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Treatment of copper converter slag with deep eutectic solvent as green chemical

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ABSTRACT

Industrial copper slag is among the most important wastes to be evaluated in terms of containing valuable metals and the amount of waste approaching 30 million tons per year. Therefore, in this study, it was aimed to propose a feasible route for copper and zinc recovery from copper converter slag (CCS) by using choline chloride (ChCl) based deep eutectic solvent which is applied on this type of slag for the first time. During the leaching experiments with the pure ChCl-2urea mixture, temperature (25–95 °C), leaching duration (2–72 h), and pulp density (1/10–1/40 g/mL) were selected as the parameters to be investigated for Cu and Zn extraction. After the experimental results, the optimized conditions for the ChCl-2urea leaching process, which gave 89.9% Cu and 65.3% Zn extraction was found at 48 h, 95 °C, 1/20 g/mL pulp density with 600 rpm stirring speed. It is noted that the iron dissolution ratio is very low (max. 4.7%) under the selected conditions. At the end of the iron cementation stage, the total recovery efficiency as a pure metallic copper was 63%. The calculated activation energy for the dissolution of the copper and zinc from CCS is 8.86 kJ mol^{-1} and 14.48 kJ mol^{-1}, respectively.

1. Introduction

In hydrometallurgical processes, acids or bases are often used to extract valuable metals from primary or secondary resources. However, many scientists have turned to the field of green chemistry instead of these conventional solvents in order to eliminate their negative effects on the environment and human health. Therefore, at the beginning of this century, imidazolium-based ionic liquids with different anions such as HSO_4^-, Cl^-, BF_4^- etc. have been frequently tested in the hydrometallurgical methods to recover valuable metals (Au, Ag, Cu, etc.) because of their superior physical and chemical properties such as non-flammability, negligible vapour pressure, high thermal stability and ionic conductivity (Li et al., 2015; Park et al., 2014; Plechkova and Seddon, 2008; Whitehead et al., 2007). However, recent studies (Docherty et al., 2007; Jordan and Gathergood, 2015) have reported that some imidazolium-based ionic liquids could exhibit high toxicity and very poor biocompatibility properties. Also, the synthesis of ionic liquids is far away to be environmentally friendly and economical since this synthesis method requires a huge amount of quaternary salt and solvent to entirely swap the anions. Furthermore, since the physical and chemical properties of ionic liquids are affected by impurities, it is very important to produce them with high purity and this adds to the additional cost which is limited their use on the industrial scale (Ramón and Guillena, 2019). To overcome the negative effects of imidazolium-based ionic liquids, many scientists have continued to search for environmentally sensitive solvents for hydrometallurgical processes. At this point, new generation solvents called *Deep Eutectic Solvents* (DESs) have started to use in the hydrometallurgical routes as well as in other fields such as catalysis, electrochemistry, material science, dissolution/separation technologies and organic synthesis. DESs are generally formed with two or more components that have low cost, low toxicity and high biocompatibility, and they can react with each other by hydrogen bond interactions to form an eutectic mixture (Dai et al., 2013; Ramón and Guillena, 2019). Generally, DESs are produced by bringing together a quaternary ammonium salt with metal salts or hydrogen bond donor (HBD) which promote to form a complex with halide anion of quaternary ammonium salt (Abbott et al., 2007; Smith et al., 2014). As one of them, choline chloride (ChCl) was broadly used as an organic component in order to obtain an eutectic mixture with cheap and safe HDB such as urea, carboxylic acids and polyols (Abbott et al., 2004; Ramón and Guillena, 2019). Due to their similar physicochemical properties to imidazolium-based ionic liquids, DESs can replace them in many

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applications.

A few numbers of studies have indicated that DESs play a considerable role as a solvent for hydrometallurgical processes. For the first time, Abbott et al.,(2003) showed the possible dissolution process of metal oxides in DESs. According to the experimental studies (Abbott et al., 2004; 2005; 2006a; 2006b; 2007), metal oxides (ZnO, CuO, NiO, CoO, TiO_2, Fe_3O_4 etc.) had different solubility in choline chloride-based DESs. For example, while CuO and Cu_2O have different and high solubility in the choline chloride and urea mixture at 60 °C, the solubility of Fe_2O_3 and Fe_3O_4 are quite low. Also, it is stated that aluminates and silicates are not soluble in DES prepared by choline chloride and urea. Due to the different dissolving properties of DESs, they are very suitable for selective leaching and electrochemically recovery process from DES. In addition, it was determined that the viscosity problem of DESs can be overcome by preparing them with different components (such as 1:1.5:0.5 ChCl:ethylene glycol:urea) without changing their solving features. Moreover, as stated in the previous studies (Abbott et al., 2006; Cao et al., 2020; Liao et al., 2016) DESs have different solvent properties to high molten salts where metal complex anion with urea formed.

As DESs provide selective metal recovery in environmentally friendly mediums, recently, very promising results on the leaching efficiency of zinc were obtained by several studies performed with industrial wastes such as electric arc furnace (EAF) and zinc plant leach residues (Bakkar, 2014; Bakkar and Neubert, 2019; Rüşen and Topçu, 2017a). It was stated by Abbott et al. (2009) selective recovery of zinc could be achieved from EAF dust over lead and iron because of the different solubility of these metal oxides. Approximately, 75% of zinc was recovered from EAF dust by the following routes; leaching with choline chloride-urea mixture, lead removal by zinc powder and electrowinning of zinc. Also, cobalt recovery from end-of-life Li-ion batteries was investigated using DESs which were prepared with different components (Peeters et al., 2020; Tran et al., 2019). While there are several studies on the metal recovery from secondary sources/wastes in the literature, none of them is related to copper or zinc extraction by using DESs from copper-containing sources such as copper minerals or industrial copper wastes. In the world, annually more than 30 million tonnes of industrial copper wastes emerge after all pyrometallurgical copper production stages (smelting, converting and refining). Especially converting slag is very important in the copper sector with including a considerable amount of copper in the range of %4–8 (Rüşen et al., 2012). An oxygen-enriched method is widely used in the converting process to obtain blister copper from the matte (Cu_2S.FeS) for pyrometallurgical copper production. However, the use of a high level of oxygen at the converter stage increases the amount of magnetite phase, which leads to rising in copper losses, namely mechanical losses, by increasing slag viscosity. In addition, physicochemical copper losses in converting stage can also occur by the insufficient dissolution of matte depending on the thermodynamic conditions of the process (Schlesinger et al., 2011). Although there have been pyrometallurgical studies to reduce copper losses (Coursol et al., 2012; Rüşen et al., 2016; Topçu et al., 2019), the hydrometallurgical methods (Arslan and Arslan, 2002; Beşe, 2007; Khalid et al., 2019; Li et al., 2008; Nadirov et al., 2013) were more commonly used for copper recovery from copper slags. However, the conventional leaching agents used in the hydrometallurgical processes have several disadvantages; the huge amount of acid consumption, recycling problem of acid waste and releasing the hazardous gases.

Therefore, it is aimed to suggest a new approach for copper and zinc recovery from CCS in the present study. In order to eliminate the negative effects of the hydrometallurgical method caused by the solution, choline chloride-based deep eutectic solvent (ChCl-urea) was used as a leaching agent. A kinetic study was performed for the first time to determine the activation energy for copper and zinc dissolution in DESs. Also, the chemical and mineralogical characterization of CCS were investigated in detail.

2. Material and experimental methods

2.1. Materials

CCS used in this work was provided from Eti Bakır copper production plant in Turkey. Before physical and chemical characterization of CCS, the sample was crushed and ground to obtain as fine particles. Choline chloride (ChCl, $C_5H_{14}ClNO$, >98%) and urea [$CO(NH_2)_2$, >99%] supplied from Merck, commercially, and were used to prepare deep eutectic solvent without any purification. Pure iron obtained from Riedel-de Haën (<212 μm, >99%) was used in cementation studies to recover copper from the leach solution.

2.2. Preparation of DES

ChCl and urea were mixed stoichiometric eutectic molar ratio 1:2, respectively, in a conical flask and synthesized as described before (Abbott et al., 2009; Bakkar, 2014). The mixture was heated quietly to 90 °C using a temperature-controlled heater equipped with a magnetic stirrer until a homogeneous colourless liquid was obtained. Thereafter, the solvent was cooled and preserved in a desiccator for leaching

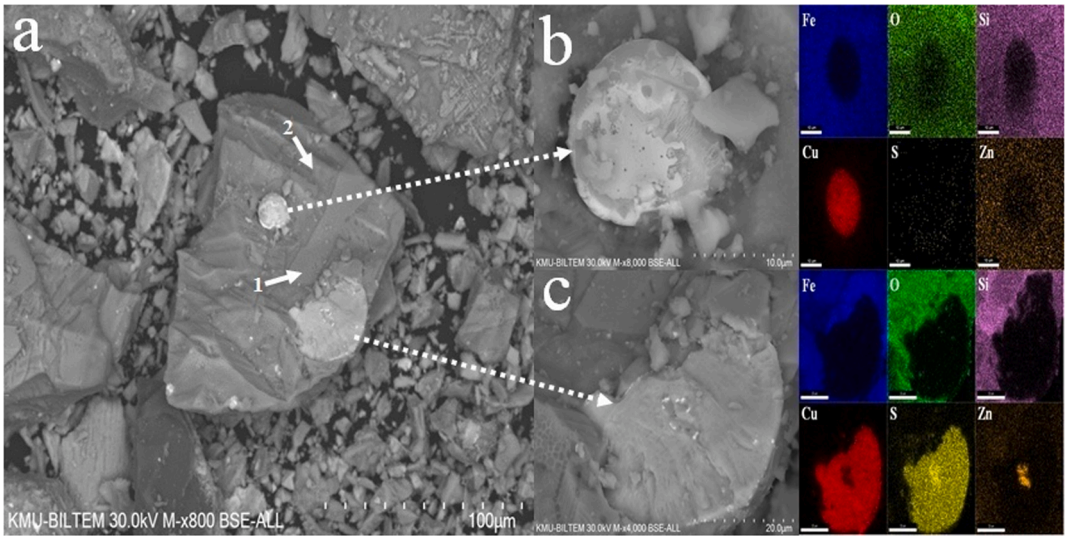

Fig. 1. a) general view of CCS, b) metallic copper and c) Cu-Zn-S complex structure images of copper converter slag.

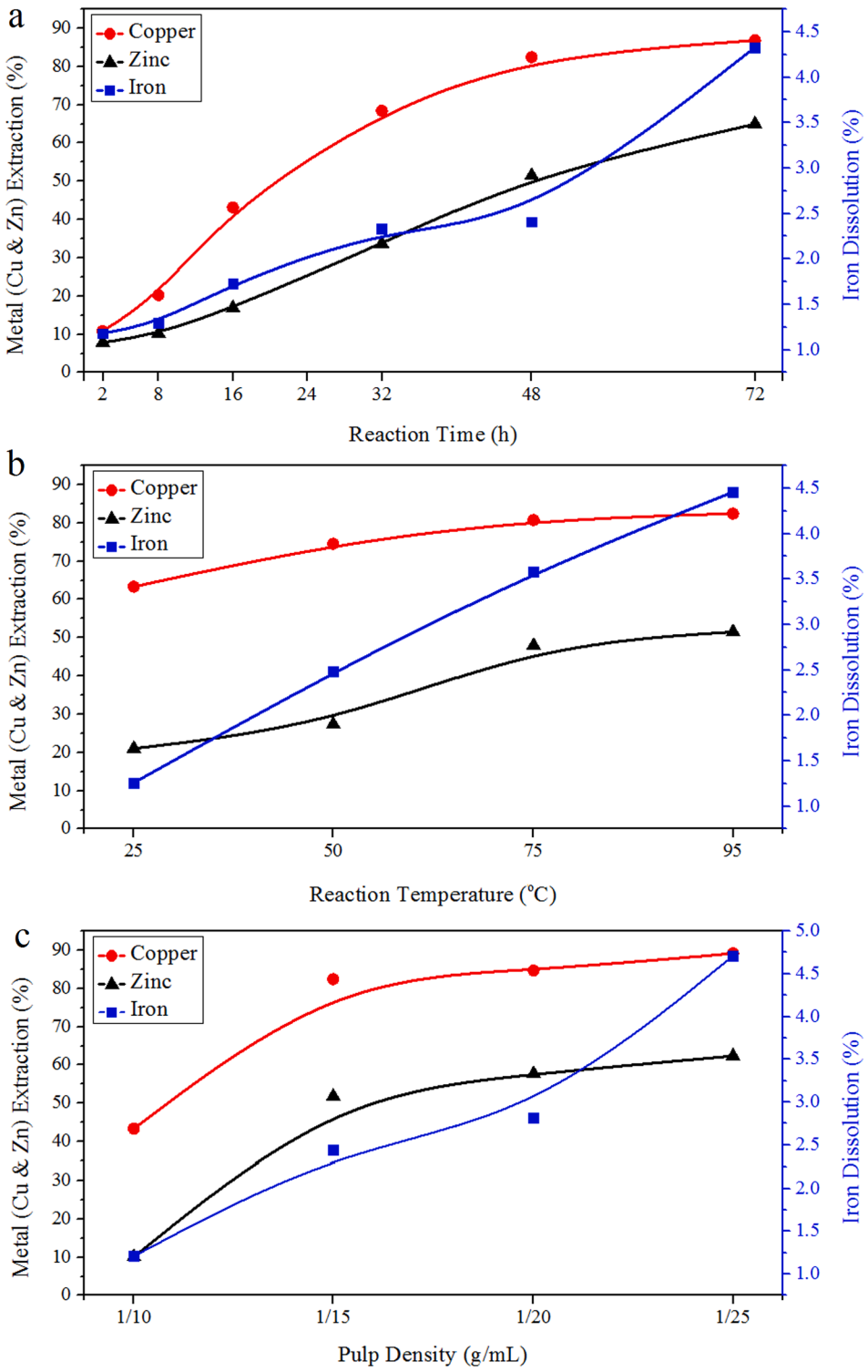

Fig. 2. Effect of a) reaction duration b) reaction temperature and c) pulp density on copper, zinc and iron extraction from CCS.

experiments.

2.3. Characterization of copper converter slag

Initially, the particle size of CCS was determined by Malvern Particle Sizer (Malvern-Mastersizer 2000 SR). According to the particle size analysis, 80% of the CCS was found to be below 100 μm. Since the particle size distribution of CCS is narrow, the effect of particle size on leaching efficiency and leaching kinetic has not been investigated in this study.

Chemical analyses of copper converter slag used in the leaching experiments were performed by inductively coupled plasma–mass spectrometer (ICP–MS) and X-ray fluorescence (XRF). According to the chemical analysis of CCS (given in Table S1), the main structure of CCS is composed of Fe and Si elements as 44.3% and 11.1%, respectively. Also, it is determined that the CCS used in the leaching experiments contains a remarkable amount of Cu and Zn. In addition, it was found that CCS contains a small amount of S, Al, Mg, Ca, Na, K and Pb.

Mineralogical analysis of CCS was detected by X-Ray diffractometer (XRD, Bruker D8 Advance with Da Vinci) with Cu Kα radiation at 30 kV, at a scanning rate of 0.4° min^{-1}. According to the XRD graph given in Fig. S1., Fayalite ($FeSiO_4$) and Magnetite (Fe_3O_4) are the main structure of the CCS. In this study, due to the high density of $FeSiO_4$ and Fe_3O_4 phases, the structure of copper and zinc could not be determined in the XRD graph. However, according to previous studies (Arslan and Arslan, 2002; Carranza et al., 2009; Muravyov et al., 2012), copper and zinc may be found in different mineralogical structures in the copper converter slag. Copper may present in the slag as metallic, oxidized and matte form, while zinc may form as complex structure.

In order to detect the detailed mineralogical analysis of CCS, the slag sample was prepared by embedding the solid part in epoxy resin and visualized it in a reflected-light microscope. Also, Hitachi SU5000 model scanning electron microscope equipped with energy dispersive X-ray (EDX) was used to determine structural properties of copper converter slag. The colour mapping method obtained by SEM and EDX data is used often by researchers to determine the possible phases in the representative samples. In this study, SEM observation and elemental distribution of copper converter slag were achieved. Thus, the distribution of the main elements (Fe, Si, O, Cu, S and Zn) in the CCS was illustrated. In the elemental mapping; iron (Fe) is represented by blue, oxygen (O) by green, silicon (Si) by purple, copper (Cu) by red, sulfur (S) by yellow and zinc (Zn) by orange. Representative SEM-EDX and optical images of CCS are shown in Fig. 1 (a-c) and Fig. 2S, respectively.

According to Fig. 1.a, the CCS does not have homogenous structures in both shape and size. Various shapes including round, spherical, flat shaped, tabular etc. were observed in the figure. The particles with the grey area, labelled as "1", indicates the fayalite phase in CCS. Fayalite exhibits dendritic growth and is seen as tabular shaped. Fayalite crystals also form as a needle-type embedded in the glassy phase. The dark grey particles in CCS, labelled as "2", show magnetite phases which mostly cause the copper losses mechanically. Apart from fayalite and magnetite phases, spherical and round type structures were detected in SEM images. As seen in Fig. 1.b, a spherical-shaped structure is determined as metallic copper with a small amount of oxygen. This may be attributed to the presence of the oxide form of copper in CCS with metallic copper. As stated before, copper droplets may lose mechanically by squeezing in the magnetite phase. In this study, a round-shaped structure surrounded by fayalite was also seen in CCS (Fig. 1.c). Elemental colour mapping corresponding to Fig. 1.c indicates that a complex structure of Cu-Zn-S and matte form is present in CCS. As seen in elemental colour mapping in Fig. 1.c, zinc is precipitated in matte to form a complex structure. This complex structure was also encircled by main phases of converter slag. In addition, previous studies (Jalkanen et al., 2003; Mihailova and Mehandjiev, 2010; Rüşen and Topçu, 2017b) on CCS pointed out that different particles or inclusions such as carbon rich phase and other oxides (CaO and Al_2O_3) could be observed in copper slags.

As seen in Fig. S2., the optical microscopic observation of copper converter slag showed that an amorphous glassy iron silicate phase is the main component with trapped magnetite. The observed copper-bearing phases are matte (Cu_2S.FeS) and metallic copper (blister copper). Copper-bearing particles of about 100 μm have been observed. Moreover, the trapped copper-bearing particles are surrounded by the main components (fayalite/magnetite species) and also contact with the magnetite phase.

2.4. Leaching experiment

After characterization of the converter slag, the leaching experiments were carried out by using the conventional hydrometallurgical method. All leaching experiments were conducted with a constant volume of leaching solution (DESs–100 mL). During the leaching experiments, heating was controlled by a contact thermometer which has ±1 °C sensitivity. In this study, the most effective leaching parameters were chosen as temperature, leaching duration and pulp density on copper and zinc recovery from CCS. The temperature, leaching duration and pulp density (solid/liquid ratio) was selected as in the range of 25, 50, 75, 95 °C; 2, 8, 16, 32, 48, 72 h and 1/10, 1/20, 1/30, 1/40 g/mL, respectively. During the leaching experiments, the stirring speed was fixed at 600 rpm. After leaching experiments, solid–liquid separation was performed carefully. The obtained pregnant leach solution was diluted with 0.1 M HCl solution for mass spectrometric measurements by Perkin Elmer PinAccle 900 T model atomic absorption spectroscopy (AAS). In order to determine the dissolution ratio of other elements in CCS such as Fe, Co and Al, the solid part obtained after solid–liquid separation was analyzed by XRF. In this study, copper and zinc recovery rates were calculated as follows:

$$\%R = \frac{C \times V \times DA}{m \times w} \quad (1)$$

where C is metal concentration in the leach solution as mg/L, V is the volume of leach solution as L, DA is dilution amount of leach solution before ICP-OES analysis, m is the weight of copper converter slag as g and w is the weight percent of the metal in copper converter slag.

3. Results and discussion

3.1. Effect of reaction duration

During the experiments conducted for the determination of the effect of reaction duration, by changing the reaction duration to 2, 8, 16, 32, 48, 72 h and the other parameters were kept constant at solid/liquid ratio (1/20 g/mL) or pulp density of (200 g/L) and reaction temperature of 95 °C with stirring speed 600 rpm. As seen in Fig. 2.a, although very low copper recovery rates were obtained with a shorter reaction duration, the copper recovery increased significantly with increasing reaction time in the ChCl-2urea leach system and reached approximately 87% after 72 h of leaching. According to the experimental results, it was observed that the copper extraction rate was obtained as 82.46% after 48 h of leaching and the increase in Cu leaching yield after 48 h was only 4.4%. So, it can be said that 48 h-leaching time is sufficient for copper recovery from CCS by using ChCl-2urea.

Zinc extraction from CCS has also been taken into account since there is a considerable amount of zinc in CCS. As understood from Fig. 2.a, zinc extraction increased with increasing reaction duration. The highest zinc extraction was obtained as 65% after 72 h leaching process. As stated before by researchers (Arslan and Arslan, 2002), zinc could be extracted from CCS up to 93% by roasting and acid leaching route. However, a leaching yield of 65% Zn can still be considered a good value without any extra roasting process. As mentioned earlier by other researchers (Abbott et al., 2006b; Bakkar, 2014), a high rate of copper and zinc solubility from metal oxides such as CuO and ZnO was obtained after 60 h of leaching time at 50 °C dissolution temperature. Therefore, it can be said that the results obtained in this study are very compatible with the literature.

On the other hand, it is seen from Fig. 2.a, that the iron dissolution from converter slag remains very low level and does not change with a longer reaction duration. Less dissolution of iron compared to the acid processes will make the iron removal step relatively easy. This situation is also very important in terms of experimental cost and time. Considering the low iron solubility and longer reaction duration, it can be said that DES is a good candidate for copper recovery from converter slag.

3.2. Effect of reaction temperature

In order to determine the effect of reaction temperature on copper and zinc recovery from CCS, the reaction temperature was chosen in a range of 25–95 °C while keeping pulp density, reaction duration and ChCl-2urea volume constant at 1/20 g/mL, 48 h and 100 mL, respectively. The variation in the copper, zinc and iron extraction with various

temperatures is shown in Fig. 2.b.

As seen in Fig. 2.b, copper and zinc extraction continuously increases with increasing temperature in the ChCl-2urea leach system and the highest extraction rate for both metals was achieved at 95 °C. A significant copper recovery (63.35%) was obtained at room temperature (25 °C) and an increase of 19.11% was observed after leaching experiments at room temperature. Although the rising in copper extraction was very low with increasing reaction temperature, the highest copper extraction value was obtained approximately 83% at 95 °C. In contrast to copper extraction, a significant increase of 30.51% in zinc extraction was obtained with increasing reaction temperature from 25 °C to 95 °C. While 21% of zinc extraction was obtained at room temperature, 51.51% of zinc extraction was achieved after leaching experiments at 95 °C. In addition, iron dissolution was very small amounts from CCS at even higher temperatures. According to experimental results, 95 °C of reaction temperature was considered as the suitable temperature for copper and zinc extraction in this study. As stated by Abbott et al. (2006b), the solubility of Cu and Zn in DES effectively depends on the reaction temperature. It is known that the number of collisions of moving particles will increase with increasing temperature in chemical processes. Deep eutectic solvents prepared by ChCl-2urea offer the opportunity to work at high temperatures due to the high thermal decomposition temperature (Delgado-Mellado et al., 2018). With this result obtained in the study, it was determined that metal recovery from converter slag can be achieved by using deep eutectic solvent prepared with ChCl and urea at different temperatures.

3.3. Effect of pulp density

The effect of pulp densities, ranging from 1/10 g/mL up to 1/40 g/mL, on the extraction efficiency of copper and zinc were studied under conditions that reaction duration and reaction temperature were kept constant of 48 h and 95 °C, respectively. Fig. 2.c. gives copper, zinc and iron extraction as a function of pulp density.

It can be concluded that copper recovery increased with decreasing pulp density. After the leaching process in pulp density of 1/10 g/mL, the copper extraction value was obtained as 45.78% and the copper recovery value increased rapidly after this point. The highest copper extraction value was obtained as 89.16% after the leach process with a pulp density of 1/40 g/mL. However, according to experimental results, there was not a significant increase after the leaching process in 1/20 g/mL pulp density. As seen in Fig. 2.c, zinc extraction showed a similar tendency with copper extraction. Also, the maximum zinc extraction was obtained 62.37% after the leaching process under the condition of 1/40 g/mL pulp density. On the other hand, the iron solubility, as in the effects of other parameters (reaction duration and temperature), remained at negligible levels in all experiments and increased with decreasing pulp density up to 4.75%.

According to the experimental results, the optimum conditions for copper and zinc recovery were chosen as 95 °C reaction temperature, 48 h reaction time and 1/20 g/ml solid/liquid ratio, and the leaching yields of approximately 90% Cu and 65% Zn were obtained. These values are compatible with copper and zinc recoveries (60–100% and 50–93%, respectively) performed with several acids from copper slags in previous studies (Arslan and Arslan, 2002; Banza et al., 2002; Beşe, 2007; Khalid et al., 2019). However, these studies involved high iron extraction, and so additional processes such as thermal decomposition and roasting using high-temperature sulfuric acid were needed before leaching to reduce iron extraction. On the other hand, the use of DESs prepared with ChCl and urea is advantageous due to negligible iron extraction and high precious metal recovery from CCS without any pretreatment. Here, although the high viscosity of DES (750 cP at 25 °C) poses a problem in the filtration stage (after leaching), it is possible to overcome this negative effect by hot filtration.

3.4. Kinetics of copper and zinc leaching

The kinetics study has an important role in the scale-up process because it demonstrates the real behaviour of a process. For the non-catalytic reaction of particles with the surrounding fluid, two simple idealized models, the progressive-conversion model (PCM) and shrinking unreacted-core model (SCM), are considered for kinetic studies. In order to investigate the kinetic parameters for copper and zinc recovery from CCS with deep eutectic solvent, some leaching experiments were analyzed with SCM because this model approximates real particles that in more closely than PCM (Fogler, 2004). The rate of non-catalytic solid–fluid reaction may be controlled by one of five successive resistances;

1. Resistance to the passage of reactant through fluid film
2. Resistance to the passage of reactant through solid product
3. Resistance to the chemical reaction of the reactant with solid on the surface of the particle
4. Resistance to the passage of fluid product through solid product film
5. Resistance to the passage of fluid product through fluid film

First three resistances are especially important and there is an integrated rate equation corresponding to each case, concerning also the particle geometry as follows;

$t/\tau = X$ for fluid film diffusion control (constant size flat plate, cylindrical and spherical particles) (2)

$t/\tau = X^2$ for product film diffusion control (constant size flat plate particles)(3)

$t/\tau = X$ for reaction control (constant size flat plate particles) (4)

$t/\tau = X + (1 - X)\ln(1 - X)$ for product film diffusion control (constant size cylindrical particles) (5)

$t/\tau = 1–3(1 - X)^{2/3} + 2(1 - X)$ for product film diffusion control (constant size spherical particles) (6)

$t/\tau = 1 - (1 - X)^{1/2}$ for reaction control (constant size cylindrical particle)(7)

$t/\tau = 1 - (1 - X)^{1/3}$ for reaction control (shrinking or constant size spherical particle) (8)

$t/\tau = 1 - (1 - X)^{2/3}$ for fluid film diffusion control (shrinking small spherical particle) (9)

Also, the following pseudo homogenous models may be applied to noncatalytic fluid–solid reactions (Tunç et al., 2007);

$t/\tau = -\ln(1 - X)$ (10)

$t/\tau = X/1 - X$ (11)

Additionally, in the shrinking core model, mixed reaction control equations are expressed as follows (Wang et al., 2017);

$t/\tau = 1/3\ln(1 - x) - [1 - (1 - x)^{-1/3}]$ for mixed control (12)

where t is the reaction time and x is the fraction reacted (leaching efficiency) of the copper and zinc.

Before the kinetic studies for copper and zinc recovery, the effect of reaction on copper and zinc recovery was determined with leaching experiments at various temperatures. The effect of reaction duration on copper and zinc recovery at various temperatures is shown in Fig. 3S(a-b). As seen in Fig. 3S.a and Fig. 3S.b, the leaching efficiency of copper and zinc increased with increasing reaction duration for all reaction temperatures. Also, it is understood from Fig. S3, copper and zinc recovery increased with rising reaction temperature. Based on experimental data in Fig. S3, the plots for the rate equations concerning all the particle geometry versus time at various temperatures are drawn for copper and for zinc recovery. It is understood after calculations that among all the models examined, and it has been found that the spherical

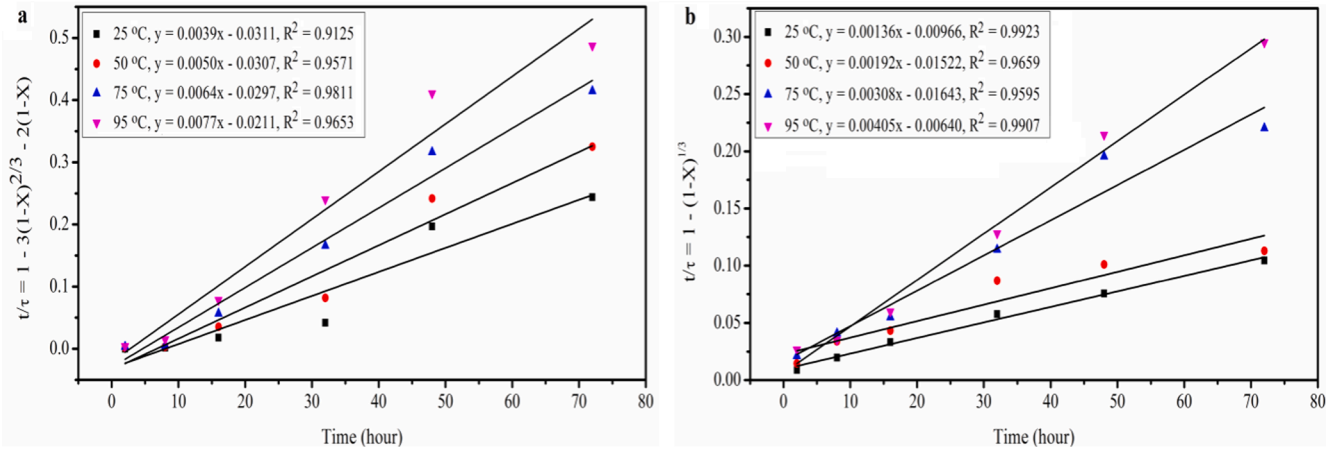

Fig. 3. a) Plot of $1–3(1 – X)^{2/3} – 2(1 – X)$ *vs* reaction time and b) plot of $1 – (1 – X)^{1/3}$ *vs* reaction time at various temperature.

Table1
R^2 values for various temperatures and their estimated activation energies.

Equation No	Models	Element	R^2 for models	Activation Energy (E), kJ.mol^{-1}
2, 4	$t/\tau = X$	Copper	0.9775	1.27
		Zinc	0.8840	12.49
3	$t/\tau = X^2$	Copper	0.9993	5.67
		Zinc	0.9218	22.23
5	$t/\tau = X+(1 – X)\ln(1 – X)$	Copper	0.9990	7.75
		Zinc	0.9275	26.81
6	$t/\tau = 1–3(1 – X)^{2/3} + 2(1 – X)$	Copper	0.9977	8.86
		Zinc	0.9105	27.39
7	$t/\tau = 1 – (1 – X)^{1/2}$	Copper	0.9979	3.57
		Zinc	0.8780	14.64
8	$t/\tau = 1 – (1 – X)^{1/3}$	Copper	0.9936	4.57
		Zinc	0.9904	14.48
9	$t/\tau = 1 – (1 – X)^{2/3}$	Copper	0,9943	2.76
		Zinc	0.8729	13.63
10	$t/\tau = -\ln(1 – X)$	Copper	0.9918	6.58
		Zinc	0.8834	17.07
11	$t/\tau = X/(1 – X)$	Copper	0.9863	13.86
		Zinc	0.8895	22.25
12	$t/\tau = \ln(1 – X) – [1 – (1 – X)^{-1/3}]$	Copper	0.9947	15.64
		Zinc	0.9069	33.11

shaped models give more uniform values for copper and zinc recovery. The well-fitted graphs for copper and zinc recovery are shown in Fig. 3.a and b. It is understood from Fig. 3.a, the mathematical model of the equation for $1 – 2/3x – (1 – x)^{2/3}$ versus time at different temperatures show that the kinetic data of copper were well fitted to the diffusion control model for the higher R^2 values (>0.97). Also, it evident from Fig. 3.b., the mathematical model of the equation for $t/\tau = 1\text{-}(1\text{-}X)^{1/3}$ seems well fitted with a regression coefficient of >0.99 for zinc recovery.

In addition, the activation energy was calculated based on Eq. (13):

$$k = A.exp^{(-Ea/RT)} \quad (13)$$

where k is the rate constant of surface reaction (s^{-1}), T the reaction temperature in Kelvin, R the universal gas constant, 8.314 J/(K·mol) and E_a is the activation energy in kJ/mol.

All the above models were applied to the experimental data for each temperature using a PC, and R^2 values were determined for each model. The correlation coefficients of the fitting results for the various models at the various temperatures are given in Table 1.

The plot of ln(k) against 1/T was drawn (shown in Fig. S4), which yields a straight line with a slope of −E/R and an intercept of ln k. Fig. S4 present a good fit ($R^2 > 0.9977$) for copper recovery. The calculated activation energy for the dissolution of the copper from CCS is 8,86 kJ. mol^{-1}. According to Fig. S4, the regression coefficient higher than

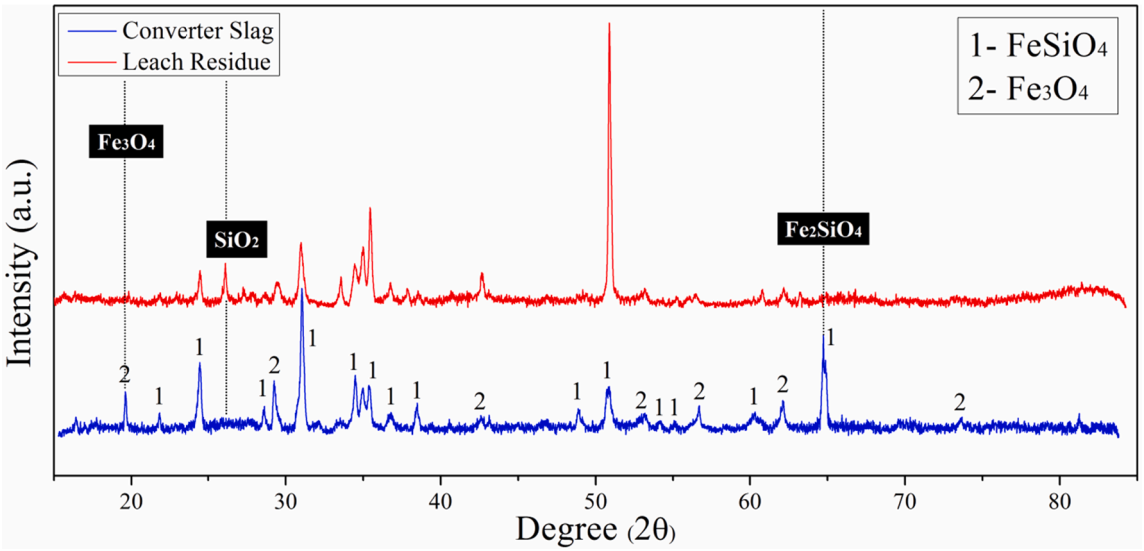

Fig. 4. XRD patterns of CCS and leach residue after the optimum leaching experiment.

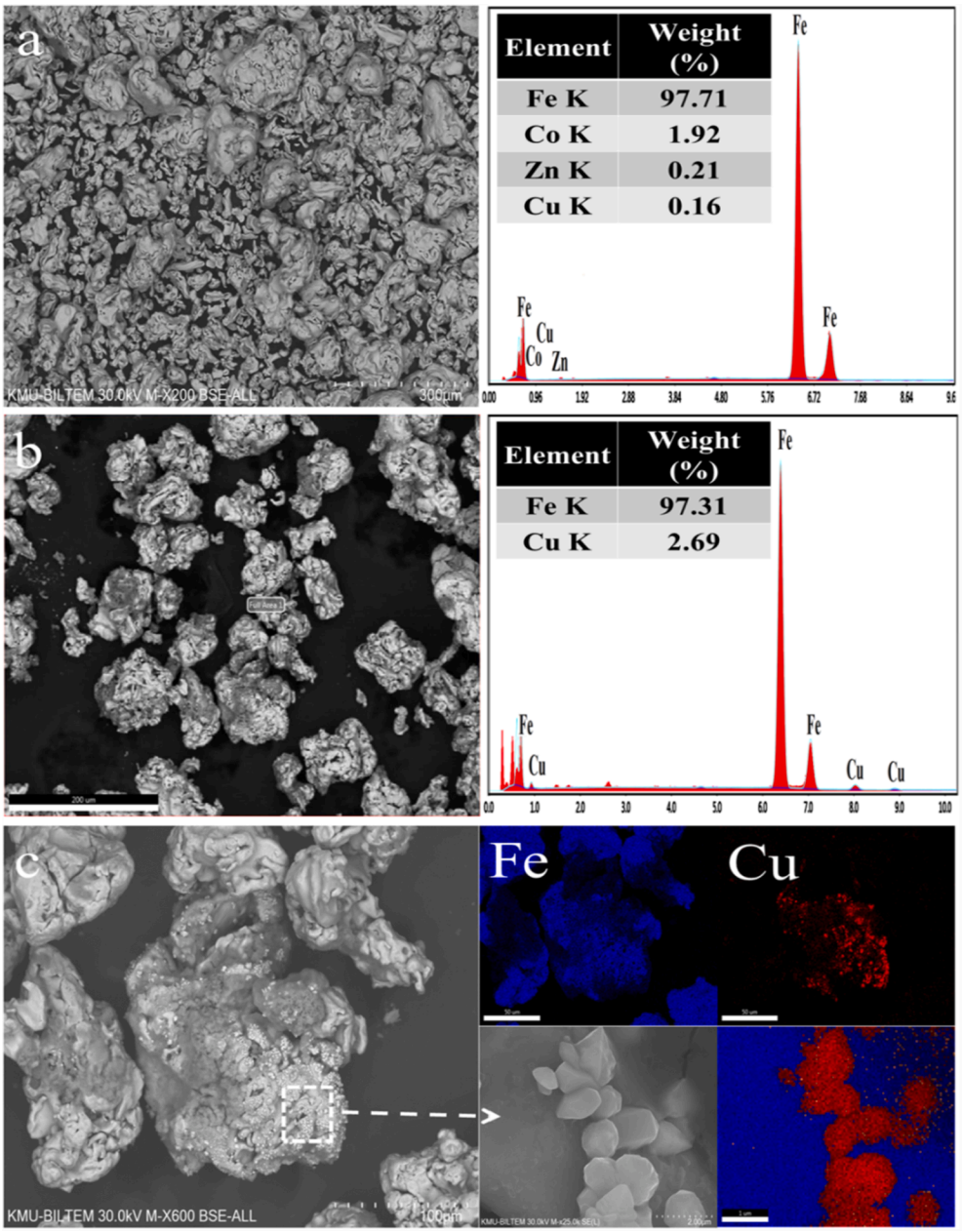

Fig. 5. a) pure powder iron, b) solid part obtained after cementation process, and c) precipitated copper particles on iron surface.

0.9904 was obtained and the activation energy was calculated as 14.48 kJ.mol^{-1} for zinc recovery. In previous studies performed with conventional acids, the activation energies for copper recovery from copper slags were obtained in the range of 11–55 kJ.mol^{-1} (Shi et al., 2020; Turan et al., 2019). Hence, it can be said that metal recovery by deep eutectic solvent needs lower activation energy.

3.5. Dissolution mechanism and metal recovery from leach solution

As stated above, copper and zinc are found in CCS as different mineralogical structures. Although the DESs are capable of donating or accepting electrons or protons to form hydrogen bonds which confers them excellent dissolution properties, the dissolution of metals in DES is not well understood as in aqueous solutions. It has been reported by several studies (Liao et al., 2016; Xie et al., 2016) that the metal complex anion $[MxClO.(urea)]^-$ is formed when MxO dissolves in ChCl-2urea regardless of the metal sources such as metallic, oxide. and sulfates. Also, it has been stated that in the leaching processes with DES prepared with choline chloride and urea, chlorine anions weaken the metal–oxygen bond and lead to the formation of metal complex anions where urea act as ligand (Abbott et al., 2005; Yang and Reddy, 2014). Hence, the following dissolution reactions for copper and zinc were proposed:

$$CuO + Ch^+ + Cl^-/urea \rightarrow [CuClO.urea]^- + Ch^+ \quad \text{(Rx. 1)}$$

$$ZnO + Ch^+ + Cl^-/urea \rightarrow [ZnClO.urea]^- + Ch^+ \quad \text{(Rx. 2)}$$

As a result, on a laboratory scale, the experimental conditions for ChCl-2urea leaching indicated that the maximum Cu and Zn extraction was nearly 90% and 65%, respectively, which could be obtained when the parameters were kept as 95 °C, 1/25 g/mL, 48 h, and 600 rpm. Meanwhile, under these conditions, Fe was dissolved in the solution up to 5%. The final residue was analyzed by XRF for Cu, Zn. and the other contents, and its composition was determined as 0.91% Cu, 1.43% Zn, 43% Fe. When compared to the XRD analysis of copper converter slags before and after leaching treatment (given in Fig. 4), it can conclude that

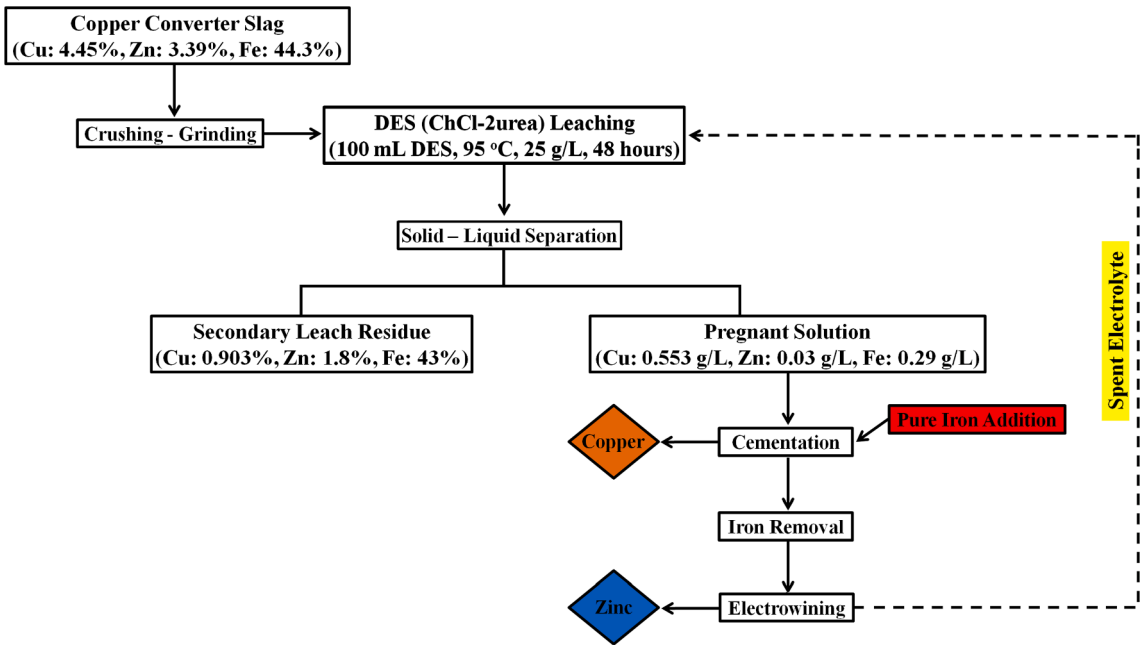

Fig. 6. Propossed process flowsheet.

almost all peaks belonging to the Fe_3O_4 and $FeSiO_4$ remained unchanged. But as seen in Fig. 4, a peak around 20° and 65° which belong to magnetite and fayalite phases disappeared and a new peak occurred around 26°. It can be said that the disappearing peaks depend on the iron solubility even if it is very low. Also, the new peak belongs to the SiO_2 phase, which occurs from the breakdown of the fayalite phase after the leaching experiment with a deep eutectic solvent.

Metal recovery from pregnant leach solution including valuable metal ions can be performed by several methods. Cementation with iron scrap is the most common method to precipitate valuable metals as a metallic form in the metal industry. For this reason, the pure iron powder was added to the leach solution at room temperature to able to extract the copper from the pregnant solution. In the cementation process, 50 mL of the pregnant leach solution was taken and 0.1 g of iron powder was added. After 2 h, a sample solution was filtered and copper concentration was analyzed by AAS. According to the experimental result, the copper concentration in the solution was decreased by %70 and a concomitant increase in the iron concentration was observed. This result showed that the total copper recovery could be achieved as 63% after the DES leaching and iron cementation steps. In addition, the solid part obtained after the filtration was investigated with SEM-EDX. The results of the SEM-EDX analysis belonging to the pure iron and precipitated metallic copper are shown in Fig. 5.

As seen in Fig. 5.a, according to the SEM images of pure iron, the sample has different sizes and shapes. Also, pure iron has a fairly small amount of copper content. As seen in Fig. 5.b, after the cementation process, metallic copper deposited on the iron surface. The amount of deposited copper depended strongly on the iron concentration and particle size of the iron. The copper deposition would be expected because of difference between $Fe^{2+/0}$ and $Cu^{2+/0}$ couples will be governed by the Nernst equation. After the leaching and cementation processes, the accumulated copper can be stripped from the iron surface. Then, zinc can be extracted from the leachate as metal form by the electrowinning method. Therefore, the process flowchart, shown in Fig. 6, can be propossed to produce pure metals (Cu & Zn) by considering the above-mentioned optimum leaching condition.

One of the most important factors for the chloro-based process is the ease of chlorine recycling. As with many processes, the recycling and reuse of DESs after metal extraction are very important for the process economy. Besides the cheap and easily available, one of the main advantages of the DES can be reused or easily disposed due to its biodegradable components. As mentioned in previous studies, choline chloride-based DESs can be reused after sulfur removal from fuel (diesel) and CO_2 capturing at least 5 times (Mohd Zaid et al., 2017; Smith et al., 2014). In addition, it has been emphasized by another study (Riaño et al., 2017) that DES based on choline chloride and lactic acid (molar ratio 1:2) can be reused for the extraction of the metals (Dy, Co and B) from the magnets without significant deviations. It is also known from the literature that imidazolium based ionic liquids can be used 4 times without any loss of metal recovery efficiency in the extraction processes (Huang et al., 2013; Whitehead et al., 2004) and the recycling of DESs is easier than ionic liquids since their formation emerges from only synthesizing the components by occurring hydrogen bondings (Satlewal et al., 2018).

Based on the above knowledge, the reusability of DES was investigated by cycling of the same leaching solution. As a result of experimental studies, it was determined that the copper extraction rates after each leaching step were 89.44%, 89.53% and, 78.65%, respectively. This study with promising results showed that DES (ChCl-2urea) can be reused at least three times in the process with low deviations. To this respect, it is labeled that the DES can be reused again for the leaching of the metals (Cu and Zn) from CCS as a spent electrolyte after the cleaning/purification stage (Fig. 6).

4. Conclusion

In this study, copper and zinc extraction from CCS was aimed by hydrometallurgical methods from CCS. For this purpose, a deep eutectic solvent which composed of choline chloride and urea mixture was used as a leaching agent which becomes attractive in recent years due to its environmental approach and interesting dissolving properties. According to chemical analyses, CCS included 44.3% Fe, 11.1% Si, 4.44% Cu, 3.39% Zn. As a result of mineralogical observation, $FeSiO_4$ and Fe_3O_4 was detected as major structures, and the CCS was also had copper-bearing structures such as metallic copper, matte copper, copper oxide, and a complex structure of Cu-Zn-S. By using ChCl-2urea mixture, approximately 90% of copper and 65% of zinc were extracted from CCS after 48 h of leaching while keeping the pulp density, reaction temperature and ChCl-2urea volume constant at 1/20 g/mL, 95 °C and 100 mL, respectively. The total copper recovery was determined as 63% after the

iron cementation as metallic copper form. The activation energy for copper and zinc recovery was calculated as 8.86 kJ.mol^{-1} and 14.48 kJ.mol^{-1}, respectively. In the light of these results, it can be expressed that copper and zinc can be extracted from CCS by using a deep eutectic solvent (ChCl-2urea) with very low iron dissolution.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2021.07.022.

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