

Comparison of conventional and microwave assisted leaching of zinc from the basic oxygen furnace dust

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Abstract

Basic oxygen furnace (BOF) dust is a hazardous metallurgical waste generated in the collection of particulate material during the steel making processes. The occurrence and recovery of metallurgical wastes from the steelmaking and the iron making processes are nowadays a great problem, mainly due to their big amount and environmental pollution by the heavy metals potential. 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. Experimental work includes full plant experiments. Extraction conditions like the effect of the microwave power, leaching agent, acid concentration, S/L ratio and the extraction time of the zinc removal efficiency were evaluated. The main goal is to set the best conditions for the transfer zinc into the solution while the iron should remain in the solid phase.

Key words: basic oxygen furnace dust, extraction, microwave assisted leaching, zinc recovery

Introduction

The primary source of iron as a feed to iron and steel facilities comes from the oxide ores containing minerals such as hematite (Fe_2O_3) and magnetite (Fe_3O_4), which usually carry a negligible amount of the non-ferrous metal as an impurity. However, some scrap is always used as a secondary source of iron and is usually carries zinc in significant amounts. Scrap originates from a variety of sources such as old cars, cans, bridges, rails and demolished buildings and in most cases it is in galvanized form, which accounts for the presence of zinc. Low vaporization temperature of zinc causes it to accumulate in the furnace off-gasses in the form of small dust particles. Regardless of the source, build-up of zinc in the steel making processes is not desirable due to its adverse effect on the process performance and eventual quality of steel. Fig. 1 represents the expanding tendency of the world steel production which is evidently associated with the waste production. It is estimated that each year, 5 – 7 million tones of the basic oxygen furnace (BOF) sludge is generated worldwide. A sludge stream is produced from the furnace dusts carried away with off-gases that are directed to scrubbers for cleaning prior to their release. This sludge is generally disposed as landfill. Two concerns here are related to the cost of landfill and the loss of iron units. Recovery of iron at acceptable zinc grade is an attractive option as long as it can be done economically. It was suggested that if the

final zinc content of BOF sludge can be reduced to below 0.4 % (wt.), it can be directly recycled in the iron-making or steel-making process (Smith et al., 2000).

At U.S.Steel Košice, s.r.o., a steel factory in Slovakia, 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 may cause contamination of groundwater; moreover, government regulations no longer tolerate longterm storage of waste on industrial areas. Several possible treatment processes for the recycling and recovery of basic oxygen furnace dust are under investigation, e.g., pyrometallurgical processes (Asadi Zeydabadi et al., 1997; Das et al., 2007). The construction of prototypes for these processes is however very expensive, working costs are high and only large quantities of the dust with a relatively high Zn concentration can be processed economically.

The fine particle fraction of the BOF dust as obtained at U.S.Steel Košice, s.r.o., has Zn content about 9.3 %; nevertheless the percentage of the zinc depends on the charge. Hydrometallurgy is therefore, in our opinion, a more suitable alternative, offering the advantage that it can be used for wastes with a low Zn concentration. This paper describes a hydrometallurgical process to remove the Zn from dust in order to recycle the Fe and to recover the Zn. First, the BOF dust was characterized: the total composition was determined, and data from an extraction procedure were obtained.

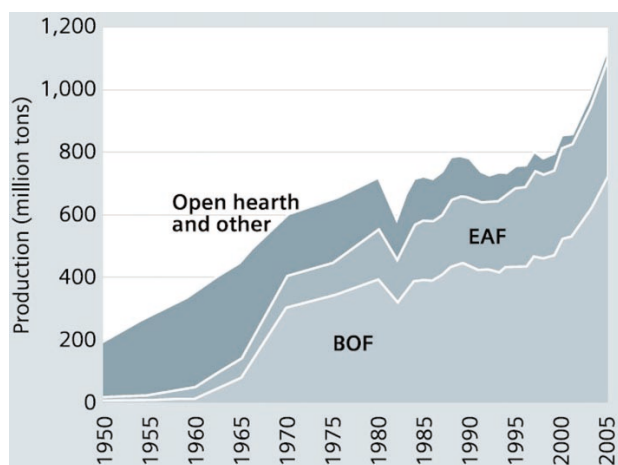


Fig. 1. World steel production.

Materials and methods

A BOF dust sample from the Steelmaking Company U.S.Steel Košice, s.r.o., was used in this investigation. First, the BOF dust was characterized: the total composition was determined, and data from an extraction procedure were obtained. The investigation was carried out by using granulometric analysis, chemical analysis, scanning electron microscopy (SEM) with EDX, X-ray diffraction (XRD) and Mössbauer spectroscopy to completely characterize the BOF dust sample.

A 10 g sample of BOF dust was mixed with 10 ml of deionized water. After 10 minute the sample was filtered and the acidity was measured using a pH meter (12.33). The granulometric analysis of BOF dust was evaluated by the Helos/LA Sympatec (Germany). The chemical characterization of BOF dust was focused in the determination of majority elements as Fe, Zn and Ca. The analysis was executed by using atomic absorption spectroscopy Varian Spectr AA-30 (Australia).

Mineralogical composition of samples was determined by XRD using a Philips PW1820 Automatic Powder Diffractometer with Cu K α radiation. Powder samples were measured on the range of 20 – 80°2 θ with a scan step 0.05° and fixed counting time of 2 s for each step. The pattern was analysed by using the Powder Cell software and the PDF database was used for the phase identification. Mössbauer spectroscopy measurements were carried out with a $^{57}\text{Co}/\text{Rh}$ 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 the energy-dispersive X-ray (EDX) was executed to get additional knowledge of the BOF dust 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 BOF dust sample were used depending on the S/L ratio. Using conventional method, the samples were leached with

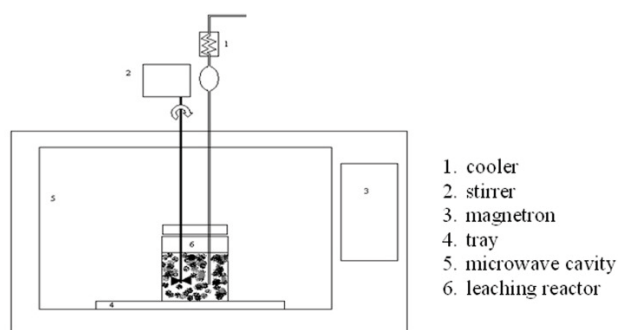


Fig. 2. Schematic diagram of the microwave leaching system.

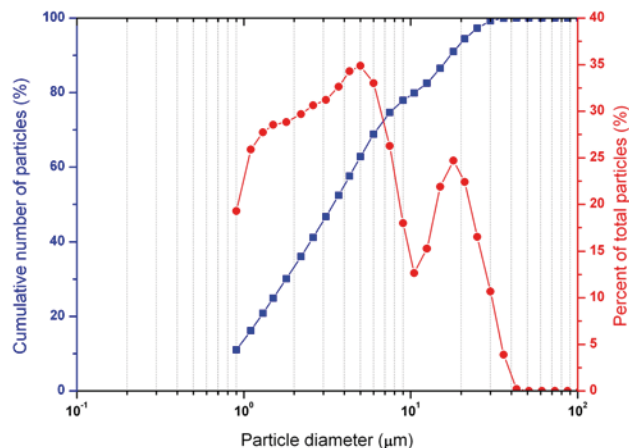


Fig. 3. Particle size distributions of the BOF dust used.

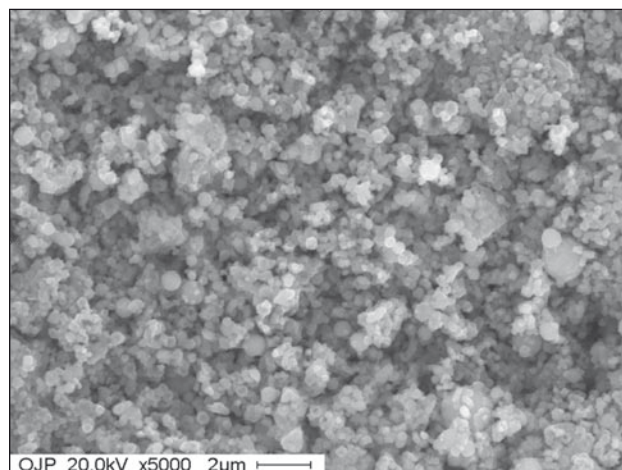


Fig. 4. Scanning electron micrograph of BOF dust particles.

sulphuric acid at temperature between 30 °C and 80 °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 the case of microwave assisted leaching a microwave oven Whirlpool AVM 434 with a power range from 90 to 650 W at frequency of 2.45 GHz was used. A schematic diagram of the microwave-leach system is presented on Fig. 2. About 5 ml solution

was removed at convenient time intervals, filtered and analysed for zinc by atomic absorption spectroscopy.

During the microwave leaching process a mechanical stirrer was used to mix the BOF dust sample with a leaching agent, with a stirring speed 350 rpm, however the leaching reactions in higher power range were very violent and the stirring was not required. After the acquired leaching time the temperature of the solution was measured immediately with a manual non-contact thermometer Raynger MX4.

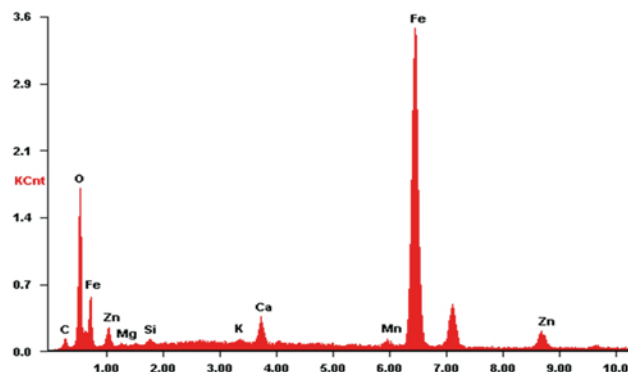


Fig. 5. EDX analysis of BOF dust sample.

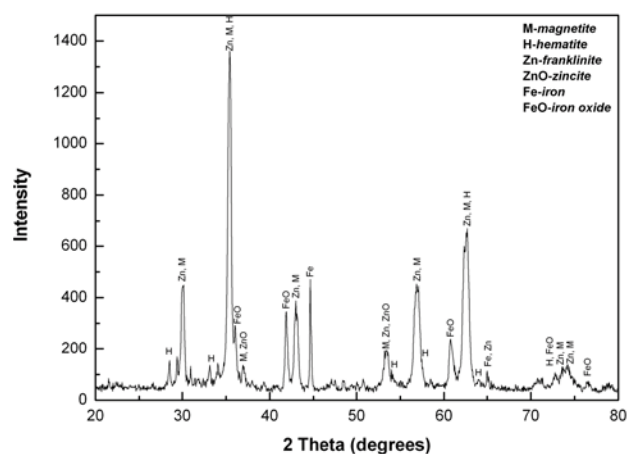


Fig. 6. X-ray diffraction pattern of BOF dust sample.

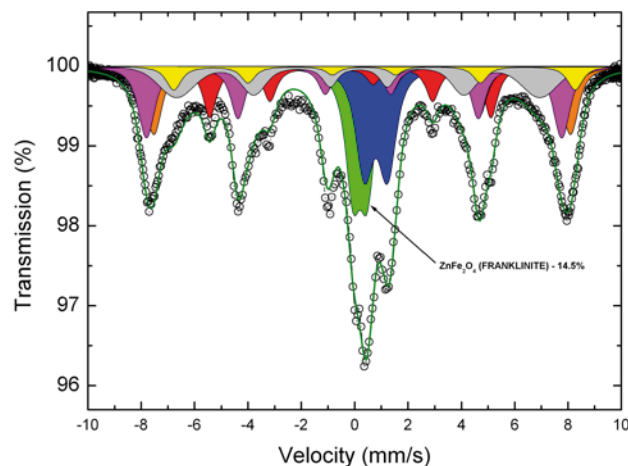


Fig. 7. Mössbauer spectrum of BOF dust.

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

Results and discussion

BOF dust is alkaline, in our case with a pH range 12.33. The particle size distribution of the examined BOF dust is

Tab. 1
Chemical composition of BOF dust

Component	Fe	C	SiO ₂	CaO	MgO	Zn	Pb
(mass %)	49.87	0.97	0.87	7.50	2.68	9.37	0.24

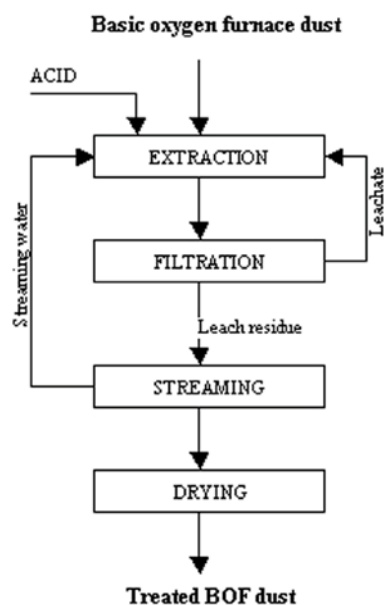


Fig. 8. Leaching diagram of the BOF dust.

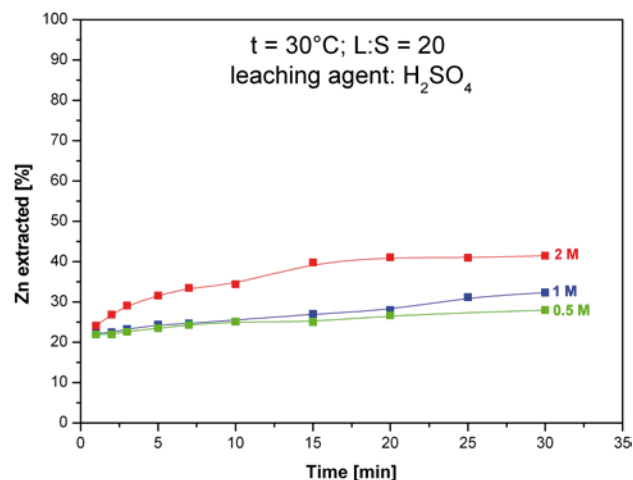


Fig. 9. Zinc dissolution percentage as a function of acid concentration on leaching time at 30 °C.

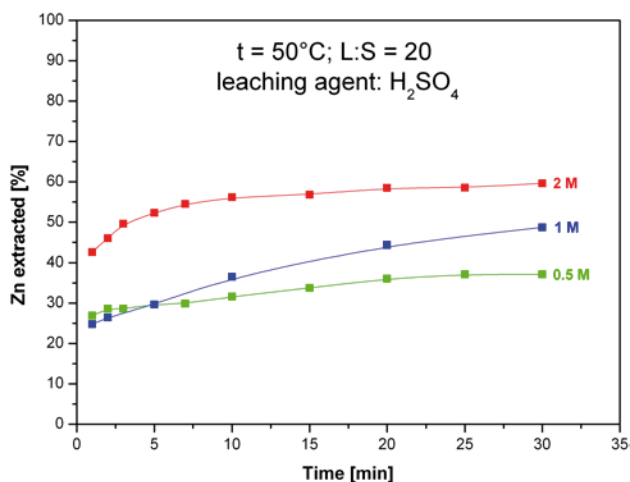


Fig. 10. Zinc dissolution percentage as a function of acid concentration on leaching time at 50°C .

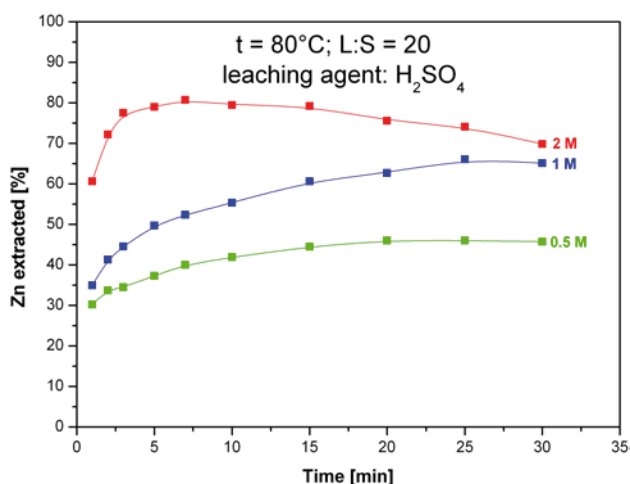


Fig. 11. Zinc dissolution percentage as a function of acid concentration on leaching time at 80°C .

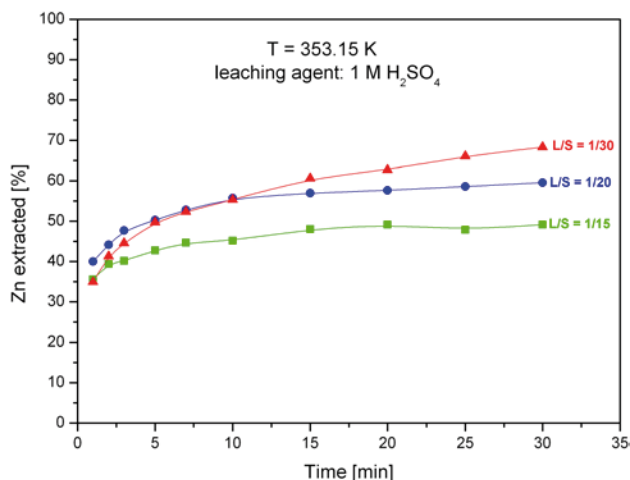


Fig. 12. Zinc dissolution percentage as a function solid/liquid ratio.

given in Fig. 3. It presents a heterogeneous distribution of particle size and contains two major size fractions: a fine grained portion ($1 - 10\text{ }\mu\text{m}$) and a coarser part ($10 - 36\text{ }\mu\text{m}$). As also known that the metals are more concentrated in the fine fraction of the waste (Machado et al., 2006), but mesh analysis was unsuccessful to separate fractions from the sludge, which could contained markedly different amount of zinc as the average composition.

It was found that 50 % of it was below $3.5\text{ }\mu\text{m}$, whereas the majority (100 %) of the particles was below $36\text{ }\mu\text{m}$. Scanning electron microscopy (SEM) with the energy-dispersive X-ray (EDX) was executed to get additional knowledge of the BOF dust particle structure, morphology and chemical composition. By the SEM observation (Fig. 4), the dust shape could be approximately spherical with some agglomerated parts. The SEM picture with EDX spectra are shown in Figs. 4 and 5.

The chemical composition of BOF dust depends mainly on the quality of steel scrap processed and the type of steel was found. Tab. 1 presents the chemical composition of the major elements of the BOF dust used. Beside iron and zinc, the dust is characterized by the relatively high content of calcium oxide, whose presence should be attributed to the lime added to the steelmaking furnace.

The X-ray diffraction pattern of the BOF dust is shown in Fig. 6. Four major phases were identified: franklinite, magnetite, hematite and iron oxide. Zinc in the examined BOF dust is in the forms of zinc oxide as zinc ferrite (franklinite – ZnFe_2O_4), whereas iron is mainly in the form of franklinite and magnetite (Fe_3O_4). Furthermore, iron, hematite, calcite and zincite are also present as minor constituents.

Iron ores are the source of iron oxide and magnetite phases. The amount of zinc is depending on the ratio of galvanized scrap utilized during the steelmaking process. Calcite is originated from limestone which is additional material added to the furnace.

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 confirm the Zn-Fe phase the Mössbauer spectroscopy was used. The Mössbauer spectrum of BOF dust sample is displayed on Fig. 7.

As it was mentioned before, zinc in BOF dust 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 . 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) and it requires relatively concentrated leaching medium (Kelebek et al., 2004). On the other hand the 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 the different methods such

as precipitation, crystallization, solvent extraction, ion exchange, electrowinning etc.

The schematic diagram of the leaching process is demonstrated in Fig. 8.

The reactions of the main species occurring in the sample and their stoichiometry can be stated as follows (Havlík et al., 2004):



In respect of the quantity of present important substances in the BOF dust, 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 the kinetic study of leachability of zinc into the solution. Effect of acid concentration and temperature on zinc leachability by conventional heating is shown in the Figs. 9 – 11. The results showed that the rates of zinc dissolution are dependent on the acid concentration and temperature. The percentage of the zinc extraction increases with increased sulphuric acid concentration and temperature up to 2M where 80 % of zinc was extracted after 7 minutes at temperature 80 °C.

The leaching efficiency of zinc is dependent on the S/L ratio. Fig. 12 shows the Zn extraction efficiency depending on the S/L ratio. Decreasing the amount of the BOF dust sample in the leaching reactor the Zn dissolution percentage has increasing tendency.

The effect of the temperature and microwave energy was studied using a modified domestic microwave oven with power levels 90, 160, 350, 650 W. In this case the temperature is dependent on the time of leaching period. In every case of the microwave assisted extraction process the temperature of the leaching solution in the beginning was at room temperature. The results are shown in Fig. 13.

The comparison between the conventional and microwave assisted leaching of the zinc dissolution percentage is shown in Fig. 14. We can conclude that the dissolution rate of zinc is strongly dependent on the temperature and in the case of microwave assisted leaching on the microwave power.

The nature of the zinc species that is easily solubilized by the acid leaching is not clear. It is speculated, however, that it involves zinc oxide in a greater proportion in the coarse fraction of the dust sample than zinc ferrite. Likewise, the inability of the fines for the zinc leaching is probably related to the presence of the zinc ferrite in much greater proportion than the zinc oxide. For the verification purposes, these points may require additional characterization work for the sludge sample currently tested. Initial batch of the dust samples indicates the presence of zinc oxide by XRD technique only as a minority phase.

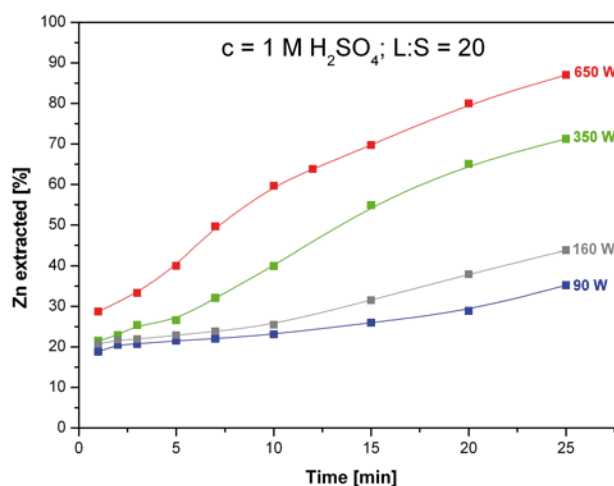


Fig. 13. Zinc dissolution percentage as a function of microwave power.

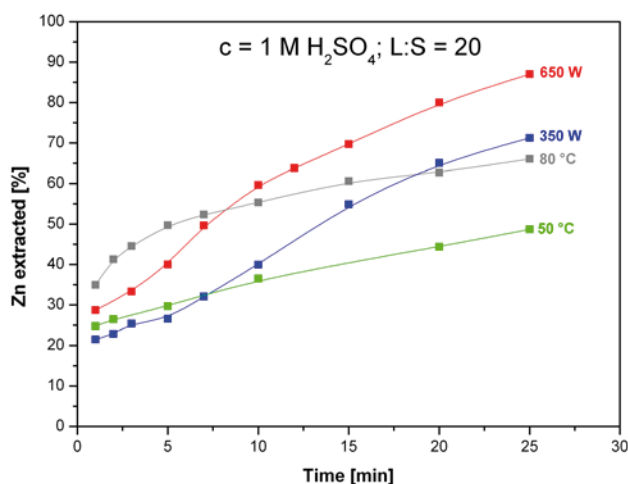


Fig. 14. Comparison of zinc leaching curves between conventional and microwave assisted leaching.

Conclusion

Recovery and separation of metals, especially zinc, from BOF dust is a practical idea in steelmaking industries. The fact that it is not possible to recycle this waste material directly or to reject it as landfill, makes it necessary to consider the proposed process used in this work, for obtaining a non-hazardous residue, which can be stored without problem or can be recycled. 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 the zinc removal from the industrial dust. The percentage of the 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 the acid extraction were the acid concentration and temperature. In the case of temperature the 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 the use of an appropriate catalyst would probably cause a dissolution of the greater amounts of zinc. However, this will probably be at the expense of the greater loss of iron units. Ability to recycle BOF dust is economically and environmentally advantageous.

Microwave treatment of BOF dust resulted in very rapid dissolution of the zinc phase. Leaching was completed within minutes, while the conventional leaching process needed much time and more electric energy in the heating process. For the comparison in the case of conventional leaching at temperature 80 °C the energy consumption was 0.8 kWh in the case of microwave assisted leaching at power level 350 W was 0.2 kWh. With the microwave heating the zinc recoveries were 10 – 20 % higher than those observed with conventional leaching. The effect of power level was significant. At the 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 BOF dust particles in the solution.

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