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## Considering the influence of calcium on EAF dust acid leaching

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**Abstract:** This work focuses on the hydrometallurgical processing of EAF steelmaking dust in laboratory conditions. The behavior of calcium under the influence of sulphuric acid as the leaching agent is discussed. Due to calcium presence the acid is continuously consumed, gradually leaching the calcium phase from EAF dust as well as other zinc- and iron-containing phases. A thorough composition analysis of the input sample of EAF dust was performed. A kinetic study of calcium showed that its leaching is a very fast process, but most of the calcium reacting with sulphuric acid is precipitated from the solution in the form of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . This causes greater sulphuric acid consumption, and therefore it is necessary to study the calcium behavior during processing of EAF dust. This work is narrowed with calcium behavior during leaching of EAF dust in sulphuric acid and effect of calcium to extraction other metals into solution.

**Keywords:** EAF dust, Leaching, Sulphuric acid, Industrial waste, Zinc, Iron, Calcium, Hydrometallurgy

### 1. Introduction

One of the most important problems encountered in steel plants throughout the world is the disposal of dusts generated during the production of steel in an electric arc furnace (EAF dusts). The steel is recovered by remelting of steel scrap containing various impurities. The presence of leachable zinc, lead, cadmium, chromium and other elements in the dust has in recent years caused the remnant material to be widely regarded as hazardous waste which is unsuitable for disposal in landfill. For the same reason it is very complicated to use this waste as secondary raw material for iron or steel production. There is a considerable content of heavy metals in steel-making dusts, for example 2 – 30 % Zn, 0.3 – 6% Pb and 0.01 – 0.2 % Cd. Moreover, a wide range of minorities is present such as Al, As, Ba, Cl, Cr, Cu, Hg, K, Mg, Mn, Mo, Na, Ni, P, Se, Si, Ti, Zr (Cruells et al., 1992). Great attention is paid in current research and subsequently in publications mostly to the recovery of iron and zinc in various forms for their reuse. Iron presence in oxide form is well known, mostly as magnetite  $\text{Fe}_3\text{O}_4$  and franklinite  $\text{ZnFe}_2\text{O}_4$ . Zinc is present mostly in two basic compounds, namely as oxide ZnO and ferrite  $\text{ZnFe}_2\text{O}_4$  and possibly as complex ferrite, e.g.  $(\text{ZnMnFe})_2\text{O}_4$ . On the other hand, EAF dusts also contain further elements, present in various forms. These also participate in the processes of EAF dust handling, although the main aim is the valorization both of iron and zinc. Lead, manganese and calcium are present in interesting amounts in addition to iron and zinc. Heavy metals are present in EAF dust due to their presence in the melted scrap, and calcium is transferred into EAF dust from fluxes. Its amount changes from case to case and varies within the range 0.4-14 %. The average amount is around 5 % (Havlik et al., 2012).

The aim of this work is to clarify calcium behavior during leaching EAF dust in sulphuric acid and effect of calcium to extraction other metals into solution.

### 2. Thermodynamics

It follows from published results that calcium in EAF dust is present in various forms such as CaO (Kukurugya et al., 2011),  $\text{Ca}(\text{OH})_2$  (Kukurugya et al., 2011),  $\text{CaCO}_3$  (Cruells et al., 1992, Lopez et al., 1993), or other complex oxides (Sofilic et al. 2004). The nature of the calcium compounds depends on

the history of origination and also on the duration of EAF dust storage or disposal and its location. Calcium ferrites originate during melting of scrap at high temperatures due to chemical reactions between scrap parts and fluxes, as well as the working atmosphere. At the melting temperature around 2100 °C the iron oxidation takes place according to (Roine, 2007).



Lime CaO is added to the scrap melting as flux. Its reaction with Fe<sub>2</sub>O<sub>3</sub> takes place according to reaction 2 and 3:



eventually



While additives such as Ca(OH)<sub>2</sub>, or CaCO<sub>3</sub> could also be present, at high melting temperatures over 2000 °C in an EAF these are thermally dissociated, producing CaO.



In fresh EAF dust the calcium is present mostly as CaO, possibly as relatively stable ferrite. When this EAF dust is stored in the open air, the lime reacts with the atmosphere at ambient temperature according to reaction 6 or by particular reaction 7, and the resulting hydroxide further reacts with CO<sub>2</sub> from the air creating CaCO<sub>3</sub> according to reaction 8.



or by particular reaction

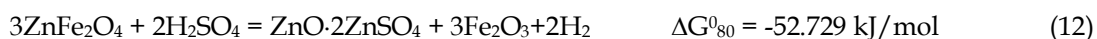
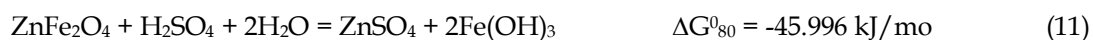
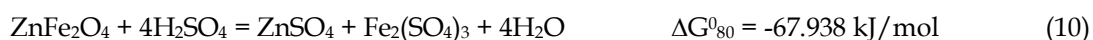


and originated hydroxide further reacts with CO<sub>2</sub> from air creating CaCO<sub>3</sub>



Basically, this is the common process of mortar hardening known from civil engineering. These reactions do not proceed immediately; the kinetics is relatively slow and depends on partial pressures of water vapor and carbon dioxide in the ambient atmosphere. It follows from the above that the reactions proceed by different kinetics on the surface and inside the volume of stored dust.

The processes of acidic hydrometallurgical processing of EAF dust are rather frequently discussed in the literature. Hydrochloric acid (Langová et al., 2009, Baik et al., 2000), nitric acid (Shawabkeh, 2010) and acetic acid (Nagib et al., 2000) are common used as lixivants in these processes, but mostly sulphuric acid is discussed as the main agent for EAF dust leaching under normal conditions of temperature and pressure (Havlik et al., 2005), or at high temperature and pressure (Havlik et al., 2004). The main components of EAF dust react in sulphuric acid according to reactions (9-16):



From the thermodynamic point of view the most stable species in the EAF leaching system in sulphuric acid is calcium sulphate. An often-used leaching temperature is 80 °C, which follows from the comparison of values of standard Gibbs energy changes in individual components' creation, and does not depend on which primary calcium compound the calcium sulphate originates from. This means that the calcium compounds present in EAF dust will react predominantly with the sulphuric acid, and hence they will consume the acid. This phenomenon is frequently used for the neutralization of waste acid solutions.

Published works focusing on material recycling of EAF dust by means of acid leaching are effectively narrowed into two directions. In one direction a relatively aggressive leaching agent is used, for example hydrochloric acid, and hence almost all EAF components go into solution from which they are gradually extracted for example through solvent extraction. The other works focus on selective extraction of chosen components into solution, mostly zinc, whereas iron stays in the solid residue and after treatment is recycled in the iron and steel production process. The latter approach is interesting from the economical point of view, but on the other hand, setting the necessary equilibrium in solution is a very difficult and sensitive task.

It follows from thermodynamic study using Eh - pH diagrams of the Zn-Fe-Ca-S-H<sub>2</sub>O system (Fig. 1-6) that under normal conditions zinc in soluble form creates a wide stability area within the pH region from 0 to 4.5. This tendency is observed with increasing temperature, whereby the equilibrium boundary between soluble Zn<sup>2+</sup> ion and insoluble ZnFe<sub>2</sub>O<sub>4</sub> shifts toward the lower value pH = 3.4. However, in the acidic area soluble iron ions form only a narrow stability area, and with increasing pH value over pH = 0.5 iron precipitates as oxide or hydroxide.

It follows from Fig. 5, 6 that calcium should precipitated from sulphuric acid solution below 77 °C and up to pH = 7.

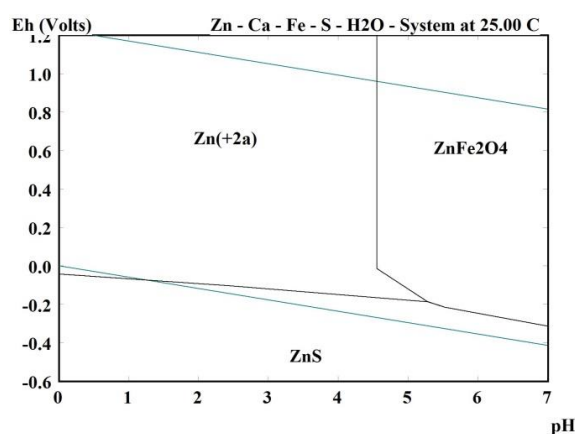


Fig. 1. Eh-pH diagrams of Zn-Ca-Fe-S-H<sub>2</sub>O system at temperature 25 °C (Roine, A., 2007)

Based on the above there exists the idea of EAF dust processing by leaching in weak sulphuric acid solution, where the individual EAF dust components will be leached out and at the same time the acid will be consumed. In this way the pH value will increase. Once pH values over ~ 1 are reached, iron is precipitated from the solution as oxide while zinc stays in the solution. After phase separation the solution is individually treated to enable zinc recovery, and solid residue goes to be recycled in the iron and steel production process (Havlik et al., 2005, Havlik et al., 2004).

### 3. Experimental

#### 3.1. Material

An EAF dust sample was used for the experiments using acidic leaching in order to transfer zinc into solution, while iron should stay in the solid residue. The chemical analysis of the material used is shown in Table 1.

In order to identify the phase composition, the EAF dust sample was subjected to X-ray (XRD) qualitative diffraction analysis on a PANalytical X'Pert PRO MRD X-ray diffractometer using CoK $\alpha$  radiation. The EAF dust contained the following phases ZnFe<sub>2</sub>O<sub>4</sub>, ZnO, Fe<sub>2</sub>O<sub>3</sub>, CaCO<sub>3</sub>, C as the results from the phase diffraction analysis.

Table 1. Chemical composition of the EAF dust

Element	Zn	Fe	Ni	Cr	Mn	Pb	Cd	Ca	LOI
Amount [%]	17.05	27.23	0	0.81	1.03	1.28	0.09	4.42	7.08

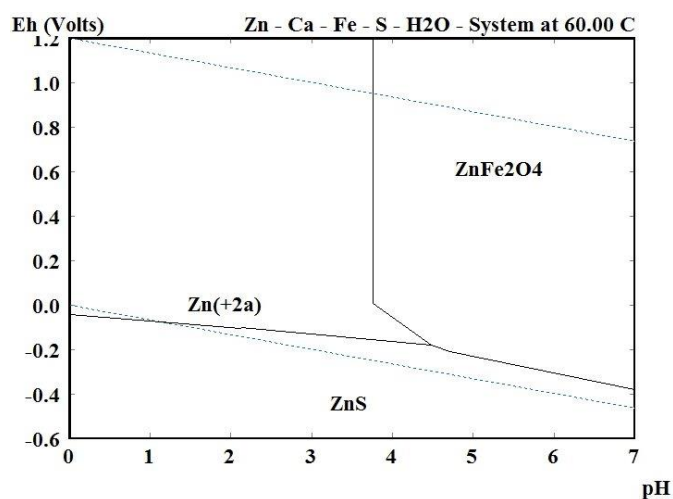


Fig. 2. Eh-pH diagrams of Zn- Ca-Fe-S-H<sub>2</sub>O system at temperature 60 °C (Roine, A., 2007)

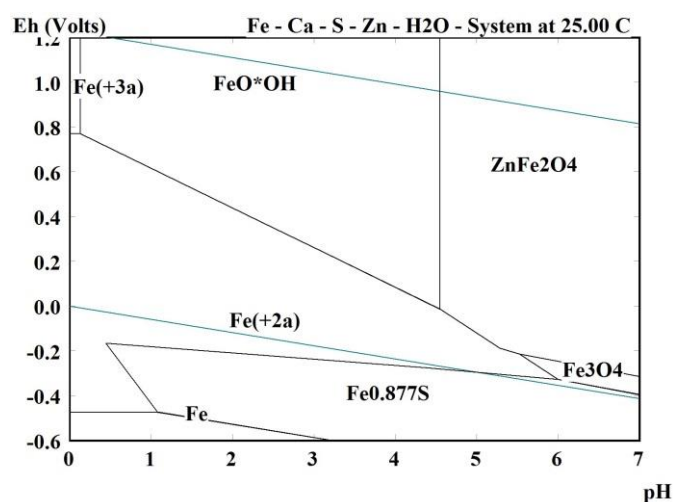


Fig. 3. Eh-pH diagrams of Fe-Ca-S-Zn-H<sub>2</sub>O system at temperature 25 °C (Roine, A., 2007)

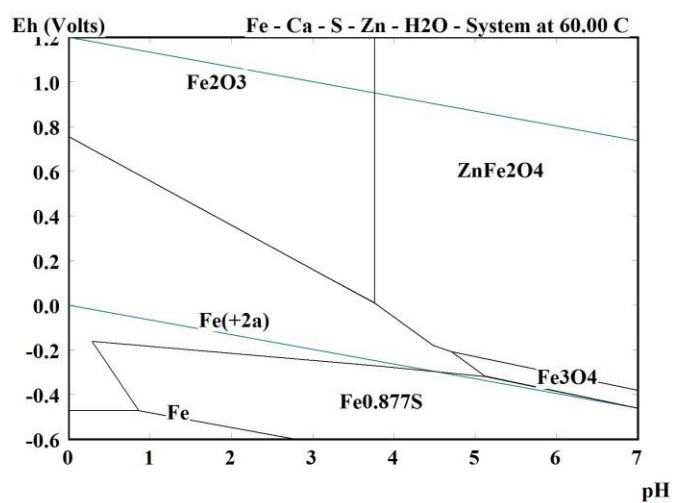


Fig. 4. Eh-pH diagrams of Fe-Ca-S-Zn-H<sub>2</sub>O system at temperature 60 °C (Roine, A., 2007)

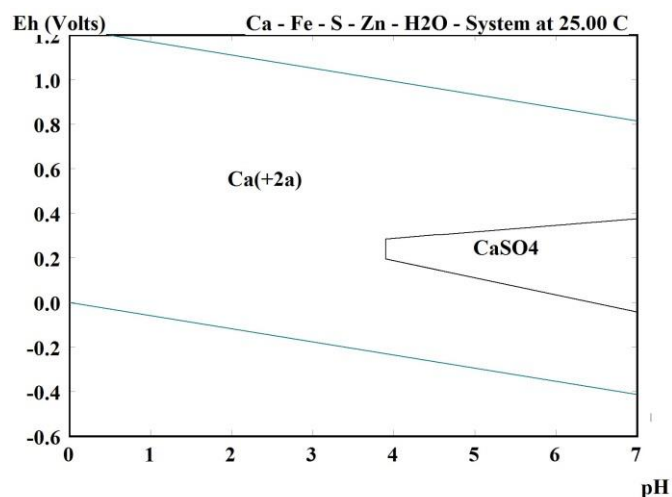


Fig. 5. Eh-pH diagram of Ca-Fe-S-Zn-H<sub>2</sub>O system at temperature 25 °C (Roine, A., 2007)

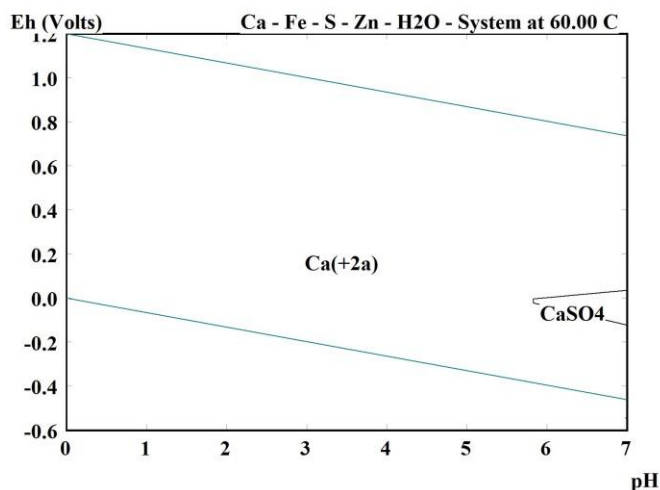


Fig. 6. Eh-pH diagram of Ca-Fe-S-Zn-H<sub>2</sub>O system at temperature 60 °C (Roine, A., 2007)

### 3.2. Experimental procedure

This sample was subjected to leaching experiments using sulphuric acid. For each experiment 500 ml of leaching solution was used. Eight different concentrations were used for this purpose, namely 0.05, 0.1, 0.25, 0.5, 0.75, 1 and 2 M H<sub>2</sub>SO<sub>4</sub>. The leaching temperature was 60 °C, solid to liquid ratio L:S = 20 (400 ml leaching solution: 20 g EAFD) and the leaching time was 30 minutes. Liquid samples were taken after 3, 5, 10, 15, and 30 minutes of leaching for analysis of Zn, Fe and Ca content using the atomic absorption spectrometry (AAS) method using Varian SpectrAA-20 Plus. The pH value was measured continuously during each experiment.

## 4. Results and discussion

### 4.1. Effect of pH and acid concentration

A leaching experiment showed that zinc, iron and calcium as well are leached out from EAF dust into solution very fast, in a matter of minutes, whereby the influence of temperature on metal extraction is not significant as was confirmed in previous works (Havlik et al., 2005, Havlik et al., 2004).

In contrast to temperature though, the solution acidity influences the process significantly (Fig. 7). However, the behaviors of zinc, iron and calcium are different. Zinc extraction is governed by a regular leaching curve, iron is not leached at low acid concentration (up to 0.1 M) and calcium is leached out at a certain level, around 22 % in this case, whereupon the process stops. The pH value change during

leaching (Fig. 8), reveals that acid consumption continues during the whole process and it is not accompanied by abrupt changes as should follow from comparison of Figs. 7 and 8.

The acid concentration does not influence metal extraction into solution significantly. However, the extraction of calcium in particular is influenced by pulp concentration change (Fig. 9). Increasing of the solid to liquid ratio (L:S) causes leaching of calcium to maximum level in a short time under given conditions.

Then the amount of leached calcium in the solution is stabilized or even slightly diminished.

The explanation of this phenomenon lies in the calcium sulphate solubility (Broul et al., 1979). The solubility of calcium sulphate dihydrate in water is  $0.26 \text{ g.dm}^{-3}$ , whereas in dilute sulphuric acid solutions around  $3 \text{ g.dm}^{-3}$  (Azimi et al, 2007).

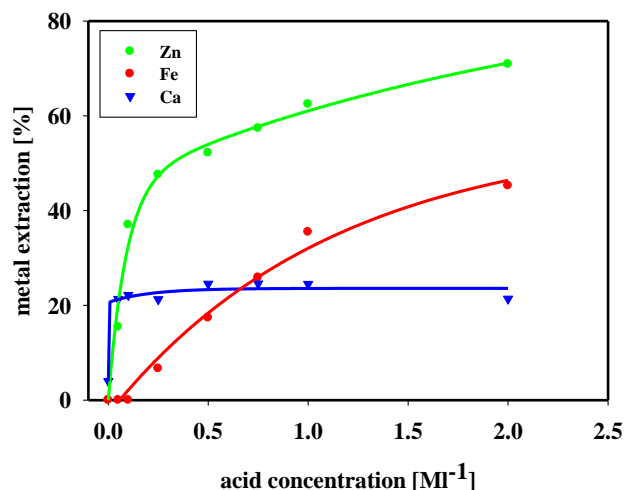


Fig. 7. Acid concentration influence on metal extraction (L:S = 20, 30 min)

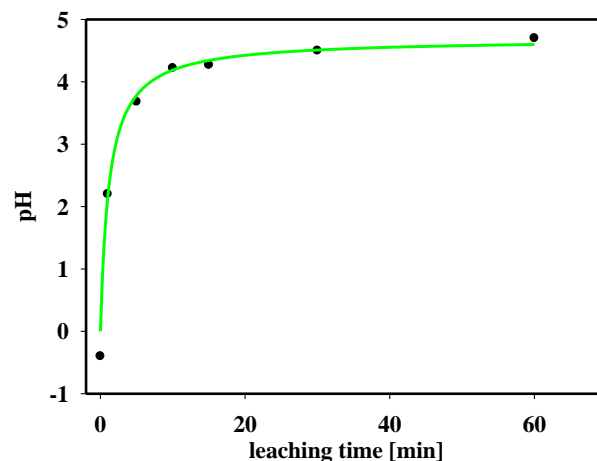


Fig. 8. pH change vs leaching time dependence L:S ratio

#### 4.2. Influence of leaching time

The key reason for EAF dust leaching in sulphuric acid is in this case as follows: zinc should pass into solution, whereas iron stays in the solid insoluble residue. This is achieved by keeping the pH of the solution in the range  $\sim 1 < \text{pH} < \sim 4$ . The original pH value of the solution is determined by the input acid concentration, but this is spent in the leaching process for  $\text{ZnSO}_4$ ,  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{CaSO}_4$  creation according to equations (9), (10), (15), and in some cases also (14) and (16). According to the measured leaching extraction values of zinc, iron and calcium (Fig. 10), the EAF dust leaching mechanism was often interpreted in the sense that it would last until the acid was spent, whereupon the leaching of components stopped.

On the other hand, the pH dependence on concentration and L:S ratio on acid concentration as well reveals another mechanism. Because of the low solubility of calcium sulphate in water, during EAF dust leaching this sulphate is precipitated from solution into solid, and for this reason the next portion of EAF dust component containing calcium is leached out. Because these reactions are thermodynamically most favorable, the acid is predominantly consumed, which is a crucial moment in the leaching of EAF dust. Fig. 11 shows solid white precipitate in the leaching solution from EAF dust leaching.

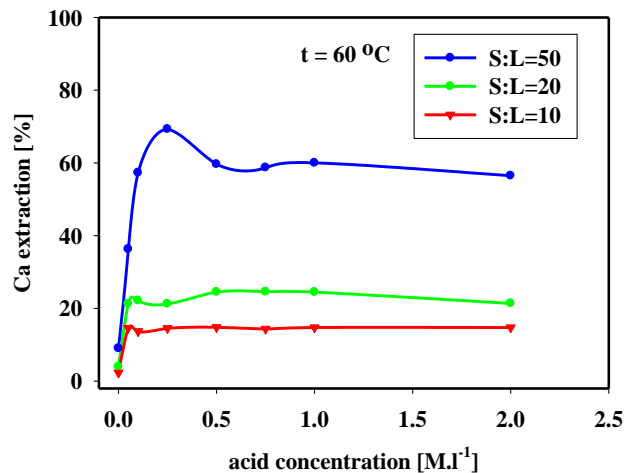


Fig. 9. Calcium extraction depending on L:S ratio

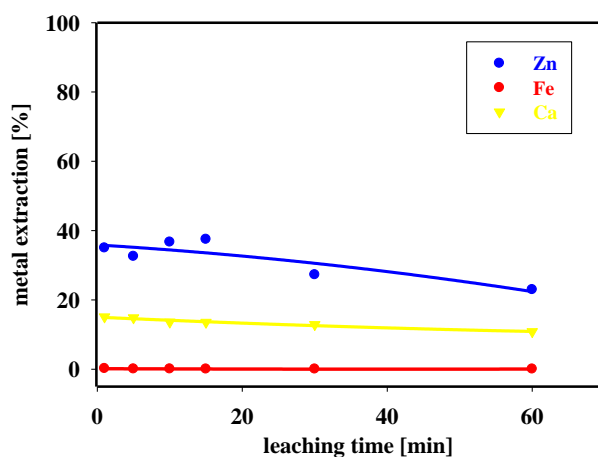


Fig. 10. Extraction curves of zinc, iron and calcium leaching from EAF dust

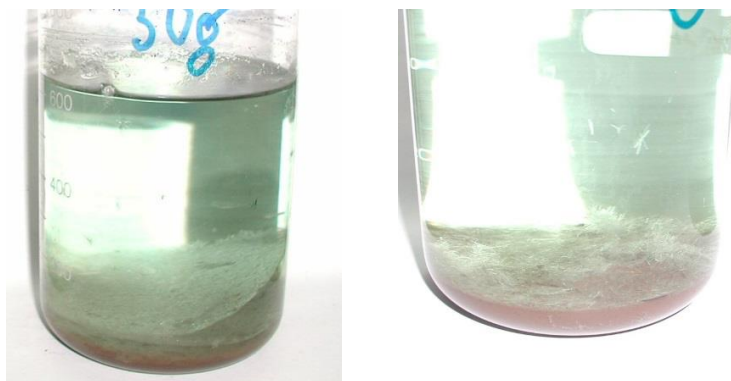


Fig. 11. White precipitate after leaching EAF dust

X-Ray diffraction qualitative phase analysis (Fig. 12) confirmed that the precipitate was the mixture of calcium sulphate dihydrate -  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . The morphological analysis and chemical microanalysis of particles as well (57 % Ca, 37.2 % S) as shown in Figs. 13 confirmed the XRD phase analysis result.

The morphological analysis obtained by scanning electron microscopy (SEM) and chemical microanalysis (EDS) of particles as well (57 % Ca, 37.2 % S) on the Fig. 13-14 confirms XRD phase analysis.

The mechanism of EAF dust leaching is controlled predominantly by leaching of phases containing calcium followed by calcium sulphate precipitation. The duration of precipitation varies within the range from a few hours to several days.

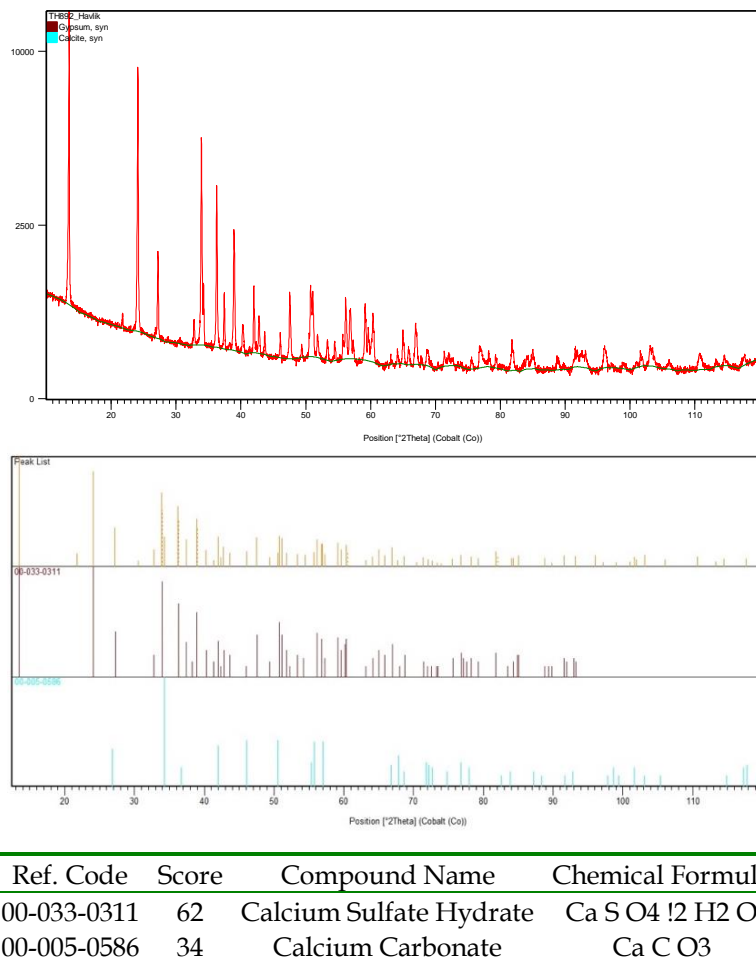


Fig. 12. X-Ray diffraction pattern of white precipitate

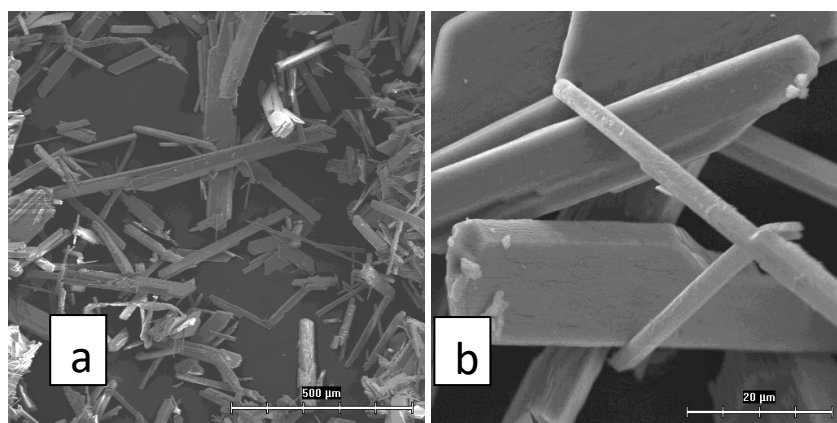


Fig. 13. Morphological observation on white precipitate



## 5. Conclusions

The process described above is that of selective recovery of zinc (and other present non-ferrous metals) using leaching solution, whereby iron stays in the solid residue. This process is significantly complicated by the calcium content in EAF dust. The calcium compounds control the leaching solution acidity during leaching. Study of zinc leaching showed that zinc passes into the solution very fast, and the maximum possible zinc extraction into the solution can be achieved in the first minutes of leaching. This study of calcium leaching showed that it is also a very fast process, but most of the calcium which reacts with sulphuric acid is precipitated from the solution in the form of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . That means the calcium content control consumption of acid in the leaching of EAF dust and considerable influences the economy of leaching.

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