Bioleaching of cobalt from sulfide mining tailings; a mini-pilot study

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ABSTRACT

Tailings are remaining processing waste streams from mines, disposed after valuable minerals extraction from the mined ore. Tailings contain varying concentrations of residual valuable metals that are currently lost due to lack of economical treatment possibilities. With sulfide containing tailings there is also a risk of acid rock drainage. In this study, iron- and sulfur-oxidizing microorganisms were utilized in bioleaching to treat pyrite-rich tailings to liberate mainly cobalt, alongside with other valuable metals. After adaptation of the microbial culture and batch bioleaching tests, the continuous-batch mode mini-pilot protocol was applied in 10 L stirred tank reactors (30 °C, 100 g/L solid content), reaching high leaching yields for the target metals (Co 87%, Zn 100%, Ni 67%, Cu 43%) in approximately 10 days retention time. The results show potential to turn challenging tailing streams into secondary resource for valuable metals.

1. Introduction

Tailings are residual material streams generated in mining activities. Regarding sulfide ore minerals, tailings are typically produced in froth flotation process, where valuable sulfide minerals are selectively separated from non-valuable gangue (Fuerstenau et al., 2007). After the separation, gangue minerals are disposed in tailing ponds (Lottermosser, 2010). General characteristics of the tailings include small particle size (< 100 μm) and formation of slurry in combination with process water (water content approximately 30%), which leads to challenges with waste management and dam structures (Lottermosser, 2010; Anderson et al., 2015). Tailings represent the largest material output in mining activities with an estimated global production of 5–14 billion tons annually (Schoenberger, 2016). Therefore, their proper management is extremely important.

The chemical and mineralogical composition of the tailings may vary greatly between different mine sites due to different mineralogy and mineral liberation, and different mineral processing technologies applied (Fuerstenau et al., 2007; Anderson et al., 2015). Nevertheless, some sulfide minerals are always lost into tailings during sulfide ore mining. If tailing ponds are not properly covered and encapsulated, water, oxygen and microorganisms can penetrate into the system and together oxidize sulfides, finally producing sulfuric acid and dissolved heavy metals (Lottermosser, 2010). This phenomenon, called acid rock drainage (ARD), is possible when the content of acid generating sulfide minerals is clearly higher than the acid neutralizing minerals (Lapakko, 2002). Due to the ARD, adverse environmental effects take place due to the release of toxic heavy metals, acidity and sulfate (Lapakko, 2002; Lottermosser, 2010; Lindsay et al., 2015).

Despite the adverse effects of tailings on the environment, they also possess a potential commercial merit due to the presence of residual valuable metals (Lottermosser, 2010; Lindsay et al., 2015). While the concentration of valuable metals is typically low, tailings utilization is encouraged by other characteristics, such as being usually discharged into an artificial pond (no mining and transportation costs), fine particle size (possibly no need of comminution), and finally enormous production volume of tailings (Lottermosser, 2010; Johnson, 2018). Even though the use of tailings has largely stayed in its infancy, the stakeholders of the mining industry have identified it as a future raw material source especially when new technologies are developed (Kinnunen and Kaksonen, 2019). The optimal solution for the tailings would be processing them to recover the valuable metals and to remove adverse environmental effects, by transforming the reactive and harmful minerals to a stable form. The risks and possibilities related to tailings have been understood for a long time and therefore solutions have been sought widely. Suggested treatment technologies or combinations thereof include flotation (Lutandula and Maloba, 2013; Leistner et al., 2016; Yin et al., 2018), magnetic separation (Bicalho da Rocha et al., 2019; Zhang et al., 2017; Zhang et al., 2020), size and density related enrichment (Kumar et al., 2009; Tripathy et al., 2013; Khalil...
et al., 2019), pyrometallurgical treatment (Lei et al., 2017; Fu et al., 2018; López et al., 2018) and hydrometallurgical extraction (Espiari et al., 2006; Antonjevic et al., 2008; Aromaa et al., 2013). Bioleaching utilizing iron- and sulfur-oxidizing microorganisms have gained a significant interest for processing of sulfide-rich tailings (Ahmadi et al., 2015; Martin et al., 2015; Falagán et al., 2017; Vardanyan et al., 2018; Borja et al., 2019). In addition to laboratory scale research, bioleaching technology has already reached industrial scale operations regarding the treatment of tailings or similar side-streams. In Kasese, Uganda, bioleaching was successfully utilized to recover cobalt from pyrite tailings using stirred tank reactors (Morin and d’Hugues, 2007). In Vuonos, Finland, talc mine’s sulfide side-stream was treated with bioleaching in stirred tank reactors to recover nickel and arsenic (Neale et al., 2017).

In the bioleaching process for sulfide minerals, both iron- and sulfur-oxidizing microorganisms are utilized. The role of iron-oxidizing microorganisms, such as Acidithiobacillus ferrooxidans and Leptospirillum ferrooxidans, is to oxidize dissolved Fe²⁺ to Fe³⁺ by dissolved oxygen from the aeration of the pulp. Fe³⁺ is a powerful oxidant that also attack on recalcitrant sulfide minerals and leach them (Monchur et al., 2009; Lindsay et al., 2015). In the sulfide mineral oxidation, Fe³⁺ is reduced back to Fe²⁺ and iron-oxidizing microorganisms reoxidize it back to Fe³⁺ allowing the leaching to continue (Sand et al., 2001; van Aswegen et al., 2007). The role of sulfur-oxidizing bacteria, such as Acidithiobacillus thiooxidans and Acidithiobacillus caldus, is to oxidize sulfur compounds to sulfuric acid. The sulfur oxidation is also very important, as it feeds the protons needed for iron oxidation and keeps the leach solution acidic and metals in dissolved form (Schippers et al., 1996; Sand et al., 2001).

In this study, sulfide-rich tailings were leached, utilizing iron- and sulfur-oxidizing microorganisms in a stirred tank application. The feed material contained several different valuable metals, namely cobalt, zinc, nickel and copper. The sample mineralogy was dominated by pyrite, but was otherwise very complex. The objectives of this study were to determine the most valuable elements of the sample material, to understand their behavior in the bioleaching system and finally to validate the developed bioleaching process in a mini-pilot (bench scale) system, utilizing a continuous-batch protocol.

2. Materials and methods

2.1. Sample materials

Material owner collected tailings sample from the tailings pond and conducted size reduction by milling (particle size d80 < 13 μm). The shipment took place approximately a year after the sampling; meantime the sample was stored as wet and in closed container. The mineralogical and elemental composition were analyzed using FE-SEM-EDS by Geological Survey of Finland and elemental analysis ICP-MS/OES by Eurofins Labtium Oy, respectively. The results are presented in Tables 1 and 2. The sample material was not sterilized in the experiments.

2.2. Microorganisms

A mixed culture of iron- and sulfur-oxidizing microorganisms, enriched from acidic mine waters (Bomberg et al., 2019) was used in the bioleaching experiments. The mixed culture contained Marinobacter sp., Acidithiobacillus spp. (At. ferrooxidans, At. thiooxidans, At. albertensis, At. ferrivorans), Leptospirillum sp. (L. ferrooxidans), Caniculiplasma sp., Nitrosonetius sp. and Ferroplasma sp. Cultivation and adaptation of the mixed culture was done in 250 mL shake flasks in an orbital shaker (Stuart SI-500; 34 °C, 150 rpm). The adaptation was started by mixing 90 mL of nutrient medium (Table 3), 10 mL of active mixed culture and 1 g of tailings sample, thus the starting solid/liquid (S/L) ratio was 10 g/L. If a pH rise was observed during the incubation, the pH was adjusted with 95% H₂SO₄ to pH 2.0. When the Eh rose to ≥ + 810 mV, the obtained culture was re inoculated with increased tailings sample mass. This was continued until the S/L ratio of 75 g/L was reached. This adapted microbial culture served as an inoculum for the bioleaching experiments. The cultivation and adaptation shake flasks were monitored with pH and RedOx potential measurements, using Consort multi-parameter analyser C3040, with Van London-pHoenix Co. pH and RedOx electrodes (Ag/AgCl in 3 M KCl; pH electrode calibration 1.68 / 4.01 / 7.00; RedOx electrode calibration + 650 mV). The Eh value was calculated by adding + 210 mV to the RedOx meter reading.

2.3. Batch experiments

The first bioleaching tests were done as duplicates in 250 mL shake flasks were monitored with pH and RedOx potential measurements, using Consort multi-parameter analyser C3040, with Van London-pHoenix Co. pH and RedOx electrodes (Ag/AgCl in 3 M KCl; pH electrode calibration 1.68 / 4.01 / 7.00; RedOx electrode calibration + 650 mV). The Eh value was calculated by adding + 210 mV to the RedOx meter reading.

Table 1

| Mineral | Wt% |
|---------|-----|
| Pyrite  | 67.5|
| Pyrophosphate | 5.6|
| Quartz  | 5.6 |
| Sphalerite | 4.9 |
| Oxidized Fe-sulfide | 2.5 |
| Tremolite | 2.0 |
| Calcite | 1.2 |
| Co-Pentlandite | 0.7 |
| Dolomite | 0.7 |
| Talc | 0.4 |
| Albite | 0.2 |
| Flagoioclase | 0.2 |
| Fe sulphate | 0.1 |
| Chalcopyrite | 0.1 |
| Pentlandite | 0.1 |
| ... | ... |
| Unclassified | 6.7 |
| Total | 100 |

Table 2

| Element | Wt% |
|---------|-----|
| S       | 43.6|
| Fe      | 35.6|
| Zn      | 4.46|
| Si      | 2.53|
| Co      | 1.17|
| Ca      | 1.13|
| Mg      | 0.732|
| Cu      | 0.04|
| Ni      | 0.374|
| K       | 0.258|
| Na      | 0.244|
| Al      | 0.145|
| As      | 0.0646|
| Mn      | 0.0292|
| P       | 0.0134|

Table 3

| Compound | Concentration (g/L) |
|----------|--------------------|
| (NH₄)₂SO₄ | 3.0 |
| K₂HPO₄   | 0.50 |
| MgSO₄·7H₂O | 0.50 |
| KCl      | 0.10 |
| Ca(NO₃)₂·4H₂O | 0.014 |
flasks in an orbital shaker (Stuart SI-500; 34 °C, 150 rpm). Tests were started by mixing 90 mL of nutrient medium (Table 3), 10 mL of active adapted microbial culture and 5 g of tailings sample (S/L ratio 50 g/L). A chemical control test was conducted without inoculation by using 100 mL of nutrient medium and 5 g of tailings sample. The chemical control and one bioleaching test had no pH adjustment, while two other bioleaching tests were manually adjusted during the first 8 h of leaching to pH 2.0 or 1.6 with 95% H2SO4. This was done to pre-leach the most reactive acid consuming minerals, such as calcite, talc and pyrrhotite. Moreover, these pH values were selected as they are generally considered suitable for the microorganisms found from the used inoculum (Rawlings, 2002).

The batch stirred tank leaching was conducted in 1 L glass reactors, equipped with heated water jacket (30 °C), teflon-coated pitch blade impeller (300 rpm), and aeration into the bottom/centre of the reactor vessel (air; 1 L/min) via a teflon tube. Tests were started by mixing 900 mL of nutrient medium (Table 3), 100 mL of active adapted microbial culture and 40 g of FeSO4·7H2O. The initial iron concentration in the stirred tank tests was selected according to the final Fe3+ concentration observed in the previous shake flask tests. After iron addition, the reactors were operated until Eh rose to +885 mV, signalling that all the iron was oxidized to Fe3+. Then, 50 g or 100 g of tailings sample was added (S/L ratio of 50 g/L or 100 g/L, respectively). The pH was manually maintained at pH 1.5–2.0 during the leaching with 95% H2SO4 or 10 M NaOH. All batch tests were monitored with pH and RedOx measurements as described in section 2.2. The elemental analysis of leachates were subcontracted (ICP-MS/OES by Eurofins Labtium Oy).

2.4. Mini-pilot

The mini-pilot study was done utilizing a continuous-batch mode testing protocol that mimics the full continuous mode operation and gives rather similar results (Sandström et al., 1997). The continuous-batch mode mini-pilot test was done in 10 L titanium reactor, equipped with baffles, pitch blade impeller (300 rpm), aeration into the bottom/centre of the reactor vessel (5 L/min) and heat plate to maintain the temperature at 30 °C. The test was started (“ramp-up phase”) by mixing 9 L of nutrient medium (Table 3), 1 L of active adapted microbial culture and 453 g of FeSO4·7H2O. The reactor was operated until the Eh rose to +875 mV, signalling that all the iron was oxidized to Fe3+. Then, the tailings sample was gradually added by 250 g doses to the S/L ratio of 50 g/L or 100 g/L, respectively). The initial Eh was slowly rising to +875 mV (data not shown). The elemental concentration of leachates in the system, as illustrated by stable dissolution of elements in the system, as shown in Fig. 1. The iron leaching was very similar compared to cobalt, in terms of both kinetics and leaching yield (data not shown). Zinc leached rapidly, reaching the complete dissolution in 4 days with inoculated shake flasks. However, in the chemical controls the Zn yield was 83% after 13 days of leaching (data not shown).

The evolution of pH and Eh in the shake flask tests is shown in Fig. 1. The mixture of nutrient medium, active inoculum and tailings sample resulted in a slurry of pH at approximately 2.0. In the chemical controls the pH was slightly higher due to the lack of acidic inoculum. The acid consumption (expressed as g 95% H2SO4 per kg of sample) for pH adjusted experiments was 27.5 g/kg and 76.9 g/kg for pH 2.0 and pH 1.6, respectively. Despite the acid addition during the first 8 h of leaching, the pH level in all bioleaching tests was rather identical from day 2 onwards. The Eh in all inoculated shake flasks showed a rising trend and the Eh reached +800 mV. However, chemical control test remained below +570 mV. The evolution of cobalt and nickel leaching in shake flask tests is shown in Fig. 1. The iron leaching was very similar compared to cobalt, in terms of both kinetics and leaching yield (data not shown).

The evolution of pH and Eh in batch stirred tank tests is shown in Fig. 2. During the first 6 days of bioleaching, the pH tend to rise. The pH was adjusted to < 2.0 with a total acid consumption of 316 g/kg (S/L ratio of 50 g/L) and 86 g/kg (S/L ratio of 100 g/L), expressed as g 95% H2SO4 per kg of sample. After 6 days, the pH started to strongly decrease in the reactors. Too low pH range for bioleaching microorganisms was prevented by NaOH addition. The total base consumption was 439 g/kg (S/L ratio of 50 g/L) and 447 g/kg (S/L ratio of 100 g/L), expressed as g 50% NaOH per kg of sample. Due to the slower increase in Eh, the test with 100 g/L S/L ratio was continued for additional 6 days.

Leaching yields for cobalt, nickel and zinc in batch stirred tank tests are shown in Fig. 3. Iron concentration rose from initial 8 g/L to 21 g/L (S/L ratio of 50 g/L) and to 23 g/L (S/L ratio of 100 g/L), respectively.

3.3. Mini-pilot study

The continuous mode bioleaching system was operated for 160 h with 79-h retention time, stable Eh at +810 mV and pH at 1.5. The acid addition during this period was 8 g 95% H2SO4 per kg of sample. During the 160-h continuous operation, all daily measurements showed stable dissolution of elements in the system, as illustrated by stable leaching yields in Fig. 4 (on the left: “Continuous mode”; please note that the continuous operation was always operated with a 79-hour retention time, which does not change with operative days). After the continuous mode, the system was turned to the batch mode and leaching was continued for another 171 h. During this phase, system generated acidity, which was compensated (214 g of 50% NaOH per 1 kg of sample) to maintain the pH 1.5. During the batch mode, the Eh rose slowly to +875 mV (data not shown). The elemental concentration of leachates in the system, as illustrated by stable dissolution of elements in the system, as shown in Fig. 1. The iron leaching was very similar compared to cobalt, in terms of both kinetics and leaching yield (data not shown).

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increased alongside with prolonged leaching time (Fig. 4; on the right: “Batch mode”; please note that the retention time increased alongside the operative days). According to the leachate analysis, leaching yields reached Co 87%, Zn 100%, Ni 67%, Cu 43% and Fe 100%. After the end of the continuous-batch test, residual solids were separated by
from pyrite and/or pyrrhotite was biologically oxidized to Fe$^{3+}$, and order for metal sul-
fidation processes. In the actual mini-pilot operation, the continuous-
batch protocol was applied. After the “ramp-up phase” the system was
operated in continuous mode with a retention time of 79 h. This phase prac-
tically mimics the first stage of reactors in a continuous bioleaching
process. During this continuous mode, the acid consumption was ex-
tremely low compared to the preliminary stirred tank batch operation
(8 g versus 86 g of 95% H$_2$SO$_4$ per kg tailings). As expected, the
leaching yields for Co, Ni, Fe and Cu were low during the continuous
operation, since the retention time was deliberately too short for effi-
cient process. However, Zn was observed to dissolve rather well with
the 79-h leaching. By changing the system to the batch mode after
continuous operation, the total retention time was increased, and the
obtained leaching profiles is expected to describe the kinetics in the
subsequent reactors in series. The cobalt and iron dissolved rather si-
imilarly, due to their partial presence in pyrite. A relatively low copper
leaching yield was expected due to its presence as recalcitrant chalco-
pyrite (Monchur et al., 2009). Moreover, the increase of dissolution rate
slowly down after the retention time of 103 h, signalling possibly chalcopyrite passivation (Stott et al., 2000). The total retention time of
the mini-pilot was 247 h (approximately 10 days), resulting in 87%
cobalt leaching yield. The industrial bioleaching processes treating
sulfide tailings or side-streams have been reported to operate with a
shorter retention time (6–7 days) with equal or higher S/L ratios
(100–150 g/L). Recovery rates of 80% for the main target elements
have been reported (Morin and d'Hugues, 2007; Neale et al., 2017) at
a similar level as in this study. The bioleaching process developed here
can be further improved in terms of leaching kinetics and treatment
capacity (S/L ratio). A clear improvement would be the usage of CaCO$_3$
instead of NaOH for pH adjustment. The tailings in this study contained
only 1.2 wt% of carbonate (Table 1). According to van Aswegen et al.
(2007), carbonate content should be at least 2 wt%, or otherwise the
purged air should be enriched with CO$_2$ or CaCO$_3$ as pH control che-
meric. As material in this research was clearly acid producing, addition
of CaCO$_3$ would be the simplest way to provide enough carbon for the
microorganisms. Another expected improvement would be temperature
elevation to 40–45 °C, which is used at industrial applications (Morin
and d'Hugues, 2007; Neale et al., 2017) and is expected to increase the
leaching kinetics.

Some challenges in mini-pilot operation with continuous-batch
mode operation were observed. Clearly lower leaching yields for cobalt,
iron and nickel and significantly higher leaching yields for copper were
obtained with solid residue analysis compared to the leachate analysis.
One possible explanation is that residual solids were collected and
analyzed only at the end of the experiment, and therefore the result is
difficult to evaluate. The reason for not taking more solid samples was
the usage of relatively small reactor (10L) together with small volume
flow. Therefore, solid sampling (50 g solid per analysis) would have
disrupted the continuous operation strongly. Moreover, the continuous
and accurate monitoring of the actual S/L ratio of the process was
challenging. It is possible that during the continuous operation slow
accumulation of solids was taking place in the stirred tank system.
Furthermore, very recalcitrant and dense sulfide minerals may have
been accumulating to the system while more reactive minerals (e.g.
pyrrhotite, sphalerite, tremolite, calcite and talc) have been slowly
depleting (i.e. system not in complete steady-state condition). However,
none of these suggestions explains why copper dissolution rate was
higher according to the solid residue analysis than leachate analysis:
chalcopyrite is very recalcitrant (Monchur et al., 2009) and would
signal the slow build-up of solids in reactor. We propose that the further
research of continuous-batch research protocol would be conducted with
≥ 20L reactor size, to increase the volume flows and enable better
analysis of the solids in the reactor. Moreover, the actual S/L ratio (as
the function of time) must be measured frequently and accurately.

**Fig. 4.** Leaching yields of metals in mini-pilot experiment, according to the
leachate measurements. The dashed vertical line indicates the change from
continuous mode to batch mode. RT = retention time. The retention time is
always 79 h in the continuous mode (standard input/output volume flows), but
increases in the batch mode alongside operative duration (no input/output
flows = increase of retention time).

4. Discussion

In shake flask experiments, all inoculated tests reached pH 1.5 and
Eh + 800 mV, while in the chemical control test, the pH was increasing
and the Eh rose only marginally. This illustrated that Fe$^{2+}$ released
from pyrite and/or pyrrhotite was biologically oxidized to Fe$^{3+}$, and
the released sulfur species were further biologically oxidized to sulfuric
acid. Both reaction routes have been explained in detail by Schippers
et al. (1996) and Sand et al. (2001). The highly acidic and oxidizing
leach solutions generated by biological reactions were beneficial for
cobalt and zinc leaching yields, compared to the chemical control test,
where the leaching took place at less aggressive conditions. Therefore,
bioleaching was considered as a promising technology and studies were
continued in batch reactors.

In stirred tank experiments, it was seen that low S/L ratio (50 g/L)
was beneficial for reaching high cobalt and nickel leaching yields more
rapidly. The reason for higher leaching yields with low S/L ratio was
expected to relate to the remarkably higher Eh values, thus providing
more oxidative power for metal sulfide leaching. This was seen especi-
ally for cobalt, which was partly incorporated into the recalcitrant
pyrite matrix. Conversely, sphalerite is known to dissolve already at
lower Eh, which was illustrated also here in both tests by the rapid and
complete leaching of zinc. The batch tests also revealed that some part
of nickel was easily dissolving: according to shake flask tests up to 40%
and stirred tank tests up to 10%. The easily dissolving part of the nickel
was expected to be incorporated into the highly reactive pyrrhotite,
while the rest was in a more recalcitrant form, e.g. as Co-pentlandite
and pentlandite. The relative resistance against oxidation and oxidizing
order for metal sulfides has been discussed in detail by Monchur et al.
(2009) and Arpalahi and Lundström (2018).

The mini-pilot was operated with S/L ratio of 100 g/L, although the
batch stirred tank experiment suggested that the S/L ratio of 50 g/L
could result in higher dissolution rate with less time, compared to S/L
ratio of 100 g/L. However, the increase of S/L ratio decreased the
consumption of chemicals (i.e. decreased costs of process). The typical
S/L ratios have been 100–150 g/L in industrial operations (Morin and
d'Hugues, 2007; Neale et al., 2017). The higher S/L ratio also allows
smaller reactor sizes, which is important for the economics of bio-
leaching processes. In the actual mini-pilot operation, the continuous-
batch protocol was applied. After the “ramp-up phase” the system was
operated in continuous mode with a retention time of 79 h. This phase prac-
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the function of time) must be measured frequently and accurately.
5. Conclusions

In this study, pyrite-rich tailings were bioleached by utilizing iron- and sulfur-oxidizing microorganisms in the stirred tank application. The main emphasis was on cobalt recovery as it was the most valuable element in the tailings by total economic value. The continuous-batch mode experimental protocol was used to reach mini-pilot scale and to evaluate the applicability of bioleaching technology for the material. According to the results, the retention time of approximately 10 days resulted in 87% cobalt leaching yield. In terms of kinetics, the process was somewhat slower than industrial bioleaching processes treating sulfide tailings or side-streams. The process illustrated here could be improved by changing the neutralizing chemical from NaOH to CaCO₃, both due to the chemical price, but also providing more carbon for the microorganisms. Moreover, elevated temperature (from 30 °C to 40–45 °C) is expected to increase kinetics. The results show the potential to turn tailings into secondary resource for valuable metals.

Declaration of Competing Interest

None.

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