



## Selective Iron Dissolution from Zinc Plant Residue

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In this study, selective extraction of metals from the zinc plant residue that supplied from the Çinkur plant was investigated. For this purpose, advanced milled of zinc plant residue was subjected to leaching in the presence of oxalic acid ( $H_2C_2O_4$ ) in atmospheric conditions. The oxalic acid salt showed different solubility effect for metal extraction. Iron was removed as iron oxalate form from zinc plant residue. However, zinc was enriched in leaching solid due to the it has low-solubility property as zinc oxalate that may be formed during leaching process. Under the optimum leaching conditions, 82.5 % of iron was extracted from zinc plant residue. In all experimental studies, it was seen that zinc extraction did not exceed to 10%. Meanwhile, lead was found to remain largely insoluble in solid leaching residue.

**Keywords:** Zinc plant residue, leaching, oxalic acid, milling.

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### 1. Introduction

Zinc is an important nonferrous metal which required for various applications such as batteries, solder, dielectric materials, and piezoelectric materials. More than 85% of zinc is produced by zinc hydrometallurgical as roast-leach-electrowinning processes all over the world. Iron-bearing sphalerite is a main raw material for this conventional process. Inevitably, spinels-oriented zinc ferrite is generated during the desulphurising roasting process of sphalerite. But, some zinc metal is produced from oxide-carbonate ores and different secondary resources such as zinc ash, zinc dross, flue dusts of electric arc furnace, leach residues, etc (Zhang et al., 2016). Pyrometallurgical and hydrometallurgical routes or their combination can be employed for treating secondary materials. The hydrometallurgical processes are regarded as more eco-friendly for treating such materials having a low zinc content. In the most common hydrometallurgical zinc process, ZnO-rich calcine is first produced from sulphide or oxide-carbonate concentrates and then leached with hot sulphuric acid solution. After liquid/solid separation, the

pregnant solution is purified and electrowon for metallic zinc production (Turan et al., 2004).

High-grade and easily concentrated ores are becoming scarcer. To meet world demands for zinc, it is necessary to develop economical and environmentally safe metallurgical technologies in where used secondary materials such as leach residues of roasted zinc concentrates and electric arc furnace dusts. The zinc in the majority of these wastes occurs in the form of zinc ferrite (franklinite,  $ZnFe_2O_4$ ), which is very stable and insoluble in most acidic and alkaline solutions. The ferrite is considered refractory (Langova et al., 2009). Consequently, zinc ferrite is always presented as a main component of zinc leaching residue, which is set aside and left as an unresolved problem. The recycling of this residue as a resource instead of a waste is notably attractive because of the depletion of zinc ores and the rapid rise of metal prices. Several pyrometallurgical and hydrometallurgical processes have been proposed for the treatment of zinc ferrites. Pyrometallurgical methods are costly owing to high energy consumption and their emissions of toxic gases are

considered an environmental problem; hydrometallurgical methods are preferred for process economy and environmental reasons. Hydrometallurgical processes such as two-stage acid leaching, high pressure acid leaching, various acids leaching microwave caustic leaching, and alkaline leaching have been developed. However, they are unsuitable for the further treatment of roasting process for the iron and many other heavy metals are left in the Zn hydrometallurgical solution so that a lengthy purification process is required before electrowinning. Moreover, this purification process produces a considerable amount of iron slag, which is a significant threatening material for environment (Peng et al., 2012).

In this study, selective iron extraction from the zinc plant residue was investigated. For this purpose, advanced milled zinc plant residue was subjected to leaching in the presence of oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) in atmospheric conditions.

## 2. Material and Methods

Zinc plant residue was obtained from Çinkur Plant located at Kayseri, Turkey. The concentrate was classified by sieving through a 200 mesh, and this fraction was used in experiments. Then, elemental analysis of the residue was performed with ICP-OES after digestion of sample (Table 1). Mineralogical analyses of the concentrate were made by using X-ray diffraction system (Shimadzu XRD-6000) and powder diffraction technique. X-ray diffraction results showed that dominant mineral phases are gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), anglesite (PbSO<sub>4</sub>), and maghemite (Fe<sub>2</sub>O<sub>3</sub>). In experiments, high-energy ball mill (known as spex mill) was used for advanced grinding. This grinding system comprised of a tungsten jar of 80 ml volume including 8 mm diameter balls. In all experiments, ball-solid ratio was kept constant as 10.

Leaching experiments were carried out in 0.3 L flasks under reflux. At the end of the leaching period, the contents were cooled and filtered. Filtered solutions were analyzed for zinc and iron using an AAS (Perkin Elmer-Analyst 400).

Table 1. Chemical composition of zinc plant residue

Pb	15.02%
Zn	7.98%
Fe	5.44%
Ag	68.4 ppm
Au	15.7 ppb
Al	1.85%
Si	6.74%
Ca	6.19%

## 4. Results and discussion

In this study, advanced milled zinc plant residue was leached in the presence of oxalic acid in atmospheric conditions. While iron oxalate and various iron salts have high

dissolution (0,008 g/100 g H<sub>2</sub>O at 20 °C), zinc compounds have low dissolution (1,38\*10<sup>-9</sup> g/100 g H<sub>2</sub>O at 20 °C). In this context, the effect of leaching parameter was examined in the range of 10-100 g/L for oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) concentration, 5-180 min for leaching time, and 318-378 K for leaching temperature. As can be seen in Figure 1, it is clear that 12% of Fe and 12% of Zn were extracted in the presence of 100 g/L oxalic acid under condition of non-advanced milling. Whereas, the iron and zinc were extracted from zinc plant residue as 17.5% and 2%, respectively under conditions of 1 min advanced milled sample and 100 g/L of oxalic acid concentration. This situation is shown in Figure 2. In the figure, it is clearly seen that the leaching efficiency of the samples obtained as a result of the advanced milled process is higher than leaching of original sample. Increase in grinding time causes agglomeration of particle surface (Turan et al., 2019). Therefore, long grinding times were not studied in the experiments. It can be said that, based on Eq. (3.1), various iron oxalate compounds/complexes (Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub><sup>3-</sup>, FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O) are formed. But, dissolved zinc ions and oxalic acid precipitate by forming low-solubility zinc oxalate (Eq 3.2):



On the other hand, the leaching time is not effective parameter in this study due to reactions ending fast. The graph of Figure 3 shows that the leaching reaction is essentially rapid. In the first 5 minutes of the leaching process, iron was extracted at a rate of approximately 16%, while the long leaching times of 180 minutes did not change much extraction. It is thought that the extraction efficiency of zinc in oxalic acid medium is as low as expected and it remains in the solid residue as zinc oxalate. In this case, the optimum leaching time was selected as 120 min, taking into account the following operating parameters. The effect of leaching temperature is given in Fig 4. It was seen that the leaching temperature was a very important parameter. It was observed that leaching efficiency did not change much at low temperatures. In addition, with the increasing leaching temperature, especially after 353 K, iron extraction efficiency increased considerably.

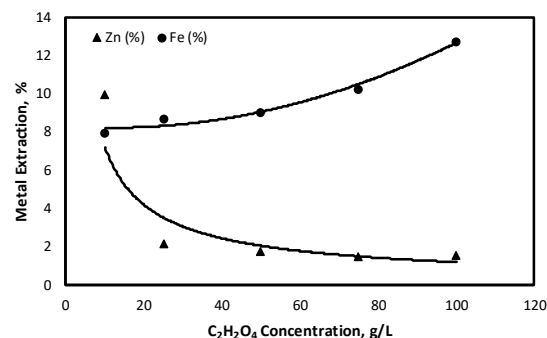
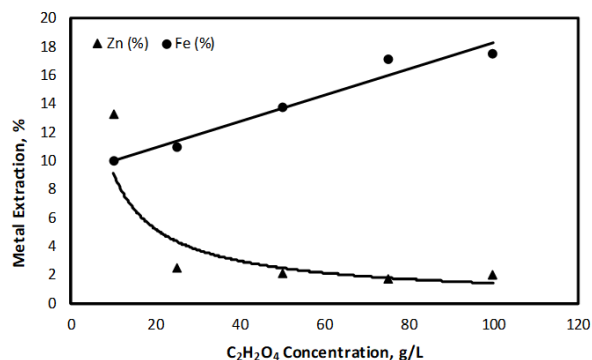
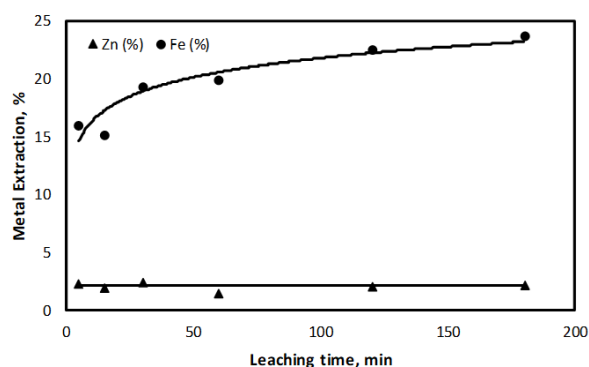


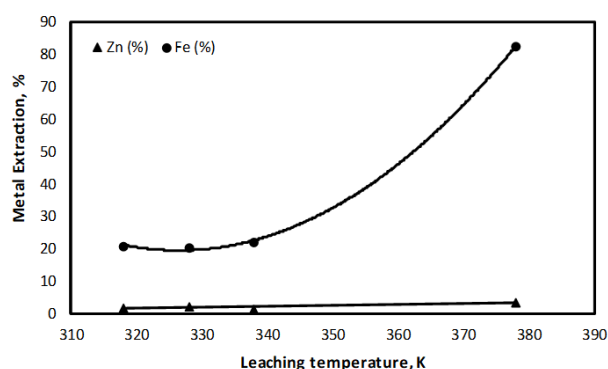
Fig 1. Effect of C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> concentration on the metal extraction (non-milled; Leaching time: 60 min; Liquid-solid ration: 25 ml/g; Stirring speed: 400 rpm; Leaching temperature: 318 K)



**Fig 2.** Effect of  $C_2H_2O_4$  concentration on the metal extraction (Milling time: 1 min; ball-concentrate ratio:10 wt/wt; Leaching time: 60 min; Liquid-solid ration:25 ml/g; Stirring speed:400 rpm; Leaching temperature:318 K)



**Fig 3.** Effect of leaching time on the metal extraction (Milling time: 1 min; ball-concentrate ratio:10 wt/wt;  $C_2H_2O_4$  concentration: 50 g/L; Liquid-solid ration:25 ml/g; Stirring speed:400 rpm; Leaching temperature:318 K)



**Fig 4.** Effect of leaching temperature on the metal extraction (Milling time: 1 min; ball-concentrate ratio:10 wt/wt;  $C_2H_2O_4$  concentration: 50 g/L; Liquid-solid ration:25 ml/g; Stirring speed:400 rpm; Leaching time: 120 min)

## 5. Conclusion

Selective extraction of metals from the zinc plant residue was investigated. For this purpose, advanced milled zinc plant residue was subjected to leaching in the presence of oxalic acid ( $H_2C_2O_4$ ) in atmospheric conditions. It is well known that ferritic metals have limited dissolution. Leaching efficiency of advanced milled samples was higher than leaching of original zinc plant residue. Selective iron dissolution based on dissolution difference of zinc and iron from zinc plant residue can be obtained by using oxalic acid. The optimal conditions were determined as oxalic acid concentration of 50 g/L, leaching temperature of 378 K, leaching time of 120 min, liquid-solid ration of 25 ml/g, milling time of 1 min and stirring speed of 400 rpm. Under the optimum leaching conditions 82.5 % of iron was extracted from zinc plant residue. In all experimental studies, it was seen that zinc extraction did not exceed to 10%. Meanwhile, lead was found to remain largely insoluble in solid leaching residue.

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