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# Recycling of brass melting slag through the high-temperature oxidation-leaching process

Fariba Maleki, Samad Ghasemi\*  and Akbar Heidarpour

## Abstract

Brass melting slag is a valuable secondary resource for the recovery of copper and zinc. The hydrometallurgical recovery process of this material is a challenge, because of its limited dissolution in sulfuric acid. The present study aimed at studying a combined pyro-hydrometallurgical treatment processes involving high temperature oxidation and sulfuric acid leaching to industrial brass melting slag to recover copper and zinc. The effect of temperature on the performance and efficiency of the high temperature oxidation process was investigated by isothermal thermogravimetry. The results revealed that by increasing the oxidation temperature, leachability improves due to the oxidation of metallic brass particles. The results obtained showed that 3 h oxidation of as-received slag at 900 °C, increased its percent leaching amount in 2 M sulfuric acid from 34 to 81%. The pregnant leach solution containing copper sulfate and zinc sulfate was subjected to the electrowining process to recover the copper as copper cathode. The zinc was also recovered as zinc sulfate via evaporation and crystallization process. Kinetic investigations showed that the 3D diffusion model has a good agreement with the isothermal oxidation results. In this model, the oxidation reaction is controlled by the outward diffusion of zinc from the brass particle. The activation energy of isothermal oxidation was obtained as 311 kJ mol<sup>-1</sup>.

**Keywords:** Brass melting slag, High-temperature oxidation, Leaching

## 1 Introduction

Regarding the increasing demand for copper and zinc, extensive research on the recovery of these metals from various secondary resources is crucial. The increase in the production rate of industrial waste has caused severe environmental issues. In addition to environmental problems, the shortage of minerals for metals extraction has highlighted the necessity of their recovery from secondary resources [1]. Recovery of metals from secondary resources can be conducted by pyrometallurgical and, or hydrometallurgical methods [2].

Copper and zinc are the major brass constituents, a famous nonferrous alloy. Brass alloy is widely employed in industrial and domestic applications. Regarding the

high amount of brass production, vast amounts of wastes will be formed during the manufacture of brass parts. One of these wastes, rich in copper and zinc, is the brass melting slag. Several researchers have addressed the recovery of copper and zinc from brass melting slag [3–10]. almost 5 wt% of remelted brass is tapped as brass melting slag, according to the data provided by brass casting plants in Iran. A significant part of brass slag is metallic brass particles. Regarding the high chemical stability of the brass alloy, it shows high resistance against leaching processes. In particular, leaching of the brass melting slag in sulfuric acid results in insignificant yield. Considerable researches have been focused on improving the leaching step of hydrometallurgical recovery of copper and zinc from brass slag. For instance, copper and zinc recovery from the brass alloy wastes by sulfuric acid was investigated by several researchers [3, 7, 11].

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Using stronger solvents is a way to improve the leaching efficiency of brass slag. In this context, the use of other solvents such as hydrochloric acid [9, 11], nitric acid [12], and sodium hydroxide [11] has been investigated for the leaching of brass slag. In the case of hydrochloric acid and nitric acid, the pregnant leach solution will be a chloride and nitrate solution, respectively. The recovery of copper and zinc from chloride and nitrate solutions is technically challenging and costly. Additionally, copper and zinc recovery from these solutions will cause environmental pollution; hence, it is unacceptable. To improve the efficiency of the leaching process, the sulfuric acid solution with oxidizing agents could be used. Hydrogen peroxide is one of the main oxidizing agents widely used to improve the leaching efficiency of corrosion-resistant metals. The use of hydrogen peroxide is reported for increasing the recovery of metals in leaching processes. For example, recovery of gold and copper from electronic kits wastes [13, 14], recovery of gold from used electronic kits [15], using  $\text{Fe}^{3+}/\text{Fe}^{2+}$  for recovery of copper from waste printed circuit boards [16], and cobalt and manganese recovery from zinc electro-winning wastes [17] are mentioned.

The other method which can substitute the use of strong leaching solvents or oxidizing agents is high-temperature oxidation of the metals and alloys as a pyrometallurgical pre-treatment method. In this method, the metal or alloy with high corrosion resistance will be converted to metal oxide due to the oxidation process. Oxides can be easily dissolved in conventional solvents such as sulfuric acid. Numerous studies have addressed the high-temperature oxidation before leaching of corrosion-resistant alloys. For instance, oxidation before tungsten and cobalt recovery from *tungsten carbide* (WC)-Co cemented carbide [18, 19], and oxidation of NdFeB magnets for recovery of neodymium and dysprosium [20] can be found.

A review of the studies on copper and zinc recovery from brass slag showed that most of these studies are only focused on the hydrometallurgical recovery of these wastes. As mentioned before, these studies failed to reach commercially and environmentally acceptable results. Even though hydrometallurgical processes have gained more attention for recovery of metals as they are economically and environmentally superior over the pyrometallurgical methods [21], but in the case of brass slag leaching in sulfuric acid solution, hydrometallurgical recovery faces a big problem at leaching process.

In this study, a pyro-hydrometallurgical process is proposed to recover copper and zinc from the brass melting slag. This process consists of high-temperature oxidation of brass slag as a pyrometallurgical pre-treatment process, followed by sulfuric acid leaching, as the hydrometallurgical step. In this study, the mechanism and

kinetics of the high-temperature oxidation of brass slag and its impact on copper and zinc recovery in the leaching process are addressed.

## 2 Materials and methods

In this study, the brass slag sample was employed from a 5 tons inductive brass melting furnace of Isfahan Brenj Co, Iran. The chemical composition of brass melt in this furnace was 60%Cu-40%Zn analyzed by the Spark-AES method. The brass slag was visually evaluated on the macroscopic scale, which indicated that this slag was a completely inhomogeneous mixture. It contains metallic brass particles, zinc oxide, copper oxide, charcoal particles, and other oxide impurities originated from the erosion of furnace refractories or the impurities of brass scraps charged to the melting furnace.

The brass slag was sieved and fractions larger than 4000  $\mu\text{m}$  were mainly the brass alloy particles that could be directly remelted. Therefore, coarse-grained fractions were not employed, and particles smaller than 4000  $\mu\text{m}$  were used in this research.

The metallic brass particles were separated from the slag by washing the oxides by water. The metallic fraction was measured (41.5 wt% of the slag was metallic particles), and the oxide fraction was analyzed by X-ray fluorescence (XRF, S4 PIONEER, Bruker). The XRF result is presented in Table 1. The *loss on Ignition* of raw slag was measured as a mass loss of raw slag after 1 h heating at 550 °C. The carbon was burned out, and no considerable oxidation of metals occurred. The phase analysis of the slag before and after oxidation experiments was identified by X-Ray diffraction (XRD, Ital Instruments APD2000), and the Cu target,  $K_{\alpha}$  radiation (40 kV, 30 mA), a 0.05° scanning step size, and 1 s time per step was used. The microstructure of samples after oxidation was investigated by scanning electron microscope (SEM, JEOL JSM850A, Japan) equipped with energy dispersive spectroscopy (EDS). The concentration of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  in the pregnant leach solution was analyzed by atomic absorption spectroscopy (AAS, Agilent FS240).

The slag oxidation was conducted in a laboratory-made thermogravimeter (TG). Since the slag is an entirely inhomogeneous mixture, a small sample (a few mg) cannot be a suitable representative of the total slag. So, if standard laboratory TG analysis equipment, which works by a few mg samples, was used for this research, the resulting thermograms were not repeatable. Therefore, we made a thermo-gravimetric apparatus capable of working with sample weight up to 30 g. Slag oxidation was examined by isothermal and non-isothermal methods. Mass measurement was carried out by a microbalance with an accuracy of 0.01 g. The balance was connected to the PC via RS232 port, and the sample

**Table 1** Chemical analysis of sieved brass slag ( $D < 4000 \mu\text{m}$ )

Compound	Brass particles (60%Cu-40%Zn)	ZnO	Cu <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	PbO	SiO <sub>2</sub>	L.O.I
wt%	41.5	38.81	4.57	2.65	4.25	2.67	2.53	2.08	0.94

weight was recorded at 1-s intervals. The slag sample was placed in an alumina pan with a 50 mm diameter, which was connected to the end of a lever. The mass of the sample was recorded in the PC as a function of time. The sample was hung down inside a vertical tube furnace (internal diameter of tube = 60 mm) with natural convection of air. The air was inserted from the bottom of the tube and vented from the top. The airflow was through natural convection and supplied oxygen for oxidation. To ensure that natural convection can deliver sufficient amounts of oxygen, we compared the overall mass gain of a slag sample after 3 h heating by natural convection air with another sample that was heated 3 h by forced convection of air. The final mass gain of both samples was almost the same. Therefore, we concluded that natural convection could supply sufficient oxygen for oxidation. The calibration and validation of the constructed thermogravimeter was conducted by a TG test on 20 g calcium oxalate as the standard TG material, which confirmed the validity and accuracy of this apparatus.

Oxidation was conducted non-isothermally on a 20 g sample of brass slag from ambient temperature to 1000 °C with a heating rate of 10 °C min<sup>-1</sup>, and isothermally (at 700, 800, 850, and 900 °C). The isothermally oxidized slags were first cooled down to room temperature; then, it was leached in a 1000 mL glass beaker by hotplate-stirrer at 1000 RPM. The other parameters for the leaching step were 2 or 3 M sulfuric acid with a pulp density of 20% (wt of slag/vol of acid solution) for 4 h at 50 °C. The particle size of the oxidized slag was almost the same as the raw slag ( $D < 4000 \mu\text{m}$ ). The pulp was then filtered, and the weight of un-dissolved slag was measured. The leaching efficiency was calculated by:

$$\text{Leaching Efficiency} = \frac{m - m_0}{m_0} \times 100 \quad (1)$$

where  $m_0$  is the initial sample weight, and  $m$  denotes the weight of un-dissolved slag after sulfuric acid leaching.

### 3 Results and discussion

#### 3.1 TG behavior of brass slag oxidation

The possible oxidation reactions with thermodynamics values for pure zinc and copper are presented in Table 2 according to Gaskell [22]. Eq. (4) in Table 2 is the difference between Eqs. (2) and (3), which indicate the relative oxidation affinity for copper and zinc. The variations in standard enthalpy,  $\Delta H$ , and Gibbs free energy,  $\Delta G$ , are also listed in Table 2. According to this table, the oxidation of pure copper and zinc is thermodynamically feasible for pure copper and pure zinc. Moreover, the driving force for the oxidation of zinc is higher than that of copper ( $\Delta G_{\text{Zn}} < \Delta G_{\text{Cu}}$ ). Thus, in the presence of copper and zinc together, and the short supply of oxygen, zinc will be preferably oxidized, and copper will be protected. The negative change in Gibbs free energy of Eq. (4) also confirms this result. The oxidation tendency of zinc in comparison to copper can be attributed to the higher reactivity of zinc. Chemical analysis results of raw slag by XRF method (Table 1) also confirms this result, as the percentage of zinc oxide (38.8 wt% ZnO) was much higher than the copper oxide (4.6 wt% Cu<sub>2</sub>O); in contrast, the copper content of the melt in an inductive furnace (60 wt% Cu) was higher than the zinc content (40 wt% Zn). This discussion shows that even though % Cu in the brass melt is more than % Zn, but during oxidation of melt and slag formation, zinc is oxidized more than copper. Therefore, the zinc oxide content of slag is higher than the copper oxide. Based on the presented thermodynamic information and the experimental observation on higher oxidation of zinc, it can be expected that the behavior of brass during high temperatures oxidation is similar to selective oxidation of zinc in the presence of copper. In the next section, selective oxidation of zinc in the brass alloy is experimentally confirmed. At room temperature and in aqueous solutions, zinc is selectively corroded from the brass alloy, where the copper part was protected against corrosion. This phenomenon is known as dezincification [23].

**Table 2** Thermodynamic values for reactions involved in the oxidation of brass slag [22]

Eq. no	Reaction	$\Delta H^0$ (kJ mol <sup>-1</sup> )				$\Delta G^0$ (kJ mol <sup>-1</sup> )			
		700 °C	800 °C	900 °C	1000 °C	700 °C	800 °C	900 °C	1000 °C
(2)	$2\text{Zn} + \text{O}_2 (\text{g}) = 2\text{ZnO}$	-356	-356	-355	-355	-251	-240	-229	-218
(3)	$2\text{Cu} + \text{O}_2 (\text{g}) = 2\text{CuO}$	-150	-150	-149	-148	-69	-60	-52	-44
(4)	$\text{Zn} + \text{CuO} = \text{ZnO} + \text{Cu}$	-205	-206	-206	-207	-182	-180	-177	-175

### 3.2 Thermogravimetric oxidation of brass slag

The non-isothermal oxidation thermogram of the brass slag is presented in Fig. 1a. At the initial stage of oxidation, i.e., up to 440 °C, almost 1.5% mass loss was attributed to the evaporation of water and gasification of remained charcoal particles in the slag. To verify the claim, a sample of brass alloy particles was heated at 440 °C for 3 h, and no weight loss or weight gain was observed. Above the temperature of 440 °C, the thermogram became ascending, and the mass gain started due to the oxidation of metallic brass alloy. The rate of mass gain until 700 °C is low, but above 700 °C, a considerable change could be found. Therefore, some temperatures above 700 °C were chosen for isothermal oxidation of the slag. Again, at temperatures higher than 850 °C, the rate of mass gain was suppressed, which could be assigned to oxidation of brass surface at lower temperatures, which decline the metallic phase exposure to oxidation and therefore, the oxidation rate decreases.

The isothermal oxidation at 700, 800, 850, and 900 °C was conducted in the air with natural convection, and the thermograms are shown in Fig. 1b. As observed in the non-isothermal case, the oxidation rate was low at temperatures below 700 °C. Therefore, the minimum temperature for isothermal oxidation was selected at 700 °C. On the other hand, the normal boiling temperature of zinc is 907 °C. Hence, oxidation at temperatures above 900 °C will result in vigorous evaporation of zinc and loss of some zinc. Therefore, the maximum isothermal oxidation temperature was selected at 900 °C.

An initial mass loss can be seen in all isothermal oxidation thermograms, which could be attributed to the evaporation of moisture and the gasification of carbon. It must be noted that carbon is added as charcoal to the induction melting furnace of brass to provide a reductive environment and reduce the oxidation of brass melt. Some part of this carbon may remain and enter the slag. During the slag oxidation in this research, this carbon was burnt and induce a weight decline in thermograms. On the other hand, until its complete burning, a reducing atmosphere containing carbon monoxide is formed in the furnace, inhibiting metal oxidation.

According to Fig. 1b, the time in which carbon burning was finished depends on the isothermal temperature. At higher temperatures, carbon burnt faster, and the diagram started its ascending trend in a shorter time. However, at lower temperatures, burning required longer times. For instance, according to Fig. 1c, at 700 and 900 °C, complete combustion of carbon took about 20 and 2 min, respectively.

After the initial mass loss in isotherm thermograms (Fig. 1b), the sample' mass gradually increased due to the oxidation of copper and zinc, according to Eqs. (2)

and (3) in Table 2. After 3 h of isothermal oxidation, samples oxidized at 700, 800, 850, and 900 °C showed 0.59, 2.7, 6.03, and 8.81 wt% mass increase, respectively. According to Tables 1, 41.50 wt% of the raw slag is the brass alloy particles. Therefore, 100 g of brass slag consists of 24.9 g copper and 16.6 g zinc, and the LOI level is 0.94%. Theoretically, complete oxidation of 41.5 wt% of brass particles according to the Eqs. (2) and (3) (Table 2) will cause a 10.38 wt% increase in the mass. Subtracting LOI value, the increase in the mass of the slag will be 9.44 wt%. This value was calculated by ignoring zinc evaporation. The oxidation progress ( $\alpha$ ) percentage can be obtained by Eq. (5):

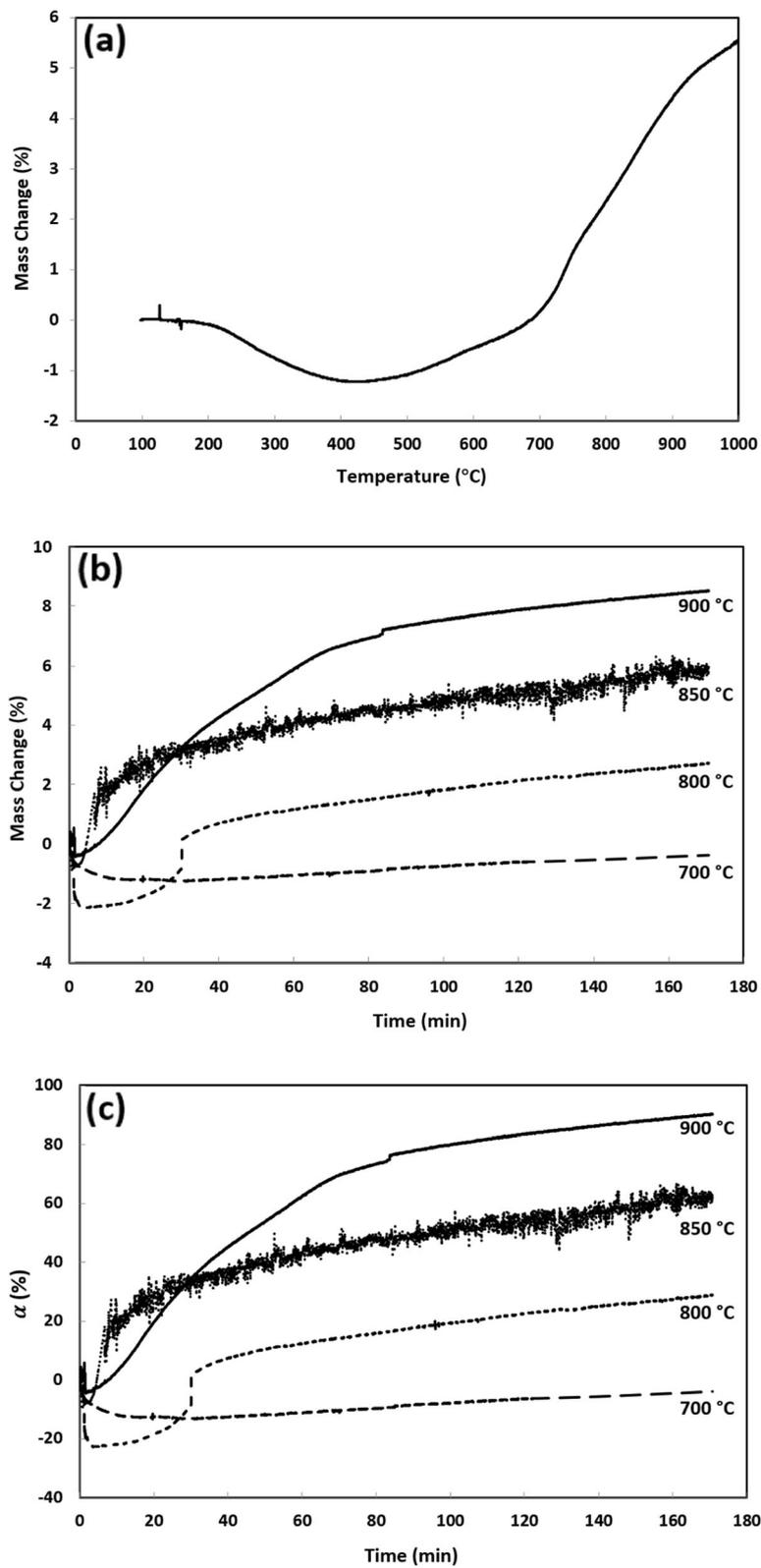
$$\alpha = \frac{\Delta m}{\Delta m_t} \times 100 \quad (5)$$

where  $\Delta m$  shows the mass increase percentage, and  $\Delta m_t$  is 9.44 wt%. According to Eq. (4) and Fig. 1b, oxidation progress can be plotted versus time for different isotherms, Fig. 1c. For oxidation at 700 °C, the oxidation rate was so low. The increase in the temperature, however, increased the oxidation rate. The only exception was in the initial stages of oxidation at 850 and 900 °C, where the oxidation rate at 850 °C was higher than that of 900 °C. The reason for this behavior is that despite higher oxidation rates at 900 °C, some parts of zinc will be evaporated and lost. Therefore, at 900 °C, the overall effect of oxidation-induced mass gain and evaporation-induced mass loss will result in lower apparent mass gain compared to 850 °C.

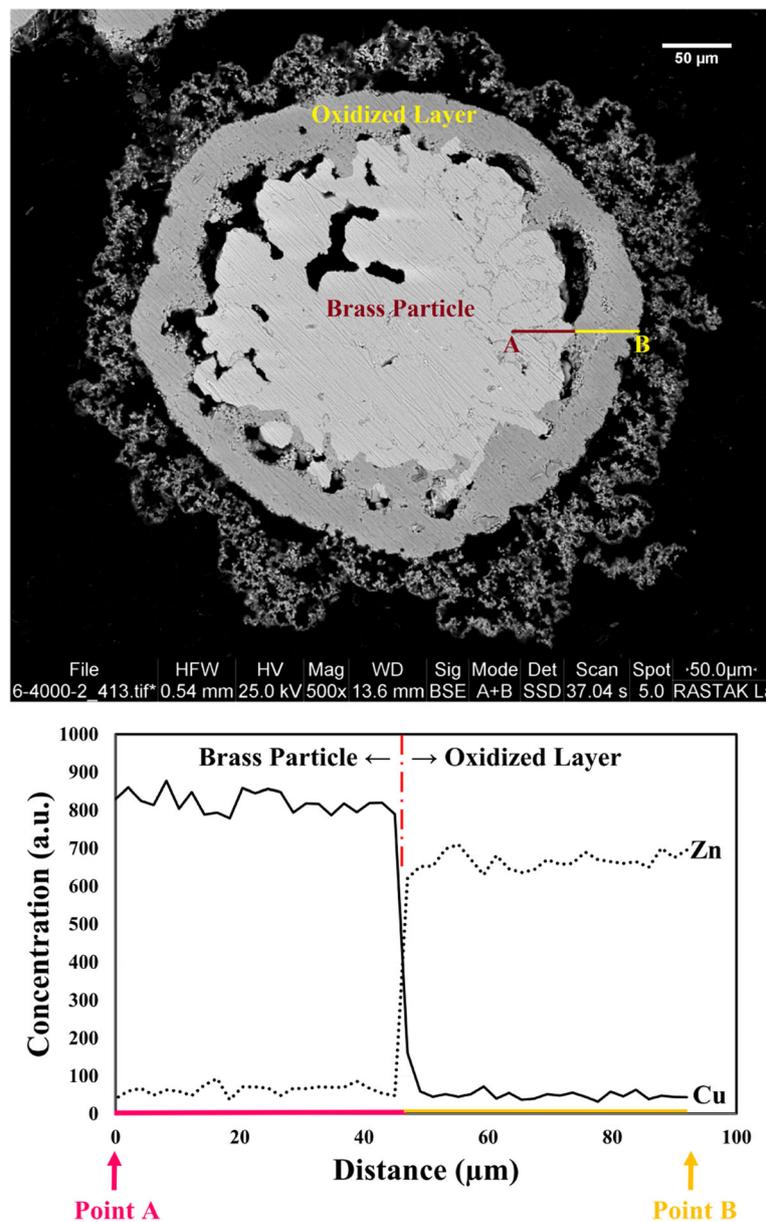
### 3.3 Mechanism of high-temperature oxidation of brass slag

According to Table 1, brass slag includes two major components: metal oxides (mainly ZnO) and brass alloy particles. The metallic phase of slag was oxidized at high temperatures. To investigate the oxidation mechanism, a sample of slag was subjected to atmospheric oxidation at 850 °C for 3 h. Then, the partially-oxidized brass particle (a brass particle oxidized 3 h at 850 °C in the air) was mounted, and its cross-section was microscopically examined by FEI Quanta 200 SEM (Fig. 2). As Fig. 2a suggests, the oxidized layer has low adhesion to the metallic substrate. Therefore, during oxidation, the oxidized layer was delaminated from the metal surface. The oxygen in the air hence can quickly diffuse to the fresh surface of the metal, and the oxidation process continued. Therefore, the oxide layer did not inhibit the oxidation, and the oxidation process was not controlled by oxygen diffusion through the oxide layer.

The linear elemental analyses across the central metallic phase and the oxidized layer are shown in Fig. 2b.



**Fig. 1** Oxidation thermograms of brass slag in the air atmosphere. **a** Non-Isothermal oxidation by a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$ , **(b)** Isothermal mass change vs. time, and **(c)** Isothermal oxidation progress,  $\alpha$ , vs. time

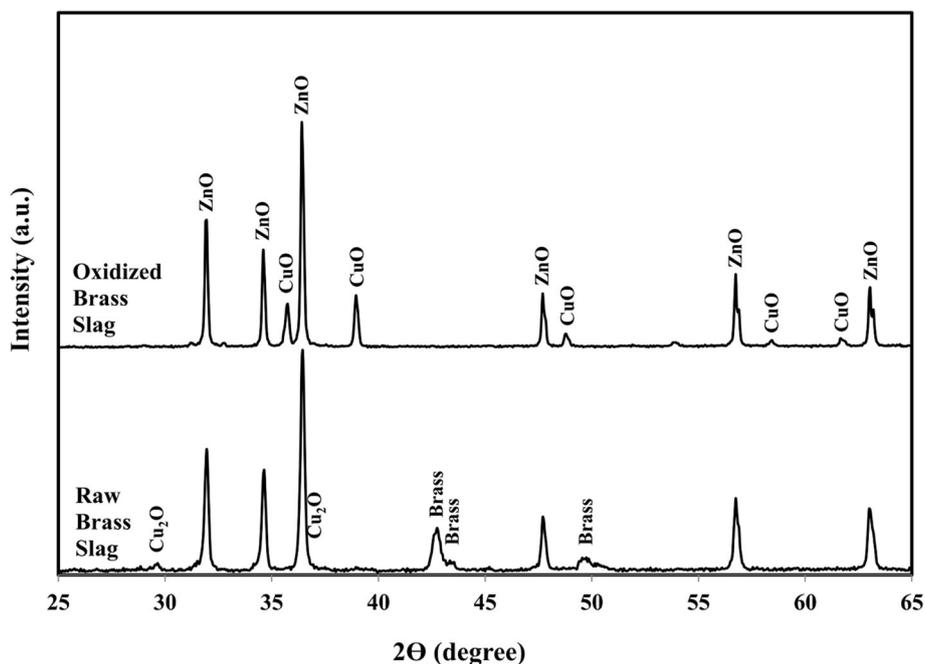


**Fig. 2** The cross-section of a brass alloy particle, partially oxidized at 850 °C in the air for 3 h. **a** SEM image from the cross-section, **(b)** the elemental line analysis across line A-B in Fig. 2b

This linear scan confirms that the concentration of copper in the central area of metal phase is much higher than the oxide layer. Mutually, the concentration of zinc atoms in the oxide layer exceeds the zinc concentration in the mid metallic fraction. These results indicate the selective oxidation of zinc from brass alloy, predicted by thermodynamic calculations shown below. Selective oxidation of zinc in the brass alloy was also reported by Yuan et al. [24] and Gao et al. [25]. They assigned it to the higher reduction ability of Cu (compared to Zn). Even if tiny amounts of CuO form, it can be easily

reduced by Zn. Because of ZnO is thermodynamically more stable than CuO.

The XRD patterns of the as-received slag and after 3 h oxidation at 850 °C are compared in Fig. 3. The raw brass slag is mainly composed of zinc oxide, cuprous oxide ( $\text{Cu}_2\text{O}$ ), and brass alloy. Cuprous oxide ( $\text{Cu}_2\text{O}$ ), and brass alloy phases are resistant to leaching in sulfuric acid solution. After oxidation, the brass alloy and cuprous oxide phases are disappeared and, cupric oxide ( $\text{CuO}$ ) and zinc oxide are identified as major phases in the oxidized slag. These phases can be readily leached in sulfuric acid.



**Fig. 3** XRD pattern of raw brass slag and oxidized brass slag (Oxidation in the air at 850 °C for 3 h)

According to microstructural examination and EDS analysis of the partially oxidized sample (Fig. 2), and XRD results (Fig. 3), the following mechanism can be proposed for oxidation:

1. In the beginning, the zinc atoms at the surface of brass particles start to oxidize selectively. Such selective oxidation of zinc atoms is consistent with the thermodynamic prediction of zinc oxidation in the presence of copper atoms. Such selective oxidation of zinc in 60%Cu-40%Zn alloy was also reported by Zhu et al. [26].

2. In the next step, the surface layer of the alloy is depleted from zinc atoms and becomes rich in copper. So, zinc atoms can diffuse from the internal layers toward the surface of brass particles; opposite to this direction, copper can diffuse toward the inner layers of the alloy. Therefore, a ZnO-rich layer forms as the oxidation product.

3. The copper content of the non-oxidized metal will increase gradually, while zinc content will decrease. By further oxidation and increase of copper content, copper can also start to be oxidized. In this way, CuO will form in the underneath layers of oxidation.

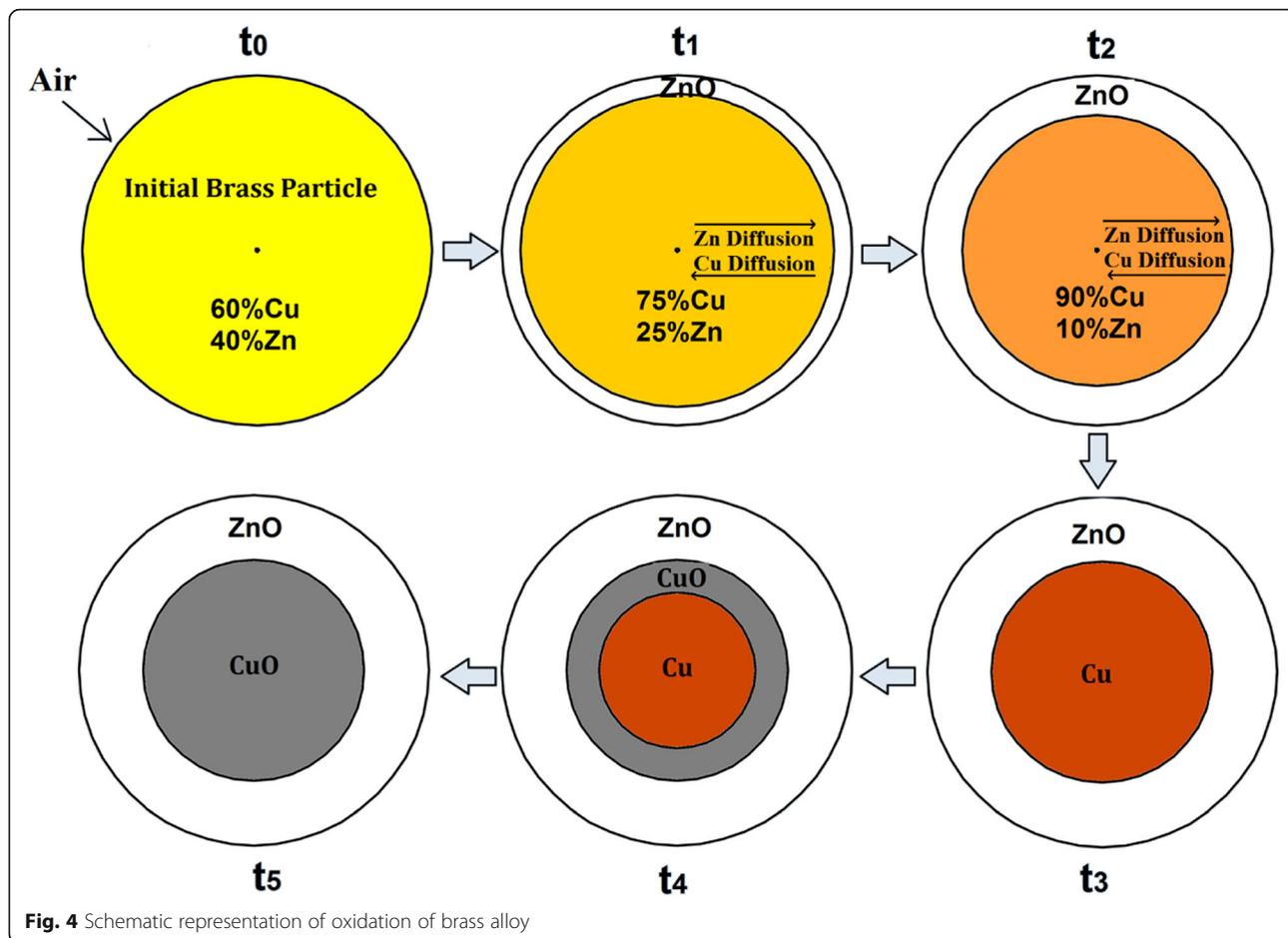
Figure 4 schematically represents the proposed mechanism for brass alloy oxidation. According to Fig. 4, at the beginning of oxidation ( $t_1$ ), the zinc content of the surface layer is oxidized in contact with air. By the progress of the oxidation process (at  $t_2$  and  $t_3$ ), zinc oxidation continues, and the thickness of the ZnO layer increases. Along with oxidation at the alloy surface, zinc content in the surface decreases while copper content is

increased. This zinc depletion behavior provides the driving force required for zinc diffusion from the internal parts of the alloy toward its surface and copper diffusion in the opposite direction. Figure 4 indicates the diffusion direction of zinc and copper elements. Further passing of time ( $t_4$ ) results in almost complete oxidation of zinc. Hence at the final stages of oxidation, a relatively pure CuO core is formed in the center of the oxidizing particle. The oxidation of the brass alloy particle finally terminates at the time of  $t_5$ .

A literature review shows that the diffusion coefficient of zinc in the brass alloy is much higher than that of copper [26, 27]. Therefore, in the brass alloy substrate, zinc atoms will move toward the surface and will be oxidized in the presence of oxygen. This phenomenon will decrease the concentration of zinc on the surface of the brass. This phenomenon is similar to the dezincification of brass in aqueous solutions. Selective oxidation is mainly due to the difference in the free energy of oxidation of the metals (Table 2). The selective oxidation at high temperatures has been reported for other alloys as well. For instance, WC-Co scraps oxidation, in which Co was first oxidized selectively [18].

### 3.4 Kinetics of high-temperature oxidation of brass slag

Isothermal oxidation results were used for selecting the kinetic model of brass oxidation. The results of 60–180 min of the isothermal oxidation experiments were put in different kinetic models, and their standard deviation values were calculated. The details of the kinetic model



governing the process are presented in ref. [28]. Based on the investigations, a 3D diffusion model (Eq. (6)) was selected as the best matching model for isotherm oxidation of brass:

$$\alpha = k t \tag{6}$$

where  $t$  and  $k$  are time and reaction rate constant, respectively. The latter depends on temperature whose value can be obtained based on the 3D diffusion model at 700, 800, 850, and 900 °C based on an Arrhenius relation [29], Eq. (7):

$$k = k_0 e^{-\frac{E}{RT}} \tag{7}$$

In which  $R$  is the global gas constant,  $k_0$  is the rate constant, and  $E$  is the activation energy of the process. The above equation can be rewritten as Eq. (8):

$$\ln(k) = \ln(k_0) - \frac{E}{RT} \tag{8}$$

If  $\ln(k)$  is plotted versus  $1/T$ , the slope of the diagram will be equal to  $(-E/R)$ ; hence, the activation energy can be obtained. Based on the results of isothermal

experiments (Fig. 1c), the activation energy for the oxidation of brass slag was  $311 \text{ kJ mol}^{-1}$  in the temperature range of 700–900 °C in this research.

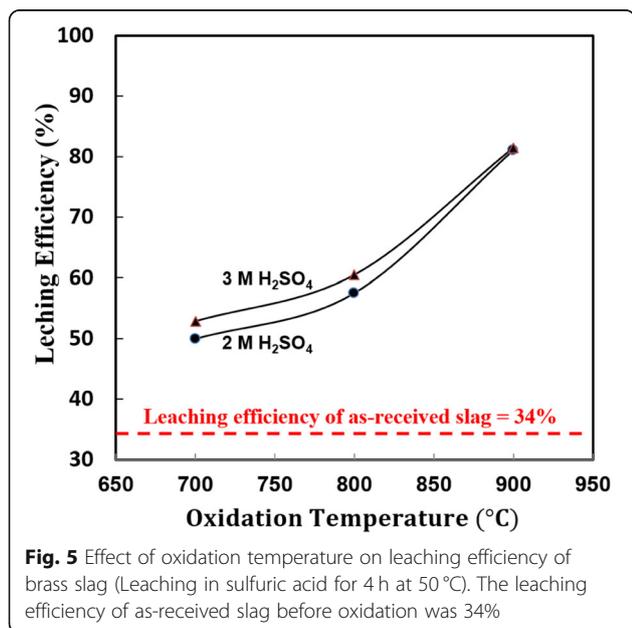
According to the Arrhenius equation, the rate constant will be increased versus temperature. The magnitude of activation energy indicates the sensitivity of the reaction rate to the temperature rise. In other words, for high activation energies, a slight increase in temperature will drastically increase the reaction rate. For small activation energies, however, temperature elevation has a small contribution to the reaction rate rise. Regarding the relatively high activation energy for high-temperature oxidation of brass, a temperature increase should induce a significant enhancement in the reaction rate. The high value of activation energy is in compliance with the results of isothermal oxidation in this research (Fig. 2c). At 700 °C and after 3 h, the reaction progress was not reasonable; however, at 900 °C, 3 h oxidation resulted in over 90% progress of the reaction. As discussed above, the brass oxidation mechanism is under the influence of the zinc diffusion rate in the brass alloy. Therefore, it can be expected that the obtained activation energy be equal to the activation energy for the diffusion of zinc in

the brass. Activation energy obtained in this research was  $311 \text{ kJ mol}^{-1}$ , which is the order of the activation energy for the diffusion of zinc in the brass alloy, reported in the previous studies as 251 [30] and  $189 \text{ kJ mol}^{-1}$  [31].

### 3.5 Leaching of oxidized brass slag

Oxidation of brass slag aimed to improve the leaching efficiency of slag in sulfuric acid. After each isotherm oxidation test, the obtained slag was leached in sulfuric acid with 2 M and 3 M concentrations for 4 h at room temperature. Figure 5 shows the results of leaching experiments. As the figure indicates, increasing the oxidation temperature improves the leach-ability of the slag.

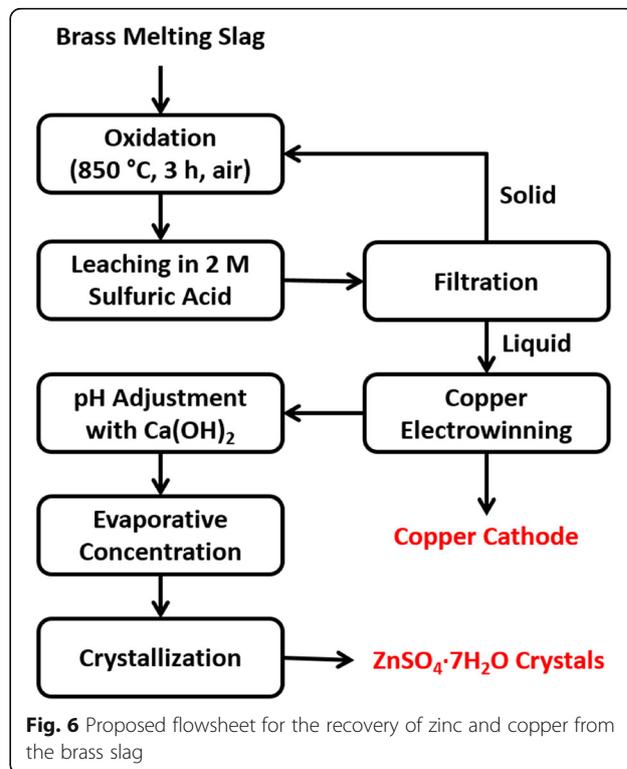
As Fig. 5 shows, the leaching efficiency of as-received slag before oxidation was measured 34%. Therefore, oxidation of the slag at  $900 \text{ }^\circ\text{C}$ , increased the leaching efficiency of the slag from 34 to 81%. The increase in acid concentration did not affect the dissolution of oxidized slag efficiency. Oxidation temperature, however, increased the leaching efficiency of brass slag. The effect of oxidation temperature on slag dissolution in sulfuric acid is a nonlinear function. Figure 5 suggests that the increase in oxidation temperature from  $700$  to  $900 \text{ }^\circ\text{C}$  resulted in a sharp and nonlinear increase of slag solubility. In other words, when the temperature was increased from  $700$  to  $800 \text{ }^\circ\text{C}$ , the solubility of slag raised from 50 to 57%, which is far less than the increase due to temperature enhancement from  $800$  to  $900 \text{ }^\circ\text{C}$  (rising from 58 to 81%). Therefore, it can be concluded that to achieve adequate solubility. The oxidation temperature has to be increased as much as possible. As can be seen, the efficiency of the slag solubility improved by



increasing oxidation temperature, but a part of zinc metal will be wasted and evaporated at  $900 \text{ }^\circ\text{C}$ . So, the optimal temperature for brass slag oxidation is reported around  $850 \text{ }^\circ\text{C}$ . Zinc and copper can be recovered from the pregnant leach solution of this slag by different processes [32, 33].

### 3.6 Process flow sheet

The sequence of operations for the recovery of zinc and copper from brass slag is shown in Fig. 6. According to this flowsheet, the brass slag is subjected to oxidation in air at  $850 \text{ }^\circ\text{C}$  for 3 h. Then, it is leached by 2 M sulfuric acid, producing a concentrated solution of zinc sulfate and copper sulfate. The concentration of copper and zinc in the pregnant leach solution was  $65 \text{ g Cu}^{2+} \text{ L}^{-1}$  and  $110 \text{ g Zn}^{2+} \text{ L}^{-1}$ , respectively. The copper is recovered from this solution as a copper cathode, through the electro-winning process. The zinc sulfate solution is subjected to evaporative concentration and crystallization to get zinc sulfate heptahydrate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ). Some part of the slag that has not been oxidized and cannot be leached in sulfuric acid, is returned to the high-temperature oxidation step. According to the flowsheet, the copper and zinc can be entirely recovered through the successive oxidation-leaching loop. Depending on the diameter of brass particles, the brass particle may be subjected to two or three oxidation-leaching cycles for the complete recovery of copper and zinc.



According to the flowsheet in Fig. 6, the specific acid consumption (kg acid per kg of brass slag) is almost independent of the acid concentration used in the leaching step. By using higher acid concentrations, a more concentrated zinc sulfate solution will be produced, which is a superior feed solution for the crystallization of zinc sulfate heptahydrate. The specific acid consumption according to the proposed flowsheet is primarily dependent on the chemical composition of raw brass slag. The brass slag is mainly composed of copper and zinc contained components (i.e., brass alloy, zinc oxide, and copper oxide). The acid consumption of brass slags with a high Zn/Cu ratio will be higher, as zinc sulfate is a zinc-containing product. Slags with lower Zn/Cu ratios show lower acid consumption. For reference, the sulfuric acid consumption of the slag having the chemical composition mentioned in Table 1 was measured as 0.82 kg H<sub>2</sub>SO<sub>4</sub> kg<sup>-1</sup> brass slag in this research.

#### 4 Conclusions

1. The chemical and mineralogical characterizations of brass melting slag demonstrate that vast amounts of copper and zinc are in the metallic form as brass alloy particles (41.5%). The brass particles resist against leaching in sulfuric acid.

2. By sulfuric acid leaching of brass melting slag, the yield of leaching was as low as 34 wt% at 2 M H<sub>2</sub>SO<sub>4</sub>, 4 h, 50 °C, while, the oxidation at 900 °C, increased the leaching efficiency of the slag up to 81%.

3. The optimal conditions for high temperature oxidation was obtained in 3 h oxidation at 850 °C in air atmosphere. It is important to note that oxidation above 850 °C, e.g., at 900 °C, results in zinc evaporation from brass slag, while oxidation at temperatures lower than 850 °C results in lower oxidation rates.

4. Copper was recovered from the leach solution as copper cathode via electrowinning, and the zinc value was recovered as zinc sulfate crystals via evaporation-crystallization.

5. A process flowsheet, given in Fig. 6, was proposed according to the above-mentioned experiments for the recovery of copper and zinc of industrial brass melting slag. The feasibility study as well as pilot plant runs of the proposed process is required to adapt it in industrial scale.

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#### Authors' contributions

All the authors have contributed to the structure, content, and writing of the paper. All authors read and approved the final manuscript.

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#### Availability of data and materials

All data generated or analyzed during this study are presented within the submitted manuscript.

#### Declarations

#### Competing interests

The authors declare they have no competing interests.

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