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AN INNOVATIVE BIOCHEMICAL ROUTE TO RECOVER COBALT FROM LATERITIC MINING WASTE

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1. Keywords
Cobalt, nickel, laterite, reductive bioleaching, mining waste

2. Highlights

- Reductive bioleaching was performed with limonite from New Caledonia.
- Cobalt and manganese were released very quickly in contrary to iron and nickel.
- Low dissolution yield of nickel might be attributed to goethite crystallinity.

3. Purpose

Cobalt (Co) and nickel (Ni) are two major components of lithium ion batteries, and their demand is expected to grow steadily over the next decade thanks to the increase of electric vehicles production. Around 60% of world's Ni reserves are contained in lateritic ores which display also significant amount of Co [1]. The treatment of this type of ore requires costly metallurgical methods that generally incur high energy or reagent consumptions and expensive capital equipment costs [2]. Despite these economic constraints, the production of Ni and Co from laterites is constantly increasing owing to the exhaustion of sulfidic deposits as well as the increase in metal demand. Laterites deposits are mainly located in tropical regions and are characterized by the presence of two distinct horizons: (i) an upper limonite zone where Ni content usually varies between 1 and 2% with also significant presence of Co; (ii) a lower saprolite zone with Ni content varying between 3 and 5%. The saprolitic ore is usually treated via pyrometallurgical reduction whereas the limonitic ore is traditionally processed through Pressure Acid Leaching (PAL) which has often proven to be very costly, plagued with technical challenges. At this time, Ni produced from laterites mainly derives from saprolite ores, the associated limonite ores being usually stockpiled and considered as a mining waste. This stockpiled material represents a vast unlocked resource.

Recent work demonstrated that Ni and Co could be extracted from limonite by using acidophilic bacteria in anoxic condition, mild acid (pH 1.8) and at ambient temperature (30°C). This method is called "reductive bioleaching" or "bioleaching in reverse gear" [3, 4]. H2020 CROCODILE research project is dedicated to the demonstration of innovative metallurgical options for the recovery of Co from primary and secondary sources. In the frame of CROCODILE, reductive bioleaching was applied to limonite from New Caledonia. The leaching mechanisms were investigated and optimised in order to design a demonstration at pilot scale.

4. Materials and methods

This study was carried out using limonite sampled in the south of New Caledonia. This material is rich in Fe (48.7%) under the form of goethite and contains also Ni (1.34%), Mn (0.91%) and Co (0.16%).
Bioleaching experiments were run in batch mode at 35°C in 2L stirred tank reactor inoculated with an acidophilic microbial consortium. It was provided by Pr. B. Johnson (Bangor acidophilic team, Bangor University) and contains *Acidithiobacillus* (*At.*) *ferrooxidans*, *At. ferriphilus*, *At. ferridurans*, *Sulfobacillus* (*Sb.*) *thermosulfidooxidans.* pH was maintained between 1.2 and 2 by adding K_2CO_3 or

H_2SO_4. The microbes were first grown on sulfur in aerobic conditions. Air injection was then switched to nitrogen to create anaerobic conditions and ferric iron was provided under the form of $Fe_2(SO_4)_3$. Finally, the limonite (5% w/v) was added to the reactor when the redox potential decreased below 650 mV (SHE). In parallel, control experiments were run without any microbial inoculation. Finally, abiotic leaching experiments were run in ferrous iron environment using the same procedure in order to clarify the dissolution mechanism.

5. Results and discussion

During the first aerobic stage of the biotic experiments, the microbial consortium exhibited very fast and significant growth associated with fast sulfur oxidation kinetics. The growth rates were substantially improved when agitation speed and air flow rate were increased, which demonstrates that mass transfers (S/L and G/L) are limiting mechanisms. The kinetics were also much faster when the air flow rate was supplemented by CO_2. Lastly, the nutrients were also identified as a limiting factor, and the initial basal medium was enriched to sustain a suitable growth of the microorganisms. When the air was switched off, dissolved ferric Fe was reduced to ferrous Fe. Amongst the tested operating parameters, the amount of biomass was the most critical one for the kinetics: the reduction rate was directly correlated to the cells concentration. After the addition of limonite, Co was dissolved very quickly (almost 80% after 24h). The dissolution kinetics of Co and Mn followed the same trend. In contrary, Ni and Fe were leached very slowly and the dissolution yields remained low (less than 10% after 3 weeks), which differs from the yields reached in previous studies with limonite sampled in other areas [3, 4]. These results might be explained by the mineralogy of the limonite. Most of Co is contained in Mn oxides such as lithiophorite and asbolane which are easily dissolved with a reducing agent. This is confirmed by the good correlation between Co and Mn dissolution kinetics. Ni is contained in goethite and to a lesser extent in Mn oxide. Fe kinetics shows that the dissolution of goethite is slow and limited, which might be attributed to the high degree of crystallinity of goethite in the sample used for this study.

In abiotic acidic conditions, dissolution is extremely slow and the yields remain below 10% for all metals in control experiments. In the presence of ferrous Fe, the kinetics of metal dissolution are similar to the kinetics obtained in biotic conditions. These results confirm that the role of bacteria is to provide the reducing agent required for Co-bearing minerals dissolution.

6. Conclusions and perspectives

The present study demonstrated that reductive bioleaching can be an efficient process to recover Co from limonite whereas Ni recovery was low compared to results obtained in previous studies. This difference might be attributed to the variation of mineralogy from one limonite deposit to another. The experiments enabled to identify the most critical operating parameters for each stage of the process (agitation, air flow, CO_2 supplementation, nutrients, biomass concentration). The results were used to design a pilot demonstration that will produce data for further economic and environmental assessment of the reductive bioleaching concept.

7. References

[1] Mudd, G.M., Jowitt, S.M.: A detailed assessment of global nickel resource trends and endowments. Economic Geology 109, 1813–1841 (2014).

[2] Asselin, E.: Thermochemistry of the Fe-Ni-Co-NH_3-H_2O system. Min. Met. Proc. 28, 169–175 (2011)

[3] Hallberg K., Grail B.M., du Plessis C.A., Johnson D.B.: Reductive dissolution of ferric iron minerals: a new approach for bioprocessing nickel laterites. Min. Eng. 24, 620–624 (2011)

[4] Johnson D.B., Grail, B.M., Hallberg, K.: A New direction for biomining: extraction of metals by reductive dissolution of oxidized ores. Minerals 3, 49–58 (2013)