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# Sulfuric acid leaching for capturing value from copper rich converter slag



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### A R T I C L E I N F O

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### ABSTRACT

In this research, a hydrometallurgical method for recovery of copper from copper rich converter slag is investigated. The main copper containing phases of the slag are cuprite (Cu<sub>2</sub>O), delafossite (CuFeO<sub>2</sub>) and metallic copper (Cu). The study investigates the effect of particle size, temperature, acid concentration, agitation and leaching time under oxidizing conditions. The results showed that at optimized conditions (40 °C, 2 M H<sub>2</sub>SO<sub>4</sub>, 60 min leaching time, 0.26 kW/m<sup>3</sup> mixing power, and 2000 mL/min oxygen flow rate), ca. 100% extraction of copper from slag into the solution was obtained. X-ray diffraction (XRD) analysis consolidated the experimental results by confirming that no Cu containing phases were present in the leach residue. Results also showed that temperature  $\leq 40 °C$  had the larger influence on Cu and Fe yield, whereas higher temperature (>40 °C) favored Ni and Zn dissolution. The acid consumption of the optimized leaching process was found to be 23.7 mol of H<sub>2</sub>SO<sub>4</sub> per kg of copper.

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### 1. Introduction

Copper is among one of base metals which has high economic importance in today's technological world. About 80% of the primary copper production comes from pyrometallurgical treatment of copper ores (Potysz et al., 2015; Gbor et al., 2000; Sarfo et al., 2017). Typically, during the copper production, for each ton of copper produced, 2–3 tons of copper slag is generated annually (Fan et al., 2013; Gyurov et al., 2011; Das et al., 2010). Usually copper slag contains about 1% Cu and 40% Fe along with silica and other elements like: Zn, Mo, Pb, Ni, As (Gbor et al., 2000; Sarfo et al., 2017). Over 80% of copper slag is land filled with or without treatment (Guo et al., 2018a, 2018b), which is a major industrial concern over space availability and copper slag management (Sarfo et al., 2017). Dumping of such large volumes of slag is not only the waste of resources but also has an adverse effect to the ecological environment (Gorai and Jana, 2003; Zhou et al., 2018).

To address the problem of land occupancy for the slag generated during copper production process and to recover values out of the slag, many research attempts aiming to meet the environmental

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solutions and recycling have been made in the past few decades (Heo et al., 2013; Banza et al., 2002; Busolic et al., 2011). In addition, pyrometallurgy has been used over the years for slag treatment (Shen and Forssberg, 2003; Hughes, 2000; Heo et al., 2016; Xian-Lin et al., 2015), since it is considered as energy efficient method to recover valuables. However, during pyrometallurgical production of copper, flux is added into the process to separate iron from the metal rich copper sulfide matte (Mackey, 1982; Gaskell, 2007; Hamuyuni, 2016). In addition, flux facilitates the impurity removal by binding them into the molten oxide phase (slag) (Mackey, 1982). However, melting the flux requires energy, which comes at a high price (Davenport et al., 2002).

A new approach for copper processing is a method that does not use flux. Lahtinen et al. (2017) in their patent, have demonstrated that if the copper converting step is carried out at such oxidation levels where part of the copper comprised in the copper containing material is oxidized to copper oxide, the use of flux can be completely avoided. The presence of copper oxide assists in liquefying the converter slag, which nullifies the need for flux. Conventionally, amount and the cost related to the flux are notable. For example, in Olympic Dam Outokumpu flash furnace located in Australia, 12–120 tonnes/day of silica flux has been used to produce 390–680 tonnes/day of copper (Davenport et al., 2002). Additionally, the oxidation step in fire refining for sulfur removal after

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converting is not needed, which decreases the utility and energy costs of copper processing. Furthermore, the absence of flux would drastically increase production capacity (reduction in slag volume) as well as waste generated (Lahtinen et al., 2017).

Typical copper content in discarded slag should be <1% (Davenport et al., 2002; Imris et al., 2005; Rüşen et al., 2012; Gorai and Jana, 2003) which necessitates further copper recovery process steps. Most common copper recovery processes from slag, use the traditional flotation method or direct reduction in electric furnace (Davenport et al., 2002; Gorai and Jana, 2003). The former process is preceded by a slag granulation procedure to facilitate recovery. The product of this process is a concentrate, which must go through the entire process of smelting and converting. The later method is a direct smelting process in electric furnace, which increases the energy requirement and consumption (Davenport et al., 2002).

Hydrometallurgical based process route for recovery of copper is preferable because it overcomes the challenges of these two recovery methods. Using this method, granulated slag can directly be treated without further pre-processing stages. Hydrometallurgical methods as demonstrated elsewhere (Davenport et al., 2002; Havlík et al., 2006; Havlik et al., 2004; McDonald and Whittington, 2008), are also selective in such a way that other valuable or toxic metals such as arsenic can be separated in an environmentally friendly manner. These methods also have the capacity for total recovery of copper from slag. Such a practice is consistent with a circular economy approach where minimal waste production is strongly emphasized.

This research aimed at efficient recovery of copper and removal of other toxic metals from slag produced during Outotec's copper production process, which is rich in copper (ca. 50%). Therefore, in this research work, factors that affect the leaching efficiency of copper such as temperature, acid concentration, mixing power and particle size have been studied systematically using sulfuric acid. The produced copper rich leach solution has the potential to be integrable into state-of-art copper electrowinning process.

#### 2. Materials and method

### 2.1. Materials

Copper rich slag used as raw material in this research, was obtained from Outotec Oyj, Finland. The chemistry of the raw material was defined by total dissolution using aqua-regia followed by solution analysis. For analysis of solutions, ICP-OES (inductively coupled plasma, optical emission spectroscopy, Perkin Elmer Optima 7100 DV, USA) was used. UV/VIS spectrophotometer (Mettler Toledo UV5 spectrophotometer) was used for SiO<sub>2</sub> analysis and Satmagan (135) magnetic analyzer was used for Fe<sub>3</sub>O<sub>4</sub> analysis. Dried residues were analyzed using SEM-EDS (scanning electron microscope, TESCAN, MIRA3) for morphological analysis and XRD (X-ray diffraction, X'Pert PRO Powder, NL) for phase analysis.

### 2.2. Leaching procedures

Leaching experiments were conducted in a 1000 mL lab scale reactor (97 mm diameter, 154 mm height) with a four-blade lab agitator (49.5 mm diameter). Temperature was kept constant using a water bath (LAUDA Aqualine AL 25) system. A Digital Glass Body pH Electrode HI 11310 (Hanna Instruments) and an InLab Ag/AgCl 3 M KCl (Mettler Toledo) redox sensor were employed for pH and redox potential measurements, respectively.

Prior to conducting experiments, the investigated raw material slag was homogenized by rotary sample divider (Quantachrome Instrument SRR II) to obtain a uniform and representative sample for analysis and leaching experiments. Two different raw material fractions with smaller (A sample sieved with 205  $\mu$ m) and larger (B sample sieved with 265  $\mu$ m) particle sizes were employed in the experimental work. The particle size distribution analysis was performed using Malvern Mastersizer (Particle Sizer) and results showed that D80 value for the sample A was 119  $\mu$ m with the average particle size of 98  $\mu$ m while for sample B, D80 value was 126  $\mu$ m with the average particle size of 118  $\mu$ m.

A summary of leaching parameters investigated is presented in Table 1. Experiments were conducted for a maximum leaching time of 120 min. Sulfuric acid  $\leq$ 99.5% assay (Sigma Aldrich, Germany), was used for all the leaching experiments.

During the leaching process, R50D overhead stirrer (CAT Scientific, Inc.) was used for agitation at 373, 490 and 613 rpm. Mixing power was determined using Equation (1):

$$P(kW) = N_P \rho n^3 D_a^5$$
<sup>(1)</sup>

where P represents agitation power (W), Np for power number,  $\rho$  is density of fluid  $(kg/m^3)$ , n is agitation speed in revolutions/second (1/s), and  $D_a$  is the diameter of impeller (m). Fluid density  $(1144-1265 \text{ kg/m}^3)$  was measured with density meter (Anton Paar DMA 40, Digital density meter) for entire temperature range (25–60 °C). Power number for agitator was 1.3. The mixing powers  $(kW/m^3)$  were calculated using Equation (1) and are listed in Table 1. Samples were collected and analyzed at 5, 15, 30, 60, 120 min intervals in order to gain insights about the leaching kinetics. At the end of leaching experiments, samples were filtered using No. 597 Whatman filter paper (240 mm in diameter) into a 1000 mL glass flask at room temperature. The slurry was shown to have good solid/liquid separation properties and it was easily filterable without the need of vacuum filtration. Analysis of leach solutions was conducted using ICP-OES and dried leach residues were analyzed by XRD (with Rietveld method, PAN analytical HighScore Plus software version 4.0) (Bish and Howard, 1988). Equation (2) was used to determine the yield of the elements present in leach solution.

$$Y = \frac{(C_1 \ \mathbf{x} \ V)}{(m_1 \ \mathbf{x} \ w_1)} \ \mathbf{x} \ 100\%$$
(2)

where  $m_1$  (g) and  $w_1$  (%) are the mass of the input materials and the composition of element, respectively;  $C_1$  and V are the concentration of element and the volume of total leach solution. Titration method was used for determining the acid concentration of the pregnant leach solution (PLS), and further this information was used to determine the acid consumption during leaching.

The toxicity characteristic leaching procedure (TCPL) test was performed on treated copper slag residue crushed to size <9.5 mm obtained after 2 M H<sub>2</sub>SO<sub>4</sub> leaching of copper slag (U.S. EPA, 2017). The TCLP test was carried out with buffered acetic acid under the conditions of pH 4.99, solid to liquid ratio of 1:20, stirring speed of 32 rpm, leaching time of 18 h and temperature of 22.5 °C. After test, samples of leachate were collected and filtered with glass fiber

 Table 1

 Experimental parameters and their respective levels.

Parameter	Range/Interval
H <sub>2</sub> SO <sub>4</sub> concentration (M)	0.1, 0.2, 0.4, 0.8, 1.0, 2.0, 3.0
Leaching temperature (°C)	25, 40, 50, 60
Mixing power (kW/m <sup>3</sup> )	0.11, 0.26, 0.54
Sampling interval <sup>a</sup> (min)	5, 15, 30, 60, 120
Solid to liquid ratio <sup>a</sup> (g/L)	100
Oxygen flow rate <sup>a</sup> (mL/min)	2000

<sup>a</sup> Fixed parameters.

filter (0.8  $\mu$ m) (Guo et al., 2018a, 2018b). The filtered samples were further analyzed with ICP-OES for their metal contents. It should be noted that TCLP can only be considered as an indicative test, as the scope of the work did not include investigation of the filtration and washing stage of the residue, which should be optimized prior to TCLP test.

### 3. Results and discussion

### 3.1. Chemistry and mineralogy

Cu and Fe were shown to be the main elements present in the slag. In addition, valuable metals like: Ni, Mg, Zn as well as toxic metals like: Pb, As were also present in small quantities in the slag (Table 2). Monitoring the behavior of As is necessary in process development due to environmental regulation. The results showed that every ton of this copper rich slag carries ca. 500 kg of copper, which is notably higher than copper concentration present in any typical slags as documented in the literature (Schlesinger et al., 2011). When compared with copper smelting slags produced in the state-of-art refineries, an estimated 98% recovery of copper metal from the investigated raw material would bring the copper level in the residue  $\leq 1\%$  copper (Forsén et al., 2017). This copper rich slag was also shown to be very low in silica.

Fig. 1 shows the QBSD (quadrant backscattering detector) micrographs of main phases present in the raw material. From Fig. 1 (SEM-EDS), it was deduced that copper was present in three phases namely cuprite (Cu<sub>2</sub>O), delafossite (CuFeO<sub>2</sub>) and metallic copper (Cu). Fig. 1c and d also showed that the copper rich slag has small amounts of lead arsenate from which the Pb originates. Other phases containing Zn and Ni present in smaller proportions are not shown in Fig. 1. The presence of dominating copper containing phases were also supported by XRD analysis as shown in Fig. 2.

The XRD pattern as shown in Fig. 2, confirmed the presence of magnetite (Fe<sub>3</sub>O<sub>4</sub>) phase, also analyzed by magnetic analyzer (Table 2). High intensity counts were observed due to the crystalline structure of the copper rich slag, which had only negligible silica content. Typical flux-based slags have lower counts in XRD compared to Fig. 2 because of silica saturation, which renders the resultant slags strongly amorphous. Absence of silica may be advantageous not only for the analysis part, but it also improves filtration properties and decreases scaling problems related to high silica content raw materials in hydrometallurgical processes (Yang et al., 2017).

### 3.2. The influence of particle size on leaching

Firstly, the effect of raw material particle size (Sample A with  $<205 \,\mu\text{m}$  and B with  $<265 \,\mu\text{m}$ ) on the leaching kinetics and copper yield was observed as shown in Fig. 3. Leaching results showed that the particle size had a significant effect on copper leaching kinetics and from Fig. 3, it could be seen that yield of copper increases with increasing leaching time in case of both the samples A and B. Copper yield percentage was increased from ca. 51%-100% in between time interval of 5-120 min in case of Sample A while for the same time interval, copper yield percentage was increased from ca. 46% to ca. 82% in case of Sample B. Results from Fig. 3 clearly showed that sample with smaller particle size (Sample A) showed better leaching kinetics compared to Sample B at similar experimental conditions. However, conventionally production of a smaller particle size fraction also requires higher energy costs in grinding of the slag. Sample A was chosen for further study based on faster copper leaching kinetics to extract copper value from the slag.

## 3.3. The influence of sulfuric acid concentration and time on leaching

The effect of initial sulfuric acid concentration  $(0.1-3 \text{ M H}_2\text{SO}_4)$ on yield of Cu, Fe, Ni, and Zn was investigated at constant temperature of 40 °C. Results are shown in Fig. 4a-d. The yield of Cu, Fe, Ni and Zn increased with increasing time up to 60 min, beyond which there was no significant increase in the yield as a function of time. Fig. 4a suggested that initial acid concentration of 1 M was not enough to facilitate sufficient copper dissolution. The highest copper yield of 61.7% was observed at 120 min leaching time. On the other hand, it can be observed that the highest acid concentration investigated (3 M) did not make any significant improvement on the Cu yields compared to 2 M acid concentration. The final acid concentration values indicated that the use of 2 M H<sub>2</sub>SO<sub>4</sub> provided sufficient amount of free acid for the leaching process. Moreover, 2 M H<sub>2</sub>SO<sub>4</sub> at 40 °C was sufficient to dissolve all the copper from the slag. The 2 M H<sub>2</sub>SO<sub>4</sub> dissolved ca. 60% of Fe, which entails poor selectivity between Cu and Fe in the investigated conditions. This condition arises from the favorable conditions for a shared stability zone of  $Cu^{2+}$  and  $Fe^{2+/3+}$  in the pH range of 0-1(Yang et al., 2010). The Ni and Zn yields were not significantly influenced by the initial acid concentration. The yields increased as a function of increasing acidity, however, not more than 22.7% and 23.8% yield were achieved for Ni and Zn, respectively. This also implies that there is a potential for good selectivity between the first two elements (Cu and Fe) and the later (Ni and Zn) elements

Table 2

Chemistry (total leaching +	ICP-OES) and the minerals f	ound to carry these elements (XRI	RD, SEM-EDS) in the investigated sl	ag samples A and B.
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Elements	A (<205 μm) (wt.%)	B (<265 μm) (wt.%)	Main minerals	Indication of mineralogy
Cu	43.6	51.8	Cu <sub>2</sub> O, CuFeO <sub>2</sub> , Cu	XRD, SEM-EDS
Fe	16.5	20.9	15.10% Fe <sub>3</sub> O <sub>4</sub> , CuFeO <sub>2</sub>	XRD, SEM-EDS
Mg	2.4	2.2	Olivine	XRD, SEM-EDS
Ni	1.31	1.21	NiFe <sub>2</sub> O <sub>4</sub>	XRD, SEM-EDS
Pb	0.64	0.52	PbAsO <sub>4</sub>	SEM-EDS
Zn	0.71	0.56	_	SEM-EDS
As	0.09	0.09	PbAsO <sub>4</sub>	SEM-EDS
Si	0.48	2.2	Olivine, 1.27% SiO <sub>2</sub>	SEM-EDS
Al	0.32	0.25	Al <sub>2</sub> O <sub>3</sub>	SEM-EDS
Na	0.01	0.01	Na <sub>2</sub> O	SEM-EDS
Ag	0.03	0.76	Metallic	SEM-EDS
Cr	0.33	0.52	_	SEM-EDS
Ca	0.18	0.15	_	SEM-EDS
SiO <sub>2</sub>	1.27	_	_	Spectrophotometer
Fe <sub>3</sub> O <sub>4</sub>	15.1	_	-	XRD, Magnetic analyzer



Fig. 1. QBSD micrographs of copper rich slag used as raw material showing the distribution of phases. The two zones highlighted in micrograph a) are magnified in micrographs b) and c). Micrographs c) and d) show the presence of lead phases.



Fig. 2. XRD pattern of the copper rich converting slag used as raw material.

during the sulfuric acid leaching process. Based on the results, leaching time of 60 min can be concluded to be sufficient leaching time for the selected process.

### 3.4. Acid consumption

Fig. 5 showed the initial (at t = 0 min) and final acid concentration (at t = 5, 15, 30, 60 and 120 min) of leach solution at experiments with initial acid concentrations of 1, 2 and 3 M H<sub>2</sub>SO<sub>4</sub>. The 2 M H<sub>2</sub>SO<sub>4</sub> acid was shown to be sufficient for completing dissolution of Cu from the copper rich slag (solid to liquid ratio = 100 g/L) with 98.7% copper yield within leaching time of 60 min. Furthermore, with 1 M H<sub>2</sub>SO<sub>4</sub>, after 30 min of leaching time, there is no increase in the copper yield due to lack of free acid i.e. all the available acid has been consumed during the leaching process. The calculated H<sub>2</sub>SO<sub>4</sub> acid consumption was shown to be 23.7 mol per 1 kg of Cu for 60 min when the initial concentration of



**Fig. 3.** The influence of particle size of granulated copper rich slag on the copper leaching ( $T = 40 \,^{\circ}$ C, acid concentration = 2 M H<sub>2</sub>SO<sub>4</sub>, mixing power = 0.26 kW/m<sup>3</sup>, oxygen flow rate = 2000 mL/min).

acid was 2 M. Further, 1.3 mol of acid per kg of Cu was consumed during the second hour of leaching and the final total acid consumption being 25.0 mol per kg of Cu at 120 min (Table 3).

### 3.5. The influence of temperature on leaching

The effect of temperature was investigated to evaluate the effectiveness on metals leaching process at four different levels (25, 40, 50 and 60 °C), as shown in Fig. 6. Results showed that copper yield  $\geq$ 98% can be achieved in only 60 min at a temperature of 40 °C. Similar results were obtained at lower temperature (25 °C) over the longer leaching process time (120 min). At higher temperature levels (50 and 60 °C), the results were in line with the results obtained at temperature of 40 °C.

Fig. 6 showed that increasing the temperature above 40 °C, did



**Fig. 4.** The effect of  $H_2SO_4$  acid concentration (0.1–3.0 M) on the yields of a) Cu, b) Fe, c) Ni, d) Zn from the copper rich converter slag (Sample A, T = 40 °C, oxygen flow rate = 2000 mL/min and mixing power = 0.26 kW/m<sup>3</sup>).



**Fig. 5.** Pregnant leach solution (PLS) acid concentration (left, pillars) and Cu yield (right, symbols) as a function of time during leaching in 1, 2 and 3 M H<sub>2</sub>SO<sub>4</sub> (Sample A,  $T = 40 \degree$ C, oxygen flow rate = 2000 mL/min and mixing power = 0.26 kW/m<sup>3</sup>).

Acid consumption per	· kg of slag at	different leaching	time intervals

Table 3

Time (min)	Acid consumption (moles/kg of Cu)				
	1 M H <sub>2</sub> SO <sub>4</sub>	1 M H <sub>2</sub> SO <sub>4</sub> 2 M H <sub>2</sub> SO <sub>4</sub>			
5	14.7	13.3	12.4		
15	19.1	16.4	17.0		
30	20.1	19.4	20.0		
60	23.1	23.7	22.1		
120	25.0	25.0	23.2		



Fig. 6. Yield of Cu, Fe, Ni and Zn as a function of temperature after 15, 30, 60 and 120 min of leaching (Sample A, 2 M  $H_2SO_4$ , oxygen flow rate = 2000 mL/min and mixing power = 0.26 kW/m<sup>3</sup>).

not improve the Cu yields significantly. The maximum copper yield was obtained at temperature of 40 °C in 60 min leaching time. At lower temperature levels (25 and 40 °C), low yield (39.3 and 56.9%) of Fe was observed while at temperature >50 °C, the yield was over 60%. Temperature >40 °C, was found to favor the yields for Ni and Zn significantly compared to other elements. This indicates that the temperature could be used to attain selectivity between Cu/Fe and Ni/Zn. Additionally, almost all the arsenic was leached at temperature of 40 °C and leaching time of 60 min (Table 4).

Table 4

The concentrations of the dissolved elements in solution after sulfuric acid leaching of copper rich converting slag (Mixing power =  $0.26 \text{ kW/m}^3$ ,  $T = 40 \degree$ C, oxygen flow rate = 2000 mL/min).

Leaching Conditions	Cu (g/L)	Fe (g/L)	Zn (g/L)	Ni (g/L)	Pb (g/L)	As (g/L)
2 M, 60 min	43.6	9.4	0.2	0.3	0.01	0.1
2 M, 120 min	45.4	10.2	0.2	0.3	0.01	0.1

### 3.6. The influence of mixing power on leaching

The increase in mixing power was shown to have significant effect on Cu yield. An increase in mixing power from 0.11 to  $0.54 \text{ kW/m}^3$  resulted in increased Cu yield by nearly 20% (Fig. 7). The yield of all the other metals was not increased significantly. The observed increase in yield of Cu could be explained by the fact that increasing the mixing power (0.11 kW/m<sup>3</sup> to 0.26 kW/m<sup>3</sup>) results in increasing the mass transfer of oxygen from the gas phase to liquid phase due to higher surface area between oxygen and process solution. However, in all the experiments oxygen feed rate was not the limiting factor, therefore increasing the power further to 0.54 kW/m<sup>3</sup> did not result in increase in Cu yield. This suggests that the mixing power of 0.26 kW/m<sup>3</sup> is the optimal intensity for the investigated research environment.

After investigating all the experimental parameters, the optimized experimental conditions for higher copper yield were found to be at  $2 \text{ M H}_2\text{SO}_4$  concentration, temperature of  $40 \,^\circ\text{C}$ , mixing power of  $0.26 \,\text{kW/m}^3$  and leaching time of 60 min, where ca. 100% yield of copper was achieved.

### 3.7. Characterization of the leach residue

The result obtained at optimized leaching conditions (2 M  $H_2SO_4$ , 40 °C, 60 min) were also validated by the XRD analysis of the leach residue (Fig. 8). The XRD analysis of leach residue confirmed that the copper containing phases Cu, Cu<sub>2</sub>O and CuFeO<sub>2</sub> were no



**Fig. 8.** XRD pattern of the leach residue from the copper rich converting slag after leaching (2 M H<sub>2</sub>SO<sub>4</sub>, T = 40 °C, t = 60 min).

longer present in the leach residue suggesting that all the copper had been leached out. The peak representing magnetite (Fe<sub>3</sub>O<sub>4</sub>) in the copper rich slag (Fig. 2) changed substantially after leaching. Remaining iron in the leach residue seem to bind itself to nickel as a double oxide (NiFe<sub>2</sub>O<sub>4</sub>) and magnesium as magnesioferrite (MgFe<sub>2</sub><sup>3+</sup>O<sub>4</sub>). The high Ni and Pb observed in the leach residue are consistent with the results from the solution analysis and suggests that the majority of these two metals remains in the leach residue. However, lead arsenate phase (Fig. 1) was converted to anglesite (PbSO<sub>4</sub>) during H<sub>2</sub>SO<sub>4</sub> leaching whereas all the arsenic was dissolved (Table 4).

Fig. 9 shows two backscatter electron micrographs of the Sample A's slag (a) and the leach residue (b). The brighter particles in Fig. 9a are the copper rich phases. As can be observed in Fig. 9b, the



Fig. 7. The influence of mixing power on yields of a) Cu, b) Fe, c) Ni, d) Zn into the solution (Sample A, 2 M H<sub>2</sub>SO<sub>4</sub>, oxygen flow rate = 2000 mL/min and T = 40 °C).



**Fig. 9.** a) Backscattered scanning electron micrographs of slag Sample A and b) leach residue obtained after leaching. ( $T = 40 \circ C$ , 2 M H<sub>2</sub>SO<sub>4</sub>, t = 60 min, and mixing power = 0.26 kW/m<sup>3</sup>).

brighter particles disappear after leaching at optimized conditions, confirming the high copper yield into the PLS from the investigated slag fraction.

### 3.8. Pregnant leach solution and the further processing options

The aim of the work was to recover copper at optimal leaching parameters from copper rich slag. Optimal leaching conditions for higher copper recovery (ca. 100%) were attained at  $2 \text{ M H}_2\text{SO}_4$  concentration and temperature of 40 °C. Table 4 presents the concentration of the metal ions (Cu, Fe, Zn, Ni, Pb, As) in the solution after sulfuric acid leaching at the optimized conditions with leaching time of 60 and 120 min, respectively. The leaching process directly produced Cu rich sulfuric acid solution, which is attractive solution for industrial operator and comparable to those concentrations used in copper electrowinning.

Typical copper electrolyte solution produced from leaching of copper ore, contains 25–60 g/L of copper and 0.1–10 g/L of iron in the electrowinning stage (Evans, 2003; Habashi, 1998). These industrial processes operate in temperatures of 40-60 °C, pH of 1 and current densities in the range of 20–45 mA/cm<sup>2</sup> are used (Moats and Free, 2007). Examples of some of the industrial copper electrolvte solutions can be seen in Table 5. After comparing Tables 4 and 5, it is suggested that leach solution produced after slag treatment in this study could be integrated into state of art process of copper production. Although, it should be noted that concentration of iron is higher in the leach solution compared to most of industrial solutions, which may increase the energy consumption. The energy consumption of the electrowinning is dependent on the current efficiency and cell voltage and ranges typically in the range of 1.8–2.5 kWh/kg Cu (Hannula et al., 2019). Iron concentration does not affect the quality of copper but has the significant effect on energy consumption during electrowinning process (Das and Krishna, 1996; Hannula et al., 2019). Therefore, iron concentration in the leach solution could be decreased by state-of-art methods such as neutralization (Izadi et al., 2017), ion exchange (Izadi et al., 2017) or solvent extraction (Agrawal et al., 2009) prior to electrowinning. The concentration of Ni and As present in the leach solution (Table 4) are well within the range of the current electrolysis operations (Table 5). As an alternative to electrowinning,

crystallization method can also be applied directly on the leach solution to recover copper as copper sulfate pentahydrate crystals (Giulietti et al., 1999; Alimohammadizadeh et al., 2018).

### 3.9. TCLP test for the leach residue

The toxicity of leach residue was determined by Toxicity Characteristic Leaching Procedure (TCLP) test (Table 6). After the test, the resultant solutions were analyzed by ICP-OES as shown in Table 6. Results from Table 6 showed that concentration of all the toxic elements in the treated slag were below the defined USEPA thresholds except for copper (U.S. EPA, 2017). Presence of copper above threshold limit shows that optimization of filtration and washing steps is required for the leach residue (Huhtanen et al., 2012; Ruslim et al., 2007). Also, leach residue of hydrometallurgical plants is generally ponded (Agrawal et al., 2004), with accumulating water recycling back to the process for metal recovery. However, it should be noted that even without optimized leach residue washing, concentration of As, Pb and Ni are below the toxicity limits.

### 4. Conclusions

Recovery of metals from a copper rich converter slag has been investigated in this experimental research by utilizing sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). Based on the results, the following conclusions can be derived:

- The dominating copper phases in the slag are Cu, Cu<sub>2</sub>O and CuFeO<sub>2</sub> (XRD and SEM-EDS). Leaching copper from these phases using sulfuric acid has a fast dissolution kinetics. Smaller particle size, higher temperature (up to 40 °C) and increasing mixing power (up to 0.26 kW/m<sup>3</sup>) enhance the leaching kinetics. XRD analysis of leach residue confirmed leaching of all copper containing phases.
- Iron in the slag is mainly present as magnetite (Fe<sub>3</sub>O<sub>4</sub>), and delafossite (CuFeO<sub>2</sub>) and copper oxide (Cu<sub>2</sub>O) in the slag.
- Nickel and zinc are present as nickel iron oxide and small amounts in olivine phase in the slag. These minerals have slower dissolution kinetics compared to copper. Nickel and zinc are

Table 5

The composition of some sulfate based industrial copper electrolyte solutions.

-		-				
Process	Cu (g/L)	Fe (g/L)	Ni (g/L)	As (g/L)	$H_2SO_4$ (g/L)	Reference
Sarcheshmeh, Iran Boliden Hariavalta Ov, Finland	33 59	3 02	0.027 17	<0.1 15	140 145	Izadi et al. (2017) Houlachi et al. (2007)
CODELCO CELLS, Chile	50-60	0.8-1	2-3	10-12	170–180	Houlachi et al. (2007)

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Table	6

TCLP test results of treated copper slag.

Elements	As (mg/L)	Bi (mg/L)	Sb (mg/L)	Cu (mg/L)	Pb (mg/L)	Ni (mg/L)	Zn (mg/L)
Treated slag	0.1	<0.2	<1.0	396.2	3.6	<0.2	<0.2
Threshold	0.5	NS	NS	100.0	5.0	1.0	70.0

least influenced by the concentration at the investigated range  $(0.1-3 \text{ M H}_2\text{SO}_4)$  whereas their dissolution is slightly favored by increasing temperature from 40 to 60 °C.

- The suggested optimal conditions for the extraction of copper from copper rich slag are: H<sub>2</sub>SO<sub>4</sub> concentration of 2 M, solid to liquid ratio (100 g/L), mixing power of 0.26 kW/m<sup>3</sup>, temperature of 40 °C, leaching time of 60 min under 2000 mL/min continuous oxygen purging. In these conditions, total acid consumption was 23.7 mol per kg of copper.
- Sulfuric acid leaching of copper rich slag with the optimized parameters can provide a copper rich process solution with iron as the main impurity metal. The solution can provide an attractive feed for integration into the industrial primary copper production with acceptable low Ni, As and Pb levels (43.6 g/L Cu, 9.4 g/L Fe, 0.3 g/L Ni, 0.1 g/L As, 0.2 g/L Zn, 0.01 g/L Pb).

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