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Non-isothermal microwave leaching kinetics of zinc removal from basic oxygen furnace dust

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The basic oxygen furnace (BOF) dust is a hazardous metallurgical waste generated in the collection of particulate material during steel making processes. The occurrence and recovery of metallurgical wastes from steelmaking and iron making processes become nowadays a great problem, mainly due to the big amount and environmental pollution by heavy metals potential. The research of non-isothermal kinetics by microwave heating was evaluated. Experimental results indicate that the most important factor that strongly affected microwave acid extraction was the microwave power input. It is shown that approximately from 22 to 50°C the process is controlled by diffusion with a low apparent activation energy value of E_a = 1.15 kJ/mol. With increasing temperature the Arrhenius slope is more steeper with the apparent activation energy value of E_a = 22.01 kJ/mol, which proves that the microwave leaching process from 50°C is under control by the surface chemical reaction. This indicates that the microwave promotes the mineral solid particle to burst effectively, makes the particle to expose a fresh surface and strengthens the leaching process.

Keywords: *basic oxygen furnace dust, extraction, microwave assisted leaching, non-isothermal kinetics, zinc recovery*

Introduction

The industrial development leads to the generation of more and more industrial waste during the production processes (Bláha et al., 2008; Vereš et al., 2009a). One of the most serious related problems is the generation of industrial sludge that contains various toxic metals. The extraction process is environmentally and economically attractive because it can detoxify industrial sludge and remove valuable metals for their reuse. Various studies have investigated the use of acids and solvents to remove metals from solid wastes using the microwave energy (Kuo et al., 2005ab; Vereš et al., 2009b; Xia and Pickles, 2000). The microwave assisted leaching which is an environment friendly process has been investigated to improve the metal recovery and to reduce the process time. To compare with the conventional leaching in the conventional thermal processing, energy is transferred to the material by the convection, conduction and radiation of heat from the surface of the material. In contrast, the microwave energy is delivered directly to materials via molecular interactions with the electromagnetic field. This difference in the manner in which energy is delivered is responsible for the numerous potential advantages in using microwaves to extract industrial sludge. Microwave heating is faster and so supports faster dissolution than conventional heating. However the temperature control inside the heated material is still a great problem (Kačur et al., 2008). The microwave energy has the potential to be used in metal recovery operations, such as heating, drying, leaching, roasting/smelting and waste management (Haque, 1999). Rapid solvent extraction (Xia and Pickles, 2000) and the fast wet dissolution of various types of solid samples (Perez-Cid et al., 1999) are some of the most well known microwave applications. Above all, the microwave leaching makes use of the advantage of characteristics such as internal heating, dielectric heating, promoting the mineral solid particles burst and exposing the fresh surface of particles (Haque, 1999; Hua et al., 2002; Zhai et al., 2009). Meanwhile, it is also able to promote the high speed vibration of polar liquid molecule, resulting in the increases of mutual collision of materials and the enhancement of the liquid-solid reaction rate (Al-Harahsheh and Kingman, 2004, 2007). In the present study, the non-isothermal leaching kinetics of zinc from the basic oxygen furnace dust by microwave heating is studied. The influence of sulphuric acid concentration, S/L ratio, microwave power level and leaching time on the leaching rate of Zn is investigated.

Calculation of non-isothermal kinetics

Kinetic analysis of solid state decompositions is usually based on a single step kinetic equation (Vyazovkin and Wight, 1999; Ebrahimi-Kahrizsangi and Abbasi, 2008):

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where t is the time, T is the temperature, α is the extent of conversion, and $f(\alpha)$ is the reaction model. Integration of the above equation gives the integral rate law:

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$$g(\alpha) = kt \tag{2}$$

Several reaction models (Ebrahimi-Kahrizsangi and Abbasi, 2008; Gao et al., 1993; Vyazovkin and Wight, 1998; 1999) using $f(\alpha)$ or $g(\alpha)$ are listed in Table 1. The explicit temperature dependence of the rate constant is introduced by replacing $k(T)$ with the Arrhenius equation which gives:

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E_a}{RT}\right)f(\alpha) \tag{3}$$

and

$$g(\alpha) = A\exp\left(\frac{-E_a}{RT}\right)t \tag{4}$$

where ***A*** (the pre-exponential factor) and $\boldsymbol{E}_\mathbf{a}$ (activation energy) are the Arrhenius parameters. These parameters 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, the explicit temporal in Eqn.(3) is eliminated through the trivial transformation (Vyazovkin and Wight, 1998):

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(\frac{-E_a}{RT}\right)f(\alpha) \tag{5}$$

where $\beta = dT/dt$ is the heating rate (Coats and Redfern, 1964; Gao et al., 1993).

Upon integration, Eqn.(5) gives:

$$g(\alpha) = \frac{A}{\beta}\int_0^T \exp\left(\frac{E_a}{T}\right)dT \tag{6}$$

If $E_a/(RT)$ is replaced by x and integration limits transformed, Eqn.(6) becomes:

$$g(\alpha) = \frac{AE_a}{RT}\int_x^\infty \frac{\exp(-x)}{x^2}dx \tag{7}$$

Eqn.(7) can be written as:

$$g(\alpha) = \frac{AE_a}{RT}p(x) \tag{8}$$

p(x) has no analytical solution but has many approximations (Chen and Lai, 2004), 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 in Eqn.(8), giving:

$$\ln\frac{g(\alpha)}{T^2} = \ln\left[\frac{AR}{\beta E_a}\left(1 - \frac{2R\overline{T}}{E_a}\right)\right] - \frac{E_a}{RT} \tag{9}$$

Plotting the left hand side of Eqn.(9), which includes ***g(α)*** versus ***1/T***, gives $\boldsymbol{E}_\mathbf{a}$ and ***A*** from the slope and intercept respectively. The model that gives the best linear fit is selected as the chosen model (Ebrahimi-Kahrizsangi and Abbasi, 2008).

Tab. 1. Solid state rate equations.

Reaction Model		f(α)	g(α)
Nucleation Models			
1	Power Law	$4\alpha^{3/4}$	$\alpha^{1/4}$
2	Power Law	$3\alpha^{2/3}$	$\alpha^{1/3}$
3	Power Law	$2\alpha^{1/2}$	$\alpha^{1/2}$
4	Avrami-Erofeev	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
5	Avrami-Erofeev	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
6	Avrami-Erofeev	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
Diffusion Models			
7	One dimensional Diffusion	$(1/2)\alpha^{-1}$	α^2
8	Diffusion control (Janders)	$2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]-1$	$[1-(1-\alpha)^{1/3}]^2$
9	Diffusion control (Crank)	$(3/2)[(1-\alpha)^{-1/3}-1]^{-1}$	$1-(2/3)\alpha - (1-\alpha)^{2/3}$
Reaction order and geometrical contraction models			
10	Mampel (first order)	$1-\alpha$	$-\ln(1-\alpha)$
11	Second Order	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
12	Contracting cylinder	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
13	Contracting Sphere	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$

Materials and methods

The basic oxygen furnace dust used in this work was dried at 105 °C for 12 h and then kept in a desiccator before the experiment. The chemical composition of BOF dust depends mainly on the quality of steel scrap processed and the type of steel produced. Table 2 presents the chemical composition of the major components 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.

Tab. 2. Chemical composition of BOF dust.

Component	Content (wt. %)
Fe_{total}	49.87
Zn	9.37
CaO	7.50
MgO	2.68
SiO_2	0.87
C	0.97
Pb	0.24

Mineralogical composition of samples was determined by XRD using a Philips PW1820 Automatic Powder Difractometer with Cu Kα radiation. It was found that zinc in this basic oxygen furnace dust is in the forms of franklinite (zinc ferrite, $ZnFe_2O_4$), zincite (zinc oxide, ZnO), and iron is in the form of magnetite, hematite, franklinite, iron oxide and elemental iron. The X-ray diffraction pattern of the BOF dust is shown in Fig. 1.

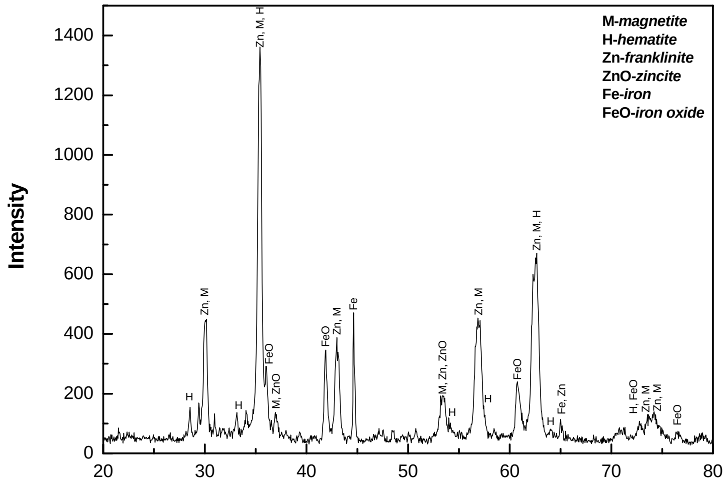


Fig. 1. X-ray diffraction pattern of BOF dust sample.

By SEM observation (Fig. 2), the dust particles shape could be approximately spherical with some agglomerated. The dust size distribution was characterized by granulometry analysis. The granulometric analysis of BOF dust was evaluated by laser analyzer Helos/LA Sympatec (Germany). The particle size distribution of the examined BOF dust is given in Fig. 3. It presents a heterogeneous distribution of particle size and contains two major size fractions: a fine grained (1–10μm) and a coarser (10–36μm) ones.

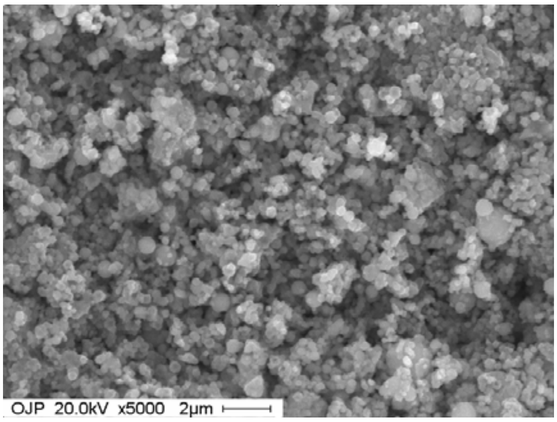


Fig. 2. SEM picture of BOF dust particles.

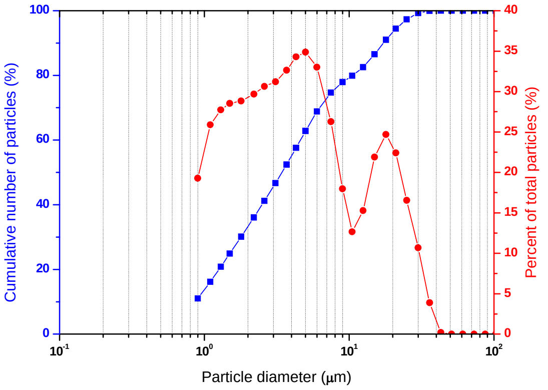


Fig. 3. Particle size distributions of the BOF dust used.

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 contain markedly different amount of zinc as the average composition. It was found that 50 % of it was below 3.5 μm, whereas the majority (100 %) of the particles was below 36 μm. During microwave assisted leaching, a microwave oven Whirlpool AVM 434 with a power range from 90 to 900 W at frequency of 2.45 GHz was used. Leaching studies to determine optimum operational conditions such as efficiency, solid-liquid (S/L) ratio, reaction time, in the reactor with volume of 300 ml were performed. During the microwave leaching process a mechanical stirrer was used to mix the BOF dust sample 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 Raytek Raynger MX-4. In all experiments, the zinc and iron concentration and dissolution percent was determined by AAS using the device Varian with accessories: Fast Sequential AAS AA240FS, Zeeman AAS AA240Z with Programmable Sample Dispenser PSD120, Graphite Tube Atomizer GTA120 and Vapor Generation Accessory VGA-77. So, the effects of leaching conditions on zinc and iron dissolution were studied.

Results and discussion

The effect of temperature and microwave energy was studied using a modified domestic microwave oven with power levels 90, 160, 350 and 650 W. In every case of microwave assisted extraction process the temperature of the leaching solution in the beginning was at room temperature. Figure 4 presents microwave assisted extraction of zinc and iron from BOF dust at various microwave powers. 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.

These experimental findings demonstrate that the most important factor in microwave acid extraction was the microwave power input. The nature of the zinc species that is easily solubilized by 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 zinc leaching is probably related to the presence of zinc ferrite in much greater proportion than the zinc oxide. For verification purposes, these points may require additional characterization work for the sludge sample currently tested. Initial batch of dust samples indicate the presence of zinc oxide by XRD technique only as a minority phase. Figure 5 demonstrates the zinc and iron dissolution dependence at various microwave powers.

The non-isothermal kinetics equation in microwave field is as (Peng and Liu, 1992; Xia et al., 2010):

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[\frac{Mc^n AR}{r_0 B\rho E_a}\left(1-\frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \qquad (10)$$

where $\boldsymbol{r}$ is the nucleus radius, $\boldsymbol{r_0}$ is the primary nucleus radius, $\boldsymbol{c}$ is the concentration, $\boldsymbol{n}$ is the order of reaction, $\boldsymbol{E_a}$ is the activation energy, $\boldsymbol{A}$ is the frequency factor, $\boldsymbol{M}$ is a constant, $\boldsymbol{T}$ is the leaching system temperature, $\boldsymbol{B}$ is the velocity constant of temperature, $\boldsymbol{\rho}$ is the density of the particles, $\boldsymbol{\alpha}$ is the leaching rate. According to Eqn.(4), the experiments on the relationship between the leaching rate of Zn in BOF dust and the temperature were carried out. The results show that the temperature of the leaching system increased gradually with increasing microwave heating time.

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.

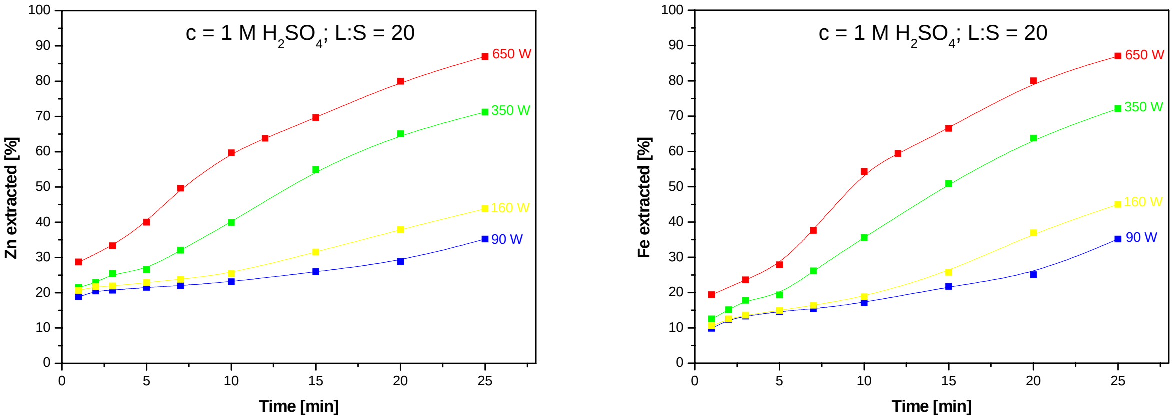


Fig. 4. Zinc and iron dissolution percentage at various microwave powers.

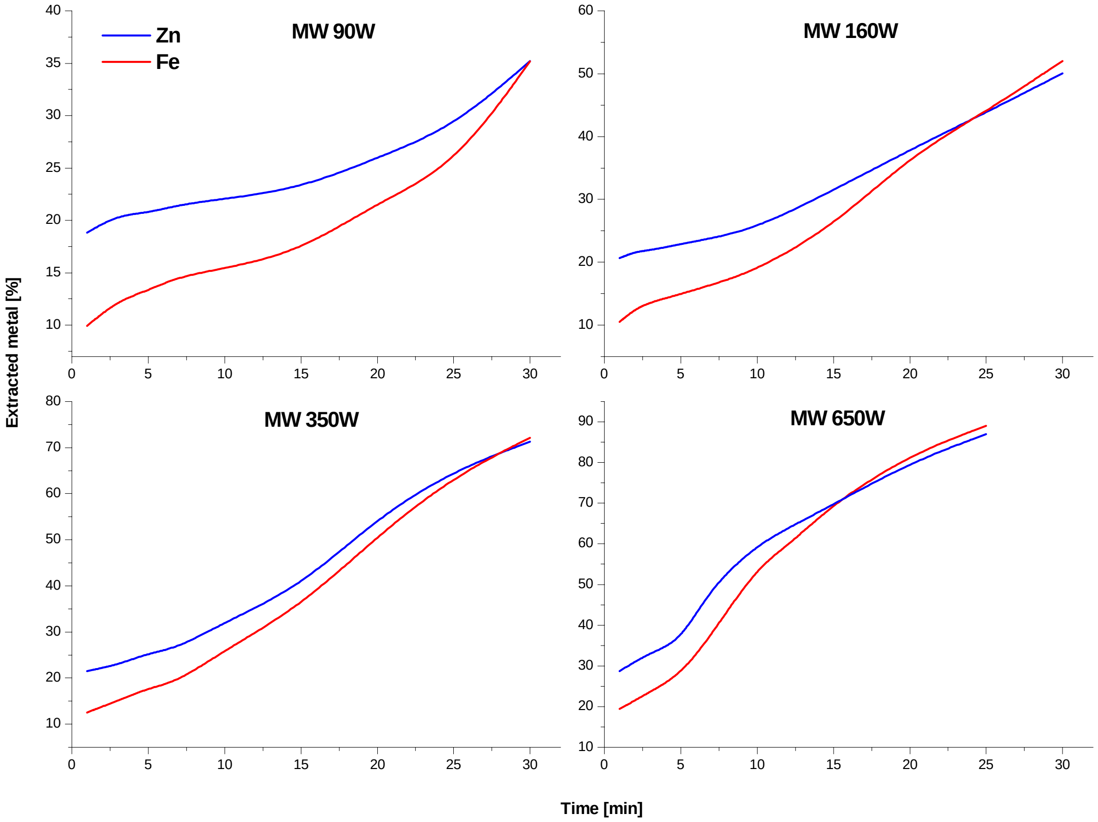


Fig. 5. Zinc and iron dissolution dependence at various microwave powers

The leaching system temperature (T), leaching rate α of Zn and calculated values of the $\ln\{[1-(1-\alpha)^{1/3}]/T^2\}$ for microwave power 160 W were listed in Table 3.

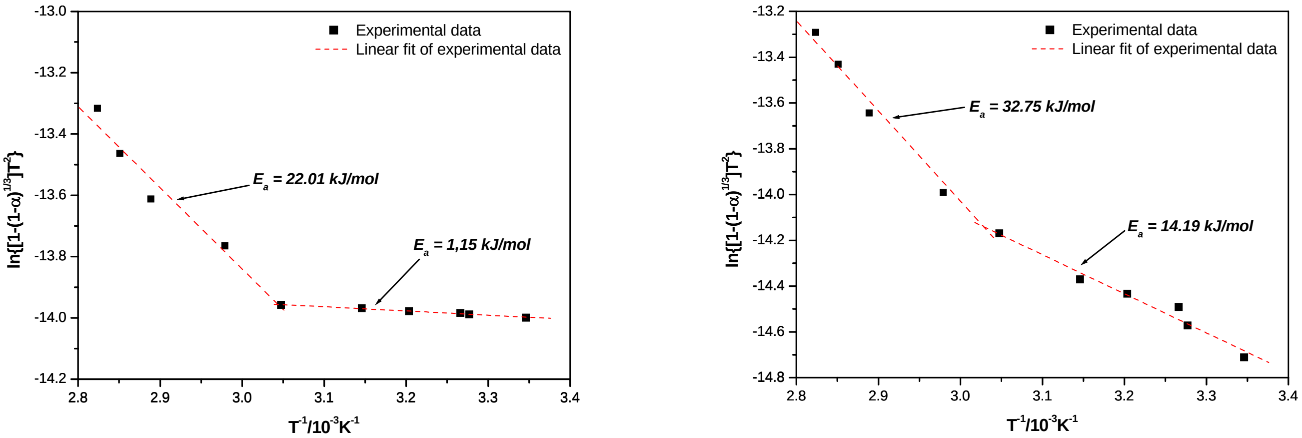
Tab. 3. Data derived from non-isothermal leaching kinetics equation.

Time/min	T/K	α/%	$\ln\{[1-(1-\alpha)^{1/3}]/T^2\}$
1	298.85	20.67	-13.9998
2	305.15	21.69	-13.9891
3	306.15	21.92	-13.9844
5	312.15	22.85	-13.9780
7	317.85	23.82	-13.9685
10	328.15	25.47	-13.9583
15	335.65	31.52	-13.7645
20	346.15	37.91	-13.6118
25	350.75	43.83	-13.4638
30	354.15	50.06	-13.3163

Using data from Table 2, the plot of relationship between 1/T and $\ln\{[1-(1-\alpha)^{1/3}]/T^2\}$ was obtained, as shown in Fig. 5, including the activation energy, calculated by the Arrhenius equation:

$$\ln k_c = -\frac{E_a}{R} \times \frac{1}{T} + \ln A \qquad (11)$$

where k_c is the apparent velocity constant.



a **b**

Fig. 6. Relationship between 1/T and $\ln\{[1-(1-\alpha)^{1/3}]/T^2\}$ at microwave power 160 W for zinc (a) and iron (b) leaching.

The kinetics of zinc dissolution in sulphuric acid has been assessed on the basis of the shrinking core model. 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.

The temperature influence on dissolution process represented by the Arrhenius relation in Figure 6 indicates that the zinc and iron 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 $E_a = 1.15$ 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 45 °C. With increasing temperature the Arrhenius slope steepness with apparent activation energy value of $E_a = 22.01$ kJ/mol.

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. The percentage of extraction of zinc increased with the 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, the particles gain more kinetic energy and collide more frequently, thus enhancing the rate of reaction. 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 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 model based on the contracting sphere (Table 1) and from the Arrhenius plot using k_c values obtained experimentally. Up to approximately 50 °C the process is controlled by diffusion with a low apparent activation energy value of E_a = 1.15 kJ/mol. With an increasing temperature, the Arrhenius slope steepness with the apparent activation energy value of E_a = 22.01 kJ/mol. The microwave treatment of the BOF dust resulted in a very rapid dissolution of the zinc phase. The effect of power level was significant. At higher power levels, the dissolution rates were higher 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 such as superheating of the liquid, interaction of the microwaves with the BOF dust particles in the solution etc.

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References

[1] Al-Harahsheh, M., Kingman, S.: The influence of microwaves on the leaching of sphalerite in ferric chloride. *Chemical Engineering and Processing: Process Intensification 46 (2007), 883-888.*

[2] Al-Harahsheh, M., Kingman S.: Microwave leaching - a review. *Hydrometallurgy 73(3), (2004), 189-203.*

[3] Bláha, V., Kaľavský, F.: Application of dry separative methods for decreasing content the residues unburned coal and separation Fe from black coal fly ash, *Acta Montanistica Slovaca, 13(2), (2008), 235-240.*

[4] Chen, H.J., Lai, K.M.: Methods for determining the kinetics parameters from nonisothermal thermogravimetry, *J. of Chem. Eng. of Japan*, *37(9), (2004), 1172-1178.*

[5] Ebrahimi-Kahrizsangi, R., Abbasi, M.H.: Evaluation of reliability of Coats-Redfern method for kinetic analysis of non-isothermal TGA. *Trans. Nonferrous Met. Soc. China 18 (2008), 217-221.*

[6] Coats, A.V., Redfern, J.P.: Kinetic parameters from thermogravimetric data. *Nature 201 (1964), 68-69.*

[7] Gao, X., Chen, D., Dollimore, D.: The correlation between the value of α at the maximum reaction rate and the reaction mechanisms: A theoretical study. *Thermochimica Acta 223 (1993), 75-82.*

[8] Haque, K.E.: Microwave energy for mineral treatment processes - a brief review. *Int. J. Miner. Process 57 (1999), 1-24.*

[9] Hua, Y., Lin, Z., Yan, Z.: Application of microwave irradiation to quick leaching of zinc silicate ore. *Minerals Engineering 15 (6), (2002) 451-456.*

[10] Kačur, J., Kostúr, K.: The algorithms for control of heating massive material, *Acta Montanistica Slovaca, 13(1), (2008), 87-93.*

[11] Kuo, C.Y., Wu, C.H., Lo S.L.: Leaching efficiency of copper from industrial sludge with traditional acid extraction (TAE) and microwave assisted treatment (MAT). *Journal of Environmental Science and Health - Part A - Toxic/Hazardous Substances and Environmental Engineering 40 (2005), 2203-2214, (2005a).*

[12] Kuo, C.Y., Wu, C.H., Lo, S.L.: Removal of copper from industrial sludge by traditional and microwave acid extraction. *Journal of Hazardous Materials B 120 (2005), 249-256, (2005b).*

[13] Machado, G.M.S.J., Brehm, F.A., Moraes, C.A.M., dos Santos, C.A. Vilela, A.C.F., Cunha, J.B.M.: Chemical, Physical, Structural and Morphological characterization of the electric arc furnace dust. *Journal of Hazardous Materials 136 (3), (2006), 953-960.*

[14] Peng, J., Liu, CH.: Kinetics of sphalerite leached by $FeCl_3$ in microwave field. *The Chinese Journal of Nonferrous Metals 2(1) (1992), 46-49.*

[15] Perez-Cid, B., Lavilla, I., Bendicho, C.: Application of microwave extraction for partitioning of heavy metals in sewage sludge. *Anal. Chim. Acta 378 (1999), 201-210*.

[16] Vereš, J., Orolínová, Z.: Study of the treated and magnetically modified bentonite as possible sorbents of heavy metals, *Acta Montanistica Slovaca, 14(2), (2009), 152-155, (2009a).*

[17] Vereš, J., Lovás, M., Jakabský, Š.: Characterization of blast furnace sludge and removal of zinc by traditional acid extraction (TAE) and microwave assisted treatment (MAT). *In: Proceedings of 13th Conference on Environment and Mineral Processing. Part II, VŠB-TU Ostrava, ISBN 978-80-248-1995-2, (2009) 283-289, (2009b).*

[18] Vyazovkin, S., Wight, C.A.: Isothermal and non-isothermal kinetics of thermally stimulated reactions of solids. *International Reviews in Physical Chemistry 17 (3) (1998), 407-433*.

[19] Vyazovkin, S., Wight, C.A.: Model-free and model fitting approaches to kinetic analysis of isothermal and nonisothermal data. *Termochinica Acta 340-341 (1999), 53-68*.

[20] Xia, D.K., Pickles, C.A.: Microwave caustic leaching of electric arc furnace dust. *Minerals Engineering 13 (2000), 79-94*.

[21] Xia, H., Peng, J., Niu, H., Huang, M., Zhang, Z., Zhang, Z., Huang, M.: Non-isothermal microwave leaching kinetics and absorption characteristics of primary titanium-rich materials. *Trans. Nonferrous Met. Soc. China 20 (2010), 721-726*.

[22] Zhai, X.J., Fu, Y., Zhang, X., Ma, L.Z., Xie, F.: Intensification of sulphation and pressure acid leaching of nickel laterite by microwave radiation. *Hydrometallurgy 99 (3/4), (2009), 189-193*.