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Title. Bioleaching of a polymetallic residue: influence of the temperature on the sulfide leaching yield.

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Abstract: The mining of non-ferrous metals produces the largest volume of metal-containing, extractive waste in Europe, and about 29% of all the waste produced in the EU-28. In the frame of the European project NEMO (Near-zero-waste recycling of low-grade sulfidic mining waste for critical-metal, mineral and construction raw-material production in a circular economy), new ways to valorise sulfidic tailings are being developed through the recovery of valuable metals and critical raw materials and the transformation of the residual in clean mineral fraction to be used for the mass production of cement, concrete and construction products. The first step of NEMO concept consists in removing the sulfides remaining in the tailings and extracting the residual metals using either enhanced bioleaching or alkaline autoclave conversion processes. This paper focuses on one of the project case study, the residues obtained at an operating heap leaching plant (Terrafame, Finland). This material still contains several sulfidic minerals (pyrrhotite, pyrite, sphalerite, pentlandite, violarite, chalcopyrite) and significant amounts of metals (Zn, Ni, Cu, Co, REEs). The study aimed at increasing metals leaching yield. Bioleaching tests were performed first in shake-flasks and then in stirred tank reactors (2L) at increasing solid concentration (from 3 to 10%) and at three temperatures using three microbial cultures growing at 42°C, 48°C, 55°C. The results show that Ni is released very quickly suggesting that part of Ni dissolved in the primary heap is re-precipitated and remains in the residues. In the contrary, Cu dissolution is much slower but the kinetics is substantially improved when the temperature is increased

Keywords: bioleaching, nickel, copper, cobalt, pyrrhotite, pentlandite, chalcopyrite, temperature, mining residues
1. Introduction
In Europe, most of the primary resources with high or moderate metal grade, reasonable accessibility and easy to process are exhausted. In today’s context of resource scarcity, complex low grade ores and metal-containing, extractive waste get more and more attention. As existing processes and technologies are often not profitable for these types of unconventional resources, alternative routes still need to be developed to address the complexity of composition while remaining cost effective. In this context, bio-hydrometallurgy appears more and more as an ecologically acceptable and yet economic alternative for the recovery of metals in low-grade sulfidic materials. However, sustainable development of biomining methods cannot target only the extraction of metals but should also include an effective strategy to valorize the non-metallic fractions and thus to reduce drastically the generation of “ultimate” wastes. The European research project NEMO (Near-zero-waste recycling of low-grade sulfidic mining waste for critical-metal, mineral and construction raw-material production in a circular economy) aims at valorizing sulfidic tailings by combining innovative hydrometallurgical processes (including bioleaching) for the recovery of valuable metals and critical raw materials and the transformation of the residual in clean mineral fraction to be used for the mass production of cement, concrete and construction products. This paper deals with the development of enhanced bioleaching methods initiated in the framework of NEMO and aiming at recovering metals remaining in the residues obtained at an operating heap leaching plant (Finland). It focuses on the comparison of three microbial cultures with different optimal temperature (42°C, 48°C, 55°C) and their influence on the leaching kinetics and the metal yields.

2. Materials and methods
Three microbial consortia selected from BRGM culture collection were used: BRGM-KCC (optimal temperature: 42°C), dominated by Leptospirillum (L.) ferriphilum, Acidithiobacillus (At.) caldus and Sulfobacillus (Sb.) spp., Tw48 (optimal temperature: 48°C) and N55 (optimal temperature: 55°C), both dominated by At. caldus and Sb. thermosulfidooxidans. The cultures were grown in a nutrient medium called “0Km” optimised for bacterial growth on sulfidic materials. Its standard composition is the following: (NH₄)₂SO₄, 3.70 g L⁻¹; H₃PO₄, 0.80 g L⁻¹; MgSO₄•7H₂O, 0.52 g L⁻¹; KOH, 0.48 g L⁻¹.

The microbial consortia were first grown in shake flasks with a solid concentration of 3%. After several sub-culturing, the biological activity and the biomass reached a steady-state and the cultures obtained in shake flasks were used to inoculate 2L stirred tank bioreactors. The agitation was performed using a dual impeller system (axial/radial) consisting of a standard 6-blade Rushton turbine in combination with a 3-blade 45° axial flow impeller. Air enriched with CO2 (1% v/v) was injected beneath the turbine at the bottom of the reactor via a stainless steel pipe at a constant gas flow rate (120L/h). The gas flow rate was chosen in order to avoid any oxygen or carbon limitations in the system. The bioreactors were operated in batch mode and two solid concentrations were tested: 5 and 10% (w/v). The bioreactors were jacketed for warm water circulation in order to maintain a constant temperature in the pulp. The pH was maintained below 1.8 by adding concentrated sulfuric acid when needed. Fe, Cu, Ni, Co and Zn concentrations in the leachate were determined daily by
atomic absorption spectroscopy using a Varian SpectrAA-300. Species-specific microbial community composition and abundance were also monitored using quantitative real-time PCR (qPCR).

3. Results

The increase of the redox potential, which denotes the microbial activity of Fe-oxidising microorganisms, was faster in the bioreactors inoculated with BRGM-KCC compared to the ones inoculated with Tw48 and N55 (Fig.1). This might be explained by the presence of *L. ferrirphilum* in BRGM-KCC consortium. This bacterium is known to oxidise Fe more quickly than other Fe-oxidising microorganisms.

![Fig.1: Redox potential and Fe leaching yield over the time at 42°C (KCC), 48°C (Tw48), 55°C (N55).](image)

The redox increase was followed by the dissolution of Fe in the first days of the tests. When dissolved Fe concentration reached 2000 mg/L, which corresponds approximately to Fe yield of 20%, it remained constant then over the time in the case of the bioreactor inoculated with BRGM-KCC consortium and maintained at 42°C. In the case of Tw48 and N55 consortia, Fe dissolved concentration decreased. This phenomenon is probably linked to the precipitation of FeIII under the form of jarosite.

As can be seen in Fig. 2, Ni leaching kinetics was very fast and Ni yield reached almost 80% after less than 2 days. Zn leaching yield reached 80% after 8 days. While 40 % of Co was leached quickly during the first day, almost no Co was released in solution until the third day. Then the Co yield followed a linear trend over the time. The final yield was closed to 100% for Ni, 85% for Zn, and 80% for Co after 13 days. Ni, Zn and Co leaching kinetics were similar at 42, 48 and 55 °C. Cu leaching kinetics was much slower compared to the other metals but the increase of the temperature had a positive impact on the leaching yield: it reached almost 50% at 55°C after 13 days whereas it reached only 36% at 42 and 48°C. The final sulfide leaching yield was close to 80% (data not shown).

![Fig. 2: Zn, Ni, Co and Cu leaching yield over the time at 42°C (KCC), 48°C (Tw48), 55°C (N55).](image)
4. Discussion

Terrafame ore is mainly dominated by pyrrhotite and pyrite whereas the nickel and zinc minerals of interest, pentlandite and sphalerite, are minor constituents of the ore. In a recent study, Arpalahti & Lundström show that Ni, Zn, Co and Cu released in the solution are partially precipitated in the current Terrafame heap operation. They suggest that these metals can react directly with pyrrhotite due to the low redox conditions encountered in the heap through a phenomenon called metathesis according to the following equation:

\[
Fe_7S_8 + Me^{2+} = Fe_6MeS_8 + Fe^{2+}
\]

The newly formed minerals can be leached quickly when the redox potential increases. The presence of these secondary metal sulfides in the residues might explain the quick release of metals at the beginning of the bioleaching tests of the present study. The metals dissolution kinetics (Fig. 2) suggest that most of the Ni remaining in Terrafame residue is contained in this kind of minerals since Ni is released very quickly in the solution at the beginning of the tests. In contrary to Ni, only a few part of remaining Zn, Cu and Co is released at the beginning of the bioleaching tests; the dissolution kinetics follow then a more conventional leaching curve. It is likely that the Zn, Cu and Co-bearing minerals (sphalerite, chalcopyrite and pyrite) originally present in the ore are not completely leached in the heap and remain in the residue. When subjected to oxidative leaching conditions, these minerals are leached following the order of nobility of sulfides as can be seen in Fig. 2: sphalerite first, and then chalcopyrite and pyrite. The limited dissolution yield of Cu is probably linked to the recalcitrant nature of chalcopyrite and to the massive Fe precipitation observed during the leaching tests. This phenomenon has been extensively reviewed and the dissolution limitation of chalcopyrite can be partially overcome by increasing the temperature as confirmed by the leaching yields obtained with the three consortia, BRGM-KCC, Tw48 and N55.

5. Conclusion

The bioleaching tests performed in aerated stirred-tank bioreactors in the frame of NEMO project enabled to understand better the leaching behavior of a complex sulfidic residue. The results show that a substantial portion of Ni, Zn and Co remaining in these residues can be recovered using this method while the sulfide content is reduced drastically. The next steps of the study will consist in (i) testing new operating conditions to improve chalcopyrite leaching and (ii) studying the use of the sulfide-free residues for the production of cement, concrete and construction products. The environmental and economic sustainability of the developed processes will be further assessed.

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