



# Application of Microwave Energy in Waste Treatment

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## Abstract

Mining and metallurgy are the most dynamic industrial sectors in the world. Mining and metallurgical industrial activities are associated with huge environmental damages of soils, water and air due to the generation of a large number of hazardous wastes. Microwave metallurgy is a new metallurgy technology which has been developed recently and now is an attractive advanced inter-disciplinary field. Taking advantages of microwave heating, it is possible to develop new metallurgy technique and process, which cannot be realized under conventional heating method. The brief purpose of this contribution is to evaluate the viability of microwave energy in metallurgical waste treatment processes with reference to recycle possibility, the cost of mineral processing, efficiency of mineral extraction in order to optimize the whole process.

Keywords: metallurgical waste, microwave, extraction, zinc recovery

## Introduction

The fundamental motto of the modern steelmakers all over the world has been transformed to the declaration: “Steelmaking industry will continue in seeking the ways of improving the energetic efficiency of the processes, the ways of the environmental pollution decreasing and the ways of decreasing the costs related to consumption of raw materials and energy inputs”. To promote this approach, that concerned also the other industrial technologies, the world community was forced to create new obligatory legal documents with direct influence on economy of the individual country (Mihok and Lešínský, 2002).

Growth of worldwide production of iron and steel in previous years (Figure 1) has led to the increased influence of metallurgy on the environment both in the area of greenhouse gasses and in the area of recycling waste products.

Mining and metallurgy are among the most dynamic industrial sectors in Europe. However, mining and metallurgical industrial activities are associated with enormous environmental damages of soils, water and air due to the generation of a large number of hazardous wastes. In last decade’s most of the waste was deposited in landfills, posing an ecological risk. Counting to these dangers it is important to develop devices and technologies which let for waste utilization (Konstanciak and Pustějovská, 2013). For this purpose, both in the global and national iron and steel making processes are observed trends for re-use cheaper, “waste” fuels and materials as substitutes of coke and iron-bearing materials. European Union has identified the harmful effects of these wastes and promotes in the Member

States the establishment of a legal framework as to protect the human health and the environment against these effects. This search is consistent with the principles of environmental burden according to the European Union Council Directive 2008/1/EC known colloquially as the „Integrated Prevention and Pollution Control (IPPC)“ with techniques which prevent or reduce pollution (Kardas, 2013).

Microwave metallurgy is a new metallurgy technology which has been developed recently and now is an attractive advanced inter-disciplinary field. Taking advantages of microwave heating, it is possible to develop new metallurgy technique and process, which cannot be realized under conventional heating method, reforming some traditional metallurgy process and technology, upgrading deep-processing level of metallurgical products, improving the product structure and finally achieving the efficient, energy-saving, and environmental-friendly metallurgical process. It can be expected that the development of microwave metallurgy will play an increasingly important role in the future metallurgical technology.

Recently, the energy of microwave leads a way to many fields of human activity. It is utilized at innovation and intensification of technologic processes in various industrial branches. In contrast to other ways of heating, where material heats up from the surface inwards, at microwave heating a thermal effect in the volume of matter generates as a result of microwave absorption (Figure 2).

Most recently, in the field of research and application of microwave energy in ore and waste processing the series of papers describing microwave heating of

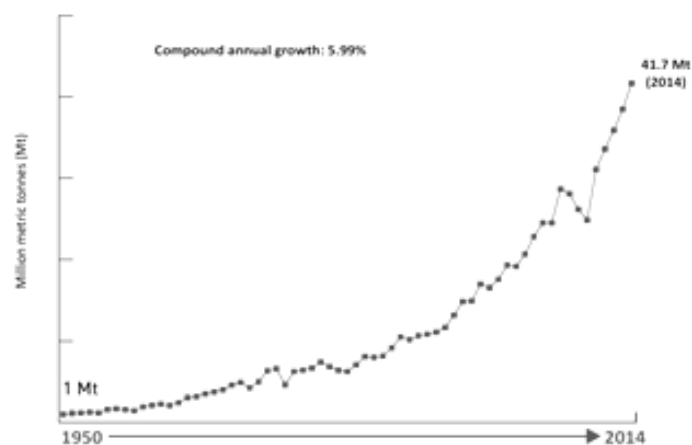


Fig. 1 Annual growth rate of world stainless steel production (Worldstainless, 2015)

Rys. 1. Produkcja stali nierdzewnej (Worldstainless, 2015)

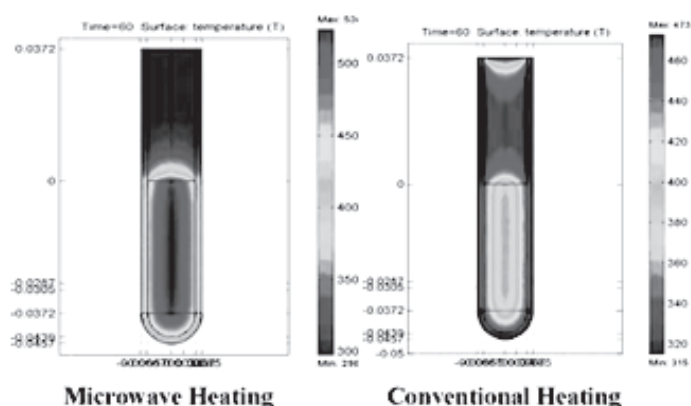


Fig. 2 Comparison of temperature differences between microwave and conventional heating (Schanche, 2003)

Rys. 2. Porównanie temperatury ogrzewania konwencjonalnego i mikrofalowego (Schanche, 2003)

various minerals, modification of physical properties, extraction processes and innovation of mineral processing technology have been published in the world (Xia et al., 2010; Vereš et al., 2012; Singh et al., 2015). Many researchers have paid attentions to the microwave heating process as an alternative recycling method due to its unique characteristics such as fast heating and direct internal heating. It is also believed that the microwave heating may provide savings in both time and energy (Vereš et al., 2011; Peng and Hwang, 2015). In modern society, the production of metals has explosively increased, and the use of metals becomes inevitable in our daily life throughout society. However, the source of metals seems to be changed from high concentrations of ores to low concentrations or industrial wastes. Along with the continuous growth in steel production, the generation of iron and steel-making industrial wastes such as mill scale, slag, dust, sludge, etc. has increased considerably. One of the most serious related problems is the generation of various industrial waste materials containing toxic metals. Considering that these wastes contain lots of useful resources such

as Fe, Zn, Pb etc., many researchers have suggested various processes recycling the valuable metallic elements.

Microwave energy has the potential to be used in metal recovery operations, such as heating, drying, leaching, roasting/smelting and waste management. Rapid solvent extraction and the fast wet dissolution of various types of solids are some of the most well-known microwave applications. The extraction processes are environmentally and economically attractive as they provide detoxification of industrial sludge and removal of valuable metals for their further reuse. Various studies have investigated the use of acids and solvents to remove metals from solid waste using microwave energy. Advantages of microwave leaching are internal heating, dielectric heating, promoting to make the mineral solid particles burst and exposing the fresh surface of particles (Vereš et al., 2010).

All of these researches are attempted with consideration on saving energy by reducing reaction time and temperature, utilization of electricity for heating without using fossil fuel and to develop effective disposal

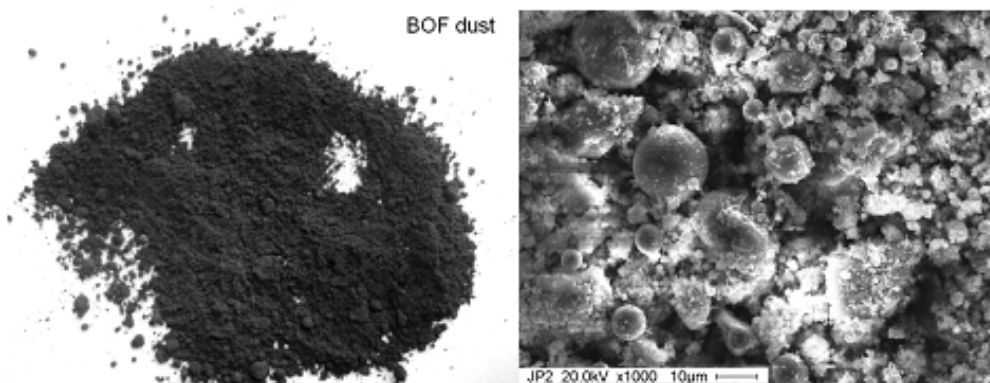


Fig. 3 BOF dust sample

Rys. 3 Próbkę pyłu BOF

Tab. 1 Chemical composition of BOF dust sample

Tab. 1. Skład chemiczny próbki pyłu BOF

Composition (wt%)	Fe	Zn	CaO	SiO <sub>2</sub>	MgO	Al <sub>2</sub> O <sub>3</sub>	C
BOF	49,87	9,37	5,50	0,87	2,68	0,07	0,97

methods of wastes. However, from studies over the past half century, it is recognized that there are still difficulties that hinder the advancement of microwave-assisted metallurgy and more broad applications of the technology to materials processing. Many challenges are confronted in the commercialization and industrialization of microwave-assisted metallurgy.

### Materials and Methods

The basic oxygen furnace (BOF) dust samples from Steelmaking Company (Slovakia) were used in this investigation. These samples were collected from the gas-cleaning system generated during the carbon making processes at a steelmaking plant (Figure 3).

The complex characterization of the sample was carried out using chemical analysis (Table 1), granulometric analysis, X-ray diffraction (XRD) for mineralogical composition and SEM. EDAX measurements were performed to get additional information on the structure, morphology and chemical composition of BOF dust particles. These results are in detail described in previous publications of the author (Vereš et al., 2015; Vereš et al., 2011).

### Results and Discussion

The effect of temperature and microwave energy was studied using a modified domestic microwave oven with different power levels. In every case of microwave assisted extraction process the temperature of the leaching solution in the beginning was at room temperature. The data obtained show that the reaction temperature (microwave power) exerts the most significant effect on the rate of zinc dissolution from BOF dust.

The conversion rate increases rapidly with increasing time and temperature.

The rate of reaction in solid-liquid systems could be determined by a non-catalytic heterogeneous model which has a number of applications in chemical and hydrometallurgical processes. The experimental data obtained at different microwave power levels have been evaluated using kinetic models listed below in Table 2, to calculate and compare the activation energy of the process.

#### Calculation of non-isothermal kinetics

Kinetic analysis of solid state decompositions is usually based on a single step kinetic equation (Vyazovkin and Wight, 1998):

$$\frac{d\alpha}{dt} = k(T) f(\alpha)$$

where  $t$  is the time,  $T$  is the temperature,  $\alpha$  is the extent of conversion, and  $f(\alpha)$  is the reaction model. Several reaction models using  $g(\alpha)$  represented in Table 2. The explicit temperature dependence of the rate constant is introduced by replacing  $k(T)$  with the Arrhenius equation which gives:

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_a}{RT}\right) f(\alpha)$$

and

$$g(\alpha) = A \exp\left(\frac{-E_a}{RT}\right) t$$

where  $A$  (the pre-exponential factor) and  $E_a$  (activation energy) are the Arrhenius parameters. These parame-

Tab. 2 Leaching kinetic models used in experiments (Vyazovkin and Wight, 1998)

Tab. 2. Model kinetyki ługowania (Vyazovkin and Wight, 1998)

Reaction model	Type of reaction model	$g(\alpha)$
Model 1 (M1)	Mampel (first order)	$-\ln(1-\alpha)$
Model 2 (M2)	Mampel (second order)	$(1-\alpha)^{-1}-1$
Model 3 (M3)	Contracting cylinder	$1-(1-\alpha)^{1/2}$
Model 4 (M4)	Contracting sphere	$1-(1-\alpha)^{1/3}$
Model 5 (M5)	Diffusion control (Janders)	$[1-(1-\alpha)^{1/3}]^2$
Model 6 (M6)	Diffusion control (Crank)	$1-(2/3)\alpha-(1-\alpha)^{2/3}$

ters together with the reaction model are sometimes called the kinetics triplet. Under non-isothermal conditions, in which a sample is heated at a constant rate, can be written as:

$$g(\alpha) = \frac{AE_a}{RT} p \quad x$$

$p(x)$  has no analytical solution but has many approximations, with one of the most popular being the Coats-Redfern method (Coats and Redfern, 1964). This method utilizes the asymptotic series expansion for approximating the exponential integral giving:

$$\ln \frac{g(\alpha)}{T^2} = \ln \left[ \frac{AR}{\beta E_a} \left( 1 - \frac{2R\bar{T}}{E_a} \right) \right] - \frac{E_a}{RT}$$

Plotting the left hand side of the equation above, which includes  $g(\alpha)$  versus  $1/T$ , gives  $E_a$  and  $A$  from the slope and intercept respectively. The model that gives the best linear fit is selected as the chosen model.

In respect of quantity of present important substances in the BOF dust, the analysis was oriented mainly on zinc extraction. Results achieved from kinetic study of leachability of zinc into the solution. The leaching rate of Zn from BOF dust gradually increased with increasing heating time and temperature, furthermore, during the microwave leaching process, the solution did not reach the constant temperature, and the leaching process was non-isothermal.

The results showed that the rates of zinc dissolution are dependent on the temperature. The percentage of zinc extraction increases with temperature. Different kinetic models were applied to the experimental data; linear plot was obtained as presented in Figures 4 and 6.

The kinetics of zinc dissolution in sulphuric acid has been assessed on the basis of the Diffusion controlled model by Crank. This model considers that the leaching process is controlled either by diffusion of reactants through the solution boundary layer or through a solid product layer, or by surface chemical reaction. Using data from measurements, the plot of relationship between  $1/T$  and  $\ln k$  was obtained, as shown in Fig. 5 and 7, including the activation energy, calculated by the Arrhenius equation.

The temperature influence on dissolution process represented by the Arrhenius relation in Figure 5 indicates that the zinc leaching from BOF dust is controlled by two mechanisms. Up to approximately 50°C the process is controlled by diffusion with a low apparent activation energy value of  $E_a = 7.51$  kJ/mol. The reaction takes place slowly without considerable increase of the amount of zinc in solution which indicates that the external diffusion of reagents to the solid/liquid interface is probably the rate controlling step at temperatures from 22 to 50°C. With increasing temperature the Arrhenius slope steepness with apparent activation energy value of  $E_a = 46.84$  kJ/mol, which means that the rate of the reaction is chemically controlled through the particle surface reaction.

The temperature influence on dissolution process represented by the Arrhenius relation in Figure 7 indicates that the zinc leaching from BOF dust is controlled by two mechanisms. Up to approximately 80°C the process is controlled by diffusion with a low apparent activation energy value of  $E_a = 10.29$  kJ/mol. With increasing temperature the Arrhenius slope steepness with apparent activation energy value of  $E_a = 70.42$  kJ/mol, which means that the rate of the reaction is chemically controlled through the particle surface reaction.

## Conclusion

The recovery and separation of metals especially zinc, from the 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 at landfills, makes it necessary to consider the proposed process used in this work i.e., to obtain a non-hazardous residue which can be stored without problem or can be recycled. Microwave assisted acid extractions were adopted to evaluate the efficiency of the zinc removal from the industrial dust. Raising the temperature of reactants will speed up a chemical reaction since the 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 dissolution of greater

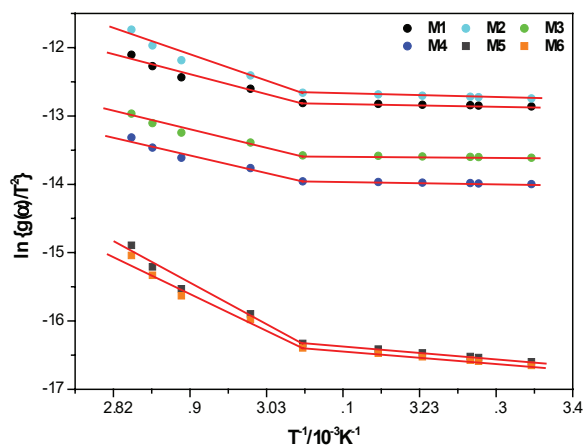


Fig. 4 Relationship between  $1/T$  and  $\ln\{g(a)/T^2\}$  at microwave power 160 W for zinc leaching using different reaction models  
Rys. 4 Zależność  $1/T$  i  $\ln\{g(a)/T^2\}$  przy 160 W dla ługowania cynku dla różnych modeli reakcji

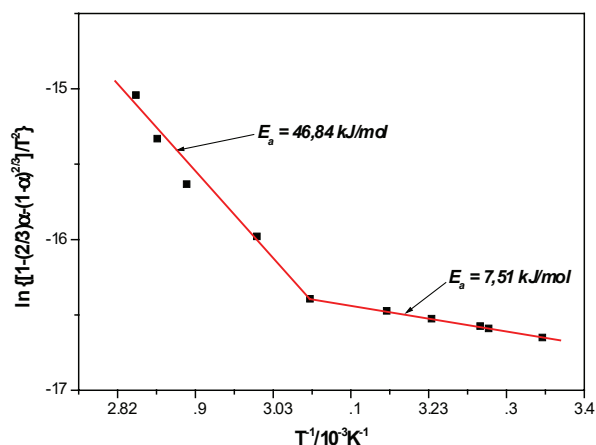


Fig. 5 Relationship between  $1/T$  and  $\ln\{[1-(2/3)\alpha-(1-\alpha)^{2.3}]/T^2\}$  at microwave power 160 W for zinc leaching  
Tab.2 Rys. 5. Zależność  $1/T$  i  $\ln\{[1-(2/3)\alpha-(1-\alpha)^{2.3}]/T^2\}$  przy 160 W dla ługowania cynku

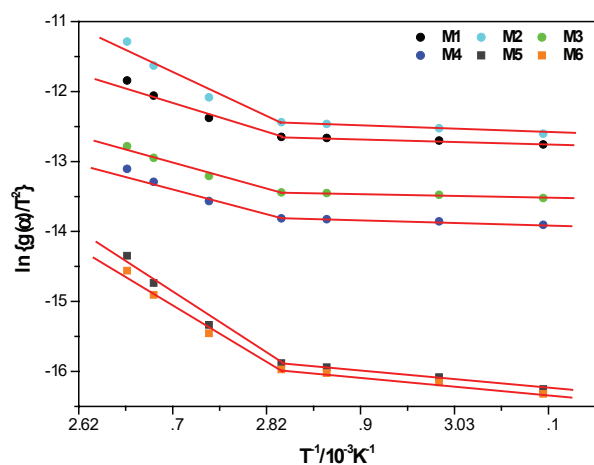


Fig. 6 Relationship between  $1/T$  and  $\ln\{g(a)/T^2\}$  at microwave power 500 W for zinc leaching using different reaction models  
Rys. 6 Zależność  $1/T$  i  $\ln\{g(a)/T^2\}$  przy 500 W dla ługowania Zn dla różnych modeli

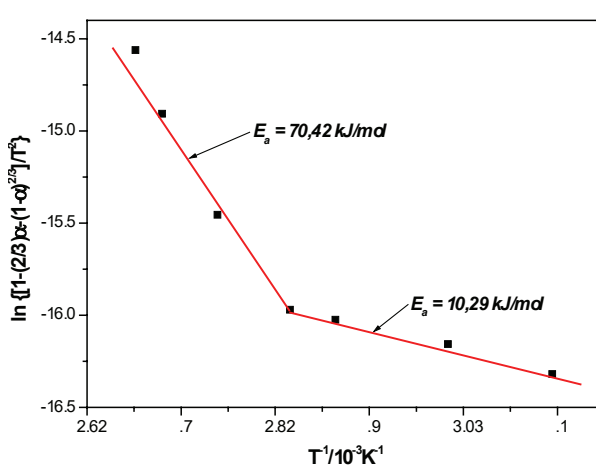


Fig. 7 Relationship between  $1/T$  and  $\ln\{[1-(2/3)\alpha-(1-\alpha)^{2.3}]/T^2\}$  at microwave power 500 W for zinc leaching  
Rys. 7 Zależność  $1/T$  i  $\ln\{[1-(2/3)\alpha-(1-\alpha)^{2.3}]/T^2\}$  przy 500 W dla ługowania Zn

amounts of zinc. However, this will probably be at the expense of a greater loss of iron units. The ability to recycle BOF dust is economically and environmentally advantageous. The kinetic equation from the evaluation of experimental data using heterogeneous and pseudo-homogeneous reaction models was determined using a kinetic model and from the Arrhenius plot obtained experimentally. Experimental results and numeric calculations indicate that the zinc leaching from BOF dust is controlled by two mechanisms. The microwave treatment of the BOF dust resulted in a very rapid dis-

solution of the zinc phase. The higher dissolution rate and also the higher zinc recoveries in the microwave leaching process could be attributed to one or more factors such as superheating of the liquid, interaction of the microwaves with the BOF dust particles in the solution etc.

#### Acknowledgements

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### *Zastosowanie energii mikrofal w przerobce odpadów*

*Górnictwo i hutnictwo to najbardziej dynamicznie rozwijające się sektory przemysłowe na świecie. Działalność górnicza i hutnicza związane są z ogromnym zniszczeniem gleb, wód i powietrza spowodowanych wytwarzaniem dużej ilości odpadów niebezpiecznych. Wykorzystanie mikrofal to nowa technologia, która została ostatnio opracowana. Korzystając z mikrofal można opracować nowe techniki i procy metalurgiczne, zastępujące konwencjonalną metodę ogrzewania. Celem artykułu jest ocena możliwości zastosowania energii mikrofalowej w procesach przeróbki odpadów metalurgicznych. Oceniono skuteczność recyklingu, koszty przeróbki odpadów i jej efektywności.*

*Słowa kluczowe: odpady metalurgiczne, mikrofałe, ekstrakcja, odzysk cynku*