T. HAVLIK*#, G. MARUSKINOVA*,**, A. MISKUFOVA*

DETERMINATION OF ZnO AMOUNT IN ELECTRIC ARC FURNACE DUST AND TEMPERATURE DEPENDENCE OF LEACHING IN AMMONIUM CARBONATE BY USING OF X-RAY DIFFRACTION

Zinc is present in electric arc furnace dust (EAFD) mainly in two basic minerals, namely as franklinite $ZnFe_2O_4$ and/or zincite ZnO. While zincite is relatively reactive and easily treatable, franklinite is considerably refractory, which causes problems during EAFD processing. In this work EAFD containing 18.53% Zn was leached in water solution of ammonium carbonate. This leaching solution selectively leaches zincite, while franklinite is refractory and stable against leaching in this case. The temperature dependence of zinc leaching from EAFD was studied and the activation energy E_A was determined by two methods:

1.) classically based on zinc chemical analyses from the leaching solution and

2.) by using of X-Ray diffraction qualitative phase analyses of leaching residues.

The determined values of activation energies 37.41 and 38.55 kJmol^{-1} match perfectly, which show the excellent possibility of using X-Ray diffraction toward the study of leaching kinetics at properly chosen experimental conditions. The important result is the determination of the amount zincite and franklinite in EAFD, which is not possible by using of classical chemical methods.

Keywords: electric arc furnace dust, zincite, franklinite, recycling, hydrometallurgy, leaching, kinetics, activation energy, XRD

1. Introduction

Worldwide steel production in 2014 was 1.665 billion tons [1]. Around 28% are produced using EAF technology, which accounts for 466 million tons [2]. During the steel production in EAF, around 15 to 25 kg of dust per 1 ton of produced steel is generated as by-product, containing 20-35% of iron oxide, which offers a good chance for its recycling in the pig iron process. Electric arc furnace dust EAFD is a hazardous waste product of the steelmaking industry with a high concentration of heavy metals. Typical composition, except of iron oxides, is 5-40% zinc oxide, 5-25% calcium oxide, 5-10% magnesium oxide, 1-5% manganese, 1-5% alumina, 0.1-1% lead, 0.1-1% chromium, etc. [3]. Existing treatment processes are industrially viable only when the zinc content is sufficiently high around 15-25%. Present hazardous components as zinc, lead, chromium, cadmium inhibit direct recycling of EAFD. On the other hand, the price of zinc is interesting and its amount of around 20% shows that globally in EAFD around 1.84 million tons of zinc are present. Nowadays, the worldwide zinc primary production is 13.3 million tons annually [4]. This is a very good reason to recycle EAFD with the aim to recover not only iron concentrate but also zinc or even other heavy metals.

The processing of EAFD can be divided into pyrometal-lurgical and hydrometallurgical methods, or their combination.

The pyrometallurgical methods are based on reductive processes, resulting in lower iron oxides or iron sponge creation. At the same time oxides of heavy metals are reduced creating zinc, lead and other easily reducible non-ferrous metals. Metals with high vapour density as zinc, lead and cadmium pass into flue dust, where they are again oxidized and captured in filters. This secondary flue dust can be used for metal recovery by hydrometallurgical methods or more infrequently pyrometallurgically. However, although higher quality ZnO can be produced, these methods require a big amount of energy due to heating and cooling of solutions.

Both, pyrometallurgical and hydrometallurgical processing of EAFD, is paid much attention to in published work, which is dealing with the theory of this processes and various kinds of technologies as well. The papers [5-9] offer a good survey about the work carried out in this field. The most practical pyrometallurgical method of processing of raw materials containing zinc is Waelz process. [2]. Further known pyrometallurgical processes dealing with zinc bearing EAFD are for example Redsmelt, Primus, RedIron [10], Fastmet [11], Radust [12], and Recumet [13].

Hydrometallurgical processes nowadays are more and more frequently taken into account mostly because of higher flexibility, fairly lower investment and operational costs and furthermore, because these processes are more environmentally friendly compared to pyrometallurgical ones. For hydrometallurgical

* TECHNICAL UNIVERSITY OF KOSICE, METALLURGICAL FACULTY, INSTITUTE OF RECYCLING TECHNOLOGIES, LETNA 9, 04200 KOSICE, SLOVAKIA
** ZP RESEARCH AND DEVELOPMENT CENTRE, KOLKAREN 35, 97681 PODBREZOVA, SLOVAKIA
# Corresponding author: tomas.havlik@tuke.sk

processing of EAFD in general acidic and alkaline processes could be used and both of them could be processed at the so called normal conditions of temperature and pressure as well as at high-temperatures and high-pressures.

Alkaline leaching seems to be a suitable method as heavy metals pass into solution while iron is inert against alkaline solution. However, there are technical problems e.g. necessity of using higher concentration of solutions, their higher price, relatively low efficiency, problematic recovery of metals from solution, and problems dealing with regeneration of solutions. When studying alkaline leaching of EAFD, NaOH is the most commonly used leaching agent.

The sulfuric acid diluted solution is the most widely used leaching agent in the case of acid leaching, which is due to its low price and relatively well-known zinc electrolysis from sulphate solutions. Several hydrometallurgical processes were described by Jha et al. as MAR, Redox, Amax, Batenus, UBC-Chaparral, Cenim-Lneti, Ezinex [6].

A very important indicator of the efficiency of EAFD processing is the form of the presence of zinc in the dust.

Zinc oxide ZnO is the compound which can easily be processed by both pyrometallurgical [16] and hydrometallurgical methods [6], but zinc ferrites such as franklinite $ZnFe_2O_4$, resp. complex franklinite as $(Me,Zn)_2O_4$, where Me = Ca,Mn, are very resistant against the majority of processing methods. Moreover, it is very problematic to predict and/or determine the mineralogical form and its quantity of zinc compounds. The comparison of pyrometallurgical and hydrometallurgical processes is as follows: generally the pyrometallurgical ones are economically acceptable when around 50 000-100 000 tons per year are processed [15]. The hydrometallurgical processes are already economic when around 16 000 tons per year are treated [5]. That is why more and more effort is paid to the design of hydrometallurgical processes of EAFD processing. On the other hand, EAFD heterogeneity and anisotropy in chemical and

mineralogical composition still does not allow to optimize the process of EAFD treatment. The form of mineralogical presence of zinc whether as zincite ZnO or franklinite $ZnFe_2O_4$ is probably determining for the process conditions, because ZnO is relatively easy leachable in almost every leaching media, while franklinite is rather refractory. Moreover, it is too complicated to determine in what amount and form the zinc in EAFD is present, as zinc is present in various mineralogical forms. Similarly, the presence of calcium in various forms and quantities seriously complicates leaching as it preferably reacts with leaching solution [16]. Due to these reasons practically no published process has achieved full-plant scale.

The aim of this work is to study the kinetics of EAFD leaching in ammonium carbonate solution and to determine basic kinetic parameters zinc leaching from EAFD. Further aim is to quantify the zinc containing mineralogical phases. For this purpose the method of X-ray diffraction analyses was used.

2. Experimental

2.1. Material

A sample of EAF dust with chemical composition 18.53% Zn, 30.07% Fe, 5.07% Ca,1.32% Pb, 1.18% Mn, 0.16% Cr, 5.12% Si was used in the experimental part. The chemical analysis was carried out by AAS (Varian Spectrometer AA 20+).

Phase analysis of the sample was carried out by the X-ray diffractometer PANanalytical X'Pert PRO using Co Kα radiation (0.1789 nm), generator settings 30 mA, 40 kV. The resulting XRD pattern is shown in Figure 1.

Other phases such as magnetite Fe_3O_4, calcite $CaCO_3$, complex franklinite $(Zn,Mn,Fe)(Fe,Mn)_2O_4$, lime CaO, sodium chloride NaCl, calcium sulfate hydrate oxide CaSO4*0.5 H_2O, and lead silicate Pb_3SiO_5 were identified.
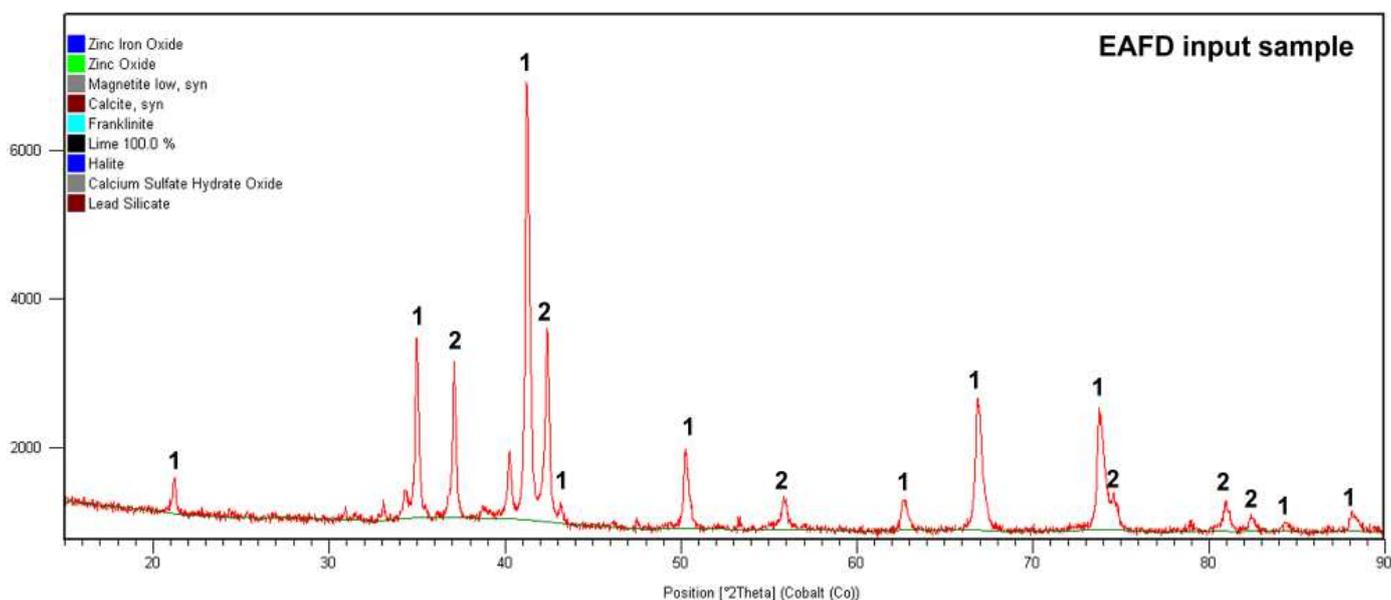

Fig. 1. The XRD pattern of the input EAFD sample, 1-ZnFe$_2$O$_4$, 2-ZnO

2.2. Experimental procedure

The experimental assumptions were as follows:
a) iron is not leached in alkaline solutions, and
b) $ZnFe_2O_4$ is refractory in alkaline solutions and can be leached difficult.

The EAFD sample was washed in water in order to remove soluble components, mostly chlorides and sulfates of calcium, chromium and lead if they were present in soluble form.

As a consequence, the distortion of XRD diffraction patterns of partly leached samples was eliminated. The sample was dried and leached according to given time and temperature schedule as shown in Table 1.

TABLE 1

The experimental matrix

Leaching time [min]	Temperature [°C]				
	20	30	40	50	60
1	x	x	x	x	x
3	x	x	x	x	x
5	x	x	x	x	x
10	x	x	x	x	x
15	x	x	x	x	x
30	x	x	x	x	x
60	x	x	x	x	x
90				x	
120				x	
150				x	
180				x	

The maximum temperature 60°C is determined by ammonium carbonate stability, because it decomposes at the temperatures around 60°C according to

$$(NH_4)_2CO_3 = NH_{3(g)} + CO_{2 (g)} + H_2O_{(g)} \qquad (1)$$

The leaching experiments were performed in a glass reactor of 800 ml, which was placed into a water thermostatic bath allowing to automatically maintain the desired leaching temperature. The pulp was mixed with a glass stirrer connected to the electric motor with variable speed. Temperature was measured by mercury thermometer.

The volume of the leaching reagent used for the experiments was 100 ml. In each experiment 20 g of sample and 100 ml of water solution of ammonium carbonate was used. The concentration of ammonium carbonate was 200 g/l. Kinetics measurements were carried out at temperatures of 20, 30, 40, 50 and 60°C. In each experiment, the pulp was stirred at a constant speed of 300 rpm. The experimental procedure was the following: The ammonium carbonate solution was poured into the reactor and heated up to the desired temperature with constant stirring. After reaching the desired temperature, a pre-weighed amount of the sample was poured into the reactor. After the sample was poured into the leaching solution, time was measured. The leaching was finished after chosen time according to Table 1, and the liquid samples were filtrated in order to remove solid

residues of the pulp. The chemical analysis, carried out in order to determine zinc and iron was made by means of the AAS method. Leaching solid residue was washed by distilled water, dried and submitted to XRDA.

3. Results and discussion

Figure 2 shows the kinetic curves of leaching zinc expressing the zinc dissolution rate at temperatures 20, 30, 40, 50, and 60°C, ammonium carbonate concentrations 200g/l and liquid to solid (L:S) ratio = 5. At the same time practically no iron was leached as maximum iron extraction was at 60°C equal to 0.099%.

It follows from the kinetic curves shapes' that the process is fast in the first stage of leaching. After a short period (two/three minutes) it is slower, even stops. It reveals even possible change of process mechanism.
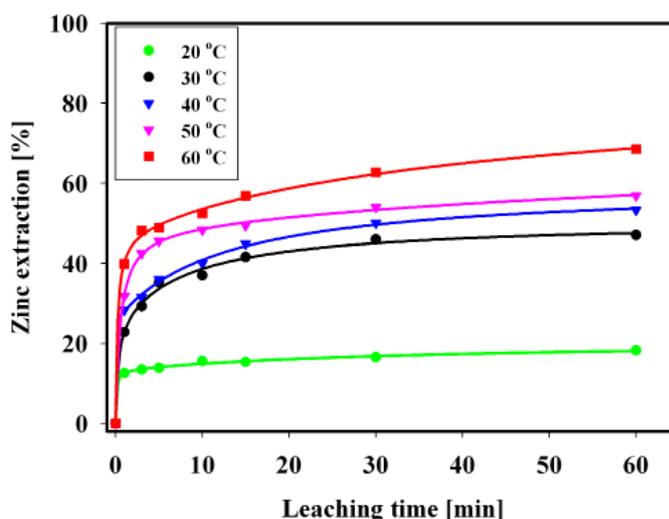

Fig. 2. Kinetic curves of zinc leaching from EAFD in dependence on temperature

As was mentioned above, all solid leaching residues were submitted to XRDA. The results in Figure 3 show that zincite ZnO is removed during leaching whereas franklinite $ZnFe_2O_4$ stays practically inert.

From this respect it is possible to consider $ZnFe_2O_4$ as internal standard which allows to quantify the kinetics of ZnO leaching from EAFD as shown in Figure 4.

Achieved kinetic dependences served in both cases for specification of temperature influence and leaching mechanism.

The kinetic dependence can be in general described as

$$R = k \cdot t^n \qquad (2)$$

where R is conversion, which will be calculated from chemical analyses results, t is known reaction time, n is reaction order and k rate constant [17,18]. By comparing kinetic equations for individual temperatures the rate constant values will be determined and the value of reaction order will be fitted.
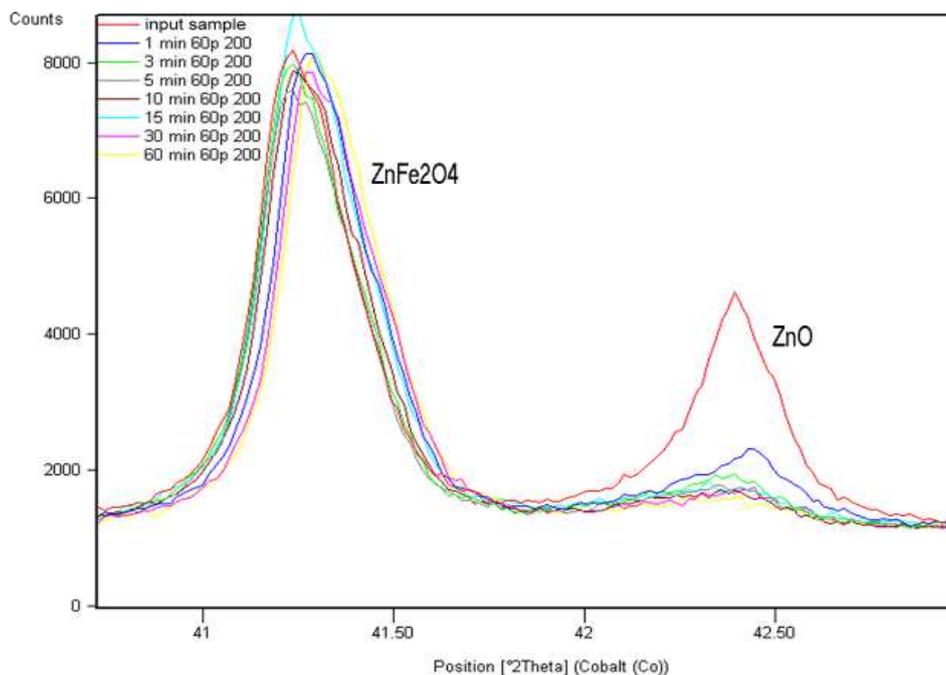
Fig. 3. Comparison of details of XRD patterns of partly leached samples
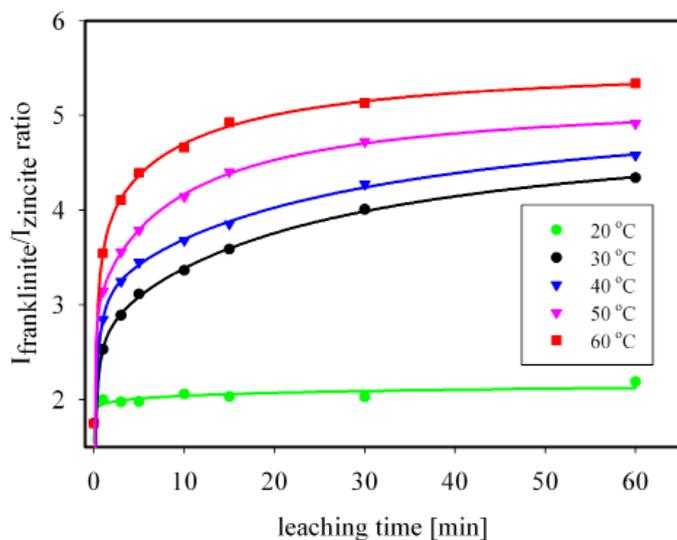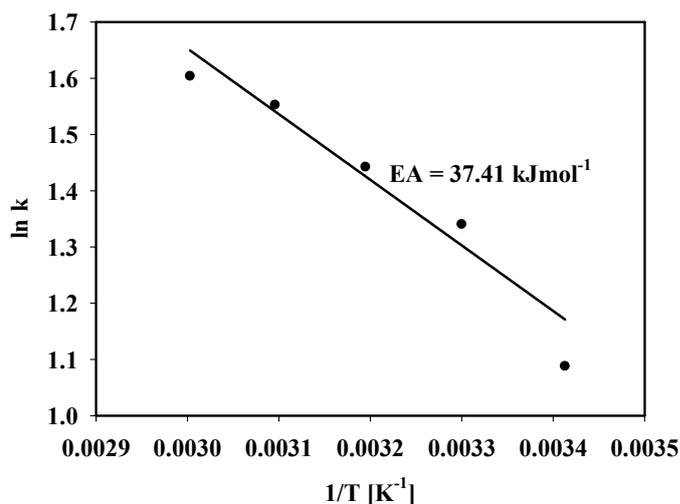

Fig. 4. Time dependences of relative intensities $ZnFe_2O_4$/ZnO ratio

Fig. 5. Arrhenius plot of zinc leaching from EAFD, estimated from chemical analyses of zinc in leaching solutions

The Arrhenius plot was constructed from calculated values of rate constants according to

$$k = A \cdot e^{-\left(\frac{E}{RT}\right)} \tag{3}$$

Taking the logarithmic form of equations and comparing them at used temperatures yields activation energy as a sloped line, what is shown on the Figure 5.

The integral of diffractions of individual phases from XRD patterns determines their relative representation in the mixture. That is why it can be used for calculation of conversion R values for rate of chemical reaction according to equation (2) as it follows from Figs. 3 and 4. The ratios D (lnk) / D (1/T) of dependences on Figs. 3 and 4 were used for the R value calculation.

From calculated values again an Arrhenius plot was constructed as shown on Fig. 6.

Determined values of activation energy in both cases reveal that the slowest, rate-controlling step is the chemical reaction; eventually, the process is running in a mixed regime of chemical reaction and diffusion. Chemical analyses of leaching solutions confirmed that zinc is leached out from EAFD, whereas XRDA of partly leached solid residues confirmed the fact that only zincite ZnO is reacted in EAFD leaching whereas franklinite $ZnFe_2O_4$ stays unreacted.

The prolongation of leaching time for 3 hours verified this fact. It follows from Figure 7 that the process practically stops and zincite ZnO was removed from leached material, Figure 3.
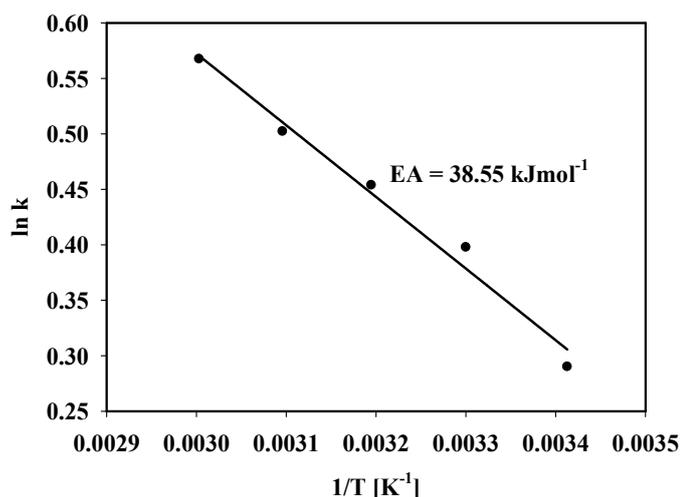
Fig. 6. Arrhenius plot of zinc leaching from EAFD, estimated from XRD profile analyses
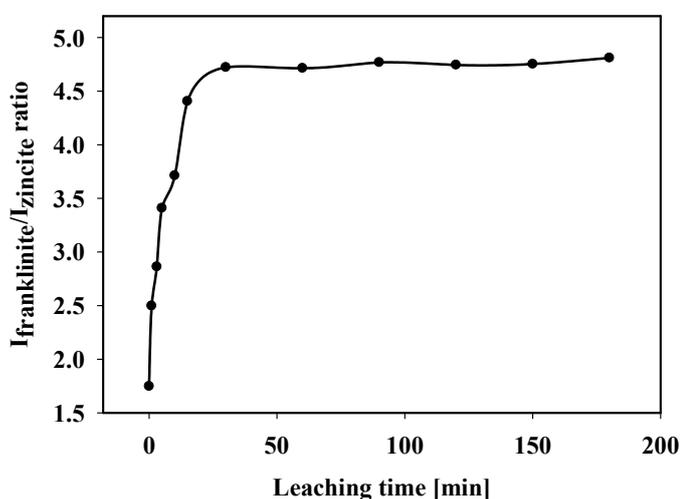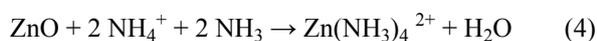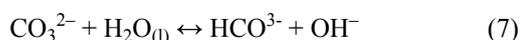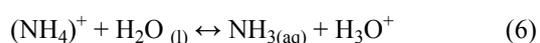

Fig. 7. Time dependences of zinc leaching from EAFD in ammonium carbonate during three hours at 50°C

It follows that the rate controlling step of zinc leaching out is the chemical reaction between ZnO and ammonium carbonate

$$ZnO + 2\,NH_4^+ + 2\,NH_3 \rightarrow Zn(NH_3)_4{}^{2+} + H_2O \qquad (4)$$

Equation (4) reveals that the process is quite complicated because ammonium carbonate is less stable at given conditions and decomposes during the process according to

$$(NH_4)_2CO_{3\,(aq)} \rightarrow 2(NH_4)^+ + CO_3{}^{2-} \qquad (5)$$

$$(NH_4)^+ + H_2O_{\,(l)} \leftrightarrow NH_{3(aq)} + H_3O^+ \qquad (6)$$

$$CO_3{}^{2-} + H_2O_{(l)} \leftrightarrow HCO^{3-} + OH^- \qquad (7)$$

As zinc is leached practically from ZnO only in this case, by using XRDA it is possible to determine the quantity of ZnO

in EAFD, which is impossible by using elemental chemical analysis, because by elemental analyses it is impossible to say if analysed zinc is resulting from zincite or franklinite. On other hand, as both, franklinite and magnetite, are present in the mixture, it is also impossible to say what part of iron belongs to franklinite. This is a very important information which significantly helps in the optimization of EAFD leaching process. In this case, the efficiency of zinc extraction was around 65% from total amount of zinc content in EAFD equal to 18.53%. That means that zinc content in studied EAFD is equal to 12% in the form of ZnO, i.e. two-thirds majority. The values of activation energy determined from both elemental chemical analyses and XRDA equal to 37.4 kJmol^{-1} and 38.55 kJmol^{-1} fit perfectly. This opens possibilities of using XRDA in leaching processes controlling mostly as multicomponent mixture is used, where it is not possible to exactly determine the composition and set-up process conditions. The result is that currently robust parameters are used in existing processes which may lead to surcharges or even preclude economic feasibility.

4. Conclusions

Some important results follow from this work, namely:
- during alkaline leaching using ammonium carbonate as leaching medium, only zincite ZnO is leached and franklinite ZnFe$_2$O$_4$ not,
- it is possible to determine the quantity of zincite present in EAFD,
- the activation energy of zincite leaching out from EAFD was determined as 37.41 kJmol^{-1} when it was calculated from chemical analyses of zinc in leaching solution,
- the activation energy of zincite leaching out from EAFD was determined as 38.55 kJmol^{-1} when it was calculated from X-Ray diffraction phase analyses of leaching residues,
- X-Ray diffraction qualitative analysis can be applied as a powerful tool for theoretical study of waste processing.

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