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Characterization and leaching behavior of mixed oxide-sulfide zinc ore from Hakkari-Türkiye

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Abstract: Besides sulfide ores, non-sulfide and mixed oxide-sulfide zinc have become important resources for zinc. Prior to processing these types of ores using non-conventional methods, chemical and mineralogical characterization is required. In this study, the chemical and mineralogical characteristics of domestic mixed zinc ore were studied using optical microscopy, SEM, XRD, ICP-OES, XRF, FT-IR and TG-DTA. The results of these analyses provide valuable information such as mineral composition, oxide percentage, grain size, mineral constituents, and thermal decomposition, which are essential for determining the mineral processing method. For instance, the ore mineralogy primarily consists of carbonate (smithsonite; ZnCO₃), and less sulfide (sphalerite; ZnS) and oxide (Zincite; ZnO). Besides, the dissolution behavior of the ore was investigated in both alkaline (NaOH, NH4OH) and acidic (HCl, H₂SO₄) solutions under different leaching conditions including concentrations (1, 2, 4, 6 M (N)), particle size (-106 µm, -300 µm), leaching time (30, 60, 120 min), leaching temperature (25, 50, 75°C), and solid/liquid ratio (1:5, 1:10, 1:15 g/dm³). In alkaline solutions, it was observed that the dissolution rate increased with higher concentrations; however, this increase was negligible in acidic solutions. The maximum leaching rates of zinc under constant conditions (-300 µm, 60 min., 25°C, 1:10 g/dm³) were achieved at 68.68%, 55.42%, 74.78%, and 75.45% for NaOH (4M), NH₄OH (6M), HCl (4M), and H₂SO₄ (4N) solutions, respectively.

Keywords: mixed oxide-sulfide zinc ore, characterization, acidic and alkaline leaching

1. Introduction

The minerals of lead and zinc are predominantly found together in three primary types of deposits: sulfide minerals, non-sulfide ores, and mixed sulfide-oxide ores. Sulfide minerals, which are mainly located in the primary sulfide ore bodies, undergo multiple stages of mineralization, and the principal sulfide minerals for zinc and lead are sphalerite (ZnS) and galena (PbS), respectively. Non-sulfide ores can be further categorized as hypogene and supergene weathering types. The main non-sulfide minerals for zinc are smithsonite (ZnCO₃), hydrozincite (Zn₅(OH)₆(CO₃)₂), hemimorphite (Zn₄Si₂O₇(OH)₂· 2H₂O), willemite (Zn₂SiO₄), and zincite (ZnO); associated with cerussite (PbCO₃), a lead carbonate mineral (Gilg et al., 2006; Jia et al., 2016; Moradi and Monhemius, 2011; Abkhoshk et al. 2014; Ehsani et al., 2021).

The mixed sulfide-oxide ores, which are the subject of this study, with complex mineralogy are found in the transition zones within deposits. Noteworthy examples of this type of deposit are the Angouran Zn-Pb ore deposit in Iran and the Lanping Pb-Zn mine in Yunnan province, China. Currently, sulfide and oxide ores are the main raw materials for zinc production, however as these supplies diminish, the exploitation of mixed sulfide-oxide ores is gaining importance. Despite their substantial reserves, the efficient utilization of mixed sulfide-oxide ores remains problematic due to challenges associated with their beneficiation (Gilg et al., 2006; Jia et al., 2016; Kaya et al., 2020; Moradi and Monhemius, 2011).

Mixed sulfide-oxide zinc and lead ores have complex mineralogy that includes sphalerite (ZnS), smithsonite (ZnCO₃), hemimorphite (Zn₄Si₂O₇(OH)₂·2H₂O), galena (PbS), cerussite (PbCO₃), pyrite

(FeS₂), goethite (Fe₂O₃ H₂O), hematite (Fe₂O₃), limonite (FeO(OH) nH₂O), calcite (CaCO₃), dolomite (CaMg(CO₃)₂), gypsum (CaSO₄ 2H₂O), quartz (SiO₂), feldspar, clays, and other minerals. Due to extraction difficulties caused by this complexity, they have been ignored for years but with the development of recent technologies, such as electrowinning (EW), solvent extraction (SX), and leach to chemical (LTC); the interest in these types of ores has increased (Hitzman et al., 2003; Jia et al., 2016; Moradi and Monhemius, 2011).

Acidic and alkaline solutions could be used for leaching of zinc ores (Frenay, 1985; Bodas, 1996; Souza et al., 2007; Wang et al., 2008; Jia et al., 2017; Yang et al., 2022; Liu et al., 2023). Alkaline systems, which include sodium hydroxide (NaOH), ammonium hydroxide (NH₄OH), and ammonia salts, offer several advantages, such as high selectivity (due to minimal iron leaching), low cost, and ease of generation. On the other hand, acidic systems, which consist of sulfuric acid (H₂SO₄), hydrochloric acid (HCl), chlorides (Cl⁻), nitric acid (HNO₃), and nitrates (NO₃⁻), provide high recovery rates, low costs, and the opportunity to utilize solvent extraction and electrowinning methods (Abkhoshk et al., 2014; Ehsani et al., 2019; Ehsani et al., 2021; Jia et al., 2016; Kaya et al., 2020; Moghaddam et al., 2005).

In Türkiye, various non-sulfide and mixed sulfide-oxide zinc ore deposits exhibit differences in mineralogy and grade (DPT, 2001; Hanilci and Ozturk, 2011; Hanilci et al., 2019; Santoro et al., 2013). While the efficient beneficiation of these resources is crucial to the sustainability of zinc production, to the authors' knowledge, there has yet to be a comprehensive study on the leaching behavior of Turkish mixed sulfide-oxide ore, particularly focusing on the dissolution behavior of zinc and lead.

The present research work aimed to comparatively investigate the dissolution behavior of zinc and lead from a local mixed sulfide-oxide (carbonate) Zn-Pb ore sample obtained from the Hakkari region, in southeast Türkiye, in both alkaline (NaOH and NH₄OH) and acidic (H₂SO₄ and HCl) media, and evaluate the effect of leaching conditions.

2. Materials and methods

2.1. Materials

The high-grade and mixed sulfide-oxide (carbonate) zinc ore used in the experiments was obtained from Hakkari Province in Türkiye. The ore sample was crushed, milled, and sieved until the size of all particles became under 300 μ m (d₈₀≈150 μ m). It was then homogenized and kept in the room for 10 days (moisture < 1%) and stored in airtight containers for further characterization analysis and leaching experiments.

2.2. Characterization and analysis

The characterization of the ore sample was conducted by optical microscopy (Olympus DP73, Japan), SEM-EDS (FEI/Philips, Quanta FEG 650, USA), XRD (Rigaku, MiniFlex 600, CuKa, Japan), XRF (Rigaku, ZSX Primus II, Japan), FT-IR (Perkin Elmer, USA) and TG-DTA (Setaram Labsys, France) analysis. To begin with, the chemical composition of the sample was determined by XRF. The XRF analysis results illustrated that the ore contains a high percentage of Fe (27.93%), Zn (11.86%), S (9.99%), Ca (7.10%) and C (4.71%), as well as smaller amount of Si (2.98%), Mg (1.29%), Pb (1.01%) Ba (0.84%), Al (0.61%) and 18.23% loss of ignition (Table 1).

Element	Fe	Zn	Ca	Si	Mg	Pb	Ba	Al	S	С	LOI
Content (%)	27.93	11.86	7.10	2.98	1.29	1.01	0.84	0.61	9.99	4.71	18.23

Table 1. Chemical composition of Zn-Pb ore sample

X-ray diffraction (XRD) analysis of the ore sample has identified the main mineralogical phases included both sulfide and nonsulfide phases; i.e., zinc (Zn) appeared in smithsonite (2θ =25.02°, 32.52°, 38.66°, 42.82°, 46.57°, and 53.60°), sphalerite (2θ =28.58°, 47.52°, and 59.02°) and zincite (2θ =34.64° and 57.56°) forms, associated with calcium is in the form of calcite (2θ =29.42°, 31.00°, 40.78° and 48.58°), dolomite (2θ =29.42°, 21.20°, 26.58°, 31.00°, 33.06°, 50.52°, 51.38°, 53.48° and 59.06°) and gypsum (2θ =11.6°) forms. On the other hand, for iron (Fe), the most abundant element in the ore, only peaks belonging to goethite (2θ =17.80°, 21.12°, 26.58°, 36.20°, 36.58°, 37.02°, 37.40° and 43.28°) could be

detected while the peaks corresponding to siderite (FeCO₃) were not distinguishable due to their similarity to smithsonite. Additionally, a few small peaks belonging to quartz (2θ =20.10° and 26.32°) occurred (Fig. 1.).

Hakkari's supergene non-sulfide Zn-Pb deposit, from which the sample was taken, was formed by the oxidation (alteration) of both sulfide and hypogene non-sulfide deposits, which are often found in carbonate host rocks. Therefore, this type of ore contains Zn (smithsonite, hydrozincite, hemimorphite, and sauconite), Pb (cerussite and Anglesite), and Fe (goethite and hematite) minerals as expected (Santoro et al., 2014).



Fig. 1. XRD pattern of Zn-Pb ore sample

Thermal analysis (TG-DTA) was fulfilled on the sample at a rate of 10 °C · min⁻¹, and the TG curve displays weight loss regions. The first small one refers to the loss of moisture and water, the second one refers to the decomposition of gypsum between 110 and 150°C (Paulik et al., 1992). The third weight loss region refers to the decomposition of goethite (Naono et al., 1987) and smithsonite (Zhang et al., 2014) which begin at about 200°C and finishes at about 450°C , the last one is observed at temperatures over 650°C refer to calcite, dolomite (Olszak-Humienik and Jablonski, 2015) and sphalerite (Gulyaeva et al., 2018) thermal decompositions. Finally, the overall mass loss reaches 17.64% at 1000°C.

According to DTA curve endothermic peaks probably assigned to decomposition reaction of gypsum (131°C; Paulik et al 1997), goethite (283°C), smithsonite (350°C), calcite and dolomite (522°C, 764°C & 822°C) and exothermic peaks relevant to the decomposition of sphalerite (554°C & 783°C; Baláž et al., 1992) accomplished with some undefined peaks at 434°C, and 911°C (Fig. 2. Left).

Fourier Transform Infrared (FTIR) spectrum of sample, the characteristic infrared band $ZnCO_3$ observed at 750 cm⁻¹, together with other vibration bands observed at 595 cm⁻¹ (Fe–O), 668 cm⁻¹ (CaCO₃), 799 cm⁻¹ (FeOOH), 872 cm⁻¹ (CO₃^{2–}), 1031 cm⁻¹ (Zn–O), 1112 (SO₄^{2–}), 1416 cm⁻¹ (CO₃^{2–}), 3180 and 3391 (OH⁻) (Frost et al., 2008; Granados Oliver et al., 2020) indicate that ore sample consists of carbonate, oxide and hydroxide phases, which is in line with the results of previous mineralogical analyses (Fig. 2. Right).

As can be seen from the optical microscope (OM) images, the ore sample consists of irregular and shapeless particles in varied sizes, mostly yellow or light brown while others are white, grey, black, dark blue, or colorless. Additionally, most of the particles are matte, and rarely transparent or metallic sheen. Besides, in SEM-EDS Spectroscopy of the sample, it is seen that some zinc-containing particles contain both C and S which means that minerals in both carbonate and sulfide phases exist (Fig. 3). Therefore, it is estimated that at least some Zn containing particles consist of both carbonate (oxide) and sulfide mineral phases. Furthermore, SEM-EDS mapping of the sample indicates that a substantial proportion of the particles include Fe, while particles with high concentrations of Ca are also present, with some having Mg as well. It is noticeable that the amount of Ca and Mg in SEM-EDS mapping is fully consistent with the results of the XRF analysis (Table 1.). Additionally, others containing Zn are mostly free of other elements, while some contain minor amounts of Fe and/or Ca (Fig. 3 down).



Fig. 2. TG-DTA pattern (Left) and FT-IR Spectrum (Right) of Zn-Pb ore sample



Fig. 3. Optical microscope image (left), SEM-EDS Spectroscopy (Right), and SEM-EDS maps of Mg, Ca, Fe and Zn (down) of the ore sample

2.3. Leaching experiments

Four reagent grade chemicals (Merck), sodium hydroxide (NaOH; 99%), ammonium hydroxide (NH₄OH; 25%), hydrochloric acid (HCl; 37%), and sulfuric acid (H₂SO₄; 95%), which used in all experiments, diluted with distilled water for preparing leaching solutions at desired concentrations (1M, 2M, 4M and 6M). It should be mentioned that for equal comparison, 1N, 2N, 4N, and 6N concentrations of sulfuric acid, a divalent acid, were utilized in the study. Then, 40 g of the ore sample was added to 400 dm³ of solution in a 600 dm³ converted glass beaker and agitated with a magnetic stirrer. The experiments were conducted under constant conditions of a solid-liquid ratio of 1:10 g/dm³, agitation speed of 650 rpm (which is enough to keep all particles in suspense), and room temperature (25°C \pm 2). Potential chemical reactions for leaching experiments are given in Table 2 and Table 3. The

(1)

dissolving ratio of metals was determined using Eq. 1, where the M is the amount of Metal (%) in the sample.

Table 2. Potential chemical reactions for leaching in alkaline solution (NaOH and NH4OH)

Reactions	Reference
$ZnCO_{3(s)} + 4NaOH_{(aq)} + 2H_2O_{(l)} \rightarrow Na_2Zn(OH)_{4(aq)} + Na_2CO_{3(aq)}$	(Ehsani et al., 2019)
$PbCO_{3(s)} + 2NaOH_{(aq)} + H_2O_{(l)} \rightarrow Na_2Pb(OH)_{4(aq)} + Na_2CO_{3(aq)}$	(Chenglong et al., 2008)
$ZnCO_{3_{(aq)}} + 4NH_4OH_{(aq)} \rightarrow Zn (NH_3)_4CO_{3_{(aq)}} + 4H_2O_{(l)}$	(Kaya et al., 2020)

Table 3. Potential chemical reactions for leaching in acidic solution (H₂SO₄ and HCl)

Reactions	Reference
$ZnCO_{3(s)} + H_2SO_{4(aq)} \rightarrow ZnSO_{4(aq)} + CO_{2(q)} + H_2O_{(l)}$	(Ozsarac et al., 2024)
$PbCO_{3(s)} + H_2SO_{4(aq)} \rightarrow PbSO_{4(aq)} + CO_{2(g)} + H_2O_{(l)}$	(Ozsarac et al., 2024)
$ZnS_{(s)} + H_2SO_{4(aq)} \rightarrow ZnSO_{4(aq)} + H_2S_{(g)}$	(Deng et al., 2022)
$ZnCO_{3(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$	(Kaya et al., 2020)
$PbCO_{3(s)} + 2HCl_{(aq)} \rightarrow PbCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$	(Hendriks et al., 2018)
$ZnS + 2HCl_{(aq)} + 1.5O_2 \rightarrow ZnCl_{2(aq)} + H_2O + SO_{2(g)}$	(Soib et al., 2019)

Dissolving ratio of metal, M (%)= $\frac{M_{ore} - M_{residue}}{M_{ore}}$ ×100

In addition to reagent type, other influencing factors such as reagent concentration, leaching time (30, 60, 120 min), leaching temperature $(25, 50, \text{ and } 75^{\circ}\text{C})$, solid-to-liquid ratio $(1:5, 1:10, \text{ and } 1:15 \text{ g/dm}^3)$, and particle size distribution of the ore, have been examined. In high temperature $(50 \text{ and } 75^{\circ}\text{C})$ experiments, a 600 dm³ sealed glass reactor and reflux condenser were used, and in tests at varied S/L ratios, the amount of solid ore samples kept constant whereas the amount of solutions changed. At the end, the residues were centrifuged, washed with distilled water, filtered, dried overnight at 105°C then weighed and kept in sealed containers for future analysis.

3. Results and discussion

3.1. Effect of concentration on dissolution rate

The effect of alkaline (NaOH and NH₄OH) and acidic (H₂SO₄ and HCl) solution concentrations was examined by measuring the Zn, Pb, and Fe content of the leaching residue. Fig. 4 shows leaching studies with various concentrations (1M, 2M, 4M, and 6M) for 60 min, S/L ratio of 1:10 g/dm³, agitation speed of 650 rpm, particle size distribution of -300μ m, and at ambient temperature of 25°C (298 K).

The concentrations of acids have a negligible effect on Zn dissolution, the highest ratios were obtained as 75.32% for $4 \text{ N H}_2\text{SO}_4$ and 74.78% for 4 M HCl acid concentration. However, lead exhibits a different dissolution behavior, while it is slightly soluble in H₂SO₄ (max. 8.56% at 4 N concentration), the dissolution in HCl increased with increasing concentration and reached 78.38% at 4 M concentration. It was also determined that acids dissolved almost all the gypsum, calcite, and dolomite in the ore (99% Ca and 95% Mg were dissolved).

The concentration of alkaline reagents (NaOH and NH₄OH) has a pronounced effect on the dissolution of zinc, as can be seen in Fig. 4 The dissolution of zinc (Zn) increased with increasing concentration and reached the maximum rate of 68.68% and 55.42% in 6 M concentration of NaOH and NH₄OH, while, for 4 M concentration these are 68.60% and 49.46%, respectively. On the other hand, the dissolution rates of lead (Pb) and iron (Fe), as well as calcium (Ca) and magnesium (Mg), in alkaline solutions are negligible. For NaOH and NH₄OH solutions, the highest dissolution ratios were attained 3.99% for Fe, 14.19% for Pb and 1.74% for Fe, 3.27% for Pb, respectively.

The leaching ratios of Zn are consistently low in all cases. This is due to the low solubility of sphalerite and zincite in acidic and alkaline media (Jia et al., 2016). Additionally, Fe has lower solubility in alkaline solvents. This leads to the conclusion that alkaline solutions selectively dissolve zinc more

effectively. Lead, on the other hand, was dissolved well only in HCl solutions, and at very low rates in other solvents.

XRD patterns of residual solids upon leaching (4N, 60 min, 25°C, S/L 1:10 g/dm³, -300μ m) of the ore sample as depicted in Fig. 5, demonstrate that sphalerite peaks remained insoluble in both alkaline and acidic solutions, hence preventing the total Zn dissolution ratio from achieving elevated levels. On the other hand, the reduction in peak intensities belongs to calcite and dolomite illustrating that they were only soluble in acidic solutions, but not in alkaline ones. Although the intensity of the goethite peaks decreases slightly, they are detected in the residues from all solutions.



Fig. 4. Effect of concentration on dissolution ratios (%) of Zn, Pb and Fe (60 min, 25°C, 1:10 g/dm³, -300 μm, 650 rpm)



Fig. 5. XRD pattern of the ore sample and leaching residues obtained after leaching in various media (4 N, 60 min, 25°C, 1:10 g/dm³, -300 μm, 650 rpm)

3.2. Effect of leaching time on dissolution rate

In this stage, the effect of leaching time on dissolution ratios of targeted metals was investigated. Fig. 6 illustrates the dissolution ratios of Zn, Pb, and Fe over leaching times of 30, 60, and 120 minutes. These experiments were conducted with a concentration of 4M (4N for H_2SO_4), S/L ratio of 1:10 g/dm³, temperature of 25°C, and stirring speed of 650 rpm. The results indicate that Zn and Pb leaching in H_2SO_4 , HCl, and NH₄OH solutions are slightly improved by increasing leaching time, reaching their highest values for Zn at 78.79%, 76.95%, and 54.83% and for Pb at 15.72%, 81.71% and 4.60% after 120 minutes of leaching time, respectively.

Conversely, in NaOH solutions leaching time has a slightly negative effect on Zn and Pb leaching ratios which are 71.18%, 68.60%, 67.62% for Zn, and 21.05%,14.19%, 10.12% for Pb, at 30, 60 and 120 minutes of stirring time, respectively. This may be due to the re-precipitation of Zn and Pb containing phases. Since the leaching time has relatively few advantages or even negative effects on dissolution ratios; the optimum leaching time in the study was determined as 60 minutes.



Fig. 6. Effect of Leaching time (min.) on dissolution ratios (%) of Zn, Pb and Fe (4 N, 25°C, 1:10 g/dm³, -300 μm, 650 rpm)

3.3. Effect of particle size on dissolution rate

The effect of the particle size distribution of ore on leaching efficiency was investigated for two different particle sizes: $-300 \ \mu\text{m} (d_{80} \approx 150 \ \mu\text{m})$ and $-106 \ \mu\text{m} (d_{80} \approx 80 \ \mu\text{m})$ under constant experimental conditions (4 N, 1:10 S/L, 60 min, 650 rpm, and 25°C). The results demonstrate that a reduction in particle size generally leads to a slight increase in the leaching ratios of Zn and Pb across all solutions, while simultaneously enhancing the leaching ratio of Fe. For particle size up to 106 μ m leaching ratio of Zn, Pb, and Fe are measured as 75.74%, 13.97%, and 24.38% for H₂SO₄; 75.58%, 81.01%, and 27.88% for HCl; 69.24%, 14.76%, and 5.03% for NaOH; and 53.17%, 1.99%, and 11.72% for NH₄OH solutions, respectively (Fig. 7). In general terms, in this study, the effect of particle size on dissolution rates of target metals (Zn, Pb, Fe) does not stand out as dominant, and significant. Thus, it does not need to go down to fine particle size (in this case, $-106 \ \mu$ m) and an efficient leaching process could be achieved at optimum particle size (i.e., $-300 \ \mu$ m).

3.4. Effect of temperature on dissolution rate

As shown in Fig. 8, leaching experiments using H_2SO_4 solution at temperatures of 25°C, 50°C, and 75°C resulted in dissolution rates of 75.32%, 77.59%, and 82.35% for Zn, 8.56%, 5.24%, and 5.04% for Pb, and 23.65%, 28.88%, and 50.49% for iron Fe, respectively. In contrast, HCl leaching tests yielded dissolution



Fig. 7. Effect of particle size (µm) on dissolution ratios (%) of Zn, Pb and Fe (4 N, 60 min, 25°C, 1:10 g/dm³, 650 rpm)



Fig. 8. Effect of temperature (°C) on dissolution ratios (%) of Zn, Pb and Fe (4 N, 60 min, 1:10 g/dm³, -300 μm, 650 rpm)

rates of 74.78%, 78.44%, and 86.71% for Zn; 8.38%, 85.09%, and 95.39% for Pb; and 23.80%, 30.92%, and 68.47% for Fe at the same temperatures. The results indicate that the leaching of Zn and Fe in the H_2SO_4 solution is significantly influenced by the reaction temperature. However, increasing the temperature has an adverse effect on the dissolution of Pb in sulfuric acid, likely due to lead re-precipitating as PbSO₄ in the residue (Moradi and Monhemius, 2011).

Similarly, the reaction temperatures affect the leaching of Zn, Pb, and Fe in HCl solutions, achieving the highest dissolution rates of Zn (86.71%) and Pb (95.39%) at 75°C. Notably, the dissolution rates of Ca, Mg, and Fe in HCl solutions increased dramatically with temperature, reaching their peaks at 75°C with rates of 99.81%, 94.60%, and 68.47%, respectively. This suggests that although HCl leaching results in high Zn and Pb dissolution at elevated temperatures, the selectivity decreases significantly, leading to an increase in undesirable ions in the leaching solution.

Conversely, the leaching experiments in NaOH and NH₄OH solutions yielded Zn dissolution rates of 68.60%, 68.02%, and 67.71% for NaOH, and 49.46%, 61.86%, and 59.19% for NH₄OH. This indicates that higher temperatures negatively affect Zn dissolution in NaOH solutions. For the ammonia solutions, although there is an increase in dissolution from 25°C to 50°C, higher temperatures result in lower Zn dissolution rates, likely due to the loss of ammonia through evaporation. Furthermore, the dissolution rates of Fe and Pb in both alkaline solutions are very low, with Fe rates below 4% and Pb rates below 16.5%, indicating a more selective leaching process for Zn and Pb. These findings align with those from the authors' previous studies. (Ehsani et al, 2019; Ehsani et al, 2021)

3.5. Effect of solid/liquid ratio on dissolution rate

The effect of varying solid/liquid (S/L) ratios (1:5, 1:10, and 1:15 g/dm³) on the dissolution of Zn, Pb, and Fe in H₂SO₄, HCl, NaOH, and NH₄OH solutions was evaluated under consistent leaching conditions (4 N, 60 min, 25°C, particle size: -300μ m, stirring speed: 650 rpm), as illustrated in Fig. 9. In acidic solutions, the leaching efficiency of Zn slightly decreased with increasing S/L ratios, while it remained relatively constant in alkaline solutions. Specifically, Zn dissolution ratios for three different S/L ratios (1:5, 1:10, and 1:15 g/dm³) were found to be 66.88%, 75.32%, and 76.22% in H₂SO₄; 70.83%, 74.78%, and 74.91% in HCl; 66.67%, 68.60%, and 68.26% in NaOH; and 46.86%, 49.46%, and 49.50% in NH₄OH solutions, respectively (Fig. 9).

In terms of Pb dissolution rates, the maximum values observed in H_2SO_4 , NaOH, and NH₄OH solutions were limited to 8.56%, 15.30%, and 4.48%, respectively. However, Pb was substantially dissolved in HCl solution, with rates ranging from 61.43% to 72.83%. For iron, considerable solubility was observed in acidic solutions, with maximum dissolution rates of up to 28.50% in H_2SO_4 and 29.74% in HCl. Conversely, in alkaline solutions, Fe barely dissolved, with rates of less than 6.58% in NaOH and 5.18% in NH₄OH. Under these experimental conditions, NH₄OH displayed the highest selectivity but the lowest efficiency.



Fig. 9. Effect of solid/liquid (S/L) ratio (g/dm³) on dissolution ratios (%) of Zn, Pb, and Fe (4 N, 60 min, 25°C, -300 μm, 650 rpm)

4. Conclusions

In this study, the characterization of mixed carbonate-sulfide Zn-Pb ore from Hakkari region of Türkiye and its leaching behavior in alkaline and acidic media was examined. The complex structure of the ore was determined by mineralogical and metallurgical analysis such as optical microscopy, SEM-EDS,

XRD, XRF, ICP-OES, FT-IR, and TG-DTA. The results showed that the main Zn minerals in the ore are smithsonite, sphalerite, and zincite, along with goethite, calcite, dolomite, gypsum, and quartz as gangue minerals.

The effect of leaching parameters, including concentration (1, 2, 4, and 6M(N)), leaching time (30, 60, and 120 min.), and particle size distribution (-300 and -106 µm), Solid-liquid ratio (1:5, 1:10 and 1:15 g/dm³) and leaching temperature (25°C, 50°C and 75°C) were investigated in four different solutions (NaOH, NH₄OH, HCl and H₂SO₄). The concentration of the solution has a positive effect on dissolving up to 4M(N), but only in NH₄OH, dissolution ratios continue to improve even at the highest concentration of 6 M. Additionally, extending the leaching time slightly improves the dissolution ratios of Zn and Pb, except in NaOH solutions, where longer leaching times result in decreased dissolution ratios. Moreover, reducing the particle size of the ore beneficially affects the dissolution rates of Zn, Pb, and Fe across all solutions. Higher temperatures improve the dissolution of Zn and Fe in acidic solutions, with HCl having the highest Zn and Pb leaching ratio at 75°C, while, in alkaline solutions, as the S/L ratio decreased, Zn dissolution rates slightly increased in acidic solution, while in alkaline solutions these rates remained comparatively constant.

The inherent complexity (consisting of both carbonate and sulfide phases) of the ore poses significant challenges in achieving optimal metal dissolution rates. Specifically, sphalerite remained undissolved in all four kinds of solutions, which limited the overall dissolution of zinc. To improve dissolution efficiencies, it is recommended to investigate the application of thermal, chemical, or mechanical pretreatments, in addition to exploring pressure or oxidative leaching techniques.

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