

## Sphalerite leaching in acid media: a review

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### ARTICLE INFORMATION :

<https://doi.org/10.30544/MMD8>

Received: 20 June 2023

Accepted: 30 June 2023

Type of paper: Review paper



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### ABSTRACT

The reserves of rich ores, from which the production of zinc by the existing conventional roasting-leaching-electrowinning process is technologically possible and economically justified, are decreasing year by year. For this reason, increasing attention has been directed towards researching the possibility of obtaining zinc from complex polymetallic ores with a low metal content, adhering to sustainable development goals following strict environmental regulations. Leaching procedures are commonly utilized for the processing of such mineral raw materials.

As sphalerite is the widespread and most significant mineral of zinc sulfide, a large part of the research focuses on studying the behavior of sphalerite in the leaching process. This paper reviews the existing knowledge about the leaching of sphalerite in acidic solutions as well as the phenomena accompanying the dissolution process. Special attention is given to research related to the kinetics and mechanism of sphalerite oxidation in an acidic medium influenced by various oxidants, such as hydrogen peroxide, oxygen, dichromate ions, nitrate and nitrite ions, ferric and cupric ions, and others. All these results enable the development of new technological procedures to produce zinc from low-grade and complex ores while meeting increasingly rigorous environmental requirements.

**Keywords:** sphalerite, acid solution, oxidative leaching, kinetics, mechanism.

### 1. Introduction

Sphalerite is the most common and significant zinc sulfide mineral. In nature, it often contains iron (up to 20%), manganese (up to 8%) and cadmium (up to 2.5%) as isomorphous impurities (Janjić and Ristić, 1995). Therefore, part of Zn is almost always replaced by Fe, commonly by Mn and Cd, and more rarely by Ba, In, Te, and Hg. For these reasons, sphalerite would be more suited to the formula (Zn, Fe, Mn, Cd)S in which, ZnS significantly outweighs the other components in quantity. Sphalerite with high iron content is known as marmatite, those with high cadmium are referred to as cristophites.

It occurs in deposits of different origins, formations, and composition in almost all major ore-bearing areas and is often found in favorable concentrations. It is a prevalent finding that all ore masses, where the formation and preservation of sulfide minerals was possible, contain sphalerite. It is mostly found in hydrothermal deposits - veins, metasomatic and impregnation, of different compositions and across all depth levels. Galena, chalcopyrite, calcite, and quartz are the most

important associated minerals. It is almost a regular phenomenon that in the deeper parts of such deposits the content of galena gradually decreases, while the content of sphalerite increases.

Sphalerite is typically associated with other sulfides, such as chalcopyrite, pyrite, and galena. They are commonly separated from each other by flotation methods. However, sphalerite can occasionally occur in a dispersed form alongside other sulfide minerals and tailings, presenting a complex mineralogical composition and fine-grained structure in the form of impregnations, inclusions, and both simple and complex intergrowths (Sokić et al, 2022).

The conventional method of obtaining zinc from sphalerite involves a roasting-leaching-electrowinning process. The roasting process emits a large amount of SO<sub>2</sub> gas that must be captured and converted to sulfuric acid. Hydrometallurgical techniques for the processing of low-grade and complex sulfide ores and concentrates are becoming more and more attractive as sulfur dioxide emission becomes more stringent (Estrada-de los Santos et al., 2016). In the leaching process, efficient extraction of zinc can be achieved regardless of the concentration of iron in zinc ores and concentrates (Souza et al., 2007).

The benefits of direct leaching include enhanced metal recoveries and the transformation of sulfide sulfur (S<sub>2</sub>-/S) into its elemental

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form (S). The latter remains in the leach residue, effectively preventing sulfur dioxide emissions. However, sulfur formed during leaching with oxidizing agents is deposited on the surface of un-leached mineral grains and hinders their further dissolution (Dutrizac, 1990; Dutrizac, 2006; Lochmann and Pedlik, 1995; Aydogan, 2005; Peng, 2005; Bobeck and Sue, 1985; Sokić et al., 2010; Sokić et al., 2012). Therefore, finding new ways to improve the dissolution rate and achieve more efficient extraction of zinc from sphalerite remains a current issue.

Acidic and alkaline solutions can be used for the leaching. Alkaline systems include caustic soda, ammonia and ammonia salts, and acidic ferric sulfate, chlorine and chlorides, nitric acid and nitrates, and sulfuric acid with and without oxidants. During the leaching of sulfide minerals, sulfide sulfur is oxidized to sulfate in an alkaline solution, and to elemental sulfur and sulfate in acidic solutions (Havlic, 2008). The maximum content of elemental sulfur during acid leaching in the presence of an oxidant is at a temperature of around 383 K. Above this temperature, the sulfate content increases at the expense of elemental sulfur.

The solution composition is a very important factor that determines the rate of the sulfide oxidation reaction, as well as the end product of the reaction. A common characteristic of all leaching solutions is that they must contain an oxidant.

Ferric and cupric ions are used as oxidants for sphalerite leaching in sulfate and chloride solutions. However, the corrosive properties of iron (III) chloride and the slow and insufficient leaching of sphalerite with iron (III) sulfate have directed research into the use of other oxidizing agents in the leaching process. In addition to the mentioned oxidants, other oxidizing agents were also used, such as hydrogen peroxide, dichromates, oxygen, nitrates and nitrites, permanganates, chlorates, ozone, and others. The application of mechanical activation, microwaves, and organic compounds has also been explored, as well as the use of silver ions to develop technological processes for zinc extraction that meet technological, economic, and ecological criteria. There are numerous studies in which the behavior of sphalerite in acidic solutions was examined. Hence, literature offers extensive knowledge on the mechanism and kinetics of sphalerite leaching in acid media.

This paper provides an overview of the outcomes of sphalerite leaching in acid solutions, with a focus on different oxidants introduced. It includes a concise review of the dissolution mechanism and kinetics of sphalerite in various media, the types of reaction products formed, and the levels of metal leaching achieved under different oxidative conditions. These conditions comprise variations in the concentration of the leaching agent and oxidant, the Solid-to-Liquid (S:L) ratio, temperature, time, and stirring speed, among others.

## 2. Effect of Fe content on sphalerite stability

Iron's presence in sphalerite significantly affects its dissolution rate. Kammel et al. (Kammel et al., 1987) and Crundwell (Crundwell, 1988) observed that the rate at which sphalerite dissolves is directly correlated with the concentration of iron impurities in the solid. Palencia Perez and Dutrizac (Palencia Perez and Dutrizac, 1991) explored how the iron content in the sphalerite structure influences its leaching in ferric sulfate and ferric chloride media. They discovered that as the iron content in the sphalerite structure increases, the sphalerite leaching rate also rises, and the activation energy required decreases, in both leaching systems.

With the increase of iron content in sphalerite from 0.04 to 12.5%, the leaching rate increases, and the activation energy decreased from 72 to 41 kJ/mol in the ferric sulfate leaching system. Leaching rates in the ferric chloride system also increased with increasing sphalerite iron content. The activation energies determined for the ferric chloride system varied from 81 to 39 kJ/mol, and the activation energy of the reaction, where ferric sulfate is the reactant, decreases with an increase of the iron content in sphalerite. Sphalerite dissolution kinetics are similar in both systems, and the reaction is controlled by charge transfer on the sphalerite surface.

Similar results were obtained by Weisener et al. (Weisener et al., 2004) when testing sphalerite leaching with different iron content in O<sub>2</sub>-purged HClO<sub>4</sub>. They found that the leaching rate increased with increasing Fe content in sphalerite. After 7 days of leaching, at 85 °C, 89% Zn was dissolved from sphalerite with 12.90% Fe, while, under the same leaching conditions, 49% Zn was dissolved from sphalerite with 0.45% Fe. With increasing Fe content in sphalerite, the dissolution activation energy decreases (i.e. 63±6 and 39±2 kJ/mol for the 0.45 and 12.90% Fe-containing sphalerite, respectively). The reason for the decrease in the dissolution rate of Zn during leaching is the formation and growth of the polysulfide surface layer, which is formed during the initial period of rapid leaching. Elemental sulfur, which is formed during the following period of slow leaching, is very porous and does not further affect the rate of leaching. As the concentration of Fe in sphalerite increases, the rate of dissolution increases, which leads to an increase in the concentration of formed polysulfide and elemental sulfur.

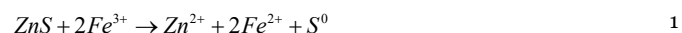
Baldwin and Demopoulos (Baldwin and Demopoulos, 1995) studied the pressure leaching of six zinc concentrates in which iron is present in very different forms. They found that if iron is present as a separate mineral, the behavior of that mineral during leaching greatly affects the efficiency of the zinc concentrate leaching process. When a sphalerite concentrate contains 5% galena, the zinc leaching rate can decrease by up to 13%, while the inclusion of 10% pyrite enhances zinc dissolution (Harvey and Yen, 1998). In contrast, Souza et al. (Souza et al., 2009) propose that the iron content only minimally impacts the leaching kinetics of silicate concentrate using sulfuric acid.

## 3. Sphalerite leaching in acid media

### 3.1. Sphalerite leaching in sulfate solutions

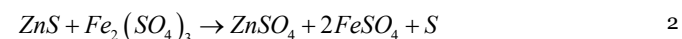
Sulfuric acid is the most commonly used sphalerite leaching agent due to its low cost and less aggressiveness compared to hydrochloric and nitric acids. However, the results of numerous studies have shown that sphalerite dissolves slowly at atmospheric pressure, which makes zinc extraction ineffective. To increase the sphalerite dissolution rate, it is necessary to add an oxidant in the acid solution, such as ferric, cupric, nitrate and dichromate ions, hydrogen peroxide, oxygen, bacteria, ozone, and other oxidants.

Leaching of sphalerite with ferric ion, either in sulfate or chloride media, takes place according to the following ionic reaction (eq. 1) (Dutrizac, 2006; Aydogan et al., 2005; Santos et al., 2010):

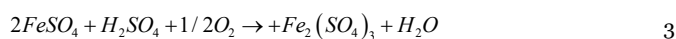


#### 3.1.1. Sulfuric acid – Fe (III) sulfate

Oxidative leaching of sphalerite with ferric ions in sulfuric acid media was investigated by many authors (Dutrizac, 2006; Lochmann and Pedlik, 1995; Kammel et al., 1987; Palencia Perez and Dutrizac, 1991; Santos et al., 2010; Rönnholm et al., 1997; Lampinen et al., 2015; Karimi et al., 2017; Cheng et al., 1994; Markus et al., 2004). Ferric ion oxidizes sulfide sulfur and reduces to ferrous ion and zinc sulfate, ferrous sulfate and elemental sulfur were obtained as leaching products (eq. 2).



To maintain the level of oxidant, ferrous ions, formed by reaction 1, are then oxidized back to ferric ion with oxidizing agents such as O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub> (Santos et al., 2010; Rönnholm et al., 1997; Lampinen et al., 2015):



Ferric ion has a significant role as an oxidant in the process, so the kinetics of the oxidation of Fe<sup>2+</sup> back to Fe<sup>3+</sup> (eq. 3) is important in the sphalerite leaching process.

The formation of elemental sulfur and its deposition on the sphalerite surface impedes mass transfer and slows down or completely blocks further reactions between zinc sulfide and ferric sulfate.

Leaching of sphalerite (Zn,Fe)S with ferric sulfate solution was tested by Dutrizac 2006. (Dutrizac, 2006) and found that the rate of leaching increases linearly with the increase of the surface area, i.e., with the decrease in the size of the sphalerite particles. The primary reaction products include ZnSO<sub>4</sub>, FeSO<sub>4</sub>, and elemental sulfur. The leaching rate escalates as the temperature rises, and the reaction exhibits an activation energy of 44 kJ/mol. The magnitude of this activation energy suggests chemical control over the rate, supported by the observation that changes in the mixing rate do not alter the reaction rate. When the leaching was performed with a 0.3 M Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution, the rate increased for acid concentrations above 0.1 M H<sub>2</sub>SO<sub>4</sub>, but remains unaffected by dilute acid concentrations. Without ferric ions, the leaching rate accelerates with a rise in H<sub>2</sub>SO<sub>4</sub> concentration and hits considerable speeds with >0.5 M H<sub>2</sub>SO<sub>4</sub> solutions. However, increased concentrations of ZnSO<sub>4</sub> or FeSO<sub>4</sub> in the ferric sulfate solution led to a decline in the rate, underlining the need to retain iron in its ferric state.

The influence of operating parameters on the leaching of sphalerite concentrate of the Angouran mine was studied by Karimi et al. (Karimi et al., 2017), where it was determined that the most influential parameter was the temperature and the least effective was acid concentration. The optimal zinc recovery from the sphalerite concentrate was 84.72% achieved at the temperature of 80 °C after 6 h of leaching with 1.2 M concentration of ferric ions and a mean particle size of 21 µm. Kinetic results showed that there were two stages in the sphalerite leaching. At the beginning of the leaching process, the kinetics of sphalerite leaching is fast and limited by both the rate of chemical reaction and the rate of diffusion through the sulfur layer. The leaching rate of sphalerite in the second stage is controlled solely by diffusion through the layer of ferrous and zinc sulfate salts. The activation energies for the first and second stages were 23.91 kJ/mol and 12.30 kJ/mol, respectively.

Kammel et al. (Kammel et al., 1987) leached sphalerite in H<sub>2</sub>SO<sub>4</sub>-Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution and examined the influence of the addition of Cu(II) ions and sphalerite grinding on zinc leaching (Kammel et al., 1987). The addition of iron (III)sulfate above the stoichiometric amount required does not increase the rate of leaching. The results also showed that zinc leaching is accelerated with increasing iron content in the sphalerite lattice. The addition of Cu(II) ions to the solution improves the dissolution of sphalerite with low iron content in its crystal lattice, while the dissolution is slowed down when the iron content exceeds 1%. Copper forms a sulfide film, which affects leaching, while grinding enhances sphalerite leaching.

Santos et al. (Santos et al., 2010) investigated the atmospheric leaching of sphalerite in both sulfate and chloride - containing solutions. Their findings revealed that, by employing a solution composed of 0.5 M H<sub>2</sub>SO<sub>4</sub> and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, and a solid/liquid ratio of 5% (v/v), they could achieve a leaching rate of 95% for zinc after 2 hours at 80 °C. Trace elements such as As, Sb, and Bi were leached as well, while Pb remained unaltered in the sulfuric medium. The leaching of Cu and Ag was more effective in the chloride medium. A further study of the Fe(II) oxidation assisted by H<sub>2</sub>O<sub>2</sub> during the leaching process found a 20% increase in zinc extraction.

Cheng et al. (Cheng et al., 1994) investigated the leaching of zinc sulfide concentrate in a solution containing ferric sulfate, sulfuric acid, and the addition of sodium chloride. They determined that the dissolution process was limited by an electron transfer reaction until the zinc leaching degree reaches 60-70%, after which the rate decreases

exponentially and becomes controlled by diffusion through the sulfur layer deposited on the sphalerite surface.

Marcus et al. in their research, point to the fact that the rate of the reaction (1) is controlled by the reaction on the surface and diffusion through the solid product layer (Markus et al., 2004). The concentration of sulfuric acid showed a decisive influence on the kinetics of the process.

In their research, Muravyov and Panyushkina (Muravyov and Panyushkina, 2023) examined the dissolution of powder samples of sphalerite, djurleite and chalcopyrite using two different solutions: chemically pure ferric sulfite reagent and ferric sulfate obtained via biooxidation of the chemically pure ferrous sulfate by an acidophilic bacterium *Leptospirillum ferriphilum*. In the case of leaching with a solution of chemical reagent of ferric sulfate, the sphalerite dissolution level after 5 h on 80 °C and 1% pulp density was 21.3% higher than in the case of the biological reagent.

Estrada-de los Santos et al. (Estrada-de los Santos et al., 2016) investigated the catalytic influence of pyrite on the dissolution kinetics of zinc sulfide concentrate with an acidified iron sulfate solution and discovered that doping with pyrite in the presence of Fe<sup>3+</sup> significantly improved the rate of zinc leaching. After 6 h of leaching, 98.9% of zinc was extracted with added pyrite and 85% of zinc was extracted after 7 h without pyrite for fine grain size. Zn extraction achieved 70% without doped pyrite and 75% in presence of doped pyrite, both in 7 h using a coarse grain size. This is due to the existence of a passivating layer on the surface of sphalerite after iron leaching in the absence of pyrite, however in the presence of pyrite, this layer was not seen, and the pyrite surface was not attacked.

Akcil and Ciftci investigated the possibilities of selective processing of polymetallic CuFeS<sub>2</sub>-PbS-ZnS concentrate by combined pyrometallurgical and hydrometallurgical process (Akcil and Ciftci, 2003). After roasting at 400 °C, the concentrate was leached with a sulfuric acid solution for 2 h, where copper leaching was over 90%, while zinc leaching was below 10%. After roasting the residue again at 600 °C and leaching again, the zinc and the rest of the copper are dissolved, while the lead remains in the precipitate as a lead concentrate. When the iron (III) sulfate was used for leaching the same fried concentrate, after 1 h of leaching, more than 85% of zinc and only 15% of copper was dissolved. With continued leaching, the dissolution of copper increased rapidly and reached 90% after 3.5 h.

Lorenzo-Tallafigo et al. (Lorenzo-Tallafigo et al., 2018) have proposed a new process for the integral treatment of polymetallic Cu-Zn-Pb sulfide ores. After flotation, the concentrate is leached in two stages with a ferric sulfate solution: sphalerite is leached in the first, and chalcopyrite in the second with the addition of silver as a catalyst. Ferric ion concentration, temperature, and particle size affect sphalerite oxidation, while the initial sulfuric acid, ferrous ion and sulfate ion concentrations do not influence the process rate. During the leaching, a layer of non-porous elemental sulfur is formed and prevents the passage of ferric ions to the sphalerite surface. At the beginning of the process, the reaction is chemically controlled with an activation energy of 51.3 kJ/mol. After achieving 30% zinc leaching, the reaction rate becomes controlled by the diffusion of ferric ions through the sulfur layer with an activation energy of 47.7 kJ/mol.

The main problem in the oxidative leaching of sphalerite with ferric sulfate is the slow rate of dissolution due to the formation of a passive layer on the surface of sphalerite. Lorenzo-Tallafigo et al. (Lorenzo-Tallafigo et al., 2018), Karimi et al. (Karimi et al., 2021) and Nikkhou et al. (Nikkhou et al., 2019) examined the sphalerite concentrate surface structure, unoxidized and oxidized in iron sulfate solution, and determined that the main by-product of the oxidation process is elemental sulfur. In addition to elemental sulfur, monosulfide, disulfide and polysulfide species and jarosite were detected on the sphalerite surface. During the bioleaching of sphalerite in iron (III)-containing sulfur environments, jarosite is often formed and slows zinc bioleaching, as shown in work from Abdollahi et al. (Abdollahi et al., 2022).

To prevent the formation of a non-porous layer of elemental sulfur, Picazo-Rodríguez et al. (Picazo-Rodríguez et al., 2020), instead of Fe<sub>3</sub><sup>+</sup>, used Fe<sub>2</sub><sup>+</sup> which was oxidized to Fe<sub>3</sub><sup>+</sup> by oxygen in the solution. A zinc extraction of 96% was obtained in a low-pressure reactor under the following conditions: 96 kPa of pressure at 353 K for 5 h with stirring rate of 350 rpm, using 1.5 M H<sub>2</sub>SO<sub>4</sub> together with 0.2 M Fe<sub>2</sub><sup>+</sup>, 200 g/L of pulp density. The elemental sulfur layer formed is porous, which is confirmed on the micrographs.

### 3.1.2. Sulfuric acid - hydrogen peroxide

The presented results of sphalerite leaching in sulfate solutions using ferric ions as oxidants at atmospheric pressure indicate that the obtained extraction values are not high, and that leaching is difficult due to the formation of a compact layer of elemental sulfur on the sphalerite surface. For this reason, a greater number of researchers in their tests, instead of ferric sulfate, used a stronger oxidant, which, due to its higher oxidation potential, can affect the sphalerite dissolution kinetics: Therefore, the oxidation of chalcopyrite was carried out using stronger oxidizing agents, which, due to higher oxidation potentials, can more effectively influence the kinetics of the dissolution process. For this purpose, the following oxidants were examined: hydrogen peroxide (Akcil and Ciftci, 2003; Lorenzo-Tallafigo et al., 2018; Karimi et al., 2021; Nikkhou et al., 2019), oxygen, ozone (Haber and Willstätter, 1931), nitrate and nitrite ion, dichromate ion (Abdollahi et al., 2022), chlorate ion (Picazo-Rodríguez et al., 2020), persulfate ion (Bogdanović et al., 2020) etc.

Hydrogen peroxide is a very strong oxidant in acidic media (E<sub>0</sub> = 1.77 V), so many researchers investigated its application in dissolving sphalerite, chalcopyrite, other sulfide minerals, and polymetallic Pb-Zn-Cu ores and concentrates (Adebayo et al., 2003).

The oxidizing effect of hydrogen peroxide in acidic solutions is based on its reduction (Greenwood and Earnshaw, 1984):



Hydrogen peroxide can also act as a reductant, where it is oxidized:



It is known that hydrogen peroxide is a relatively unstable compound. The decomposition products are oxygen and water:

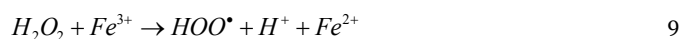
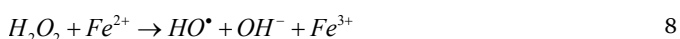


and this (eq. 6) represents the sum of half reactions (eq. 4 and 5).

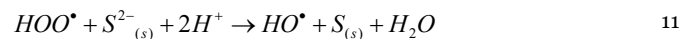
Hydrogen peroxides oxidative activity is dependent on its homolytic cleavage products reactive hydroxyl and hydroperoxyl radicals. (Haber and Willstätter, 1931):



The decomposition is catalyzed in the presence of Fe<sup>2+</sup>/Fe<sup>3+</sup> ions, Cu<sup>+</sup> ions, platinum, silver, etc. In the presence of Fe<sup>2+</sup>/Fe<sup>3+</sup> ions, hydrogen peroxide dissociates into hydroxyl and hydroperoxyl radicals (Fenton reaction) according to the following reactions (Haber and Willstätter, 1931; Lin and Luong, 2004):

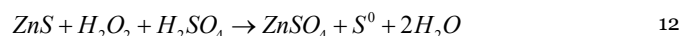


The resulting hydroperoxyl radical reacts with the sulfide sulfur according to reaction (11):

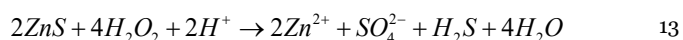


releasing hydroxyl radical and elemental sulfur.

Abramov and Avdohin (Abramov and Avdohin, 1997) state that the oxidation of sphalerite proceeds to the formation of elemental sulfur according to eq. (12):



Contrary to them, Aydogan S (Aydogan, 2006) proposes the following equation for sphalerite leaching:



Kinetic investigations have revealed that sphalerite leaching can be described by the shrinking core model and that the leaching rate is controlled by surface reaction at temperatures ranging from 10 to 60 °C. The estimated activation energy was 43 kJ/mol.

Reactions 7 and 8 usually occur simultaneously, and process parameters influence which of the equations will be dominant.

Habashi proved that hydrogen peroxide has a substantial influence on sulfide oxidation by boosting ore solubility by partially converting the sulfide to elemental sulfur and then to sulfate (Habashi, 1999). Other researchers have explored the dissolving process in the presence of H<sub>2</sub>O<sub>2</sub>, and it has been discovered that sulfide is oxidized in two phases (Adebayo et al., 2003; Jiang et al., 2002; Olubambi et al., 2006). Sulfide is transformed to elemental sulfur in the first phase, and sulfur is turned to sulfate in the second.

Using XRD analysis of the residue after chalcopyrite leaching in a solution containing H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>, Antonijević et al. (Antonijević et al., 2004) have found that most of the sulfide sulfur is transformed into sulfate. On the other hand, Misra and Fuerstenau (Misra and Fuerstenau, 2005) established that most of the sulfide sulfur is transformed into elemental forms. Olubambi and Potgieter (Olubambi and Potgieter, 2009) noticed that the increase in the porous and crystalline nature of the residues with increasing hydrogen peroxide concentration reduced the passive nature of chalcopyrite and accelerated leaching through the porous nature of the dissolution products. Sokić et al. (Sokić et al., 2019) concluded that an increase in temperature, the concentration of hydrogen peroxide and sulfuric acid, as well as a decrease in particle size and stirring speed, all contribute to the dissolution of chalcopyrite in the H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O<sub>2</sub> system. The diffusion of the lixiviant via the sulfur layer deposited on the surface of the chalcopyrite particles controls the reaction rate, as shown by XRD and qualitative and quantitative mineralogical analyses. The determined value of activation energy is equal to 80 kJ/mol.

The elemental sulfur formation and its deposition on unleached sulfide mineral grains makes leaching difficult and prevents the dissolution of trapped mineral grains. Balaž and Ebert investigated the leaching of mechanically activated sphalerite concentrate in a vibrating mill and determined significantly higher leaching of zinc compared to the non-activated concentrate (Balaž and Ebert, 1991). Mechanical activation of sphalerite by vibration grinding mill results in changes in the surface and volume properties of this mineral, which directly affects its leaching with sulfuric acid and hydrogen peroxide. Sphalerite that was previously activated by grinding in a vibrating mill for 7.5-150 min,

65-100% dissolves in 4% hydrogen peroxide solution after 120 min at atmospheric pressure and room temperature.

To increase the efficiency and rate of dissolution, some organic and synthetic compounds can be added to the solution, which **either** prevents the formation of a compact sulfur layer or leads to its dissolution (Mahajan et al., 2007; Peng et al., 2005; Fan et al., 2019).

Mahajan et al. (Mahajan et al., 2007) used ethylene glycol for chalcopyrite leaching with 1 M H<sub>2</sub>SO<sub>4</sub>–0.26 M H<sub>2</sub>O<sub>2</sub> solution. They confirmed the presence of elemental sulfur at the chalcopyrite surface in the form of individual crystalline particles rather than a continuous sulfur layer. Estimated activation energy in their studies was 30 kJ/mol, and the leaching rate was regulated by surface reaction. At the same time, they avoided the quick breakdown of hydrogen peroxide at high temperatures by adding ethylene glycol. At 65 °C, the copper extraction went from 20% to 60% during 240 min of leaching.

Peng et al. (Peng et al., 2005) studied the addition of tetrachloroethylene (C<sub>2</sub>Cl<sub>4</sub>) to the leaching process of sphalerite with a sulfuric and nitric acid solution to dissolve elemental sulfur from leach residue and increase the leaching efficiency. With the addition of tetrachloroethylene, the rate of leaching is significantly increased and is controlled by the reaction on the surface; without its addition, it is controlled by diffusion through the sulfur layer.

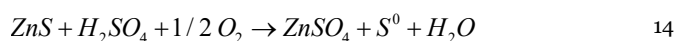
Organic solvents are usually toxic, volatile, flammable, and explosive and can cause environmental pollution and are consequently unsafe to use. Therefore, Fan et al. (Fan et al., 2019) employed liquid paraffin to separate elemental sulfur during the leaching process, demonstrating that liquid paraffin is an effective and safe organic solvent that could separate and purify elemental sulfur from the leach residue.

Investigating the extraction of zinc from sphalerite concentrates using hydrogen peroxide as an oxidant in sulfuric acid solutions, Pecina et al. (Pecina et al., 2008) determined that oxidative leaching from sphalerite follows a shrinking core model, and despite the layer of elemental sulfur surrounding the particles, dissolution was controlled by the reaction of surface with an activation energy of 50 kJ/mol. They also showed that the addition of complexation agents such as oxalic acid, citric acid, phosphorus acid, and phosphonic acid increases the extraction of zinc from sphalerite concentrate.

Petrović et al. (Petrović et al., 2018) examined the leaching of chalcopyrite concentrate with a solution containing hydrochloric acid and hydrogen peroxide and showed that part of the copper remains undissolved; the maximum extraction of copper was 33%. The obtained activation energy value of 19.6 kJ/mol indicates that the leaching process is controlled by diffusion through the elemental sulfur layer deposited on the surface of chalcopyrite, which was confirmed by XRD and SEM/EDS analysis. The decomposition of hydrogen peroxide is catalyzed Fe(III) ions, chlorine and solid mineral particles, leading to a decrease in the oxidizing power of hydrogen peroxide and a decrease in the dissolution rate.

### 3.1.3. Sulfuric acid - other oxidants

*Sulfuric acid – oxygen pressure leaching.* Oxygen pressure leaching in sulfuric acid has been reported in several publications (Harvey et al., 1993; Habashi, 1980; Kawulka et al., 1975, Li et al., 2010), and it is represented by the following chemical reactions:



With increasing temperature, elemental sulfur formed is oxidized according to the following equation (Petrović et al., 2018):



McDonald and Muir (McDonald and Muir, 2007) showed that when chalcopyrite is oxidized in an autoclave at low temperatures (100-120 °C), sulfide sulfur is oxidized to elemental form, while at temperatures above 180 °C, sulfide sulfur is oxidized to sulfate. When leaching at 108 °C, 80-90% of sulfide sulfur is oxidized to elemental form and this percentage increases in the presence of chloride ions. At leaching temperatures higher than 180 °C, all sulfur is oxidized to sulfate, with the rate of sulfate formation decreasing in the presence of chloride ions.

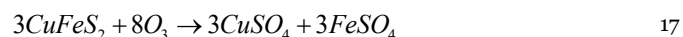
Habashi (Habashi, 1980) studied the mechanism of the sphalerite oxidation process and discovered that the dissolving rate is independent of oxygen pressure, but depends solely on sulfuric acid concentration when acid concentration is low. The dissolving rate with higher concentrations of sulfuric acid is solely determined by the oxygen pressure.

Because molten sulfur would enclose un-leached sulfide and impede dissolution, pressure leaching temperatures were kept below the melting point of sulfur. Certain surface-active compounds prevent molten sulfur from sulfide particles, allowing leaching at temperatures exceeding sulfur's melting point (Kawulka et al., 1975). Li et al. (Liu et al., 2010) explored the oxygen pressure leaching process of sphalerite concentrate in sulfuric acid solution with the addition of sodium lignosulfonate. The addition of lignosulfonate enhanced zinc extraction to 96-98%. Under an oxygen partial pressure of 800 kPa and a leaching temperature of 150 °C for 2 hours, 99% zinc was leached from the concentrate, with 81% of the sulfide sulfur oxidizing to sulfate.

Xie et al. (Xie et al., 2007) examined the effect of stirring speed, particle size, temperature, oxygen partial pressure, acid concentration, iron content in the concentrate and Fe<sup>2+</sup> concentration in the solution on the leaching rate of zinc under oxygen pressure in sulfuric acid solution. They found that a stirring speed above 600 rpm does not affect the leaching rate, indicating that diffusion is not the control step of the leaching process. The optimal temperature is 140-150 °C, and the optimal pressure is 1.2-1.4 MPa. In the mentioned conditions, the rate of Zn leaching decreases with the increase in the initial concentration of sulfuric acid, the rate increases with a rise of iron content in the concentrate and the concentration of Fe<sup>2+</sup> in the leaching solution. The activation energy was 55.04 kJ/mol.

*Sulfuric acid – ozone.* The use of ozone as a strong oxidizing agent during the leaching of sulfide minerals with ferric ions in a sulfuric acid solution to increase the rate of regeneration of ferric ions and oxidation of elemental sulfur, which blocks the dissolution of sulfide mineral grains, was examined by several researchers (Havlik et al., 1999; Carillo-Pedroza et al., 2010; Carillo-Pedroza et al., 2012; Mubarak et al., 2018).

Havlik et al. (Havlik et al., 1999) studied the leaching of a chalcopyrite concentrate in sulfuric acid solution using O<sub>3</sub> as an oxidizing agent. The global reaction can be represented by eq. 17 which occurs through several intermediate steps:



The formation of elemental sulfur or any other product that would block the leaching of non-leached chalcopyrite mineral grains was not proven. The authors stated that the reaction rate was controlled by the diffusion of O<sub>3</sub> in the interface solid-liquid, and that ozone solubility decreases with increasing temperature.

Dissolution of low-grade chalcopyrite ore in an acid medium with Fe<sup>3+</sup> and O<sub>3</sub> as oxidizing agents was investigated by Carillo-Pedroza et al. (Carillo-Pedroza et al., 2010; Carillo-Pedroza et al., 2012). The continuous addition of O<sub>3</sub> to the solution favors oxidation of Fe<sup>2+</sup> formed according to equation 17.



The mechanism of chalcopyrite dissolution in the presence of  $\text{Fe}^{3+}$  and  $\text{O}_3$  is that  $\text{Fe}^{3+}$  quickly reacts with the surface of the mineral, resulting in the formation of  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  ions and a layer of elemental sulfur on the surface of chalcopyrite (Carillo-Pedroza et al., 2010). The diffusion of the oxidizing agents  $\text{Fe}^{3+}$  and  $\text{O}_3$  through the sulfur layer is the rate-controlling step of the entire process. The results showed that the presence of ozone reduces the leaching time and allows the use of lower concentrations of  $\text{Fe}^{3+}$  and  $\text{H}_2\text{SO}_4$  compared to leaching without ozone. The use of ozone in the oxidation of sulfide ores containing gold, silver and copper has been shown to increase the extraction of gold and silver by at least 15%, with less cyanide consumption (Carillo-Pedroza et al., 2012). The extraction of copper increased by 16% and in less operation time.

Mubarak et al. (Mubarak et al., 2018) investigated the effect of particle size, acid concentration, stirring speed, feed gas injection rate, temperature, and slurry density on the leaching of sphalerite with the addition of ozone in a sulfuric acid solution under atmospheric pressure. The experimental results showed that the leaching efficiency depends on all operating parameters except the stirring speed. High zinc extractions (~100%) were achieved, along with the generation of independent elemental sulfur that can be floated and easily separated rather than adhered as a dense layer on the particle surface. Dissolved ozone was found to play a key role in improving the dissolution rate of zinc from the concentrate which was controlled by a surface reaction.

*Sulfuric acid – persulfate ions.* Babu et al. (Babu et al., 2002) studied the oxidative leaching of sphalerite in sulfuric acid media with ammonium, sodium, and potassium persulfates. They extracted 95% zinc from a concentrate with particle size 150  $\mu\text{m}$  at 60 °C for 5 h in the presence of 20% (w/v) ammonium persulfate and 5% (v/v) sulfuric acid concentration. As the temperature increases above 70 °C, zinc leaching decreases due to enhanced decomposition of ammonium persulfate. Kinetic analysis showed that the leaching of zinc followed a diffusion-controlled model, and the rate is regulated by the diffusion of the lixiviant through the sulfur layer. The activation energy was  $41 \pm 2$  kJ/mol. Ammonium persulfate was found to be a more effective oxidant than sodium persulfate and potassium persulfate. Similar results of leaching of zinc sulfide concentrate from the Ganesh-Himal deposit of Nepal with ammonium persulfate were obtained by Sahu et al. (Sahu et al., 2006). Zinc extraction increased up to a temperature of 60 °C, and a further increase in temperature resulted in a decrease in metal extraction. Kinetic analysis showed that the zinc leaching followed a mixed controlled kinetic model with activation energy of 43 kJ/mol.

Crundwell (Crundwell, 2021) investigated the effect of light on the dissolution mechanism and leaching of sphalerite, pyrite and chalcopyrite in sulfuric acid and found that light increased the rate of dissolution of natural sphalerite, pyrite, and chalcopyrite minerals. Irradiation of sphalerite with UV light increases the rate of dissolution. The presence of iron impurities in sphalerite has a notable influence on its color, and therefore on the dissolution rate.

### 3.2. Sphalerite leaching in chloride solutions

The use of chloride systems in investigations of hydrometallurgical processing of sulfide minerals is significant (Watling, 2013). Of the chlorides, ferric chloride, cupric chloride, sodium chloride, hydrochloric acid and elemental chlorine are most often used for oxidation (Aydogan et al., 2005).

The oxidation potential in the ferric chloride system leads to the formation of elemental sulfur as one of the main products of leaching, which from an ecological point of view is a more acceptable form than sulfur dioxide in pyrometallurgical processing, i.e. sulfates in hydrometallurgical processing under pressure. Ferric chloride is far more aggressive than ferric sulfate and significantly accelerates the decomposition of sulfide minerals. On the other hand, Wilson and Fisher (Wilson and Fisher, 1981) found that chalcopyrite leaching is

more efficient in Cu(II) chloride solutions than in sulfate solutions in the presence of Fe(III) as an oxidant. The redox potential of the  $\text{Cu}^{2+}/\text{Cu}^+$  couple is significantly higher in chloride than in sulfate solution (Wang, 2005). Also, the redox potential of  $\text{Cu}^{2+}/\text{Cu}^+$  is higher than the redox potential of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  in a saturated chloride solution.

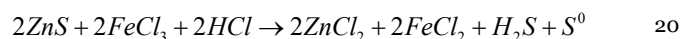
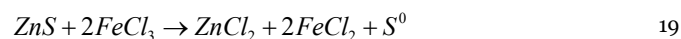
The advantages of using chloride systems compared to sulfate systems are: a) high solubility of zinc and iron; b) faster oxidation of ferrous ions to ferric ions; c) the formation of a porous sulfur layer that enables the diffusion of reactants to the sulfide surface, d) faster leaching kinetics compared to sulfate systems and e) low pyrite reactivity in chloride systems (Watling, 2013; Watling, 2014; Dreisinger, 2003). The application of chloride solutions for leaching is limited due to their high corrosiveness towards most metals, although this problem can be overcome by using plastic materials.

Regardless of the mentioned advantages, leaching processes in chloride systems have not been applied at the industrial level due to limitations such as (Watling, 2014; Bogdanović et al., 2020): a) the corrosive effect of chloride, which requires the use of expensive materials for reactors; b) the necessity of fine grinding the concentrate to small size classes because the process is carried out under atmospheric pressure, c) the lack of selectivity of leaching, which requires additional treatment of the solution, d) the difficult electrolysis of copper from chloride solutions, and e) the environmental concerns associated with chloride effluents.

#### 3.2.1. Ferric chloride solutions

During the sphalerite leaching with a solution of ferric chloride and hydrochloric acid, zinc chloride or zinc chloride complexes, elemental sulfur, ferrous chloride, ferric and ferrous complexes, and hydrogen sulfide can be formed, which mainly depends on the pH of the solution (Aydogan et al., 2005).

Oxidation of sphalerite with ferric chloride proceeds according to reactions (Aydogan et al., 2005; Hu et al., 2003):



The reactivity of sphalerite depends on the iron content in its lattice and increases with increasing iron content. Aydogan et al. (Aydogan et al., 2005) have shown that the leaching rate increases with an increase in Fe(III) ion concentration, temperature and mixing speed, as well as with a decrease in the solid-liquid ratio and particle size. Thus, zinc leaching after 4 h of leaching was 14.2 and 82.0% at 40 and 80 °C, respectively. The sphalerite dissolution rate is controlled by the reaction rate on the surface, with an activation energy ( $E_a$ ) of 45.3 kJ/mol in the range of 40-80 °C. Examining the dissolution kinetics of sphalerite in ferric chloride and hydrochloric acid solutions in the temperature range from 25 to 100 °C, Dutrizac and MacDonald (Dutrizac and MacDonald, 1978) also determined that the reaction was chemically controlled with an activation energy of about 42 kJ/mol. The leaching rate was relatively insensitive to low levels of HCl, but increased dramatically at higher acid concentrations. Most oxidized sulfide sulfur is present in leach residues in elemental form (Dutrizac, 1990; Dutrizac and MacDonald, 1978). In their research, Al-Harashseh and Kingman (Al Harashseh and Kingman, 2008) found that the reaction rate increases with increasing temperature, mixing speed, ferric chloride concentration, and particle size reduction. The shrinking core model was applied to the experimental results. The reaction was found to be controlled by a chemical reaction with an activation energy of 44.8 kJ/mol.

A similar value of  $E_a$  (46.9 kJ/mol) for sphalerite leaching in acidic ferric chloride solution in the temperature range from 320 to 360 K was obtained by Bobeck and Su (Bobeck and Su, 1985). On the other hand, they found that during the initial stage of the process, the

chemical reaction on the surface of the mineral controls the reaction rate, while in the later stages, diffusion through the sulfur layer as a product controls the reaction rate.

Complex sulfide ores often have a small free surface with finely dispersed mineralization. The leaching of each individual mineral depends on its nature and association with other sulfides and gangue minerals. During the leaching of CuFeS<sub>2</sub>-ZnS-PbS concentrate with iron (III) chloride, galena leaches very quickly and easily, unlike chalcopyrite, whose leaching is quite slow, while the rate of sphalerite leaching mostly depends on the iron content in its structure (Dutrizac, 1992).

Mandre and Sharma (Mandre and Sharma, 1993) investigated the dissolution behavior of galena, sphalerite, and pyrite by direct leaching of an Indian lead-zinc complex sulfide ore using ferric chloride solution and confirmed that the leaching characteristics of individual sulfide minerals depend on their nature of association with other sulfides. Galena dissolves faster than sphalerite and pyrite due to the liberation of mineral grains and lower activation energy. By maintaining low temperature and FeCl<sub>3</sub> concentration, selective dissolution of galena is possible. However, an increase in iron chloride concentration over 0.15 M and an increase in temperature leads to the simultaneous dissolution of galena and sphalerite. Kinetic analysis showed that the leaching of galena and sphalerite followed a linear kinetic model with Ea of 22 and 38 kJ/mol, respectively.

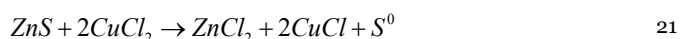
Tkačova et al. (Tkačova et al., 1993) determined that zinc, copper and iron show different leaching rates after mechanical activation, thus increasing the selectivity of leaching. The differences in the leaching rate are related to the different degree of amorphization of the minerals during grinding. They also observed that the leaching selectivity decreases with increasing oxidant concentration (FeCl<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, etc.). Mechanical activation of the CuFeS<sub>2</sub>-ZnS-PbS concentrate causes a change in the leaching mechanism of chalcopyrite and sphalerite (from mixed to diffusion at 70 °C), while galena leaching is chemically controlled even after activation (Godočikova et al., 2002).

Application of microwaves in extractive metallurgy has published by many authors (Weian et al., 1997; Al Harahsheh and Kingman, 2004; Al-Harahsheh, 2005). In these papers it has been concluded that microwave energy can have a positive influence on the kinetics of the leaching process of metals from sulfide ores and concentrates.

Peng and Liu (Peng and Liu, 2001) investigated the influence of microwaves on sphalerite leaching kinetics in a solution of 1.0 M FeCl<sub>3</sub> and 0.1 M HCl at 95 °C. After 1 h of leaching with microwave treatment, zinc extraction reached 90%, while with conventional leaching without the effect of microwaves, the maximum zinc extraction was about 52%. Al-Harahsheh and Kingman (Al Harahsheh and Kingman, 2008) also noted an improvement in zinc leaching when leaching was carried out under microwave irradiation. An increase in zinc dissolution after microwave-assisted leaching was more obvious under stagnant conditions as compared to that in conventionally heated systems.

### 3.2.2. Cupric chloride solutions and ammonium chloride solutions

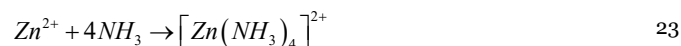
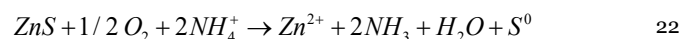
During the leaching of sulfide minerals in copper chloride leaching systems, elemental sulfur is formed as one of the main products, which is generally more environmentally friendly than sulfur dioxide from pyrometallurgy or sulfate from hydrometallurgy under pressure (Guy et al., 1983):



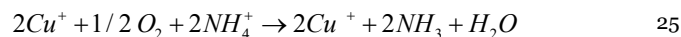
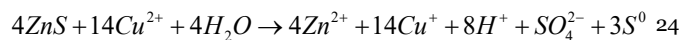
Leaching of complex CuFeS<sub>2</sub>-ZnS-PbS-FeS<sub>2</sub> concentrates with copper(II)-chloride solution at 100 °C is significant in the first hours, while after 12 h it practically stops (Tchoumou and Roynette, 2007). If leaching is carried out without oxygen, pyrite leaching will be prevented. Galena leaches at the highest rate, followed by sphalerite and finally chalcopyrite, very slowly. The leaching of complex Cu-Zn-Pb sulfide ore in the copper-chloride system was investigated by Guy et al. (Guy

et al., 1983) and they determined that zinc, in the case of leaching of very small particles of ore, leaches out very quickly and that the leaching reaches 98%. When coarse ore was leached, 16-20 h of leaching were required to achieve high leaching rates. The reason for this is the fact that chalcopyrite and sphalerite are intergrowths with pyrite, as well as with each other and other minerals. The activation energies for the dissolution of zinc from CuFeS<sub>2</sub>-ZnS-PbS-FeS<sub>2</sub> was 26 kJ/mol and indicate that diffusion through the formed layer of sulfur around the mineral grains controls the reaction rate.

Limpo et al. (Limpo et al., 1990a; Limpo et al., 1990b) worked on the development of a two-stage ammonium chloride-O<sub>2</sub> leaching process of complex sulfide ores (CENIM-LNETI process), whereby more than 95% of Zn, Cu, Pb and Ag were converted into solution. Leaching is carried out at 105 °C and under a 150 kPa O<sub>2</sub> pressure and initially occurs in near-neutral solution according to the reaction:



The initial leach is accelerated by the presence of low concentrations (e.g., 1.5 g/l Cu<sup>2+</sup>) of cupric chloride, and it seems likely that a cupric chloride leach is actually involved:



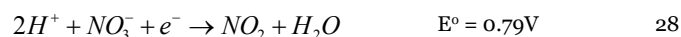
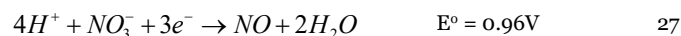
From solution, zinc is extracted at 50 °C using solvent extraction with di(2-ethylhexyl)phosphoric acid (DEHPA).

### 3.3. Sphalerite leaching in nitrate solutions

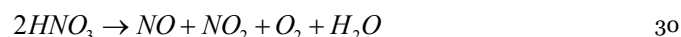
Nitric acid and nitrates are strong oxidizing agents. Reactions with sulfides vary greatly depending on the sulfides treated, acid concentration, and temperature. By gradual oxidation in dilute acid and at a lower temperature, nitrates are formed, sulfur is oxidized to sulfate, and the nitrate ion is reduced to nitrogen monoxide. By using a more concentrated acid and a higher temperature, the reaction is accelerated, most of the sulfur is oxidized to its elemental form, metal nitrates are formed, and the nitrate ion is reduced to nitrogen dioxide. This is understandable, because concentrated nitric acid oxidizes nitrogen monoxide into nitrogen dioxide while passing through it (Habashi, 1999).

Habashi believes that the oxidation of metal sulfides with nitric acid takes place in two ways (Habashi, 1999):

- oxidation by nitrate ion (NO<sub>3</sub><sup>-</sup>):

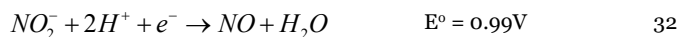


- oxidation with oxygen, which is produced by the decomposition of nitric acid:

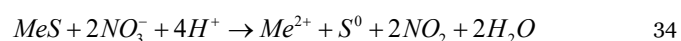
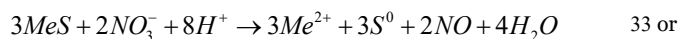




Application of nitric acid for leaching sulfide minerals has not found any significant application until today. On the other hand, nitrate and nitrite ions, due to their high oxidation potential, see (eq. 27, 28 and 32) (Filipović and Lipanović, 1987), are used as oxidizing agents in the leaching of sulfide minerals with sulfuric acid:



Sulfide concentrate oxidative dissolution using solution containing nitrate as an oxidant in sulfuric acid, results with formation of elemental sulfur, and it can be represented by one of the following chemical reactions (Bredenhann and Van Vuuren, 1999; Sokić et al., 2009; Peng et al., 2005):

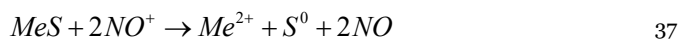


A small part of the sulfide sulfur, under certain conditions, is oxidized to sulfate (Droppert and Shang, 1995).

Company "Sunshine Mine" Kellogg, Idaho (Ackerman and John, 1990) uses  $H_2SO_4$ - $HNO_3$  mixture for leaching Ag-Cu-Fe sulfide concentrate. The process is carried out in an autoclave at 155 °C and a pressure of 620 kPa, during which Cu and Ag are dissolved, and sulfide sulfur is oxidized to elemental form. Prater et al. (Prater et al., 1973) investigated the leaching of chalcopyrite in a mixture of  $H_2SO_4 + HNO_3$  at elevated temperatures and confirmed high leaching of copper, with the conversion of about 60% of sulfide sulfur to its elemental form. Copper was separated from the solution by solvent extraction, iron was deposited in the form of jarosite, and nitric acid was regenerated through NOx gases. Regeneration of nitric acid is carried out by oxidation of NO gas and its dissolution in water:



There are opinions that the sulfide oxidation process is much faster in the presence of nitrosyl ions ( $NO^+$ ) (Anderson et al., 1993):



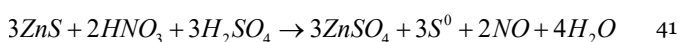
and are because leaching is faster if the mixture of  $HNO_3$  and  $H_2SO_4$  is replaced by a mixture of  $NaNO_2$  and  $H_2SO_4$ . Adding  $NO_2^-$  instead of  $NO_3^-$  accelerates the formation of  $NO^+$  ions:



Oxidation of chalcopyrite in the presence of  $NO^+$  in an autoclave at 150 °C takes place with the formation of elemental sulfur (Anderson et al., 2003):

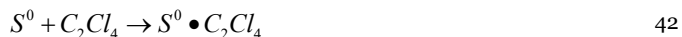


Leaching of sphalerite in  $H_2SO_4$ - $HNO_3$  solution takes place according to the equation (Peng et al., 2005):



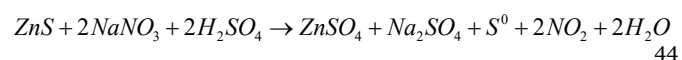
At 2.0 M  $H_2SO_4$ , 0.2 M  $HNO_3$ , 85 °C and 0.1 MPa  $O_2$ , 70.1% of zinc was leached after 1 h, or 99.2% after 6 h of leaching. The reaction rate is controlled by diffusion through the sulfur layer formed on the

sphalerite surface. With the addition of tetrachloroethylene ( $C_2Cl_4$ ) the leaching rate was significantly increased and under the same conditions was 88.2% after 1 h and 99.6% after 3 h of leaching. The effect of increasing leaching rates is the result of the extraction of sulfur formed during leaching by  $C_2Cl_4$ :



Diffusional resistances no longer exist and the leaching rate is controlled by the rate of reaction at the surface.

The kinetics and mechanism of sphalerite leaching with  $H_2SO_4$ - $NaNO_3$  solution at standard conditions was investigated by Sokić et al. (Sokić et al., 2012). Following chemical reactions can represent the sphalerite dissolution process:



The ratios of NO to  $NO_2$  in gaseous products and the elemental sulfur to sulfate that are formed after leaching depend on the concentration of the nitrate ion (Droppert and Shang, 1995).

When the temperature was raised from 60 to 90 °C, the zinc leaching rose from 25.23% to 71.66% after 2 h, and from 59.40% to 99.83% after 4 h (Sokić et al., 2012). The kinetic study revealed that the rate of leaching was controlled by the lixiviant diffusion through the sulfur layer, which precipitated at the particle surfaces. The activation energy was estimated to be 55 kJ/mol.

Lizhu and Huiqin (Lizhu and Huiqin, 1998) studied the leaching process of a sulfide zinc concentrate using Fe(III) ions in sulfuric acid solution and with the addition of Cu(II) ions and nitric acid as a catalyst. The process was carried out at atmospheric pressure and at a temperature of 353K. After two hours of leaching, more than 95% of zinc was leached. Baldwin and Van Weert (Baldwin and Van Weert, 1996) investigated the influence of nitrates ( $KNO_3$ ,  $HNO_3$ ) and nitrites ( $NaNO_2$ ) on the oxidation of iron(II)-sulfate in a sulfuric acid solution in an autoclave. They came to the conclusion that the presence of nitrates does not affect the oxidation of iron(II)-sulfate, while nitrites act catalytically and accelerate the oxidation of Fe(II) ions.

Table 1 shows activation energy values and leaching mechanism obtained in experiments of sphalerite leaching in acid solutions in the presence of different oxidants.

#### 4. Conclusion

Bearing in mind the numerous results of research on the chemical dissolution of sphalerite in acidic solutions in the presence of oxidants, the following can be concluded:

1. The presence of iron in the sphalerite structure significantly affects its stability. A greater amount of iron present in the sphalerite structure induces an increase of the sphalerite leaching rate, and the required activation energy decreases in ferric sulfate and ferric chloride leaching systems.
2. Sphalerite leaches relatively slowly in ferric sulfate solutions. The ferric ion oxidizes sulfide sulfur and reduces it to ferrous ions, and zinc sulfate, iron sulfate and elemental sulfur are obtained as leaching products. The ferric ion has an important role as an oxidant in the process, so the kinetics of  $Fe^{2+}$  oxidation back to  $Fe^{3+}$  (eq. 3) is important in the sphalerite leaching process. The formation of elemental sulfur and its deposition on the surface of sphalerite hinders the contact between zinc sulfide and iron sulfate and slows down or completely stops its leaching. The values of zinc extraction are different under similar experimental conditions (leaching time, temperature, size of particles) and range up to 98%. This difference



**Table 1.** Activation energy values and leaching mechanism of sphalerite leaching in acid solutions

Sphalerite sample	Solution	Temperature, °C	Activation energy, kJ/mol	Process that determines the reaction rate	Bibliography
Sphalerite with 0.04% Fe	H <sub>2</sub> SO <sub>4</sub> -Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	50-90	72	chemical control	Palecia Perez and Dutrizac, 1991
Sphalerite with 12.5% Fe			41		
Sphalerite with 0.45% Fe	HClO <sub>4</sub> -O <sub>2</sub>	25-85	63±6	diffusion control	Weisener et al., 2004
Sphalerite with 11.40% Fe			50±7		
Sphalerite with 12.90% Fe			39±2		
Sphalerite concentrate	H <sub>2</sub> SO <sub>4</sub> -Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	40-80	44	chemical control	Dutrizac, 2006
Sphalerite concentrate	H <sub>2</sub> SO <sub>4</sub> -Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	70-110	112	chemical control	Lampinen et al., 2015
High Fe sphalerite concentrate	H <sub>2</sub> SO <sub>4</sub> -Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	40-90	27.5 (Zn leaching < 40%)	chemical control	Souza et al., 2007
			19.6 (Zn leaching > 40%)	diffusion control	
Sphalerite concentrate	H <sub>2</sub> SO <sub>4</sub> -Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> -NaCl	60-90	49	chemical control	Cheng et al., 1994
			/	mixed control	
Sphalerite concentrate	H <sub>2</sub> SO <sub>4</sub> -Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	80	23.9 (1st stage)	mixed control	Karimi et al., 2017
			12.3 (2nd phase)	diffusion control	
Bulk concentrate	H <sub>2</sub> SO <sub>4</sub> -Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	50-90	51.3 (Zn leaching < 30%)	chemical control	Lorenzo-Tallafigo et al., 2018
			47.7 (Zn leaching > 30%)	diffusion control	
Sphalerite concentrate	H <sub>2</sub> SO <sub>4</sub> -H <sub>2</sub> O <sub>2</sub>	10-60	43	chemical control	Aydogan, 2006
Sphalerite concentrate	H <sub>2</sub> SO <sub>4</sub> -H <sub>2</sub> O <sub>2</sub>	25-60	50	chemical control	Pecina et al., 2008
Sphalerite concentrate	HNO <sub>3</sub> -H <sub>2</sub> O <sub>2</sub>	30-50	28.7	chemical control	Adebayo et al., 2006
High Fe sphalerite concentrate	H <sub>2</sub> SO <sub>4</sub> -O <sub>2</sub>	140-150	55	chemical control	Xie et al., 2007
Sphalerite concentrate	H <sub>2</sub> SO <sub>4</sub> -(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	30-60	43	mixed control	Sahu et al., 2006
Sphalerite concentrate	H <sub>2</sub> SO <sub>4</sub> -(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	30-70	41±2	diffusion control	Babu et al., 2002
Sphalerite with 0.04% Fe	FeCl <sub>3</sub> -HCl	50-90	81	chemical control	Palecia Perez and Dutrizac, 1991
Sphalerite with 12.5% Fe			39		
Sphalerite concentrate	FeCl <sub>3</sub> -HCl	40-80	45.3	chemical control	Aydogan et al., 2005
Pure sphalerite	FeCl <sub>3</sub> -HCl	51-91	44.8	chemical control	Al-Harabs-heh and Kingman, 2008
Sphalerite concentrate	FeCl <sub>3</sub> -HCl	47-87	46.9	chemical control (initial stage)	Bobeck and Su, 1985
				diffusion control (later stage)	
Cu-Zn-Pb sulfide ore	FeCl <sub>3</sub> -HCl	20-100	26	diffusion control	Guy et al., 1983
Pb-Zn sulfide ore	FeCl <sub>3</sub> -HCl	30-100	38	chemical control	Mandre and Sharma, 1993
Sphalerite concentrate	H <sub>2</sub> SO <sub>4</sub> -HNO <sub>3</sub>	45-85	/	diffusion control	Peng et al., 2005
Sphalerite concentrate	H <sub>2</sub> SO <sub>4</sub> -NaNO <sub>3</sub>	60-90	55	diffusion control	Sokić et al., 2012

can be explained by the fact that different sphalerite concentrates were used in which sphalerite is associated in different ways with other sulfide minerals and gangue minerals.

- The oxidation of sphalerite in the presence of strong oxidizing agents such as hydrogen peroxide is much faster compared to ferric sulfate and with increasing oxidant concentration it increases and reaches 99% in a relatively short time. Increasing the mixing speed and temperature above 50 °C has a negative effect on the sphalerite leaching rate, because it accelerates the decomposition of hydrogen peroxide.
- Chloride systems have several advantages over sulfate systems: a) Fe(III) chloride and Cu(II) chloride are far more aggressive than ferric sulfate b) high solubility of zinc and iron; c) faster oxidation of ferrous ions into ferric ions; d) the formation of a porous layer of sulfur that enables the diffusion of reactants to the sulfide sur-

face, e) faster leaching kinetics compared to sulfate systems and f) low reactivity of pyrite in chloride systems. Regardless of the mentioned advantages, leaching processes in chloride systems have not been applied at the industrial level due to the corrosive effect of chloride, the non-selectivity of leaching, and the difficult electrolysis of copper from chloride solutions.

- The use of nitric acid for leaching sulfide minerals has not been widely used to date. On the other hand, nitrate and nitrite ions are used as oxidizing agents in the leaching of sulfide minerals with sulfuric acid. During leaching, most of the sulfide sulfur is oxidized to elemental form, and a smaller part to sulfate. This slows down the leaching process and the diffusion of reactants through the sulfur layer reduces the sphalerite dissolution rate.

## Acknowledgement

This study was financed by the Ministry of Science, Technological Developments and Innovation of the Republic of Serbia (Contract number: 451-03-47/2023-01/200023).

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