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Highlights

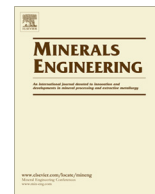
• Bioleaching of sulfidic mining wastes enables to produce lixiviant solution that can be used further for e-wastes leaching. • Biological re-oxidation of iron greatly enhances metals dissolution kinetics and yields during PCBs leaching. • Copper extraction above 90% was achieved in 24 h of PCBs leaching. • Microbiologically assisted leaching of waste PCBs is a promising way for metals recycling. • Decoupling the lixiviant production from the leaching process enables to avoid toxicity issues.



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Co-processing of sulfidic mining wastes and metal-rich post-consumer wastes by biohydrometallurgy

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ABSTRACT

The consequence of a strong economic growth in emerging countries combined with the rise of the world population is an increase in the demand for raw materials, leading to growing concern regarding their availability and the global efficiency of the supply chain. These tensions reinforce the need to associate the development of the recycling industry to the identification of new resources which could be used for the recovery of valuable materials. The purpose of this study is to develop a novel biological co-processing approach for the recovery of strategic metals in both sulfidic mining wastes and post-consumer wastes (WEEE). The principle of this treatment is based on two steps: mine wastes are biologically oxidized, resulting in the production of a ferric iron-sulfuric acid lixiviant solution which is used to leach base and other soluble metals contained in e-scrap. Batch tests were carried out using flotation tailings wastes containing 60% of pyrite and grinded Printed Circuit Boards (PCB < 750 μm) with a solid load of 2.5%. Two series of tests were conducted in order to study the influence of the ferric iron concentration and of the bacterial activity on metals dissolution. Results showed that a higher ferric iron concentration led to an increase in the dissolution rate of copper which is the main metal contained in the PCBs. Moreover, a dissolution yield of 98.3% was reached for copper after 2 days when bacterial activity was observed, corresponding to an increase of about 20% compared to the tests without bacterial activity. Finally, this study highlights the importance of the availability of ferric iron and of the bacterial oxidation of ferrous iron for the feasibility of this bioleaching process dealing with the recycling of PCBs.

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1. Introduction

Among the different types of secondary post-consumption wastes, e-wastes represent the fastest growing and most problematic waste stream in the world. In the EU, 9.7 million tons were produced in 2009 and this is estimated to grow to a projected 12.3 million tons per year by 2020 (Huisman et al., 2008). Recovering metals from e-waste is potentially more energy efficient than mining raw material. However, they are highly complex in terms of structure and composition as very little consideration is given to end-of-life reprocessing during the design and construction of electronic goods. As a result it is not always possible to feed such waste into conventional recycling streams. Many of the metals on the “criticality” list are found in significant quantities in e-wastes (EU, 2014). The majority of the value in e-waste is in the printed circuit boards (PCBs). On average 90% of the intrinsic economic value of PCBs is in the precious metals that they contain (Cui and Zhang, 2008). They also contain some critical metals such as

gallium. 65% of the world's gallium production ends up in PCBs and no current process for its recovery exists. Copper is also very important: it is much more abundant in e-wastes and PCBs than the higher value metals, that is why its recovery and recycling are crucial given the increasing scarcity and complexity of copper ore.

Pyrometallurgy is the traditional choice for metal refining from processed (usually upgraded) e-waste, resulting in the production of precious metal-bearing copper bullion (Tuncuk et al., 2012). It can be done within existing smelters treating mineral concentrates, where e-waste may be combined (10–15%) with a copper concentrate (Cui and Zhang, 2008). However, it is energy intensive and requires a relatively high grade feed material, and the ceramics from e-waste contribute to increase the final slag volume. Compared to pyrometallurgy, hydrometallurgical processes offer relatively low capital cost and are particularly suitable for small-scale installations (Tuncuk et al., 2012). An added advantage is their flexibility, offering a possibility for selective extraction of base and precious metals of interest in e-waste and PCBs. Since major metals exist in their elemental or alloy form in PCBs, their hydrometallurgical extraction has been tested

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using various oxidants (lixiviants; hydrogen peroxide, oxygen, ferric iron, etc.) under acidic (HCl, H₂SO₄, HNO₃ etc.) or ammoniacal and chloride leaching environments (Quinet et al., 2005; Deveci et al., 2010; Huang et al., 2009; Kasper et al., 2011; Tuncuk et al., 2012). These studies have shown a different degree of base and precious metals recovery efficiency. However, these processes require the consumption of a high amount of chemicals. The use of microorganisms for the recovery of metals could then be an economic and environmental alternative. Biohydrometallurgy is an established technology for concentrates and mineral processing wastes. It has been recognized as a potential technology for the treatment of metallic wastes (Bryan et al., 2012). It has been used to recover copper and zinc from slags, galvanic sludge, fly ash and filter dust with recoveries close to 100% (Krebs et al., 2006). Studies into the bioleaching of e-waste have mainly involved the treatment of printed circuit boards (PCBs). The use of organic acids produced by various fungi or biogenic cyanide has been examined, particularly for the recovery of gold and other noble metals (Brandl et al., 2001; Faramarzi et al., 2004; Brandl et al., 2008; Chi et al., 2011). However, such approaches require the selective cultivation of specific microorganisms in circum-neutral media rich in organic substrates. This often requires aseptic growth conditions and is unlikely to be practical when treating large volumes of non-sterile e-wastes. Further, the majority of the cyanide produced is consumed by the copper which is in much higher concentrations relative to target metals such as gold. Therefore, the use of ferric iron and/or proton lixiviants produced by extreme acidophiles would be preferable and more practical. Indeed, there is no need for sterile conditions and culture media are relatively simple comprising key nutrients such as sources of nitrogen, potassium and phosphorus. In mineral bioleaching the source of iron and sulfur which are oxidized by the microbial community to produce the oxidizing acidic lixiviant solution is contained in pyrite or other sulfide minerals. In the current e-waste bioleaching practices, this source of iron and sulfur must be provided in addition to the nutritive medium. This is usually realized in the form of ferrous sulfate with acidity provided via pH control with sulfuric acid or through addition of elemental sulfur. The studies published so far (Zhu et al., 2011; Yang et al., 2009; Xiang et al., 2010; Liang et al., 2010; Karwowska et al., 2014; Hong and Valix, 2013; Ilyas et al., 2010; Cerruti et al., 1998) were carried out in shake flasks in liquid media containing ferrous iron, sometime amended with elemental sulfur and inoculated with pure or mixed cultures of iron- and sulfur-oxidizing microorganisms. Ground e-waste (usually PCBs) was either added immediately, in a one-step process, or following initial substrate oxidation (and thus lixiviant production) in an indirect two-step or multi-step process. The toxicity of the e-waste on the microorganisms has been shown to be the major problem preventing efficient leaching. Staggering the production of the lixiviant and the addition of the e-waste in a two-step process could then greatly increase leaching rates. Furthermore, PCBs are highly acid-consuming and require a high degree of pH modification to maintain an acidic environment necessary for the microbial action and metal solubility. The necessary addition of chemical products will increase the operating cost of such processes.

In addition to deposits of secondary post-consumer wastes (the classical target of the urban mining concept), old waste deposits

related to past mining and metallurgical activities can also be significant reserves of valuable base or strategic metals as well as mineral substances. Before the 20th century, only a single or, at best, a couple of metals were extracted from any given mine. The other elements were either not detected by contemporary analytical methodology or considered as mineralogical “exotica”. As demonstrated by European FP7 research project ProMine (<http://ptrarc.gtk.fi/ProMine/default.aspx>) these types of mining and metallurgical residues contain not only rare and precious metals but also appreciable amounts of “residual” base metals (Cu, Ni, Zn, Co...) which must not be neglected in today’s context of resource scarcity and the environmental management of post mining activities.

While current laboratory-scale studies provide evidence that biohydrometallurgical reprocessing of e-wastes and mining wastes are technically possible, the wider economics of such type of processes are unlikely to be favorable with the current state-of-the-art and the competition with “classical” pyro and hydro options. Using an industrial ecology approach and including the potential costs associated with the “no action scenario” in terms of waste management, a co-processing concept was envisaged.

The purpose of this study is therefore to develop a novel biological co-processing approach for the recovery of strategic metals in both sulfidic mining wastes and post-consumer wastes (e-scrap). The principle of this treatment is based on two steps: mine wastes are biologically oxidized, resulting in the production of a ferric iron-sulfuric acid lixiviant solution which is used to leach base and other soluble metals contained in e-scrap. By decoupling lixiviant production from PCB leaching in a two-step process, it is assumed that issues of toxicity will be avoided.

Bioleaching batch tests were performed using flotation tailings wastes containing 60% of pyrite in a first step, and, in a second step, grinded Printed Circuit Boards (PCB < 750 μm) with the lixiviant produced by the bioleaching of the sulfidic wastes. The results were compared to those obtained in abiotic conditions using a synthetic leaching solution instead of a solution produced biologically.

2. Materials and methods

2.1. Wastes

The mining wastes used in this study are flotation tailings mainly composed of pyrite (60%). They contain also cobalt (0.06%), copper (0.19%) and gold (1 g/t). These wastes have been chosen for their high content of pyrite, which makes them particularly suitable for bioleaching. The electronic wastes are computer PCBs grinded first under 3 mm using a shear shredder and then under 750 μm using a laboratory knife mill (Retsch, model SM2000).

2.2. Bacterial culture and nutrients

The tests were run using BRGM-KCC acidophilic and moderate thermophilic (40 °C) microbial consortium which has already been fully described (Battaglia et al., 1994; d’Hugues et al., 2003). The predominant organisms in the culture are affiliated to the genera *Leptospirillum*, *Acidithiobacillus* and *Sulfobacillus*. These bacteria are autotrophic and known as iron-oxidizer. They are also known for their tolerance to high concentrations of various metals espe-

Table 1
Average metal content in PCBs used for this study.

| Cu | Fe | Ni | Pb | Zn | Sn | Ag | Au | Pd | Ga | Co | Mo |
|-------|------|-----|------|------|------|-------|-------|------|-----|------|------|
| g/kg | | | | | | ppm | | | | | |
| 215.1 | 24.3 | 2.4 | 17.5 | 14.6 | 34.6 | 393.6 | 143.9 | 42.4 | 7.9 | 29.2 | 11.2 |

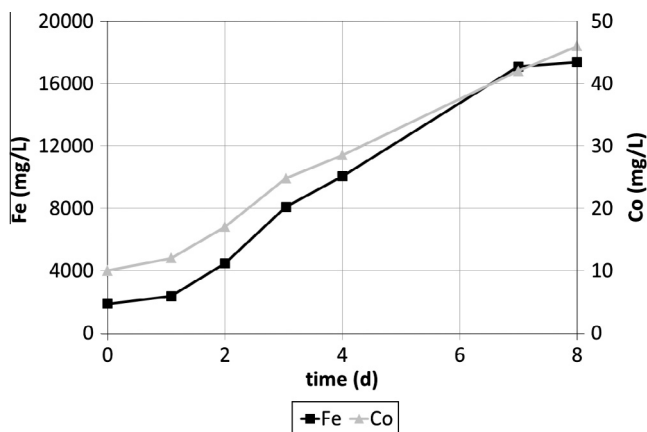


Fig. 1. Iron and cobalt concentration vs. time in solution during the bioleaching of the sulfidic mining wastes.

cially copper (Guezennec et al., 2014). The culture used as an inoculum originated from BRGM stock culture, stored at -80°C . The culture was subcultured several times in batch mode and on pyrite from 2 mL up to 2 L prior to the beginning of the batch test.

The culture was grown in a nutrient medium called "0Km" medium. It is a modified "9 K" medium (9 K without iron, "m" indicating modification of the basal salts) and was optimized for bacterial growth on cobaltiferous pyrite. Its standard composition is the following: $(\text{NH}_4)_2\text{SO}_4$, 3.70 g L^{-1} ; H_3PO_4 , 0.80 g L^{-1} ; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.52 g L^{-1} ; KOH , 0.48 g L^{-1} .

2.3. Metal content in solid fractions

The metal content of initial PCBs and of leached residues was determined using an analytical procedure derived from standard NF EN 13657. The size of the PCBs particles after comminution is one of the main issues that must be encountered in PCBs analysis. The size of the samples must be sufficient to avoid uncertainties linked to the sampling representativeness. The analytical procedure was tested using several amounts of comminuted PCBs (1 g, 3 g and 5 g). From the results (data not shown) samples of 3 g were finally selected for the following of the study. The quartered samples of 3 g of materials (comminuted PCBs or leached residue) were dissolved in aqua regia using a closed system with reflux to avoid reagents losses. The contact time between the samples and aqua regia was about 24 h at room temperature and then 2 h at 200°C . After cooling, samples were carefully filtered and weighed. The insoluble portion indicates ceramic and polymers. The leached portion represents the soluble metals and was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) and atomic adsorption spectrometry (AAS). The analyzed metals were: copper, iron, nickel, lead, zinc, tin, silver, gold, palladium, gallium, cobalt and molybdenum. The final solid residues were also characterized using optical microscopy as well as Scanning Electron Microscopy to check the presence of undissolved metals, which was not the case. The average metal content of PCBs samples used in this study is given in Table 1.

Table 2

Characteristics of the biological lixiviant solutions.

| Type of PCB leaching test | pH | Eh (SHE) mV | Fe_{tot} mg L^{-1} | Fe^{2+} mg L^{-1} | Cu^{2+} mg L^{-1} | Ni^{2+} mg L^{-1} | Pb^{2+} mg L^{-1} | Zn^{2+} mg L^{-1} | Co^{2+} mg L^{-1} |
|----------------------------|-----|-------------|---|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| Erlenmeyer flasks (500 mL) | 1.1 | 862 | 10966 | 8 | 109 | 8.5 | 1.5 | 6.4 | 28 |
| | 1.2 | 826 | 18145 | 42 | 135 | 16 | 6 | 11 | 45 |
| Reactor (1 L) | 0.9 | 800 | 18430 | 151 | 112 | 14.7 | 5.9 | 15 | 46 |

2.4. Laboratory apparatus

2.4.1. Bioleaching of mining wastes

Bioleaching of the mining wastes was performed in order to produce the lixiviant solution used for the biotic leaching of PCBs. The tests were carried out in batch mode using 2 L laboratory scale glass reactors thermostated at 40°C . The reactors were baffled; the agitation was performed using a dual impeller system consisting of a standard 6-blade flat Rushton turbine in combination with a 6-blade 45° axial flow impeller. The impeller speed was set at 400 rpm. Air (120 L h^{-1}) enriched with CO_2 (1%) was injected beneath the impeller at the bottom of the reactor via a stainless-steel pipe. The tests were run in triplicate at 10% (w/w) pulp density and the inoculation was performed by adding 200 mL of the BRGM-KCC culture in each reactor. When the Fe^{3+} concentration in the pregnant leach solution (PLS) reached the targeted value, reactors agitation and aeration were stopped. After natural decantation (around 12 h) the supernatant solution was filtered at $0.65\text{ }\mu\text{m}$ to remove particles while enabling bacteria to remain in the solution. This solution was then used as lixiviant solution for the biotic treatment of PCBs.

2.4.2. PCBs leaching

Two series of PCBs leaching tests were performed in batch conditions using comminuted samples of PCBs with a solid load of 2.5%.

2.4.2.1. 1st series of PCBs leaching tests. The aim of the first series of experiments was to test the influence of initial Fe^{3+} concentration as well as the type of lixiviant solutions (biological or chemical) on the PCBs leaching. For this purpose, the experiments were carried out in 500 mL Erlenmeyer flasks containing 10 g of comminuted PCBs and 400 mL of the biogenic lixiviant solution produced from the bioleaching of mining wastes (biotic tests) or 400 mL of a synthetic lixiviant solution (abiotic tests). For the biotic tests, two concentrations of Fe^{3+} were tested: 11 g L^{-1} and 18 g L^{-1} . The initial pH of the lixiviant solution was respectively 1.12 and 1.19, the initial Eh being respectively 862 and 826 mV (SHE). The synthetic solution was prepared by mixing deionized water with $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ salt in order to have a concentration of Fe^{3+} of about 18 g L^{-1} . The initial pH of the synthetic solution was 1.38 and the initial Eh was 914 mV (SHE). Biotic and abiotic tests were carried out in triplicate at ambient temperature and under magnetic stirring. Plastic paraffin film was used for sealing the Erlenmeyer flasks in order to prevent excessive evaporation.

2.4.2.2. 2nd series of PCBs leaching tests. The aim of the second series of experiments was to enhance the bacterial activity during PCBs leaching by providing bacteria with more appropriate conditions (i.e. temperature and oxygen transfer) and to compare the results with those obtained in the first series of PCBs leaching experiments. The tests were carried out in duplicate using laboratory scale glass reactors containing 1 L of the biogenic lixiviant solution with a Fe^{3+} concentration of 18 g L^{-1} and 26 g of PCBs. The agitation device used in these tests had the same characteristics as the one described for the production of the lixiviant solution. The initial pH of the lixiviant solution was 0.90 and the initial Eh was

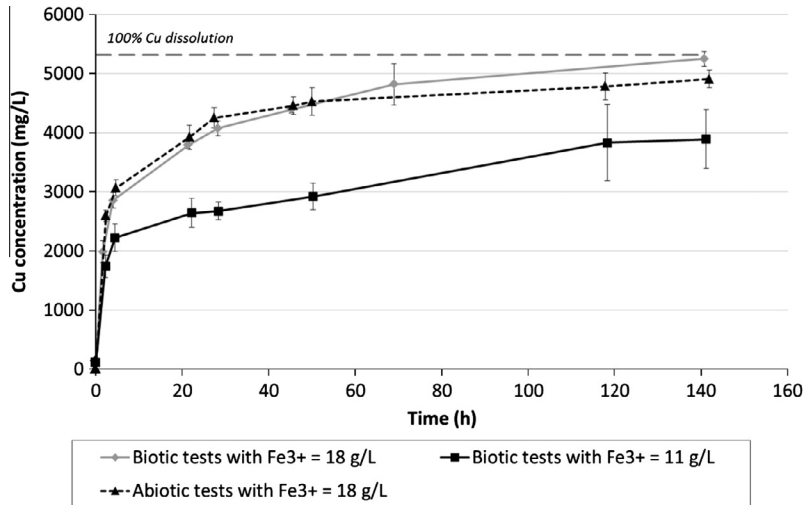


Fig. 2. Cu^{2+} concentration vs. time during biotic and abiotic leaching of PCBs in Erlenmeyer flasks.

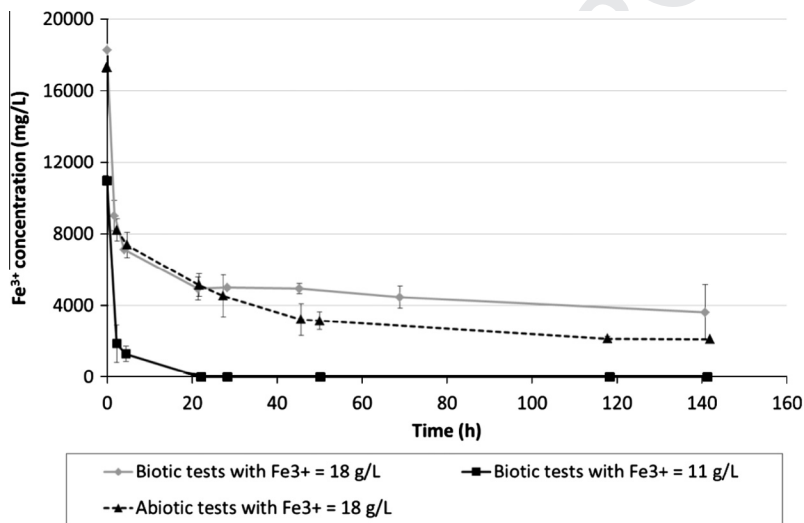


Fig. 3. Fe^{3+} concentration vs. time during biotic and abiotic leaching of PCBs in Erlenmeyer flasks.

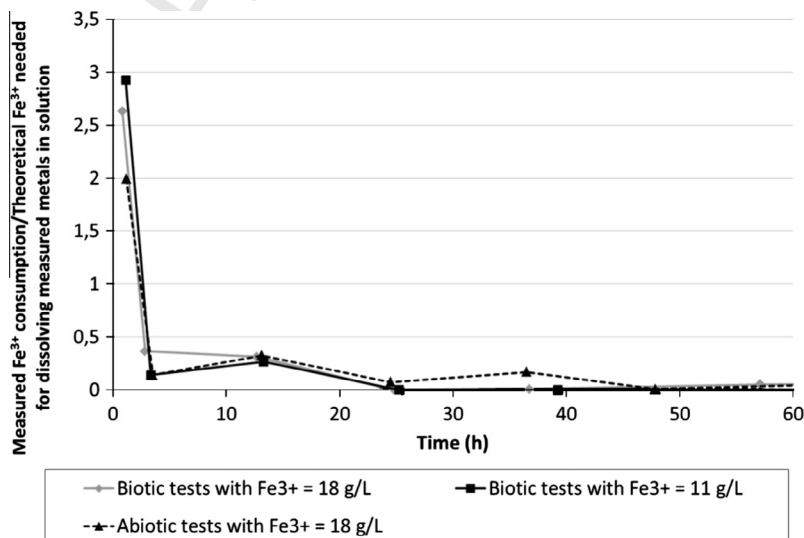


Fig. 4. Ratio “Measured Fe^{3+} consumption/Theoretical Fe^{3+} needed for dissolving measured metals in solution” vs. time during biotic and abiotic leaching of PCBs.

800 mV (SHE). The temperature of the reactors was maintained at 40 °C and the air flow rate was set at 0.5 L/h.

2.5. Reactor monitoring

Each type of reactors was monitored regularly for temperature, pH (adjusted below 1.8 by adding H₂SO₄ (96%)) and redox potential. Several samples of solution were taken and filtered at 0.45 μm in order to monitor the concentrations of Fe, Cu, Ni, Zn, Pb and Co (measured by AAS) and of Fe²⁺ (determined by titration using cerium(IV) sulfate). Bacterial cells were counted regularly in biotic slurry samples. The leach residue was collected at the end of each batch test and analyzed using the procedure described in Section 2.3. The final liquor of the biotic tests was also analyzed by ICP-OES to determine Sn, Au, Ag, Ga, Mo and Pd final concentrations. These data were used further for the calculation of mass balance and metal dissolution yields.

3. Results

3.1. Production of the lixiviant solution by bioleaching of sulfidic mining wastes

Fe and Co concentration follow-up during the bioleaching of the sulfidic mining waste is shown in Fig. 1. The operating conditions were not optimized since the objective of these tests was only to produce lixiviant solution, but the curve is similar to the one obtained in previous study using KCC-BRGM microbial consortium on this pyritic waste with first a lag phase of one day, and then a regular increase of metal content. Experiments were stopped when the Fe concentration in the solution reached the targeted value: 11 or 18 g L⁻¹. These values were chosen by calculating the stoichiometric amount of oxidant (Fe³⁺) required to leach the metals contained in the PCBs. Indeed several authors showed that in presence of Fe³⁺, the dissolution of PCBs metals is governed by an oxidative mechanism based on the following equation (Yang et al., 2014; Zhu et al., 2011; Bas et al., 2013):



Ferric iron in aqueous solution exhibits a standard reduction potential (Eh) as high as +0.77 V and could readily solubilize base metals contained in electronic scraps. Knowing the content of Cu, Ni, Zn, Pb, Fe and Sn in the PCBs it can be easily calculated from Eq. (1) that Fe³⁺ concentration of 11 g L⁻¹ corresponds to a stoichiometric ratio of 1.2 and 18 g L⁻¹ to a stoichiometric ratio of 2.

The lixiviant solution obtained from the bioleaching of the sulfidic wastes is characterized by low pH (<1.3) and high redox

potential (800–862 mV), which indicates a good biological oxidizing activity (Table 2). This is confirmed by the low concentration of Fe²⁺ compared to total iron. The solution also contains small amounts of Cu, Ni, Pb, Zn and Co (Table 2).

3.2. PCBs leaching tests

3.2.1. Effects of Fe³⁺ concentration and of lixiviant solution type (chemical or biological) on leaching

The first series of leaching tests aimed first at studying the influence of lixiviant solution production method (chemical or biological) on the metals dissolution by performing biotic PCBs leaching tests using the biogenic lixiviant solution obtained from the bioleaching of mining wastes and abiotic tests using a synthetic solution containing ferric iron and sulfuric acid. The concentration of Fe³⁺ was set to 18 g L⁻¹ in both solutions. The 2nd aim was to study the influence of Fe³⁺ concentration on the metals dissolution. Therefore biotic tests were also carried out using the biogenic lixiviant solution with a ferric iron concentration of 11 g L⁻¹. Biotic and abiotic experiments were performed in Erlenmeyer flasks at ambient temperature and without air injection.

The dissolved Cu²⁺ and Fe³⁺ concentrations were monitored with time (Figs. 2 and 3). Copper dissolution and ferric iron consumption are very similar in biotic and abiotic tests with an initial Fe³⁺ concentration of 18 g L⁻¹. The Cu²⁺ concentration increased rapidly during the first 5 h. A slower dissolution was then observed before the curve leveled off after 120 h with a final copper dissolution rate of about 96%. Ferric iron follows an inverse trend with a sharp decrease in the first hours of the tests followed by a slower decrease afterwards. In biotic tests no re-oxidation of Fe²⁺ ions in Fe³⁺ ions was observed. Moreover, the number of bacterial cells displayed no significant changes during the biotic tests remaining to a level closed to 10⁸ bact/mL.

These results underline that there was no significant bacterial activity in tests performed with the biogenic lixiviant solution. This could be explained by the fact that the ambient temperature and the oxygen content in solution were too low for any activity of moderate thermophilic bacteria. Therefore, it can be concluded that, if carried out at ambient temperature, the ferric ion production method (chemical or biological) had no influence on the metals dissolution.

Regarding the influence of the Fe³⁺ concentration, Fig. 2 shows that higher Fe³⁺ concentration leads to increase the kinetics of the copper dissolution and the final recovery. Similar results were found by several authors (Yang et al., 2009; Zhu et al., 2011; Bas et al., 2013).

By comparing Figs. 2 and 3 it can be seen that in the biotic test with a Fe³⁺ concentration of 11 g L⁻¹, Cu dissolution rate was lower than the consumption rate of Fe³⁺. Indeed, even if the initial Fe³⁺ concentration of 11 g L⁻¹ corresponds to a stoichiometric ratio of 1.2, all Fe³⁺ was consumed after one day whereas Cu dissolution rate was only about 50% at that time. In biotic and abiotic tests with a Fe³⁺ concentration of 18 g L⁻¹, the consumption of Fe³⁺ is not complete: Fe³⁺ concentration decreases more slowly after 5 h of leaching and reaches a steady state even if all metals are not completely dissolved. This seems to indicate that ferric iron is no more involved in the leaching. One hypothesis could be that ferric iron forms complexes and is therefore not available for metals dissolution.

The ferric iron consumption was analyzed by calculating the ratio “Measured Fe³⁺ consumption/Theoretical Fe³⁺ needed for dissolving measured metals in solution” vs. time (see Fig. 4). This ratio take into account only the dissolution of Cu, Pb, Ni and Zn since they are the main metals contained in PCBs. In the first hours of leaching, this ratio is equal to 2 in the abiotic tests, which confirms that the metal dissolution corresponds to the oxidative process

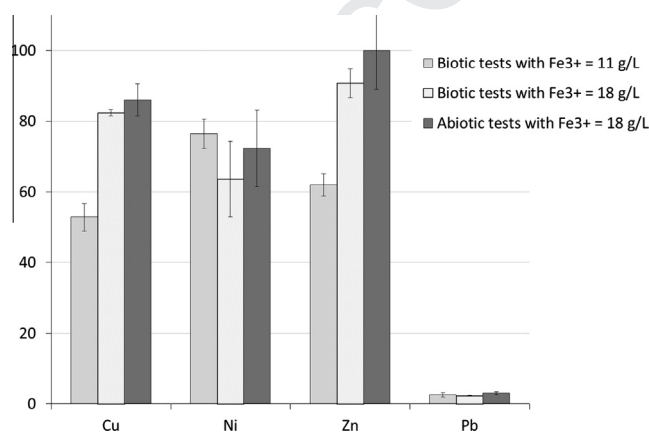


Fig. 5. Metal dissolution yields after 2 days of PCBs leaching in Erlenmeyer flasks.

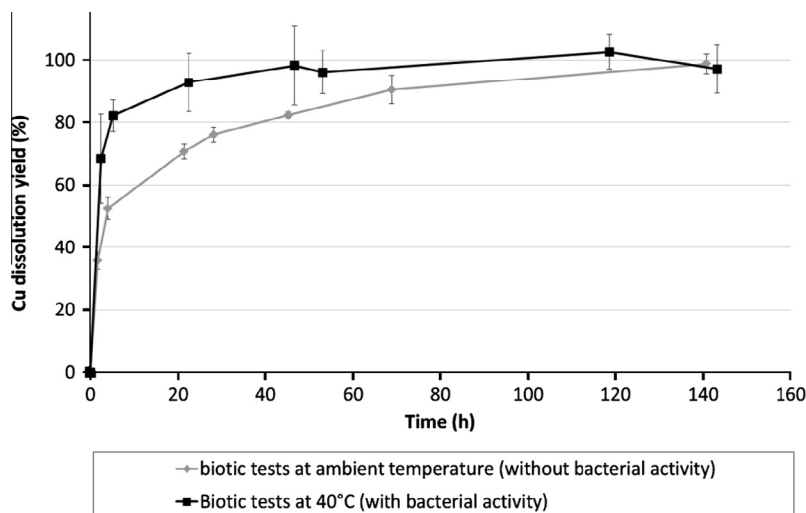


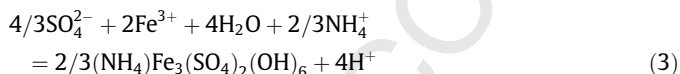
Fig. 6. Evolution of Cu dissolution yields with time during biotic tests at 40 °C and at ambient temperature (initial Fe³⁺ = 18 g L⁻¹).

Table 3
Metal dissolution yields (in%) and absolute standard deviation σ (in%) after 2 days and at the end of tests of PCBs leaching at 40 °C and at ambient temperature (initial Fe³⁺ = 18 g L⁻¹).

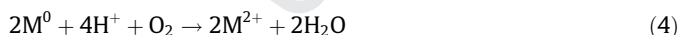
| | After 2 days of leaching | | At the end of the leaching tests (about 6 days) | |
|----|--|---|---|---|
| | Biotic test at 40 °C (with bacterial activity) | Biotic test at ambient temperature (without bacterial activity) | Biotic test at 40 °C (with bacterial activity) | Biotic test at ambient temperature (without bacterial activity) |
| Cu | 98.3 ($\sigma = 12.8$) | 82.3 ($\sigma = 0.9$) | 97.7 ($\sigma = 5.3$) | 98.6 ($\sigma = 3.2$) |
| Ni | 100 ($\sigma = 2.8$) | 63.5 ($\sigma = 10.7$) | 100 ($\sigma = 5.9$) | 84.3 ($\sigma = 11.8$) |
| Zn | 95.3 ($\sigma = 14.0$) | 90.7 ($\sigma = 4.1$) | 95.2 ($\sigma = 6.7$) | 98.5 ($\sigma = 5.8$) |
| Pb | 2.7 ($\sigma = 0.1$) | 2.3 ($\sigma = 0.1$) | 3.3 ($\sigma = 0.1$) | 2.6 ($\sigma = 0.1$) |
| Ga | NA | NA | 68.6 ($\sigma = 5.3$) | 42.9 ($\sigma = 7.4$) |
| Sn | NA | NA | 59.4 ($\sigma = 1.6$) | 6.8 ($\sigma = 1.8$) |

NA: Not analyzed.

presented in Eq. (1). In biotic tests, whatever the Fe³⁺ concentration, the ratio is higher than 2 in the first hours, underlining the presence of other reactions consuming Fe³⁺. One hypothesis which is reported by several authors (Yang et al., 2014; Zhu et al., 2011; Xiang et al., 2010; Vestola et al., 2010; Wang et al., 2009) could be the formation of jarosite precipitates (see Eqs. (2) and (3)), a reaction which is favored by the presence of ions such as K⁺ or NH₄⁺ brought by the nutrient medium:



After about 5 h, this ratio falls under 0.5 meaning that metals dissolution not only occurs through the oxidative action of Fe³⁺ initially present in the flasks but also through other phenomena. For example, part of zero-valence metals could be directly leached out based on the following overall reaction, with H⁺ coming from sulfuric acid:



As mentioned by several authors (Hong and Valix, 2013; Zhu et al., 2011; Yang et al., 2014; Bas et al., 2013) Eq. (4) has a low kinetics which could explain the decrease in copper dissolution rate after the rapid consumption of Fe³⁺ at the beginning of the leaching experiments.

The metal dissolution yields obtained after 48 h of leaching are summarized in Fig. 5. After 2 days, the Cu extraction was 82.5% in

biotic tests with an initial Fe³⁺ concentration of 18 g L⁻¹, 86% in abiotic tests and 52.8% in biotic tests with an initial Fe³⁺ concentration of 11 g L⁻¹. Zn showed the same behavior as Cu in all types of experiments. Fe³⁺ concentration seems to have no influence on the dissolution of Ni. Pb dissolution yields are significantly lower than what can be expected given the pH and the redox of the solution, probably because of Pb precipitation phenomenon (Ilyas et al., 2010; Ilyas et al., 2013). Ilyas et al. (2013) reported in particular the formation of PbSO₄ precipitates during PCBs bioleaching in shake flasks.

3.2.2. Effects of bacterial activity on leaching

Since no bacterial activity was detected in the first series of biotic tests, a second series of leaching tests was run in order to enhance bacterial activity and to favor biological oxidation of ferrous iron produced by the oxidative leaching of PCBs. The experiments were performed using the biogenic lixiviant solution ([Fe³⁺]₀ = 18 g L⁻¹) at 40 °C which is known to be the optimal temperature for BRGM-KCC consortium. A small amount of air was injected (0.5 L h⁻¹) in order to provide oxygen to bacteria. The results obtained were compared to those obtained with the biotic tests of the first series of PCBs leaching experiment run with the same biogenic lixiviant solution in shake flasks at ambient temperature. Cu concentration over time is shown in Fig. 6. A higher dissolution yield of copper is observed. After 4 h of leaching, Cu dissolution yield reached about 76% in these tests against 53% in the tests in flasks at ambient temperature. A complete extraction of copper, nickel and zinc is obtained after 2 days of leaching, whereas the extraction in flask tests is only 82.3% for Cu, 63.5%

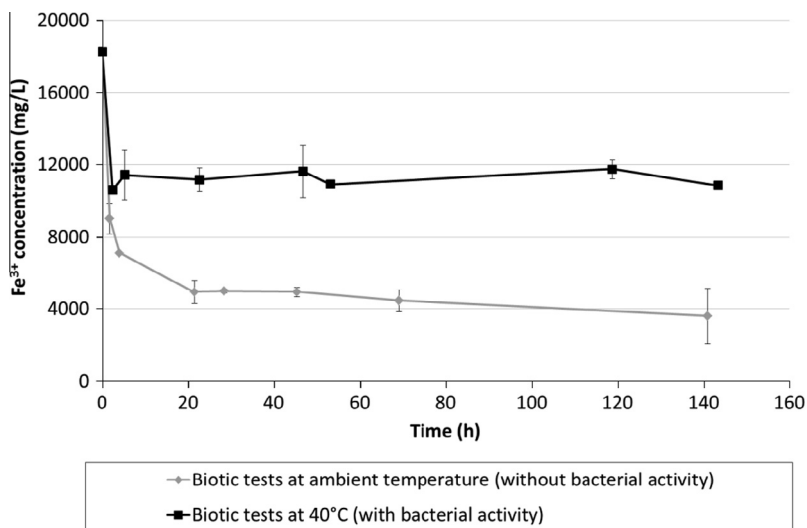


Fig. 7. Fe³⁺ concentration vs. time during biotic tests at 40 °C and at ambient temperature (initial Fe³⁺ = 18 g L⁻¹).

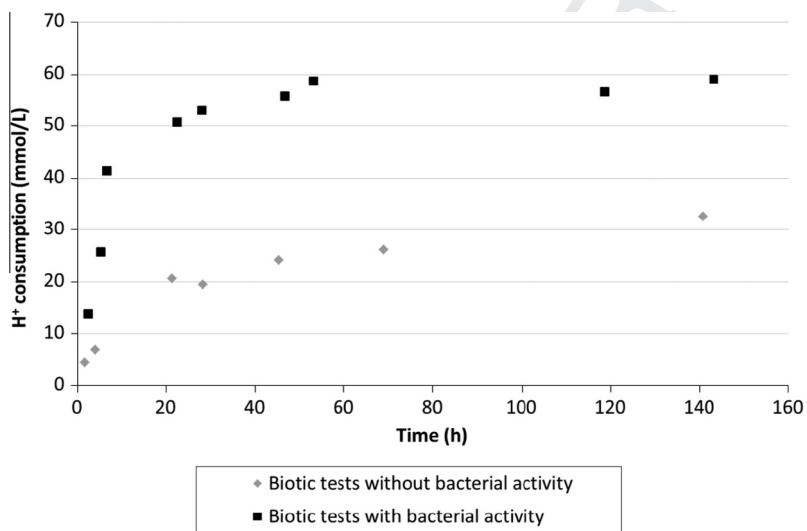


Fig. 8. H⁺ consumption vs. time during biotic tests with and without bacterial activity (initial Fe³⁺ = 18 g L⁻¹).

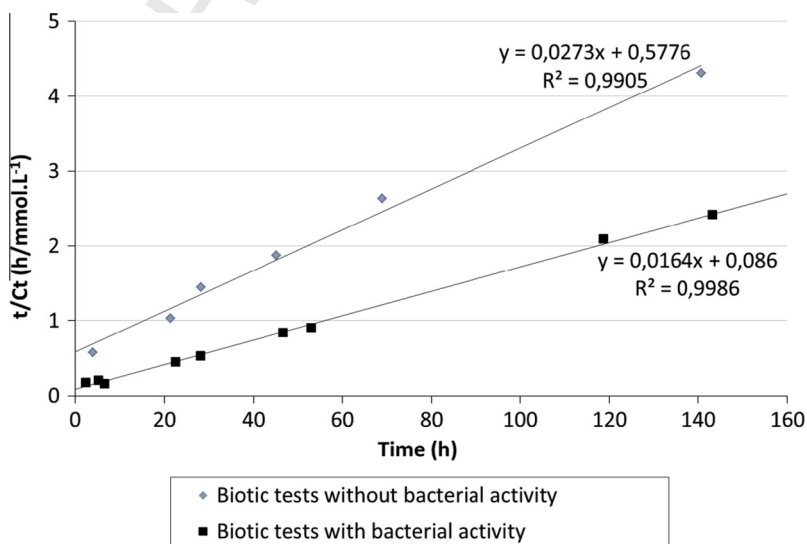
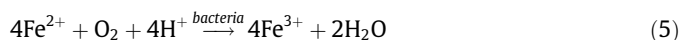


Fig. 9. Second-order model of H⁺ consumption during biotic tests with and without bacterial activity (initial Fe³⁺ = 18 g L⁻¹).

Table 4
Comparison between Cu extraction obtained by several authors and our results.

| | One-step leaching | | | | | Two-step leaching | | |
|----------------------------------|---------------------|---------------------|---------------------|--------------------|-------------------|--------------------|------------|---------|
| | Xiang et al. (2010) | Ilyas et al. (2007) | Ilyas et al. (2013) | Wang et al. (2009) | Zhu et al. (2011) | Yang et al. (2009) | This study | |
| PCB content (g L ⁻¹) | 20 | 10 | 100 | 7.8 | 8 | 25 | 25 | |
| Time (day) | 16 | 18 | 12 | 5 | 3 | 1 | 1.5 | 1 2 |
| % Diss. Cu | 95% | 74% | 90% | 70% | 92.9% | 90% | 100% | 93% 99% |

for Ni and 90.7% for Zn (Table 3). As previously observed, Pb dissolution yield is very low, probably due to phenomenon of precipitation. Results of metals extraction at the end of the tests (about 6 days) is also given in Table 3. After about 6 days, both cases have similar dissolution yields for Cu, Zn and Pb. Regarding extraction of Ni, Ga, Sn (both are only analyzed at the end of the experiments) after 6 days of leaching, higher values are reached in tests at 40 °C; in particular, the Sn extraction rate is more than 8 times higher. As can be expected with an acid ferric lixiviant solution, no dissolution was obtained for Au, Ag, Pd and Mo (results not shown). Fig. 7 shows that this is correlated with a higher level of Fe³⁺ in solution. Indeed, even if both cases exhibit a drastic decrease of Fe³⁺ concentration in the first 2 h, Fe³⁺ stabilizes then at about 11 g L⁻¹ all along the tests at 40 °C whereas the concentration of Fe³⁺ decreases in the tests at ambient temperature. This difference is probably linked to the re-oxidation of ferrous iron by the oxidizing bacteria contained initially in the biological lixiviant solution according to the following equation:



According to Bas et al. (2013), Fe²⁺ is the only energy-yielding substrate for bacteria to support the bacterial growth and activity in bioleaching process. A cycle between Fe³⁺ and Fe²⁺ is then built and metals are continually leached out. This could explain the increase in dissolution kinetics and in dissolution rates observed in tests with bacterial activity compared to the ones carried out at ambient temperature where no bacterial activity was detected. The ratio between FeIII and FeII in the solution ([FeIII]/[FeII]) is also an important parameter which must be encountered to interpret these results. In the test at 40 °C this ratio decreases to a value of 1.1 after 30 min and then increases to reach a value of 1.6 at the end of the experiments (7 days of leaching). In the tests at ambient temperatures this ratio decreases constantly to reach a value of 0.2 at the end of the experiments, which is much less favorable to metal leaching. These results highlight the central role of ferric iron in the metal dissolution process as well as the influence of the biological recycling of ferric iron on the leaching kinetics of PCBs.

3.2.3. H⁺ consumption during PCBs leaching

Since the recycling of ferrous iron into ferric iron consumes H⁺ (see Eq. (5)), the consumption of protons during PCBs leaching and its influence on metal dissolution efficiency were examined. As indicated by Yang et al. (2014), the PCB leaching process can lead to several pathways of H⁺ consumption: a direct H⁺ consumption through reactions with substances of PCB such as alkaline substances, and an indirect H⁺ consumption with bacterial oxidation of Fe³⁺. H⁺ consumption over time is plotted in Fig. 8. Fig. 8 confirms that H⁺ consumption is faster and higher in tests with bacterial oxidation of ferrous iron compared to the ones without this oxidation. Yang et al. (2014) suggested that H⁺ consumption kinetics can be described by the following second-order kinetic model:

$$\frac{t}{C_t} = \frac{t}{C_e} + \frac{1}{k_2 C_e^2} \quad (6)$$

where t represents the time; C_t represents the amount of H⁺ consumption; k_2 represents the reaction rate constant of second-order kinetics; C_e represents the total H⁺ consumption in the whole process of bioleaching.

Fitting results of this second-order kinetic model are shown in Fig. 9. In both cases, the correlation coefficient is over 0.99 suggesting that the second-order kinetic model is able to adequately describe the progress of H⁺ consumption during leaching. Calculation of the reaction rate constant k_2 gives 0.0031 [mmol/L]⁻¹ [h]⁻¹ for tests with bacterial activity and 0.0013 [mmol/L]⁻¹ [h]⁻¹ for tests without bacterial activity. Eq. (5) also allows evaluating the total H⁺ consumption in the whole process of leaching and then the potential of metal dissolution rate. Potential value of the total H⁺ consumption is strongly increased when bacteria are allowed to oxidize ferrous iron with a value of 60.9 mmol L⁻¹ compared to 36.6 mmol L⁻¹ for tests without bacterial activity, meaning that favorable conditions for bacterial oxidation of Fe²⁺ greatly enhances the overall extraction of metals. It must be noted also that given the importance of proton consumption during PCBs leaching, lixiviant solutions produced from the bioleaching of sulfidic mining wastes are not only interesting for their content in ferric iron but also because they provide high amounts of protons under the form of sulfuric acid.

3.3. Comparison of this study with results from the literature

Cu extraction obtained in the 2nd series of PCBs leaching experiments were compared to results from the literature. This comparison is not easy since experimental conditions are rather different. For example, the initial PCBs content in the reactor can vary from less than 1% to more than 10%. The particle size distribution is also very different: PCBs are usually grinded under 250 μm; in some cases only the finest fraction is used in the tests. These factors can of course have a great influence on the results of leaching. It must be noted also that in most of the papers dedicated to PCBs bioleaching, experimental tests are performed in one step mode, which means that the lixiviant solution is not produced in a first reactor prior to PCBs leaching. Only a few papers propose PCBs leaching in two steps mode. As can be seen in Table 4, in the case of one-step leaching the final copper dissolution yield varies between 70% and 95% for a leaching time ranging from 3 to 18. The two-steps mode enables to reach better kinetics and higher metal dissolution yield since the copper dissolution is almost complete in 2 days of leaching. Only Zhu et al. (2011) reached extraction yield above 90% after 3 days of one-step leaching, but initial PCBs content was 3 times smaller (8 g L⁻¹ against 25 g L⁻¹). In most of papers dealing with one-step leaching problems of metal toxicity impacting bacterial activity were mentioned to explain low leaching efficiency. The results obtained by Yang et al. (2009) in 2-steps mode using a culture of *A. ferrooxidans* are very similar to the results obtained in this study, which highlights the interest of this method of leaching. It confirms that decoupling lixiviant production and leaching process could limit problems of metal tolerance and thus greatly enhance leaching efficiency in terms of kinetics but also in terms of metals dissolution yields.

4. Conclusions

The lixiviant solutions obtained from the bioleaching of sulfidic mining wastes using KCC-BRGM consortium showed a good performance for base metal recovery from waste PCBs (Cu, Ni, Zn, Pb, Sn, Ga). The tests were carried out using a two steps approach (bio-generation of the lixiviant oxidative solution/microbiologically assisted leaching of the PCBs). The results indicated that microbial assisted leaching was significantly more effective than a pure chemical leaching of PCBs. The extraction of metals was mainly accomplished indirectly through oxidation by ferric iron. The bacterial activity helped regenerating and maintaining a higher concentration of ferric iron in solution. The comparison with data from the literature is significantly encouraging since the rate and kinetics obtained in this study were much higher and quicker than those obtained in previous studies. It must be noted that in most of them, bioleaching was carried out using a one-step approach, which confirms the interest of decoupling the lixiviant production from the leaching process to avoid toxicity issues.

5. Uncited reference

Fujita et al. (2013).

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