

## Characterization of the effects of acetic acid on the recovery of valuable contents from flotation tailings of non-sulfide metals

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**Abstract:** Non-sulfide lead flotation tailings draw attention in terms of their valuable contents. Dissolution studies have been carried out with strong inorganic acids, especially in ore form, but these acids have been unfavorable in removal in the context of metal recovery processes. Organic acids, on the other hand, are notable for their environmentally friendly properties and selective metal recovery opportunities. In this study, the effects of acetic acid on metal recovery from oxidized waste were investigated with different experimental parameters at a laboratory scale. Optimal conditions were determined depending on the increase in acetic acid concentration. At 0.75-1.0 M acid concentrations, 49-55% Pb and 49-54% Zn recovery efficiencies were obtained with grades of 7.0-7.2% and 19.5-19.7%, respectively. The recovery of Pb/Zn by the leaching process with acetic acid and the selective non-recovery of iron were also observed through characterization studies. With the Rietveld XRD method, an increase in iron minerals such as goethite and a decrease in smithsonite-hydrozincite minerals were determined. These changes were seen as a decrease in the contents of these minerals in SEM/EDX analysis and as a decrease in smithsonite mineral bond structures in the FT-IR analysis. This study showed that acetic acid has many advantages in the utilization of zinc-lead-containing oxide flotation tailings, which have high economic value, such as selective metal recovery, easy biodegradability, environmental friendliness, and non-corrosiveness.

**Keywords:** flotation tailing, acetic acid, recovery, zinc/lead, characterization

### 1. Introduction

Lead and zinc have been used in many fields such as metallurgy, military, and medicine for many years (Nanda et al., 2022). These metals are non-ferrous metals that are very commonly used after aluminum and copper and are also found together in nature. Lead has the advantage of being soft, easily machinable, and heavy, whereas zinc has the advantage of low melting/boiling points and resistance to corrosion (Nayak et al., 2021).

The most prevalent ores containing these metals are sulfide ores (Moradi and Monhemius, 2011). However, the decrease in the availability of these ores has increased the interest in the utilization of other low-grade and more difficult-to-enrich oxidized and mixed-type ores (Hussaini et al., 2021) and secondary wastes (Tang et al., 2020). In particular, recycling processes have many advantages. Some of these advantages are reducing the environmental impact of harmful components in waste (Kaya et al., 2020), recycling valuable ingredients such as zinc (Alkan et al., 2023), and reducing the need for the landfill processing of fine-sized waste (Mikula et al., 2022; Yoğurtcuoğlu, 2023a).

The most common enrichment method for these ores is the physicochemical (flotation) method (Yoğurtcuoğlu, 2023b) where the surface is sulfurized, and anionic collectors such as xanthates (Ahmed et al., 2021) are applied (Şentürk et al., 1993; Önal et al., 2005). There are also zinc recovery studies in which anionic and cationic collectors have been applied together for oxide and mixed-type ores (Hosseini and Forssberg, 2006; Hosseini and Forssberg, 2007; Hosseini and Taji, 2015; Magela et al., 2021; Henrique et al., 2022). However, while only lead can be recovered in these ores industrially, zinc and other metals can still be found in the wastes (Yarluğkal Altınışık et al., 2022; Yoğurtcuoğlu, 2022a).

Hydrometallurgical and pyrometallurgical processes, which are among other enrichment methods, have been found to be effective in research on the recovery of zinc (and its contained ore) from both mine tailings (three types) and secondary sources (such as EAF-electric arc furnaces) (Sinha et al., 2016; Onukwuli and Nnanwube, 2022). There are three stages (roasting-leaching-electrowinning) that are used in zinc recovery in the world (Aparajith et al., 2010). In the first step, ZnO calcine is produced from concentrates, and in the second step, the zinc in the calcine is leached with a hot sulfuric acid solution. After liquid-solid separation by a rotary filter, a charged leaching solution and a solid leach residue are obtained. In the third stage, the pregnant solution is purified, and zinc is recovered by electrolysis (Turan et al., 2004; Şahin and Erdem, 2015).

In one example of a pyrometallurgical process, the sulfurization of carbonate and oxide structures was achieved by sulfation roasting with elemental sulfur in the range of 600-900°C from refractory lead-zinc ore. Recovery rates of approximately 96-97% for lead and zinc were obtained under the optimum conditions (Zheng et al., 2015). Chlorination roasting was carried out for the recovery of lead and zinc found in copper melting slags, which are important secondary sources. In the experiments, 74.74% Zn and 94.72% Pb recovery rates were obtained at a roasting temperature of 850°C, a roasting time of 60 min, an airflow rate of 100 mL/min, and a 30% CaCl<sub>2</sub> concentration by weight (Guo et al., 2021).

Hydrometallurgy is a more advantageous process due to the requirement of high energy and dust/gas systems in pyrometallurgical processes, as well as the corrosive effect of the presence of chloride/fluoride in the powder content. While sulfuric acid and ammonia solutions are effective solutions, sodium hydroxide is a selective reagent (Jha et al., 2001). As a different operational process, after zinc was recovered with sulfuric acid (hydrometallurgical process) in an Angouran (Iran) oxide lead-zinc deposit, lead-containing cerussite, mimetite, and beudantite were recovered using the flotation method (Rashchi et al., 2005). Zinc recovery from sphalerite ore with nitric acid was carried out using a statistical design of experiments. As a result of leaching, a zinc recovery rate of 87.67% was achieved (Onukwuli and Nnanwube, 2022). The powerful acids mentioned above have drawbacks as well, such as their potential to easily evaporate, high consumption rates, and difficulties in recycling, while they dissolve several contaminants during the leaching process (Alkan et al., 2023).

Instead of these acids, organic acids such as acetic (Nagib and Inoue, 2000), citric (Hussaini et al., 2023), malic (Hussaini et al., 2021), formic, and oxalic acids (Halli et al., 2017), which are compatible with green technologies, biodegradable, cleaner (Vidra and Németh, 2018; Hu et al., 2021), financially affordable, and acceptable acids (Zhu et al., 2013), are more remarkable (Xiao et al., 2021; Niskanen et al., 2022). One of the main features of these reagents is their high selectivity due to their low dissolution capacity (Hürşit et al., 2009). Acetic acid, another weak solvent, was determined have pH values of 2.4, 2.9, and 3.4 at 1.0, 0.1, and 0.01 M concentrations, respectively. Oxides, carbonates, metals, and salts dissolve in this solution. This dissolution process is slower than those in acids such as HCl and H<sub>2</sub>SO<sub>4</sub> but 10-11 times faster compared to most other organic acids (Laçin et al., 2005).

In a study by Dreisinger et al. (1990), by applying dilute acetic acid to the dust of carbon steel EAF, lime was precipitated as calcium acetate, and then zinc was recovered by ammonia leaching. Additionally, before this process, chlorides are separated by washing with water, while other metals are purified after the zinc process. In the study of Barrett et al. (1992), calcium and magnesium removal from steel-made EAF powder with strong acetic acid, iron recovery from zinc ferrite and sent to the furnace was provided. Additionally, it was ensured that the unwanted metals from among others were separated, and useful products were obtained at the zinc recovery stage.

Along with the above-mentioned studies, although there are metal recovery processes with acetic acid reported in different secondary sources in the literature (Steer and Griffiths, 2013; Sethurajan et al., 2017; Halli et al., 2017; Xue et al., 2022), no studies where this acid was used for oxidized flotation wastes could be found in the review of the literature. For this reason, in this study, the effects of acetic acid, an organic acid with many advantages such as being cheap, selective, and environmentally friendly, on metal recovery from oxidized Pb/Zn flotation wastes were investigated. In this study, characterization tests were also carried out to determine changes in mineral contents, bond structures, and phases. This way, it is thought that by emphasizing the recovery of both metals from these wastes and their structural features, together with the positive effects of these acids, this study can shed light on the industry and the literature.

## 2. Materials and methods

### 2.1. Material

The oxidized lead-zinc flotation tailing sample (about 30 kg) was obtained from the Yahyalı/Kayseri (Turkey) region of the Pb/Zn deposits along Zamantı-Aladağlar (Hanilçı and Öztürk, 2005; Hurşit et al., 2009). The dried sample (105°C) was divided using sample division techniques, and the feed sample used in the experiments was obtained as 25-30 g. The representative sample was subjected to FT-IR analyses, chemical analyses (XRF), and particle size distribution tests. In magnetic stirrers, the experiments were conducted while controlling the temperature and steam at a stirring speed of 750–1000 rpm (in a fume hood).

The leaching tests, which could be considered as approximately the middle value of all the experiments, were done. These values were acetic acid (CH<sub>3</sub>COOH) concentration: 0.5M, leaching temperature: 60°C, leaching time: 60 min, and solid-to-liquid ratio: 10%. The results determined by this experiment were compared to the results of all other experiments. Additionally, in each parameter analysis, one of these values was changed, and the others were kept constant to analyze the effects of these changes on the outcomes. The parameter ranges were determined as acetic acid concentrations of 0.125-1M, leaching temperatures of 25-95°C, leaching times of 15-120 min, and solid ratios of 5-40%. Additionally, error bars were added by calculating the % error values according to the three results of the Pb/Zn/Fe values for each data.

### 2.2. Methods

Analyses were made in NOHU (Niğde Ömer Halisdemir University) Central Research Laboratory to determine the structures of the feed and the waste samples obtained after the process. Using an XRF (X-ray fluorescence) device branded Panalytical/Zetium, the feed sample's chemical composition was examined. The Mastersizer MU 3000 instrument was used to analyze the particle size distribution of the sample. The results were computed by averaging the results of three analyses. XRD (X-ray diffraction) Rietveld's analyses were performed to identify the mineralogical structures of the feed and the waste samples. The device was a Panalytical Empyrean branded device, and the analyses were carried out with the parameters at 2°/min, 45 mA, 40 kV, and 5-90°. To examine the bond structure of the samples, FT-IR (Fourier transform infrared spectroscopy) analyses were performed. The analyses were carried out with a Bruker-Vortex 70 device in the measurement range of 4000-400 cm<sup>-1</sup>. SEM/EDX analyses were carried out on the samples using a field emission scanning electron microscope (FESEM) at Kayseri Erciyes University Technology Research and Application Center. The point elemental analysis was performed with a Zeiss brand and Gemini 500 model analyzer. The purpose of this analysis was to determine the morphological changes of the two samples and the minerals they contained by point analysis. The PerkinElmer PinAAcle 500 AAS (Atomic absorption spectroscopy) equipment was used to conduct the analyses of metals from the liquid solutions at the end of the experiment based on the average results of three analyses. Additionally, after the experiment, solid tailing sample analysis results were confirmed in the plant.

## 3. Results and discussion

### 3.1. The feed sample characterization analyses

According to the XRF analysis results (Table 1), ZnO and PbO were detected at concentrations of 7.82% and 2.46%, respectively.

Table 1. XRF analysis of the feed sample

Weight, %	Chemical composition
55.48	Fe <sub>2</sub> O <sub>3</sub>
9.39	SiO <sub>2</sub>
7.82	ZnO
3.68	Al <sub>2</sub> O <sub>3</sub>
3.23	CaO
2.46	PbO

The particle size analysis revealed a particle size value of  $d_{90}=112.98 \mu\text{m}$  in the feed sample (Fig. 1). It is an important advantage for these hydrometallurgical methods that there is no need for (re)grinding, which is the greatest source of energy consumption in the ore preparation and enrichment process, since the test samples were wastes originating from the flotation process.

The XRD Rietveld's analysis results of the feed sample are shown in Fig. 2. The minerals determined in the analysis of this sample were dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) at a concentration of 21.0%, goethite ( $\text{FeOOH}$ ) at 41.8%, quartz ( $\text{SiO}_2$ ) at 14.0%, calcite ( $\text{CaCO}_3$ ) at 0.7%, smithsonite ( $\text{ZnCO}_3$ ) at 17.2%, hydrozincite ( $\text{Zn}_5(\text{CO}_3)_2(\text{OH})$ ) at 4.4%, and plumbojarosite ( $\text{PbFe}_6(\text{SO}_4)_2(\text{OH})_{12}$ ) at 1.0%.

The O, Al, Si, Fe, and Zn were detected in the SEM/EDX analyses of the first marked point of the feed sample (Figs. 3 and 3-a). According to the results of this analysis, the presence of quartz, smithsonite, goethite, and hydrozincite was detected. In the analyses of the second point (Figs. 3 and 3-b), O, Mg, Al, Si, K, Fe, and Zn were identified. According to the results of these analyses, the sample included silicate minerals (such as muscovite, kaolinite, quartz) and oxide/carbonate iron-zinc minerals.

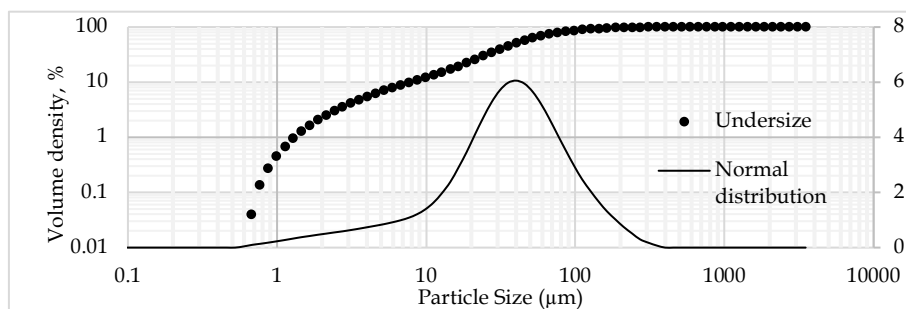


Fig. 1. The particle size distribution of the feed sample

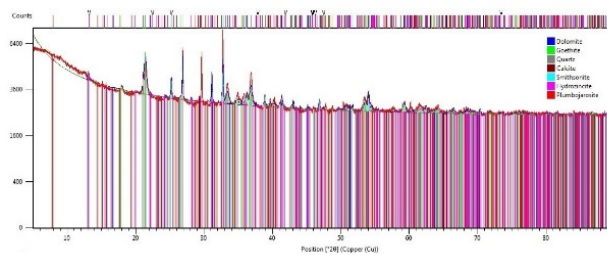


Fig. 2. XRD Rietveld's analysis of the feed sample

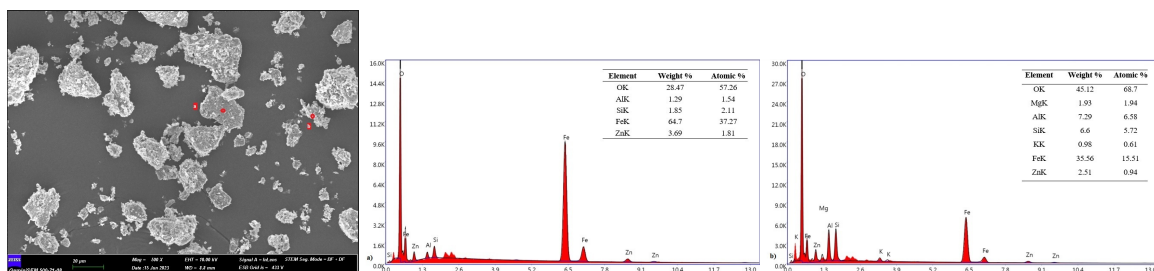


Fig. 3. SEM/EDX analysis of the feed sample (a- EDX1, b- EDX2)

The results of the FT-IR analyses of the feed sample are given in Fig. 4. The  $3618.30 \text{ cm}^{-1}$  peak belonged to montmorillonite clay (El Ouardi et al., 2019), the  $3125.57 \text{ cm}^{-1}$  (Akyildirim et al., 2019) and  $2359.24 \text{ cm}^{-1}$  (Nandiyanto et al., 2019) peaks belonged to the NH component, and the peak of montmorillonite (Ojima, 2003) at  $1634.83 \text{ cm}^{-1}$  indicated HOH deformation (of Pb-jarosite) (Smith et al., 2006). The  $1434.71$  ( $1435.00$ )  $\text{cm}^{-1}$  peak suggested that ZnS formed on the smithsonite surface after the  $\text{Na}_2\text{S}$  treatment (Hosseini and Forssberg, 2006). The peaks at  $998.98 \text{ cm}^{-1}$  and  $875.59 \text{ cm}^{-1}$  were a C-O stretching peak (MalligArjuna Rao et al., 2021) and a specific calcite peak (Luo et al., 2011; Kiefer et al., 2018), whereas the  $909.57 \text{ cm}^{-1}$  peak belonged to hydroxyl group bonds (Yoğurtcuoğlu, 2023c). The

peaks at  $797.00\text{ cm}^{-1}$  were the peaks of goethite (Zviagina et al., 2020) and quartz minerals (Ojima, 2003; Sbihi et al., 2014). The  $523.87\text{ cm}^{-1}$  peak indicated Al-O-Si group deformation (Aslan and Gurocak, 2022) and COH vibration (Dikmen and Alver, 2021).

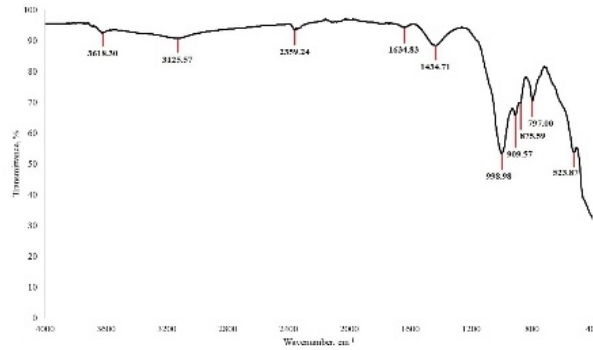


Fig. 4. FT-IR analysis of the feed sample

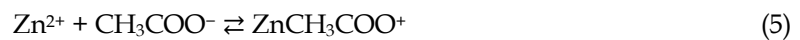
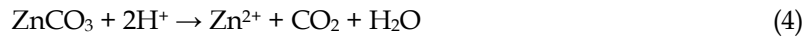
### 3.2. Metal analyses

In the characterization studies, it was observed that the test sample contained oxidized/carbonated Pb/Zn/Fe metals.

Therefore, the dissolution of acetic acid in aqueous medium according to Eq. 3 (Yoğurtcuoğlu, 2022b) are as follows:



Additionally, the reaction of smithsonite in aqueous (acidic) media denoted by Eq. 4 (Hurşit et al., 2009) and that in acidic environments denoted by Eq. 5 (Jiao et al., 2011) are shown below.



The dissolution reaction of lead oxide in an acetic acid medium is as follows (Eq. 6) (Zhu et al., 2013):



#### 3.2.1. Leaching test parameters

Using the experimental parameters based on the other experiments (Table 2), namely a 0.5M acetic acid concentration, a  $60^\circ\text{C}$  leaching temperature, 60 min of leaching time, and a 10% solid-to-liquid ratio, the recovery rates were 31.30% for Zn, 31.80% for Pb, and 14.12% for Fe. Metal grades were determined as 5.54% for Pb, 15.94% for Zn, and 17.77% for Fe.

Table 2. Leaching test parameters

Parameters	Acetic acid concentration	Leaching temperature	Leaching time	Solids	Results (%)		
Values	0.5M	$60^\circ\text{C}$	60 min	10%	<u>Zn</u> 31.30	<u>Pb</u> 31.80	<u>Fe</u> 14.12

#### 3.2.2. Effects of parameters

According to numerous studies, the concentration effect of the leaching chemicals is the most important factor in the ability of the hydrometallurgical method to recover metals from waste or ore. Additionally, other parameters in which this method is generally examined are leaching time, leaching temperature, and solid-liquid separation (Havlik and Friedrich, 2004; Onol and Saridede, 2013; Alkan et al., 2023). The experiments on the effects of the acetic acid concentration were carried out at  $60^\circ\text{C}$ , with a 10% solid-to-liquid ratio, for 1 h, and at acid concentrations of 0.125, 0.25, 0.5, 0.75, and 1.0M (Fig. 5-a). In the experiments of this parameter, the error rates were determined to be  $\pm 6.93\%$  for Pb,  $\pm 0.27\%$  for Zn, and  $\pm 3.8\%$  for Fe. Zinc recovery efficiency values (9.05-53.64%) increased with an increase in acid concentrations. Similarly, Pb solubility showed a recovery value of 17.62% at the 0.125M acetic acid

concentration, while it reached 55.10% at 1M. It was seen that the recovery rates of Fe decreased as the acid concentrations increased, and this decrease was observed to be from 16.5% to 13.30%. Metal grades changed in the ranges of 4.68-7.21% for Pb, 6.74-19.67% for Zn, and 38.02-15.06% for Fe as the concentration increased. As seen here, with the increase in concentration, the recovery efficiency and grade of zinc increased, these values also increased relatively in case of lead, but they decreased for iron. In conclusion, these changes in metal recovery values indicated that lead was recovered at higher efficiency rates than zinc.

An important factor in hydrometallurgical operations is the leaching temperature. Because temperature increases the number of particle collisions that contribute to the dissolution mechanism (Topçu et al., 2021a; Topçu et al., 2021b). In the experiments on the effects of the leaching temperatures in the range of 25-60-95°C (Fig. 5-b), an acetic acid concentration of 0.5M, 1 h of leaching time, and a solid-to-liquid ratio of 10% were kept constant. The error rates in the analyses were found to be  $\pm 8.37\%$  for Pb,  $\pm 0.18\%$  for Zn, and  $\pm 7.47\%$  for Fe. The increase in temperature positively affected the recovery efficiency values of the metals. It was determined that the solubility of zinc reached 34.02%. Lead solubility, on the other hand, increased by approximately 6.5-7% from the initial value of 28.94%. Iron solubility increased from 13 to 16%. As with the difference in acid concentrations, zinc recovery rates were lower than those of lead. With the increase in temperature, zinc grades increased from 10.68% to 16.5%. As for lead, the values remained between 5.42 and 5.64%. The values for iron decreased from 25.92% to 17.38%. These results showed similar increases in grade and recovery with the acetic acid concentration.

Another parameter whose effects were determined was the leaching time, and the determination of the optimum test time is especially important to reduce the energy costs. As seen in Fig. 5-c, in the experiments where the effects of different leaching times, namely 15, 30, 45, 60, and 120 min, were investigated, other operating conditions were kept constant at a 0.5M acetic acid concentration, a 60°C leaching temperature, and a 10% solid-to-liquid ratio. The error rates in the analyses were found to be  $\pm 6.77\%$  for Pb,  $\pm 0.26\%$  for Zn, and  $\pm 4.27\%$  for Fe. Depending on the increases in leaching time, the zinc and lead recovery efficiency values were close to each other, and they were in a range of 33.6-33.7%. The recovery efficiency of iron increased from 10.54 to 14.64%. In the examination of grades depending on time, although there was an increasing trend in the grades of all metals, lower grades (14.06-18.5%) were observed for iron than the other two parameters. The grade of zinc was in the range of 11.62-16.50%, and the grade of lead was in the range of 4.16-5.65%.

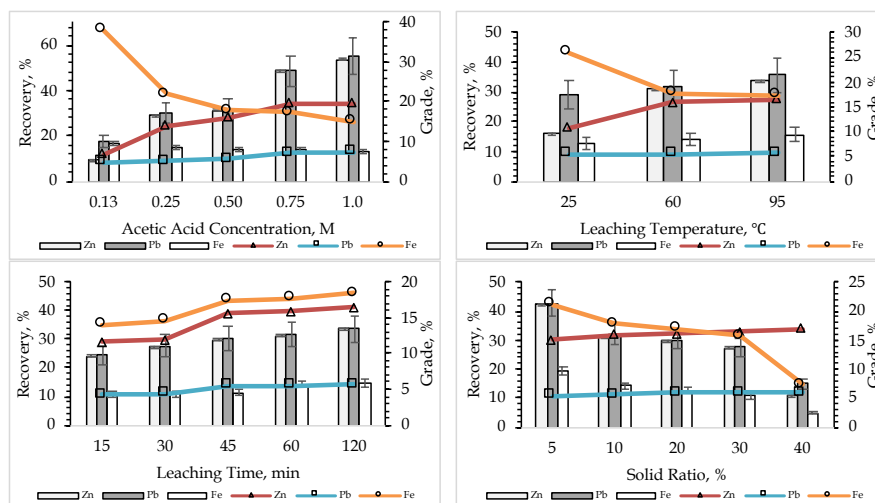


Fig. 5. Effects of acetic acid concentration (a), leaching temperature (b), leaching time (c), and solid-to-liquid ratio (d) on %metal recovery/grade

Fig. 5-d presents the results of the experiments conducted at solid-to-liquid ratios of 5, 10, 20, 30, and 40%. Other parameters were kept constant at a 0.5M acetic acid concentrations, 1 h of leaching time, and a 60°C leaching temperature. The error rates in the analyses were found to be  $\pm 5.34\%$  for Pb,  $\pm 0.35\%$  for Zn, and  $\pm 3.88\%$  for Fe. Compared to the other three experiments, it was observed that the increases in

the solid-to-liquid ratio values negatively affected the recovery rates in the experiments. In these experiments, it was observed that the solubility of zinc decreased from 42.49% to 11.07% from a solid-to-liquid ratio of 5% to a ratio of 40%. The solubility of lead, on the other hand, was found to be 14.84% at a 40% solid-to-liquid ratio, while it was around 28% at a solid-to-liquid ratio of 20%. Iron recovery efficiency values also decreased from 19.26% to 4.64%. Unlike the time parameter, the iron grade decreased from 21.14 to 7.30% in the solid rate parameter, like the other two parameters. The grades of lead and zinc also increased from 5.43 to 5.93% and from 15.10 to 16.92%, respectively.

In light of all these metal analysis data, optimal results were obtained at the highest concentration of acetic acid. For the acetic acid concentration of 1M, the recovery and grade values were found respectively as 53.64% and 19.67% for zinc, 55.10% and 7.21% for lead, and 13.30% and 15.06% for iron. Throughout the entire study, the lowest and highest values of iron recovery and grade were observed in the solid-liquid ratio parameter. Correspondingly, as the parameter value increased, Fe recovery values changed from 19.26 to 4.64%, and Fe grades changed from 21.14 to 7.31%. Metal recovery values of lead and zinc were also obtained in inverse proportion to the solid-liquid ratio. The general reason why metals cannot dissolve in high solid-to-liquid ratios is thought to be the difficulty of reacting the reagents and water with the solid surface. Similar improvements were observed in terms of the metal recovery and grade values of these two metals with increases in all other parameter values.

For the recovery of zinc and low-grade iron from iron powders formed in iron and steel manufacturing, dissolution with organic carboxylic acids was carried out. Among these acids, 58.1% Zn and 2.7% Fe were obtained with ethanoic (acetic) acid at pH 2.9 (Steer and Griffiths, 2013). The dissolution of different types of zinc structures from zinc plant leach waste (ZLR) was investigated. It was determined that dissolution occurred for zinc silicates (Sethurajan et al., 2017). Lead and zinc recovery rates were investigated at different acetic acid concentrations by Halli et al. (2017) using the EAF, and it was determined that lead was more soluble in acetic acid leaching. It was found that iron recovery was not affected by concentration differences and had low values. In a similar study by Xue et al. (2022), the advantage of acetic acid was reported as its selectivity for Pb and Zn, but the solubility of Zn decreased in the presence of structures such as  $ZnFe_2O_4$ . According to Nagib and Inoue (2000), it was determined that the acid concentration in the acetic acid dissolution of Zn, Pb and Fe in PFA and SFA samples found in municipal wastes was effective in the solubility of lead (especially) and zinc, but did not affect the solubility of iron. In addition, it was observed that the % solids parameter of this study had a negative effect on metal recoveries. However, in the study of Hamuyuni et al., (2018), it was observed that high acid concentration had a negative effect on metal recovery. In this study, metal recoveries increased up to 1 M concentration. Alkan et al. (2023) studied Pb/Zn metal extraction and recovery by the leaching of ammonium acetate (AmAc) from zinc filter cakes (ZFCs). As the temperature increased over time, the recovery efficiency of both metals increased. Correspondingly, according to Aydoğan et al., (2007), in the study of dissolution of galena obtained from Sivas Koyulhisar complex sulfur enrichment facility in acetic environment, temperature and time parameters had a positive effect on metal extraction rates.

Similarly, in this study, it was determined that the metal recovery efficiency values decreased with the increase in the solid-to-liquid ratio. Likewise, the recovery efficiency values of lead and zinc were close to each other at all test parameter values except for the solid-to-liquid ratio, while the recovery of lead was slightly higher depending on an increase in this parameter. Iron recovery rates were found to be lower, which could be attributed to the usage of an organic acid.

As seen in the results of other studies in the literature, lead recovery efficiency values would be expected to be higher than those of zinc as a result of the efficiency of acetic acid experiments (Hamuyuni et al., 2018; Kaya et al., 2020). In addition, in the study of Halli et al. (2017), the recovery efficiencies of this acid were obtained with similar results as this study. However, Nagib and Inoue's (2000) study suggested that low sample grain sizes may be effective in metal recovery efficiencies.

### 3.3. Leaching waste characterization analyses

In the XRD Rietveld's analysis of the waste sample after leaching (Fig. 6), mineral contents were found to be 9.0% for dolomite, 68.7% for goethite, 14.3% for quartz, 3.1% for smithsonite, 1.6% for hydrozincite, and 3.4% for plumbojarosite. Calcite could not be detected.

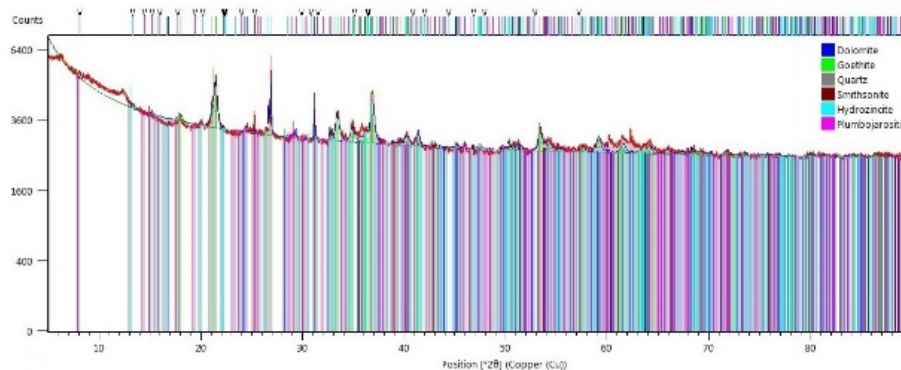


Fig. 6. XRD Rietveld's analysis of the waste sample after leaching

It was determined that calcite was dissolved in the acetic acid medium in a pH range of 2.3-4.6 (Fredd and Fogler, 1998). The dissolution reactions in calcite (Eq. 1) or mainly lime (Eq. 2) (Dreisinger et al., 1990) in acetic acid are as follows:



Therefore, the main reasons why calcite could not be determined in the results shown in Fig. 6 was thought to be that it was dissolved as calcium acetate by leaching. In the results of the analysis, a decrease in zinc minerals and an increase in iron minerals were observed. In relation to the recovery efficiencies of zinc, when evaluated along the Rietveld XRD results, these results seem to agree with each other. Especially the decrease in the contents of smithsonite and hydrozincite supports these data. Additionally, although the goethite contents increased further than the values given in Fig. 2, the increase in the amount of iron after lead and zinc were obtained from the waste sample showed parallel results with the recovery efficiency values.

At the first point of the SEM/EDX analyses of the leaching waste sample (Figs. 7 and 7-a), C, O, Al, Si, K, Ca, Fe, and Zn were determined. In the analyses of the second point (Figs. 7 and 7-b), O, Al, Si, Fe, and Zn were observed. In the results of these analyses, besides the presence of carboxylic acid, non-recoverable zinc and especially iron minerals, silicate structures, and feldspar group structures were observed. In the SEM/EDX analyses of the waste sample, the determination of Fe, Al, and small amounts of zinc (lead not determined) was an indication that this acid-leaching process was effective.

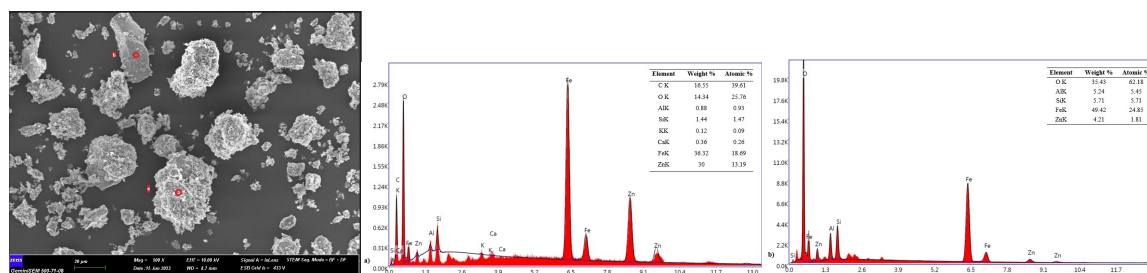


Fig. 7. SEM/EDX analysis of the waste sample after leaching (a- EDX1, b- EDX2)

Compared to the feed sample, waste sample weights decreased by approximately 8.5-18%. In connection with this situation, the presence of this metal at the highest levels in these images increased further with the content of dissolved solids, as a result of the low iron recovery rate in the dissolution results. In other words, by separating the valuable contents of the feed sample from the solid, more iron was observed on the waste surface. However, the observation of zinc was due to the dissolution of the solid and increasingly more evident appearance on the surface.

After the leaching process, the 3125 and 1435  $\text{cm}^{-1}$  peaks of the waste sample decreased, and the 2359 and 875  $\text{cm}^{-1}$  peaks disappeared (Fig. 8). These peaks indicated that carbon-containing C-H, C-N, and C-O bonds, and bonds of montmorillonite and smithsonite were removed from the structure (Hu et al., 2023).



Due to the positive results for zinc and lead in metal recovery, the decrease in the smithsonite peak determined in the FT-IR analysis also revealed the effectiveness of organic acid with its bond structure.

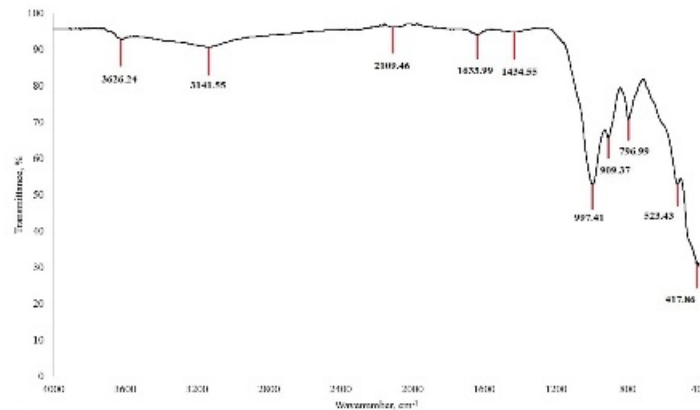


Fig. 8. FT-IR analysis of the waste sample after leaching

#### 4. Conclusions

In this study, an acetic acid leaching process was investigated for the recovery of valuable contents from fine-sized flotation wastes. In addition to parameter studies, characterization studies were also carried out for the feed sample and waste sample. The particle size of the feed sample was  $d_{90} = 113$  microns, and the chemical analysis results showed 2.2-2.5% Pb and 6.2-6.5% Zn. In the Rietveld XRD analysis, quartz, smithsonite, hydrozincite, and goethite were determined at high levels. In the SEM/EDX analysis, similar contents of these minerals were determined. The FT-IR analysis also confirmed the bond structures of these minerals, and calcite peaks were also observed.

According to the midpoints of the experimental parameters, a leaching test was performed with 0.5 M acetic acid, 60°C temperature, 60 min leaching time, and 10% solids. As a result of this experiment, metal recoveries and grades were found to be 31.3 and 15.94% for zinc, 31.8 and 5.54% for lead, and 14.1 and 17.77% for iron, respectively. In the parametric experiments, only one parameter of the experiment was changed, and the others were kept constant. There were significant improvements in metal recovery and grades in the experiments conducted by changing acid concentrations. In the analyses performed by changing the leaching temperature parameter, the highest recoveries were obtained at 95°C. However, this parameter was less effective. In the leaching time experiments, the recovery efficiency values of Pb and Zn remained around 35-40%. The solid-liquid ratio parameter also affected the reaction in the opposite direction, and the highest recovery efficiency was obtained at a ratio of 5%. As a result, the highest recovery efficiency values were determined by changing the acid concentrations among all parameters. This optimum experiment was carried out at a 1M acid concentration, and metal recovery rates (and grades) were obtained at 53.64% for Zn (19.67%), 55.10% for Pb (7.21%), and 13.30% for Fe (15.06%).

From the characterization studies of the waste sample, the results of the Rietveld XRD analysis showed that the calcite mineral was completely dissolved, some of the dolomite was dissolved, the smithsonite and hydrozincite contents substantially decreased, and the goethite content increased. The increase in goethite mineral content was another proof of low iron recovery efficiency rates. Similarly, in the SEM/EDX analysis, increases were observed in the gangue minerals and iron structures, while the zinc structures decreased, and lead was not observed. The FT-IR results showed that smithsonite, clay structures, and carbon bonds decreased with acetic acid leaching. A remarkable point is that during the experiments, it was observed that the mass of the sample decreased. Additionally, it was shown that the recovery efficiency and grades for Pb/Zn improved, and these were consistent with the results of the waste characterization studies.

Consequently, it was observed that lead was recovered more effectively in the metal recovery processes carried out in an acetic acid environment, zinc had similar recovery efficiency values in the same environment, and the solubility of iron with this organic acid was low under the same conditions. The industrial use of these inexpensive and easily degradable acids will provide an economic

contribution, thanks to the recovery of precious metals from these oxidized flotation wastes that do not require grinding. The recovery efficiencies of the metals in these oxidized wastes showed reached results in parallel with the literature, and it is thought that researching different chemicals for increasing the efficiency of this environmentally friendly acid can allow researchers and professionals to increase the efficiency of the process.

### Acknowledgments

The author wishes to thank Havadan Mining for their support.

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