The 56th International October Conference on Mining and Metallurgy
22-25 October 2025, Bor Lake, Bor, Serbia
www.ioc.tfbor.bg.ac.rs

DOI: 10.5937/IOC25255A *Original scientific paper*

INNOVATIVE OXIDATIVE SYSTEM FOR LEACHING OF Fe^{2+} FROM SPHALERITE CONCENTRATE

Dimitrije Anđić[1a], Aleksandar Jovanović[1b], Nikola Vuković[1c], Ivana Jelić[1d], Mladen Bugarčić[1e], Vaso Manojlović[2a], Miroslav Sokić[1f]

[1] Institute for Technology of Nuclear and Other Mineral Raw Materials, Belgrade, Serbia
[2] University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, Serbia
[1a] d.andjic@itnms.ac.rs, 0009-0001-6824-5202
[1b] a.jovanovic@itnms.ac.rs, 0000-0001-9867-9282
[1c] n.vukovic@itnms.ac.rs, 0000-0002-3607-5907
[1d] i.jelic@itnms.ac.rs, 0009-0000-9901-9323
[1e] m.bugarcic@itnms.ac.rs, 0000-0002-6119-4414
[2a] v.manojlovic@tmf.ac.bg.rs, 0000-0002-3009-2909
[1f] m.sokic@itnms.ac.rs, 0000-0002-4468-9503

Abstract
Sphalerite is a sulfide zinc mineral, which also contains supporting metals such as iron, copper and lead. In this work, we dealt with the extraction of iron from sphalerite in a new oxidation system. Manganese dioxide was used as the primary oxidant, and KI was used as a secondary oxidizing agent with the aim of creating an I_2/I^- oxidation cycle in a sulfuric acid medium. The thoughtful characterization (XRD, SEM, EDS) of the initial sample, as well as the precipitate formed after leaching was done. During the leaching tests, process parameters were varied.

***Keywords**: hydrometallurgy, chemical oxidation, leaching efficiency*

1. INTRODUCTION

Sphalerite is often found in a dispersed form alongside other sulfide minerals and tailings, characterized by a complex mineralogical composition and fine-grained texture. It can appear as impregnations, inclusions, and both simple and complex intergrowths within the ore matrix. Conventional hydrometallurgical techniques typically involve leaching sphalerite concentrates in an acidic medium, most commonly sulfuric acid combined with various oxidants. These processes enhance metal recovery while also minimizing air pollution risks. The main byproducts of these reactions include sulfuric acid and/or elemental sulfur, along with the formation of soluble sulfate salts. However, due to the inherent resistance of sphalerite in acidic solutions, oxidizing agents are required to promote its oxidative dissolution [1]. In addition to sphalerite, the concentrate may contain trace amounts of other metals, such as iron, which is most commonly present in the form of pyrite. The chemical composition of pyrite is iron (II)-sulfide (FeS_2), which contains 46.6 % Fe and 53.4 % S [2]. When leaching sulfides with sulfuric acid, oxygen or some other compound with very strong oxidizing abilities (H_2O_2, MnO_2, $KMnO_4$...) can be used as an oxidant [3, 4]. A. Chandra et al. [5] found that pyrite leaching occurs more slowly when sulfuric acid is used as leaching agent. Therefore, the goal of this work is to introduce a new oxidation system (MnO_2-KI) during the leaching of sphalerite with sulfuric acid, in order to increase the extraction yield of iron.

2. EXPERIMENTAL

Zinc concentrate was taken from the ore deposit "Rudnik" (Rudnik), Serbia. Prior leaching tests, the concentrate was ground with a vibro mill (KHD Humboldt Wedag AG, Germany). Chemicals used for experiments are manganese dioxide (Alkaloid, purity > 95%, North Macedonia) and

potassium iodide (Merck, purity > 95%, Germany) and 1.5 M analytically prepared sulfuric acid solution (Zorka, PA, Serbia).

2.1. Structural characterization

Surface morphology was determined by scanning electron microscopy (SEM) using a JEOL JSM-7001F (Japan) instrument coupled with an energy-dispersive spectrometer (EDS) (Oxford Xplore 15, UK). Additional structural insights were gained through qualitative ore microscopic analyses conducted with a polarizing microscope (Carl Zeiss-Jena Axioscope 5 Pol, Germany). The microscope featured a color camera (Axiocam 105 color, USA), and photomicrographs were captured using the Carl Zeiss AxioVision SE64 Rel. 4.9.1 software with the "Multiphase" module. The mineral compositions of the concentrate and leaching residues were analyzed using X-ray diffraction (XRD) to determine the phase composition (Philips PW 1710/1820, Netherlands).

2.2. Leaching experiments

For leaching experiments, a 1.2 dm^3 glass reactor (Zhengzhou Great Wall, China) was employed. Detail experimental procedure of all leaching tests was presented in work of Bugarčić et al. [5]. At specified intervals, aliquots were taken and analyzed using atomic absorption spectrophotometry (AAS, PERKIN ELMER 703, USA). The AAS results were used to calculate the iron extraction rate (%).

3. RESULTS AND DISCUSSION

3.1. Materials characterization

Under the optical microscope (Figure 1), it was noted that around 80 % of the sphalerite exists as free grains, while the rest is found in simple to complex intergrowths with other minerals. Chalcopyrite is the mineral most commonly associated with sphalerite in this concentrate, followed by pyrite, galena, gangue minerals, and chalcopyrite impregnations. The size of the sphalerite grains ranges from approximately 10 μm to more than 350 μm.

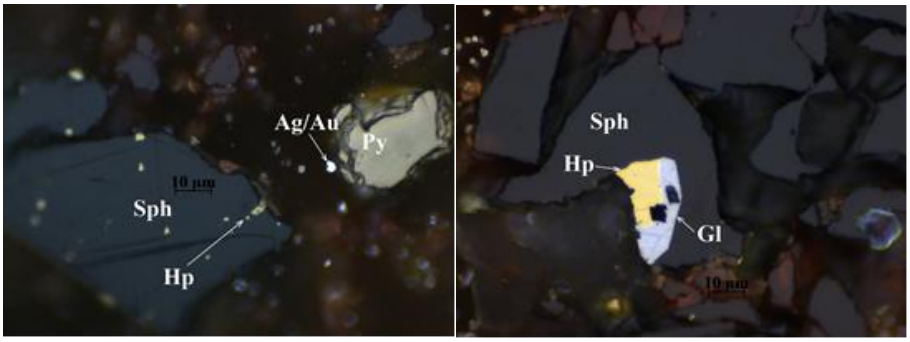

Figure 1. Native silver/gold (Ag/Au) next to pyrite (Py) in the Zn concentrate sample (left subfigure) and complex assemblage of sphalerite (Sph), chalcopyrite (Hp) and galena (Gl) in the Zn concentrate sample (right subfigure)

The minerals identified in the examined sample by XRD included sphalerite, chalcopyrite, pyrite and quartz (Figure 2). Sphalerite was by far the most dominant mineral, while chalcopyrite, pyrite, and quartz were present in much smaller quantities.

The SEM image (Figure 3) reveals that the concentrate particles have distinct, smooth edges. Constituents are in the diameter range 50 – 100 μm.

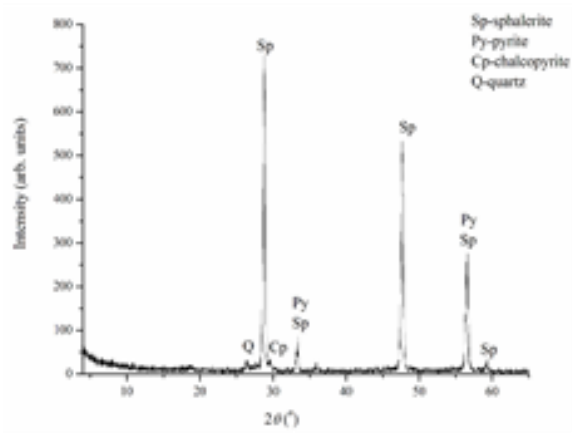

Figure 2. Powder diffractogram of the ZnS sample [6]

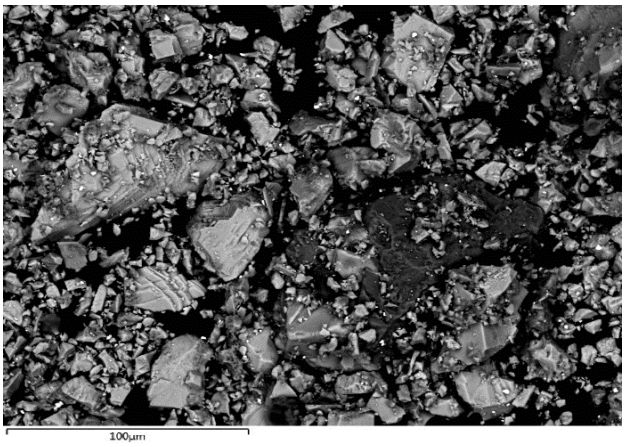

Figure 3. SEM micrograph of ZnS sample

3.2. Leaching experiments

The leaching efficiency of iron (Fe) from zinc concentrate rises with temperature, ranging from 40 °C to 80 °C. Increased temperatures provide extra thermal energy, promoting particle movement and increasing the frequency of effective collisions between sulfide minerals and the intermediary oxidant (I_2). This leads to more efficient leaching of iron from zinc concentrate.

Figure 4. shows the XRD analysis of the precipitate after leaching the zinc concentrate at lower temperatures.

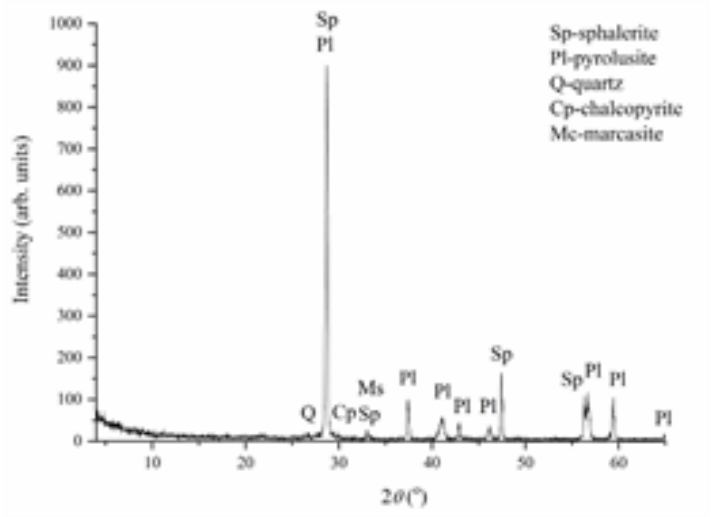

Figure 4: XRD pattern with legend for leaching residue; experiment parameters (3 wt. % KI + stoichiometric amount of MnO_2 at 40 °C) [6]

Based on the qualitative mineralogical composition, it can be concluded that the most abundant phase in the precipitate after leaching is pyrolusite. After pyrolusite - 54.3 wt.%, the most abundant is sphalerite - 41.2 wt.%, followed by quartz - 0.8 wt.%, chalcopyrite - 1.1 wt.%, and marcasite - 1.0 wt.%.

The microscopic image (Figure 5) clearly shows that, in addition to the phases that make up the initial concentrate, pyrolusite is also present in the precipitate largely.

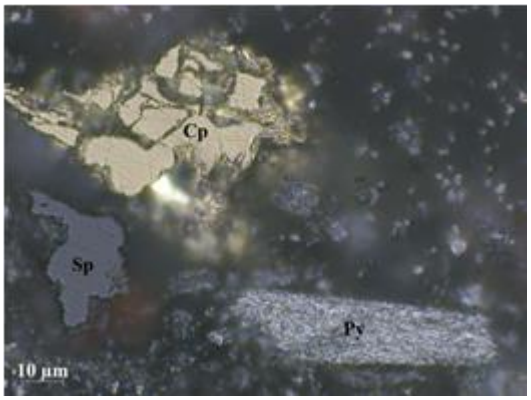

Figure 5. Liberated grains of sphalerite (Sp), chalcopyrite (Cp) and pyrolusite (Pl)

Using the XRD method (Figure 6), was established that elemental sulfur is released during leaching at a high temperature (80 ^{o}C). The explanation for this phenomenon is that the crystallization and formation of elemental sulfur is temperature dependent. At elevated temperatures, oxidation reactions lead to rapid migration of sulfur atoms from the sphalerite surface, where they are grouped into crystal structures.

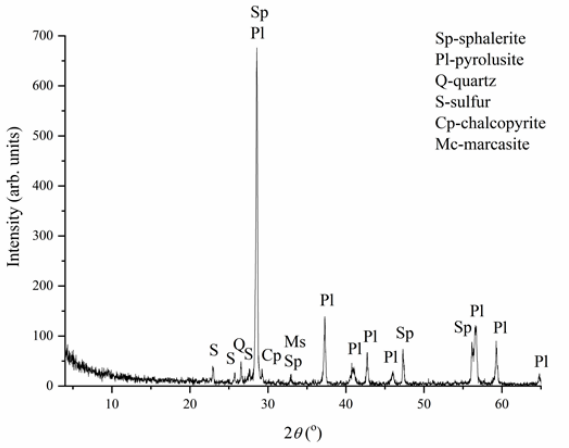

Figure 6: XRD pattern with legend for leaching residue; experiment parameters (3 wt. % KI + stoichiometric amount of MnO_2 at 80 °C) [6]

Based on Figure 6, it can be seen that the most abundant phase in the analyzed sample is pyrolusite, and below it is sphalerite, quartz, sulfur, chalcopyrite and marcasite. In Figure 7, we can see that elemental sulfur is separated in the form of irregular grains.

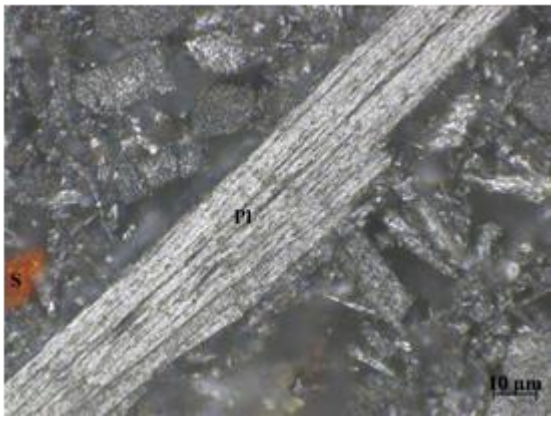

Figure 7. Irregular grain of sulfur [6]

Figure 8 shows the influence of temperature and time on the degree of leaching of Fe and sphalerite concentrate. Based on the obtained results, we can conclude that the degree of iron leaching

increases with the increase in temperature. The reason for this is that with an increase in temperature, the particles move faster, and therefore the leaching agent comes into contact with a larger number of particles of the initial concentrate, and thus the degree of valorization of iron increases. According to the identical principle, time has an influence on the degree of iron leaching.

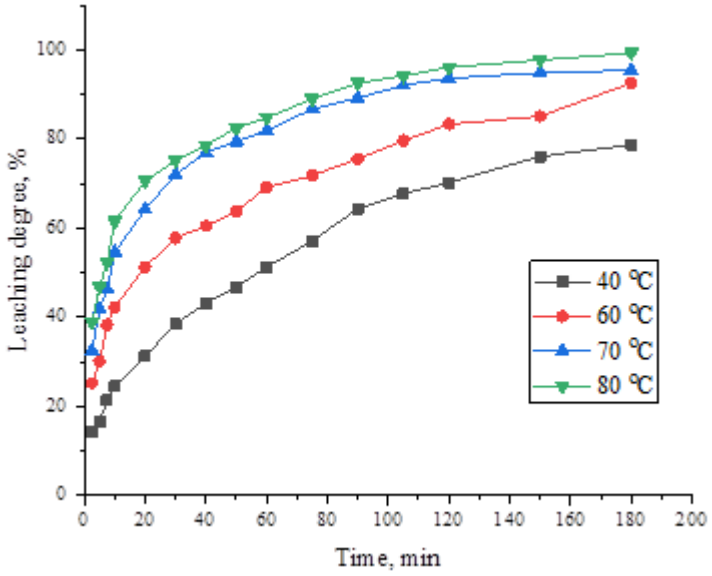

Figure 8. Influence of temperature and reaction time on leaching degree of Fe (3 wt. % KI + stoichiometric amount of MnO_2)

4. CONCLUSION

This research examined the dissolution characteristics of iron (Fe) from sphalerite concentrates in a sulfuric acid solution, utilizing manganese dioxide (MnO_2) as the main oxidizing agent. The process was conducted at temperatures ranging from 40 °C to 80 °C under atmospheric pressure, with the presence of potassium iodide (KI). Increasing the temperature enhanced Fe leaching efficiency due to faster reaction kinetics. However, XRD analysis identified crystalline sulfur phases at 80 °C, whereas no such phases were observed at 40 °C. This suggests that higher temperatures facilitate the crystallization of elemental sulfur, leading to the formation of detectable crystalline structures. In contrast, at lower temperatures, sulfur remains in an amorphous or finely dispersed form, which is not detectable by XRD but can be observed using reflected light microscopy. This research leaves the possibility of finding a new system that would enable the maximum degree of valorization of iron from sphalerite concentrate.

ACKNOWLEDGEMENTS

This work was supported by the Ministry of Science and Technological Development and Innovation of the Republic of Serbia (Contract No. 451-03-136/2025-03/200023).

REFERENCES

[1] M. Sokić, M. Bugarčić, A. Jovanović, MMD, 1 (2023) 33–43.
[2] S. Janjić, P. Ristić, Mineralogija, Naučna knjiga, Beograd, 1995, 217.
[3] M. Sokić, The mechanism of leaching of polymetallic Pb-Zn-Cu concentrates with sulfuric acid in the presence of selected oxidants. TMF UB 2008.
[4] S. Aydogan, J. Chem. Eng., 123 (2006) 65–70.
[5] A.P. Chandra, A.R. Gerson, GCA 75 (22) (2011) 6893-6911.
[6] M. Bugarčić, A. Jovanović, D. Anđić, I. Jelić, M. Miletić, B. Marković, M. Sokić, Metals, 15 (1) (2025) 50.