



## Effects of operational parameters on the bio-assisted leaching of metals from pyrolyzed printed circuit boards



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### ARTICLE INFO

#### Keywords:

Printed circuit boards  
Pyrolysis  
Recycling  
Bio-leaching

### ABSTRACT

End-of-life printed circuit boards have been subjected to proprietary pyrolysis resulting in a copper-rich char containing liberated metals. For downstream processing and copper recovery, the char was exposed to two different leaching solutions: one containing mixed microbial consortia originating from bioleaching of coal spoils and a cell-free chemical solution for comparative purpose. The influence of char pre-treatment, reactor type, temperature and type of leaching solution on the dissolution of the zero-valent copper was studied. It was found out, that for bringing copper in solution, the type of leaching solution had less pronounced effect than the type of reactor. Other than ferric iron concentration and temperature, the bacterial presence has shown effect on copper leaching kinetics and process efficiency. The fact that copper was continuously dissolved by ferric iron at initial concentrations well below the stoichiometric required ratio, demonstrated microbial regeneration of ferric iron and its back-cycling in the system. In case of the absence of microbe, the regeneration of ferric iron is driven by oxidation in the presence of O<sub>2</sub> and H<sup>+</sup>. A simplified kinetic model of copper dissolution suggested that the reaction order depends upon the initial concentration of ferric iron.

### 1. Introduction

Waste electronics and electrical equipment (WEEE) generated by man present a growing waste stream over the past years, estimated to be 44.7 million metric tonnes in 2016 globally (Baldé et al., 2017). As a response to this situation, the Directive 2012/19/EU on recovering metals from WEEE streams has been established by the European Parliament on 4 July 2012, aiming to reduce this waste stream efficiently and recover valuable metals. However, the complex and heterogeneous mix of various materials along with the increasing volumes and complexities of WEEE still remain a challenge in WEEE recycling and management (Gupta et al., 2008; Tsydenova and Bengtsson, 2011).

Among different types of WEEE, printed circuit boards (PCBs) hold the majority of intrinsic value. Recycling of PCBs has been motivated by the content of precious and non-ferrous metals and their potential for commercial valorisation. Although the processing of PCBs is widely researched, the problem with their hydrometallurgical processing lies on the entrapment of metals beneath plastics and ceramic material (mainly glass fibres), limiting the contact between metal surface and extractive reagents. Pyrolysis offers promising solution to this issue through thermal degradation of the organic fraction of the waste. In the absence of oxygen, PCBs pyrolysis degrades the plastics and

disintegrates the fibre, producing oil and combustible gases, while leaving behind a solid residue in the form of carbonaceous char, from which metals and other solid materials can be recovered (Williams, 2010). Unlike the crude PCB, most of metals in the char are fully liberated, thus rendering them much more accessible for recuperation by physical or chemical processes.

Metals in PCBs exist as zero-valent or compound (alloy) form. One way to process them to recover metal values is through hydro-metallurgical approaches. In order to extract and bring in solutions contained metals, various reagent systems (e.g. sulphate, chloride, nitrate, iodide, ammonia, cyanide, thiourea, and thiosulphate) in combination with suitable oxidants (e.g. H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>, Cu(II), Cl<sub>2</sub>) have been developed and explored (Bas, 2012; Cui and Zhang, 2008; Kim et al., 2010; Kumar et al., 2014; Madenoglu, 2005; Tuncuk et al., 2012; Yazici, 2012). Despite few positive results, various issues need to be sought, e.g. relatively high cost and consumption of reagents, corrosion resistant systems and problems in solutions purification and metals recovery from solutions.

In response to these challenges, biohydrometallurgy has appeared a promising alternative route. It offers a more environmental-friendly approach involving utilization of microbes with their natural capability to extract metals for their own metabolic functions. Development of

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metal bioleaching using micro-organisms has been intensively studied over the past few years, recovering metals from a wide variety of WEEE sources, e.g. fine shredder residue (Lewis et al., 2011), spent batteries (Mishra et al., 2008; Tanong et al., 2016), waste electric cables (Lambert et al., 2015) and PCBs (Guezennec et al., 2015; Liang et al., 2010; Pradhan and Kumar, 2012; Saidan et al., 2012; Wang et al., 2009; Xiang et al., 2010; Yang et al., 2009). However, no research has been published on bioleaching of pyrolyzed PCBs.

Regardless the number of papers being published on bioleaching processes, only few of them focused on the design of reactors (Rossi, 1999). The key to enhance bioleaching efficiency is to provide the appropriate environment to the microbes being either suspended (planktonic) or attached to particles (Bailey, 1993). From the engineering point of view, the appropriate environment means availability of sufficient amount of dissolved oxygen and carbon dioxide (Boon and Heijnen, 1998) and moderate effects of agitation on microorganisms. This forms an important principle that guides the design and operation of gas–liquid–solid–microbes bioreaction system. At present, bioreactors applied in bioleaching processes are stirred tank and airlift bioreactors (Pachuca tank) (Rossi, 1999). As a rule, suspended mineral particles would damage bioleaching microbes in both stirred tank bioreactor and air-lift bioreactor. Other authors found that viability of microbes decreased very rapidly when solids concentration exceeded 20%w/w in a bench-scale stirred tank bioreactor, meaning increasing solids concentration in stirred tank bioreactors would lead to a severe loss of microbial activities, which in turn would deteriorate the bioleaching processes (Deveci, 2004, 2002).

This limitation of stirred tank bioreactors is considered as a major drawback of the related extractive processes since it affects overall costs (bioreactor size, power input and maintenance). As a consequence, the design of a new bioreactors, capable of treating high solids concentration while at the same time keeping the activity of microbes is very important for industrial application of bioleaching processes. Researchers have explored the application of rotating drum bioreactors in a plant cell culture, solid substrate fermentation (Mitchell et al., 2002), bioleaching processes (Herrera, 1998; Loi, 1997; Rossi, 1999) and bioremediation (Banerjee et al., 1995) because of low shear/collision effects in rotating drum bioreactor. This opens an avenue for application of similar type of reactors in WEEE bioleaching.

On the background of the above, the current paper aims to investigate on comparative basis the performance of two reactors: a stirred-tank (STR) and a rotating-drum (RDR) system for hydro-metallurgical recovery of the copper remaining in pyrolyzed PCB's. The key objective is to evaluate the feasibility of using acidic solution originating from acid-mine drainage (AMD) prone coal spoil as a lixiviant source. Otherwise this stream is regarded as a waste solution and hence needs an appropriate management. To this end, selected process parameters such as concentration of ferric and total iron, leaching temperature and char pre-treatment are studied and compared with pure chemical leaching to outline the role of the microorganisms being present in the bio-lixiviant.

## 2. Materials and methods

### 2.1. PCBs origin and preparation

Depopulated low-grade PCBs (non-saleable to smelters due to gold grade below cut-off) provided by Comet Traitements S.A. were shredded to a size below 40 mm and pyrolyzed at their proprietary installation in Obourg (Belgium). The pyrolysis lead to decomposition of plastics/resins into a liquid hydrocarbon (oil) leaving a solid residue (carbonaceous char) which contains metals and solid materials such as fibre glass remnants. Compared to non-treated PCBs the pyrolysis apart from liberating the metals is leading to significant increase in their content in the char - Table 1. As preparation for the leaching, the char was further sieved into several size fractions. The fraction of +8 mm

**Table 1**  
Elemental composition of the as received and pyrolyzed PCBs.

Elements	Unit	As received	Pre-treated
Al	%	2.8	4.6
Cu	%	27.7	49.1
Fe	%	3.5	6.7
Ni	%	0.3	0.5
Pb	%	0.6	0.9
Sn	%	3.7	6.3
Zn	%	1.3	1.9

**Table 2**  
Elemental composition of the sieved char (+8 mm) and effect from magnetic separation.

Elements	Unit	Fraction + 8 mm	Magnetic (35.7%)	Non-magnetic (64.3%)
Al	%	6.6	0.8	9.8
Cu	%	30.3	21.4	35.2
Fe	%	12.9	23.2	7.1

was ultimately chosen as a most suitable candidate for leaching, the remaining fractions being deemed as commercial products for smelters and metal traders.

To remove excessive iron, the char was further processed using high-intensity magnetic separation (HIMS). The reason behind was to minimize the consumption of  $\text{Fe}^{3+}$  present in the lixiviant by lowering Al and Fe concentration, thus copper remaining the only targeted metal for dissolution. Magnetic separation was able to remove the majority of iron in char while keeping the copper in non-magnetic fraction -Table 2.

### 2.2. Bacterial culture and nutrients

The mixed bacterial culture originated from the coal tailing storage facility at Tauron Wydobycie, Poland. Cultures containing *Sulfobacillus thermosulfidooxidans* and unidentified species were used. The nutrient medium used to maintain bacterial growth contained:  $(\text{NH}_4)_2\text{SO}_4$  0.4 g/L, KOH 0.48 g/L,  $\text{H}_3\text{PO}_4$  85% 0.81 g/L,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  0.52 g/L.

### 2.3. Production of biolixiviant from coal waste

The production of biolixiviant was performed by bioleaching of the coal waste utilizing the mixed culture mentioned above. This bioleaching was performed at 10% w/v solid density inside a 2-L double-walled vessel at 48 °C with addition of 60 L/hour air +1% v/v  $\text{CO}_2$ . After 10–14 days of leaching, the solution was left overnight to let the solid settle. The supernatant was then recovered and kept at ambient temperature for 24 h at most, before being transferred to char leaching reactors.

### 2.4. Experimental setup

Six runs for char leaching were performed under batch conditions at 10% solid density (w/v) - Table 3. The technological parameters tested were: material pre-treatment by magnetic separation, type of reactor (STR - stirred-tank and RDR - rotating-drum), leaching conditions (abiotic and biotic) and working temperature (30 and 48 °C). Biotic tests were performed by utilizing the bio-derived solution from coal bioleaching, while the abiotic were carried out using cell-free solution resembling the composition of the bio-lixiviant. The synthetic solution was prepared by mixing deionized water with  $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$  for reaching an  $\text{Fe}^{3+}$  concentration as close as possible to that of the bio solution.

The stirred-tank reactor (STR) experiments were carried out at 10% solid density inside a 1-L thermostated double-walled vessel fitted with a 4-propeller blade run at stirring speed of 600 rpm. Reactor aeration

**Table 3**  
Process parameters used for the char leaching.

Test n <sup>a</sup>	Reactor	Feed pre-treatment	Inoculum	Nutrients	Temp.	Init. Eh	Initial pH	Initial Fe <sup>3+</sup>	Initial Cu <sup>2+</sup>	Initial Al <sup>3+</sup>
			(%)	(%)						
1	STR	No	0	100	48	614	1.67	3.08	0.13	0.03
2	STR	No	10	90	48	544	1.52	4.28	0.03	0.14
3	STR	Yes	10	90	30	777	1.83	5.81	0.11	0.21
4	STR	Yes	10	90	48	478	1.52	5.46	0.02	0.21
5	RDR	No	0	100	30	638	1.30	6.94	0.03	0.01
6	RDR	No	10	90	30	754	1.73	6.13	0.00	0.20

was achieved by using a stainless-steel sparger placed at the bottom of vessel.

The rotating-drum reactor (RDR) consisted of a perforated trommel submerged inside a tubular vessel with 5L working volume. The solid material to be leached was placed inside the trommel which was rotated at 60 rpm by means of a shaft connected to a DC motor. Similar to the STR tests, both bio-lixiviant and a synthetic chemical solution were tested at 10% solid density and at 30 °C working temperature.

Both reactors were fitted with pH and redox probes, the pH probe being connected to a peristaltic pump dosing diluted sulphuric acid and controlled in pH-stat mode by a computerized unit. The pH was set to 1.7 aiming to ensure optimal bacterial growth and prevent copper losses through build-up of iron precipitates and cementation. Regular solution sampling enabled determination of copper concentration in the pregnant leach solution.

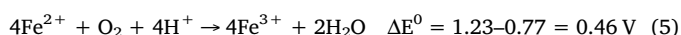
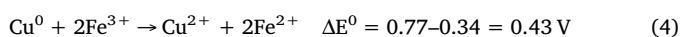
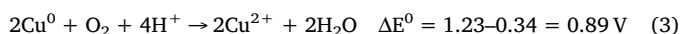
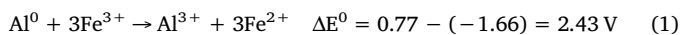
### 2.5. Analysis

The char subjected to leaching and the leached solid residues was pulverised and sieved at 150 µm prior to chemical assay. The metallic alloys retained on the sieve underwent a double nitric acid/aqua regia digestion. The material passing through the 150 µm aperture was submitted to an oxidative fusion (sodium peroxide) and solubilised in diluted hydrochloric acid. Solutions were assayed by Atomic Absorption Spectrometry (AAS) and by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) for major elements. Ferrous iron was determined by K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> titration. Ferric iron was estimated based on the difference between total and ferrous iron. Acid consumption (gram H<sub>2</sub>SO<sub>4</sub> per gram of solid and gram H<sub>2</sub>SO<sub>4</sub> per gram of leached copper) was calculated in each experiment.

## 3. Results and discussions

### 3.1. Electrochemical considerations

In order to better understand the chemical environment under which the leaching takes place, the standard reduction potentials for the full-reactions ( $\Delta E^0$ ) occurring in the system (Cu<sup>0</sup>-Cu<sup>2+</sup>, Fe<sup>2+</sup>-Fe<sup>3+</sup>, Al<sup>0</sup>-Al<sup>3+</sup>) under the presence of O<sub>2</sub>, H<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> can be presented as follows.



When the  $\Delta E^0$  values of the above reaction are considered, it appears that the oxidation of Al<sup>0</sup> by Fe<sup>3+</sup> (Eq. (1)) and the cementation of Cu<sup>2+</sup> on Al<sup>0</sup> (Eq. (2)) possess the highest  $\Delta E^0$ . Similarly, based on the  $\Delta E^0$  values only these two reactions should be the ones occurring right at the beginning in the studied system. In such a way, aluminium is in

competition with copper regarding: (1) Fe<sup>3+</sup> consumption and (2) cementation of dissolved copper. Cementation on aluminium could be avoided through bringing aluminium in solution completely before copper starts to dissolve. Typically, zero-valent copper met in electronic waste should be in competition with aluminium, zinc and iron in terms of leachability. In our system we observe that copper in electronic waste is in competition with the aluminium only, which will be dissolved first.

It is known that oxidation of copper can be realized through two principally different ways. i.e. oxidation by O<sub>2</sub> - Eq. (3) and oxidation by Fe<sup>3+</sup> - Eq. (4). From a thermodynamic point, due to the higher difference in standard potentials  $\Delta E^0$ , the reaction expressed by Eq. (3) is more likely to occur than the one pictured by Eq. (4). However, due to limitations on O<sub>2</sub> transfer rate from the gas to the liquid phase, an oxidation by Fe<sup>3+</sup> is much more likely. In our system the absence of ferric iron does not hinder copper dissolution entirely. However, in other studies a significant decrease in copper dissolution kinetics during tests without addition of ferric iron has been documented (Lambert et al., 2015). In addition to the chemical mechanisms linked to metals dissolution, the oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> also takes place - Eq. (5). This reaction naturally occurs in chemical systems and is known to be catalysed when iron-oxidizing bacteria are present.

### 3.2. Kinetic aspects of copper leaching

Assuming that the principal mechanism leading to the dissolution of copper may be presented by the reaction given as Eq. (4), it becomes possible to derive a simplified kinetic model of copper recovery. With concentrations given in mol/L, the rate of copper leaching follows the following law:

$$\frac{d[\text{Cu}^{2+}]}{dt} = -\frac{d[\text{Fe}^{3+}]}{2 \cdot dt} = k \cdot [\text{Cu}^0]^a [\text{Fe}^{3+}]^b \quad (6)$$

where k - kinetic constant for the rate equation, a and b - kinetic orders relative to Cu<sup>0</sup> and Fe<sup>3+</sup> respectively. In the current system the concentration of Cu<sup>0</sup> is in large excess and remains constant at the beginning of the leaching. Therefore, the influence of Cu<sup>0</sup> could be neglected in a first approach. Regarding the influence of Fe<sup>3+</sup>, two different models are proposed depending on the initial Fe<sup>3+</sup> concentrations in each system. The first model assumes that the ferric iron is in large excess, thus the kinetics of copper leaching does not depend on Fe<sup>3+</sup> concentration. By modifying the kinetic constant of ferric iron  $k' = k \cdot [\text{Fe}^{3+}]^b$  and given the concentration of Cu<sup>2+</sup> at time 0 (t = 0) is zero, the zero-order model could be solved by the equation given below:

$$[\text{Cu}^{2+}] = k' \cdot t \quad (7)$$

The second model considers that the kinetics of copper leaching depends linearly on the concentration of ferric iron. In this model, ferric iron content acts as a limiting factor thus it needs to be considered in the kinetic rate equation. Similar to the case of the zero-order model, the first-order model can be solved through:

$$[\text{Fe}^{3+}] = [\text{Fe}^{3+}]_0 e^{-2kt} \quad (8)$$

Last but not least, Cu<sup>2+</sup> concentration can be expressed as function

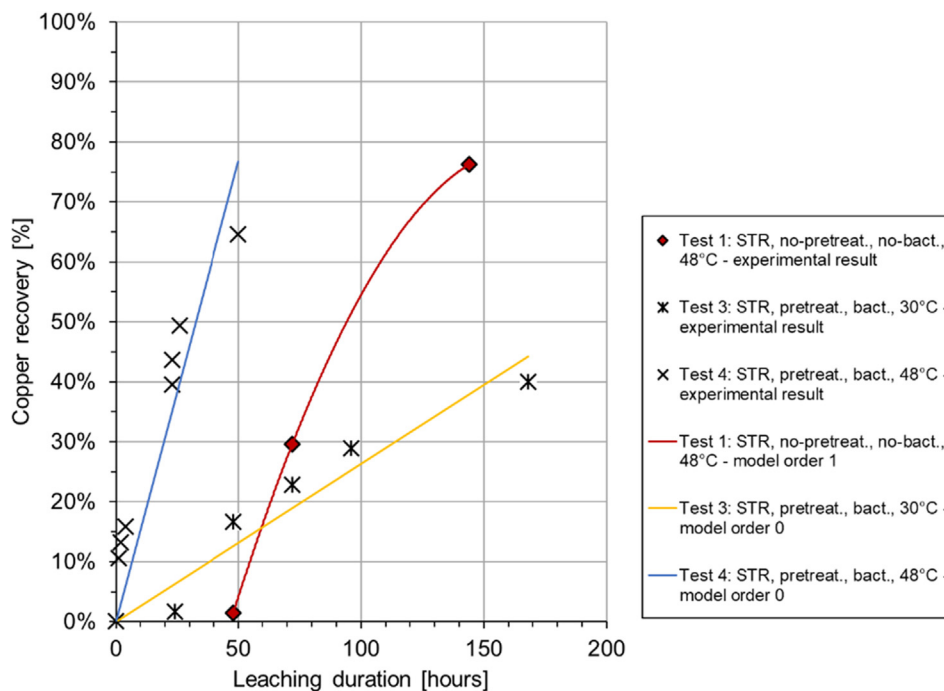


Fig. 1. Comparison between experimental and modelled results.

of the  $Fe^{3+}$  concentration as follows:

$$[Cu^{2+}] = \frac{[Fe^{3+}]_0 - [Fe^{3+}]}{2} = \frac{1}{2}[Fe^{3+}]_0 \cdot (1 - e^{-2kt}) \quad (9)$$

Fig. 1 presents the recovery of copper ( $R_{Cu}$ ) over time, by considering that copper recovery (%) is defined as  $R_{Cu} = m_{\text{recovered Cu}} / m_{\text{total Cu}}$ . In order to provide experimental grounds for establishment of a model, three tests providing contrasting process conditions were performed. Test 1 represents low  $Fe^{3+}$  concentration and high content of aluminium (no pre-treatment), test 3 is characterized by high  $Fe^{3+}$  concentration, but low presence of aluminium, while test 4 is similar to test 3 however realized at higher temperature. Fig. 1 confirms the relevance of using two different approaches (zero-order and first-order kinetic model), when comparing the effect of  $Fe^{3+}$  concentration on copper recovery. Comparing the experimental to model fitting data coming from test 1 to those derived from tests 3 and 4, it becomes evident that  $Fe^{3+}$  availability and presence of aluminium do influence leaching kinetics. When ferric iron concentration is relatively low ( $\sim 3$  g/L  $Fe^{3+}$ ), ferric iron seems to be largely consumed by aluminium before copper starts to react (test 1). In such case the model follows first-order trend. On the other hand, when the  $Fe^{3+}$  concentration is relatively high ( $\sim 7$  g/L  $Fe^{3+}$ ), there is an excess of ferric iron and the leaching rate does not depend on the concentration of iron anymore (tests 3 and 4), hence follows a zero-order path. Another observation worth to note, is the way how the kinetic constant is affected by the process temperature: i.e. test 4 with higher temperature clearly shows higher kinetic constant ( $k'$ ) compared to test 3.

### 3.3. Effect of operational condition on copper leaching

Fig. 2 provides a comparison between biotic and abiotic copper leaching taking into consideration the redox potential evolution. The first impression from the redox potential trend is the lack of significant difference between biotic and abiotic systems. This is somehow unexpected given the fact that bacterial activity strongly correlates with the oxidation of  $Fe^{2+}$  to  $Fe^{3+}$ , which ultimately reflects in redox potential increase. The results in Fig. 2 show that at the beginning of the experiment the solution contains predominately  $Fe^{3+}$  (redox between

600 and 800 mV), which is further gradually converted into  $Fe^{2+}$  with concomitant decrease of redox value over time. The lack of a clear trend for redox potential increase indicates that the consumption rate of  $Fe^{3+}$  through metals dissolution is faster to one of  $Fe^{2+}$  re-oxidation by bacteria, resulting in a stagnant trend after rapid decrease at the beginning.

By comparing tests 1 and 2, as well as tests 5 and 6, it could be noted that bio-leaching mode outperformed cell-free leaching in terms of copper recovery under both RDR and STR conditions, in the case when non-pre-treated char was processed. Fig. 3 suggests that at the beginning of the process, both systems show little to no copper dissolution due to the fact that the oxidative medium ( $Fe^{3+}$ ) was consumed in majority by aluminium ahead of copper. After 24 h of leaching, copper starts to dissolve promoted by the bacterial regeneration of ferric iron, while in the cell-free system copper appeared in solution after 48 h. This observation indicates that there is a microbial contribution towards  $Fe^{2+}$  to  $Fe^{3+}$  re-oxidation. Fig. 3 also summarizes the effect from the operational conditions on copper leaching. As expected, on comparative basis, the stirred-tank reactor has demonstrated better copper dissolution compared to the rotating-drum reactor. However, due to equipment restriction, the effect from the operational temperature was followed for the case of the stirred-tank reactor only.

Fig. 4 presents the evolution of  $Fe^{3+}$  concentration for the six tests being done. The immediate impression is that the regeneration of  $Fe^{3+}$  inside the rotating-drum reactor is slightly better than the one in the stirred-tank reactor. Operating at lower agitation speed, the rotating-drum reactor provides less shear- and attrition effects potentially harmful to bacterial cells, thus maintaining better growth conditions. However, the copper dissolution reactions in the rotating-drum reactor are much slower than those in the stirred-tank system. Aside from the fact that the working temperature of the former reactor is lower ( $30^\circ C$  vs.  $48^\circ C$ ), the latter one provides higher agitation speed meaning increased chances of contact between  $Fe^{3+}$  and zero-valent metals. Since the re-oxidation rate of  $Fe^{2+}$  through bacteria is relatively slow, it is difficult to trace  $Fe^{3+}$  regeneration effects in the stirred-tank reactor - (i.e. Test 3 and 4), the  $Fe^{3+}$  being rapidly consumed through copper oxidation.

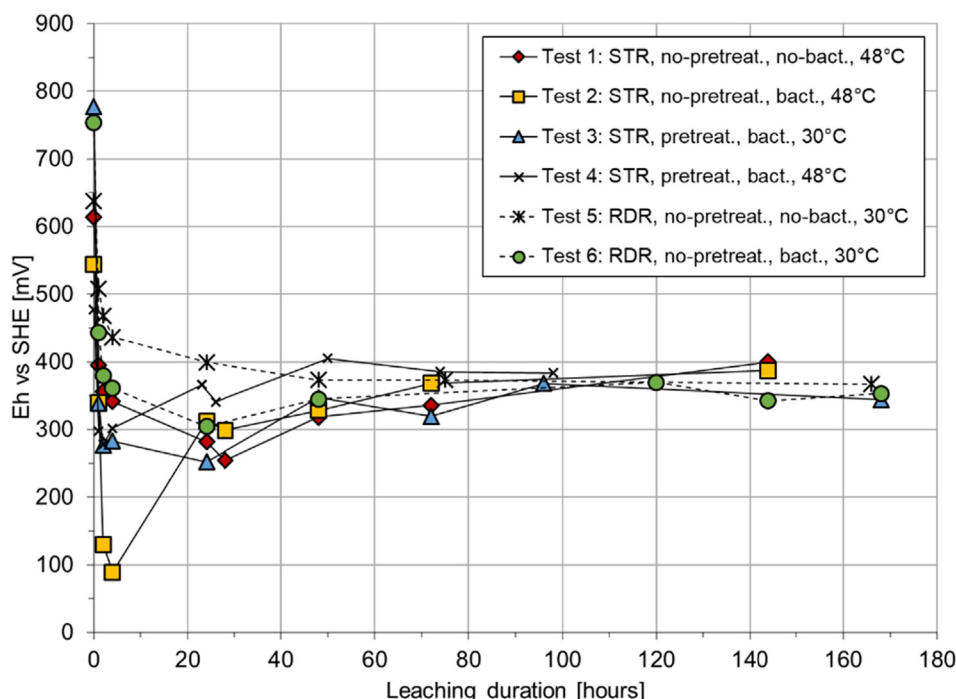


Fig. 2. Evolution of redox potential during biotic and abiotic leaching.

3.4. Effect of temperature on copper recovery during STR leaching

As a rule, the choice of an optimal temperature range promotes bacterial activity during bioleaching and increases the iron oxidation rate (IOR). Fig. 3 shows that at higher temperature (48 °C) the leaching performs better reaching 70% Cu recovery after 100 h, while at lower temperature only 30% is reached. The isolated consortia used in this study are known to have an optimum growth at 48 °C which could also explain the observed difference, regardless of the fact that higher temperatures do promote chemical reactions kinetics as well.

3.5. Effect of char pre-treatment on copper leaching

As mentioned above, char pre-treatment aimed to reduce the amount of metals other than copper, which will possibly react with the Fe<sup>3+</sup>, thus increasing the final copper recovery. Fig. 3 clearly indicates that the pre-treatment increases the initial copper dissolution kinetics. For the un-treated char, copper dissolved only after all (non-inert) aluminium and iron had been dissolved, which under test 2 conditions happened after 24 h of leaching. For the pre-treated char, copper is brought into solution right at the very beginning. After nearly 100 h,

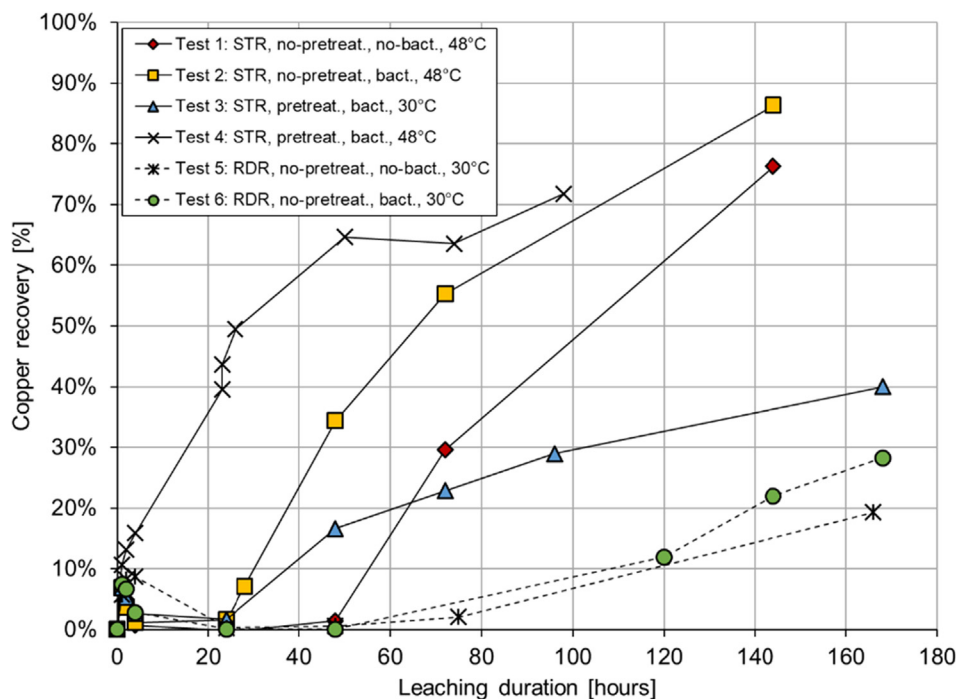


Fig. 3. Evolution of copper recovery during leaching in stirred-tank and rotary-drum reactor under different conditions.

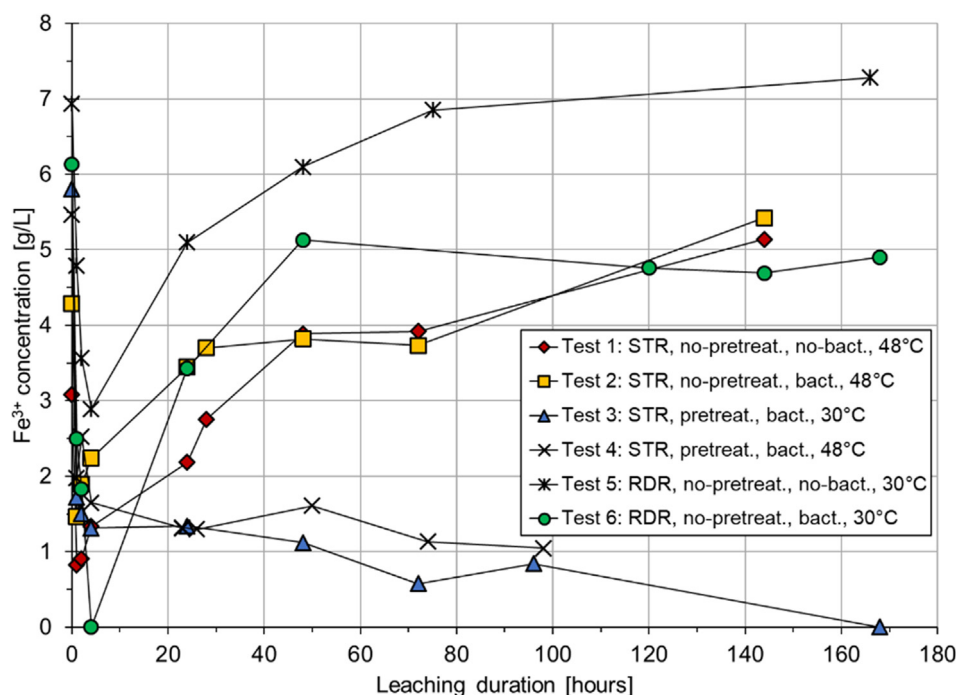


Fig. 4. Evolution of the  $\text{Fe}^{3+}$  concentration for the abiotic and biotic tests.

leaching of pre-treated char shows slightly better recovery (70%) compared to that for the un-treated char (66%).

### 3.6. Sulphuric acid consumption

Diluted sulphuric acid was added to keep the pH value at around 1.7 in order to prevent iron precipitation and to provide favourable conditions for bacterial growth. From the copper recovery perspective, the overall acid consumed during leaching could be divided under two directions: a first one that enables copper dissolution (stoichiometric acid consumption), and a second part that corresponds to the acid allocated to side reactions. For the sake of simplicity, only the useful part of the current acid consumption is discussed below.

According to Eqs. (4) and (5), 2 mol of  $\text{Fe}^{3+}$  are required to dissolve 1 mol of  $\text{Cu}^0$  and the regeneration of these 2 mol of  $\text{Fe}^{3+}$  requires 1 mol of  $\text{H}_2\text{SO}_4$ . Hence, the stoichiometric acid consumption can be calculated as:

$$\text{H}_2\text{SO}_4 \left( \frac{\text{mol}}{\text{molCu}^{2+}} \right) = \frac{n_{\text{Cu}^0_{\text{initial}}}(\text{mol}) - \frac{1}{2}n_{\text{Fe}^{3+}_{\text{initial}}}(\text{mol})}{n_{\text{Cu}^{2+}_{\text{final}}}(\text{mol})} \quad (10)$$

Table 4 shows that the actual acid consumption is higher than the stoichiometrically predicted one for all the tests. This suggests that the sulphuric acid serves to other than copper dissolution chemical reactions only. In this case, it is known that bacterial regeneration of ferric iron from ferrous iron is an acid-consuming reaction, despite it is harder

to quantify the stoichiometric of this reaction in the system. By comparing the acid consumption during biotic and abiotic tests realized under same conditions, it can be noted that within the biotic tests, consumption is lower (2.36, 2.50, 2.04, and 5.12 mol  $\text{H}_2\text{SO}_4/\text{mol Cu}^{2+}$  for Test 2, 3, 4, 6 respectively) than that calculated for the abiotic tests (2.52 and 6.99 mol  $\text{H}_2\text{SO}_4/\text{mol Cu}^{2+}$  - for Test 1 and 5 respectively). One possible explanation for this observation is that bacteria generate acid alongside  $\text{Fe}^{3+}$  regeneration, contributing to lowering both pH and acid consumption as well.

The effect from char pre-treatment on acid consumption is also notable, with leaching of un-treated char requiring more acid (2.36 mol  $\text{H}_2\text{SO}_4/\text{mol Cu}^{2+}$  for Test 2) than the pre-treated one (2.04 mol  $\text{H}_2\text{SO}_4/\text{mol Cu}^{2+}$  for Test 4). To note also, that in the case of pre-treated char, the major part of acid is possibly allocated to copper dissolution rather than to leaching other metals and gangue consumption.

Finally, it appears that the increase of temperature does not contribute to higher acid consumption needed to stabilize the pH in the system. Test 3 at lower temperature is seen to consume more acid (2.50 mol  $\text{H}_2\text{SO}_4/\text{mol Cu}^{2+}$  for Test 3) than the one at higher temperature (2.04 mol  $\text{H}_2\text{SO}_4/\text{mol Cu}^{2+}$  for Test 4). This is somehow not in entire agreement with results reported earlier (Lambert et al., 2015), the reason may be due to the optimum temperature used in the current study stimulating bacterial growth and hence contributing towards acid generation which keeps pH at low level.

Table 4

Extraction level of Cu and Al and acid consumption during abiotic and biotic char leaching.

Test	Total leach time (h)	Cu extraction (%)	Al extraction (%)	$\text{H}_2\text{SO}_4$ consumption (g/g char)	Cu dissolution rate (g/L-h)	$\text{H}_2\text{SO}_4$ consumption (mol/mol $\text{Cu}^{2+}$ )	Stoic. $\text{H}_2\text{SO}_4$ consumption (mol/mol $\text{Cu}^{2+}$ )
1	144	76	50	3.48	0.26	2.52	1.16
2	144	86	38	3.69	0.25	2.36	0.97
3	168	40	42	2.82	0.19	2.50	2.15
4	98	72	33	2.66	0.36	2.04	1.33
5	166	19	35	2.44	0.05	6.99	4.02
6	168	28	44	2.62	0.06	5.12	2.86

#### 4. Conclusions

The presented results reaffirm the importance of choosing the optimal process conditions when leaching zero-valent copper found in pyrolyzed PCB's using bio-lixiviant derived from AMD-prone coal spoil. Although preliminary, the following conclusions could be drawn which could be used as guidelines in other projects dealing with utilization of acidic-solutions from coal bioleaching in recovering metals from secondary raw materials:

- Char pre-treatment is an important step to ensure high copper dissolution degree and fast kinetics;
- At optimum temperature range stimulating bacterial growth and activity, copper leaching proceeds much more efficiently;
- Stirred-tank reactor proved to be a better option for char leaching, although rotating-drum reactor still has room for improvement;
- Acid consumption varies as function of leaching conditions and their optimization to bring it to an economically acceptable level will be beneficial for the entire process.

#### Acknowledgment

The financial support from the EU within the “CEReS - Co-processing of Coal Mine and Electronic Wastes” project funded under the RFCS scheme is gratefully acknowledged.

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