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Testing of 17-different leaching agents for the recovery of zinc from a carbonate-type Pb-Zn ore flotation tailing

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ABSTRACT

The recovery of zinc from a flotation tailing using 17-different leaching agents, including inorganic and organic acids, alkaline solutions and chelating agents, was investigated. The effects of the lixiviant type, acid concentration, leaching temperature, leaching time, and solid-to-liquid ratio on the metals dissolution were studied. The use of sulfuric acid resulted in 91% of zinc extraction with a high selectivity against lead. The major impurities of lead, iron, calcium and arsenic precipitated during the leaching process as a segnisite, beudantite, gypsum, and goethite in this lixiviant. It was seen that the addition of oxidants in sulfuric acid solution slightly increased zinc dissolution. The citric acid dissolved 90.1% of zinc along with 9.1% lead. 90% of zinc dissolution was achieved by using malic acid, and high selectivity between zinc and lead dissolutions was also observed. The citric and malic acid leach residues contained a substantial amount of segnitite, beudantite, and quartz as the major phases. In term of zinc and lead dissolution selectivity, the best inorganic agents were determined in the following order: sulfuric acid > hydrochloric acid > perchloric acid > nitric acid. With organic agents, the best zinc and lead selectivity was achieved in the following order: sulfosalicylic acid > citric acid > malic acid > formic acid > tartaric acid > ascorbic acid. The best simultaneous zinc and lead dissolutions were achieved using sodium hydroxide agent. Using 5 M sodium hydroxide at 80 °C and 1/10 solid-to-liquid ratio for 180 min. leaching time, 81.4% of zinc and 47.4% of lead were dissolved while leaving a considerable amount of iron in the residue. When the ammonium chloride was used as a lixiviant, the silver and zinc were taken into the leach solution. 61.3% of zinc dissolution was obtained by using 50% ammonia as lixiviant, whereas no iron and lead dissolutions were observed. Using 0.37 M EDTA at 80 °C, 1/10 solid-to-liquid ratio for 180 min. leaching time, more than 90% of zinc dissolved along with a substantial amount of iron, arsenic and lead co-dissolutions. 47.4% of zinc dissolution was obtained at 80 °C and 1/10 solid-to-liquid ratio for 180 min. leaching time when sodium citrate was used as lixiviant, whereas less than 20% of zinc dissolved using ammonium oxalate at similar leaching condition. 39% zinc was dissolved using 3 M ammonium acetate at 80 °C, 1/10 solid-to-liquid ratio for 180 min., while 23.1% of zinc dissolution was achieved when the ammonium acetate was tested under similar experimental conditions. As a result, sulfuric, citric, malic, sulfosalicylic and formic acids were deemed to be the most promising leaching agents for the selective recovery of zinc from the lead–zinc flotation tailing.

1. Introduction

The most used non-ferrous base metals in the world after copper and aluminum are zinc and lead. These two metals are usually present together in lead–zinc ores as well as in the tailings and wastes from the processing of the metals. Approximately, 95% of the global mined lead and zinc productions were derived from sulfide type of ores, i.e. galena (PbS) and sphalerite (ZnS), whereas only 5% of lead and zinc came from oxidized, i.e. non-sulfide, ores (Kaya et al., 2020a). In 2019, the global refined zinc and lead productions were estimated to be 13.49 Mt and 11.76 Mt, and the metal consumption was estimated to be 13.67 and 11.81 Mt, respectively (Klochko, 2020; Tolcin, 2020). The differences between the production and consumption figures were met by the recycling of the metals from secondary resources. In the USA, about 73% of its lead domestic consumption, equivalent to about 1.2 Mt of the metal, was recovered from secondary resources mainly from lead-acid

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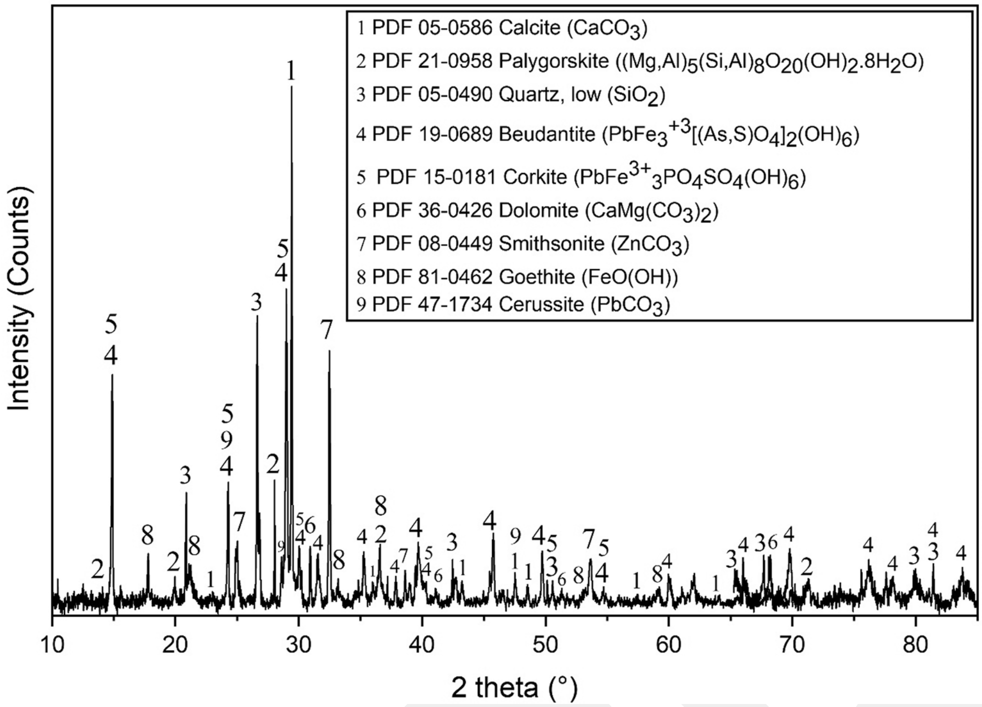


Fig. 1. XRD spectra of the flotation tailing.

batteries in 2019 (Klochko, 2020). In the same year, the USA recovered about 30,000 tons of refined zinc, equivalent to 25% of its domestic consumption, from secondary resources such as galvanizing residues and electric arc furnace (EAF) dust (Tolcin, 2020).

Mohr, et al. (2018) estimated that the global lead and zinc productions from the currently known resources will be peaked before the year 2031 and hence, it is important to find alternative resources of these two metals to meet the future demands. One of the promising alternative resources is the mine tailings of low-grade lead–zinc ores. The average annual mined zinc and lead in the last decade were 12.6 Mt and 4.6 Mt, respectively. Based on these figures, about 1.7 Mt of zinc and 0.5 Mt of lead may potentially be discarded in the flotation tailings each year. Mixed sulfide-oxide and oxidized ores are the main sources of lead and zinc after sulfides type ores and are generally found in silicate or carbonate forms in different parts of the world. Over the last decade, many processes have been utilized for the treatment of oxidized ores, such as differential flotation, gravity separation combined with flotation, hydrometallurgy, and pyrometallurgy. It is known that oxidized minerals of lead and zinc are more difficult to float than their sulfide counterparts (Moradi et al., 2011; Kaya et al., 2020a). Differential froth flotation is difficult owing to the fine-grained nature of the mixed/oxidized ores. Therefore, ultrafine grinding, which entails extra costs, is required for the adequate liberation of the phases prior to the production of the zinc and lead concentrates (Frias et al., 2008). Also, during the flotation of oxides, activation is required as slimes may coat the surface of the particles and prevent their floatability. Moreover, since oxides can dissolve easily, mineral surfaces hydrate extensively and collectors react with metal cations in the pulp. This leads to an increase in reagent consumption (Liu et al., 2011; Abkhoshk et al., 2014).

The pyrometallurgical and hydrometallurgical methods have been used to recover zinc from zinc-bearing secondary resources such as galvanizing ash (40–70% Zn), Waelz oxides (49–59% Zn), EAF dust (7–40% Zn) and other zinc and copper-bearing residues (35–50%) (Cole and Sole, 2003; Kaya et al., 2020a,b). Both the pyrometallurgical and hydrometallurgical methods have their advantages and disadvantages. The former, for example, is able to provide more rapid and efficient attainment of the metals than the latter but it is suitable only for treating high-grade resources and emits hazardous acid gas during smelting at high temperatures. Given the increasing global environmental awareness in addition to the decreasing grades of the secondary resources, hydrometallurgical methods are considered more attractive for recycling lead and zinc (Moradi et al., 2011).

In Turkey, lead and zinc ore reserves are approximately 0.86 Mt and 2.5 Mt, respectively (Sop, 2001). In 2016, Turkey produced about 1.6% of the world's zinc concentrate (0.2 Mt/y) and about 26% of lead and zinc come from oxidized lead–zinc ores, which present in the central Anatolia area, Kayseri region. There are small mining companies with underground mines and flotation concentrators and the yearly ore production capacity of each company varies from 0.1 to 0.3 Mt.

Cinkur lead–zinc plant was started in 1976 in Kayseri, Turkey, which could produce 35,000 tpy zinc, 6000 tpy lead along with 4.5 tpy silver and 125 tpy cadmium from oxide-carbonated zinc-based metals using the Waelz process (Roast-Leach-Electrowinning-RLE). Due to economic reasons, the plant was shut down in 1999. Currently, approximately 1.0 Mt zinc and lead flotation tailings in the Kayseri region are stored in huge tailing ponds. Lead and zinc mine tailings are frequently rich in toxic heavy metals, such as lead, zinc, copper, cadmium, manganese, arsenic and nickel. As the solid wastes formed from naturally dehydrated slurry after mineral separation, stocked lead–zinc flotation tailings usually threaten the local environment and adversely affect the sustainable development of the eco-system (Kursun et al., 2017). Therefore, it is important to develop a simple and environment-friendly methods to reuse and reduce the toxicity of these zinc industrial wastes. The use of hydrometallurgical process to recovery zinc from such a resource may be potentially more efficient that the conventional physical separation methods (Kaya et al., 2019; 2020a).

The use of acidic agents (Terry and Monhemius, 1983; Bodas, 1996; Abdel-Aal and Shukry, 1997; Abdel-Aal, 2000; Nagib and Inoue, 2000; Espiari et al., 2006; Souza et al., 2007; Souza et al., 2009; Safari et al., 2009; Moradi et al., 2011; Asadi et al., 2017; Atia and Spooren, 2020), alkaline agents (Zhao and Stanforth, 2000; Chen et al., 2009; Santos et al., 2010; Zhang et al., 2014; Liu et al., 2014; Ghasemi and Azizi, 2018; Ehsani et al., 2019), ammonium chloride/ammonium carbonate/ammonium hydroxide agents (Moghaddam et al., 2005; Ju et al., 2005;

Feng et al., 2007; Wang et al., 2008; Ding et al., 2010; Rao et al., 2015) have been investigated to leach zinc from zinc or lead–zinc oxide ores. In this study, we focused on the recovery of zinc from a carbonate-type flotation tailing produced from a concentrator that treated a complex ore comprising both sulfide and carbonate forms of the zinc and lead (See Fig. S1). Leaching tests using 17-different lixiviants (inorganic, organic, alkaline and chelating) were carried out to determine the most effective leaching agent to selectively leach zinc from a carbonate tailing leaving the bulk of lead, iron, arsenic, and silver in the leach residue. This work is important to develop a suitable hydrometallurgical method to recycle the tailing with low environmental impact and competitive production cost. The determination of the best leaching agent from the flotation tailing would be of interest to metallurgical and environmental engineers who are interested in the downstream processing of zinc from pregnant leach solutions such as selective precipitation and solvent extraction. Reference, where oxalic acid has been used to dissolve the zinc from the flotation tailing (Kursunoglu et al., 2021), have been excluded from the current paper as the oxalic acid has extracted a substantial amount of iron together with zinc from the flotation tailing.

2. Materials and method

2.1. Materials

A representative sample of a carbonate-type Pb-Zn ore flotation tailing was collected from the tailing dump of Orex Mining Co. in Yahyali, Kayseri, Turkey. The sample was crushed for deagglomeration and air-dried in the laboratory. After drying, the sample was ground and homogenized. The particle size of the ground sample was analyzed by a particle size analyzer (Mastersizer 2000). Most of the particles were fine with more than 90% of them were smaller than 99 µm. The chemical composition of the sample was analyzed by Bureau Veritas Mineral Laboratory in Vancouver, Canada, via digestion and solution analysis using inductively coupled plasma mass spectroscopy (ICP-MS). The chemical analysis shows that the sample consisted of 7.5% Pb, 5.77% Zn, 21.3% Fe, 5.6% As, and 101 ppm Ag. The mineralogical compositions were determined using Empyrean, PANalytical XRD and Bruker D8 Discover (XRD) with Cu Kα1 (wavelength 1.54060 Å) radiation source and calibrated with a silicon standard for alignment of the 2θ = 10°–70° radiation generated at 40 mA and 45 kV. The mineral phases were identified using Diffrac Suite EVA software equipped with the current ICDD PDF-2/Minerals database. The major mineral phases were found to be smithsonite ($ZnCO_3$), cerussite ($PbCO_3$), goethite ($FeO(OH)$), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), quartz (SiO_2), palygorskite ($(Mg,Al)_5(Si,Al)_8O_{20}(OH)_2{\cdot}8H_2O$), corkite ($PbFe^{3+}{}_3(PO_4)(SO_4)(OH)_6$) and beudantite ($PbFe_3(OH)_6\ SO_4AsO_4$) (Fig. 1). The main components of the sample were Zn, Pb, Fe, As and Ag, as well as Si, Al, S, Ca, K, and Na. The total concentration of the alkali metals such as Na, K, Ca, and Mg in the sample was around 5.5%, while that of Si and Al was about 7.6%.

The particle morphology and surface composition of the flotation tailing were analysed by scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS). SEM-EDS analyses were carried out using Hitachi-Requlus 8230 SEM and Oxford instrument EDS at 5–10 kV. The surface morphology of particles was very rough, porous, and complex. Most of the lead–zinc metals were observed to be intergrown with calcite and some of them are impregnated with iron oxides. A more detailed description of the sample morphology is presented elsewhere (Kursunoglu et al., 2021).

2.2. Method

The sample was not exposed to any metallurgical pretreatment operations before leaching unless otherwise stated. The leaching experiments were carried out in a 500 mL three-necked Pyrex reactor equipped with a glass condenser inside a temperature-controlled hot mantle (MTOPS). Analytical and technical grade chemicals were used in this study. Deionized water was used for dilution.

The leaching tests were performed using 25 g of the sample at a solid-to-liquid ratio of 1/10 (w/v) and a stirring speed of 400 rpm for 180 min. unless otherwise stated. At 30, 60, 120, and 180 min. time intervals, 5 mL of the slurry was taken and the slurry sample was immediately centrifuged at 5000 rpm. The supernatant was analyzed by ICP-MS at ALS Minerals in Izmir-Turkey or Atomic Absorption Spectroscopy (AAS) at Eskisehir Osmangazi University, Mining Engineering Department.

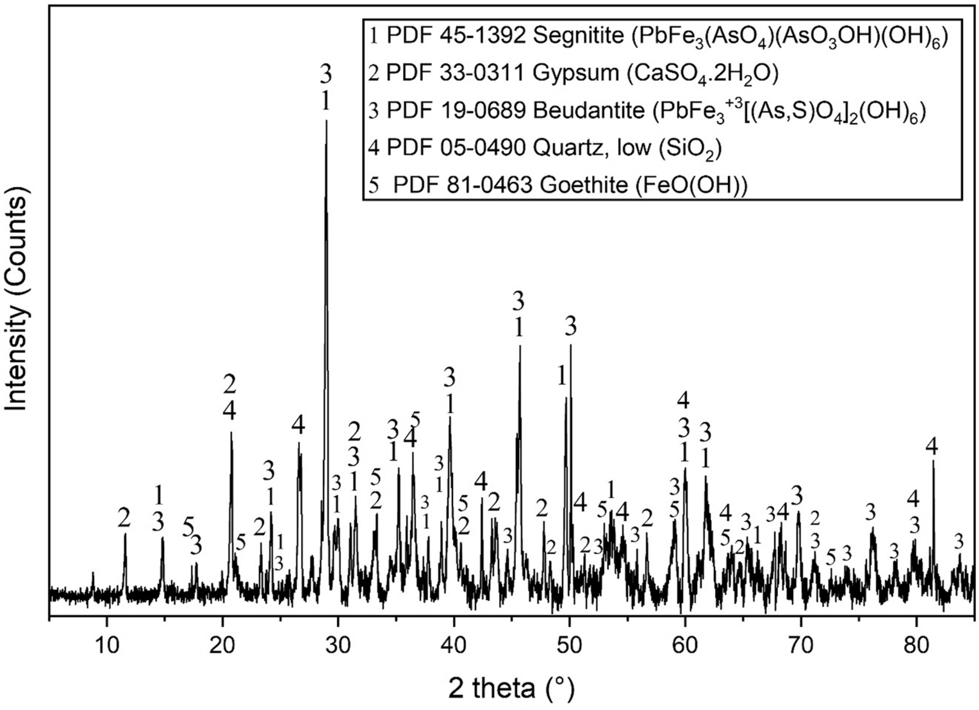


Fig. 2. XRD spectra of the leached residue at optimum conditions (1.0 M sulfuric acid, 40 °C, 30 min. and 2/10 solid to liquid ratio).

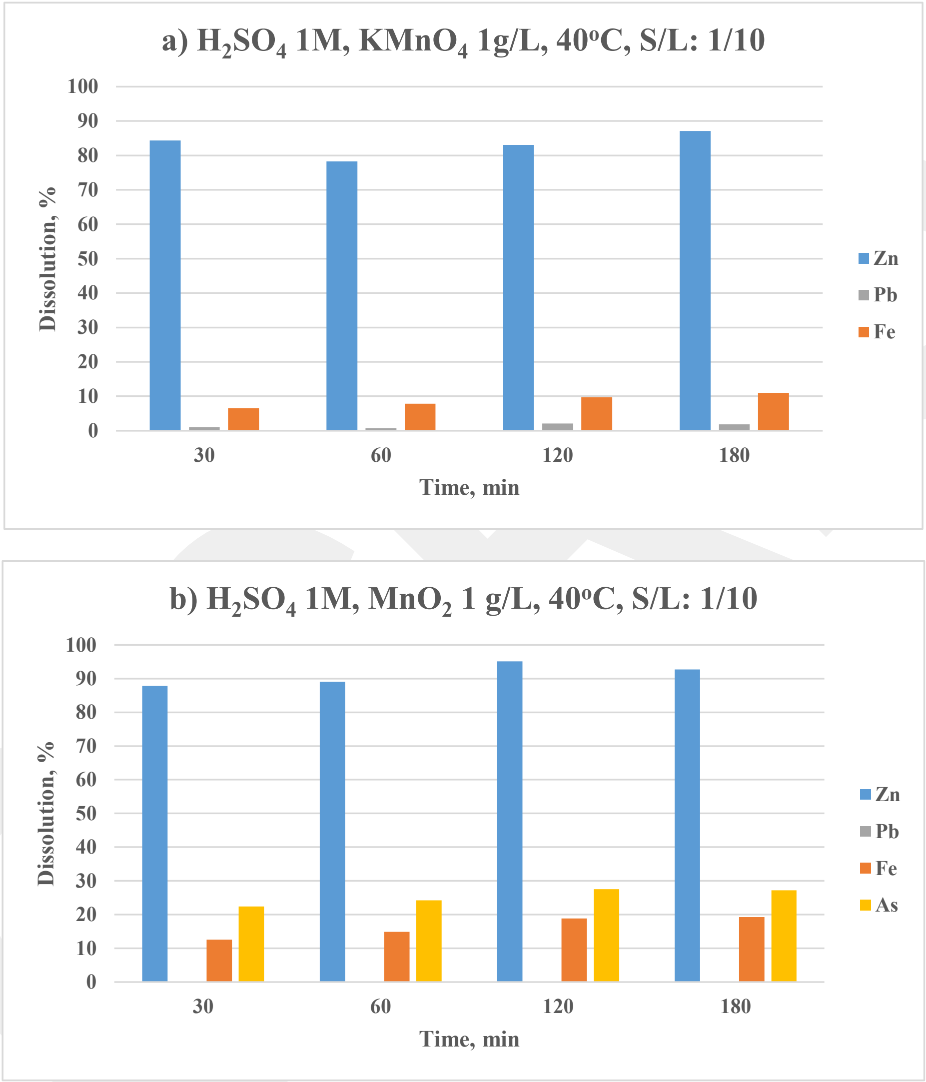


Fig. 3. The effect of four different oxidants on the dissolution of zinc from the flotation tailing (a-$KMnO_4$ addition, b-MnO_2 addition, c- $Na_2O_5S_2$ addition, d-H_2O_2 addition).

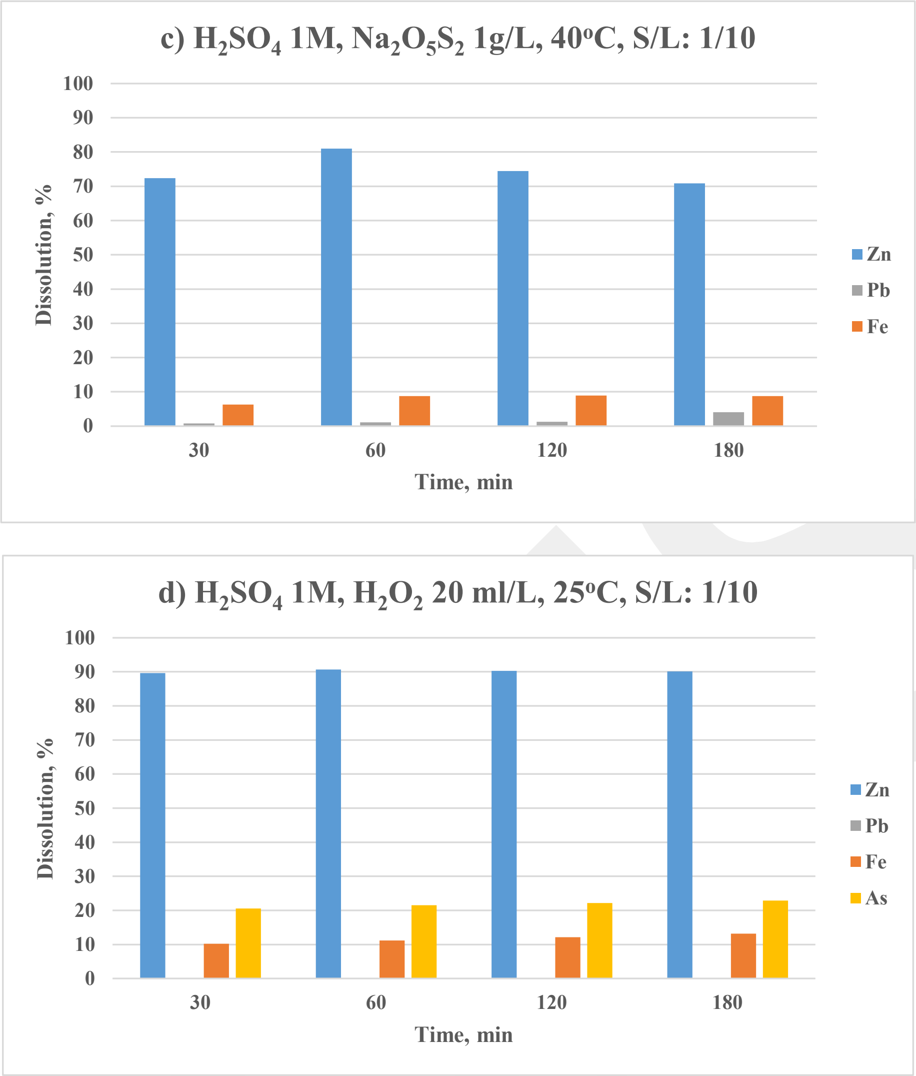


Fig. 3. (*continued*).

The pH measurement was performed using a pH meter equipped with IntelliCAL PHC 28,101 pH probe (Hach, HQ40d). The mineralogical and elemental composition of the leached residue was analyzed by XRD and an X-ray fluorescence spectrometer (XRF) (Minipal 4 Panalytical), respectively. Some of the leaching tests were triplicated to assess the reproducibility of the test results. The dissolution percentage was determined using the following equation:

$$Dissolution(\%) = \frac{c_l \times V_L}{c_s \times M_S} \times 100\% \qquad (1)$$

where c_l is the metal concentration in the leachate (mg/L), V_L the volume of the analyzed leachate (L), c_s the metal concentration in the tailing (mg/kg), and M_S the weight of the tailing sample (kg).

3. Results and discussion

3.1. Inorganic acids

3.1.1. Leaching of zinc and lead from the tailing in the presence or absence of oxidant in sulfuric acid (H_2SO_4) solution

The effect of leaching temperature and leaching time on metal dissolutions were carried out using 0.25–1.0 M sulfuric acid. The metal dissolution order was previously found to be Zn > As > Fe with no Pb and Ag dissolution was observed (Kursunoglu et al., 2021). The dissolution of zinc with sulfuric acid was a very fast process. Most of the zinc was dissolved into the solution in the first 30 min., and the zinc dissolution process slowed down afterwards. At sulfuric acid concentration below 0.5 M, the very slight and fluctuating influence of the temperature on the zinc dissolution was observed, whereas the temperature has a significant effect on iron dissolution. This phenomenon indicates a different mechanism of leaching zinc and iron from the tailing in a sulfuric acid solution. The significant effect of temperature on iron dissolution was observed especially at concentrations 0.5 M and 1.0 M sulfuric acid concentrations, which is consistent with the findings of Kukurugya et al., (2015). The researchers reported that most of the iron remains in the residue as $Fe_2(SO_4)_3$ and Fe_2O_3. These compounds occurred slowly at room temperature.

With increasing sulfuric acid concentration, zinc dissolution increased significantly under the conditions examined. The temperature effect is obvious at 0.5 and 1.0 M concentrations. The lead dissolution was almost zero for all tested temperatures and leaching times due to the precipitation of lead as a sulfate formation. Iron and arsenic co-dissolutions started after 0.5 M sulfuric acid concentration and drastically increased at 1.0 M. Arsenic dissolutions were higher iron at low temperatures at 120 min. The maximum zinc dissolution (92%) along with iron (14.6%) and arsenic (24.6%) dissolutions were obtained at 1.0 M sulfuric acid concentration, 40 °C leaching temperature and 60 min.

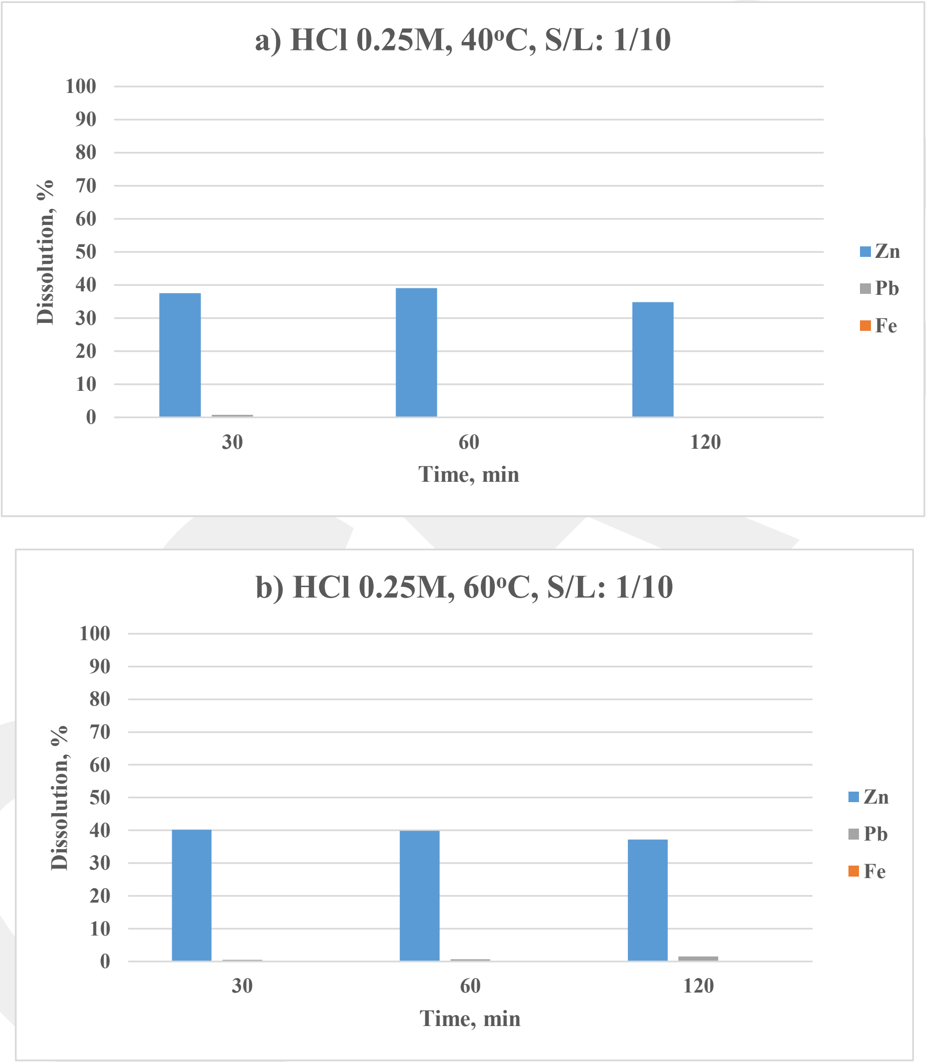
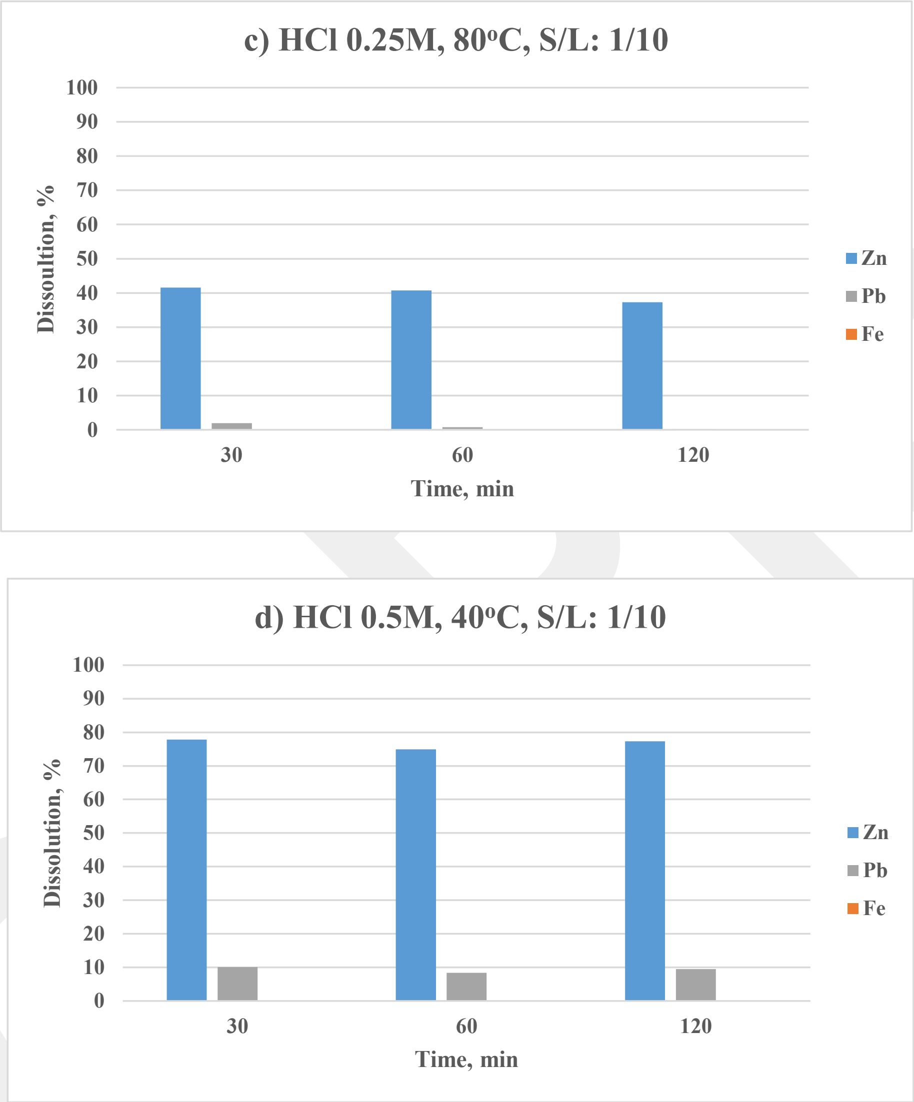


Fig. 4. The effect of leaching temperature and time on the dissolution of metals from the flotation tailing using hydrochloric acid solution.



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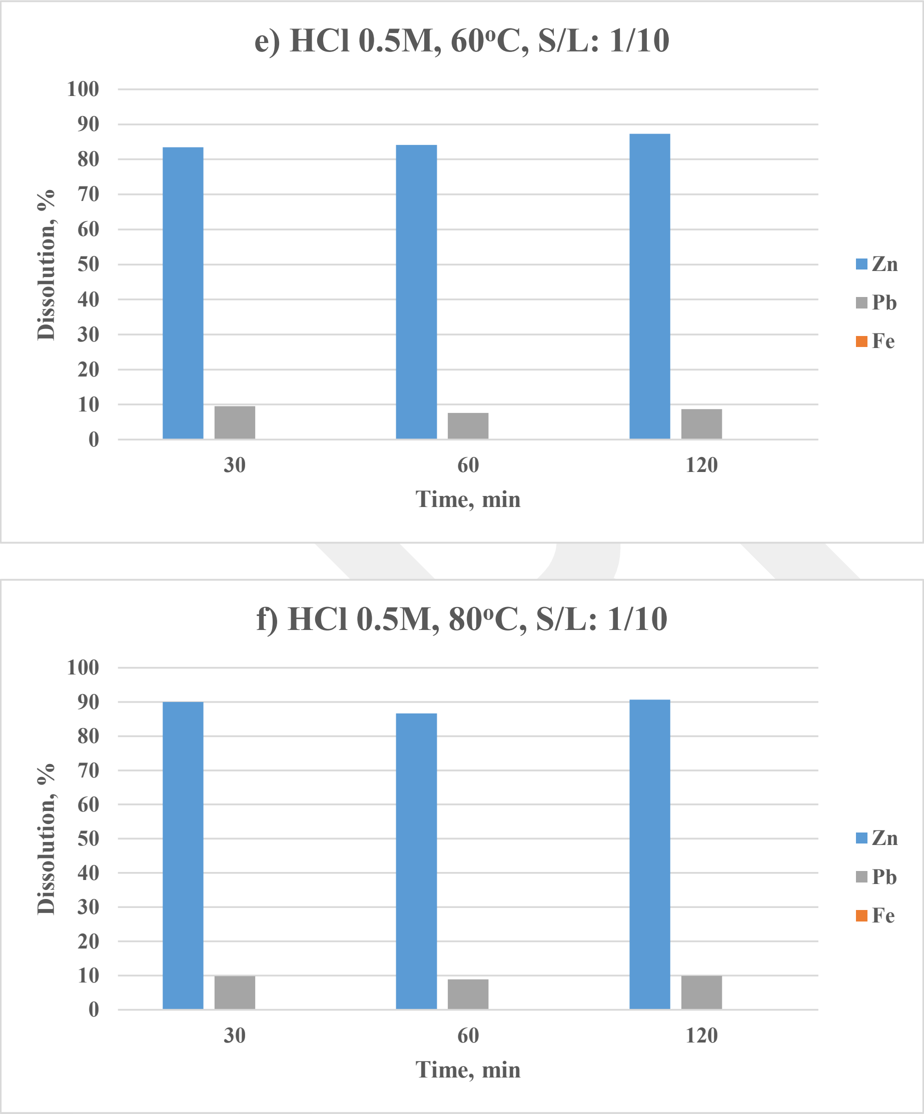

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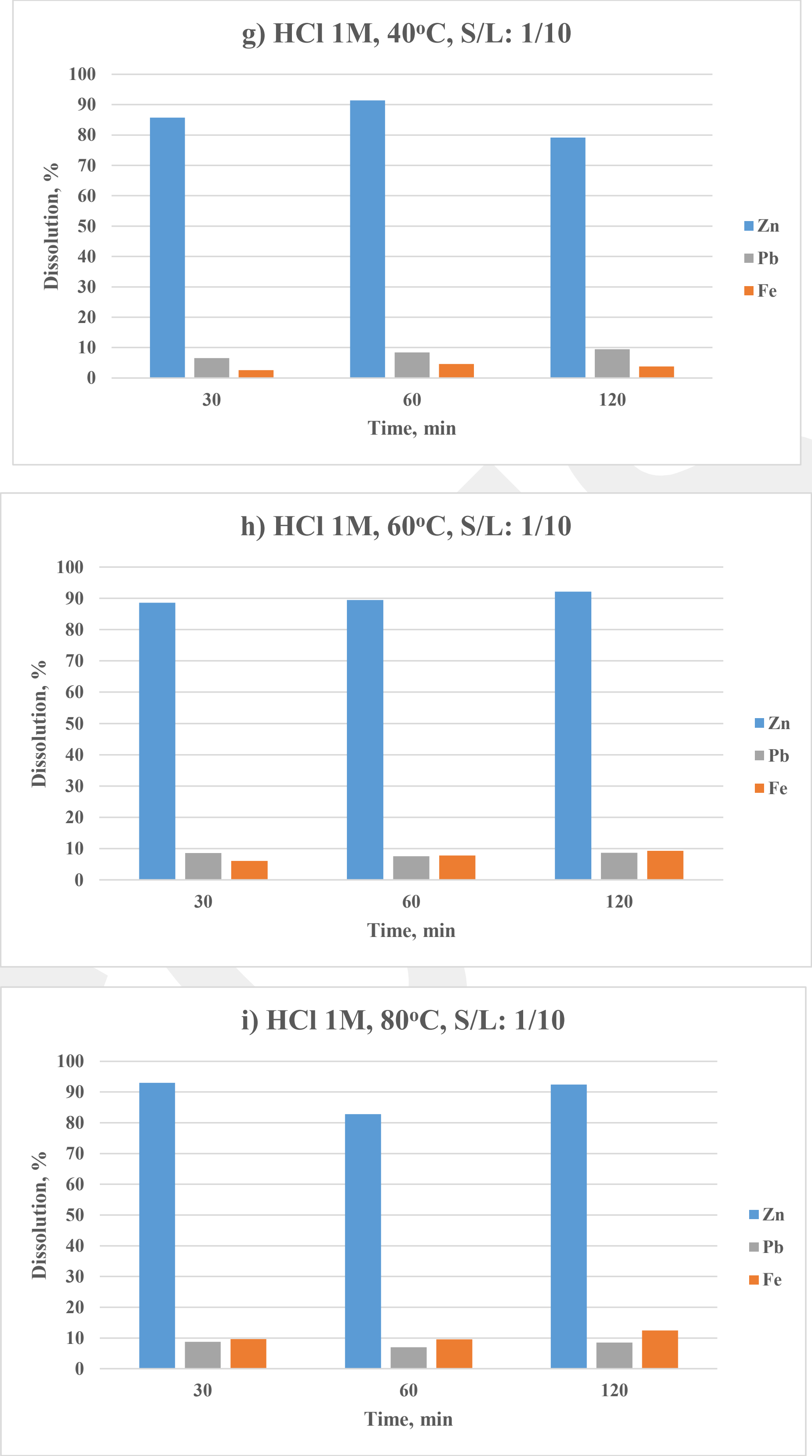

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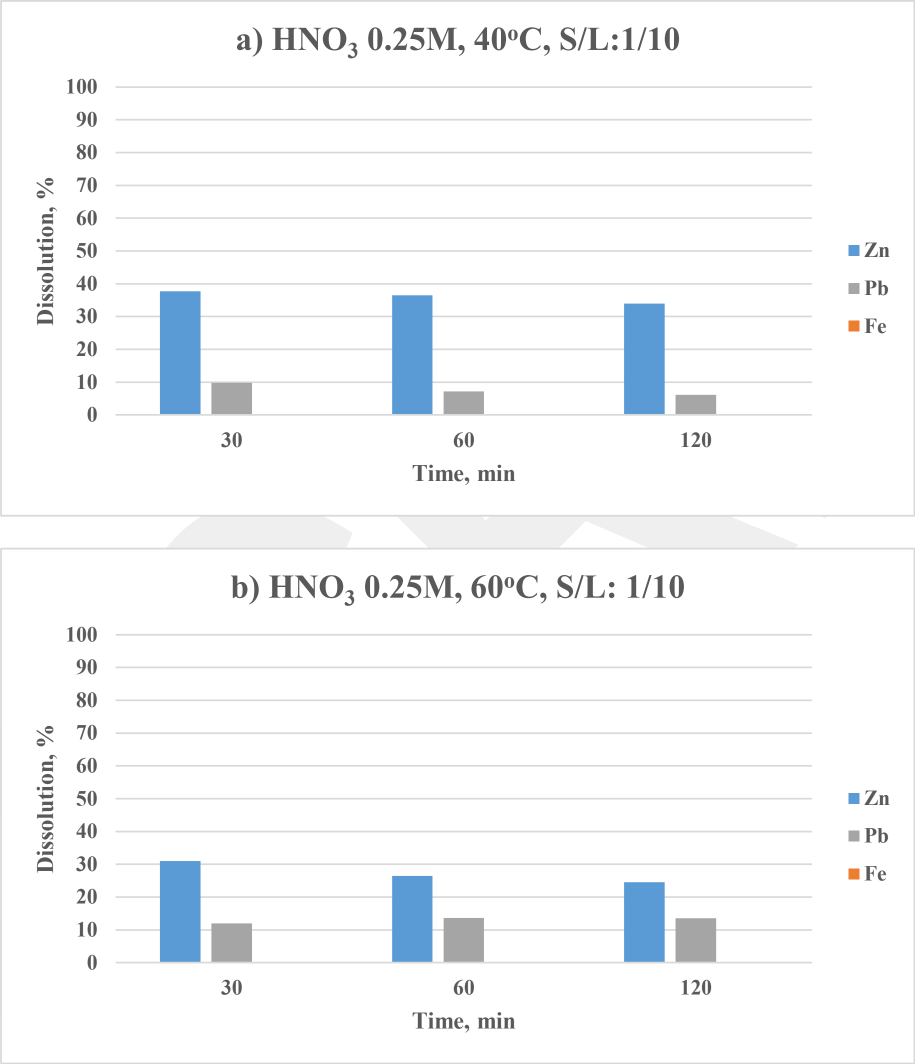
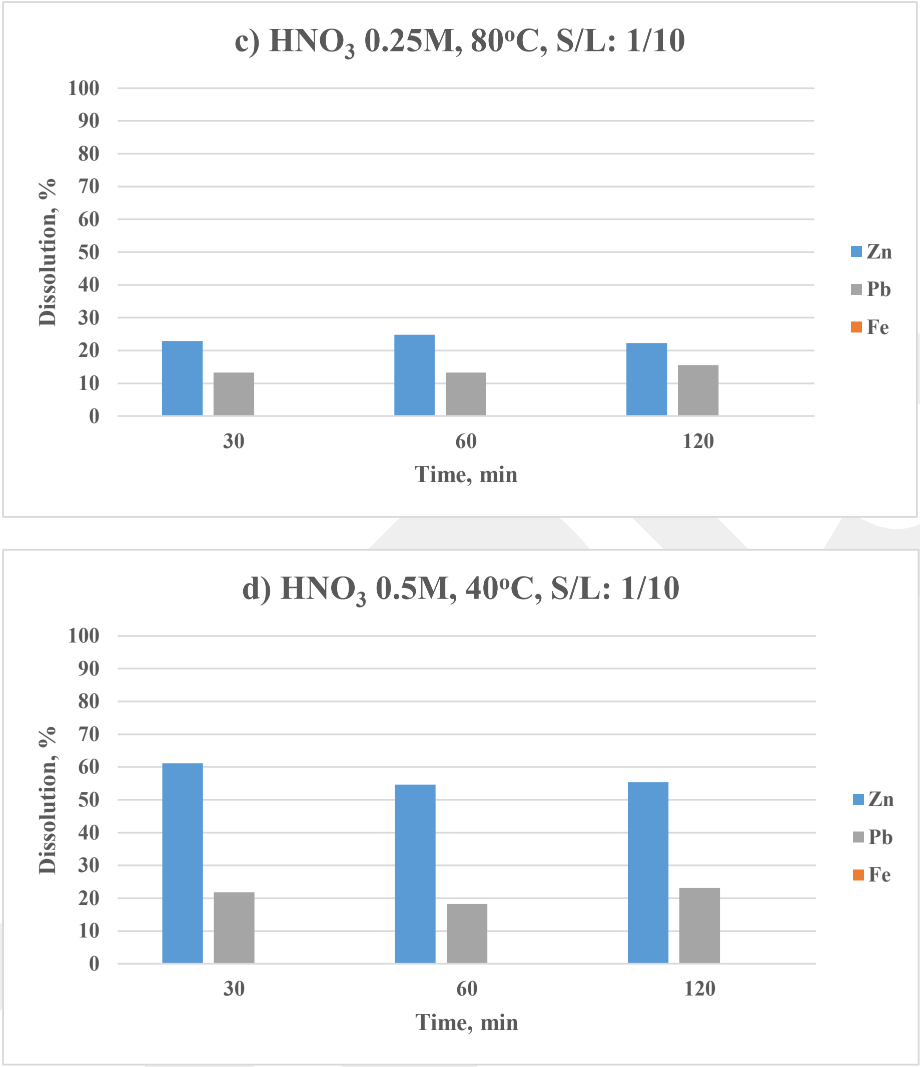


Fig. 5. The effect of leaching temperature and time on the dissolution of metals from the flotation tailing using nitric acid solution.



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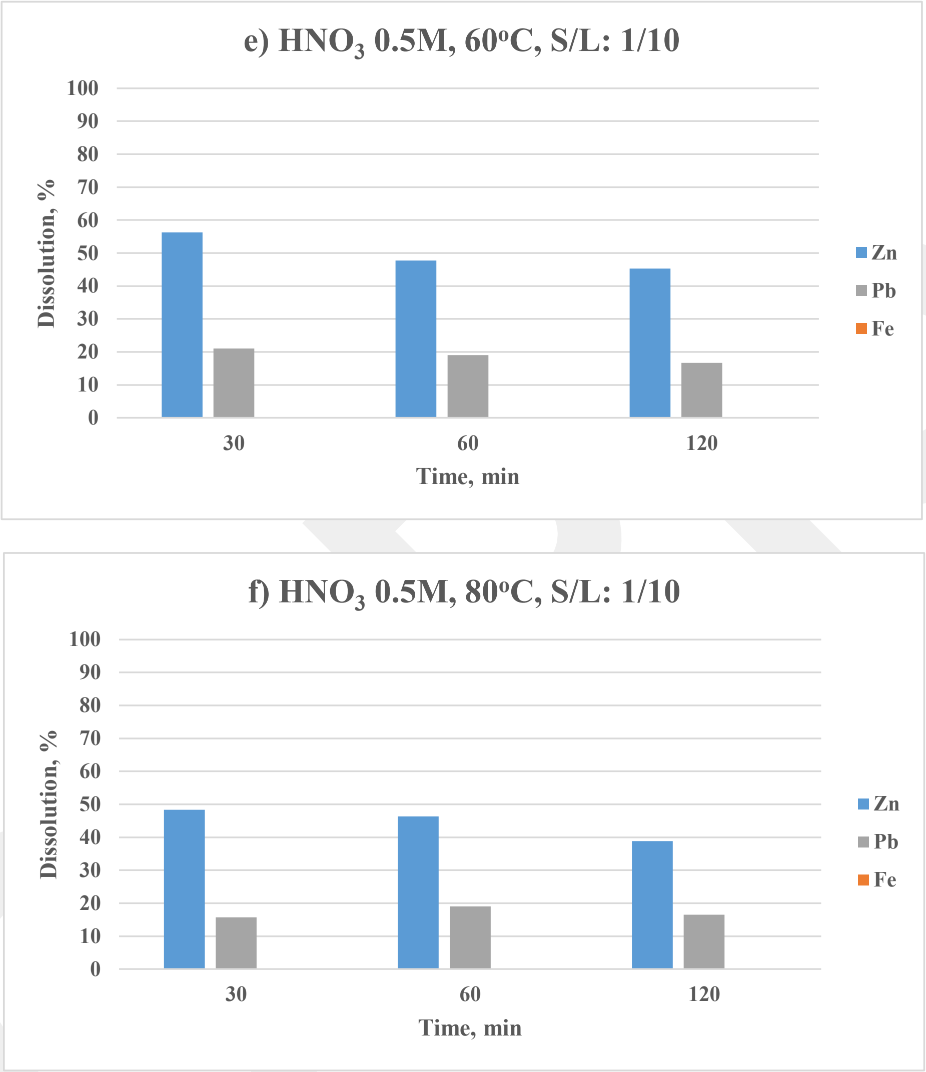

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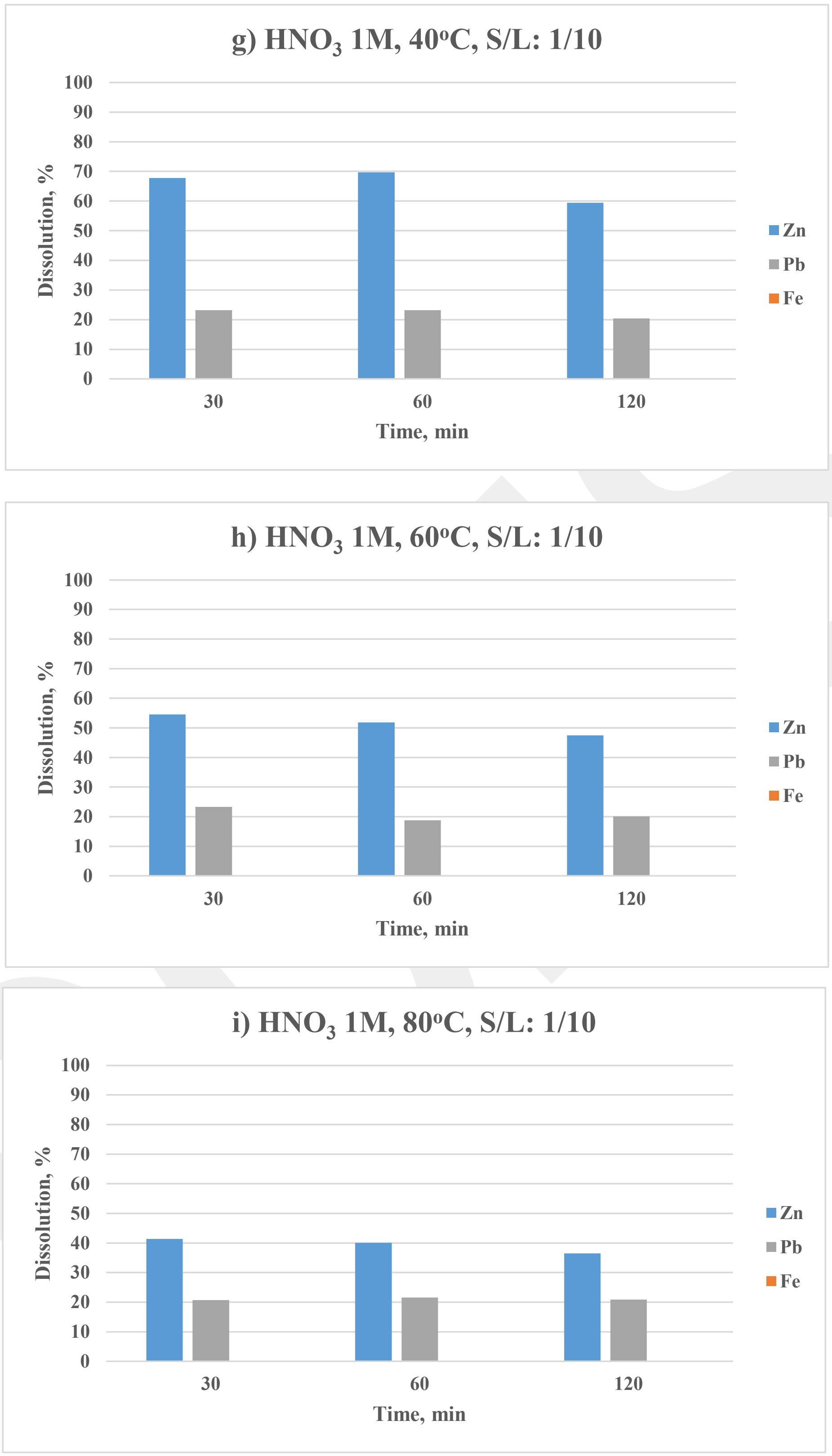

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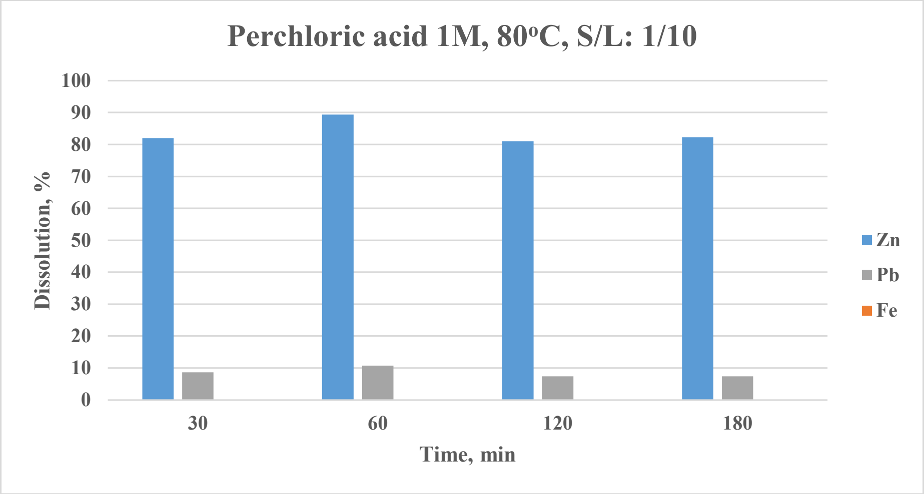


Fig. 6. The dissolution of metals from the flotation tailing using perchloric acid solution.

Table 1
The comparison of inorganic acid types and optimum conditions for the zinc and lead dissolutions from the flotation tailing (a: analytical grade).

Agent/Agent + Oxidant	Zinc Dis., %	Lead Dis., %	Optimum parameters
Sulfuric acid[a]	91	–	Con.: 1 M, T: 40 °C, t: 30 min., S/L: 2/10
Nitric acid[a]	69.7	23.2	Con.: 1 M, T: 40 °C, t: 60 min., S/L: 1/10
Hydrochloric acid[a]	90	9.8	Con.: 0.5 M, T: 80 °C, t: 30 min., S/L: 1/10
Perchloric acid[a]	89.3	10.7	Con.: 1 M, T: 80 °C, t: 60 min., S/L: 1/10
1.0 M sulfuric acid + 1 g/L $KMnO_4^a$	87.1	1.9	T: 40 °C, t: 180 min., S/L: 1/10
1.0 M sulfuric acid + 1 g/L $Na_2O_5S_2^a$	81.8	1.1	T: 40 °C, t: 60 min., S/L: 1/10
1.0 M sulfuric acid + 1 g/L MnO_2^a	95.1	–	T: 40 °C, t: 120 min., S/L: 1/10
1.0 M sulfuric acid + 20 mL/L $H_2O_2^a$	90.6	0.5	T: 25 °C, t: 60 min., S/L: 1/10

leaching time.

Increasing solid to liquid ratio from 1/10 to 2/10 at 1.0 M sulfuric acid concentration, 40 °C leaching time, and 30 min. leaching time resulted in 91.0% Zn dissolution with 11.2% Fe and 18.4% As co-dissolutions. Thus, 1.0 M sulfuric acid concentration, 40 °C leaching temperature, 2/10 solid to liquid ratio and 30 min. leaching time was deemed as the optimum condition. Under the selected optimum condition, the PLS contained 13100 mg/L Zn, 7.1 mg/L Pb, 3320 mg/L Fe, and 1915 mg/L As. The XRF analysis of the residue shows that it consisted of 1.67% ZnO, 13.2% PbO, 6.27% As_2O_3, 39.2% Fe_2O_3 and 6.29% CaO. Fig. 2 shows the XRD spectra of the leached residue at the optimum condition. The major mineral phases were identified as segnitite, gypsum, beudantite, quartz, and goethite. Note that segnitite and beudantite are difficult to distinguish as the sulfate and arsenate anions readily exchangeable with each other.

The effect of four different oxidants on the dissolution of zinc from the flotation tailing in sulfuric acid solution was tested (Fig. 3(a-d)). 87.1% Zn, 1.9% Pb and 11% Fe dissolutions were obtained using 1 g/L potassium permanganate ($KMnO_4$) as an oxidant addition in 1.0 M sulfuric acid solution at 40 °C leaching temperature and solid-to-liquid ratio of 1/10 for 180 min. leaching time (Fig. 3(a)). 95.1% Zn, 0% Pb,18.8% Fe, 27.5% As and 0% Pb dissolutions were achieved at the addition of 1 g/L manganese dioxide (MnO_2) in 1.0 M sulfuric acid solution at 40 °C leaching temperature and solid to liquid ratio of 1/10 for 120 min. leaching time (Fig. 3(b)). 81.8% Zn, 1.1% Pb and 8.8% Fe dissolution were obtained at 1 g/L sodium metabisulfite ($Na_2O_5S_2$) addition in 1.0 M sulfuric acid solution at 40 °C leaching temperature and solid to liquid ratio of 1/10 for 60 min. leaching time (Fig. 3(c)). 90.6% Zn, 0.5% Pb, 11.2% Fe and 21.5% As dissolved when the 20 mL/L hydrogen peroxide (H_2O_2) addition in 1.0 M sulfuric acid solution at 40 °C leaching temperature and solid to liquid ratio of 1/10 for 60 min. leaching time (Fig. 3(d)). These results showed that the addition of oxidant slightly increased the zinc dissolution.

3.1.2. Leaching of zinc and lead from the tailing in hydrochloric acid (HCl) solution

Fig. 4(a-i) shows the effect of leaching temperature and time on the dissolution of metals from the flotation tailing using hydrochloric acid as lixiviant. The metal dissolution order was determined to be Zn > Pb without any Fe dissolution up to 0.5 M. The zinc dissolution generally increases with increasing leaching temperature that results in faster leaching kinetics, but this effect was especially visible for hydrochloric acid concentrations of below 1.0 M. The solubility of metals in the hydrochloric acid increased to facilitate the leaching of metals. The viscosity of the slurry and diffusion resistance decreased with increasing temperature. Yoshida (2003) found that increases of hydrochloric acid concentration and leaching temperature increased zinc dissolution from a zinc oxide powder and the activation energy of the zinc oxide leaching by hydrochloric acid was 11.6 kJ/mol, which is consistent with the present study that there is no beneficial effect of leaching time on the zinc dissolution from the flotation tailing. It seems that 30 min. leaching is enough to dissolve 93% zinc together with 8.8% lead, 9.3% iron using 1.0 M hydrochloric acid solution at 80 °C temperature and solid to liquid ratio of 1/10 (Fig. 4 (i)). On the other hand, increasing leaching temperature and time affected the dissolution of iron. From these tests, two optimum conditions were selected as follows: 0.5 M hydrochloric acid concentration, 80 °C leaching temperature, and 30 min. leaching time (Fig. 4(f)) or 1.0 M hydrochloric acid concentration, 80 °C leaching temperature, and 30 min. leaching time (Fig. 4(i)). However, considering the acid consumption and neutralization of PLS in the downstream process, the former one is selected as the optimum conditions for the hydrochloric acid leaching process. Possible reactions between ZnO/$ZnCO_3$/PbO and hydrochloric acid are given below:

$$ZnO(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2O \tag{2}$$

$$ZnCO_3(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + CO_2(g) + H_2O \tag{3}$$

$$PbO(s) + 2HCl(aq) \rightarrow PbCl_2(s) + H_2O \tag{4}$$

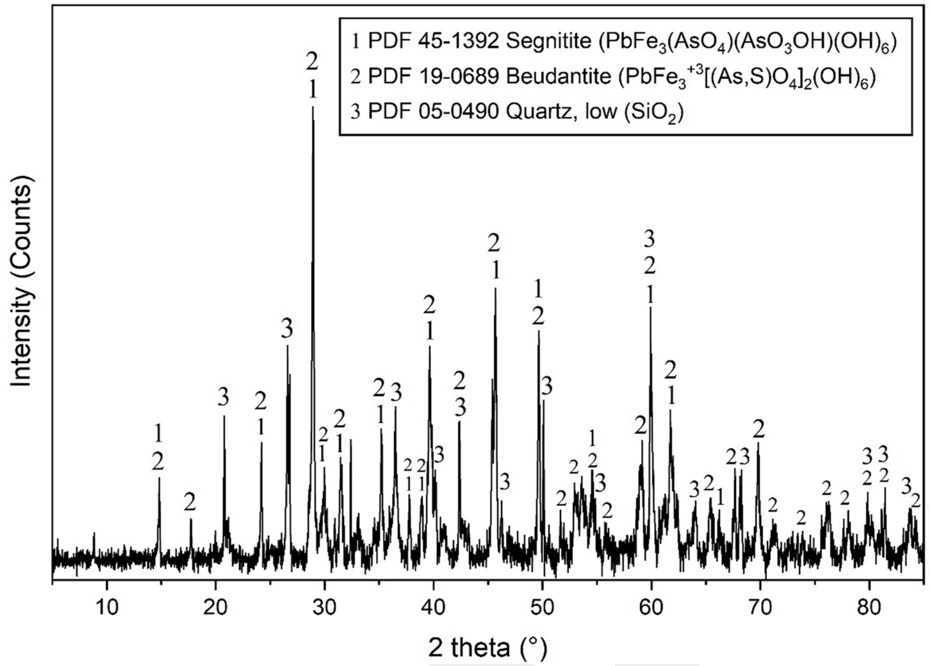


Fig. 7. XRD spectra of citric acid leached residue at the optimum conditions.

3.1.3. *Leaching of zinc and lead from the tailing in nitric acid (HNO_3) solution*

Fig. 5(a-i) shows the effect of leaching temperature and time on the dissolution of metals from the flotation tailing using nitric acid as lixiviant. As can be seen from Fig. 5 (a-i), increasing nitric acid concentration from 0.25 M to 1.0 M increased zinc dissolution from 38% to 70%, whereas increasing leaching temperature and time decreased zinc dissolution. This may be due to the passivization of the mineral surfaces with fine mineral particles. Since the metals contacted with nitric acid, it cannot be oxidized any further and the reaction rate slowed down. Increasing nitric acid concentration increased lead co-dissolution from 7% to 23%. There was no iron co-dissolution at any tested conditions. It was seen that the nitric acid dissolved not only zinc but also lead together. The metal dissolution followed the descending order: Zn > Pb > Fe. The following reactions take place during the nitric acid leaching process.

$$ZnO(s) + 2HNO_3(aq) = Zn(NO_3)_2(aq) + H_2O \tag{5}$$

$$PbO(s) + 2HNO_3(aq) = Pb(NO_3)_2(aq) + H_2O \tag{6}$$

3.1.4. *Leaching of zinc and lead from the tailing in perchloric acid ($HClO_4$) solution*

Perchloric acid is an inorganic acid and a stronger acid than sulfuric and nitric acid as well as a powerful oxidizer. Using 1.0 M perchloric acid at 80 °C and 1/10 solid to liquid ratio for 60 min. leaching time achieved a maximum 89.3% zinc dissolution along with 10.7% lead dissolution (Fig. 6).

Table 1 shows the comparison of inorganic acid types and optimum conditions for the zinc and lead dissolutions from the flotation tailing. From tested different leach conditions, 1.0 M sulfuric acid concentration, 40 °C leaching temperature, 30 min. leaching time and 2/10 solid to liquid ratio were chosen as the best condition. The zinc dissolution was determined as 91% along with 11.2% Fe and 18.4% As dissolutions. At 0.5 M hydrochloric acid concentration, 80 °C leaching temperature, 30 min. leaching time, and 1/10 solid to liquid ratio achieved 90% zinc dissolution together with 9.6% lead dissolution. 69.7% Zn and 23.2% Pb were taken into the leach solution using nitric acid as a solvent under the following conditions: 1.0 M nitric acid concentration, 40 °C leaching temperature, 60 min. leaching time and 1/10 solid to liquid ratio. The results demonstrated that the addition of oxidant to the sulfuric acid solution slightly increased the zinc dissolution percentages from the tailing. The maximum zinc selectivity between lead was achieved at the following inorganic agent order: sulfuric acid > hydrochloric acid > perchloric acid > nitric acid.

3.2. *Organic acids*

3.2.1. *Leaching of zinc and lead from the tailing in citric acid ($C_6H_8O_7$) solution*

The effect of citric concentration on the dissolution of metals from the tailing was determined in our previous research paper (Kursunoglu et al., 2021). 90.6% zinc dissolution was taken into the leach solution along with 9.3% lead, 14.5% arsenic and 19.2% iron at 1.0 M citric acid concentration, 80 °C leaching temperature and 2/10 solid to liquid ratio for 180 min. leaching time. Under these conditions, the zinc, lead, iron and arsenic concentration in the PLS was 12100 mg/L, 1220 mg/L, 8410 mg/L and 1670 mg/L, respectively. The metal dissolution order using citric acid was as follow: Zn > Fe > As > Pb > Ag. The pH of the medium is less acidic with citric acid ($2 < pH < 3$) than sulfuric acid ($0.5 < pH < 1$). Fig. 7 shows the XRD spectra of the citric acid leached residue at the optimum leaching conditions. The precipitate contains segnitite ($PbFe_3(AsO_4)(AsO_3OH)(OH)_6$)), beudentite $PbFe_3^{3+}[(As,S)O_4]_2\ (OH)_6$) and quartz as the major phases. XRD result shows that the segnitite and beudentite predominantly formed in the residue. XRF analysis revealed that the citric acid leach residue contains 14.8% PbO, 2.25% ZnO, 44.1% Fe_2O_3, 8.12% As_2O_3 and 0.78% CaO. According to XRF results, no calcium precipitate was seen in the residue as compared to the sulfuric acid leaching process where calcium precipitated as gypsum.

3.2.2. *Leaching of zinc and lead from the tailing in malic acid ($C_4H_6O_5$) solution*

The effect of temperature and leaching time on the dissolution of metals from the flotation tailing was investigated (Fig. 8(a-c)). 86.1% Zn, 8.9% Pb and 6.6% Fe dissolutions were achieved using 1.0 M malic acid at 80 °C leaching temperature and 1/10 solid to liquid ratio for 180 min. leaching time. Metal dissolution order was found to be Zn > Pb > Fe. The optimum leaching conditions were as follows: 1.0 M malic acid,

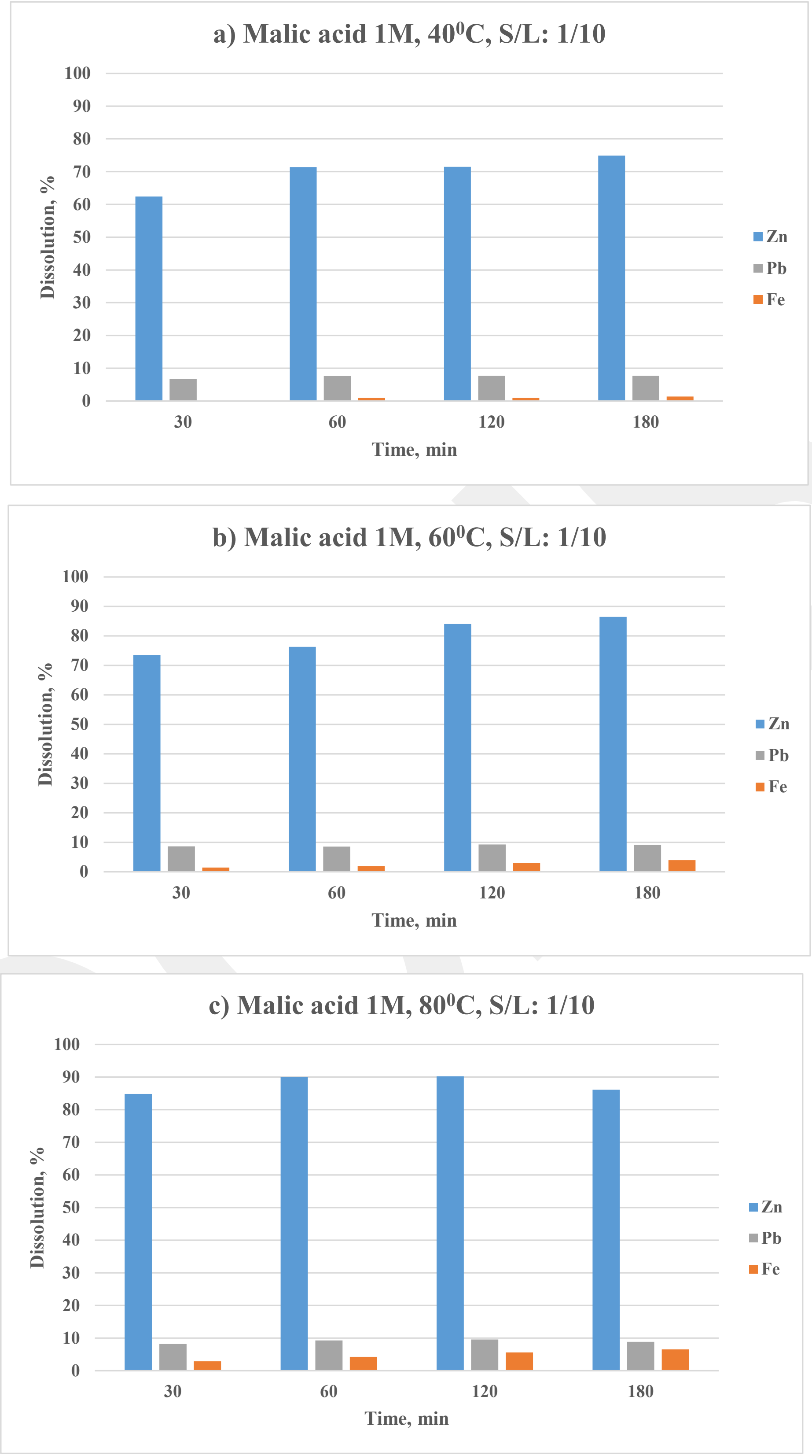


Fig. 8. The effect of temperature and leaching time on the dissolution of metals from the flotation tailing using malic acid.

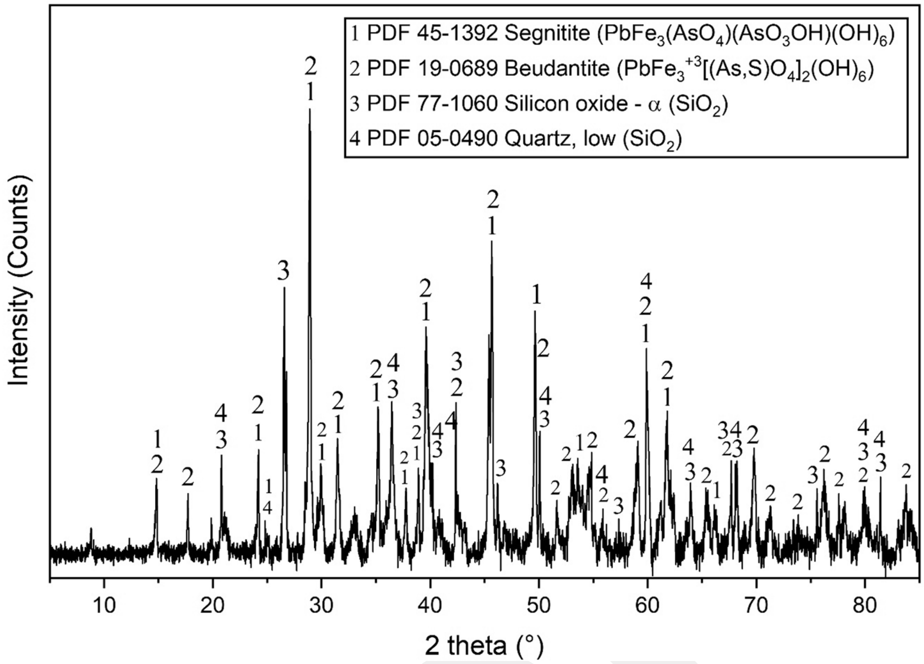


Fig. 9. XRD spectra of the leach residue using malic acid at the optimum conditions.

1/10 solid to liquid ratio, 80 °C leaching temperature and 60 min. leaching time. Under these conditions, 90% Zn, 9.3% Pb and 4.3% Fe were extracted into the leach solution (Fig. 8(c)). The metal concentration in the PLS was determined as 5050 mg/L Zn, 387 mg/L Pb, 1200 mg/L Fe and 470 mg/L As. The pH of the solution was determined as 2.2. Fig. 9 shows the XRD spectra of the leach residue using malic acid at the optimum conditions. The residue contains segnitite, beudentite, silicon oxide, and quartz as major phases. The XRF results of the leach residue contained 16.4% PbO, 2.89% ZnO, 52.8% Fe_2O_3, 9.8% As_2O_3 and 0.85% CaO. Yan et al., 2014 indicated that the leaching ability of citric acid is supposed to be higher than that of malic acid from contaminated sediment. Similar results were obtained when lead and zinc were leached using citric acid and malic acid (Li et al. 2010), which is consistent with our experiment that citric acid is a more remarkable leaching ability than malic acid. The malic acid ionization is represented as the following reaction:

$$HCO_2H(aq) + H_2O(l) \leftrightarrow H_3O^+(aq) + HCO_2^-(aq) \tag{7}$$

The zinc oxide with an organic acid reaction can be written as (Song and West Chester, 2004):

$$2H_XA + XZnO \rightarrow XZnA_{2/X} + XH_2O \tag{8}$$

where A is an organic acid, and X is an integer that varies from 1 to 2.

The effect of solid to liquid ratio on the dissolution of metals was also investigated using 1.0 M malic acid at 80 °C leaching temperature, and solid to liquid ratio of 2/10 and 3/10 (Fig. 10(a-b)). At high solid ratio, stirring difficulties arise with increasing pulp viscosity and particles may not be completely surrounded by the solution. Thus, the zinc dissolution decreased with increasing solid ratio. With increasing solid ratio, zinc dissolution decreased from 82.1% (Fig. 10(a)) to 63.5% (Fig. 10(b)) using 1.0 M malic acid at 80 °C leaching temperature for 180 min. leaching time. Not only lead but also iron dissolutions were less than 10%. The pH of the solution changed from 2.68 to 3.06.

3.2.3. *Leaching of zinc and lead from the tailing in formic acid (CH_2O_2) solution*

The effect of temperature and leaching time on the dissolution of metals from the flotation tailing was investigated using formic acid as an organic agent (Fig. 11(a-c)). When the leaching time and temperature increased, the zinc dissolution increased slightly. The lead dissolution was less than 5% under the tested all leaching conditions while no iron dissolution was observed. The zinc was very selectively extracted from the flotation tailing, leaving a considerable amount of lead and iron in the residue. The optimum leaching conditions were determined as 1 M formic acid concentration, 60 °C leaching temperature, 1/10 solid to liquid ratio and 120 min. leaching time (Fig. 11(b)). 82.3% Zn and 3.5% Pb dissolutions were achieved under these conditions. Metal dissolution order was determined to be Zn > Pb > Fe. The formic acid ionization and diffusion H + ions are represented as the following reactions:

$$CH_2O_2 \leftrightarrow H^+ + CHO_2^- \tag{9}$$

$$2H^+ + ZnCO_3 \leftrightarrow H_2CO_3 + Zn^{2+} \tag{10}$$

3.2.4. *Leaching of zinc and lead from the tailing in different organic acid solutions*

The dissolution of metals from the flotation tailing was tested using tartaric acid ($C_4H_6O_6$) as an organic agent (Fig. 12). When the tartaric acid was used as lixiviant, the zinc, lead and iron dissolutions remained relatively constant. The zinc dissolutions were found to be less than 35%. The lead dissolutions increased up to 11.7% while the iron dissolutions were less than 7% under the tested conditions. Metal dissolution order was as follows: Zn > Pb > Fe. The solution pH was around 2.

The dissolution of metals from the flotation tailing was carried out using ascorbic acid ($C_6H_8O_6$) as a lixiviant (Fig. 13). When the ascorbic acid was used as an organic agent, the zinc, lead, iron and arsenic showed the same dissolution trend under the investigated conditions. Slight fluctuations were observed during the zinc dissolution. 34.4% zinc dissolution was obtained using 1 M ascorbic acid at 80 °C leaching temperature, 1/10 solid to liquid ratio and 30 min. leaching time. The lead dissolution was less than 12% under the tested all leaching conditions while the iron dissolution increased up to 18.3% along with 12.1% arsenic dissolution for 180 min. It was revealed that there is no good selectivity between zinc and other impurities such as iron and arsenic when the ascorbic acid was used as an organic agent. Metal dissolution order was found to be Zn > Fe > As > Pb. The pH of the solution was around 3.5.

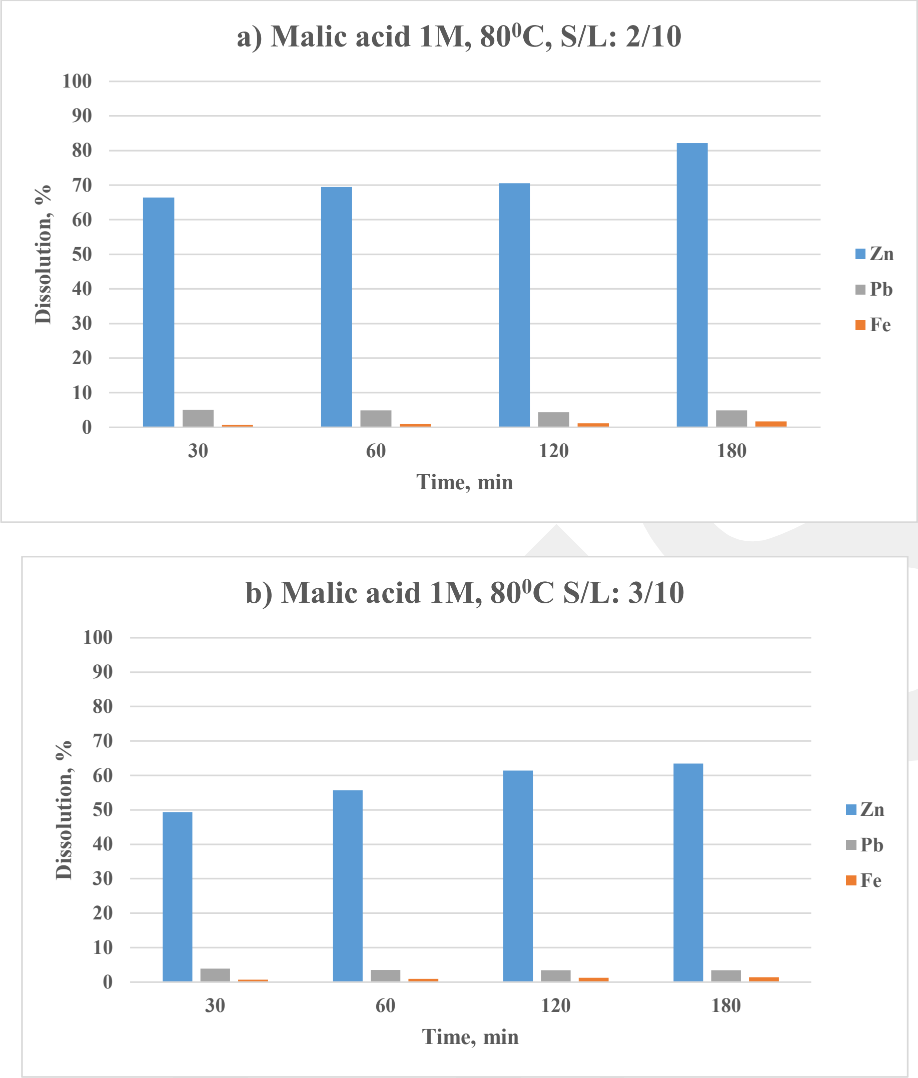


Fig. 10. The effect of solid to liquid ratio on the dissolution of metals using malic acid solution.

The dissolution of metals from the flotation tailing was performed by using sulfosalicylic acid ($C_7H_6O_6S$) (Fig. 14). When the sulfosalicylic acid was tested, the zinc dissolutions remained relatively constant under the examined conditions. More than 87% Zn dissolutions were achieved using 1 M sulfosalicylic acid concentration at 80 °C leaching temperature, 1/10 solid to liquid ratio and 30 min. leaching time. 88.7% Zn dissolution was obtained within 30 min. leaching time, whereas 6.4% Fe was extracted from the flotation tailing. No lead co-dissolution was observed during the leaching process under the tested conditions. Deng et al., 2017 observed that when the reaction time and temperature extended, copper leaching rates demonstrated upward tendencies using sulfosalicylic acid from a copper oxide ore. The sulfosalicylic acid is completely ionized as the following reaction equations (Eqs. (11)–(12)). It was seen from the current study that there is a pretty good selectivity between zinc and lead as well as iron when the sulfosalicylic acid was used as an organic agent. Metal dissolution order was determined to be Zn > Fe > Pb.

$$C_7H_6O_6S(s) \rightarrow C_7H_3O_6S^{3-}(aq) + 3H^+(aq) \quad (11)$$

or

$$C_7H_6O_6S(s) + 3H_2O(aq) \rightarrow C_7H_3O_6S^{3-}(aq) + 3H_3O^+(aq) \quad (12)$$

Table 2 shows the effect of different organic acids on the dissolution of metals from the flotation tailing. The results indicated that citric and malic acid were superior leachates to other tested organic acids as the dissolution percentages of zinc is greater than 90% under the conditions examined. However, the maximum selectivity between zinc and lead was obtained at the following organic agent order: sulfosalicylic acid > citric acid > malic acid > formic acid > tartaric acid > ascorbic acid.

3.3. *Alkaline solution*

3.3.1. *Leaching of zinc and lead from the tailing in sodium hydroxide (NaOH) solution*

The effect of sodium hydroxide concentration and leaching time on the dissolution of metals from the flotation tailing was investigated at 80 °C leaching temperature, a sodium hydroxide concentration in the range of 1 M to 7 M, solid to liquid ratio of 1/10 for 180 min. leaching time (Fig. 15(a-d)). 81.4% Zn and 47.5% Pb were simultaneously taken into the leach solution without any Fe co-dissolution using 5 M sodium hydroxide for 180 min. (Fig. 15(c)), which is consistent with the findings of Zhao and Stanforth, 2000. The authors found that the best leaching results were obtained in 5 M NaOH, at 90–95 °C and a reaction time of 90 min. for the production of zinc powder by alkaline treatment of

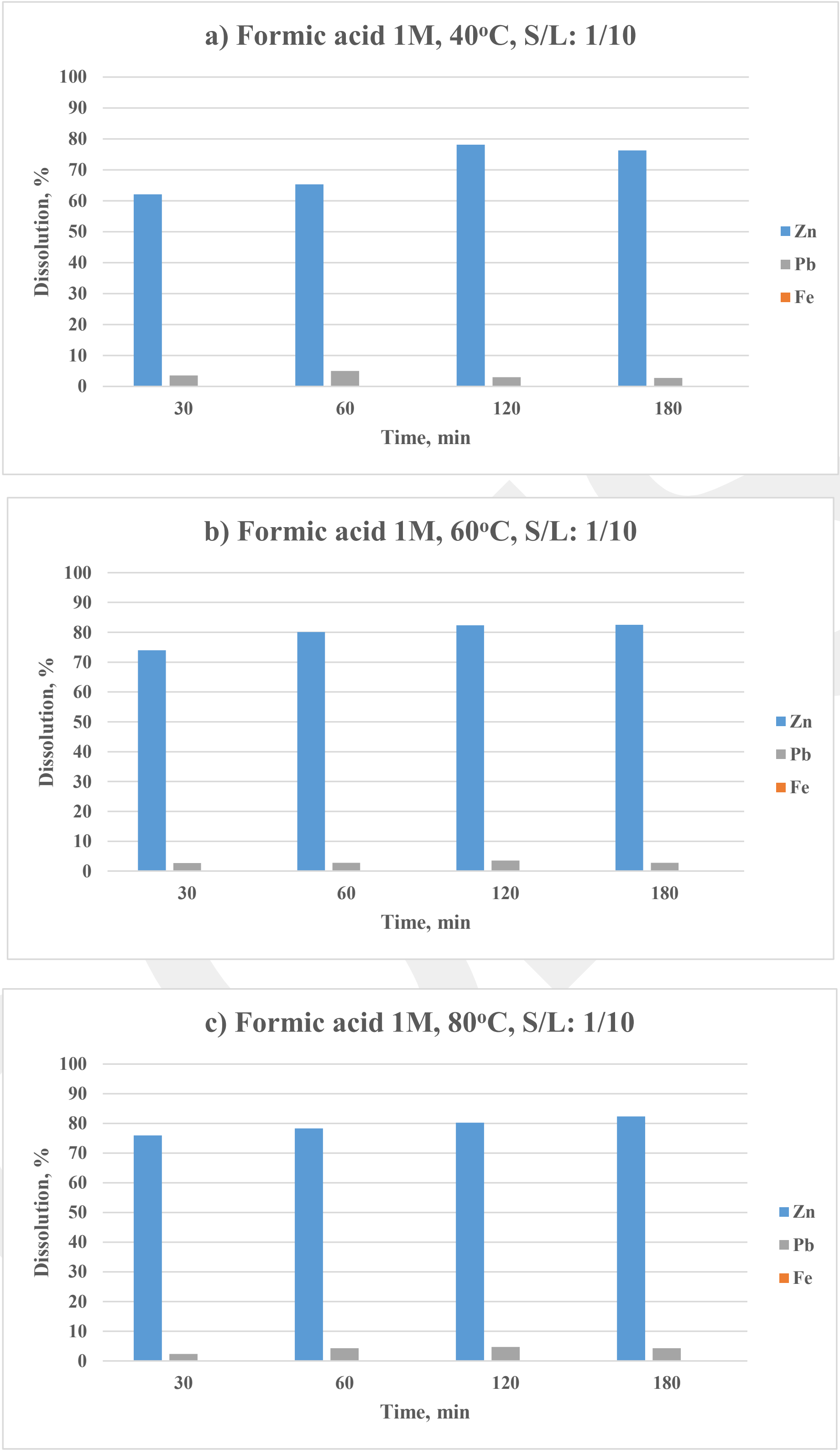


Fig. 11. The effect of temperature and leaching time on the dissolution of metals from the flotation tailing using formic acid.

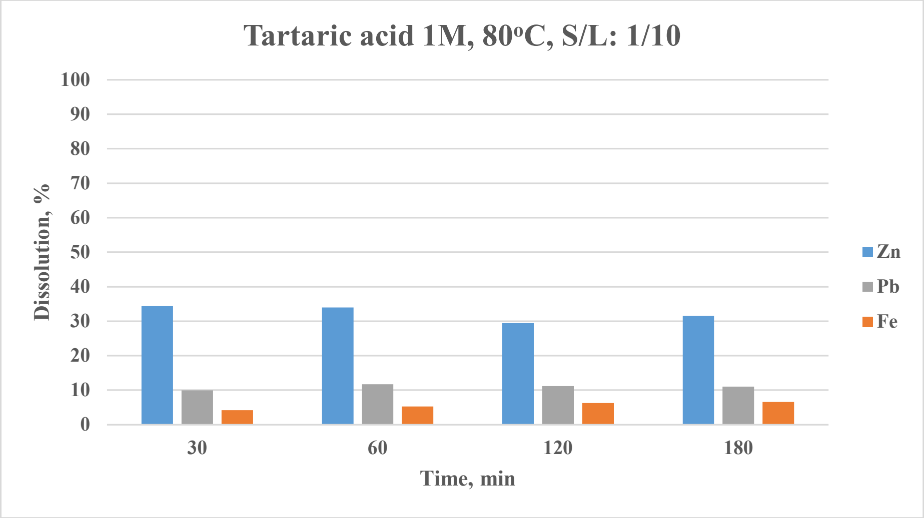


Fig. 12. The dissolution of metals from the flotation tailing was tested using tartaric acid.

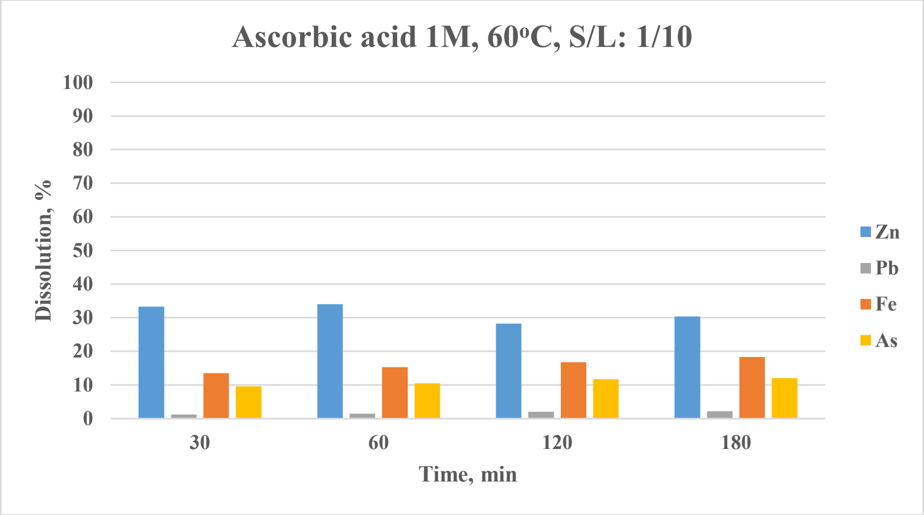


Fig. 13. The dissolution of metals from the flotation tailing using ascorbic acid.

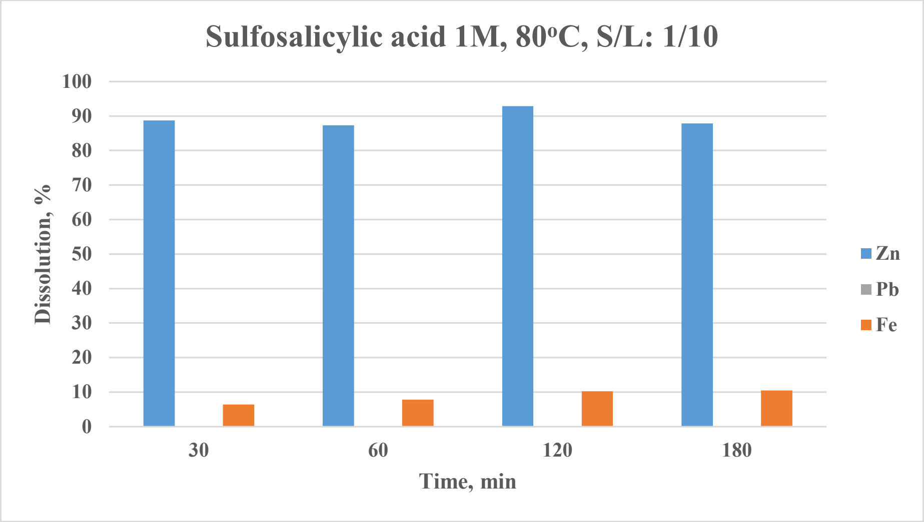


Fig. 14. The dissolution of metals from the flotation tailing using sulfosalicylic acid.

Table 2
The effect of organic acid on the dissolution of zinc and lead from the flotation tailing (t: technical grade).

Agent	Zinc Dis., %	Lead Dis., %	Optimum parameters
Citric acid[a]	90.6	9.3	Con.: 1 M, T: 80 °C, t: 180 min., S/L: 2/10
Malic acid[t]	90	9.3	Con.: 1 M, T: 80 °C, t: 60 min., S/L: 1/10
Sulfosalicylic acid[t]	88.7	–	Con.: 1 M, T: 80 °C, t: 30 min., S/L: 1/10
Formic acid[t]	82.6	2.8	Con.: 1 M, T: 60 °C, t: 180 min., S/L: 1/10
Tartaric acid[t]	34.4	10	Con.: 1 M, T: 80 °C, t: 30 min., S/L: 1/10
Ascorbic acid[t]	34.1	1	Con.: 1 M, T: 60 °C, t: 60 min., S/L: 1/10

smithsonite ores. The lead dissolution was slightly decreased at 7 M sodium hydroxide concentration as the high concentration of sodium hydroxide has a strong oxidation characterization and converts a part of PbO in PbO_2, which has a little solubility in sodium hydroxide solution (Badanoıu et al., 2013). At high alkali concentration, ZnO converts into $NaZn(OH)_3$ and the solubility of $NaZn(OH)_3$ decreases with increasing alkali concentration at the same temperature. Ghasemi and Azizi, 2018 found that the hydroxyl ions are enough due to the further formation of $Zn(OH)_4^{2-}$ and $Pb(OH)_4^{2-}$ at 4 M sodium hydroxide concentration. Metal dissolution order was determined to be Zn > Pb. The dissolution of cerrusite and smithsonite in sodium hydroxide solution is described as follows:

$$ZnCO_3(s) + 4OH^-(aq) \rightarrow Zn(OH)_4^{2-}(aq) + CO_3^{2-}(aq) \tag{13}$$

$$PbCO_3(s) + 4OH^-(aq) \rightarrow Pb(OH)_4^{2-}(aq) + CO_3^{2-}(aq) \tag{14}$$

3.4. *Ammonia/Ammonia compound and chelating solutions*

3.4.1. *Leaching of zinc and lead from the tailing in ammonia (NH_3) solution*

The effect of ammonia concentration and leaching time on the dissolution of metals was investigated at 80 °C leaching temperature and 1/10 solid to liquid ratio (Fig. 16(a-c)). The zinc dissolution remained relatively constant under the examined conditions. No iron and lead co-dissolutions were observed during the leaching process. Wang et al., 2008 found that the dissolution of zinc from a low-grade zinc oxide ore increased with increasing ammonia concentration, which is not consistent with the findings of the present study. This can be due to the high volatilization rate of ammonia at the high leaching temperature of the current study. At 50% ammonia concentration, 61.3% zinc dissolution

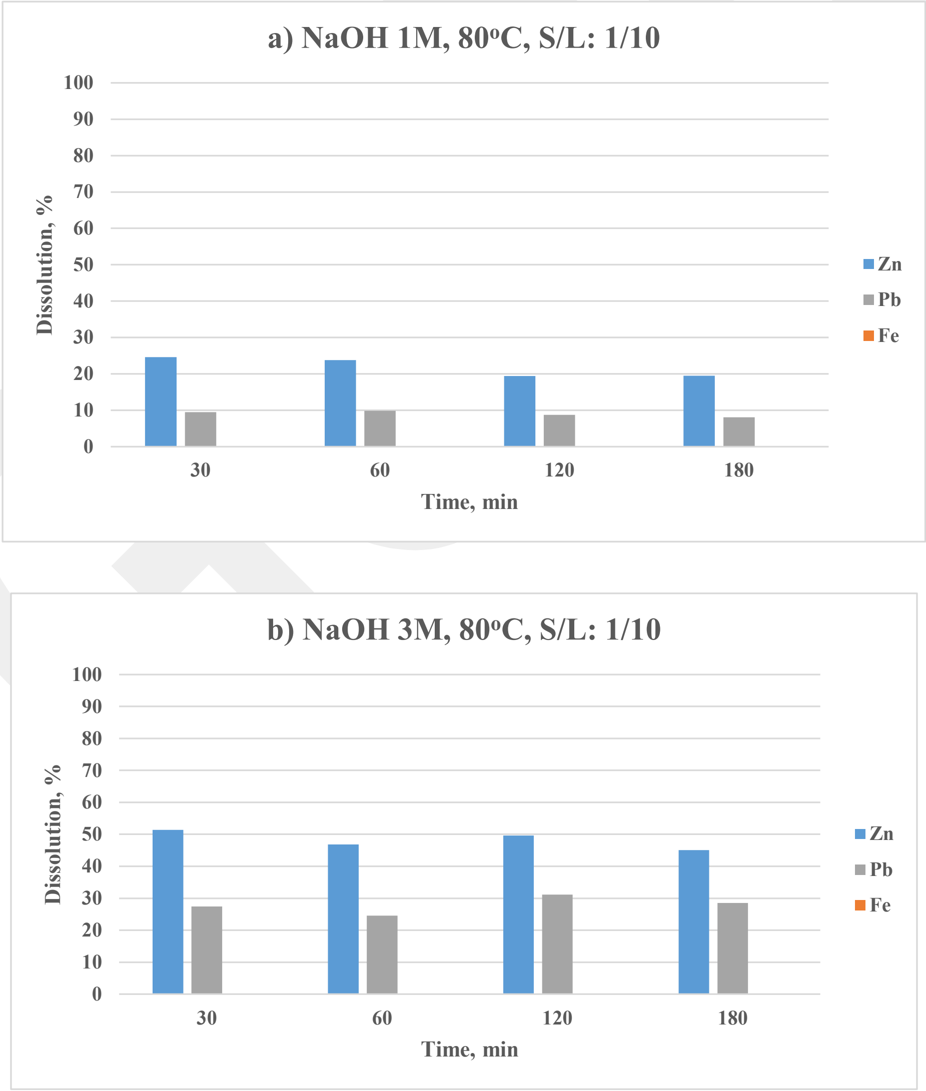


Fig. 15. The effect of sodium hydroxide concentration and leaching time on the dissolution of metals from the flotation tailing.

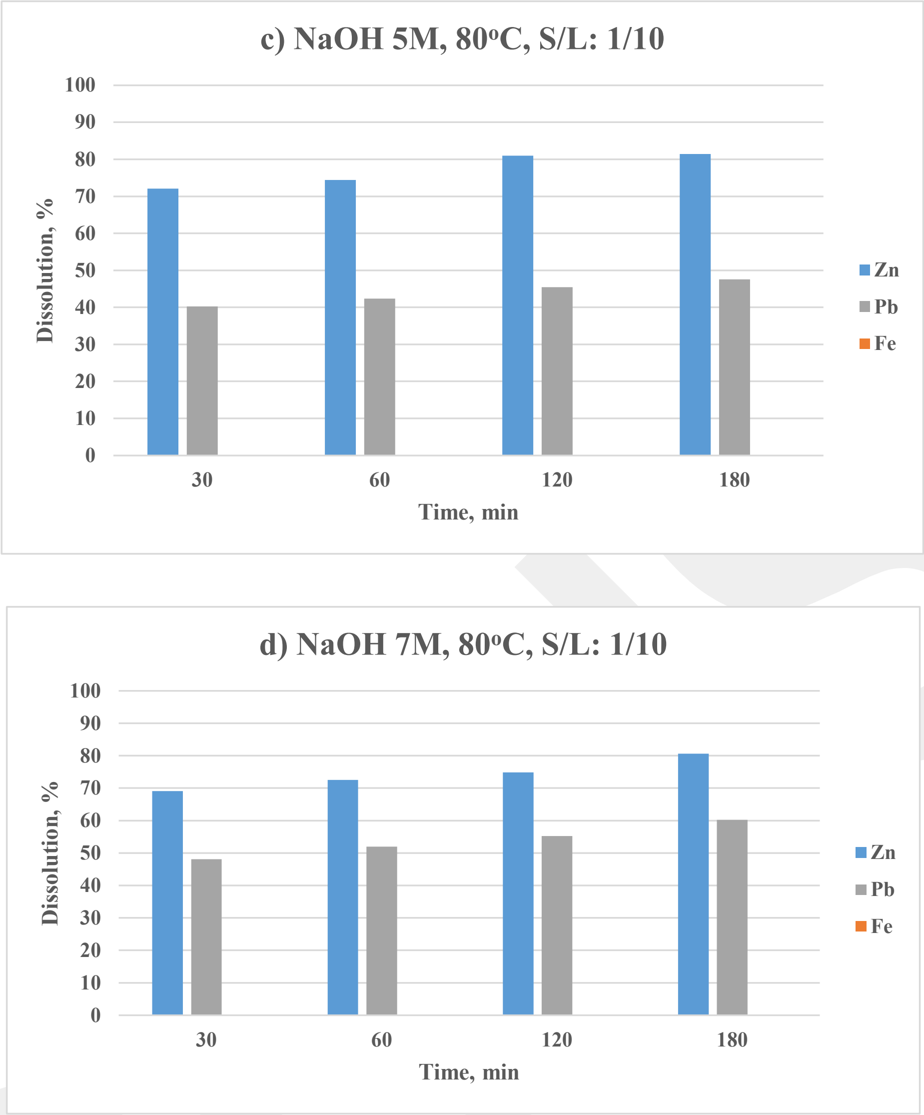


Fig. 15. (*continued*).

was achieved within 180 min., remaining all lead and iron in the leach residue (Fig. 16(c)). The reactions between smithsonite and ammonia in an aqueous solution are as follows:

$$ZnO(s) + 2NH_3(aq) + H_2O = [Zn(NH_3)_2]^{2+}(aq) + 2OH^- \tag{15}$$

$$ZnO(s) + 2NH_4^+(aq) + 2NH_3(aq) \Leftrightarrow Zn(NH_3)_4^{2+}(aq) + H_2O \tag{16}$$

$$ZnCO_3(s) + 4NH_3(aq) = [Zn(NH_3)_4]^{2+}(aq) + CO_3^{2-} \tag{17}$$

$$ZnSO_4(s) + iNH_3(aq) = [Zn(NH_3)_i]^{2+}(aq) + SO_4^{2-} \tag{18}$$

where i: 1, 2, 3, 4.

3.4.2. Leaching of zinc and lead from the tailing in ammonium chloride (NH_4Cl) solution

The effect of leaching temperature and leaching time on the dissolution of metals was investigated using 5 M NH_4Cl at a solid to liquid ratio of 1/10 (Fig. 17(a-d)). The zinc and silver dissolutions increased with increasing leaching temperature and time. Ju et al. 2005 found that zinc dissolution increased with increasing leaching temperature in ammonium chloride solution. This is most probably due to the large activation energy for a surface chemical reaction and sublimation of ammonium chloride into ammonia and hydrochloric acid at high temperatures. When the leaching temperature ascended from 60 °C to 80 °C, no lead, iron and arsenic dissolutions were observed. 73% Zn and 34.8% Ag dissolution was achieved at 80 °C within 120 min. leaching time (Fig. 17(d)). Metal dissolution order was as follows: Zn > Ag. The pH of the solution changed between 6.4 and 6.9.

3.4.3. Leaching of zinc and lead from the tailing in ethylenediaminetetraacetic acid ($C_{10}H_{16}N_2O_8$) (EDTA) solution

The effect of leaching temperature and leaching time on the dissolution of metals from the flotation tailing using ethylenediaminetetraacetic acid ($C_{10}H_{16}N_2O_8$) (EDTA) was investigated at a solid to liquid ratio of 1/10 (Fig. 18(a-c)). The effect of EDTA (0.37 M), which is low biodegradability, high metal removal efficiency, availability of proper recycling techniques, on the dissolution of metals from the flotation tailing was tested. 96.6% Zn dissolution along with 27.1% Pb and 20% Fe co-dissolutions were obtained at 80 °C leaching temperature using 0.375 M EDTA for 180 min. leaching time (Fig. 18(c)). The EDTA achieved more than 90% zinc dissolution along with lead and iron co-dissolutions, which is consistent with the findings of Sun et al., 2001. The researcher found that the recovery of zinc from contaminated surface soils collected from four different sites is greater than lead at low EDTA concentration. Metal dissolution order was determined to be Zn >

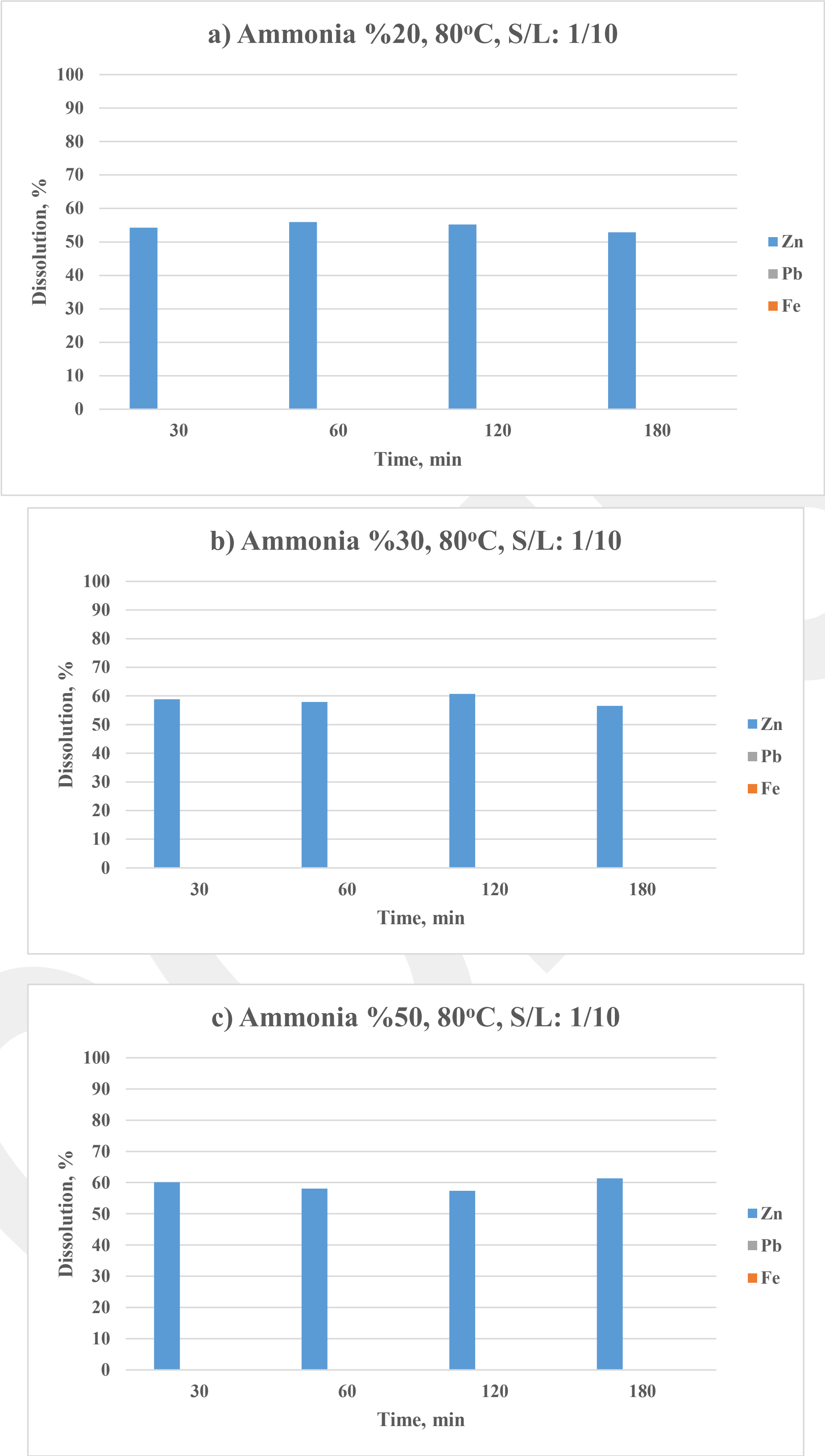
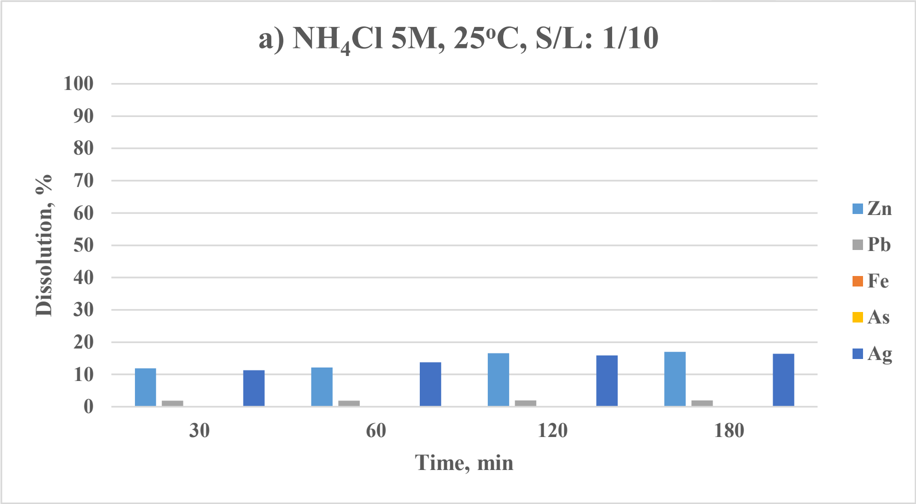


Fig. 16. The effect of ammonia concentration and leaching time on the dissolution of metals from the flotation tailing.



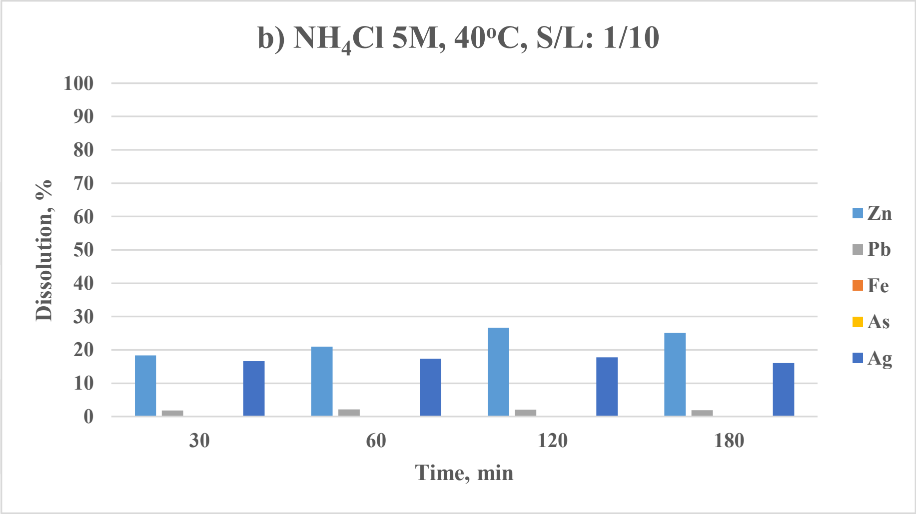


Fig. 17. The effect of leaching temperature and leaching time on the dissolution of metals from the flotation tailing using ammonium chloride.

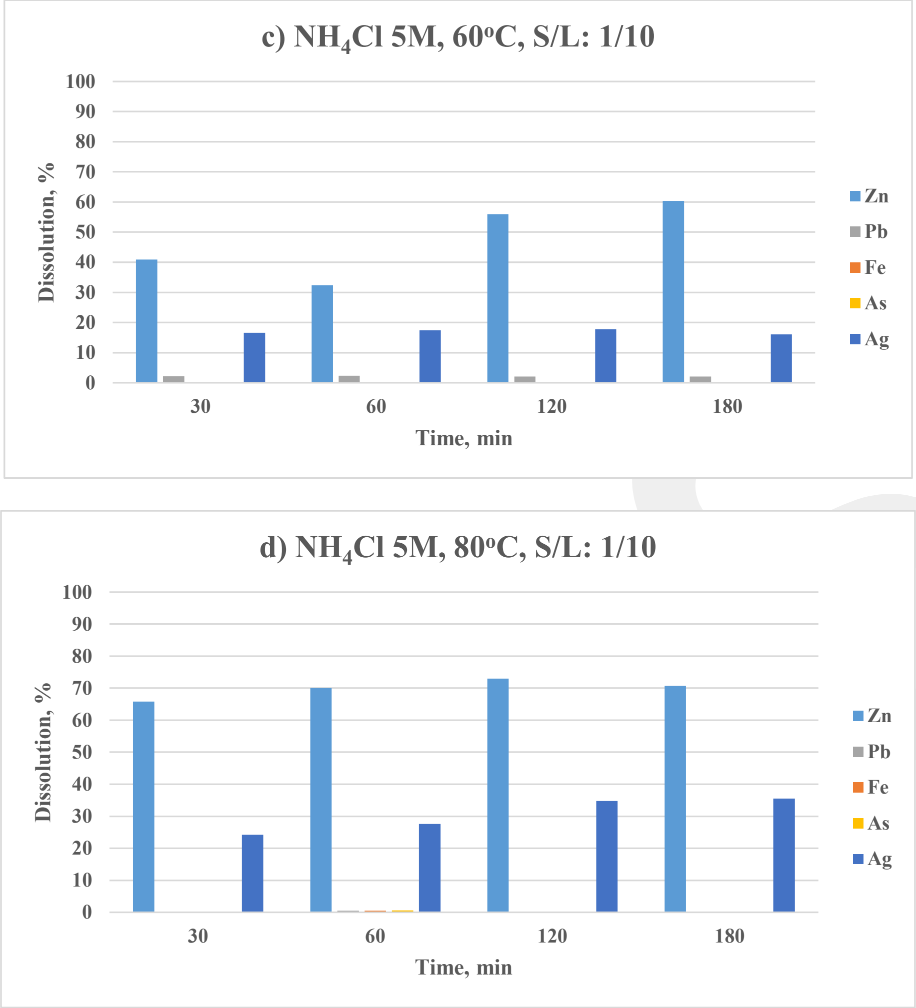


Fig. 17. (*continued*).

Pb > Fe. The solution pH changed between 5 and 6. EDTA cannot bind with zinc oxide if lead oxide is present in the flotation tailing due to the lower EDTA affinity for Zn^{2+} than Pb^{2+}, as seen in Eq. (19). The concentration of EDTA exceeds a certain point, excessive EDTA can bind with zinc, which leads to a considerable increase in zinc concentration (Liu et al., 2014).

$$Zn - EDTA + PbO + H_2O = Pb - EDTA + Zn(OH)_2 \tag{19}$$

3.4.4. *Leaching of zinc and lead from the tailing in different solutions*

Fig. 19 shows the dissolution of metal from the flotation tailing using ammonium oxalate ($(NH_4)_2C_2O_4$) at different leaching time. As can be seen from Fig. 19, the zinc dissolution was less than 20% using 1 M ammonium oxalate at 80 °C, 1/10 solid to liquid ratio for 180 min. leaching time. Less than 3% of lead dissolution was obtained under the tested conditions. No iron co-dissolution was observed.

The effect of ammonium acetate ($C_2H_7NO_2$) and sulfate ($(NH_4)_2SO4$) concentration and leaching time on the dissolution of metals from the tailing was studied at 80 °C, solid to liquid ratio of 1/10 (Fig. 20(a-b)). The dissolution of zinc slightly increased with increasing leaching time. The maximum zinc dissolution (39%) was achieved using ammonium acetate for 180 min. leaching time (Fig. 20(a)). The lead and iron co-dissolutions were less than 5% under the examined conditions. The maximum zinc dissolution (23.1%) was obtained for 180 min. leaching time when the ammonium sulfate was used as a leach solution (Fig. 20 (b)). The lead and iron co-dissolutions were determined to be less than 5%. Feng et al., 2007 found that the ammonium sulfate leaching of the low-grade zinc oxide pellets is controlled by the diffusion of the leach liquor through the gangue layer in the whole leach process. Not only ammonium acetate but also ammonium sulfate showed a similar effect on the metal dissolutions from the flotation tailing. It was seen that there is no beneficial effect of ammonium acetate and ammonium sulfate on the dissolution of lead and iron. The zinc dissolutions were in the range of 15% and 40% along with pretty low lead dissolutions.

Table 3 summarizes the effect of ammonia or sodium compound and chelating agents on the zinc and lead dissolution from the flotation tailing. The ammonia or sodium compound and chelating agents were not considered as a lixiviant for the dissolution of zinc and lead from the flotation tailing as the good selectivity or recovery between the zinc and lead were not obtained.

4. Conclusions

The beneficiation of lead–zinc oxide ores using flotation is rather hard compared to sulfides as oxides can dissolve and their surfaces become hydrated easily. Lead can be recovered to some extend by flotation from non-sulfide lead–zinc ores; however, zinc oxides remain in the flotation tailings. The major zinc extraction method from fine and complex lead–zinc flotation tailings is the hydrometallurgical process. The recovery of zinc from a non-sulfide lead–zinc flotation tailing was investigated using 17-different leaching agents via the bench-scale study. The main parameters affecting major metal extractions were

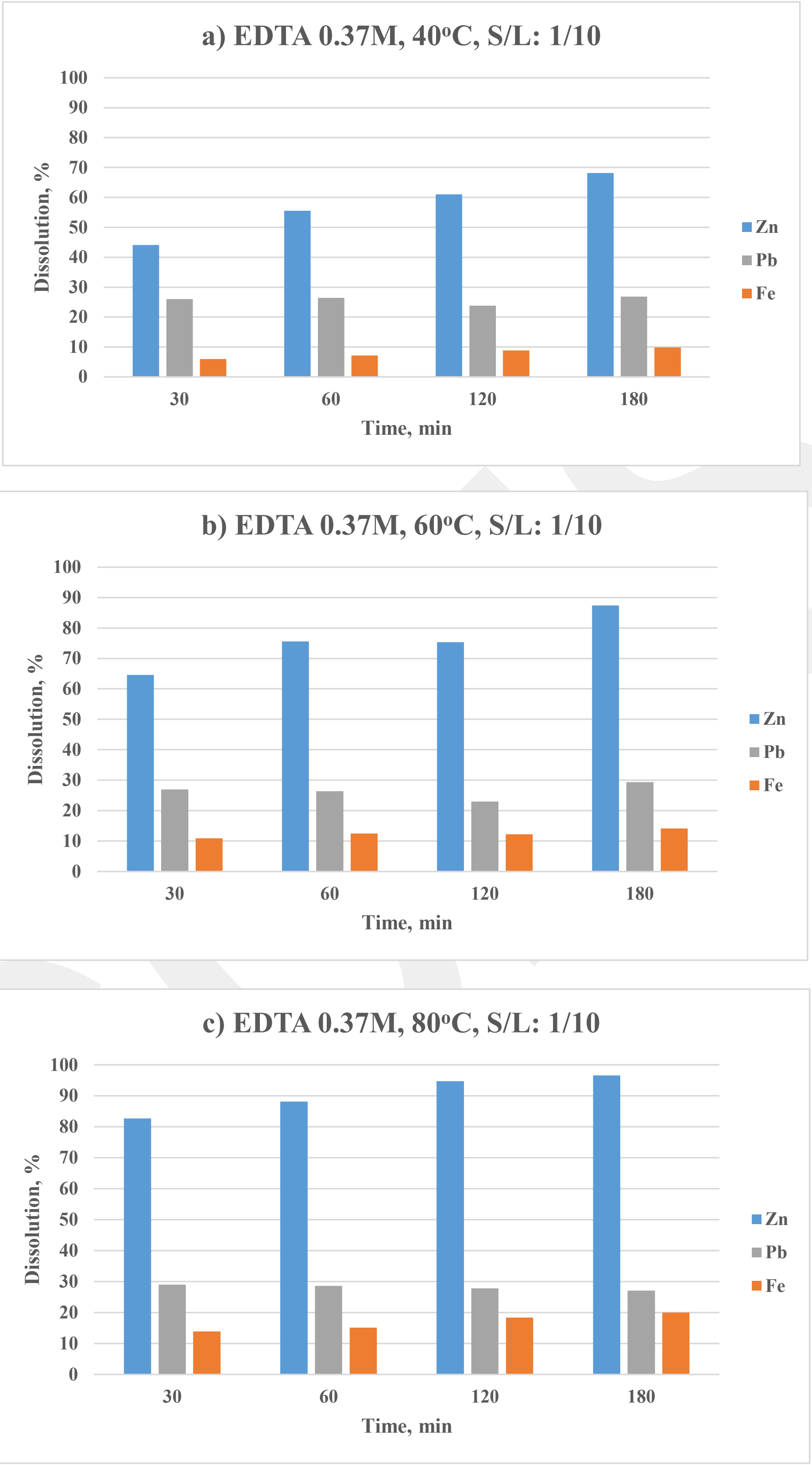


Fig. 18. The effect of leaching temperature and leaching time on the dissolution of metals from the flotation tailing using EDTA.

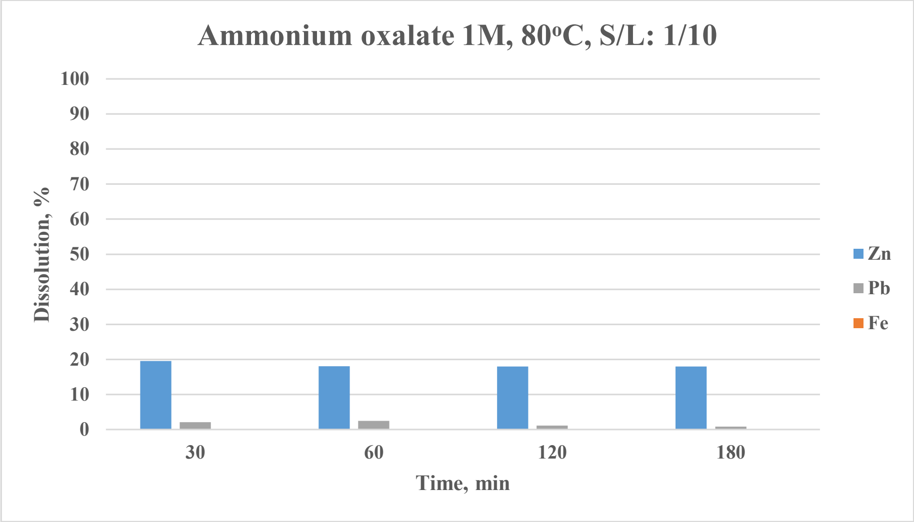


Fig. 19. The dissolution of metals from the flotation tailing using ammonium oxalate.

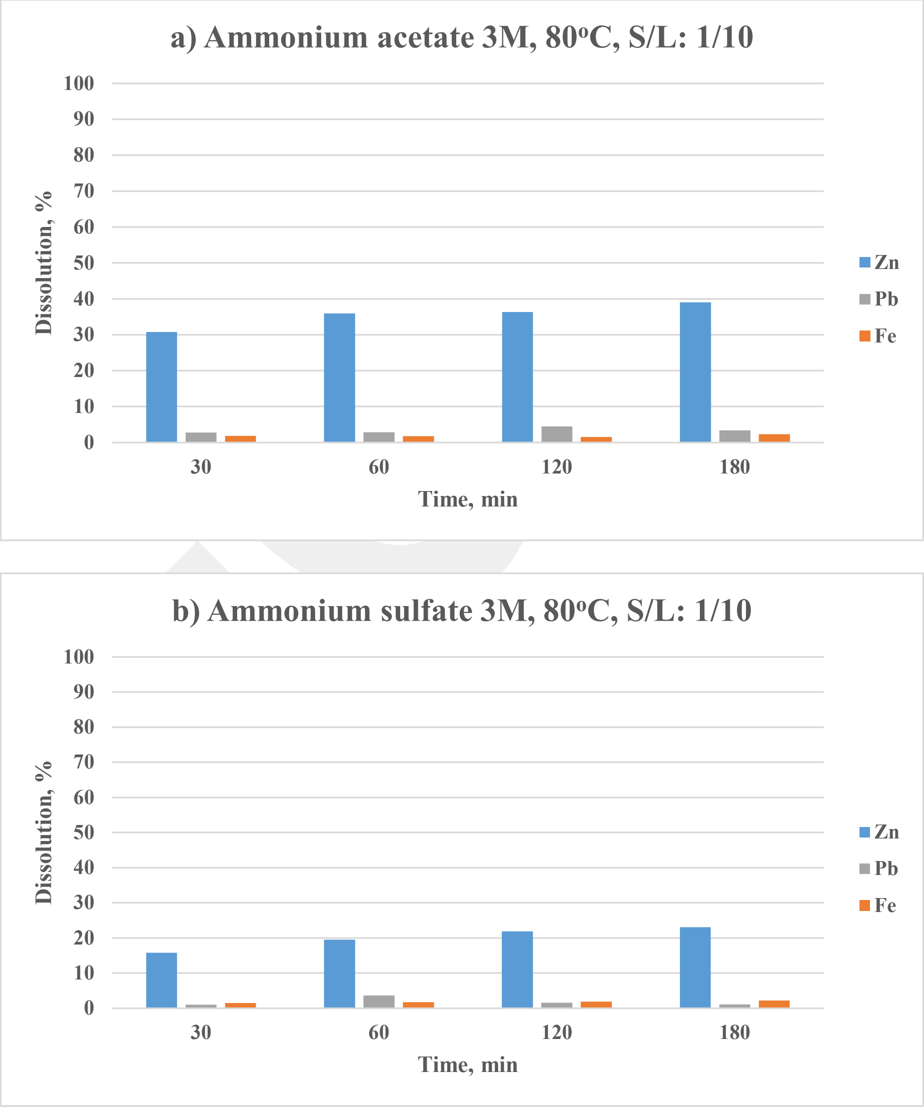


Fig. 20. The effect of ammonium acetate and sulfate concentration and leaching time on the dissolution of metals from the tailing (a-ammonium acetate, b-ammonium sulfate).

Table 3
The effect of ammonia or sodium compound and chelating agents on the zinc and lead dissolution from the flotation tailing (a: analytical grade).

Agent	Zinc Dis., %	Lead Dis., %	Optimum parameters
Ammonia[a]	61.3	–	Con.: 50% NH_4, T: 80 °C, 180 min., S/L: 1/10
Ammonium chloride[a]	73	–	Con.: 5 M, T: 80 °C, t: 120 min., S/L: 1/10
Ammonium acetate[a]	39	3.4	Con.: 3 M, T: 80 °C, t: 180 min., S/L: 1/10
Ammonium oxalate[a]	19.6	2.1	Con.: 1 M, T: 80 °C, t: 30 min., S/L: 1/10
Ammonium sulfate[a]	23.1	1.1	Con.: 3 M, T: 80 °C, t: 180 min., S/L: 1/10
EDTA[a]	96.6	27.1	Con.: 0.375 M, T: 80 °C, t: 180 min., S/L: 1/10

considered as agent concentration, leaching temperature, leaching time and solid-to-liquid ratio. Sulfuric, malic, sulfosalicylic, formic and citric acids were determined to be the most promising lixiviants for the zinc recovery from the flotation tailing. The maximum zinc dissolution order was determined as sulfuric acid (91%) > citric acid (90.6%) > hydrochloric (90%) ~ malic acid (90%) > sulfosalicylic acid (88.7) > formic acid (82.6%) under the conditions explored. The lowest lead dissolution was obtained in the following order: sulfuric acid ~ sulfosalicylic acid (0%) > formic acid (2.8%) > citric acid (9.3%) ~ malic acid (9.3%) > hydrochloric (9.8%). 81.4% of zinc and 47.4% of lead were simultaneously extracted into the leach solution, remaining a considerable amount of iron in the residue using 5 M sodium hydroxide at 80 °C and 1/10 solid to liquid ratio for 180 min. leaching time. Therefore, sulfuric, citric, malic, sulfosalicylic and formic acids were determined as the best leach solutions for the recovery of zinc from the flotation tailing. The maximum lead dissolution was observed by using a sodium hydroxide solution.

CRediT authorship contribution statement

Shokrullah Hussaini: Investigation, Writing - original draft, Visualization, Data curation. **Sait Kursunoglu:** Conceptualization, Methodology, Investigation, Writing - original draft, Writing - review & editing, Visualization, Supervision. **Soner Top:** Investigation, Writing - review & editing, Visualization. **Zela Tanlega Ichlas:** Writing - original draft, Writing - review & editing, Visualization. **Muammer Kaya:** Conceptualization, Methodology, Writing - original draft, Writing - review & editing, Visualization, Resources, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mineng.2021.106935.

References

Abdel-Aal, E.A., Shukry, Z.E., 1997. Application of quick leaching method to Egyptian zinc silicate ore. Trans. Inst. Min. Metall., Sect. C 1997 (106), 89–90.

Abdel-Aal, E.A., 2000. Kinetics of sulfuric acid leaching of low-grade zinc silicate ore. Hydrometallurgy 55, 247–254.

Abkhoshk, E., Jorjani, E., Al-Harahsheh, M.S., Rashchi, F., Naazeri, M., 2014. Review of the hydrometallurgical processing of non-sulfide zinc ores. Hydrometallurgy 149, 153–167.

Asadi, T., Azizi, A., Lee, J., Jahani, M., 2017. Leaching of zinc from a lead-zinc flotation tailing sample using ferric sulphate and sulfuric acid media. J. Environ. Chem. Eng. 5, 4769–4775.

Atia, T.A., Spooren, J., 2020. Microwave assisted chloride leaching of zinc plant residues. J. Hazard. Mater. 398, 122814.

Badanoıu, G., Buzatu, T., Buzatu, M., Butu, M., 2013. Study concerning PbO solubility in NaOH solution for the treatment of sulfate-oxide pastes obtained from dismantling used lead-acid batteries. Revita De Chimie 64 (9), 1004–1010.

Bodas, M.G., 1996. Hydrometallurgical treatment of zinc silicate ore from Thailand. Hydrometallurgy 40, 37–49.

Chen, A., Zhao, Z.W., Jia, X., Long, S., Huo, G., Chen, X., 2009. Alkaline leaching Zn and its concomitant metals from refractory hemimorphite zinc oxide ore. Hydrometallurgy 97, 228–232.

Cole, M.P., Sole, K.C., 2003. Zinc solvent extraction in process industries. Min. Proc. and Ext. Met. Review 24 (2), 91–137.

Deng, J., Wen, S., Yin, Q., Wu, D., Sun, Q., 2017. Leaching of malachite using 5-sulfosalicylic acid. J. Taiwan Inst. Chem. Eng. 71, 20–27.

Ding, Z., Yin, Z., Hu, H., Chen, Q., 2010. Dissolution kinetics of zinc silicate (hemimorphite) in ammoniacal solution. Hydrometallurgy 104, 201–206.

Espiari, S., Rashchi, F., Sadrnezhaad, S.K., 2006. Hydrometallurgical treatment of tailings with high zinc content. Hydrometallurgy 82, 54–62.

Ehsani, I., Ucyildiz, A., Obut, A., 2019. Leaching behaviour of zinc from a smithsonite ore in sodium hydroxide solutions. Physicochem. Problems Miner. Process. 2019 (55), 407–416.

Feng, L., Yang, X., Shen, Q., Xu, M., Jin, B., 2007. Pelletizing and alkaline leaching of powdery low grade zinc oxide ores. Hydrometallurgy 89, 305–310.

Frias, C., Frades, M., Pechharroman, E., Diaz, G., 2008. Improving polymetallic ores beneficiation by means of the primelead process. In: Young, C.A., Taylor, R. P., Anderson, C.G., Choi, Y. (Eds.), Hydrometallurgy, 2008, Proceeding of the sixth International Symposium, SME, Colorado, USA, pp: 378-386.

Ghasemi, S.M.S., Azizi, A., 2018. Alkaline leaching of lead and zinc by sodium hydroxide: kinetics modelling. J. Mater. Res. Technol. 7, 118–125.

Ju, S., Motang, T., Shenghai, Y., Yingnian, L., 2005. Dissolution Kinetics of Smithsonite Ore in Ammonium Chloride Solution. Hydrometallurgy 80, 67–74.

Kaya, M., Gul, E., Kursunoglu, S., Hussaini, S., 2019. Leaching of oxidized Turkish Pb-Zn flotation tails by inorganıc acids, IMPC-Eurasia-2019, 1st Regional Mineral Processing Conference. In: Bulut, G., Yuce, A.E., Onal, G. (Eds.), Proceedings 31 Oct.-2 Nov. Antalya-Turkey pp: 491-502.

Kaya, M., Hussaini, S., Kursunoglu, S., 2020. Critical review on secondary zinc resources and their recycling technologies. Hydrometallurgy 195, 105362.

Kaya, M., Kursunoglu, S., Hussaini, S., Gül, E., 2020b. Leaching of Turkish Oxidized Pb–Zn Flotation Tailings by Inorganic and Organic Acids, In book: PbZn 2020: 9th International Symposium on Lead and Zinc Processing, San Diago, USA, 23-27 Feb., pp: 447-468. Published in book PbZn-2020 by Springer-TMS.

Klochko, K., 2020. Lead. In: U.S. Geological Survey, Mineral Commodity Summaries 2020. pp. 94-95. https://doi.org/10.3133/mcs2020.

Kukurugya, F., Vindt, T., Havlik, T., 2015. Behavior of zinc, iron, and calcium from electric arc furnace (EAF) dust in hydrometallurgical processing in sulfuric acid solutions: thermodynamic and kinetic aspects. Hydrometallurgy 154, 20–32.

Kursun, I, Ozdemir, M.F., Hacıfazlıoglu, H., Terzi, M., 2017, Dissolution of lead from lead-zinc tailings with HNO3, XVII Balkan Mineral Processing Congress, XVII BMPC, Tiran-Albania, 493-498.

Kursunoglu, S., Kursunoglu, N., Hussaini, S., Kaya, M., 2021. Selection of an appropriate acid type for the recovery of zinc from a flotation tailing by the analytic hierarchy process. J. Cleaner Prod. https://doi.org/10.1016/j.jclepro.2020.124659.

Li, P., Zeng, G.M., Xu, W.H., Zhang, C., Jiang, M., 2010. Effects of organic acids on zinc and lead leaching from contaminated sediments. China Environmental Science 30, 1235–1240.

Liu, Q., Zhao, Y., Zhao, G., 2011. Production of zinc and lead concentrates from lean oxidized zinc ores by alkaline leaching followed by two-step precipitation using sulfides. Hydrometallurgy 110, 79–84.

Liu, Q., Yang, S., Chen, Y., He, J., Xue, H., 2014. Selective recovery of lead from zinc oxide dust with alkaline Na2EDTA solution. Trans. Nonferrous Met. Soc. China 24, 1179–1186.

Moghaddam, J., Sarraf-Mamoory, R., Yamini, Y., Abdollahy, M., 2005. Determination of the Optimum Conditions for the Leaching of Nonsulfide Zinc Ores (High-SiO_2) in Ammonium Carbonate Media. Ind. Eng. Chem. Res. 44, 8952–8958.

Moradi, S., Monhemius, A.J., 2011. Mixed sulphide–oxide lead and zinc ores: Problems and solutions. Minerals Engineering, 24, 1062-1076.

Mohr, S., Giurco, D., Retamal, M., Mason, L., Mudd, G., 2018. Global projection of lead-zinc supply from known resources. Resources 7, 17.

Nagib, S., Inoue, K., 2000. Recovery of lead and zinc from fly ash generated from municipal incineration plants by means of acid and/or alkaline leaching. Hydrometallurgy 56, 269–292.

Rao, S., Yang, T., Zhang, D., Liu, W., Chen, L., Hao, Z., Xiao, Q., Wen, L., 2015. Leaching of low grade zinc oxide ores in NH_4Cl–NH_3 solutions with nitrilotriacetic acid as complexing agents. Hydrometallurgy 158, 101–106.

Safari, V., Azarpeyma, G., Rashchi, F., Mostoufi, N., 2009. A shrinking particle-shrinking core model for leaching of a zinc ore containing silica. Int. J. Miner. Process. 93, 79–83.

Santos, F.M.F., Peina, P.S., Porcaro, A., Oliviera, V.A., Silva, C.A., Leao, V.A., 2010. The kinetics of zinc silicate leaching in sodium hydroxide. Hydrometallurgy 102, 43–49.

Song, B.X., West Chester, W., 2004. Process of preparing in-situ water-soluble zinc salt for use in automatic dishwashing compositions. Patent, US 2004 (0176269), A1.

Sop, 2001. Specialization Commission Metallic Mines Sub-Commission Lead-Zinc-Cadmium Study Group Report. Ankara.

Souza, A.D., Peina, P.S., Lima, E.V.O., Dasilva, C.A., Leao, V.A., 2007. Kinetics of sulphuric acid leaching of a zinc silicate calcine. Hydrometallurgy 89, 337–345.

Souza, A.D., Peina, P.S., Santos, F.M.F., Dasilva, C.A., Leao, V.A., 2009. Effect of iron in zinc silicate concentrate on leaching with sulphuric acid. Hydrometallurgy 95, 207–214.

Sun, B., Zhao, F.J., Lombi, E.S.P., McGrath, S.P., 2001. Leaching of heavy metals from contaminated soils using EDTA. Environ. Pollut. 113 (2001), 111–120.

Terry, B., Monhemius, A.J., 1983. Acid dissolution of willemite (Zn, Mn)$_2$ SiO$_4$) and hemimorphite ($Zn_4Si_2O_7(OH)_{2\ H}2O$). Metall. Trans. B 14, 335–346.

Tolcin, A.C., 2020. Zinc. In: U.S. Geological Survey, Mineral Commodity Summaries 2020. pp. 190-191. https://doi.org/10.3133/mcs2020.

Wang, R., Tang, M., Yang, S., Zhagn, W., Tang, C., He, J., Yang, J., 2008. Leaching Kinetics of Low Grade Zinc Oxide Ore in NH_3-NH_4Cl-H_2O System. Journal of Central South University 2008 (15), 679–683.

Yan, Y., Gao, J., Wu, J., Li, B., 2014. Effects of inorganic and organic acids on heavy metals leaching in contaminated sediment. An Interdisciplinary Response to Mine Water Challenges - Sui, Sun & Wang (eds), China University of Mining and Technology Press, Xuzhou, ISBN 978-7-5646-2437-8.

Yoshida, T., 2003. Leaching of zinc oxide in acidic solution. Mater. Trans. 44, 2489–2493.

Zhang, Y., Deng, J., Chen, J., Yu, R., Xing, X., 2014. A low-cost and large-scale synthesis of nano-zinc oxide from Smithsonite. Inorg. Chem. Commun. 43, 138–141.

Zhao, Y., Stanforth, R., 2000. Production of Zn powder by alkaline treatment of smithsonite Zn–Pb ores. Hydrometallurgy 56, 237–249.