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Research Paper

# A Comparative Study on the Mechanism and Kinetics of Acidic Leaching of Sphalerite Concentrate in the Presence of Different Iron Salts

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***Abstract:*** As the main resource of zinc metal production, zinc sulfide mineral has poor sulfuric acid dissolution due to an inactive sulfur layer. This research has done a comparative study on the mechanism and kinetics of acid leaching of sphalerite concentrate in the presence of iron salts such as nitrate, chloride, and iron sulfate. For this purpose, studies were done on a sphalerite concentrate containing 41.23% Zn, 26.15% S, and 6.06% Fe. The investigated parameters include ferric ion concentration, sulfuric acid concentration, temperature, time, solid-to-liquid ratio, and oxygen injection rate, each evaluated at 5 levels. The results indicate that the parameters of temperature, solid-liquid ratio, and ferric ion concentration had the greatest effect on the sphalerite dissolution rate. In the optimal conditions of sulfuric acid concentration 0.51 M, ferric iron 0.9 M, oxygen injection rate 2 L/min, reaction temperature 90°C, time 12 h, and the solid-to-liquid ratio of 50 g/L, recovery of zinc was obtained to be 94.85%. Kinetic investigations showed that, based on the shrinking core model, the sphalerite leaching rate control is based on the diffusion mechanism due to the high correlation coefficient compared to the chemical reaction mechanism.

***Keywords:*** Sulfide concentrate, Zinc, Atmospheric leaching, Ferric ion.

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## INTRODUCTION

One of the important resources for producing zinc metal is sphalerite mineral, which supplies more than 70% of zinc metal in the world. Zinc sulfide minerals have little dissolution in common acids due to the presence of an inactive layer around the surface of the particles [1]. Hydrometallurgical methods for extracting zinc metal from its sulfide resources include direct leaching of the concentrate. These methods include leaching in high temperature-pressure and atmospheric conditions. Pressure and atmospheric leaching methods are carried out in reactors designed for this purpose and used on an industrial scale. Atmospheric leaching has lower kinetics and efficiency compared to pressurized leaching, and because of that, different oxidants are used for the oxidation process [2]. Extensive research has been done in the field of sphalerite leaching to develop a hydrometallurgical process, although no literature study has been conducted regarding the comparative study on the mechanism and kinetics of acid leaching of sphalerite concentrate in the presence of different iron salts such as iron nitrate, chloride, and sulfate. The most important parameters involved in zinc dissolution are temperature, concentration and type of oxidizing agent, solid-to-liquid ratio, acid concentration, and particle size. In the present study, the leaching of sphalerite concentrate in the presence of different iron salts has been investigated from the viewpoint of mechanisms, kinetics, and leaching parameters.

## METHODS

Since the leaching efficiency of sphalerite depends on the amount and type of oxidizing agent, different sources of iron supply and the type of iron charges (at the beginning of the experiments) were investigated on the leaching rate. Also, the effect of important parameters such as iron concentration, type of iron charges, and type of reagent providing iron in sphalerite leaching was investigated. In addition, the effect of other parameters such as acid concentration, temperature, oxygen injection rate, time, and solid-to-liquid ratio was investigated. The composition of sphalerite used in this study has been illustrated in Table 1. The range of investigated parameters is given in Table 2. The middle point of the ranges was considered as the starting point. In the leaching medium, ZnS participates in the oxidation-reduction reaction by $Fe_2(SO_4)_3$, which leads to the oxidation of zinc, the production of $ZnSO_{4(aq)}$, the reduction of iron, and the production of $FeSO_4$. $FeSO_4$ produced reacts with sulfuric acid and oxygen in the leaching medium, which causes oxidation to $Fe_2(SO_4)_3$. This cycle continues until the layer formed on the surface of the particles has a suitable porosity.

**Table 1.** Chemical composition of zinc sulfide concentrate (%)

| Zn | S | Fe | Mg | Mn | Pb | Ni | Co | Cd |
|---|---|---|---|---|---|---|---|---|
| 41.23 | 26.15 | 6.06 | 0.33 | 0.09 | 2.30 | 0.004 | 0.005 | 0.135 |

**Table 2.** The range of investigated parameters in the zinc sulfide concentrate leaching in the presence of ferric ions

| | |
|---|---|
| Temperature (ºC) | 30 – 45 – 60 – 75 – 90 |
| Oxidant concentration | 0.5-1-1.5-2-5 |
| Ferric iron (Molar) | 0.18 –0.36 – 0.54 –0.72 – 0.9 |
| Sulfuric acid (Molar) | 0.31 – 0.41– 0.51 –0.71 – 1.1 |
| Oxygen injection flow rate (L/min) | 1 - 2 – 3 – 4 – 5 |
| S:L ratio (g/L) | 50 - 75 – 100 – 125 – 150 |
| Reaction time (h) | 12 |

## FINDINGS AND ARGUMENT

In this study, the effect of ferric iron concentration in the range of 0.18 to 0.9 M in the reaction temperature of 90 °C, sulfuric acid 0.51 M, solid to liquid ratio 100 g/L, and oxygen injection rate 2 L/min on sphalerite leaching was investigated. The results indicate that the leaching efficiency increases with the increase of iron (ferric iron) concentration. By increasing iron concentration from 0.18 to 0.54 M and from 0.72 to 0.9 M, the leaching efficiency after 12 hours of reaction time increased from 60.32 to 65.76% and from 72.95 to 75.55%, respectively. The results are in agreement with the results of Lorenzo and his colleagues in 2018 [3]. If ferrous iron sulfate ($FeSO_4$) is used instead of ferric sulfate ($Fe_2(SO_4)_3$) in the leaching medium, the leaching efficiency decreases from 75.55 to 52.14% after 12 hours. In other words, if the iron used in the experiment is trivalent from the beginning, it increases the sphalerite leaching reaction kinetics. If the iron is ferrous (bivalent), first this iron must be oxidized to ferric iron. Oxidation of iron by oxygen at ambient pressure does not have a high kinetic rate and depends on the proper distribution of oxygen in the solution. In the continuation of the research, in addition to the type of iron consumed ($Fe_2(SO_4)_3$ or $FeSO_4$) in the dissolution of sphalerite, the resource types, including iron sulfate ($Fe_2(SO_4)_3$), chloride ($FeCl_3$) or nitrate ($Fe(NO_3)_3$) were also examined in this research. The results are shown in Figure 1. As can be seen, the leaching efficiency is higher if iron(III) chloride and iron(III) nitrate are used. At a concentration of 0.9 M ferric iron, the leaching efficiency of $Fe_2(SO_4)_3$, $FeCl_3$, and $Fe(NO_3)_3$ was found to be 77.55, 84.76, and 94.12%, respectively. The results are consistent with the results of the research of Nikkhou and his colleagues in 2019 [4], who investigated the oxidation of sphalerite by ferric iron ions.

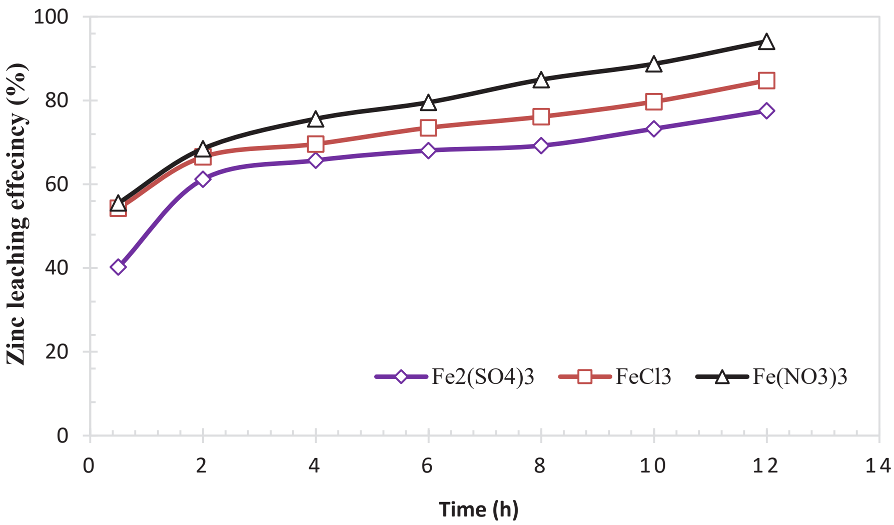


**Figure 1.** The effect of the type of iron reagents on the leaching efficiency in the conditions of 0.9 M of ferric iron at time 12 hours, temperature 90 °C, sulfuric acid 0.51 M, solid to liquid ratio 100 g/L, oxygen injection rate 2 L/min, stirring speed 500 rpm, and particle size less than 50 microns

The diffusion kinetic model can be introduced as a reliable model in sphalerite ore leaching in this research. According to the rate constants obtained, iron nitrate has the highest diffusion rate with a rate constant of 0.0256. In the next rank, iron chloride has a kinetic constant of 0.195. Ferric iron sulfate and ferrous iron sulfate have the lowest diffusion rates with 0.0146 and 0.0045, respectively.

By increasing the concentration of sulfuric acid from 0.31 to 0.51 M after 12 hours of reaction time, the leaching efficiency increased from 63.44 to 77.78%, but after that, by increasing the concentration of sulfuric acid from 0.51 to 1.1 M during 12 hours of reaction time, sphalerite leaching efficiency has not changed much and reached an equilibrium state. Considering that increasing the concentration of acid will increase its consumption rate, this matter is also considered one of the limiting factors on the industrial scale. Thus, the concentration of 0.51 M sulfuric acid was chosen as its optimal limit for further investigation.

In this investigation, the effect of temperature on the leaching of sphalerite in the range of 30-90 $^{o}$C under the conditions of 0.51 M sulfuric acid concentration, iron concentration of 0.9 M, solid to liquid ratio of 100 g/L and oxygen injection rate of 2 L/min was investigated. As a result, by increasing the temperature from 30 to 90 °C after 12 hours of reaction time, the leaching efficiency has increased from 20.49 to 77.78%, respectively. According to the response variable that the maximum efficiency is assumed, the temperature of 90 °C was considered as its optimal condition.

The effect of the injection rate of pure oxygen into the leaching medium in the range of 1 to 3 L/min was investigated under the conditions of sulfuric acid concentration of 0.51 M, iron concentration of 0.9 M, a temperature of 90 °C, a solid-to-liquid ratio of 100 g/L. The results show that by increasing the rate of oxygen from 1 to 2, and 3 L/min after 12 hours, the leaching efficiency has increased from 68.48 to 77.78 and 80.37%, respectively. With the increase of oxygen in the medium, the possibility of contact of ferrous iron ions with oxygen in the medium increases and ultimately raises the conversion rate of ferrous iron to ferric. As the concentration of ferric iron increases in the medium, the leaching efficiency of zinc also increases.

The effect of the solid-to-liquid ratio on leaching efficiency in the range of 50-150 g/L was investigated under the conditions of 0.51 M sulfuric acid concentration, 0.9 M ferric iron concentration, 90 °C reaction temperature, and a 2 L/min oxygen injection rate. The results show that as the solid to liquid ratio increases, the leaching efficiency decreases. So, the efficiency decreased from 94.85% to 58.83% after 12 hours with the increase of the solid-to-liquid ratio from 50 to 150 g/L.

## CONCLUSIONS

In this research, the effect of parameters of ferric iron concentration, sulfuric acid concentration, temperature, time, oxygen injection rate, and the solid-to-liquid ratio on the leaching of sphalerite concentrate was investigated. In the optimum conditions, sulfuric acid concentration of 0.51 M, ferric iron of 0.9 M, an oxygen injection rate of 2 L/min, a reaction temperature of 90 °C, a time of 12 hours, and the solid-to-liquid ratio of 50 g/L were obtained. The results showed that the key factors in achieving high efficiency in sphalerite leaching are ferric iron concentration, temperature, and the solid-to-liquid ratio, which in general increases with an increase in oxidant concentration and temperature and a decrease in solid-to-liquid ratio.

It was also observed that the type of iron added to the medium ($Fe^{2+}$ or $Fe^{3+}$) as well as the source of its supply ($Fe_2(SO_4)_3$, $FeCl_3$ or $Fe(NO_3)_3$) are the effective parameters on sphalerite leaching rate. Kinetic analysis showed that, based on the shrinking core model, sphalerite leaching was controlled by the diffusion mechanism due to the high correlation coefficient compared to the chemical reaction mechanism. According to the rate constants obtained from the results, iron nitrate has the highest diffusion rate with a rate constant of 0.0256. In the next rank, iron chloride has a constant of 0.195. Ferric iron sulfate and ferrous iron sulfate have the lowest diffusion rates with values of 0.0146 and 0.0045, respectively. According to the results, by increasing the concentration of sulfuric acid to a certain extent, the kinetics and efficiency of leaching increased. However, higher acid concentrations did not have much effect on the efficiency and leaching rate of sphalerite. Temperature is one of the most important parameters in achieving high efficiency, so increasing it from 30°C to above 85°C increases the efficiency by about 4 times. The results showed that the leaching efficiency decreased with the increase in the solid-to-liquid ratio. Thus, the leaching efficiency decreased from 94.85% to 58.83% after 12 hours with the increase of the solid-to-liquid ratio from 50 to 150 g/L.

## REFERENCES


[1] Bernasowski, M., Stachura, R., and Klimczyk, A. (2022). *"Fuel Consumption Dependence on a Share of Reduction Processes in Imperial Smelting Furnace"*. Energies, 15: 9259.

[2] Karimi, S., Rashchi, F., and Ghahreman, A. (2021). *"The Evaluation of Sphalerite Surface Formed During Oxidative Leaching in Acidic Ferric Sulfate Media"*. Journal of Sustainable Metallurgy, 7: 1304-1313.

[3] Lorenzo-Tallafigo, J., Iglesias-Gonzalez, N., Romero, R., Mazuelos, A., and Carranza, F. (2018). *"Ferric leaching of the sphalerite contained in a bulk concentrate: Kinetic study"*. Minerals Engineering, 125: 50-59.

[4] Nikkhou, F., Xia, F., and Deditius, A. P. (2019). *"Variable surface passivation during direct leaching of sphalerite by ferric sulfate, ferric chloride, and ferric nitrate in a citrate medium"*. Hydrometallurgy, 188: 201-215.