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Selection of an appropriate acid type for the recovery of zinc from a flotation tailing by the analytic hierarchy process

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ABSTRACT

The selection of acid type for metal dissolution from minerals is an important issue in leaching operations. Acids are used to recover valuable elements from the minerals by dissolving them in a solution. The acid must offer a high recovery at marginal cost and a low environmental effect. Many parameters can affect the acid type selection for high leaching recovery and low environmental effect and thus, the selection of an acid type is complex. In this study, based on the experimental results obtained from the bench-scale laboratory studies, the selection of acid type for the recovery of zinc from a flotation tailing was investigated using the analytic hierarchy process (AHP). The utilization of AHP was supported by the use of ExpertChoice® 2000 software. The outcomes demonstrated that sulfuric acid is the most desirable acid type with a ranking of 0.541, tracked by citric acid, and oxalic acid with scoring of 0.282 and 0.177, respectively. Furthermore, analyses of sensitivity were performed to examine the influence of the main criteria on the different acid type. It emerged that citric acid can be used when the environmental main criterion ascended from 7.8% to 75.3%.

1. Introduction

Approximately, 95% of the global production of metallic Pb and Zn derived from their respective sulfide ores namely galena and sphalerite, respectively, and only 5% of these two metals production came from oxide ores. In 2018, the global Zn reserve was about 230 Mt, while its production and consumption were estimated to be 13.42 and 13.74 Mt, respectively (USGS, 2018). In 2018, 32.000 tons of secondary Zn from galvanizing residues and crude Zn-oxide recovered from electric arc furnace (EAF) dust recycled in the USA.

The recovery of valuable metals from secondary materials has a double effect on natural resources. Using secondary diminishes the pressure on the earth's fast exhausting raw deposits, thereby guaranteeing a prolonged supply of metals for a predictable future. As secondary materials are emanated from wastes, removing resources from them warrants cleaner surroundings (Hamuyuni et al., 2018). Using secondary's also retains metals in circulation, a process is often known as a sustainable circular economy. Rising waste volumes require metal recycling concepts. An increasing amount of production waste, steel scrap, batteries, e-waste, industrial residues, mine tailings, metallurgical slags/dust, bottom ash process residues, etc. require efficient recycling technologies. In these wastes, heavy metals threaten the environment, create risks for human health and induce significant storage problems. These wastes also have a significant amount of valuable metals, which makes recycling economically feasible and lucrative.

Although developed countries have established regulatory programmes for the disposal of solid wastes, they have generally continued to use unsophisticated methods such as open dumps, landfills, incinerators and sanitary landfills which represent a significant source of metals released into the environment (Baran and Antonkiewicz, 2017). There are millions of tonnes of lead-zinc sulphide ore treated by flotation techniques in metallurgical industries, which are contained substantial amounts of non-ferrous and precious metal losses. Currently, metallurgical tailings can be considered as a secondary source of metals due to the depletion of natural mineral resources in the most industrialized countries (Lutandula and Maloba, 2013). The most important secondary sources of the zinc and lead are anodes, electric arc furnace dust, galvanizing plants, spent lead-acid batteries, pipes, solders, and dry cells, etc. The minerals of zinc and lead are of course linked with

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each other. The mineralization of every lead and zinc deposit divided into three main categories: (a) sulphide ores, (b) mixed sulphide—oxide ores, (c) non-sulphide ores, which formed two types, hypogene or supergene weathering. Zinc oxide ores, such as willemiyte (Zn_2 SiO_4), smithsonite ($ZnCO_3$), hemimorphite (Zn_2 SiO_3 H_2O), hydrozincite ($2ZnCO_3$ $3Zn$ $(OH)_2$) and zincite (ZnO), are considered as a vital source of zinc. Since oxide and carbonate minerals are generally amenable to atmospheric acid leaching, hydrometallurgical processes are preferred to treat such complex and low-grade source of metals containing finely disseminated lead and zinc, which are chemically similar. They are more attractive than pyrometallurgical processes as they are more environmentally friendly given the process emit no hazardous dust and toxic gas, and require much lower capital for small scale operation (Jha et al., 2001; Sethurajan et al., 2016).

The use of acidic reagents such as sulfuric acid solutions (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; Safari et al., 2009; Souza et al., 2009; Moradi and Monhemius, 2011; Asadi et al., 2017) and hydrochloric acid (Nagib and Inoue, 2000) have been reported to leach zinc from zinc or lead-zinc oxide ores. With the use of sulfuric acid solutions as lixiviant, the reports show that zinc in its oxide, silicate and carbonate forms are readily soluble whereas lead sulfate is poorly soluble in sulfuric acid solution forcing lead to reprecipitate after its dissolution with the acid (Moradi and Monhemius, 2011). There is an increasing interest in the use of organic acids to recover zinc from low-grade zinc ores and zinc plant tailings (Hursit et al., 2009; Irannajad et al., 2013; Larba et al., 2013; Deng et al., 2015; Yang et al., 2017). The use of citric acid, gluconic acid, trichloroacetic acid, nitrilotriacetic acid, and acetic acid have been investigated for this purpose. Although organic acids are not usually utilized as lixiviates because of their low dissolution recoveries, they are attractive in terms of easy biodegradation (Li et al., 2010; Larba et al., 2013; Musariri et al., 2019; Kaya et al., 2020; Pathak et al., 2020). Besides, they are used at much milder settings such as at pH 3—5 (Larba et al., 2013).

The choice of the most suitable acid type is a multi-objective and multi-criterion decision assured by a set of restrictions. In the present work, we utilize the Analytic Hierarchy Process (AHP) to interpret the three acid type options (sulfuric, citric and oxalic). This method can be carried out by a Multiple Criteria Decision Making (MCDM) method. MCDM aims to aid a decision-maker to choose an appropriate alternative among a set of options (Saaty, 1990). Selecting an appropriate acid type is a multi-objective decision process considering constraints, preferences, and priorities. AHP is a possible solution to solve this type of selection problem. Due to the AHP method is easy to use, it has found acceptance between decision-makers. The AHP method helps in providing a systematic decision process using multiple criteria based on the decision-makers' subjective preferences.

In recent years, numerous researchers have performed by the utilization of decision-making systems in mining operations. For example, Adebimpe et al. (2013) and Kursunoglu and Onder (2015) have used the AHP method for the selection of mine equipment. Zoran et al. (2011) and Owusu-Mensah and Musingwini (2010) have carried out the AHP for the selection of ore transport systems. Alpay and Yavuz (2009) has selected an underground mining method. Musariri et al. (2019) has determined the location of a mineral processing plant. Kursunoglu et al. (2017) has predicted a leaching method for a laterite ore. Stirbanovic et al. (2019) has determined an appropriate flotation machine selection by Topsis and Vikor method. Kazemi et al. (2020) has selected an appropriate mineral processing plant site by fuzzy analytical hierarchy process. Sitorus and Brito-Parada (2020) has used a fuzzy multiple criteria decision-making model for the selection of appropriate equipment in mineral processing. However, no study has been reported on the selection of an appropriate acid type for the recovery of zinc from the flotation tailings or ores by the AHP method. In the present study, based on the available experimental results obtained from the bench-scale studies, the AHP method was applied for the selection of the most appropriate acid type for the recovery of zinc from the flotation tailing, leaving a considerable amount of iron and arsenic in the residue.

2. Materials and method

The tailing sample was supplied by Orex Mining Co. in Kayseri, Turkey. The supplied sample was ground in a laboratory ball mill and the particle size distribution of the ground ore was measured using a laser diffraction particle analyzer (Musariri et al., 2019). The elemental composition was analyzed by ALS Mineral Laboratory in Izmir, Turkey, via digestion and solution analysis using inductively coupled plasma mass spectroscopy (ICP-MS). The morphology of the sample was analyzed via scanning electron microscopy (SEM, Hitachi-Requlus 8230) and energy dispersive spectrometry (EDX, Oxford Instrument) analysis at 5—10 kV.

The leaching tests were performed in 500-mL round-bottom glass flasks with reflux condensers attached to minimize evaporative losses. The flasks were placed in heating mantles (METOPS) equipped with magnetic stirrers (Fig. 1). The temperature of the slurry was monitored regularly using a glass thermometer. In each experiment, 250 mL of a solution at a pre-determined concentration was put into the flask. The heating mantle was automatically increased to the preferred temperature. Then, 25 g of the ground tail was into the flask. Sampling was performed by withdrawing 5 mL of the slurry at selected time intervals, and the withdrawn sample was subsequently centrifuged at 5000 rpm for 10 min. The obtained supernatant was then analyzed using ICP-MS.

The used lixiviants in this study were prepared from analytical grades of sulfuric acid (H_2SO_4, Sigma Aldrich), citric acid ($C_6H_8O_7$, Merck) or oxalic acid ($C_2H_2O_4$, Merck). Deionized water was used for diluting these acids. In the tests, solid/liquid ratio (S/L), mixing speed was kept constant at 1/10, 400 rpm, respectively, unless stated otherwise.

2.1. Analytic hierarchy process (AHP)

The AHP method depends on a series of pair-wise comparisons, considering the perception and evaluation of decision-makers. The

Fig. 1. Experimental set-up.

comparisons are carried out using a scale of certain sentences that exhibits how much one factor controls another concerning a given feature (Saaty, 2008). The AHP method is practiced in its simple system as follow (Saaty, 1990):

1. Determine decision criteria C_i to be used to assess and rank options.
2. Determine a set of options to be ranked.
3. Construct an n x n pair-wise comparison matrix A(a_{ij}) with (i,j = 1,2,. . .,n), where n is the number of elements to be compared. The matrix equation is

$$A = \begin{bmatrix} a_{11} & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2n} \\ \dots & \dots & \dots & \dots \\ a_{n1} & a_{n2} & \dots & a_{nn} \end{bmatrix}$$

where $a_{ij} > 0$, $a_{ij} = 1/a_{ji}$, $a_{ii} = 1$, and a_{ij} is the ranking of the comparative importance of criterion i respect criterion j defined by the decision-maker. The comparative significance of the two components is compared using the Saaty's 9-point scale shown in Table 1.

$$W = [w_1, w_2, \dots, w_n] \tag{1}$$

where W is the normalized principal eigenvector of matrix A.

5. The consistency of matrix A is defined as calculating the Consistency Index (CI) defined as

$$CI = (\lambda_{\max} - n) \, / \, (n - 1) \tag{2}$$

where $\lambda_{\max}$ is the maximum eigenvalue and n is the size of the matrix. The consistency fraction (CR) is calculated as

$$CR = CI \, / \, RI \tag{3}$$

where, RI denotes Saaty's unsystematic index values for different matrix sizes (n). If the CR values of the matrices are fewer than or equivalent to 0.10, contrasts formed by the decision-maker are appreciable. If higher rates than 0.10 are obtained, the judgments of the decision-maker then need to be rechecked to improve consistency (Kursunoglu and Onder, 2015; Kursunoglu et al., 2017). Random reliability indicators are given in Table 2.

3. Results and discussion

3.1. Materials characterization

The XRD analysis revealed that the major mineral phases were smithsonite ($ZnCO_3$), cerussite ($PbSO_4$), goethite ($FeO(OH)$), calcite ($CaCO_3$) and quartz (SiO_2). The other major mineral peak with 100% intensity was determined to be beudantite ($PbFe_3(OH)_6SO_4AsO_4$) as an arsenic bearing mineral. The chemical composition of the flotation tailing used in this study consists of 7.5% Pb, 5.77% Zn, 21.3% Fe, 5.6% As and 101 ppm Ag (Hussaini et al., 2019). The main components present in the tailing were Zn, Pb, Fe, As and Ag. Alkali metals (such as Na, K, Ca and Mg) exist in tailings around 5.5%. Si and Al are about 7.6%. The SEM image and the EDX area analysis are given in Fig. 2. These images show that most of the particles were fines. This is supported by the result obtained from the particle size analysis that revealed that 90% of the particles were lesser than 99 μm. The surface morphology of the particles was rough, porous and complex. Different particle shapes and sizes were observed. Based on the colour intensity of the particles, three distinct phases were identified. The brightest particles contained a high level of Pb and O. They were identified as cerrusite. The light grey particles, which contained high Zn and O contents, were identified as smithsonite, while the darkest particles had a high amount of O, Ca and Si and most probably represent calcite and quartz. There was only a little fraction of liberated Zn and/or Pb containing particles as most of the Pb-Zn metals are intergrown with calcite and some of them are impregnated with iron oxide due to oxidation process.

3.2. Effects of sulfuric acid on the dissolution of the flotation tailing

The flotation tailing was leached in sulfuric acid solution. It was chosen as a lixiviant owing to its effectiveness for the dissolution of zinc compounds and the ability to reject lead and calcium from the pregnant leach solution as well as its low cost and commercial

Table 1
Scale for pair-wise comparisons (Saaty, 2008).

4. Determine the qualified primacies of the criteria or options. The relative primacies are accomplished using the eigenvector theory. The relative weight of matrix A is obtained as

Intensity of Importance	Definition	Explanation
1	Equal Importance	Two actions contribute equally to the objective
2	Weak or slight	
3	Moderate importance	Experience and judgments slightly favor one activity over another
4	Moderate plus	
5	Strong importance	Experience and judgments strongly favor one activity over another
6	Strong plus	
7	Very strong or demonstrated importance	An activity is favored very strongly over another; its dominance established in practice
8	Very, very strong	
9	Extreme importance	The proof favoring one activity over another is of the highest possible order of affirmation
Reciprocals of above	If action i has one of the above non-zero numbers apportioned to it when in comparison with action j, then j has the reciprocal value when compared with i	
1.1–1.9	If the actions are very close	May be tough to ascribe the best value but when compared with other contrasting actions the size of the small numbers would not be too perceptible, yet they can still show the the relative importance of the actions.

Table 2
Random reliability indicators (Saaty, 1999).

6. Constitute the pair-wise comparison matrix between alternatives to determine how much an alternative dominates another based on a criterion.
7. Calculate the final ratings of the alternatives.

Matrix Size (n)	1, 2	3	4	5	6	7	8	9	10	11	12	13	14	15
RI value	0.00	0.58	0.90	1.12	1.24	1.32	1.41	1.45	1.49	1.51	1.48	1.56	1.57	1.59

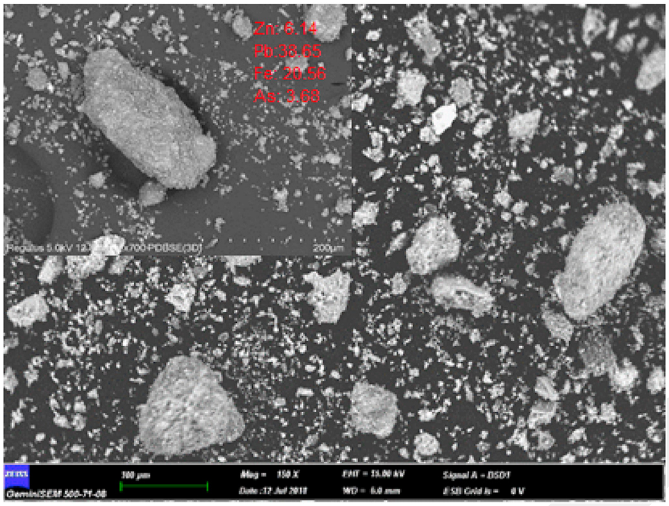


Fig. 2. SEM images and EDX analyses of the tailing.

availability (Jha et al., 2001).

Zinc oxides, carbonates, silicates, and iron oxides can dissolve in sulfuric acid solution according to Eqs. (4)–(7) whereas lead oxides or carbonates can dissolve in sulfuric acid solution but will then precipitates as lead sulfate according to Eqs. (8) and (9) (Moradi and Monhemius, 2011). Fig. 3 shows changes of dissolutions of four main metals identified in the sample, namely Zn, Pb, Fe and As, at various leaching temperatures ranging from 25 to 80 °C, leaching duration ranging from 30 to 180, and concentration of acid ranging from 0.5 to 1.0 M, while the solid/liquid ratio was fixed at 1/10.

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O \quad \Delta G_{298} = -95.593\ kJ \tag{4}$$

$$ZnCO_3 + 2H_2SO_4 \rightarrow 2ZnSO_4Si(OH)_4 \quad \Delta G_{298} = -78.855\ kJ \tag{5}$$

$$Zn_2SiO_4 + 2H_2SO_4 \rightarrow 2ZnSO_4 + Si(OH)_4 \quad \Delta G_{298} = \ -134.570\ kJ \tag{6}$$

$$2FeO(OH) + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 4H_2O \quad \Delta G_{298} = -164.731kJ \tag{7}$$

$$PbCO_3 + H_2SO_4 \rightarrow PbSO_4\downarrow + CO_2\uparrow + H_2O \tag{8}$$

$$PbO + H_2SO_4 \rightarrow PbSO_4\downarrow + CO_2\uparrow + H_2O \tag{9}$$

It was determined that zinc dissolution in the lixiviant was able to reach an appreciable level in 0.5 M sulfuric acid. More than 80% of zinc was dissolved at 40 °C after 60 min of leaching, and the zinc dissolutions were only increased slightly after 120 and 180 min. Iron and arsenic dissolutions were less than 15% in 0.5 M sulfuric acid solution within the studied temperature range. The dissolution of these metals, however, increased significantly while the acid concentration was raised to 1.0 M. Zinc dissolution was also increased when the acid was increased to 1.0 M but the extent of this increase was much smaller than iron and arsenic. Understandably, no lead was detected in the leach solution given the limited solubility of lead sulfate in an acidic medium. Based on these results, it was determined that acid concentration of 0.5 M, leaching duration of 60 min and temperature of 40 °C was the most optimum condition, which dissolved 84.7%, 14%, 5.1% of Zn, As and Fe into the pregnant leach solution, respectively, at an S/L of 1/10.

Fig. 4 shows the dissolutions of zinc, lead, iron, and arsenic at different S/L values. The concentration of sulfuric acid and leaching temperature was maintained at 1.0 M and 80 °C, respectively. When the solid/liquid ratio was increased, zinc dissolution decreased slightly. However, the iron and arsenic dissolutions were decreased to a more significant extent when the solid/liquid ratio was increased. Thus, S/L of 2/10 was determined to be the most appropriate condition for the dissolution of zinc from the flotation tailing, which was able to leave a considerable amount of iron and arsenic in the leach residue. 89.3% Zn, 12.3% Fe, 18.8% As were extracted into the leach solution using an acid concentration of 1.0 M sulfuric acid, a temperature of 40 °C, a solid/liquid ratio of 2/10 and a leaching duration of 60 min.

3.3. *Effect of citric acid on the dissolution of flotation tailing*

Citric acid with low molecular weight can be found naturally in fruits, produced by microbial fermentation and is a biodegradable organic product. It is also a relatively less costly and more environmentally friendly lixiviant. The ability to recover metals from mineral phases with this acid depends on the metals' chemical reactivities toward the acid. There are few reports on leaching of non-sulfide flotation tailings or ores with citric acid. Despite being a weak acid, the smithsonite minerals found in flotation tailings or ores can be dissolved in dilute citric acid due to the coordination of citrate with zinc ions, which causes the increase of smithsonite solubility. The reaction between citric acid and smithsonite can be represented as shown in Eqs.(10)–(12).

$$C_6H_8O_7 = 2H^+ + C_6H_6O_7^{2-} \tag{10}$$

$$ZnCO_3 + 2H^+ = Zn^{2+} + CO_2 + H_2O \tag{11}$$

$$ZnCO_3 + C_6H_8O_7 = Zn^{2+} + C_6H_6O_7^{2-} + CO_2 + H_2O \tag{12}$$

Larba et al. (2013) detected that when the concentration decreased, citric acid can extract 90.4% of ZnO within 1 h leaching time and at 50 °C leaching temperature. The sulfates, nitrates, chlorides, and addition heightened the dissolution to 67%, 84%, and 98%, respectively, after only 15 min of leaching at 40 °C. H^+ ion from citric acid and Cl^- and NO^{3-} anions have significant effects in the dissolution of Zn, and these anions have catalytic effects in the zinc dissolution. The results of the citric acid leaching found in the present study are shown in Fig. 5. The experiments were carried out using 0.5 M citric acid, solid/liquid ratio of 1/10 at different leaching temperatures in the range of 25–40 °C. These results show that Zn, Pb, Fe and As dissolutions were increased with increasing leaching temperature and leaching duration. 74.7% Zn, 6.31% Pb, 11.5% Fe and 12.6% As were dissolved into the leach solution at 60 °C for 120 min.

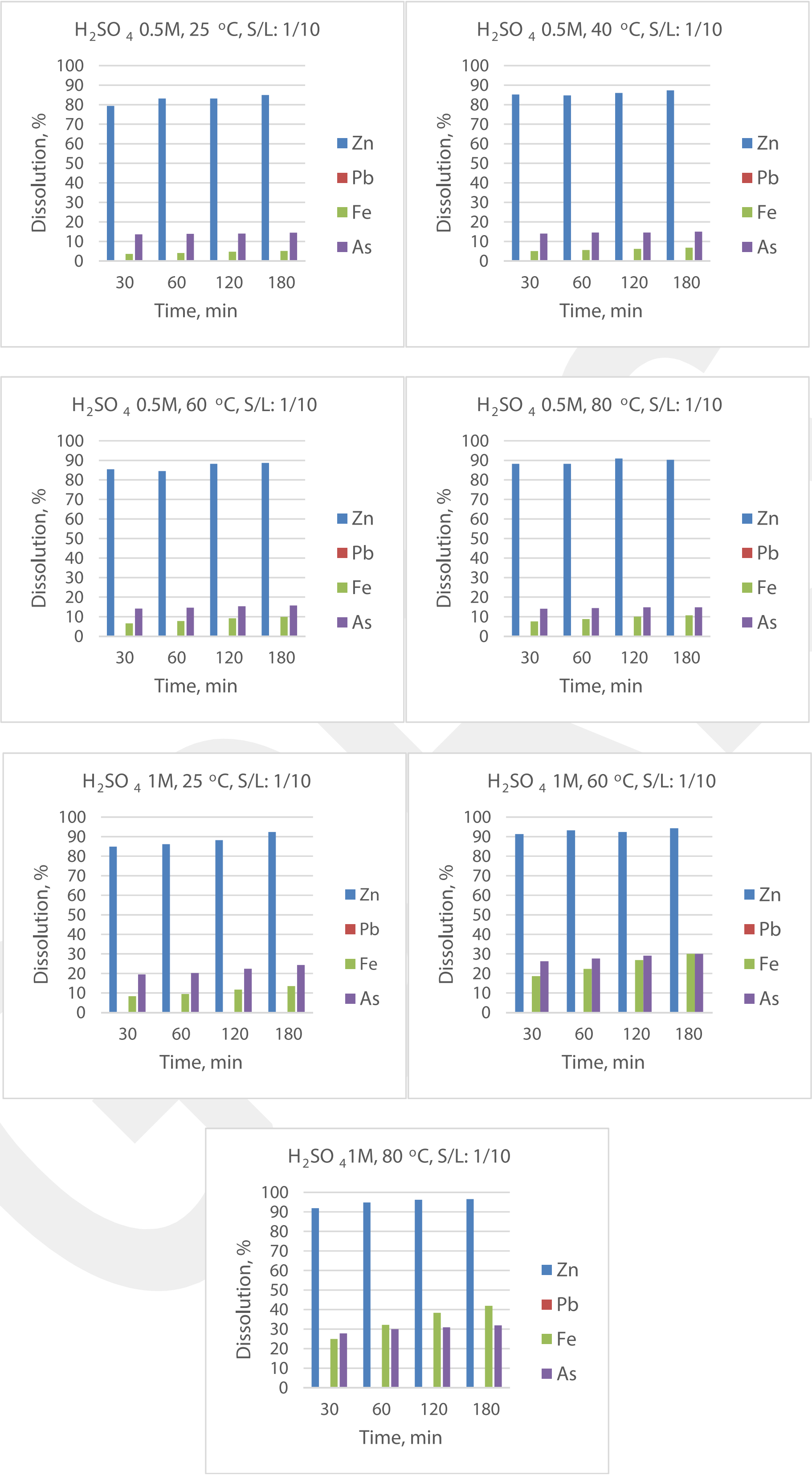
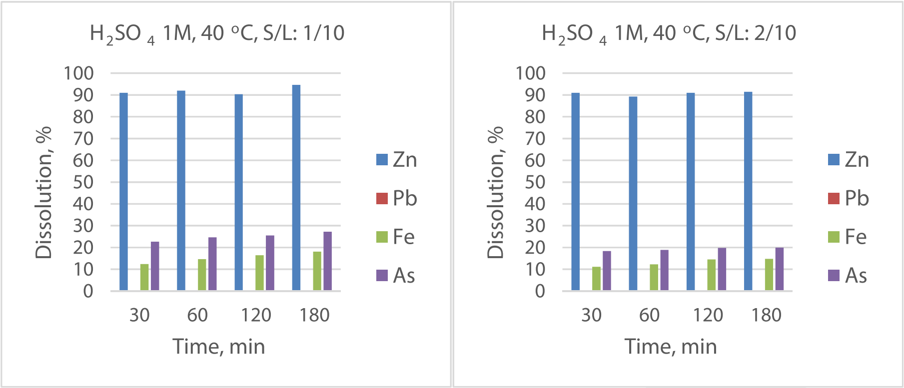


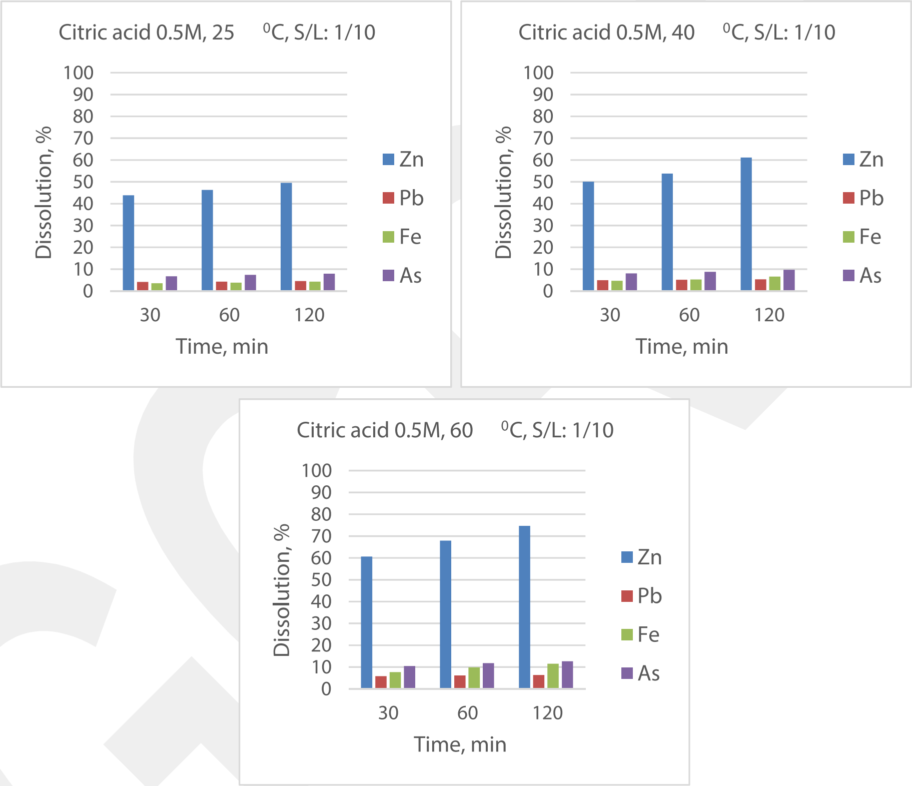
Fig. 3. Effect of temperature on dissolution at 0.5 M and 1 M sulfuric acid concentration.



H_2SO_4 1M, 40 °C, S/L: 1/10

H_2SO_4 1M, 40 °C, S/L: 2/10

Fig. 4. Effect of solid/liquid ratio on dissolution at 40 °C and 1 M sulfuric acid concentration.



Citric acid 0.5M, 25 °C, S/L: 1/10

Citric acid 0.5M, 40 °C, S/L: 1/10

Citric acid 0.5M, 60 °C, S/L: 1/10

Fig. 5. Effect of temperature on dissolution at 0.5 M citric acid concentration.

Fig. 6 shows the results of leaching in 0.5 and 1.0 M citric acid using two different solid/liquid ratios, 1:10 and 1:20. The results show that the dissolution rates of Zn, Pb, Fe and As were increased with decreasing solid/liquid ratio. The zinc dissolution decreases from 89.3% at S/L of 1/10 to 74.8% at S/L of 1:20 after 120 min of leaching in 0.5 M of the acid. When the value of S/L was increased, the amounts of metals present in the ore per unit lixiviant increased and consequently, the metal dissolution decreases. These findings are consistent with the results of Chen et al. (2009) and Espiari et al. (2006) who studied the leaching of zinc oxide ores by alkaline and acidic lixiviants, respectively. Fig. 6 also shows that the zinc dissolution raised while the concentration of citric acid raised from 0.5 to 1.0 M, but only slight differences can be observed when the leaching duration was kept at 120 min or longer. Therefore, it was determined that the dissolution of the metals in citric acid was optimum when the concentration of acid was 0.5 M, the solid/liquid ratio was 1/10, the leaching temperature was 80 °C and the leaching duration was 120 min.

3.4. Effect of oxalic acid on the dissolution of flotation tailing

Tests were conducted at 25 and 40 °C while the other experimental parameters were fixed (oxalic acid concentration of 1.0 M and solid/liquid ratio of 1/10). The dissolution of zinc, lead, iron, and arsenic as a function of leaching time for the above temperatures is given in Fig. 7.

These results show that the dissolution of iron and arsenic are extremely reliant on the leaching temperature. At 40 °C the iron and arsenic dissolutions increased gradually, indicating that the reaction proceeds through a mechanism of autocatalytic. At 25 °C,

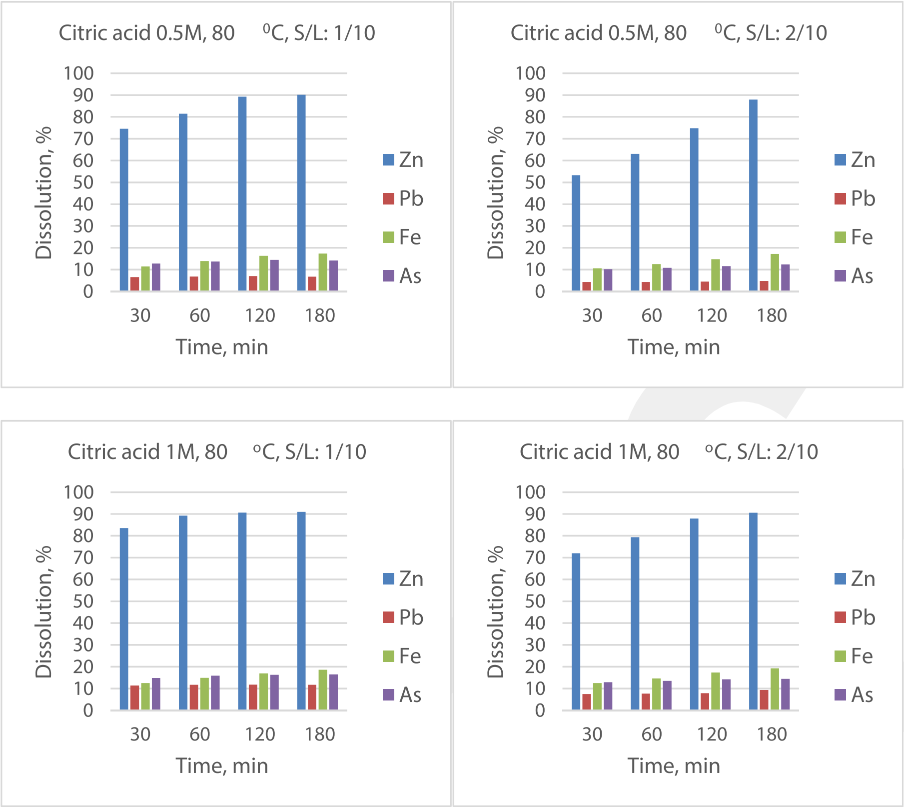


Fig. 6. Effect of solid/liquid ratio on dissolution at 80 °C, and 0.5 M and 1 M citric acid concentration.

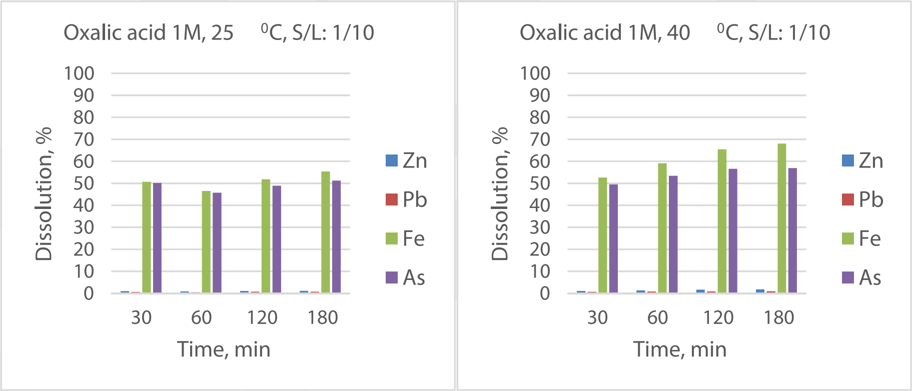


Fig. 7. Effect of temperature on dissolution at 1M oxalic acid concentration.

the iron and arsenic are slightly concave shape, which is considered by a protracted induction age. 68.1% Fe and 57% As were taken from the tailing under the following conditions: 1.0 M oxalic acid, 40 °C leaching temperature, 180 min leaching time. The effect of solid/liquid ratio on dissolution was studied through a series of tests performed at 60 °C and 1.0 M. The metal dissolutions in the oxalic acid solution as a function of leaching time for these tests is designed in Fig. 8.

As is shown in Fig. 8, the iron and arsenic dissolutions are practically dependent on the leaching temperature and oxalic acid concentration, meaning that the solid/liquid ratio is a significant parameter for the iron and arsenic dissolution from the flotation tailing. Compared to 25 and 40 °C leaching temperature, the iron and arsenic dissolutions were slightly increased at 60 °C when the solid/liquid ratio was kept at 1/10.74.3% Fe, 60% As were recovered by using 1.0 M oxalic acid, 1/10 solid/liquid ratio, 60 °C leaching temperature and 180 min leaching time while the zinc and lead dissolutions were determined as less than 10%. Goethite (α-FeOOH), which is a dominant mineral phase in the flotation tailing, has a slightly different free energy of formation. The thermodynamics of goethite dissolution was investigated by Cornell and Schwertmann (1996). A slightly acidic oxalic acid solution (pH 2.0–4.0), the dissolution of goethite is represented by the following equation:

$$FeOOH + HC_2O_4^- + 3H^+ = [FeHC_2O_2]^{2-} + 2H_2O \tag{13}$$

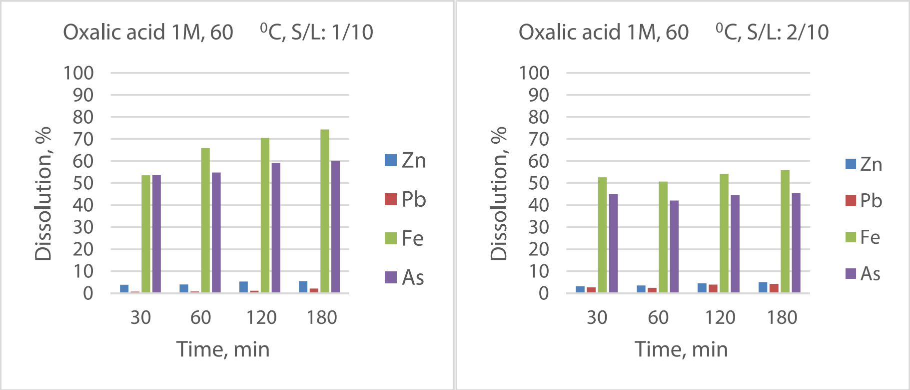


Fig. 8. Effect of solid/liquid ratio on dissolution at 60 °C and 1 M oxalic acid concentration.

3.5. Development of the AHP model

In the present study, three main criteria were determined as the main factors to select an acid type for the dissolution of zinc from the flotation tailing, namely leaching parameters, dissolution, and environmental, each with explicit sub-criteria. The main criteria and sub-criteria for these selections are given in Table 3. Firstly, the AHP model should be established to govern the hierarchical construction of the decision-making problem (Kursunoglu and Onder, 2015; Kursunoglu et al., 2017). This model categorizes the objective, all decision criteria, and options into three main degrees. The upper degree (Degree 1) denotes the main objective of choosing an acid type. Degree 2 indicates the main criteria and sub-criteria. Degree 3 covers the decision options that affect the acid type selection. The AHP diagram for selecting the optimum acid type for processing the flotation tailing is shown in Fig. 9.

3.6. Pair-wise comparisons

The objective of the present work is to predict that acid type is the most appropriate for the dissolution of zinc, lead, iron, and arsenic from the flotation tailing. The problem of acid type selection split into a hierarchical assembly (Fig. 9). Espiari et al. (2006) was handled for the determination of pair-wise matrices and sensitive examination. The pair-wise comparison matrices are divided into the criteria by the specialists that are professional in the field of hydrometallurgical processes. comparison Saaty's 9-point scale factor is given in Table 1. The pair-wise comparison matrices are mutual (in allocating a rate from 1 to 9 to the comparison matrix between the criteria i and j, the mutual value relates to the comparison between j and i). Calculations of *CR, CI and* λ_{max} are utilized with relating to the theoretic description shown in Section 2.1. Parallel stages are reiterated for stabilizing and shaping of primacies of the other pair-wise comparison matrices, which are recognized for acid type choice. *CR* rates of pair-wise comparison matrices change between 0 and 0.10 in the present work. It is concluded that all comparisons are reliable. Table 4 demonstrates the pair-wise comparison matrix concerning the main criteria.

Table 4 shows the concluded outcomes. It is obvious that the leaching parameters main criterion is the most crucial factor (primacy rate: 0.635), tracked by the dissolution and environmental main criteria, respectively. Tables 5–7 demonstrate the primacy rates of each sub-criterion. Acid concentration is the greatest vital sub-criterion with a grade of 0.540 in the leach parameters main criterion. Zinc and lead are the greatest significant sub-criteria with a grade of 0.450 in the dissolution main criterion. Selectivity and Potential toxicity have equal importance with a grade of 0.500 in the Environmental main criterion.

Options were confronted with pair-wise in accordance to each of the sub-criteria. Tables 8–17 depict the research professional team's judgment of options contrary to each of the sub-criteria.

The goal of the acid type selection is shown in Fig. 10. It is decided from Fig. 10 that sulfuric acid, with a ranking of 0.541, is the most favored, tracked by citric acid and oxalic acid. The proportion primacies of sulfuric acid, citric acid and oxalic acid are 54.1%, 28.2% and 17.7%, respectively.

The action diagram (Fig. 11) shows the primacies of the final options in light of the main criteria. When the leach parameters and dissolution main criteria are conceived, sulfuric acid is superior to citric and oxalic acid. When the environmental main criterion is imagined, citric and oxalic acid is better than sulfuric acid. However, it can be seen from the oxalic acid leaching tests (section 3.4), when oxalic acid was used, zinc was poorly dissolved and iron and arsenic co-dissolutions increased significantly. These increases create a problem in the downstream process such as impurity removal stages followed by solvent extraction (SX) and

Table 3
Main criteria and sub-criteria utilized in the AHP model.

Main Criteria	Sub-Criteria	Depiction
Leach Parameters(C_1)	Temperature (SC_1)	Comprises the temperature affecting dissolution.
	Time (SC_2)	Comprises the amount of time during each metal dissolution.
	Acid Concentration (SC_3)	Comprises the acid concentration affecting dissolution.
	Solid Liquid Ratio (SC_4)	Comprises the solid/liquid ratio affecting dissolution.
Dissolution(C_2)	Zinc (SC_5)	Comprises the zinc dissolution during each acid.
	Lead (SC_6)	Comprises the lead dissolution during each acid.
	Iron (SC_7)	Comprises the iron dissolution during each acid.
	Arsenic (SC_8)	Comprises the arsenic dissolution during each acid.
Environmental (C_3)	–	The environmental main criterion is an important factor that is taken into consideration for strict environmental legislation.

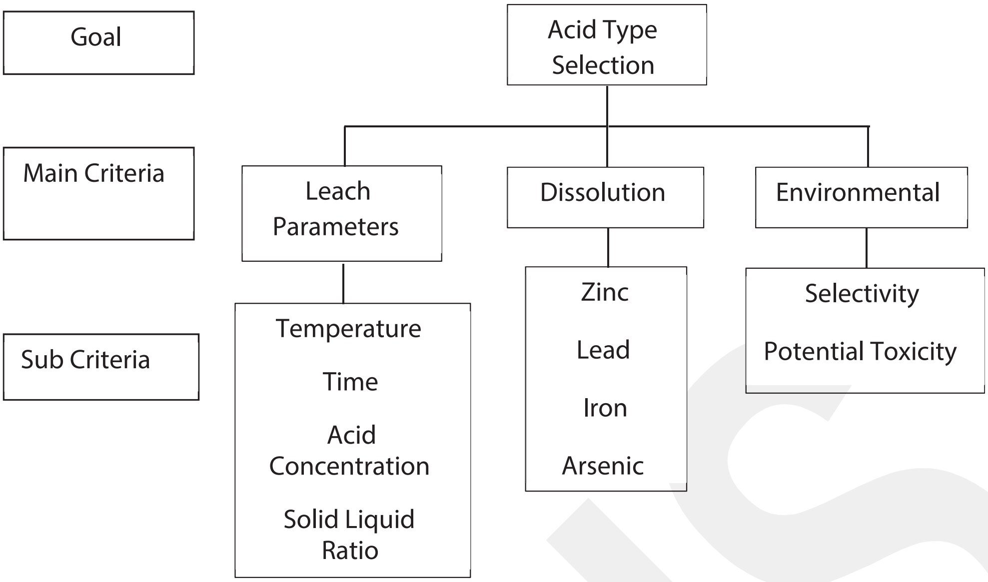


Fig. 9. An appropriate acid type selection by the AHP model.

Table 4
Comparison of the pair-wise matrix by main criteria.

	Leach Parameters	Dissolution	Environmental	Local Primacies
Leach Parameters	1	3	6	0.635
Dissolution	1/3	1	5	0.287
Environmental	1/6	1/5	1	0.078
CR = 0.09				

Table 6
Comparison of sub-criteria by the “Dissolution” main criteria.

	Zinc	Lead	Iron	Arsenic	Local Primacies
Zinc	1	1	9	9	0.450
Lead	1	1	9	9	0.450
Iron	1/9	1/9	1	1	0.050
Arsenic	1/9	1/9	1	1	0.050
CR = 0.00					

Table 7
Comparison of sub-criteria by the “Environmental” main criteria.

	Selectivity	Potential Toxicity	Local Primacies
Selectivity	1	1	0.500
Potential Toxicity	1	1	0.500
CR = 0.00			

Table 8
Comparisons of the options by “Temperature” sub-criteria.

	Sulfuric Acid	Citric Acid	Oxalic Acid	Local Primacies
Sulfuric Acid	1	9	2	0.582
Citric Acid	1/9	1	1/9	0.051
Oxalic Acid	1/2	9	1	0.367
CR = 0.05				

electrowinning (EW). When the dissolution main criteria are thought, sulfuric and citric are superior to oxalic acid.

3.7. *Sensitivity analysis*

To analyze the resistance of the conclusion, decision-makers performed sensitivity analyses. The final primacies of the options are extremely reliant on the primacy masses apportioned to the main criteria; therefore, varying the main criteria primacy rates (i.e., either ascending or descending it) will subsequently change the conclusions or grades of the options. A sensitivity analysis is used to detect the impact of the main criteria on the different acid types. Espiari et al. (2006) Software can afford a sensitivity analysis of the problem. In the sensitivity analysis, it is possible to see how the other criteria, alternatives, and the overall results are affected when a criteria priority is changed. The main criteria and active sensitivity are shown in Fig. 12. Alternatives are presented linear and numerical depending on priorities of main criteria values. The main criterion of environmental (7.8%) is in the third row. Fig. 13 shows the main criteria changes when the environmental criterion increases from 7.8% to 75.3%. It is seen that when the environmental criterion increase to 75.3%, the criteria of leaching parameters decrease from 63.5% to 17% and the main criteria of

Table 5
Comparison of sub-criteria by the “Leach Parameters” main criteria.

	Temperature	Time	Acid Concentration	Solid/Liquid Ratio	Local Primacies
Temperature	1	5	1/3	4	0.289
Time	1/5	1	1/7	1/3	0.055
Acid Concentration	3	7	1	4	0.540
Solid/Liquid Ratio	1/4	3	1/4	1	0.117
CR = 0.07					

Table 9
Comparisons of the options by “Time” sub-criteria.

	Sulfuric Acid	Citric Acid	Oxalic Acid	Local Primacies
Sulfuric Acid	1	4	7	0.696
Citric Acid	1/4	1	4	0.229
Oxalic Acid	1/7	1/4	1	0.075
CR = 0.07				

Table 10
Comparisons of the options by “Acid Concentration” sub-criteria.

	Sulfuric Acid	Citric Acid	Oxalic Acid	Local Primacies
Sulfuric Acid	1	4	7	0.705
Citric Acid	1/4	1	3	0.211
Oxalic Acid	1/7	1/3	1	0.084
CR = 0.03				

Table 11
Comparisons of the options by “Solid/Liquid Ratio” sub-criteria.

	Sulfuric Acid	Citric Acid	Oxalic Acid	Local Primacies
Sulfuric Acid	1	2	8	0.586
Citric Acid	1/2	1	7	0.353
Oxalic Acid	1/8	1/7	1	0.061
CR = 0.03				

Table 12
Comparisons of the options by “Zinc” sub-criteria.

	Sulfuric Acid	Citric Acid	Oxalic Acid	Local Primacies
Sulfuric Acid	1	4	9	0.709
Citric Acid	1/4	1	5	0.231
Oxalic Acid	1/9	1/5	1	0.060
CR = 0.07				

Table 13
Comparisons of the options by “Lead” sub-criteria.

	Sulfuric Acid	Citric Acid	Oxalic Acid	Local Primacies
Sulfuric Acid	1	1/3	1/2	0.157
Citric Acid	3	1	3	0.594
Oxalic Acid	2	1/3	1	0.249
CR = 0.05				

Table 14
Comparisons of the options by “Iron” sub-criteria.

	Sulfuric Acid	Citric Acid	Oxalic Acid	Local Primacies
Sulfuric Acid	1	1	7	0.500
Citric Acid	1	1	4	0.415
Oxalic Acid	1/7	1/4	1	0.086
CR = 0.03				

Table 15
Comparisons of the options by “Arsenic” sub-criteria.

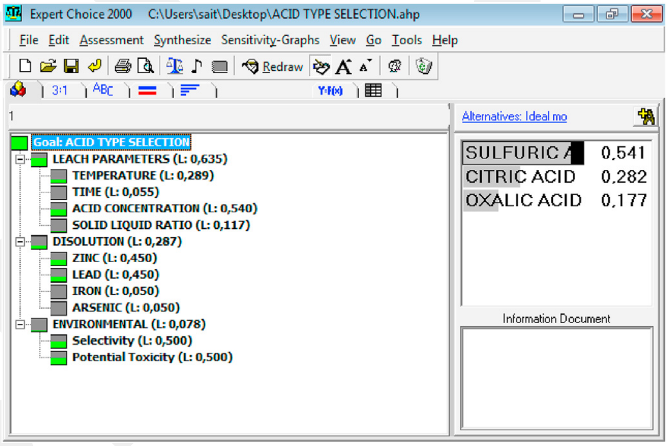
	Sulfuric Acid	Citric Acid	Oxalic Acid	Local Primacies
Sulfuric Acid	1	1	7	0.500
Citric Acid	1	1	4	0.415
Oxalic Acid	1/7	1/4	1	0.086
CR = 0.03				

Table 16
Comparisons of the options by “Selectivity” sub-criteria.

	Sulfuric Acid	Citric Acid	Oxalic Acid	Local Primacies
Sulfuric Acid	1	1/2	9	0.367
Citric Acid	2	1	9	0.582
Oxalic Acid	1/9	1/9	1	0.051
CR = 0.04				

Table 17
Comparisons of the options by “Potential Toxicity” sub-criteria.

	Sulfuric Acid	Citric Acid	Oxalic Acid	Local Primacies
Sulfuric Acid	1	1/7	1/7	0.067
Citric Acid	7	1	1	0.467
Oxalic Acid	7	1	1	0.467
CR = 0.00				

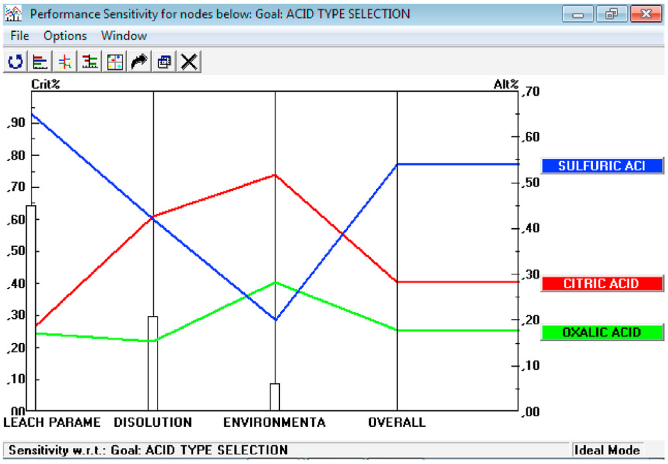

Expert Choice 2000 C:\Users\sait\Desktop\ACID TYPE SELECTION.ahp

Goal: ACID TYPE SELECTION
- LEACH PARAMETERS (L: 0,635)
  - TEMPERATURE (L: 0,289)
  - TIME (L: 0,055)
  - ACID CONCENTRATION (L: 0,540)
  - SOLID LIQUID RATIO (L: 0,117)
- DISOLUTION (L: 0,287)
  - ZINC (L: 0,450)
  - LEAD (L: 0,450)
  - IRON (L: 0,050)
  - ARSENIC (L: 0,050)
- ENVIRONMENTAL (L: 0,078)
  - Selectivity (L: 0,500)
  - Potential Toxicity (L: 0,500)

Alternatives: Ideal mo

SULFURIC A	0,541
CITRIC ACID	0,282
OXALIC ACID	0,177

Fig. 10. The goal of the acid type selection.


Performance Sensitivity for nodes below: Goal: ACID TYPE SELECTION

Sensitivity w.r.t.: Goal: ACID TYPE SELECTION

Ideal Mode

Fig. 11. The action diagram of the acid type selection.

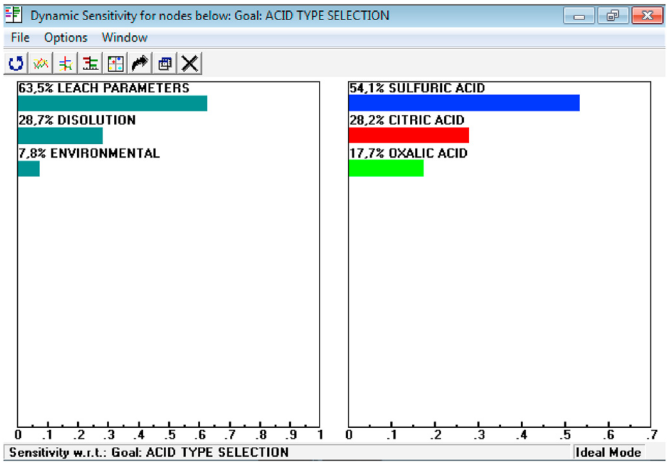


Fig. 12. Main criteria and active sensitivity.

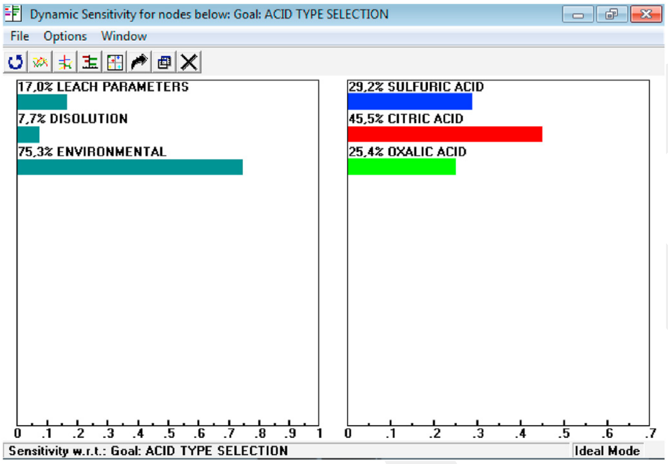


Fig. 13. Main criteria and changes of sensitivity.

dissolution falls from 28.7% to 7.7%. Priorities of alternative acid types for the sulfuric acid decrease from 54.1% to 29.2%, whereas citric and oxalic acid increase from 28.2% to 45.5% and 17.7% to 25.4%, respectively. Therefore, the sub-criteria based on the selectivity and potential toxicity of the pregnant solution obtained, sulfuric acid (29.2%) is better than oxalic acid (25.4%), while the citric acid (45.5%) is the best lixiviant providing high selectivity of valuable components without the leaching of harmful elements.

4. Conclusions

This present work has depicted the utilization of the AHP method for the selection of a suitable acid type to recover zinc and lead from flotation tailing. As a more systematic route, the AHP method can be used for the selection of the most proper acid type. The method is easily implemented by decision-makers as it has a flexible mechanism as well as perceptible. In the given AHP model, sulfuric acid, citric acid, and oxalic acid options were assessed concerning three main criteria and sub-criteria. The assessment publicized that compared to dissolution and environmental main criteria, decision-makers take care of leaching parameters. The AHP data demonstrate that sulfuric acid is appointed as the most suitable acid for the dissolution of metals from the flotation tailing, leaving a considerable amount of iron and arsenic in the residue. Citric and oxalic acids are potentially less harmful to the environment than sulfuric acid as sulfuric acid application leads to such problems as poor selectivity, corrosivity, high acid consumption, the requirement of elevated temperatures and low metal recovery and problematic leach residue. However, in the present study sulfuric acid provided a better zinc dissolution than oxalic acid and better selectivity. Moreover, leaching with oxalic acid led to the high dissolutions of iron and arsenic in the solution. These elements are not valuable components of the tailings. Their extractions lead to the formation of toxic solutions. At the same time, sulfuric acid solution may be re-used after zinc extraction and therefore could not create a real environmental problem. A sensitivity analysis was performed by the AHP software results. It was revealed that when the environmental main criterion increased from 7.8% to 75.3%, the scores of options are obtained as follows: citric acid (45.5%)>sulfuric acid (29.2%)>oxalic acid (25.4%).

CRediT authorship contribution statement

Sait Kursunoglu: Conceptualization, Methodology, Software, Validation, Investigation, Writing - original draft, Writing - review & editing, Supervision, Visualization. **Nilufer Kursunoglu:** Conceptualization, Methodology, Software, Validation, Formal analysis, Writing - review & editing, Visualization. **Shokrullah Hussaini:** Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Writing - original draft, Visualization. **Muammer Kaya:** Conceptualization, Writing - review & editing, Supervision, Visualization.

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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