

# Bioleaching and chemical leaching of lateritic ore in small percolators

Srdjan Stanković, Axel Schippers\*

Federal Institute for Geosciences and Natural Resources, Stilleweg 2, 30655 Hannover, Germany

## ARTICLE INFORMATION :

<https://doi.org/10.30544/MMD9>

Received: 25 June 2023

Accepted: 30 June 2023

Type of paper: Research paper



Copyright: © 2023 by the authors, under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons-mons.org/licenses/by/4.0/>).

## ABSTRACT

This work presents results of an initial exploration of nickel and cobalt bioleaching from lateritic ores in small percolators, which serve as simulations of the heap leaching process. Heap leaching offers an attractive alternative to high-pressure acid leaching of laterites, owing to its relatively simple technology, reduced capital and operational expenses, and lower carbon dioxide emissions. Conventional heap leaching of laterites relies on sulfuric acid leaching. Typically, this process consumes 400-500 kg/t of ore, necessitating the construction of a costly on-site sulfuric acid plant. However, the metabolic activity of sulfur-oxidizing bacteria can generate sulfuric acid while reducing ferric to ferrous iron, facilitating mineral dissolution through a combined protonation and reduction effect. Implementing this process eliminates the need for a sulfuric acid production plant, as the bacteria oxidize sulfur within the leaching heap. The results presented in this paper demonstrate comparable efficiencies between bioleaching and chemical leaching with sulfuric acid for nickel extraction, underscoring the importance of ferrous iron in enhancing leaching efficiency.

**Keywords:** cobalt, bioleaching, laterites.

## 1. Introduction

Two dominant technologies for processing of lateritic material are either pyrometallurgical processing in smelters or hydrometallurgical processing by the application of high pressure acid leaching with sulfuric acid (HPAL). Heap leaching of laterites is an emerging alternative approach to HPAL. It is a relatively simple technology characterized by substantially lower capital and operational expenses, as well as carbon-dioxide emission in comparison to HPAL (Oxley et al. 2013, Norgate and Jahanshahi, 2011). The main disadvantages of the heap leaching process are the long leaching time and relatively high acid consumption (Stanković et al. 2020). Considering the enormous amounts of material that needs to be processed, consumption of sulfuric acid of the industrial scale heap leaching operations is enormous and requires construction of a capital-intensive sulfuric acid production plant. One possible alternative to heap leaching of laterites with sulfuric acid might be the application of heap bioleaching. Acidophilic sulfur-oxidizing bacteria that belong to the genus *Acidithiobacillus* can oxidize elemental sulfur under aerobic and anaerobic conditions (Wang et al., 2019). Bacterial sulfur oxidation generates sulfuric acid and ferrous iron as outcomes of bacterially mediated reduction of ferric iron in

leaching solution under aerobic or anaerobic conditions (Marrero et al., 2015, Santos et al., 2020, Malik and Hedrich, 2022). Previous experiments conducted in bioreactors showed that bioleaching of nickel and cobalt from laterites is based on acidic dissolution of main nickel bearing phases (mostly serpentine group minerals and to some extent iron(III)oxide phases) and rapid reductive dissolution of MnO-rich phases (asbolane-lithiophorite) that host the majority of cobalt and a significant part of nickel (Stanković et al., 2022). The idea behind the preliminary experiments described in this paper was to mix lateritic material with sulfur, and test the ability of bacteria to produce sulfuric acid and ferrous iron, thus promoting bioleaching of nickel and cobalt from lateritic ore in small laboratory column percolators.

## 2. Materials and methods

### 2.1. Laterite sample

The Brazilian Nickel company provided the sample from the Piauí deposit in Brazil for the experiment. The sample was sent to BGR in two barrels, each containing approximately 70 kg of material. The chemical composition analyzed by XRF comprised 62.23% SiO<sub>2</sub>, 19.12% of Fe<sub>2</sub>O<sub>3</sub>, 5.84% of MgO, 2.26% of Al<sub>2</sub>O<sub>3</sub>, 9193 mg/kg Ni and 370 mg/kg Co. The most abundant mineral phases identified by quantitative XRD analysis were quartz (38 wt%), smectite (24 wt%), goethite (14 wt%), chlorite (8

\* Corresponding author.  
E-mail address: axel.schippers@bgr.de (Axel Schippers).

wt%), kaolinite (5 wt%), hematite (4 wt%), lizardite (3 wt%), K-feldspar (2 wt%), and chromite (2 wt%) (Stanković et al., 2023).

## 2.2. Preparation of bacterial culture and „wet“ sulfur

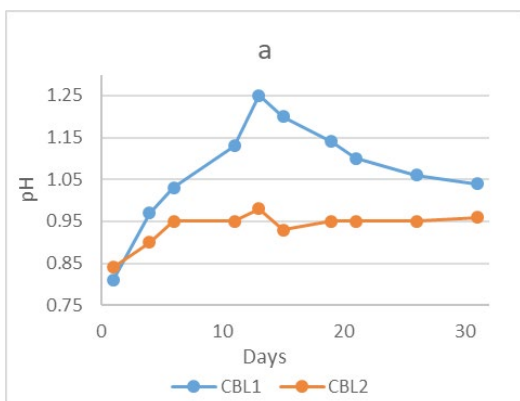
A bioreactor vessel with a total volume of 2 L was filled with 1.6 L of basal salts solution (Wakeman et al., 2008), 30 g of elemental sulfur and inoculated with 200 mL of an active culture of sulfur-oxidizing bacteria *Acidithiobacillus thiooxidans* DSM 9463. Bacteria were cultivated for seven days under the following conditions: temperature 30 °C, air supply 1 L/min, stirring speed 250 rpm. The amount of sulfur was determined based on the estimated sulfuric acid consumption of 400 g per kg of ore.

## 2.3. Setup of the bioleaching experiment

After seven days of cultivation in the bioreactor, 900 mL of bacterial culture was transferred into each of two double-walled Duran® reactor bottles with magnetic stirrers and placed on a magnetic stirring plate with steering speed of 50 rpm. The bottles were connected to a water bath with water recirculation (Julabo, Germany) to maintain a constant temperature at 30 °C. Air was supplied to the liquid bacterial culture medium in bottles at a rate of 1 L/min. Lateritic material (200 g) was mixed with bacterially colonized, „wet“ sulfur collected from the bioreactor vessel using a laboratory drum agglomerator and 3 M sulfuric acid as a binder (Stanković et al., 2023). Half of the agglomerated material was put into each column. The height of the columns was 50 cm, and the internal diameter was 2.5 cm. The lixiviant (bacterial culture) was applied at a rate of 3 mL/min in recirculation mode using 4-channel peristaltic pumps Reglo ICC digital (Cole Parmer, USA). The setup of the bioleaching experiment is presented in Figure 1.



Fig. 1. Setup of the small column percolator bioleaching experiment.



## 2.4. Setup of chemical leaching experiment

For the chemical leaching experiment in small column percolators, one bottle was filled with 900 mL of 1 M sulfuric acid, and one bottle was filled with 900 mL of 1 M sulfuric acid with 5 g/L ferrous sulfate heptahydrate dissolved as a reducing agent (Moro et al., 2023). Experiments were conducted at 30 and 3 mL/min liquid flow rate.

## 2.5. Liquid sample analyses

Liquid samples were obtained in leaching experiments. Concentrations of dissolved metals were determined with a Thermo Fisher iCAP Pro ICP-OES, operated simultaneously in radial and axial view mode. Quality control was achieved by continuously measuring a Bernd Kraft Multielement Standard (Analytichem GmbH, formerly Bernd Kraft GmbH), containing 22 elements at known concentrations in 2 M HNO<sub>3</sub>, after each sample batch. Deviations for the reported analytes from known concentrations were below approximately 5 %. Ferrous iron concentrations were measured by a colorimetric assay using ferrozine (Lovely and Philips, 1987). Total iron was quantified by adding an excess of ascorbic acid to reduce soluble ferric iron to ferrous iron, and ferric iron was determined from the difference between the total and ferrous iron concentrations. The pH was measured with electrodes, and the redox potential (ORP) was measured with platinum-silver/silver chloride electrodes; the given values are relative to Ag/AgCl.

## 3. Results and discussion

### 3.1. Results of the bioleaching experiments

Changes of pH and redox potential of the two small column bioleaching percolator experiments, designated as CBL1 and CBL2, are shown in Figure 2. During the bioleaching experiment, the consistently low pH values confirmed that bacteria were able to oxidize elemental sulfur that was mixed with lateritic material in the columns. Visual inspection of leaching residues after finishing the experiment after one month did not reveal any traces of unoxidized sulfur.

On the 11th day of experiment CBL1, a sudden increase in pH and a decrease in ORP were detected (Figure 2). The percentage of ferrous iron relative to total iron in this experiment reached 100 % and remained high throughout the course of the experiment (Figure 3). In experiment CBL2 the redox potential was higher in comparison to CBL1. The decrease in redox potential in CBL1 corresponded with an increase in the proportion of ferrous iron in leaching solution; the share of ferrous iron in CBL2 was low throughout experiment (Figure 3). As the concentration of ferrous iron in solution decreased after

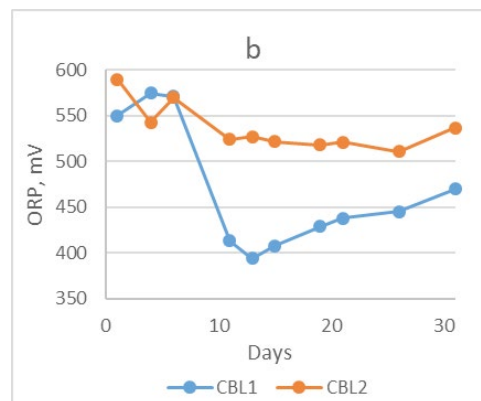
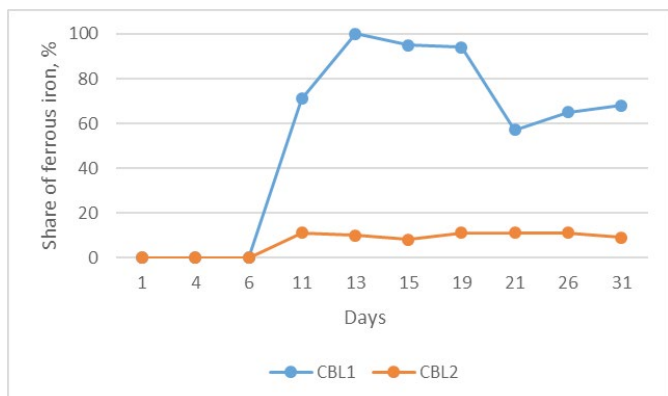


Fig. 2. Changes in pH (a) and redox potential (b) during bioleaching experiment.

the 11th day, the pH also dropped, indicating that the acid consuming capacity diminished over time, due to completion of chemical reactions. Conducted under non-sterile conditions, the experiments may have experienced growth of various bacterial contaminants in the two columns. Bacteria that belong to the species *Acidithiobacillus ferrooxidans* can utilize sulfur as an electron donor and ferric iron as an electron acceptor in a respiratory chain under anaerobic conditions (Kucera et al., 2016). These bacteria can efficiently reduce ferric iron under anaerobic conditions. The differing chemistry of the leaching solution in experiment CBL1, as compared to CBL2, could be attributed to contamination with *Acidithiobacillus ferrooxidans*, potentially under anaerobic conditions within the column.



**Fig. 3.** Changes in share of ferrous iron expressed as percentage of the total iron concentration in the leaching solution of the two bioleaching experiments.

Two chemical leaching small column percolation experiments were designated as CCL (chemical leaching with 1 M sulfuric acid) and CCLFe (chemical leaching with 1 M sulfuric acid and 5 g/L ferrous sulfate heptahydrate). Changes in pH and redox potential (ORP vs. Ag(AgCl)) during chemical leaching experiments are presented in Figure 4.

During the chemical leaching experiments, the pH was slightly higher in the CCLFe experiment. The redox potential was relatively constant in the leaching solution of the CCL experiment; however, in the leaching solution of the CCLFe experiment, the redox potential increased as result of the oxidation of ferrous iron, which reacted with certain mineral phases.

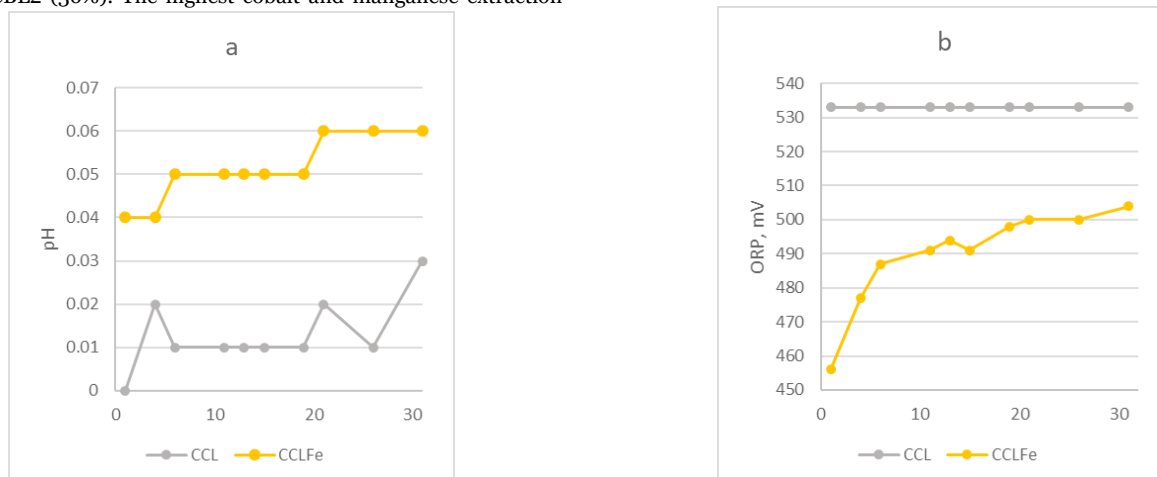
Figure 5 shows changes in nickel, magnesium, cobalt, and manganese extraction during bioleaching and chemical leaching experiments.

Nickel extraction ultimately reached 68 % in both chemical leaching experiments (CCL1 and CCLFe), 64 % in CBL1 and 40 % in CBL2 experiments. Magnesium extraction was similar in CBL1, CCL and CCLFe experiments (49%, 49%, 47% respectively) and substantially lower for CBL2 (36%). The highest cobalt and manganese extraction

occurred in CBL1 leaching solution (83% and 86%, respectively), and lowest was observed in CBL2 leaching solution (60% and 56% respectively). Cobalt and manganese extraction was comparable in CCL and CBL2 - 69 % and 58%, respectively. The CCLFe experiment performed better due to the presence of ferrous iron, which reductively dissolves Mn-rich phases hosting cobalt in laterites (Stanković et al., 2022): 77% of Co and 70% of Mn were extracted. The correlation coefficient between Mg and Ni extractions was higher ( $R^2=0.967$ ) than the correlation coefficient between Fe and Ni extractions ( $R^2=0.883$ ) during bioleaching experiments. This data indicates that most of the nickel was bioleached from Mg-rich mineral phases (such as serpentine group minerals). As expected, the correlation coefficient between Mn and Co extractions was high ( $R^2=0.985$ ) indicating that most of the cobalt came from Mn-rich mineral phases.

Figure 6 shows changes in concentrations of extracted iron during bioleaching and chemical leaching experiments. The amount of extracted iron was highest after leaching in the CCLFe experiments (32%), and lowest for CBL2 (6%). The concentration of ferrous iron was substantially higher for CBL1 than for CCLFe (Figure 7). Iron extraction during leaching of laterites in the CBL1 and CBL2 experiments remained comparable until day 11, when a complete reduction of iron in the leaching solution of the CBL1 experiments occurred. After that day, the concentration of iron in the CBL1 leaching solution increased more rapidly than that for CBL2 and the final iron extraction reached 19.5 %, which was comparable to that achieved with 1 M sulfuric acid (23%).

The results clearly indicate the importance of ferrous iron for efficient bioleaching of nickel and cobalt from laterites. The effect of ferrous iron on effective reductive dissolution of Mn-rich cobalt bearing phases is well documented (Stanković et al., 2022; Moro et al., 2023), and confirmed in this study. The effect of ferrous iron on dissolution of other mineral phases is less clear. According to MacDonald and Whittington (2008) ferrous iron can facilitate protonation based dissolution of iron(III)oxide minerals. Senanayake et al. (2011) tested leaching of nickel from synthetic iron oxides in presence of ferrous iron, and concluded that ferrous iron had a beneficial effect on nickel extraction, which is also confirmed by results of this study. The amounts of extracted iron and magnesium were substantially higher with leaching in the ferrous iron rich CBL1 experiments in comparison to the ferrous iron depleted CBL2 experiments. Despite the lower acid concentration during the bioleaching experiment, the extraction of nickel in the CBL1 experiments was comparable to that of the nickel extraction from laterites in the chemical leaching experiments CCL and CCLFe. Cobalt extraction was most efficient during bioleaching in the CBL1 experiments. The extraction of all measured chemical elements were lowest after bioleaching of the lateritic sample in the CBL2 experiments. These results suggest that a lower acid concentration during bioleaching might be compensated by the reducing power of ferrous iron.



**Fig. 4.** Changes in pH of the leaching solution (a) and redox potential (b) during chemical leaching experiments.

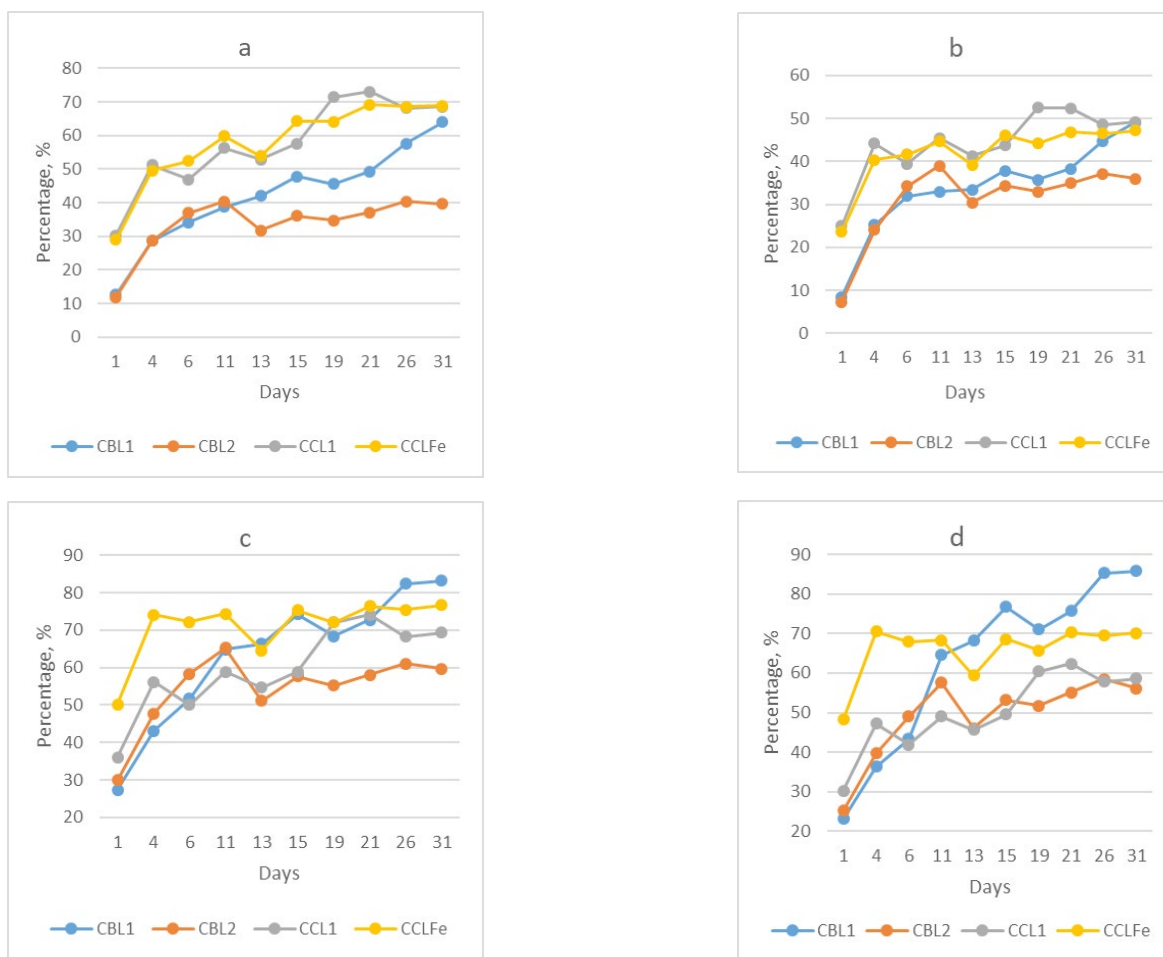


Fig. 5. Changes in nickel (a), magnesium (b), cobalt (c) and manganese (d) extraction during bioleaching and chemical leaching experiments.

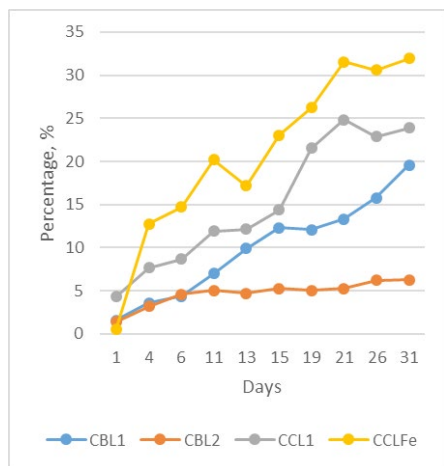


Fig. 6. Changes in iron extraction during bioleaching and chemical leaching experiments.

4. Conclusion

The experiments indicate that bioleaching nickel and cobalt from laterites at the Piauí deposit is feasible. Under controlled reducing conditions, bioleaching may approach sulfuric acid leaching nickel extraction rates while recovering more cobalt. Given lower environmental impact of bioleaching and operational costs, this seems like a significant benefit. Eliminating sulfuric acid production on-site reduces costs and promotes environmentally friendly mining.

The increased demand for cobalt in rechargeable batteries makes cobalt extraction using bioleaching particularly noteworthy. The transition to a heap bioleaching system is difficult, especially in establishing and maintaining large-scale reducing conditions. To ensure

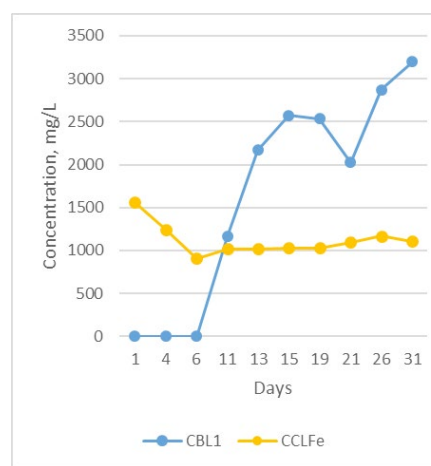


Fig. 7. Changes of ferrous iron concentration in leaching solutions of the CBL1 and CCLFe experiments.

consistent and efficient metal recovery, future research should optimize operational parameters and manage microbial communities to scale this process. Practical application requires studying the bioleaching system's long-term stability and environmental resilience.

Acknowledgements

We thank the company Brazilian Nickel and Anne Oxley for providing the sample, and Reiner Neumann (CETEM, Brazil) and Herwig Marbler (BGR-DEIRA, Germany) for organizing transportation, and for scientific discussions. This research was financially supported by the German Mineral Resources Agency (DEIRA) within BGR.

## References

- Kucera, Jiri, Eva Pakostova, Jan Lochman, Oldrich Janiczek, and Martin Mandl. "Are there multiple mechanisms of anaerobic sulfur oxidation with ferric iron in *Acidithiobacillus ferrooxidans*?" *Research in microbiology* 167, no. 5 (2016): 357-366.
- Lovley, DR. "Rapid assay for microbially reducible ferric iron in aquatic sediments." *Appl. Environ. Microbiol.* 52 (1987): 751-757.
- McDonald, R. G., and B. I. Whittington. "Atmospheric acid leaching of nickel laterites review: Part I. Sulphuric acid technologies." *Hydrometallurgy* 91, no. 1-4 (2008): 35-55.
- Malik, Luise, and Sabrina Hedrich. "Ferric iron reduction in extreme acidophiles." *Frontiers in Microbiology* 12 (2022): 818414.
- Marrero, J., O. Coto, S. Goldmann, T. Graupner, and A. Schippers. "Recovery of nickel and cobalt from laterite tailings by reductive dissolution under aerobic conditions using *Acidithiobacillus* species." *Environmental science & technology* 49, no. 11 (2015): 6674-6682.
- Moro, Kofi, Frank Haubrich, Mirko Martin, Marlies Grimmer, Nils Hoth, and Axel Schippers. "Reductive leaching behaviour of manganese and cobalt phases in laterite and manganese ores." *Hydrometallurgy* (2023): 106101.
- Norgate, T., and S. Jahanshahi. "Assessing the energy and greenhouse gas footprints of nickel laterite processing." *Minerals Engineering* 24, no. 7 (2011): 698-707.
- Oxley, Anne, Mark E. Smith, and Omar Caceres. "Why heap leach nickel laterites?" *Minerals Engineering* 88 (2016): 53-60.
- Santos, Ana Laura, Agnieszka Dybowska, Paul F. Schofield, Richard J. Herrington, and D. Barrie Johnson. "Sulfur-enhanced reductive bioprocessing of cobalt-bearing materials for base metals recovery." *Hydrometallurgy* 195 (2020): 105396.
- Senanayake, G., J. Childs, B. D. Akerstrom, and D. Pugaev. "Reductive acid leaching of laterite and metal oxides—A review with new data for Fe (Ni, Co) OOH and a limonitic ore." *Hydrometallurgy* 110, no. 1-4 (2011): 13-32.
- Stanković, Srđan, Srećko Stopić, Miroslav Sokić, Branislav Marković, and Bernd Friedrich. "Review of the past, present, and future of the hydrometallurgical production of nickel and cobalt from lateritic ores." *Metallurgical & Materials Engineering* 26, no. 2 (2020): 199-208.
- Stanković, Srđjan, Mirko Martin, Simon Goldmann, Hans-Eike Gäbler, Kristian Ufer, Frank Haubrich, Vivian Fernandes Moutinho et al. "Effect of mineralogy on Co and Ni extraction from Brazilian limonitic laterites via bioleaching and chemical leaching." *Minerals Engineering* 184 (2022): 107604.
- Wakeman, Kathryn, Hannele Auvinen, and D. Barrie Johnson. "Microbiological and geochemical dynamics in simulated-heap leaching of a polymetallic sulfide ore." *Biotechnology and bioengineering* 101, no. 4 (2008): 739-750.
- Wang, Rui, Jian-Qiang Lin, Xiang-Mei Liu, Xin Pang, Cheng-Jia Zhang, Chun-Long Yang, Xue-Yan Gao et al. "Sulfur oxidation in the acidophilic autotrophic *Acidithiobacillus* spp." *Frontiers in microbiology* 9 (2019): 3290.