ZnO does not cause any problems to neither alkaline nor acid leaching. However, zinc ferrite is considerably refractory against leaching. Although alkaline leaching seems to be advantageous (due to the low iron leaching) it requires relatively concentrated leaching medium (Kelebek S. et al., 2004). On the other hand acid leaching does not need so concentrated solution as the alkaline one, but iron is partially transferred into solution in this case. However, choosing the sulphuric acid leaching route, the highly reactive

species of zinc are dissolved. After the purification of the leach liquors, the metal from the leach solution can be recovered by different methods such as precipitation, crystallization, solvent extraction, ion exchange, electrowinning etc.

Tab. 2. Mössbauer parameters used in the spectrum fit of BFS at room temperature.

Sample	Phase	IS [mm.s^{-1}]	QS [mm.s^{-1}]	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	------

In leaching process the first and most important step is to transfer zinc from solid phase into solution. Selective solubility of zinc relative to iron compounds in this case is critical. The aim of the present leaching process is to propose such conditions of hydrometallurgical treatment under which zinc will be transferred from BFS into the solution while iron remains in the form of a solid residue. Resulting solution is can be further treated to recover zinc and solid residue is recycled into iron making process. The schematic diagram of the leaching process is demonstrated on Figure 7.
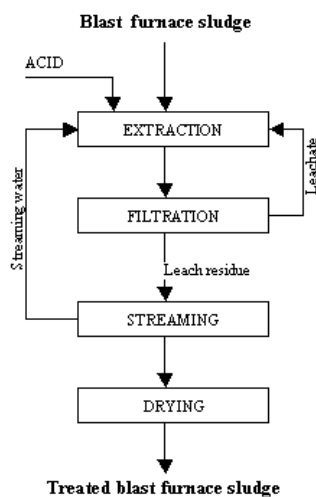

Fig. 7. Block diagram of the recycling BFS.

In respect of quantity of present important substances in the BFS, the analysis was oriented mainly on zinc extraction. Moreover, in one case the comparison of zinc and iron extraction at chosen conditions and possibility of their selective extraction was studied. Results achieved from kinetic study of leachability of zinc into the solution. Optimum values for various leaching agents are established experimentally and shown in the following subsections (Tab. 3.).

Tab. 3. Leaching efficiencies of zinc and iron from BFS depending on the various leaching agents and microwave power.

leaching agent	Time [min]	Power [W]	L/S ratio	Zn extracted [%]	Fe extracted [%]
1 M H_2SO_4	5	90	20	78.71	2.97
		160		85.74	4.26
1 M HNO_3	5	90	20	67.66	2.05
		160		78.31	2.37
1 M HCl	5	90	20	69.84	2.96
		160		79.25	3.70

Comparison between different leaching agents (mineral acids) showed that sulphuric acid is an ideal leachant for separation of zinc from the BFS. Selective leaching of zinc with respect to iron and low cost are the main characteristics of the sulphuric acid leaching process.

The effect of sulphuric acid concentration was determined experimentally. The results showed that the rates of zinc dissolution are dependent on the acid concentration. The Zn dissolution dependency on acid concentration is shown on Figure 8.
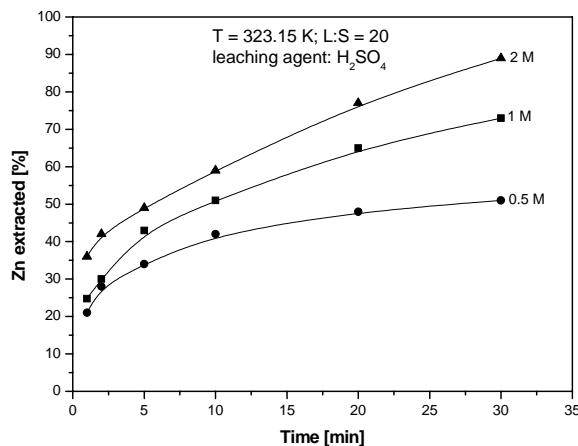

Fig. 8. Zinc dissolution percentage as a function of acid concentration on leaching time at 50 °C.

The effect of temperature on amount of dissolution was studied at 20 and 50 °C with conventional heating and with microwave owen in power levels 90, 160 W, in this case the temperature is dependent on the time of leaching period. We can conclude that the dissolution rate of zinc and iron is dependent on the temperature and microwave power. The results are shown on Fig. 9.
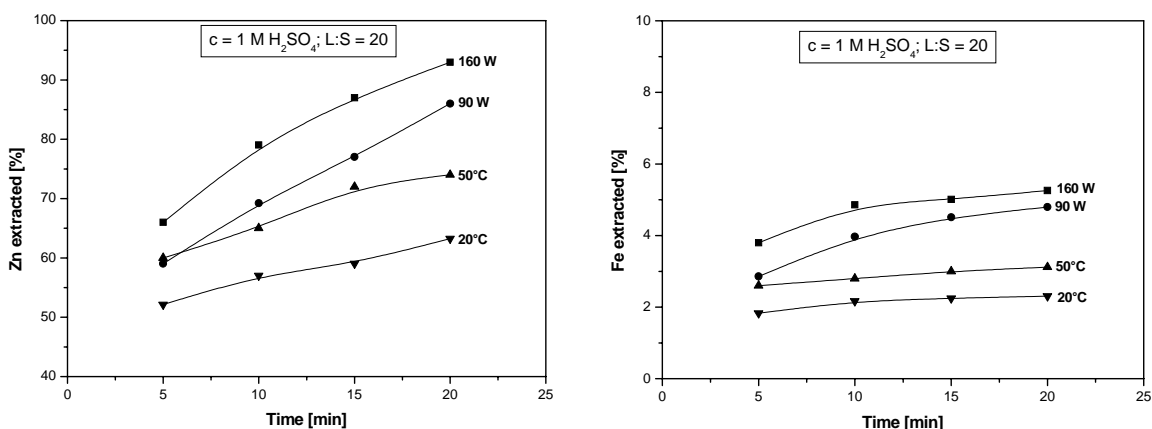

Fig. 9. Zinc (a) and iron (b) dissolution percentage as a function of temperature and microwave power on leaching time.

The leaching efficiency of zinc and iron is dependent on the S/L ratio. Table 4 show the Zn and Fe extraction efficiency depending on the S/L ratio. Decreasing the amount of the BFS sample in the leaching reactor the Zn and Fe dissolution percentage has increasing tendency in both examples.

Tab. 4. Leaching efficiencies of zinc and iron from BFS depending on the S/L ratio.

Acid	Microwave power	Residence time	S/L ratio	dissolution of Zn [%]	dissolution of Fe [%]
1 M H$_2$SO$_4$	160 W	5 min	12.5	75.36	3.80
			20	85.74	4.26
1 M HNO$_3$			12.5	69.38	2.12
			20	78.31	2.37

Conclusion

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 used in this work, 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 many different techniques increase the reliability in the results and also give more conditions to decide about the best possible recycling method.

Conventional and microwave assisted acid extractions were adopted to evaluate the efficiency of zinc removal from industrial waste. The percentage of extraction of zinc increased with the acid concentration and temperature (microwave power). At higher temperatures, the dissolution rates were faster and more zinc was dissolved. These experimental results demonstrated that the most important factors in acid extraction were the acid concentration and temperature. In the case of temperature particles only react when they collide. When a substance is heated particles gain more kinetic energy and collide more frequently thus speeding the rate of reaction. Raising the temperature of reactants will speed up a chemical reaction since activation energy is achieved easily. The reaction is highly exothermic due to the alkaline nature of the sample. Harsher chemical conditions involving a higher dose of acid, high temperatures and use of an appropriate catalyst would probably cause dissolution of greater amounts of zinc. However, this will probably be at the expense of greater loss of iron units. Ability to recycle BFS is economically and environmentally advantageous.

Microwave treatment of BFS resulted in very rapid dissolution of zinc phase. Leaching was completed within minutes, while the conventional leaching process needed much time and more electric energy for heating process. For the comparison in the case of conventional leaching at temperature 50 °C the energy consumption was 0.6 kWh in the case of microwave assisted leaching at power level 160 W was 0.1 kWh. With microwave heating the zinc recoveries were 10-20 % higher than those observed with conventional leaching. The effect of power level was significant. At higher power levels, the dissolution rates were faster and more zinc was dissolved. The higher dissolution rate and also the higher zinc recoveries in the microwave leaching process could be attributed to one or more factors: - superheating of the liquid, - interaction of the microwaves with the BFS particles in the solution.

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