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Comparison of Different Leaching Media on Calcium, Iron, Magnesium and Manganese Removal from Flotation Tails

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ABSTRACT

Intense mining activities involving different mining sectors are operated in worldwide and a large amount of waste is generated. In addition to the problems caused by the accumulation of these wastes, environmental problems arise due to the metal content of the wastes. Leaching studies was one of the methods applied to evaluate elements. The main factor in the selection of the reactants used in the leaching studies is to improve the removal efficiency of the elements. In this study, HCl, HNO_3, H_3PO_4 and HNO_3 with 2 g/L citric acid was used to leach calcium (Ca), iron (Fe), magnesium (Mg) and manganese (Mn) elements from the flotation tails. While effective leaching yields for Ca, Mg, and Mn elements could be obtained with all inorganic acids tested, the removal of the Fe element was limited. However, studies with HNO_3 and citric acid yielded important results regarding Fe removal. As a result of the leaching studies, optimum leaching condition was determined as 240 minutes of reaction time at 60 °C, 2 M HNO_3 with 2 g/L citric acid. The leaching efficiency of Fe element was 11.97% at 20 °C, 13.48% at 40 °C, 45% at 60 °C at a concentration of 1 M HNO_3 with 2 g/L citric acid. Ca, Mg and Mn elements removal was about 80-100% at all tested conditions with HNO_3 and 2 g/L citric acid. These results show that the types of reagents, experimental conditions, and also waste type was important to determine best leaching conditions.

Keywords: leaching; flotation tails; iron; manganese; calcium; magnesium.

INTRODUCTION

Mining has been one of the oldest and most traditional economic activities responsible for obtaining raw materials for different purposes (Xavier et al., 2020). Due to the exploitation of non-renewable resources as a result of mining-related studies, many experts consider mining activities as unsustainable activities. However, these effects could be reduced with some improvements and initiatives. Considering the potential impacts of mining activities, there may be environmental, health and economic impacts on those living in the immediate surroundings.

Metal/heavy metals originating from mining or other industries could enter the receiving environment, which is one of the serious environmental problems. According to the calculations of the European Union, about 23.4% of the total waste produced in Europe consists of mining and quarrying sectors (EU, 2020). The flotation tailing is considered an environmental problem as a result of its great volume and mineralogical species contained (Santander and Valderrama, 2019). These contaminants could accumulate in the aquatic flora and fauna environment and easily enter the food chain, as they are non-degradable, stable and highly resistant. They could have negative and highly toxic effects on biological systems even at very low concentrations (Choińska-Pulit et al., 2018; Fernandez-Gonzalez et al., 2018; Meseldzija et al., 2019). While metal wastes mostly emerge from the metallurgical industries as primary mineral resources; also it is formed in different amounts of various other wastes (Lottermoser, 2010). While transition metals such as iron, copper, nickel and zinc can be found in high concentrations; these kinds of waste also contain precious metals such as gold and silver (Ahmadi et al., 2015).

It is also known that acidic wastewaters contain high concentrations of dissolved metals and sulfates as a result of the contact of mine wastes with oxygen and water, after the dissolution of sulphide minerals (Falagán et al., 2017).

Flotation tails containing metals and other contaminants have to leached before recovery processes. There has been used several leaching methods for this purpose. Acidic leaching is a kind of method used to effectively take metals into solution from solid wastes such as basic oxygen furnace sludge, electric furnace sludge, blast furnace sludge and dust, fly ash, and metallurgy sludge (Che et al., 2010; Brunelli and Dabalà, 2015; Zheng et al., 2016; Shen et al., 2016, Xie et al., 2018; Kurklu and Sayilgan, 2020).

Falagán et al. (2017) investigated the combination of oxidative and reductive bioleaching of copper from mine tailings and found that this process could be used effectively at low pH values and at 45 °C temperature. Ong et al. (2018) investigated the recovery of manganese and iron from groundwater treatment sludge and Mn (100%) leaching was obtained using sulfuric acid and hydrogen peroxide at 25 °C. Terrones-Saeta et al. (2020) searched copper leaching from mining wastes and found that 80% of the Cu removal with 0.20 molar sulphuric acid solution after 2 h reaction time and they did not obtain important rates of recovery of magnesium, manganese and titanium.

The mining process of iron ore generates various amounts of sulfides, the major component of which is pyrite (FeS_2), and also significant amounts of iron oxide minerals (Nakhaei and Irannajad, 2017). Besides, dolomite is the main impurity mineral in magnesite ore, affecting the quality of products (Hu and Zhu, 2020). The reaction that occurred between HCl and dolomite was displayed as a two-step reaction. Also, $CaCO_3$ could dissolve faster than $MgCO_3$ (Busenberg and Plummer, 1982; Hu and Zhu, 2020). Considering the XRD results in this study, dolomite and pyrite compounds were observed. Possible reactions of these minerals in flotation tails with investigated acids in experimental studies are given below (Eq. 1-6).

Reactions of with HCl (Busenberg and Plummer, 1982; Hu and Zhu, 2020):

$$CaMg(CO_3)_2+H^+ \rightarrow MgCO_3+Ca^{2+}+HCO_3^- \quad (1)$$

$$MgCO_3+H^+ \rightarrow Mg^{2+}+HCO_3^- \quad (2)$$

Reactions with H_3PO_4 (Shaskova et al., 2000):

$$CaMg(CO_3)_2+H_3PO_4 \rightarrow CaHPO_4 \cdot 2H_2O+MgHPO_4 \cdot 3H_2O+CO_2 \quad (3)$$

Reactions with HNO_3 (Kadıoglu et al., 1995; Pultar et al., 2019):

$$CaMg(CO_3)_2+4HNO_3 \rightarrow Ca(NO_3)_2+Mg(NO_3)_2+2CO_2+2H_2O \quad (4)$$

$$FeS_2+4HNO_3 \rightarrow Fe(NO_3)_3+2S+NO+2H_2O \quad (5)$$

Pyrite solubility at low pH values is expressed as (Demoisson et al., 2005; Dogaroglu, 2010):

$$FeS_2+2H^+ \rightarrow Fe^{2+}+S(0)+H_2S \quad (6)$$

As mentioned in literature, many studies have been carried on the leaching of various elements from different kinds of wastes and wastewaters. To the best of our knowledge, there are no comprehensive studies about investigating the acidic leaching conditions of magnesium, iron, calcium and manganese elements from lead-zinc-copper flotation tailings with different acids. Also, each flotation tails have its own individual mineralogical and chemical composition and consequently its optimal leaching conditions could differ from one type of mining waste to another. In this work, leaching of magnesium, calcium, iron and manganese elements from flotation tails with 4 different acids (HCl, HNO_3, H_3PO_4 and HNO_3+citric acid) was investigated. The leaching efficiency of inorganic and organic acids at different temperatures (20, 40 and 60 °C) and different molarities (0.5, 1 and 2 M) were investigated.

MATERIALS AND METHODS

Characterization of mining flotation tails

A flotation tails sample was obtained from a Lead-Zinc-Copper Flotation (Enrichment) Mining Corporation in Turkey. The dry sample was used in all experiments after dried at 60 °C for 24 hours (FN 500, Nuve). The metal contents of the sample were analyzed with ICP-OES (Agilent 5100 SVDV, USA) device in the ALS laboratory in Czech Republic according to S-METAXHB1 and METAXHB2 methods (Sayilgan and Karacan, 2018). XRD (Bruker D8 Advance Twin-Twin) analysis of the sample was analyzed using CuKα x-rays at the YETEM Laboratory in Suleyman Demirel University (SDU). Ca, Mg, Fe and Mn concentrations in leaching solutions were analyzed using inductively coupled plasma (ICP-OES) (Perkin Elmer, Optima DV2100) in SDU. The composition of mining flotation tails was analyzed using SEM-EDX (FEI QUANTA, FEG 250). The chemicals used in the experiments, HNO_3 (Merck), HCl (Merck), H_3PO_4 (Merck), citric acid (Merck), and NaOH (Merck) were provided in analytical purity.

Acidic leaching experiments

Inorganic acidic leaching experiments were performed with hydrochloric acid (HCl), nitric acid (HNO_3) and phosphoric acid (H_3PO_4). In addition, leaching experiments were carried out with citric acid together with HNO_3 in a set of experiments in order to investigate the effect of organic acids on leaching yield with inorganic acid (HNO_3). The experimental procedure is shown in Table 1. Acidic leaching tests were carried out by adding 2 g/L waste sludge in 500 mL high-density polyethylene flasks in an orbital incubator (Gallenkamp) controlled temperature under constant stirring (150 rpm). The leaching behavior of Ca, Mg, Mn and Fe elements from waste sludge was assessed by experiments using a waste sludge concentration of 2 g/L and an acid concentration of 0.5, 1, and 2 M, and at different temperatures (20, 40, and 60 °C). For example, for conducting acidic leaching tests with 1 M HCl, firstly, after the temperature of the orbital incubator was adjusted to the desired temperature, the solution containing 2 g/L flotation tails and 1 M HCl was shaken in the incubator. At the end of the determined test period, 10 mL of sample was taken from the leaching solution. Then samples were centrifuged at 6,000 rpm for 5 minutes (Hettige Centrifuge, Rotofix32, Germany) to precipitate waste sludge. After separation, leach solutions were diluted 1:10 using nitric acid solution (pH ~1.5-2) to prevent precipitation of metals remaining in the solution, and samples were kept at 4 °C in the refrigerator until analysis. Then, element analysis was performed with the ICP-OES device (Perkin Elmer, DV2100). The best leaching efficiencies are obtained at 2M acid concentration, thus the results obtained with 2 M acid are given in this study. Reaction times of 0, 20, 60, 120, 180, and 240 minutes were used for the kinetics experiments. Each leaching experiment was carried out separately with HCl, HNO_3, H_3PO_4 and HNO_3 with citric acid under specified conditions.

RESULTS AND DISCUSSION

Characterization of mining flotation tails

Elemental analysis of mine flotation tails is shown

Table 1. Experimental procedure of acidic leaching tests.

Flotation tails concentration	Acids	Mixing rate (rpm)	Acid concentration (M)	Temperature (°C)	Reaction time (min)
2 g/L	HCl H_3PO_4 HNO_3 HNO_3+ citric acid	150	0.5-1-2	20-40-60	0-20-60-120-180-240

in Table 2. As seen in Table 2, flotation tails contains 170,000 mg/kg calcium, 86,300 mg/kg iron, 91,500 mg/kg magnesium, 20,600 mg/kg manganese and 95,200 mg/kg sulfur. Flotation tails also contain 4,260 mg/kg zinc and 3560 mg/kg lead. Other element concentrations are at relatively low values (not shown Table). Kurşun et al. (2017) determined that lead-zinc flotation residues obtained from Balıkesir contains 13% Fe_2O_3, 8% Al_2O_3, 23% CaO, 2.5% MgO, 1500 mg/L lead and 1500 mg/L zinc. Cichy et al. (2016) found that 2-6% Zn compounds, 0.2-1% Pb compounds, 10-44% Fe compounds, 2.4% CaO, 0.9% MgO in the flotation waste of zinc-lead oxides in Poland. These results and our work result show that zinc-lead flotation wastes mainly contain iron, magnesium, zinc, calcium, lead and manganese elements.

Table 2. Elemental analysis of flotation tails.

Elements	Concentrations (mg/kg dry matter)
Calcium	170,000
Iron	86,300
Magnesium	91,500
Manganese	20,600
Sulphur	95,200
Aluminum	1,040
Lead	3,560
Zinc	4,260

Flotation tails also include other elements in small quantities.

Figure 1 shows XRD pattern of mining flotation tails. As it seen in Figure 1, flotation tails mainly consists of dolomite and iron sulphide compounds. These peaks are expected for flotation tails due to the dolomite compounds containing calcium, magnesium, iron and the pyrite compound containing iron sulfide. Nayak et al. (2020) determined the mineral content as zinc-containing halerite, iron-containing pyrrhotite and sodium-rich feldspar from a lead-zinc mine deposit, in India. Kurşun et al. (2017) determined high levels of magnetite (Fe_3O_4) and galena (PbS) compounds as a result of XRD analysis of the mine waste obtained from the Balıkesir Region (Turkey) with similar characteristics. The compounds identified in this study and in other studies are the expected compounds in lead-zinc flotation wastes as the main content. It may be due to the fact that flotation tails contain similar or different components with each other caused by presence of flotation tails in different regions and countries and they may be due to different concentrations of element

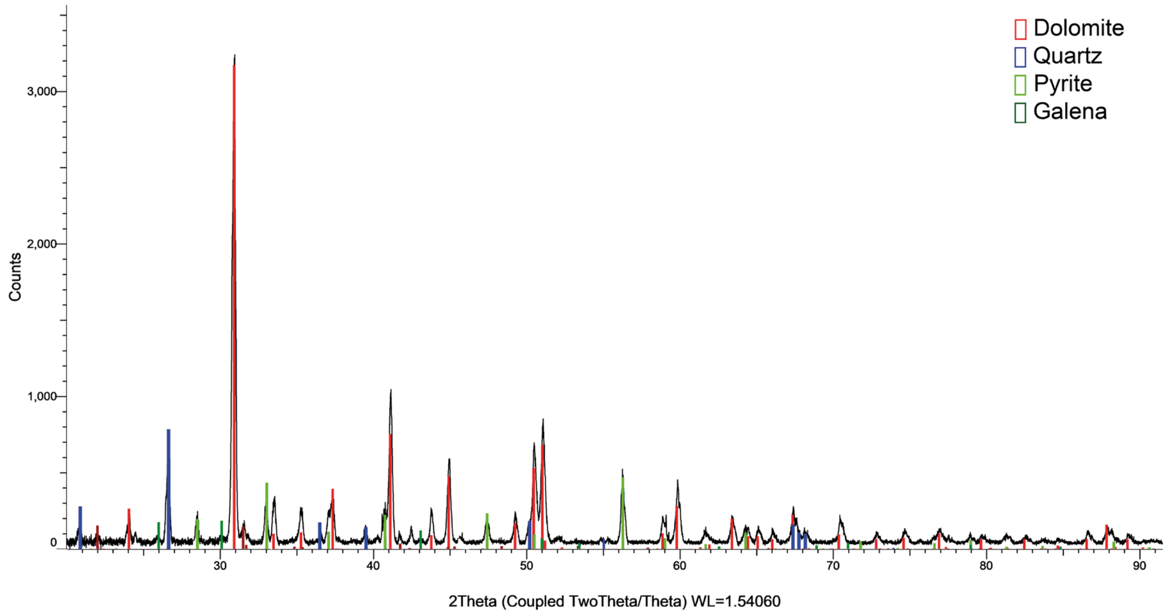

Figure 1. XRD pattern of mining flotation tails.

contents in the main ore.

Figure 2 shows the surface morphology of mining flotation tails. The SEM images in Figure 2 show that the flotation tails mainly contain quartz, feldspar and galena. As a result of SEM images, it was seen that the particles forming the sample showed a wide range of distribution in the range of 0.5-100 µm. Galena is euhedral or subhedral, about 70 µm in size, larger than other compounds. Nayak et al. (2020) stated that the size of galena varies between 75-960 µm and it is observed with quartz with typical cubic crystal feature. In our study, quartz particles were observed on galena, and it is consistent with literature studies. Feldspar particles appear as dispersed, small or medium sized, semi-shaped or amorphous particles (Nayak et al., 2020). In EDX peaks, it was seen that the flotation tails contain Ca, Mg, Al, Fe, Cr, Si, C and O elements.

Acidic leaching results

The mining sector has an important sector in the worldwide because it constitutes raw material for many technologies. As a result of large-scale production, a large amount of waste is generated. In order to recover valuable or harmful elements from these wastes, it is frequently applied around the worldwide firstly hydrometallurgical methods to leach the elements into solution. Effective leaching yields could be obtained with acidic leaching studies. In this study, acidic leaching experiments were conducted to evaluate the solubility of Ca, Mg, Fe, and Mn elements from flotation tails with 4 different acids (HCl, H_3PO_4, HNO_3, HNO_3 with citric acid) at three different concentrations (0.5, 1, 2 M), and three different temperatures (20, 40, and 60 °C). The best leaching efficiencies are obtained at 2M acid concentration, thus the results obtained with 2 M acid are given in this study. All leaching experiments, the leaching efficiencies of the elements were calculated by considering the formula below (1):

$$\text{Leach. yield (\%)}= \frac{\text{Or. min. waste el. conc.} (\frac{mg}{L}) - \text{El.conc. after leach.} (\frac{mg}{L})}{\text{Original mining waste conc.} (\frac{mg}{L})} \text{ x100}$$

Acidic leaching results of HCl

The results of the leaching experiments with hydrochloric acid are shown in Figure 3.

As it can be seen in all graphs in Figure 3, as the reaction time increased, the concentrations of Ca, Mg, Fe and Mn transferred (leached) to the solution, and thus the leaching efficiency was increased. In general, yields did not change much after 120 min leaching time for all elemental species. Ca, Mg, Fe and Mn leaching yield ranged from 19-97%; 4-93%; 2-13%, and 15-100%, respectively. In Ca, Mg and Mn removal efficiencies, leaching efficiencies with HCl could be obtained successfully, while Fe leaching efficiencies could be obtained around 13% maximum. It was observed that increasing the temperature values from

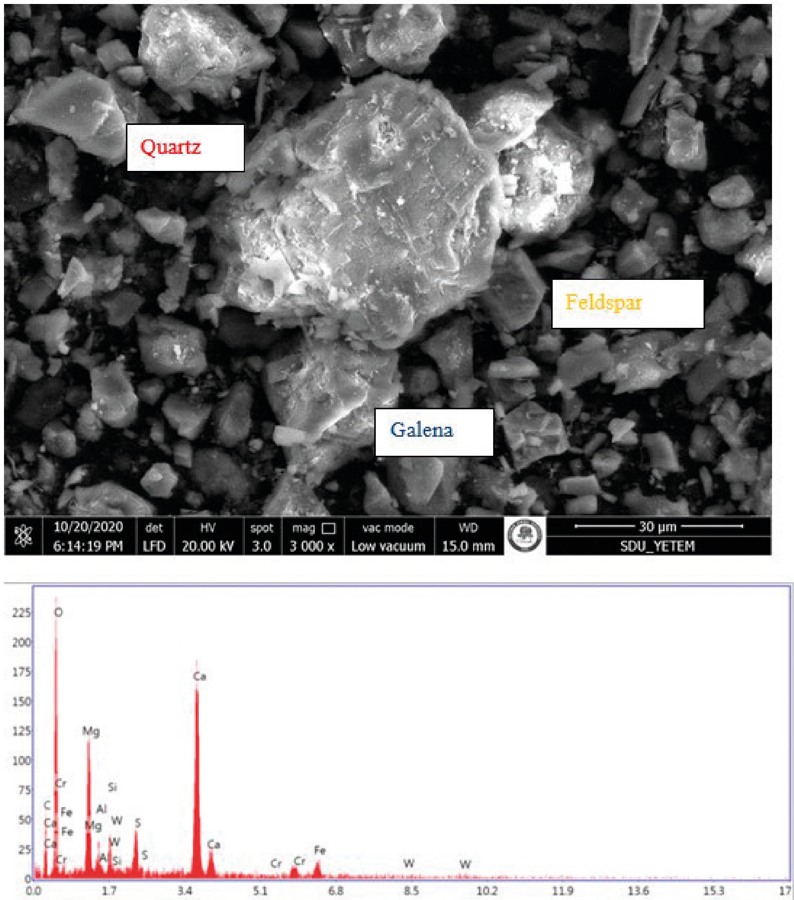

Figure 2. SEM-EDX image of mining flotation tails.

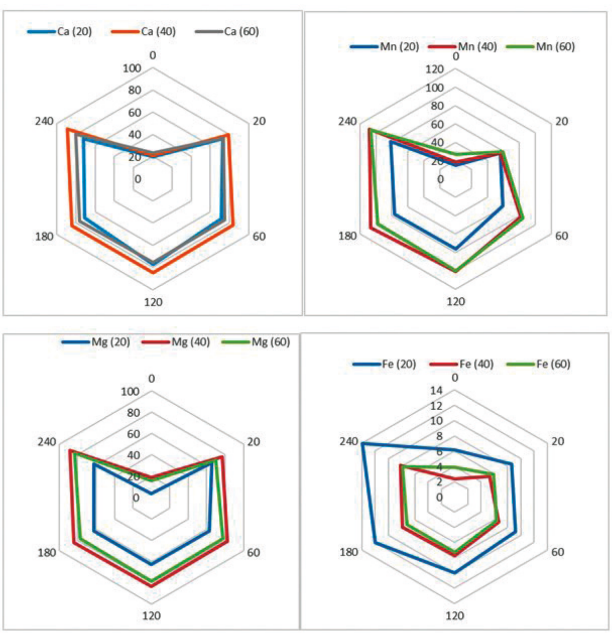

Figure 3. Leaching results of the Ca, Fe, Mg and Mn elements with 2 M HCl.

20 °C to 60 °C did not increase the Fe leaching efficiency. In literature studies, it was seen that the leachability of Fe element was lower than other elements. Studies show that Fe extraction is highly dependent on pH, and that inorganic acids have a lower pH value than organic acids, and thus have an effect on better Fe leaching efficiency (Elomaa et al., 2019). The lower leachability of Fe leaching efficiency compared to other elements can be considered as an advantage in terms of enabling selective leaching. Also, Fe could know as dominated and costly impurity metal in hydrometallurgical processes and good selectivity could directly decreased in process costs (Elomaa et al., 2019).

Acidic leaching results of H_3PO_4

The results of the leaching experiments with phosphoric acid are shown in Figure 4.

As the duration of the experiment increased, the concentrations of Ca, Mg, Fe and Mn, which were leached into the solution, and thus the leaching efficiency increased. In general, it was observed that the leaching efficiencies for all elemental species increased during

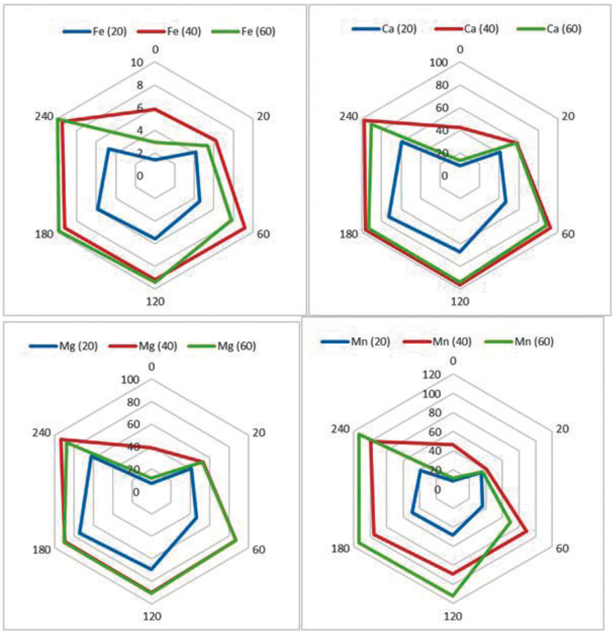

Figure 4. Leaching results of the Ca, Fe, Mg and Mn elements with 2 M H_3PO_4.

the experimental periods in the studies performed at 20 °C. Optimum leaching was obtained in 120 minutes in the studies performed at 40 and 60 °C. Since H_3PO_4 is a relatively weak acid compared to HCl, it was possible to observe the effect of reaction time and temperature in experimental studies with H_3PO_4. At all three temperatures, 90-100% Ca, Mg and Mn removal was obtained within 120 minutes; Fe removal remained around 10% under the same conditions. Li et al. (2021) also found that the solubility of Si, Fe, Al, and S were not as soluble as those of fluorapatite, calcite, and dolomite in phosphoric acid solution. Fe removal was about 40%, while Mg ve Ca removal was about totally 100% with H_3PO_4. Other studies also showed that the minerals containing Si, Fe, Al, and S were not as soluble as those of fluorapatite, calcite, and dolomite in phosphoric acid solution. It may indicate that part of pyrite was dissolved in the acid hydrolysis solution (Li et al., 2021).

Acidic leaching results of HNO_3

The results of the leaching experiments with nitric acid are shown in Figure 5.

Figure 5 shows that the leaching yields of Mg and Ca elements follow a similar trend at all temperatures investigated and a leaching efficiency of approximately 80% is obtained in 30 minutes reaction time. Mn leaching efficiency reached its maximum values of about 100% in 120 minutes. In some of Mn leaching efficiency, leaching efficiencies were founded as more than 100% this may be due to analytical measurement errors since it was worked with real flotation tails. In terms of Fe leaching efficiency, it was observed that Fe leaching was increased with increasing reaction time. After 240 minutes reaction time with 2M HNO_3, maximum 50% Fe leaching efficiencies were obtained. Similarly, Liu et al. (2014) also stated with 1 M sulfuric acid concentration, the Mn leaching efficiency increased between 10-180 minutes, while it did not change between 180-240 minutes and was approximately 96%. They stated that the Fe leaching efficiency increased rapidly in the first 100 minutes, but continued to increase slowly in the advancing reaction time, and the Fe leaching efficiency was around 13%. Although, Liu et al. (2014) did not work with the same acid and concentration, it is noteworthy that Mn and Fe elements indicate similar leaching tendencies with our study. Ahn et al. (2011) also found that Pb, Ba, Ag, Zn, Bi and Co were highly reactive with HNO_3 resulting in 80-90% dissolution, while Al and Fe were much less reactive with HNO_3 resulting in only 30-40% dissolution.

Acidic leaching results of HNO_3 with citric acid

Leaching experiments were conducted with HNO_3 and 2 g/L citric acid. As an organic acid, citric acid was chosen due to the literature studies and the experience we gained from our previous studies (Sayılgan et al., 2010; Zaleckas et al., 2013). Zaleckas et al. (2013), in their studies on the

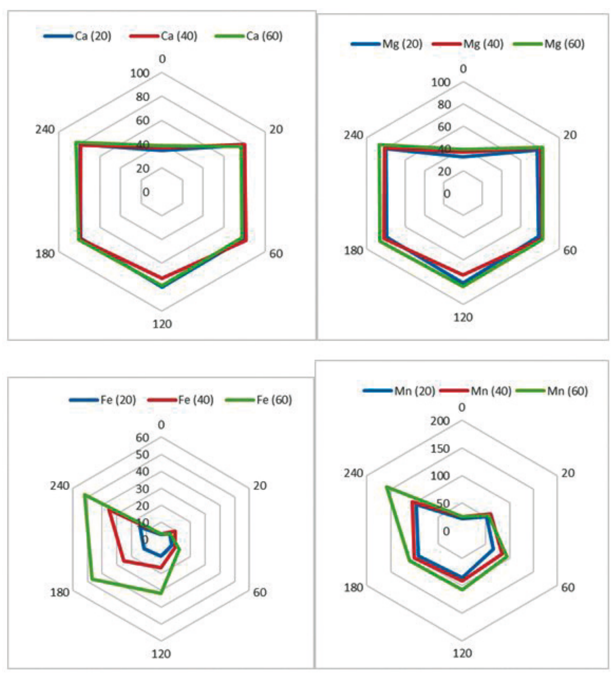

Figure 5. Leaching results of the Ca, Fe, Mg and Mn elements with 2 M HNO_3.

leaching of metals from sewage sludge, stated that citric acid, a tricarboxylic acid, provides stronger extraction than oxalic acid, which is dicarboxylic acid. Also, in our previous studies, it has been determined that oxalic acid precipitates in the form of metal oxalate, and no precipitate is formed with citric acid (Sayılgan et al., 2010). The results of the leaching experiments of nitric acid with citric acid are shown in Figure 6.

Figure 6 shows that the leaching yields are quite successful according to the conditions where only inorganic acids are used. While increasing HNO_3 concentration with 2 g/L citric acid concentration and increasing reaction temperature, removal of elements was increased, especially in Fe removal, which is quite successful findings. 96.47% Ca, 94.73% Mg, 84.36% Fe, 133.05% Mn element recovery was obtained with 2 M HNO_3+2 g/L citric acid concentration at 60 °C. All elements removals were increased with increasing acid concentration at 20 °C. However, an increase was observed for removal of only Fe element with increasing acid concentrations, and no significant effect was observed in the removal of other elements at 40 °C and 60 °C. This may be due to the already 80-100% removal of Ca, Mg and Mn elements under the specified conditions. The leaching efficiency of Fe element was 11.97% at 20 °C, 13.48% at 40 °C, 45% at 60 °C at a concentration of 1 M HNO_3+ 2 g/L citric acid, after a reaction time of 240 minutes. Similar results were obtained in literature studies. Jensen et al. (2007) stated that the Mn element was completely extracted with organic acids, while the Fe and Al elements could be extracted in lesser amounts. They stated that the most effective removal efficiencies were obtained with citric acid and malic acid, and the extraction efficiencies increased when the acid concentrations were increased from 0.5 M to 1 M. As inorganic acid, they stated that nitric acid significantly increased the removal efficiency. Shi et al. (2020) examined the removal of heavy metals by washing the soil with citric acid and ferric chloride and stated that soil elements such as Al, Mn, Fe and organic substances dissolved with citric acid.

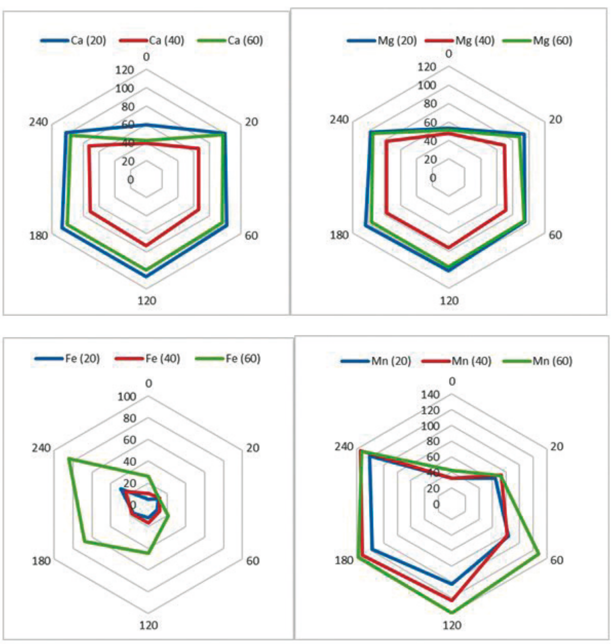

Figure 6. Leaching results of the Ca, Fe, Mg and Mn elements with 2 M HNO_3 and 2 g/L citric acid.

In the literature studies, nitric acid, hydrochloric acid, sulfuric acid come to the fore in terms of leaching efficiency in extraction processes. However, it was stated that besides the leaching efficiency, the advantages of acids in terms of cost and usage should also be taken into account. From an economic point of view, it was stated that nitric acid and sulfuric acid were better reactants due to their higher extraction rate compared to acetic acid. More effective leaching yields are obtained by completely ionizing inorganic acids due to their stronger strength. Strong inorganic acids such as H_2SO_4, HNO_3 and HCl could react with metals in the waste sludge and cause dissolving and leaching through proton exchange. Organic acids such as acetic acid and citric acid act through additional mechanisms in the form of complexation of metal ions and organic acid anions (Wu et al., 2004). However, while quite good removal efficiencies can be obtained for Mn removal with organic acids such as oxalic acid; it can affect the leaching efficiency quite negatively by causing the formation of zinc oxalate (Sayılgan et al., 2010). In this respect, the element contents of the waste to be leached are also very important issue for selection of organic acids. Overall, in this study, when the recovery of Ca, Mg, Mn, and Fe elements from flotation tails with different inorganic acids and HNO_3+citric acid was investigated, it was observed that all elements could leach significantly. In this sense, it comes to the fore to make the necessary acid selection depending on the waste to be investigated and the element to be recovered. Considering the waste and acids investigated in this study, if the first priority is selective leaching of Fe only inorganic acids could be applied for leaching studies and Fe could remain in residues. If Fe and other elements such as Ca, Mn, and Mg required to be taken into solution, HNO_3+citric acid could be applied.

CONCLUSIONS

Mining activities have been a very important role in worldwide. However, environmental factors should also be carefully considered in addition to the economic inputs. In this study, the solubility of Ca, Mg, Fe and

Mn elements, which are found in high concentrations in the flotation tails formed in the Lead-Copper-Zinc Enrichment Plants, by different acidic leaching methods was investigated. The flotation tails contain 170000 mg/kg Ca, 86300 mg/kg Fe, 91500 mg/kg Mg, 20600 mg/kg Mn. Flotation tails creates both environmental risk and economic value with its high concentration of element content. Leaching studies were carried out with HCl, H_3PO_4, HNO_3 and HNO_3+citric acid to investigate the solubility of the elements. All experimental results showed that Ca, Mg and Mn elements could be leached effectively under the investigated experimental conditions with inorganic acids, however, Fe removal was at low concentrations. However, an increase in Fe removal was obtained in experimental conditions when 2 g/L citric acid was added to nitric acid. 96.47% Ca, 94.73% Mg, 84.36% Fe, 133.05% Mn element recovery was obtained with 2 M HNO_3+2 g/L citric acid concentration at 60 °C. This promising result could an effectively solution for more difficult leachable elements such as Fe if it is desired to be recovered together with other elements. However, it is very important to choose the organic acid to be selected based on the elements and characterization of the waste. If the iron is desired to remain in the residue and Ca, Mg, Mn elements are desired to be leached from the waste, the waste could be leached with low concentration inorganic acids.

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