



Behavior of zinc, iron and calcium from electric arc furnace (EAF) dust in hydrometallurgical processing in sulfuric acid solutions: Thermodynamic and kinetic aspects

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ABSTRACT

This work is focused on the behavior of zinc, iron and calcium during leaching EAF dust in sulfuric acid solutions. The influences of leaching time, temperature, sulfuric acid concentration and L:S (Liquid:Solid) ratio on the extraction of zinc, iron and calcium were studied. The leaching experiments were preceded by a thermodynamic study consisting of calculations of ΔG^0 and E–pH diagrams of the Zn–Fe–Ca–S–H₂O system. A thorough characterization of the input sample of EAF dust was performed. The highest zinc extraction, 87%, was achieved by using 1 M H₂SO₄ at the temperature of 80 °C and L:S ratio 50. From the perspective of a selective leaching of zinc, where no iron is passing into the solution, concentration 0.1 M H₂SO₄ at L:S ratio = 50 and 0.25 M H₂SO₄ at L:S ratios = 20 and 10 can be considered as optimal concentrations. The calculated values of the activation energy confirmed different mechanisms of leaching zinc, iron and calcium. The rate limiting step in the case of zinc and calcium is represented by a rate of diffusion, while in the case of iron it is a rate of chemical reaction.

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1. Introduction

In 2013, more than 1.6 billion tons of crude steel was produced worldwide, while almost 30% of this amount was produced in EAF (Worldsteel Association, 2012). The steelmaking industry, like any other industrial production, generates waste. Approximately 20 kg of fine-grained dust containing iron and non-ferrous metals (Zn, Cd, Pb, and Cr) is generated per 1 ton of steel produced in EAF (International Zinc Association, 2013a). Due to the content of heavy non-ferrous metals and high dust levels during disposal, EAF dust is classified, according to European Waste Catalogue and Hazardous Waste List, as hazardous waste (category 10 02 07) (National Waste Collection Permit Office, 2014).

Despite the hazardous nature of EAF dust there are three main reasons for its processing. The first reason is recovery of iron concentrates suitable as a raw material in the production of steel or pig iron.

The second main reason for its processing is the recovery of zinc for commercial products. The current price of zinc on the LME (London Metal Exchange) is 2070 \$/ton (London Metals Exchange, 2014) and market price of ZnSO₄·7H₂O is in the range of 400–600 \$/ton (Alibaba.com, 2014). Content of zinc in EAF dust is, according to Table 1, in the range of 8–33%, which is significantly higher than that in primary raw materials (5–15%) (International Zinc Association, 2013b).

The third reason to process EAF dust is to reduce the amount of hazardous waste and/or its transformation to non-hazardous waste, i.e. saving disposal costs.

The most common phases of metals present in EAF dust are listed in Table 2.

In general, there are three basic ways of processing EAF dust: pyrometallurgical, hydrometallurgical and a combined method. A product of pyrometallurgical processing is usually represented by impure ZnO which has minimal commercial value. This product has to be further processed by the hydrometallurgical method in order to obtain high purity metallic zinc. Hydrometallurgical processes are mainly based on acid or alkaline leaching. The form of the presence of zinc is a key indicator of the efficiency of the processing of EAF dust. Zinc can be present in EAF dust, according to Table 2, as an oxide (ZnO) and/or as a ferrite (ZnFe₂O₄). Selective extraction of zinc into a solution, with iron remaining in a solid residue, is the ideal result of hydrometallurgical processing. This selective extraction of zinc can be achieved by alkaline leaching, as metals like Zn, Pb, and Cd, pass into a solution while iron remains in a solid residue. However, these methods require very concentrated solutions, which cause technical problems. Moreover, zinc in the ferritic form is not leached out during alkaline leaching and therefore, it is necessary to use pyrometallurgical reduction as an intermediate step. Complicated recycling of solutions and high cost of reagents are other disadvantages of alkaline leaching (Havlik et al., 2004, 2005, 2006).

Acid leaching is generally characterized by better kinetics, better recycling of solutions after leaching and the benefit of not requiring concentrated solutions compared to alkaline leaching. Relatively low cost of

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Table 1
Chemical composition of EAF dust, according to various sources.

Content [wt.%]										Source
Zn	Fe	Ca	Pb	Cr	Mn	Si	Cd	Ni	Cu	
33	26.5	0.9	2.17	0.2	2.3	n.a.	n.a.	0.1	0.2	Havlík et al. (2006)
28.47	36.46	1.73	4.05	0	1.95	1.12	0.07	0.04	0.35	Martins et al. (2008)
29.1	24	3.16	3.64	0.14	4.11	0.34	0.11	n.a.	0.25	Shawabkeh (2010)
8.08	45.24	n.a.	2.12	n.a.	n.a.	n.a.	0.04	n.a.	n.a.	Langová et al. (2007)
17.99	45	3.85	0.2	0.46	1.94	0.42	<0.01	0.03	0.14	Sun et al. (2008)
8	45	3.7	2.1	n.a.	n.a.	n.a.	0.04	n.a.	n.a.	Langová and Matýšek (2010)
18.96	32.09	3.42	2.05	0.12	1.68	2.5	0.05	0.07	0.3	Sedláková et al. (2006)
20.32	n.a.	n.a.	5.59	0.13	n.a.	n.a.	0.04	0.02	n.a.	Oustadakis et al. (2010)

n.a. – Not analyzed.

reagents and higher metal extraction into a solution are additional benefits. A disadvantage, however, is that high zinc extraction leads to a significant amount of iron passing into a solution.

In addition to already mentioned hydrometallurgical methods also new methods of processing EAF dust are recently studied in a laboratory scale. These new approaches include using of deep eutectic ionic solvents based on choline chloride for dissolution of zinc and lead from EAF dust (Abbott et al., 2009; Bakkar, 2014).

Currently, no hydrometallurgical technology is used on an industrial scale, which is mainly due to the lack of research aimed at the behavior of individual compounds of EAF dust in leaching reagent (Havlík et al., 2004, 2005, 2006). Studying the behavior of the main compounds of EAF dust is a fundamental prerequisite for choosing the most suitable conditions of hydrometallurgical processing.

This work is focused on the influence of temperature, sulfuric acid concentration and L:S ratio on the leaching kinetics of zinc, iron and calcium into sulfuric acid solutions. Based on the shape of kinetic curves, the value of activation energy, as the main indicator of leaching mechanism, was estimated.

2. Experimental

2.1. Material

A sample of EAF dust with chemical composition listed in Table 3, was used in the experimental part. The chemical analysis was carried out by the AAS method using Varian Spectrophotometer AA20 +.

Chemical composition of the sample used in this work corresponds to a chemical composition listed in a technical literature (Table 1). Phase analysis of the sample was carried out by the X-ray diffractometer PANanalytical X'Pert PRO MPD using Co K α radiation. Resulting XRD pattern is shown in Fig. 1.

As a result of XRD phase analysis and its evaluation, five main phases were identified – ZnO, ZnFe₂O₄, Fe₃O₄, CaO and SiO₂. These phases correspond to that identified in other published works (Table 2). The

reasons why no phase of manganese and chromium were identified in the sample could be the following:

- A content of Mn and Cr in the sample was under detecting limit of the method;
- Mn and Cr can be present in ferritic form whose peaks can be covered by the peaks of magnetite and franklinite – coincidence of peaks;
- Mn and Cr can be present in the spinel phase lattice of franklinite and magnetite and not as separate phases.

Fig. 2 shows the sample of EAF dust at magnifications 20 $\times$ and 195 $\times$. These images were captured using a digital microscope Dino-Lite PRO AM 413T. It can be seen from Fig. 2, that particles of EAF dust create agglomerates predominantly with a spherical shape. These agglomerates are created mostly by fine particles forming aggregates or covering larger particles, which is confirmed by the granulometry (two peaks in distributive curve, Fig. 3). In order to find out the size and distribution of the particles, granulometric analysis was carried out using Scanning-photo-sedimentograph, Fritsch GmbH, Analysette. The results of granulometric analysis are shown in Fig. 3 in the form of a distributive and cumulative curve.

It can be seen from Fig. 3, that there are two major grain-size fractions in the sample, a finer fraction ($-22 + 2 \mu\text{m}$) which represents 37% and a coarse fraction ($-47 + 28 \mu\text{m}$) which represents 35%. Almost 99% of the particles are below 50 μm .

The sample of EAF dust was observed through the SEM–EDX analysis where the morphology and chemical analysis of surface areas were studied. The observation was carried out using scanning electron microscope JEOL JMS-35CF with EDX analyzer LINK ANALYTICAL AN10/85S. Figs. 4 and 5 show images from the SEM with analysis of selected areas listed in Tables 4 and 5.

A spherical particle marked in Fig. 4 as TH82 shows high iron content (89%) on its surface, which could indicate that this given particle comes from metal bath. The surface of the particle TH83 contains 45.2% iron and 31.5% zinc, which indicates the presence of Fe–Zn phases. A ratio between zinc and iron content is very close to that in ZnFe₂O₄, which indicates the presence of this phase on the surface of the particle TH83.

In the case of the rectangular particle showed in Fig. 5 (TH89) the common presence of calcium, iron and silicon could indicate the presence of Ca–Fe–Si based phases. XRD analysis carried out in this work did not confirm the presence of this kind of phase, but according to literature the presence of such a phase could be possible in this kind of

Table 2
The most common phases present in EAF dust (Martins et al., 2008; Oustadakis et al., 2010; Dutra, 2006; Machado et al., 2006; Xia and Picles, 2000).

Element	Phase
Fe	Fe ₃ O ₄ , ZnFe ₂ O ₄ , Fe ₂ O ₃ ,
Zn	ZnFe ₂ O ₄ , ZnO
Ca	CaO, Ca(OH) ₂ , CaCO ₃
Si	SiO ₂
Mn	MnO ₂ , Mn ₃ O ₄
Cr	FeCr ₂ O ₄
Pb	Pb(OH)Cl, PbO

Table 3
The result of chemical analysis of the sample.

Element	Zn	Fe	Ca	Pb	Cd	Mn	Cr	Si	LOI
Content [wt.%]	17.05	27.23	4.42	1.28	0.09	1.03	0.81	3.22	7.08

LOI – Lost of ignition.

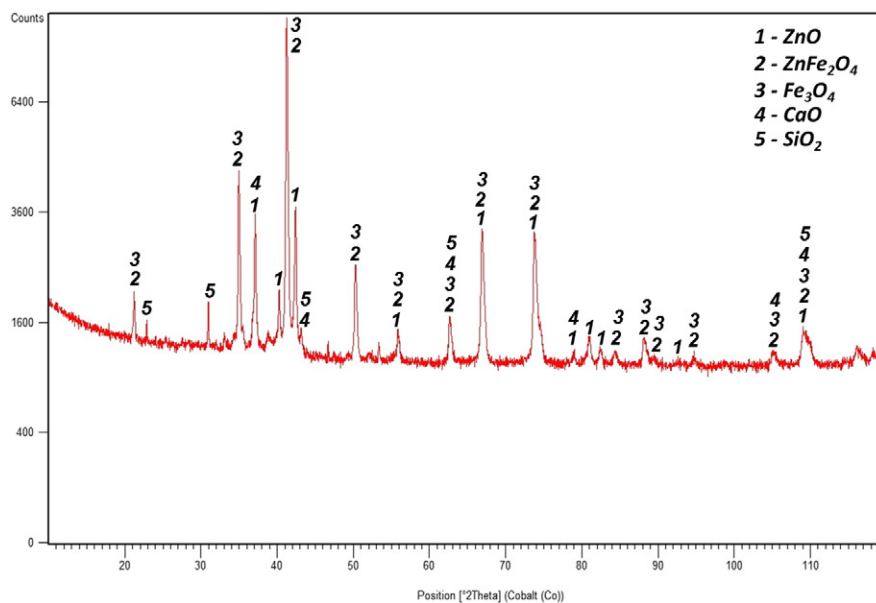


Fig. 1. The XRD pattern of the EAF dust sample.

material (Sofilic et al., 2004). Since these phases are significantly resistant to leaching, they can reduce the efficiency of leaching zinc into the solution.

As it results from the SEM–EDX observations, there is a close relationship between the shape of the particle and its chemical composition. Particles with high content of zinc and iron have mostly spherical shape while rectangular particles contain significant amounts of calcium. It confirms different mechanisms of formation of dust particles as described in (Guezennec et al., 2004; Guezennec, 2005). Formation of spherical particles with high iron and zinc content is most likely carried out by bubble-burst mechanism, while rectangular calcium bearing particles get into EAF dust mainly by direct fly-off.

2.2. Thermodynamic study

A thermodynamic study presented in this work was focused on the determination of the values of standard Gibbs free energy change (ΔG^0) and study of E–pH diagrams in order to find out the stability areas of zinc, iron and calcium in the Zn–Fe–Ca–S–H₂O system. The value of ΔG^0 is the main criterion for spontaneity of a reaction in a closed system at constant pressure and temperature. When $\Delta G^0 < 0$, then the reaction will proceed spontaneously toward the

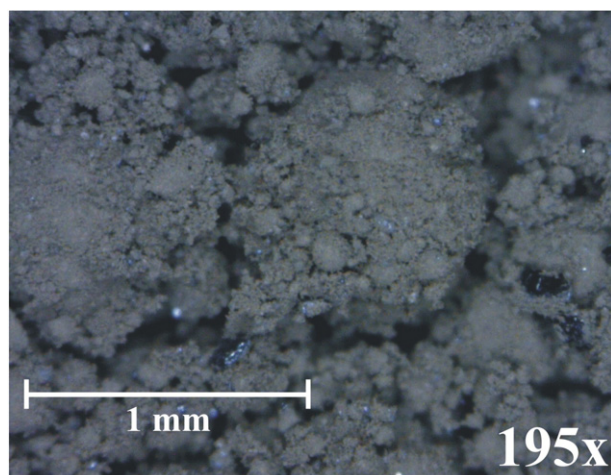
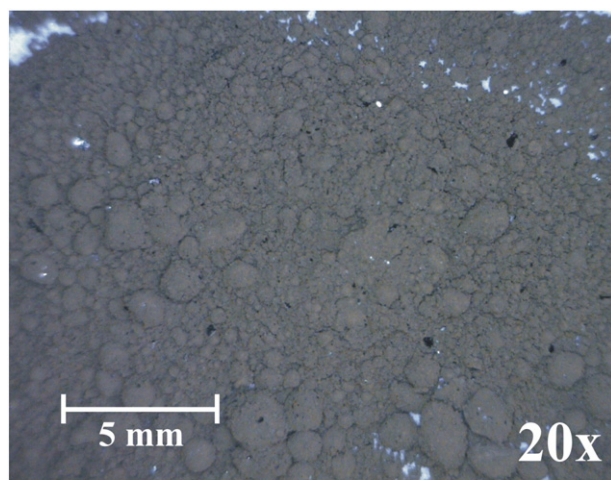


Fig. 2. The sample at magnification 20 and 195×.

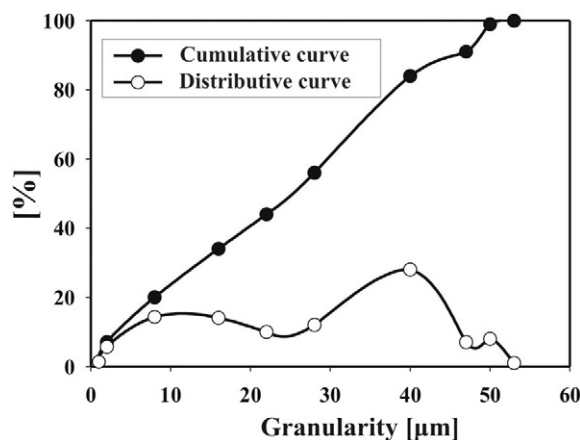


Fig. 3. Cumulative and distributive curves.

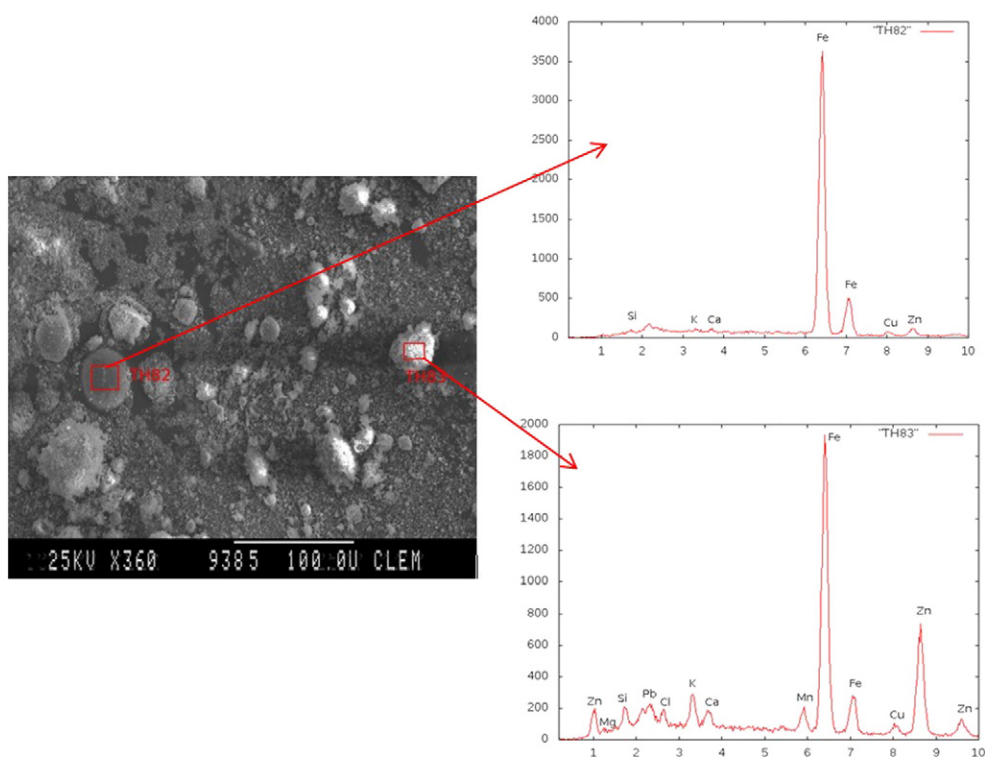


Fig. 4. Images from the SEM-EDX analysis – magnification 360×.

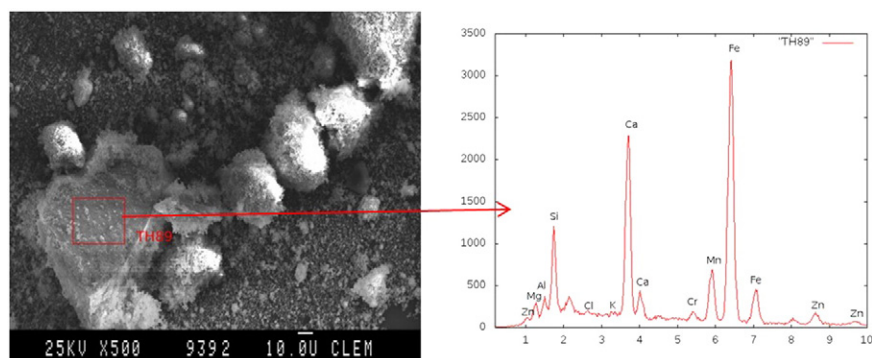
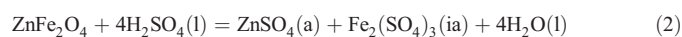
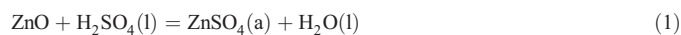


Fig. 5. Images from the SEM-EDX analysis – magnification 500×.

production of products. If $\Delta G^0 > 0$, the reaction will proceed spontaneously in the opposite way. In case that $\Delta G^0 = 0$, the reaction is in equilibrium.

Table 6 shows the values of ΔG^0 at 20, 40, 60, 80 and 95 °C. The values of ΔG^0 refer to 1 mol of sulfuric acid. The following reactions describe the possible reactions of zinc in a sulfuric acid solution:



Iron passes into the solution together with zinc from franklinite (reaction (2)) and/or from iron oxides according to:

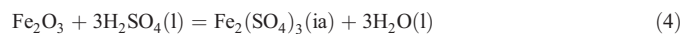


Table 4

Chemical composition of the areas selected in Fig. 4.

Area	Content [wt.%]									
	Mg	Al	Si	Ca	Cr	Mn	Fe	Zn	Pb	Cd
TH82	0	0	0.7	0.6	0	0.3	89	4.9	0.8	0.8
TH83	2.2	0.5	3.7	1.7	0.3	2.9	45.2	31.5	2.7	0

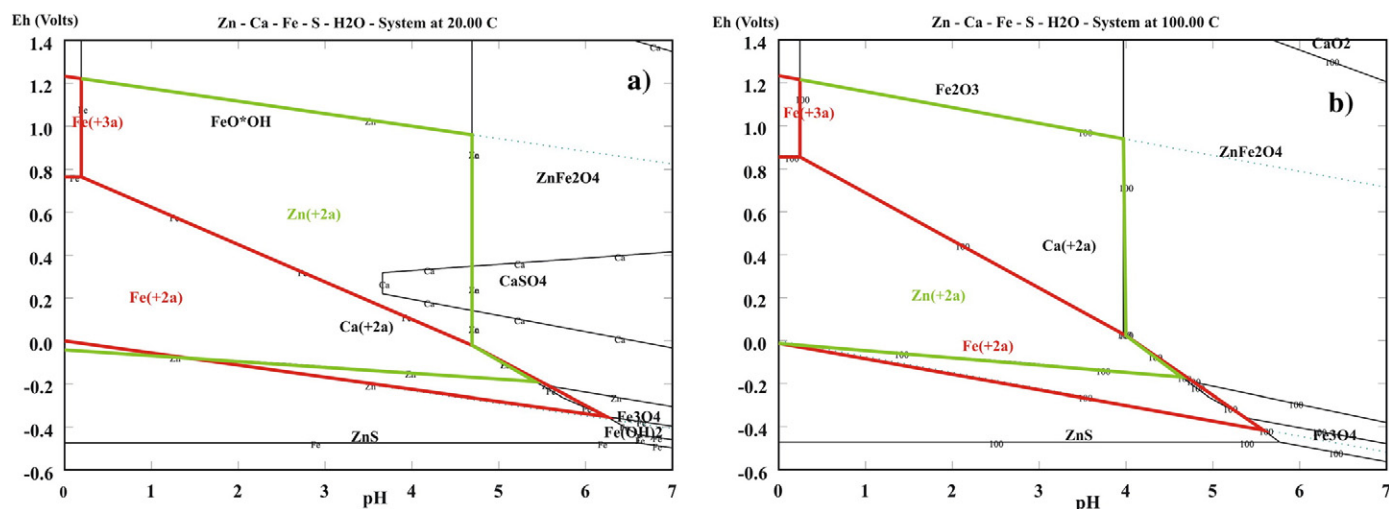
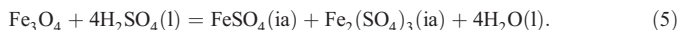
Table 5

Chemical composition of the area selected in Fig. 5.

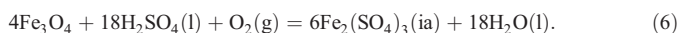
Area	Content [wt.%]									
	Mg	Al	Si	Ca	Cr	Mn	Fe	Zn	Pb	Cd
TH89	7	3.1	11.4	20	0.9	7.6	44.5	3.1	0	0.1

Table 6The values of ΔG^0 for the reactions (1) to (9)*.

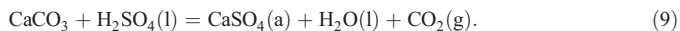
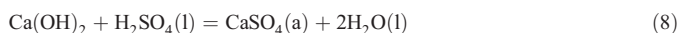
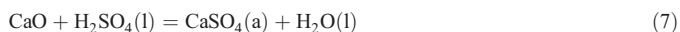
Temperature [°C]	The values of ΔG^0 for the reactions (1)–(9), [kJ]								
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
20	–134.57	–67.07	–74.66	–36.24	–62.19	–71.51	–253.62	–195.70	–122.40
40	–132.04	–61.70	–69.90	–31.62	–56.24	–65.05	–251.47	–194.05	–123.45
60	–129.36	–56.20	–64.90	–26.90	–50.15	–58.46	–249.08	–192.19	–124.25
80	–126.55	–50.57	–59.65	–22.08	–43.94	–51.74	–246.46	–190.16	–124.82
95	–124.36	–46.27	–55.58	–18.40	–39.19	–46.61	–244.37	–188.52	–125.12

* The values of ΔG^0 were calculated through HSC Chemistry® 7.14 software.**Fig. 6.** E–pH diagrams for the Zn–Ca–Fe–S–H₂O system at 20 and 100 °C. (E–pH diagrams were calculated through the software for thermodynamic calculations HSC Chemistry® 7.14).

In the presence of oxygen from the atmosphere:



Calcium can pass into the solution according to the following reactions:

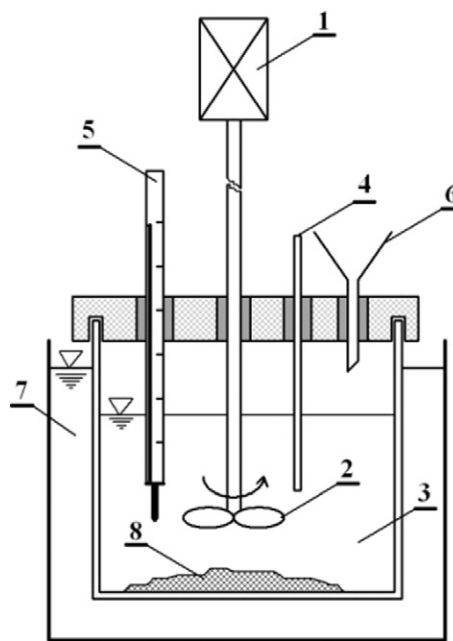


It results from the thermodynamic values in Table 6 that the reactions (1) to (9) are probable as their values of ΔG^0 are negative at all given temperatures. Reaction (7) has the highest probability of proceedings, which indicates that acid can be preferably consumed by leaching of calcium from its oxide. If only values of ΔG^0 would be taken into account, neglecting other factors (kinetics, system complexity and side effects), the main elements should pass into the solution in the following order $\text{Ca} \rightarrow \text{Zn} \rightarrow \text{Fe}$.

Given values describe the situation in the equilibrium state and relate only to individual phases. However, the real system consists of more than one phase, so it is necessary to verify how the system will behave under specified conditions. For this purpose, thermodynamic study through E–pH diagrams was carried out. The resulting E–pH diagrams of the Zn–Fe–Ca–S–H₂O system at 20 and 100 °C are shown in Fig. 6.

It results from given E–pH diagrams that zinc is present in the form of soluble compounds in a wide range of pH, from 0 to 5, practically in

the whole range of the water stability area. Similarly, calcium is also present in the form of soluble compounds in that area. However, the case of iron is more complex. In very acidic areas, with pH close to 0 and with potential higher than 0.77 V, iron creates the area of ferric

**Fig. 7.** The scheme of the equipment used for the leaching experiments (Havlík et al., 2006). 1 – Mechanical stirrer; 2 – propeller; 3 – pulp; 4 – sampler; 5 – thermometer; 6 – feeder; 7 – water thermostat; 8 – sample of EAF dust.

ions. Increasing the pH value causes hydrolytic precipitation of iron. Practically, it means that after leaching out zinc, iron and calcium into the solution, according to Eqs. (1), (2), and (7), free acid is partially consumed what leads to increasing pH and subsequent hydrolytic precipitation of iron from the solution. Zinc and calcium remain in a soluble form while the pH value is in the range 0 to 4. In the case of an increase of the pH value over 4, there could be precipitation of zinc, which should be avoided by choosing suitable leaching conditions.

2.3. Experimental procedure

The leaching experiments were carried out on the equipment shown in Fig. 7.

A glass reactor of 800 ml, which was placed in a water thermostat, was used for the leaching experiments. Leaching experiments were carried out with 500 ml solution of 0.05, 0.1, 0.25, 0.5 and 1 M H_2SO_4 at temperatures of 20, 40, 60, 80 and 95 °C. The sample weights for the leaching experiments were 10, 25 and 50 g, which represents L:S ratios of 50, 20 and 10. All experiments were carried out at atmospheric pressure. Duration of one leaching experiment was 90 min. As this study was focused on the kinetics of leaching zinc, iron and calcium, liquid samples of 10 ml were taken at the fixed time intervals after 1, 5, 10, 15, 30, 60 and 90 min. All taken samples were analyzed by the AAS (atomic absorption spectroscopy) method to determine the

concentration of zinc, iron and calcium in the solution. All results were recalculated due to the change of the pulp volume caused by sampling and evaporation. Stirring speed was kept constant 300 rpm during all experiments.

3. Results and discussion

3.1. Behavior of zinc

Fig. 8 shows the kinetic curves of leaching zinc expressing the percentage of zinc passing into the solution at temperatures 20 to 95 °C, sulfuric acid concentrations 0.05–1 M and L:S ratio = 50.

It results from Fig. 8 that leaching zinc into the solution is a very fast process. All zinc, which could possibly pass into the solution, will do so in the first 15 min. After that, the zinc leaching process stops. At sulfuric acid concentration below 0.5 M only very slight influence of the temperature on the zinc leaching process can be observed. This influence significantly increases in the sulfuric acid concentration over 0.5 M. Maximal zinc extraction 87% was reached at the following conditions: 1 M H_2SO_4 , 80 °C and L:S ratio = 50. Kinetic curves in Fig. 8 indicate that extension of leaching time would not result in a significant increase in the zinc extraction into the solution.

Fig. 9 shows that L:S ratio is one of the key factors in determining optimum sulfuric acid concentration in the leaching solution. While at L:S

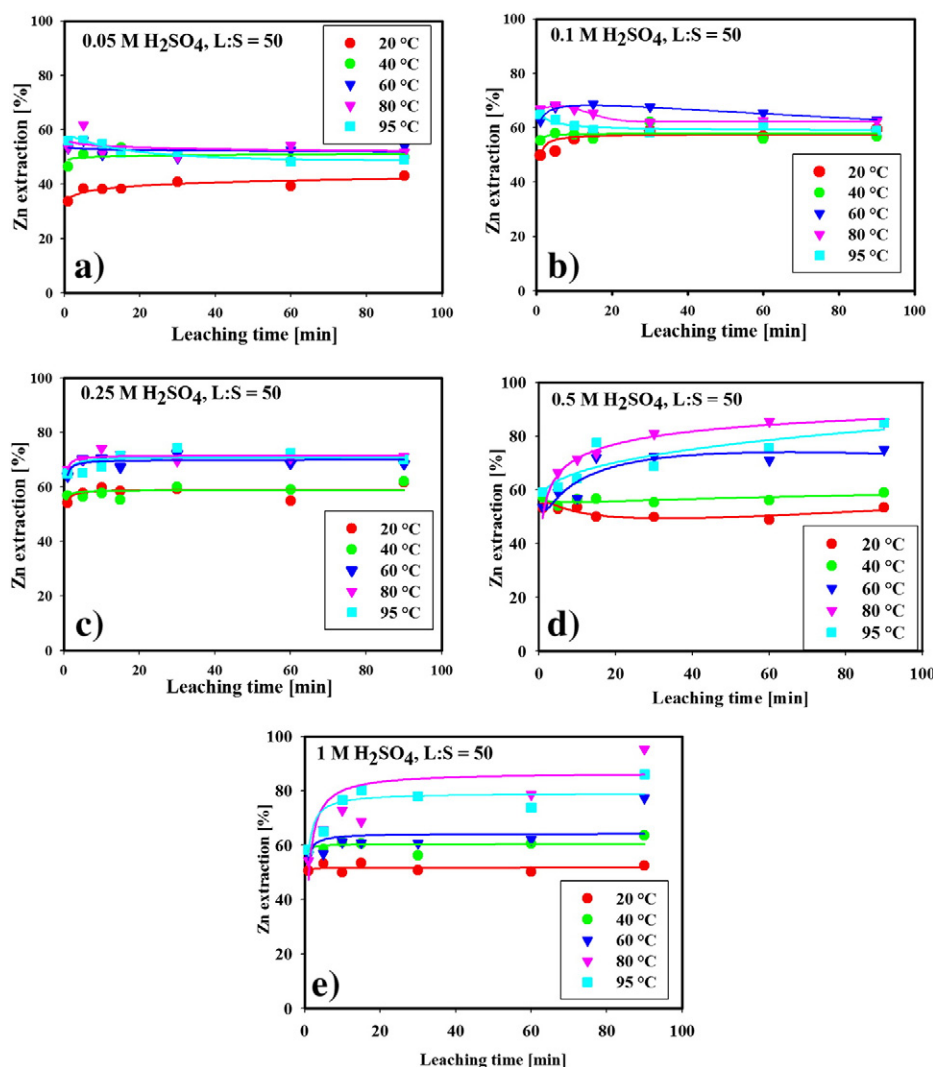


Fig. 8. Kinetic dependencies of the Zn extraction at temperatures 20–95 °C, sulfuric acid concentrations 0.05–1 M and L:S ratio = 50.

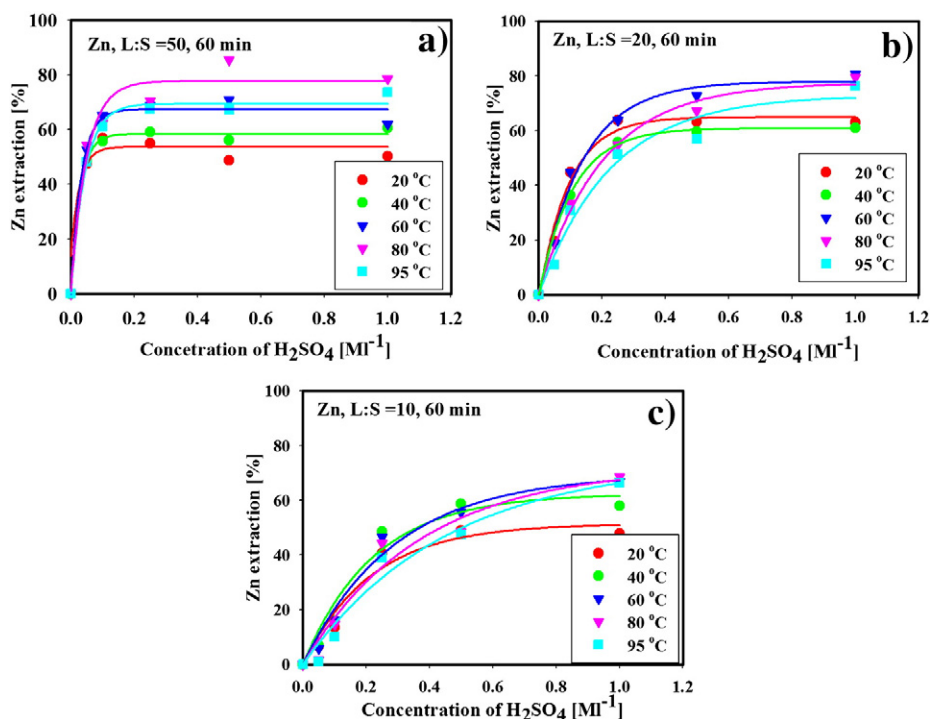


Fig. 9. Effect of sulfuric acid concentration on the Zn extraction at various temperatures and L:S ratios = 50, 20, 10 (in 60th minutes of leaching).

ratio = 50, maximum zinc extraction can be reached using 0.25 M H_2SO_4 , in the case of L:S ratio = 20, 0.5 M H_2SO_4 must be used in order to achieve the maximum zinc extraction. In case of the lowest L:S ratio = 10, the highest zinc extraction was reached by using 1 M H_2SO_4 , while further increasing of the concentration could lead to further slight increase in the zinc extraction.

3.2. Behavior of iron

Leaching kinetics of passing iron into the solution is, according to Fig. 10, not as fast as in the case of zinc. Sulfuric acid concentration and temperature have a significant effect on the amount of iron passing into the solution. The significant effect of the temperature can be

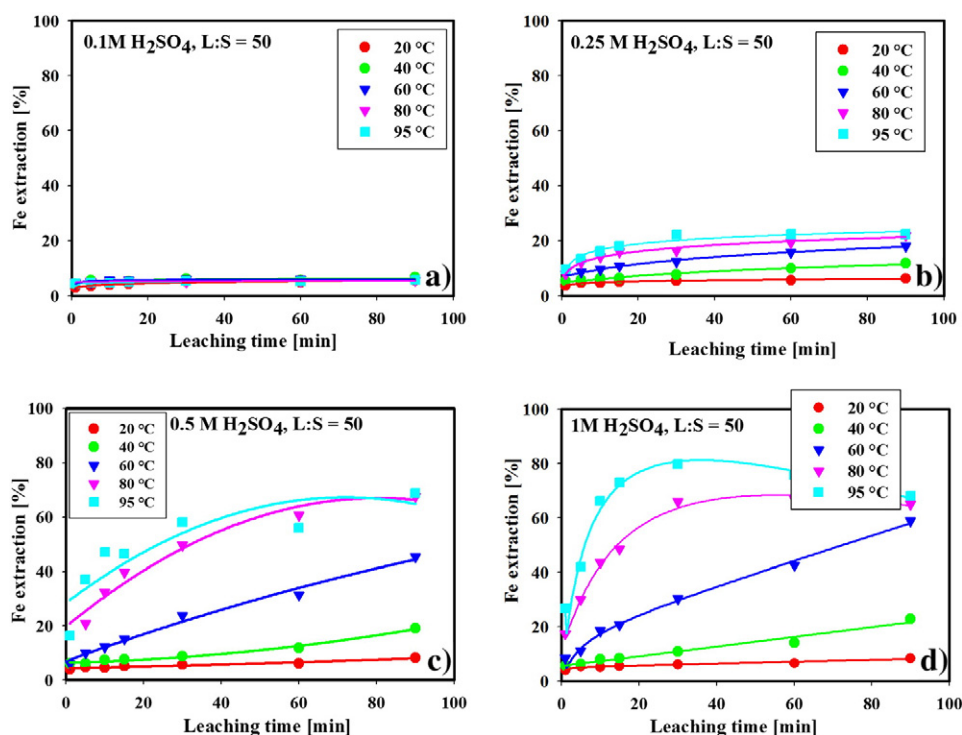


Fig. 10. Kinetic dependencies of the Fe extraction at temperatures 20–95 °C, sulfuric acid concentrations 0.05–1 M and L:S ratio = 50.

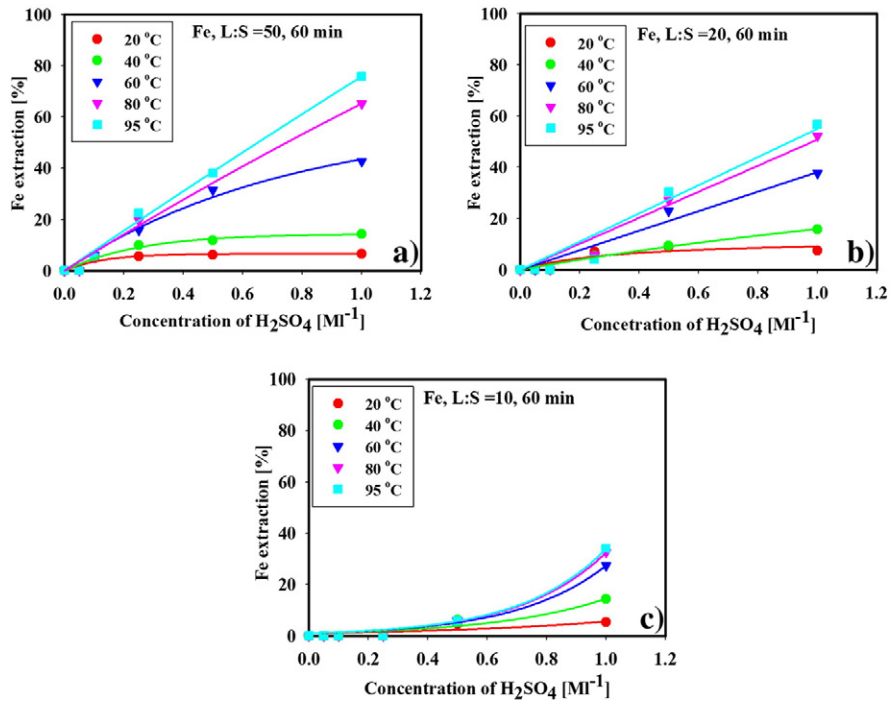


Fig. 11. Effect of sulfuric acid concentration on the Fe extraction at various temperatures and L:S ratios = 50, 20, 10 (in 60th minutes of leaching).

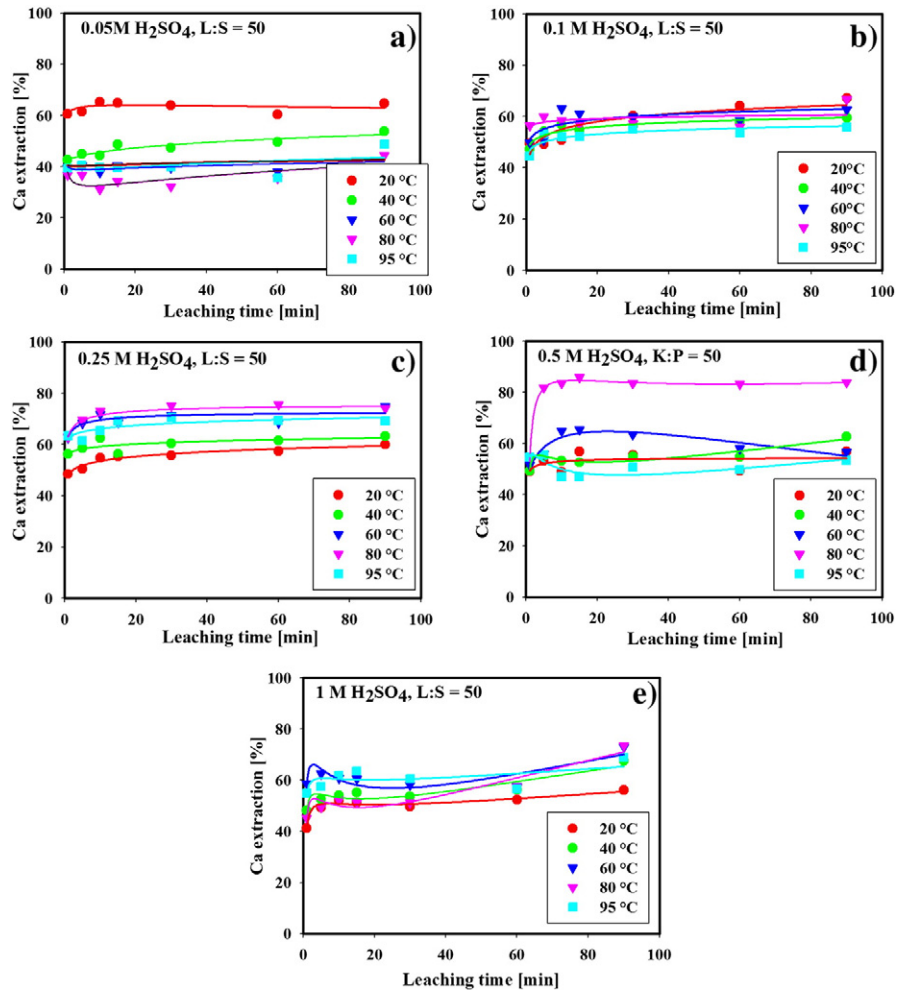


Fig. 12. Kinetic dependencies of the Ca extraction at temperatures 20–95 °C, sulfuric acid concentrations 0.05–1 M and L:S ratio = 50.

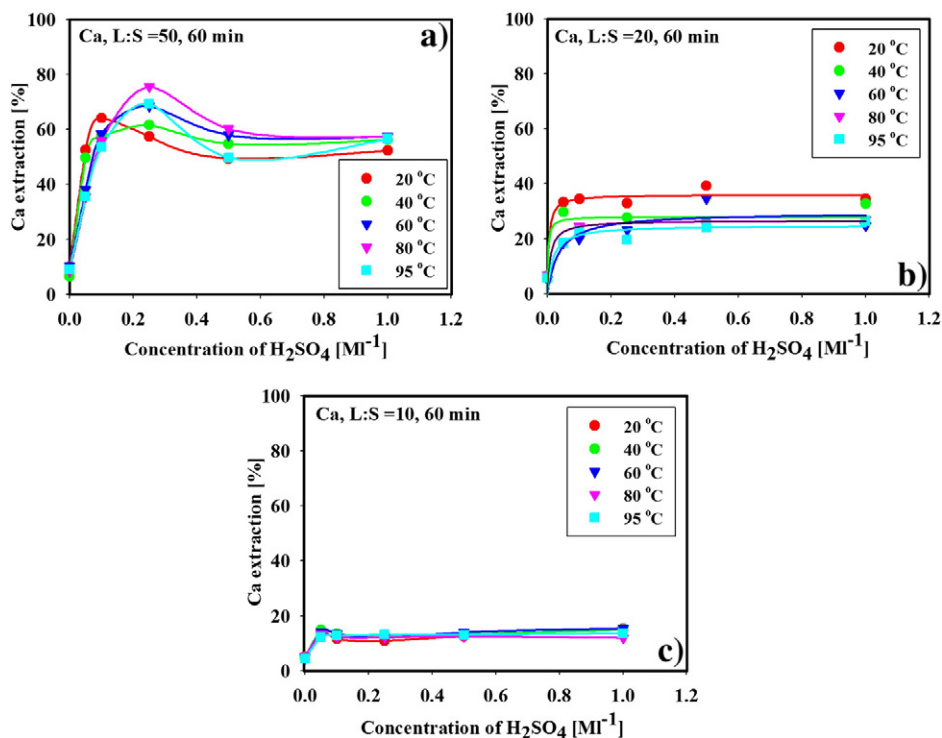


Fig. 13. Effect of sulfuric acid concentration on Ca extraction at various temperatures and L:S ratios = 50, 20, 10 (in 60th minutes of leaching).

observed especially at concentrations 0.5 and 1 M H₂SO₄. The highest iron extraction, ~ 80% was achieved using 1 M H₂SO₄ at 95 °C after 30 min of leaching. After 30 min of leaching at the given temperature, a slight decrease of iron concentration in the solution can be observed. Curves of iron extraction at temperatures up to 60 °C indicate that even after 90 min the process of leaching iron is not finished and extending the leaching time could lead to higher iron extraction into the solution.

In case of iron, the influence of the temperature rises with increasing acid concentration. This phenomenon can be observed in Fig. 11, which

shows the influence of sulfuric acid concentration on the iron extraction at various temperatures and L:S ratios = 50, 20 and 10.

It results from Fig. 11, that in contrast to zinc, in the case of iron the increase in sulfuric acid concentration leads to higher iron extraction into the solution at all L:S ratios. Comparing graphs in Figs. 9 and 11, there is a difference in the character of the curves, which indicates a possibility of selective leaching zinc at the minimal amount of iron passing into the solution. In the case of L:S ratio = 10 and 0.25 M H₂SO₄ it is possible to leach out approximately 50% of zinc without iron significantly passing into the solution.

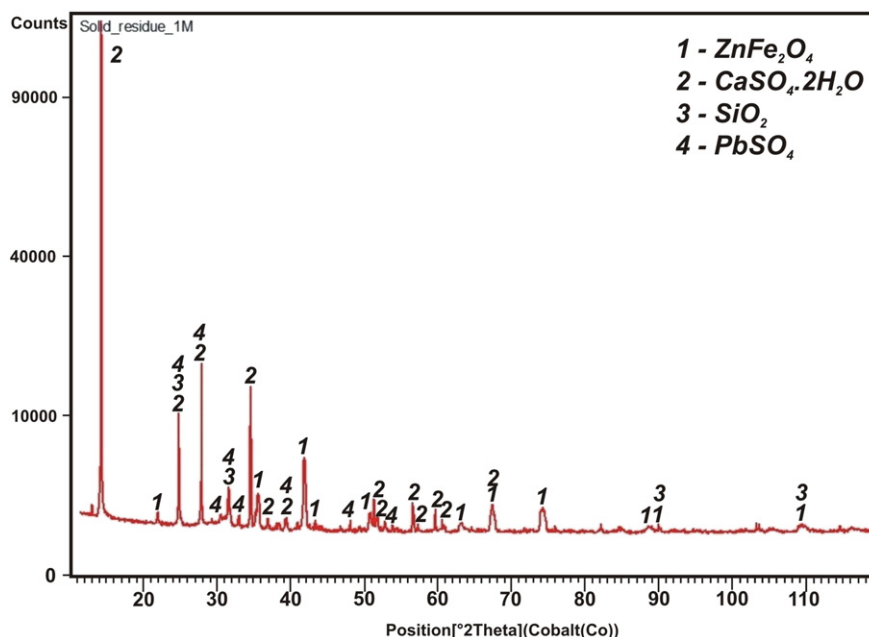


Fig. 14. The XRD pattern of the solid residue.

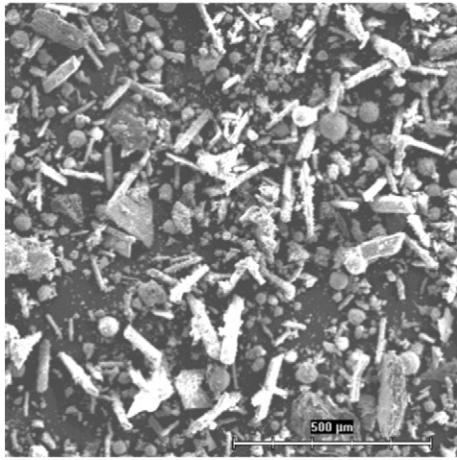


Fig. 15. Crystals of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in the solid residue.

Table 7

The values of the activation energy for leaching zinc, iron and calcium.

Acid concentration	Ea(Zn) [$\text{kJ} \cdot \text{mol}^{-1}$]		Ea(Fe) [$\text{kJ} \cdot \text{mol}^{-1}$]	Ea(Ca) [$\text{kJ} \cdot \text{mol}^{-1}$]
	Stage I	Stage II		
0.5 M H_2SO_4	0.99	58.74	47.03	1.28
1 M H_2SO_4	1.72	42.28	35.64	3.99

3.3. Behavior of calcium

Fig. 12 shows the kinetic curves of calcium, displaying the amount of leached calcium depending on the temperature at sulfuric acid concentration in the range of 0.05 to 1 M and L:S ratio = 50.

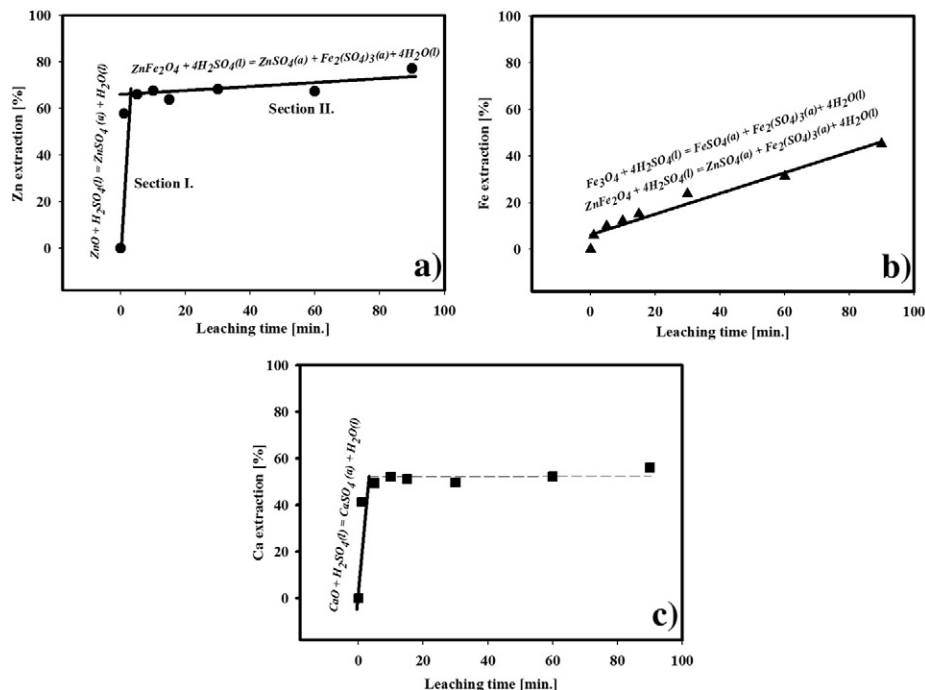


Fig. 16. Partition of the kinetic curves of leaching zinc, iron and calcium.

As the amount of calcium in the solution is determined by its limited solubility, most of the calcium that is leached out into the solution precipitates in the form of gypsum crystals (Fig. 15). Therefore, the amount of calcium that is remaining in solution (Fig. 12) is not the same as the amount of calcium which has been leached.

The influence of the sulfuric acid concentration on calcium extraction into the solution at various temperatures and L:S ratios = 50, 20 and 10 is shown in Fig. 13.

It can be seen from Fig. 13, that the amount of calcium in the solution cannot be affected by any leaching parameter like temperature, leaching time and acid concentration. The L:S ratio is the only one parameter affecting the amount of calcium passing into the solution. Maximal calcium extraction, ~ 80%, was reached at L:S ratio = 50 at 80 °C in the solution of 0.5 M H_2SO_4 . During the analysis of calcium by the AAS method, gradual precipitation of calcium in the form of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ should be considered. As an evidence of calcium precipitation, XRD analysis (Fig. 14) of solid residue was carried out. The solid residue came from the experiment carried out in the following conditions: 1 M H_2SO_4 , 95 °C and L:S ratio = 10. Fig. 15 shows the crystals of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in the sample of the solid residue.

3.4. Mechanism of leaching zinc, iron and calcium

The effect of temperature is the biggest difference between leaching zinc and iron. In the case of zinc, the temperature has only minimal influence while in the case of iron the influence of the temperature is significant. This phenomenon indicates a different mechanism of leaching zinc and iron from EAF dust in a sulfuric acid solution. The influence of temperature on the rate of chemical reactions can be expressed by Arrhenius equation.

In order to determine the mechanism of leaching zinc, iron and calcium, a calculation of the activation energy E_a was carried out. In the first step, a rate constant was determined at various temperatures from the shape of the kinetic curves. Subsequently, the value of the activation energy was determined through the logarithmic form of the Arrhenius equation (Havlik, 2008). These calculations were carried out for L:S ratio = 50 and sulfuric acid concentrations 1 and 0.5 M

H_2SO_4 . The calculated values of E_a are listed in Table 7. Fig. 16 shows the typical kinetic curves of leaching zinc, iron and calcium. It results from the shape of the curves that zinc, unlike iron, passes into the solution in two stages. According to the kinetic curves of leaching calcium, calcium passes into the solution only in the first minutes. After reaching the saturated solution, it starts to precipitate in the form of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Besides the kinetic curves also possible reactions are shown in Fig. 16.

In the case of leaching zinc, the most important stage is *stage I* in which almost all zinc, that can possibly pass into the solution will do so within the first minute. It can be stated that in *stage I* diffusion is limiting step. On the other side, in *stage II*, where zinc passes into the solution only slightly, the values of the activation energy indicate that the rate limiting step in this case is represented by the rate of the chemical reaction, which is, according to Arrhenius equation, exponentially dependent on temperature. Based on the values of the activation energy above and shape of kinetic curves of leaching zinc, it can be stated that *stage I* corresponds to leaching zinc from its oxide – ZnO , while *stage II* corresponds to leaching zinc from its ferritic form – ZnFe_2O_4 .

The values of the activation energy indicate that the rate limiting step in leaching iron is dependent on the rate of the chemical reaction. It is a similar mechanism as in the case of zinc (*stage II*), which means that this mechanism is typical for leaching zinc ferrite where zinc is interstitially located in the structure of ZnFe_2O_4 .

Diffusion rate is the rate limiting step in the case of leaching calcium too. Contrary to leaching zinc, calcium after reaching saturated solution precipitates as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

For determining optimal leaching conditions also the influence of sulfuric acid concentration must be taken into account. The influence of sulfuric acid concentration on the extraction of zinc, iron and calcium at L:S ratios = 50, 20 and 10 is shown in Fig. 17.

Determining optimal conditions of hydrometallurgical processing of EAF dust is often a compromise between the highest zinc extraction and the lowest iron extraction into the solution. From this perspective,

concentration of 0.1 M H_2SO_4 at L:S ratio = 50 and 0.25 M H_2SO_4 at L:S ratios = 20 and 10 can be considered as an optimal concentration, as shown in Fig. 17.

4. Conclusion

EAF dust studied in this work was subjected to the elemental analysis (AAS). The following contents of the main compounds were discovered: 17.05% Zn, 27.23% Fe, 4.42% Ca and 6.88% Si. The subsequent XRD analysis confirmed the presence of the following phases: ZnFe_2O_4 , ZnO , Fe_3O_4 , SiO_2 and CaO .

Granulometry analysis showed that EAF dust is fine-grained materials where 90% of all particles are below 50 μm .

Kinetic study of zinc leaching showed that zinc passes into the solution very fast and maximum possible zinc extraction into the solution can be achieved in the first minutes of leaching. Leaching of zinc takes place in two stages (Fig. 16a), where the rate limiting step in the first stage of leaching zinc (from ZnO) is represented by diffusion while in the second stage (from ZnFe_2O_4) it is the rate of chemical reaction. Maximum zinc extraction, 87%, was achieved at the following conditions: 1 M H_2SO_4 , 80 °C and L:S ratio = 50. Achieving higher zinc extraction was prevented by encapsulation of zinc phases in resistant Ca–Si–Fe matrix.

Kinetic study of iron leaching showed that iron passes into the solution significantly slower than zinc. Temperature has a significant effect on iron extraction into the solution. The rate limiting step in leaching iron is represented by the rate of chemical reaction.

Kinetic study of calcium showed that leaching of calcium is a very fast process, but most of the calcium which reacts with sulfuric acid precipitates from the solution in the form of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Final calcium concentration in the solution, regardless of experimental conditions, was about 600 $\mu\text{g/ml}$.

From the results of this work, the scheme of hydrometallurgical processing EAF dust can be designed (Fig. 18), which can serve as a basis for

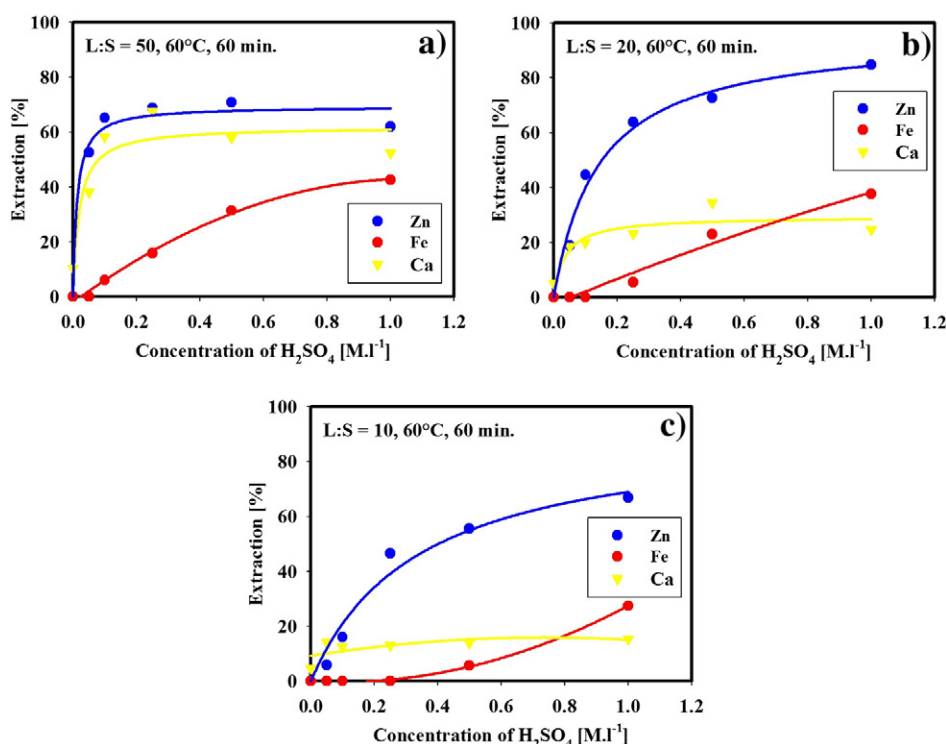


Fig. 17. The influence of sulfuric acid concentration on extraction of zinc, iron and calcium at L:S = 50, 20 and 10.

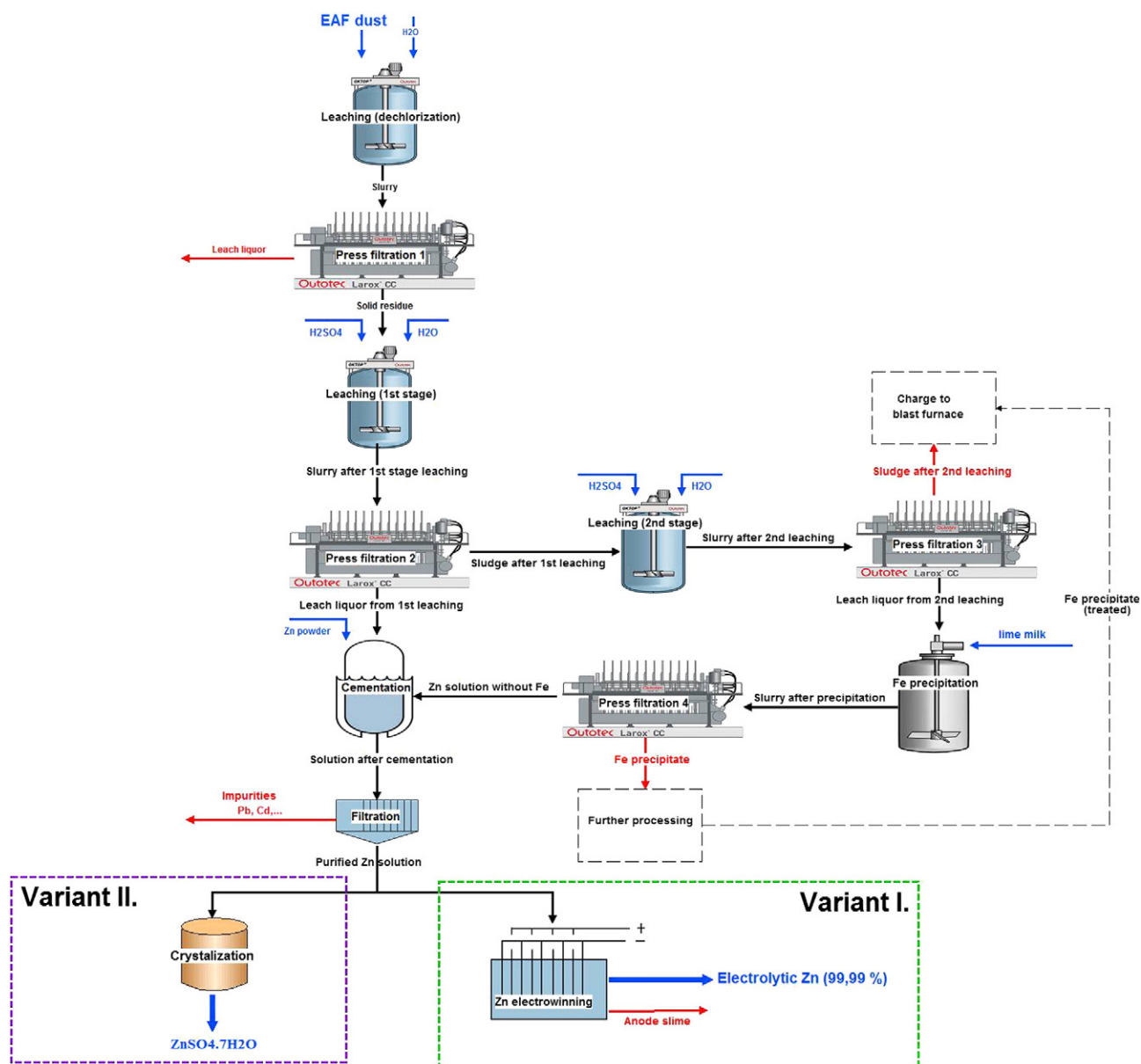


Fig. 18. The scheme of complex processing EAF dust.

the technical realization of processing of this hazardous industrial waste with the aim to recover metallic zinc or other commercial products.

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