

Article

Leaching of Copper Shaft Furnace Dust Using Deep Eutectic Solvents (DESs)

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Abstract

This study investigates the hydrometallurgical recovery of valuable metals from copper shaft furnace dust (SFD), a complex industrial waste containing approximately 40 wt.% Zn, 16 wt.% Pb, and 1 wt.% Cu. In contrast to conventional inorganic leaching processes that rely on aggressive acids and bases, this research explores the use of deep eutectic solvents (DESs) as eco-friendly and selective lixiviants. Deep eutectic solvents based on choline chloride combined with citric acid and lactic acid were evaluated as leaching media for metal recovery from SFD. The effects of temperature, leaching time, stirring intensity, and the DES:SFD ratio on metal extraction were systematically investigated. Analytical characterization of the raw material, leaching residues, and pregnant leach solutions was performed using Atomic Absorption Spectroscopy (AAS), X-ray Fluorescence Spectrometry (XRF), and Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS). The experimental results demonstrated efficient recovery of Zn, Pb, Cu, and Sn under mild leaching conditions. For the citric acid–choline chloride system, the highest extraction efficiency was obtained at 60 °C using a DES:SFD ratio of 30, whereas increasing the temperature to 70–80 °C did not significantly improve metal extraction. The lactic acid–choline chloride system exhibited different leaching behaviour, with the highest recoveries achieved after short leaching times. These findings indicate that DES-based systems represent a promising, sustainable alternative for the selective leaching of heavy metals such as Zn, Pb, Cu, and Sn, from metallurgical secondary raw materials, contributing to the development of greener circular economy practices.

Keywords: deep eutectic solvents; metals recovery; circular economy; leaching; dust; zinc



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1. Introduction

The strategic importance of copper has been growing in recent years, driven primarily by the energy transition, the electrification of transport, the development of renewable energy sources, and digitalization, as these sectors are characterized by high material intensity and a rising demand for primary copper resources [1,2]. In 2025, global copper mine production reached an estimated 23 million metric tons, while worldwide refined secondary copper production increased by 13.5 percent year-over-year to an estimated

5.3 million metric tons [3]. It is expected that copper production will continue to rise due to its irreplaceable role in modern information technologies and growing electromobility. Consequently, this increasing copper production will also lead to a higher generation of solid wastes, such as dusts and slags, which would pose a serious risk to the environment if left unvalorized [4,5]. Fine-grained solid metallurgical waste, such as dusts from pyrometallurgical copper or steel production, represents one of the most significant environmental challenges in the metallurgical industry [6,7]. These wastes represent a secondary source of valuable metals (Zn, Pb, and Sn), the efficient recovery of which requires the implementation of innovative and environmentally acceptable technological processes [8–10]. The processing of these dusts is technologically demanding. In hydrometallurgical treatment, leaching is the key step, and its efficiency is often limited by slow kinetics. Therefore, there is a growing need to intensify hydrometallurgical methods in order to increase metal recovery, accelerate leaching, and simultaneously reduce the energy and environmental intensity of processing oxidic materials [11,12].

One of the promising approaches in this field is Deep Eutectic Solvent (DES) extraction, which represents a modern and environmentally friendly method for recovering valuable components from both natural and industrial raw materials or wastes. DESs (Deep Eutectic Solvents), formed by mixing two or more components such as natural acids, sugars, or urea, create a mixture that exhibits a significantly lower melting point than its individual components, which is a consequence of strong intermolecular interactions between the constituent [13–15].

DES represent mixtures of components whose combination forms a liquid system with a melting point significantly lower than that of the individual pure substances. They are most commonly composed of a hydrogen bond acceptor (HBA), such as the organic salt choline chloride, and a hydrogen bond donor (HBD), which includes urea, citric acid, or other organic acids. The exact composition of the mixture at which the transition to the liquid phase occurs at the lowest temperature is referred to as the eutectic point Figure 1.

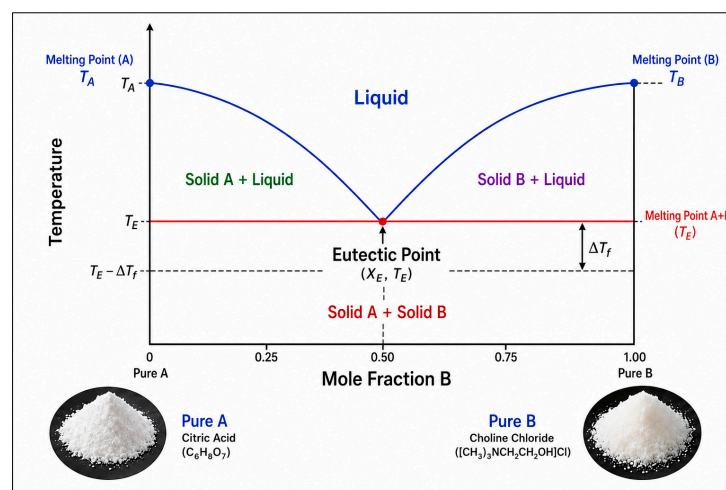


Figure 1. Eutectic phase diagram of the citric acid and choline chloride mixture.

This extreme decrease in the melting point in the diagram is caused by charge delocalization via hydrogen bonds between the chloride anion (Cl^-) of choline chloride (HBA) and the carboxylic groups ($-\text{COOH}$) of citric acid (HBD). This prevents the components from reforming a rigid crystal lattice.

The decrease in the melting point of eutectic solvents is primarily related to the formation of strong hydrogen bonds between the components, which disrupt the crystal structure of the starting substances [16,17]. Thanks to the ability to vary the type and ratio

of HBA and HBD, DES are highly customizable, which allows for tuning their physico-chemical properties and expands their application in catalytic, separation, electrochemical, and leaching processes [16,18]. The preparation of DES typically consists of mixing the HBA and HBD in a suitable molar ratio, optionally with the addition of a small amount of water. The mixture is then heated until it homogenizes and forms a stable liquid phase, which, with an appropriate composition, can remain stable even at room temperature as illustrated in Figure 2.

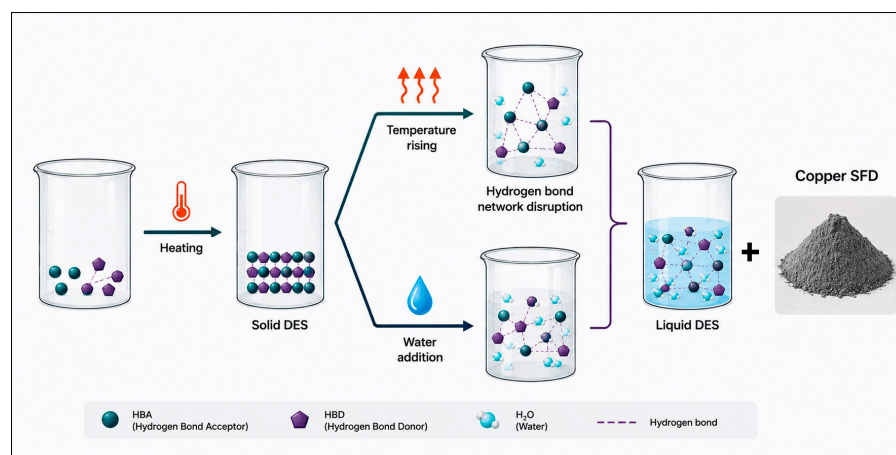


Figure 2. Preparation of DES by mixing the HBA and HBD in a suitable molar ratio.

Among the most commonly used components in the preparation of DES are choline chloride, urea, glucose, lactic acid, and various fatty acids [15,19].

The main advantages of DESs include high extraction efficiency, which makes it possible to increase the solubility and yield of various natural substances such as phenols, flavonoids, or polysaccharides. Another significant benefit is their low toxicity, biodegradability, and often their origin from renewable sources. Furthermore, DES contribute to the stabilization of extracted compounds, protecting them from degradation and allowing for the reuse of the solvent after its regeneration. A disadvantage can be the higher viscosity of some systems, which may complicate handling and reduce the extraction rate; however, this drawback can be partially eliminated by adding water or applying gentle heating. Another limitation remains the still insufficiently researched behavior of DES on an industrial scale, whereby their effective application requires thorough optimization of the composition depending on the specific extraction process [20,21].

DESs represent a promising alternative to conventional extraction media, mainly due to their low toxicity, favorable environmental profile, and the possibility of tailored modification of their properties. Their application in the processing of metal-bearing wastes proves to be efficient, particularly in the selective recovery of metals such as Zn, Pb, Cu, and Sn. For these reasons, DES can be considered a modern and promising tool in the field of sustainable processing of secondary raw materials, such as metallurgical dusts, slags, and other metal-bearing industrial wastes [22–24].

Table 1 summarizes representative studies on the application of deep eutectic solvents for the recovery of valuable metals from various primary and secondary raw materials. Although some of the investigated materials, such as waste printed circuit boards, differ significantly from copper shaft furnace dust in terms of composition and origin, these studies were included because they demonstrate the applicability of DES systems to the selective recovery of metals from complex metal-bearing matrices.

Table 1. Overview of studies on DESs applied in the leaching of metal-bearing raw materials.

Authors	Materials	Reagent	Conditions	Efficiency
Wang Ch. et al. [15]	Zn oxide dust	Ethylene glycol:urea (2:1)	T = 80 °C t = 12 h	85% Zn
	Goethite residues	ChCl:Levulinic acid (1:3)	T = 30 °C t = 2 h	65% Zn
	Blast furnace sludge	ChCl:malonic acid (1:1)	T = 60 °C t = 3 h	85% Zn
Zhao Q. et al. [25]	Mixture of metals	ChCl:glycolic acid (1:2)	T = 50 °C t = 2 h	90% Zn 87% Pb 17% Cu
	Second phase—precipitation	ChCl:oxalic acid (1:2)	T = 50 °C t = 8 h	75% Cu
	A mixture of metal oxides	ChCl:ethylene glycol (1:2)	T = 50 °C t = 8 h	<20% for most metals
Shakiba B. et al. [16]	Polymetallic sulfide concentrate	ChCl: p-toluenesulfonic acid (2:1)	T = 100 °C t = 72 h L:S 1:50 pH = 0.7	99% Pb 96.8% Zn 73% Au
Behnajady B. et al. [17]	Polymetallic sulfide concentrate	ChCl:NaPTS (1:1)	T = 100 °C t = 24 h DES:concentrate = 50 g/g	>90% Zn, Pb, Fe
		ChCl: maleic acid (1:1)	T = 100 °C t = 24 h	63% Zn 98% Pb
		ChCl: malonic acid (1:1):	T = 100 °C t = 24 h	44% Zn, almost 0% Fe
		ChCl:EG, glucose, urea	T = 100 °C t = 24 h	only 9–14% Zn
Li J. et al. [18]	Lead-contaminated soil	ChCl:oxalic acid (1:1) + 0.2 mol/L citric acid	Preparation of DES: T = 80 °C t = 3 h Leaching: T = 25 °C t = 2 h pH = 0.9 DES:soil 6:1	91% Pb
Rashid S.N. et al. [26]	Contaminated mangrove soil	ChCl: lactic acid (1:2)	pH = 1.43 a viscosity 140 cP T = 25 °C t = 3 h soil:DES 1:15 40% aqueous solution pH = 2.05 Viscosity 118 cP	97% Pb
		ChCl:levulinic acid	T = 25 °C t = 3 h soil:DES 1:10 60% aqueous solution	99% Pb
Huang K. et al. [27]	Lead-contaminated soil	ChCl: ethylene glycol (0.75:1)	T = 40 °C t = 2 h soil:liquid 1:6 DES:water 1:2	>95% Pb

The main objective of this study is to investigate the hydrometallurgical recovery of zinc, lead, and copper from complex industrial waste (copper shaft furnace dust) using eco-friendly Deep Eutectic Solvents (DESs). The research focuses on optimizing leaching conditions (temperature (60–80 °C), stirring, solid-to-liquid ratio) utilizing a choline chloride and citric acid mixture, followed by a detailed product analysis via AAS, XRF, and SEM-EDS.

The major novelty and significance of this work lie in ground-breaking replacement of aggressive inorganic acids and bases with a highly sustainable, eco-friendly, and environmentally compatible DES-based system designed for treating flue dust from copper production. This work delivers valuable original experimental data, demonstrating ex-

ceptional extraction efficiencies (up to 85.6% for Zn), and strongly confirms the powerful potential of multi-stage heavy metal recovery within a circular economy framework.

2. Materials and Methods

Chemical analysis of solid and liquid samples was performed using a combination of X-ray fluorescence spectrometry (XRF) (SPECTRO Analytical Instruments GmbH, Kleve, Germany) and atomic absorption spectroscopy AAS (iCE 3300 AA-ThermoFisher Scientific, Grand Island, NY, USA), depending on the elemental composition and detection requirements. Samples of CSF dust and produced precipitates were characterized by scanning electron microscope (SEM) (MIRA 3 FE-SEM TESCAN, Brno, Czech Republic) equipped with a high-resolution cathode (Schottky field emitter), a three-lens Wide Field Optics™ design, and an Energy-dispersive X-ray detector (EDX) (Oxford Instruments, Abingdon, UK). The redox potential (Eh) and pH were measured using an Orion Lab Star PH111 pH meter (Thermo Fisher Scientific, Waltham, MA, USA). Particle size analysis of the sample was performed using a Malvern Mastersizer 3000 laser diffraction analyzer (Malvern Instruments Ltd., Malvern, UK). Morphological analysis of the particles under magnification using a Dino-Lite ProAM413T optical microscope (AnMo Electronics Corporation, Hsinch, Taiwan) revealed that the sample consisted of two fractions—coarse and fine spherical grains—and that the larger grains were covered by smaller ones. The particle size range obtained from the particle size analysis (approximately 4–200 µm), together with the information that most particles were distributed within the 70–100 µm range (Figure 3d).

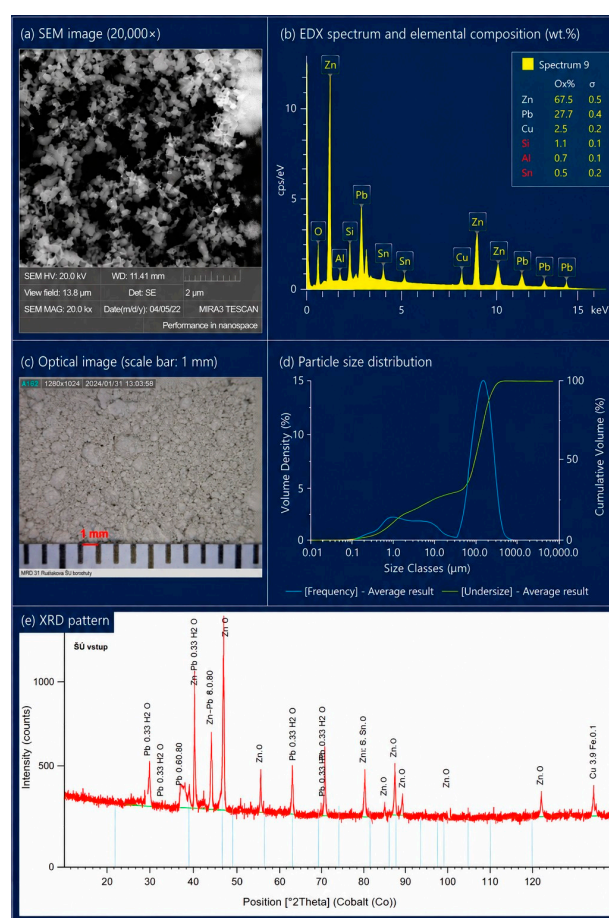


Figure 3. Characterization of the CSF dust sample: (a) SEM; (b) EDX; (c) particle morphology; (d) particle size analysis; (e) XRD analysis (The peak at position ≈ 70 on the x -axis is $\text{Pb}_{0.33}\cdot\text{H}_2\text{O}$).

Two types of deep eutectic solvents (DES), specifically citric acid (CA) and lactic acid (LA), both combined with choline chloride (ChCl), were used as leaching media in the leaching experiments. The preparation of the leaching medium was performed by mixing the respective acid with choline chloride in a ratio of 1 to 2.8. For the experiment itself, a total of 100 g of this mixture was prepared, corresponding to 33.3 g of citric acid or lactic acid and 66.6 g of choline chloride. To adjust the rheological properties and reduce the high viscosity inherent to DES, 10 milliliters of distilled water were added to the prepared medium. The addition of distilled water served to decrease the high viscosity of the DES system, thereby enhancing mass transfer and promoting efficient solid–liquid contact during the leaching process [28,29].

The leaching process itself was carried out under constant stirring at a speed of 400 rpm, ensuring sufficient contact between the phases. The process was conducted at a stable temperature of 60 °C for a duration of 60 min. Through these experiments, the effects of three key process parameters such as time, temperature, and the liquid-to-solid ratio on the overall extraction efficiency were systematically examined.

3. Results and Discussion

Characterization of the copper SFD sample is a fundamental requirement for developing an effective leaching process. In this subsection, the chemical composition, phase composition, and particle size distribution of the sample were analyzed to identify the content of individual metals. The results of the characterization serve as a reference point for determining the optimal conditions for DES leaching.

The copper SFD samples were subjected to chemical analysis using atomic absorption spectrometry (AAS); the average values and their standard deviations are shown in the table below (Table 2). The highest contents are Zn at 44.02% and Pb at 14.57%.

Table 2. Chemical analysis of copper SFD using AAS.

Element [wt.%]	Zn	Pb	Sn	Fe	Cu	Ni	Cl [−]	L.O.I.
Average	44.02	14.57	1.59	0.232	1.2	0.02	30.54	7.788
SD	5.642	1.791	0.04	0.024	0.081	4×10^{-3}	3.51	-
Variance	31.83	3.207	0.002	0.021	0.007	2×10^{-3}	12.37	-

A sample of the copper SFD was subjected to SEM analysis (Figure 3a), EDX analysis (Figure 3b), observation under an optical microscope (Figure 3c), particle size analysis (Figure 3d), and X-ray phase-qualitative diffraction analysis (Figure 3e). The X-ray analysis (Figure 3e) shows that Zn is present in the SFD as zinc oxide (ZnO), Sn is present as stannous oxide (SnO₂), and lead is present as lead oxide (PbO) and hydrated lead oxide (PbO·0.33 H₂O).

The morphology of the SFD sample was analyzed using SEM (Figure 3a), which indicated the presence of smaller particles, while EDX (Figure 3b) analysis identified the local elemental composition of zinc, lead, and copper. It should be noted that the elemental composition obtained by SEM–EDX represents only the selected analysed area and therefore differs from the bulk chemical composition determined by AAS (Table 2). These differences reflect the heterogeneous nature of the copper shaft furnace dust and the localized character of the SEM–EDX analysis. The particles are smaller than 1 µm and nearly spherical in shape.

The average particle size values are D10 = 4.09 µm, D50 = 69.0 µm, D80 = 96.4 µm, and D90 = 112 µm, with the maximum recorded particle size being 200 µm (Figure 3d). Based on the analysis results, a frequency plot of the particle size distribution and a cumulative sieve plot of the particle size distribution were constructed. The distribution graphs shown here indicate that the largest volume of particles is found in the 70–100 µm range, and most particles are smaller than 130 µm.

The leaching of copper SFD using DES represents an alternative method to the hydrometallurgical processing of this waste. The objective of this chapter is to evaluate the possibility of extracting selected metal components from copper SFD using a suitable extraction mixture and to assess its impact on the efficiency and selectivity of the process. This processing method can contribute to more efficient metal recovery and, at the same time, to the utilization of waste material with a high metal content.

The following part of the experiment examines the effect of parameters on the leaching of copper SFD using DES. The contact time between the solid and liquid phases is one of the key parameters that influences the amount of metal components leached into the solution and, consequently, the overall efficiency of the process. Therefore, studying the time dependence of leaching allows for a better understanding of the process kinetics and determining the time at which the most significant migration of metals into the leachate occurs. The effect of this parameter was investigated in a leaching medium consisting of a mixture of CA and ChCl at a temperature of 60 °C. Subsequently, the effect of temperature and leaching time was investigated in two DES leaching mixtures: a mixture of citric acid and choline chloride, and a mixture of lactic acid and choline chloride. Temperature is one of the key parameters that significantly influence the course of SFD copper leaching using DES. Increasing the temperature accelerates the kinetics of the process, which can lead to more intensive release of metal components into the solution and, consequently, to higher leaching efficiency. At the same time, temperature can also affect the selectivity of the process; therefore, optimizing the temperature is essential for obtaining the highest possible efficiency.

3.1. Leaching in Acid Citric

When leaching SFD using DES, the ratio of DES to the solid phase—or to the SFD—also has a significant role, as this parameter can significantly affect the rate of dissolution of metal components and the overall efficiency of the process. A change in the DES:SFD ratio is also related to the accessibility of the active components of the leaching system in contact with the solid matrix, and thus to the rate at which individual metals are released into the solution. This section therefore examines how different DES:SFD ratios affect the leaching process, metal recovery, and the system's behavior in an acidic environment. For this experiment, a mixture of citric acid and choline chloride was selected as the leaching medium.

Figure 4 shows that at lower DES:SFD ratios, there is a significant increase in the concentrations of both zinc and lead in the leachate. At a DES:SFD ratio of 30, the lowest concentration of both metals is obtained, while at a ratio of 10, their dissolution into the solution increases noticeably, with the most pronounced increase observed especially for zinc. Compared to Zn and Pb, Cu leaches only to a minimal amount and its concentration remains low throughout the experiment. The results show that a lower DES:SFD ratio promotes more efficient and effective leaching of SFD; however, technological problems occurred during the process. Since SFD is a hydrophobic material, agglomerates (small balls) formed even with continuous stirring, which reduced the specific surface area of the material and made the dissolution of metals into the solution more difficult and less efficient. This phenomenon did not occur at a DES:SFD ratio of 30. Therefore, this ratio was selected for further experiments.

Figure 5 shows the time dependence of SFD leaching in a mixture of citric acid and choline chloride at a temperature of 60 °C and a DES:SFD ratio of 30. The results indicate that the concentration of all studied metals increased over time, with a 100% recovery rate for all metals after 120 min. A chemical analysis of the initial sample reveals that Zn is the most represented metal in it. The results indicate that, under the given conditions, it is sufficient to leach the sample in a CA–ChCl mixture for 15 min, at which point the recovery

of Zn into the solution is 88%. Further extending the leaching time is ineffective in this case. Although the recovery is 96.3% after 60 min and 100% after 120 min, it is necessary to take into account the energy intensity of the process at elevated temperatures and under constant stirring.

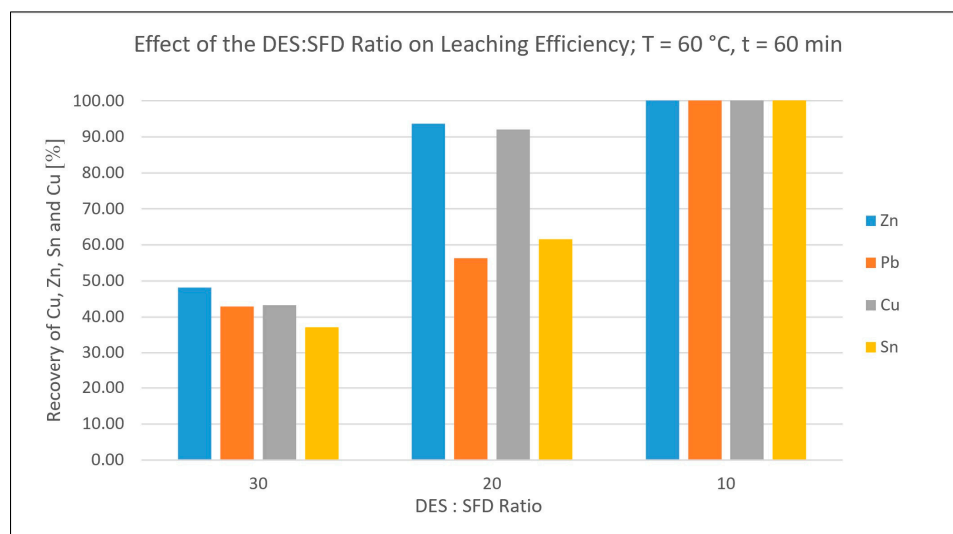


Figure 4. The effect of the DES:SFD ratio on leaching in citric acid at T = 60 °C. Data represent mean values of triplicate experiments (SD < 2%).

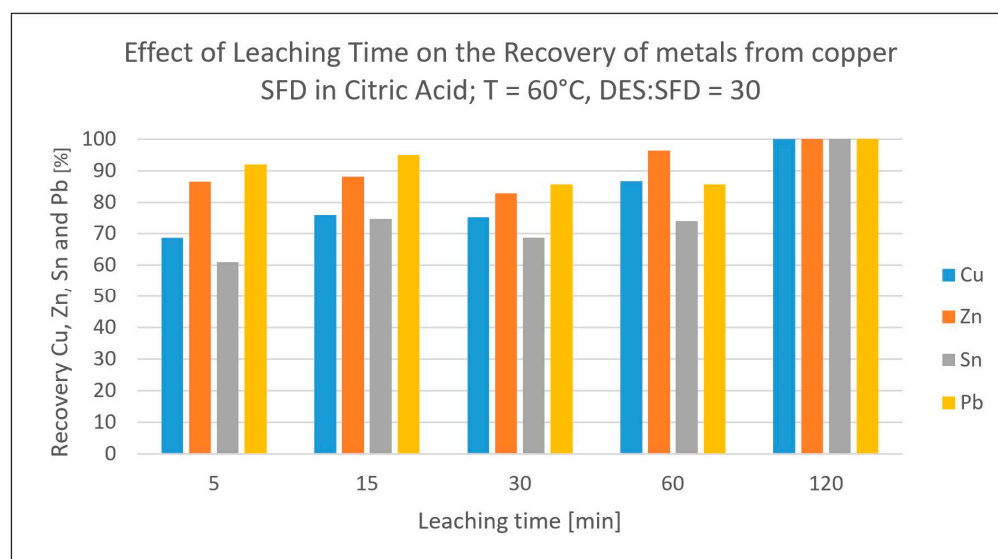


Figure 5. The effect of Leaching time on the Recovery of metals from copper SFD in Citric Acid at 60 °C. Data represent mean values of triplicate experiments (SD < 2%).

Figure 6 shows the dependence of recovery on temperature during the leaching of SFD in a mixture of citric acid and choline chloride for 30 min at a DES:SFD ratio of 30. The results indicate that temperature slightly increased the recovery of metals into the solution; however, the increase is not very significant. At 60 °C, the recovery rates were 37.6% for Cu, 41.4% for Zn, 34.3% for Sn, and 42.8% for Pb. At 70 °C, the recovery rates were 44.5% for Cu, 49.1% for Zn, 40.6% for Sn, and 51.4% for Pb. At 80 °C, the recovery rates were 49.3% for Cu, 50.8% for Zn, 64.5% for Sn, and 53.5% for Pb. The results suggest that the increase in temperature had the greatest effect on Sn recovery into the solution; however, the recoveries of the other metals increased by a maximum of 12% for Cu, 9% for Zn, and

10% for Pb, with recoveries hovering around 50% for all metals. Therefore, increasing the energy intensity of the process for the CA–ChCl mixture is ineffective.

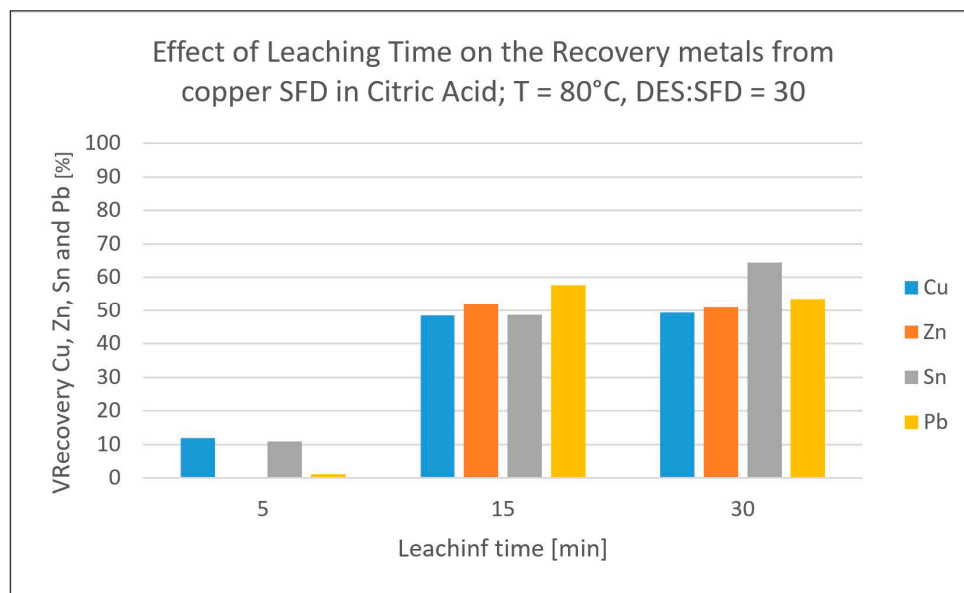


Figure 6. Effect of temperature on the leaching of Copper SFD in a mixture of citric acid and choline chloride after 30 min. Data represent mean values of triplicate experiments (SD < 2%).

Figure 7 shows the dependence of recovery on time at an increased temperature of 70 °C during the leaching of SFD in a mixture of citric acid and choline chloride at a DES:SFD ratio of 30. The results indicate that the temperature slightly increased the recovery of metals into the solution; however, the increase is negligible. At 70 °C, the recoveries after 5 min were up to 43% for Cu, Zn, and Sn, and up to 50% for Pb; after 30 min, the recoveries ranged from 40–50% for all metals. Based on the obtained results, it appears that the increase in temperature did not have a significant effect on the leaching of metals into the solution. This means that increasing the energy demand of the process for the CA–ChCl mixture is also ineffective.

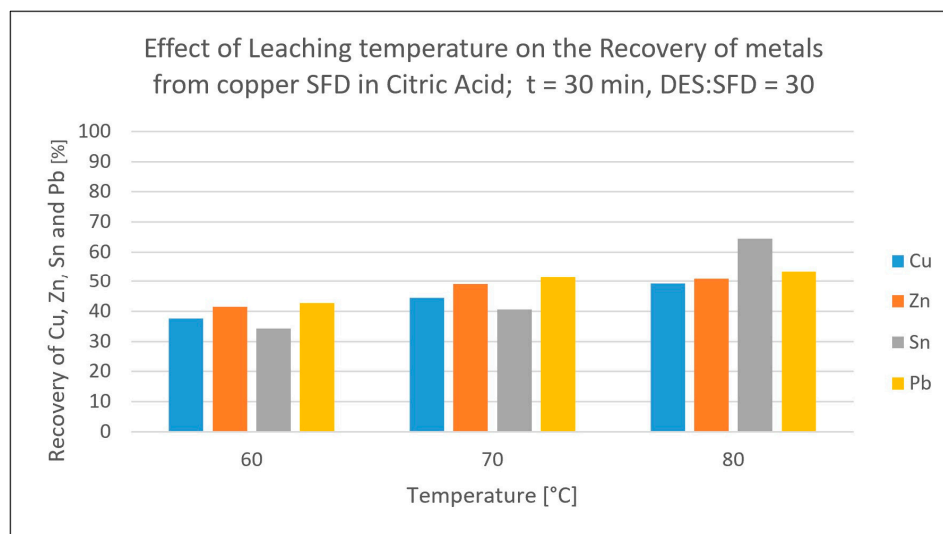


Figure 7. The effect of time on the leaching of SFD in a mixture of citric acid and choline chloride at 70 °C. Data represent mean values of triplicate experiments (SD < 2%).

Figure 8 shows the dependence of recovery on time at an elevated temperature of 80 °C during SFD leaching in a mixture of citric acid and choline chloride at a DES:SFD ratio

of 30. The results indicate that the temperature did not increase the recovery of metals into the solution. At 80 °C, the recoveries after 5 min were up to 10% for Cu and Sn and <1% for Zn and Pb, and after 30 min, the recoveries ranged from 50–65% for all metals. The results indicate that increasing the temperature had only a limited effect on the leaching of metals into the solution. Although elevated temperature generally enhances leaching kinetics, deep eutectic solvent systems may exhibit more complex behaviour than conventional aqueous leaching systems. Possible factors include changes in solvent structure, hydrogen-bond interactions, viscosity, and the stability of metal–ligand complexes, which may influence the overall extraction efficiency. Since these phenomena were not directly investigated in the present study, the proposed explanation should be regarded as a possible interpretation and requires further experimental verification. Therefore, increasing the energy consumption of the process in the case of the CA–ChCl mixture is also ineffective.

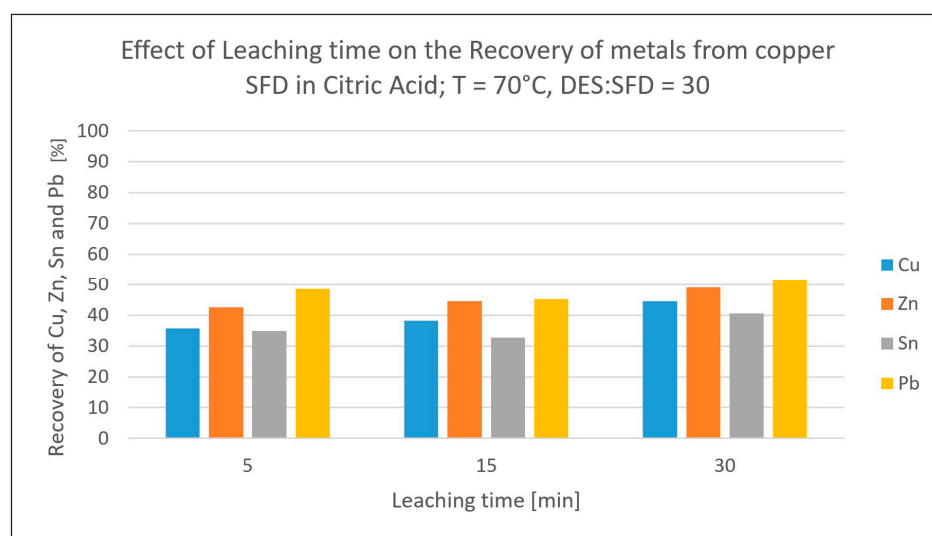


Figure 8. The effect of time on the leaching of SFD in a mixture of citric acid and choline chloride at 80 °C. Data represent mean values of triplicate experiments (SD < 2%).

3.2. Leaching in Lactic Acid

Figure 9 shows the time dependence of the leaching of SFD in a mixture of lactic acid and choline chloride at a temperature of 60 °C and a DES:SFD ratio of 30. The results indicate that the concentration of all monitored metals decreased over time; after 5 min, the recovery rates were 68.7% for Cu, Zn 61.4%, Sn 46.8%, and Pb 55.5%. After 120 min, the recovery rates were 53% for Cu, 51.9% for Zn, 75.6% for Sn, and 51.7% for Pb. The results indicate that, under the given conditions, it is sufficient to leach SFD in a mixture of LA–ChCl for 5 min, at which point the recovery of metals into the solution is highest. Further extension of the leaching time is ineffective in this case, as the recovery of metals decreases.

Figure 10 shows the dependence of recovery on temperature during the leaching of SFD in a mixture of lactic acid and choline chloride for 30 min at a DES:SFD ratio of 30. The results indicate that temperature slightly increased the recovery of metals into the solution; however, the increase is negligible. At 60 °C, the recovery rates were 53.7% for Cu, 54.9% for Zn, 49.3% for Sn, and 56.0% for Pb. At 70 °C, the recovery rates were 57.1% for Cu, 55.4% for Zn, 74.2% for Sn, and 52.9% for Pb. At 80 °C, the recovery rates were 56.1% for Cu, 54.9% for Zn, 76.1% for Sn, and 50.4% for Pb. The results suggest that temperature had the greatest influence on Sn recovery into the solution; however, the recovery rates of the other metals increased by a maximum of 2.5% for Cu, 0% for Zn, and resulted in a 6% decrease in Pb recovery, with recovery rates ranging up to 60% for all metals. Therefore,

increasing the energy consumption of the process in the case of the LA–ChCl mixture is also ineffective.

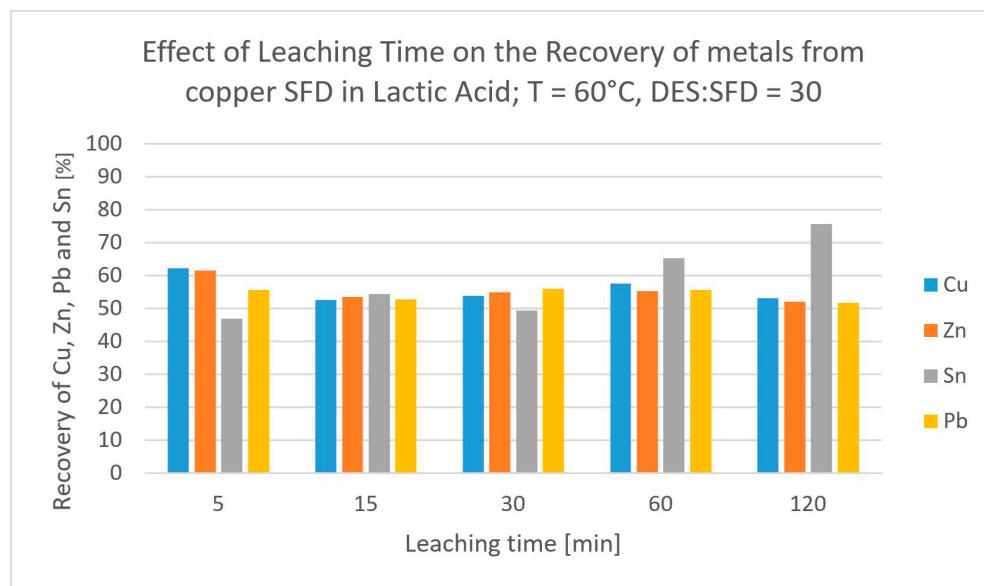


Figure 9. The effect of leaching time on the leaching of SFD in a mixture of lactic acid and choline chloride at 60 °C. Data represent mean values of triplicate experiments (SD < 2%).

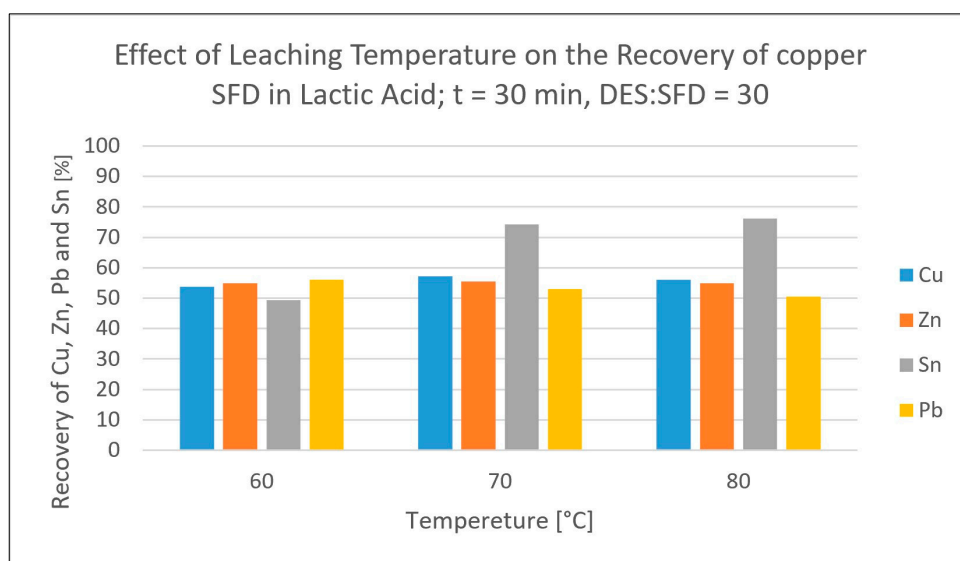


Figure 10. The effect of temperature on the leaching of SFD in a mixture of lactic acid and choline chloride after 30 min. Data represent mean values of triplicate experiments (SD < 2%).

Figure 11 shows the dependence of recovery on time at an elevated temperature of 70 °C during the leaching of SFD in a mixture of lactic acid and choline chloride at a DES:SFD ratio of 30. The results indicate that the temperature did not increase the recovery of metals into the solution. At 70 °C, the recoveries after 5 min were up to 60% for Cu, Zn, Sn, and Pb, and after 30 min, the recoveries ranged from 50–60% for all metals. The results indicate that increasing the temperature had no significant effect on the leaching of metals into the solution. Therefore, increasing the energy consumption of the process in the case of the LA–ChCl mixture is also ineffective.

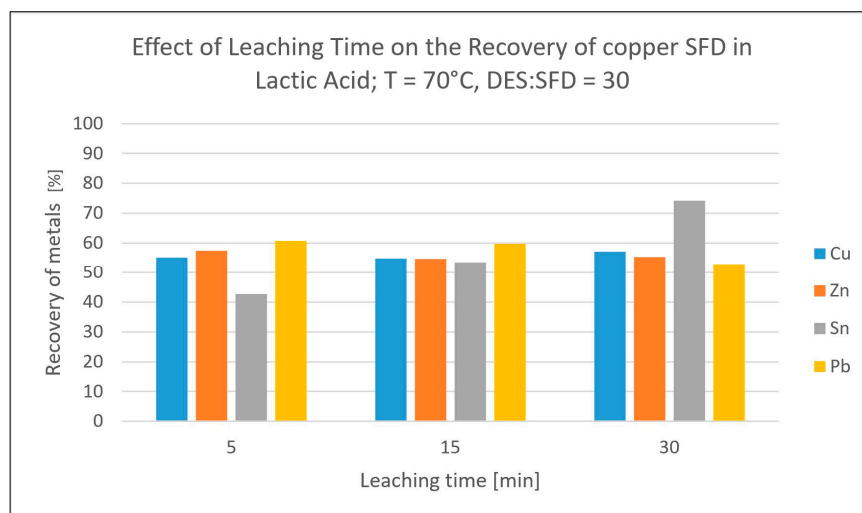


Figure 11. The effect of time on the leaching of SFD in a mixture of lactic acid and choline chloride at 70 °C. Data represent mean values of triplicate experiments (SD < 2%).

Figure 12 shows the dependence of recovery on time at an elevated temperature of 80 °C during the leaching of SFD in a mixture of lactic acid and choline chloride at a DES:SFD ratio of 30. The results indicate that the temperature did not increase the recovery of metals into the solution. At 80 °C, the recoveries after 5 min ranged from 56 to 63% for all metals. After 30 min, the recoveries ranged from 51–57% for Cu, Zn, and Pb, and 76% for Sn. The results indicate that increasing the temperature had no significant effect on the leaching of metals into the solution. Therefore, increasing the energy consumption of the process in the case of the LA–ChCl mixture is also ineffective.

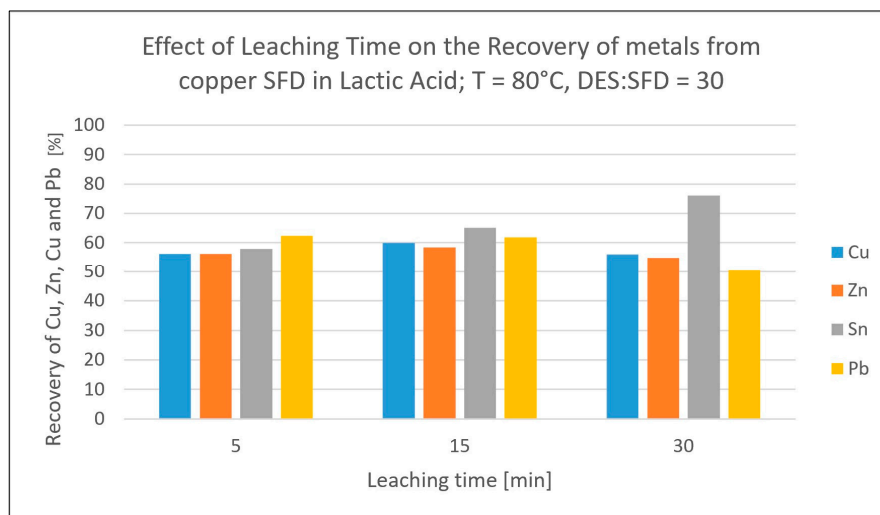
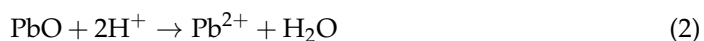


Figure 12. The effect of time on the leaching of SFD in a mixture of lactic acid and choline chloride at 80 °C. Data represent mean values of triplicate experiments (SD < 2%).

A possible leaching mechanism of copper SFD containing zinc and lead oxides using a deep eutectic solvent (DES) prepared from choline chloride (ChCl) and citric acid (H₃Cit) is proposed. This solvent may serve simultaneously as an environmentally friendly solvent, a source of protons, and a complexing agent. During the leaching process, citric acid provides the dissolution of metal oxides through acid-base reactions according to Equations (1) and (2):





In the DES environment, citric acid undergoes gradual deprotonation to form citrate species capable of binding metal ions, as shown in Equations (3)–(5):



where the citrate anion has the structure shown in Equation (6):



and functions as a multidentate ligand. The released metal cations may subsequently be stabilized by the formation of soluble citrate complexes (Equations (7) and (8)):



The result of leaching is not the formation of a single, precisely defined chemical compound, but rather a DES-type liquid phase containing dissolved metal complexes. The overall process can be schematically represented as follows (9) and (10):



↓



The insoluble residue may contain low-solubility mineral phases, such as iron oxides, silicates, or other impurities present in copper SFD. The resulting liquid phase is a DES based on choline chloride and citric acid, enriched with zinc and lead ions, with the extracted metals stabilized in the system primarily in the form of citrate complexes. This proposed mechanism provides a possible explanation for the DES's high ability to dissolve and simultaneously stabilize metallic components originating from the oxide phase of metallurgical waste. By stabilizing ionic species, DES promotes higher leaching selectivity during metal extraction [30]. The hypothesized reaction mechanism is based on published findings on citrate–metal complexation and was not directly verified by spectroscopic methods in this study. Theoretical schematic of copper SFD leaching in DES is shown in Figure 13.

The leaching of copper SFD using DES has been confirmed as a prospective alternative approach to the hydrometallurgical processing of this type of waste. Based on the experiments, it can be concluded that the process efficiency was significantly influenced by the leaching medium used, the DES:SFD ratio, the leaching time, and the temperature, with different system behaviors observed for the CA–ChCl and LA–ChCl mixtures.

When leaching in a mixture of citric acid and choline chloride, a DES:SFD ratio of 30 proved to be the most suitable, as lower ratios led to the formation of agglomerates and, consequently, to a reduction in the dissolution of metals into the solution. In terms of time, a 15 min leaching period proved sufficient, and further prolonging the contact time did not result in a significant improvement in efficiency. Although raising the temperature to 70–80 °C in this system slightly increased extraction, the energy consumption of the process surpassed the achieved effect; therefore, this approach does not appear to be optimal.

In the case of a mixture of lactic acid and choline chloride, the leaching profile was different, with the highest efficiency being achieved after just 5 min, and further prolonging the leaching time led to a decrease in metal recovery. Here, as well, the increase in temperature from 60 °C to 80 °C had only a limited effect, confirming that increasing the energy consumption of the process does not provide an appropriate technological benefit. Overall, it can therefore be concluded that DES represent an effective medium for processing copper SFD; however, precise optimization of individual process parameters, such as leaching temperature, contact time, and the DES:SFD ratio is essential to achieve the desired efficiency and selectivity.

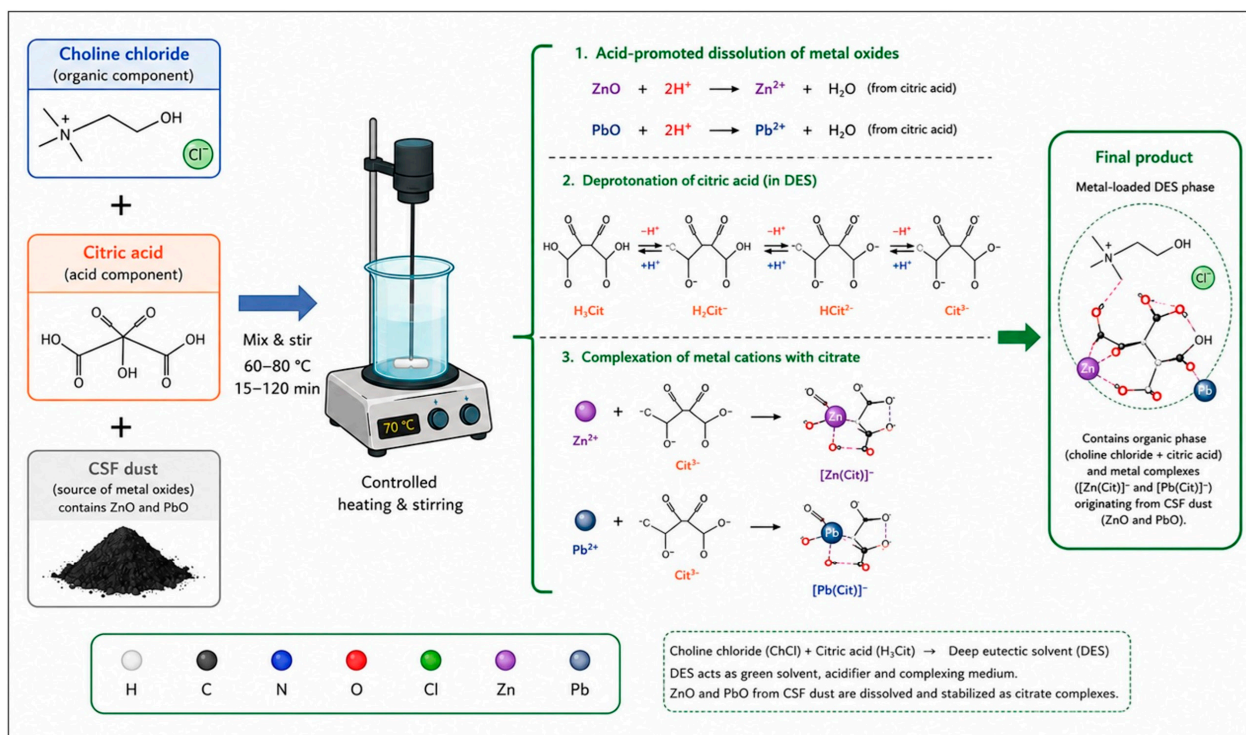


Figure 13. Theoretical schematic of copper SFD leaching in DES.

4. Conclusions

This research investigated the feasibility of utilizing deep eutectic solvents (DES) for the leaching of copper shaft furnace dust to recover valuable metals and valorize this secondary raw material source. Sample characterization confirmed a high content of zinc (44.02 wt.%) and lead (14.57 wt.%), with the dominant phases being zinc oxide (ZnO), lead oxide (PbO), hydrated lead oxide, and tin dioxide (SnO₂).

Experimental results indicated that leaching efficiency is influenced by DES composition, contact time, temperature, and the liquid-to-solid ratio. For the citric acid and choline chloride (CA–ChCl) system, a DES:dust ratio of 30 proved to be optimal, achieving high zinc recovery after just 15 min of leaching at 60 °C. Although extending the leaching time led to a further increase in yield, it came at the expense of higher energy consumption of the process.

In the case of the lactic acid–choline chloride (LA–ChCl) system, the highest recoveries were achieved after only 5 min of leaching, whereas further extension of the process led to a decrease in metal concentration in the leachate. Increasing the temperature to 70 °C and 80 °C had only a limited effect on metal recovery in both investigated systems and was therefore not justified from both technological and economic standpoints.

Based on the obtained results, deep eutectic solvents represent a promising and environmentally acceptable alternative for the hydrometallurgical processing of metallurgical waste. Compared with conventional inorganic leaching systems, DESs offer the potential for more selective metal extraction while reducing the use of aggressive mineral acids. DESs achieve high selectivity through the formation of specific metal complexes. This significantly simplifies downstream metal separation from the leachate, making DESs a more efficient and environmentally friendly alternative [15,31]. Their utilization enables efficient metal recovery from shaft furnace dust under relatively mild process conditions, while simultaneously contributing to the reduction in the environmental burden associated with the disposal of these wastes. However, further optimization of process parameters, as well as a more detailed study of the dissolution mechanisms and subsequent separation of individual metals, is essential for industrial application. The results of this work indicate the potential of DES as a modern tool for the sustainable processing of secondary raw material sources and support further research into their application in the field of metal-bearing waste recycling.

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References

1. Podobińska-Staniec, M.; Wiktor-Sułkowska, A.; Kuśtra, A.; Lorenc-Szot, S. Copper as a Critical Resource in the Energy Transition. *Energies* **2025**, *18*, 969. [CrossRef]
2. Seck, G.S.; Hache, E.; Bonnet, C.; Simoën, M.; Carcanague, S. Copper at the crossroads: Assessment of the interactions between low-carbon energy transition and supply limitations. *Resour. Conserv. Recycl.* **2020**, *163*, 105072. [CrossRef] [PubMed]
3. Doris Dokua Sasu Copper Mine Production Worldwide 2010–2025. Available online: <https://www.statista.com/statistics/254839/copper-production-by-country/> (accessed on 18 June 2026).
4. Tian, H.; Guo, Z.; Pan, J.; Zhu, D.; Yang, C.; Xue, Y.; Li, S.; Wang, D. Comprehensive review on metallurgical recycling and cleaning of copper slag. *Resour. Conserv. Recycl.* **2021**, *168*, 105366. [CrossRef]
5. Yang, F.; Wu, Y.; Zhang, Q. Towards resource regeneration: A focus on copper recovery from electronic waste. *J. Clean. Prod.* **2024**, *484*, 144286. [CrossRef]
6. Orac, D.; Laubertova, M.; Pirošková, J.; Klein, D.; Bures, R.; Klimko, J. Characterization of dusts from secondary copper production. *J. Min. Metall. Sect. B Metall.* **2020**, *56*, 221–228. [CrossRef]
7. Gao, W.; Xu, B.; Yang, J.; Yang, Y.; Li, Q.; Zhang, B.; Liu, G.; Ma, Y.; Jiang, T. Comprehensive recovery of valuable metals from copper smelting open-circuit dust with a clean and economical hydrometallurgical process. *Chem. Eng. J.* **2021**, *424*, 130411. [CrossRef]
8. Oráč, D.; Klimko, J.; Klein, D.; Pirošková, J.; Liptai, P.; Vindt, T.; Miškufová, A. Hydrometallurgical recycling of copper anode furnace dust for a complete recovery of metal values. *Metals* **2022**, *12*, 36. [CrossRef]

9. Znamenáčková, I.; Dolinská, S.; Hredzák, S.; Briančin, J.; Kožárová, V. Possibilities of Obtaining Zinc from Steel Making Wastes and Galvanizing Using Microwave Energy. *Inz. Miner.* **2025**, *3*, 1–5. [\[CrossRef\]](#)
10. Laubertova, M.; Havlik, T.; Parilak, L.; Derin, B.; Trpcevska, J. The effects of microwave-assisted leaching on the treatment of electric arc furnace dusts (EAFD). *Arch. Metall. Mater.* **2020**, *65*, 321–328. [\[CrossRef\]](#)
11. Havlik, T. *Hydrometallurgy: Principles and Application. Chapter 12—Leaching of Copper Sulphides*, 1st ed.; Woodhead Publishing Series in Metals and Surface Engineering; Woodhead Publishing Limited: Cambridge, UK, 2008; ISBN 978-1-84569-407-4.
12. Matkarimov, S.T. Hydrometallurgical Processing of Copper-Smelting Dust. *Int. J. Emerg. Trends Eng. Res.* **2020**, *8*, 3088–3094. [\[CrossRef\]](#)
13. Zhang, Q.; De Oliveira Vigier, K.; Royer, S.; Jérôme, F. Deep eutectic solvents: Syntheses, properties and applications. *Chem. Soc. Rev.* **2012**, *41*, 7108–7146. [\[CrossRef\]](#)
14. Qin, H.; Hu, X.; Wang, J.; Cheng, H.; Chen, L.; Qi, Z. Overview of acidic deep eutectic solvents on synthesis, properties and applications. *Green Energy Environ.* **2020**, *5*, 8–21. [\[CrossRef\]](#)
15. Wang, C.; Zhou, Z.; Zhang, X.; Guo, H.; Boczkaj, G. Metal extraction using deep eutectic solvents for metal recovery and environmental remediation—A review. *Sep. Purif. Technol.* **2025**, *364*, 132533. [\[CrossRef\]](#)
16. Shakiba, G.; Abdollahi, H.; Gharabaghi, M.; Mahroomi, M.; Kiani, F. High performance-green extraction of base metals (Zn and Pb) and gold from polymetallic sulfide concentrate using p-toluenesulfonic acid-based deep eutectic solvents. *Sep. Purif. Technol.* **2025**, *373*, 133538. [\[CrossRef\]](#)
17. Behnajady, B.; Karimi, S.; Hoseinpour, H. Leaching of sphalerite concentrate by Binary deep eutectic solvents based on choline chloride with MD and DFT insights. *Miner. Eng.* **2026**, *241*, 110162. [\[CrossRef\]](#)
18. Li, J.; Li, S.; Chen, C.; Kan, R.; Li, F.; Li, Y. Ternary deep eutectic solvent combining Ch-O and citric acid for lead leaching from contaminated soil: Optimization, kinetics, and mechanism. *Colloids Surf. A Physicochem. Eng. Asp.* **2026**, *738*, 140029. [\[CrossRef\]](#)
19. Sudová, M.; Sisol, M.; Kanuchova, M.; Marcin, M.; Kurty, J. Environmentally Friendly Leaching of Antimony from Mining Residues Using Deep Eutectic Solvents: Optimization and Sustainable Extraction Strategies. *Processes* **2024**, *12*, 555. [\[CrossRef\]](#)
20. Panić, M.; Damjanović, A.; Radošević, K.; Cvjetko Bubalo, M.; Dujmić, F.; Škegro, M.; Radojčić Redovniković, I.; Brnčić, M. Enhanced Preparative-Scale Extraction from Graševina Grape Pomace Using Ultrasound-Assisted Extraction and Natural Deep Eutectic Solvents. *Appl. Sci.* **2024**, *14*, 6185. [\[CrossRef\]](#)
21. Dai, Y.; Witkamp, G.J.; Verpoorte, R.; Choi, Y.H. Tailoring properties of natural deep eutectic solvents with water to facilitate their applications. *Food Chem.* **2015**, *187*, 14–19. [\[CrossRef\]](#) [\[PubMed\]](#)
22. Nowińska, K.; Kokowska-Pawłowska, M. Mineralogy of Zinc and Lead Metallurgical Slags in Terms of Their Impact on the Environment: A Review. *Minerals* **2024**, *14*, 852. [\[CrossRef\]](#)
23. Iluțiu-Varvara, D.A.; Aciu, C. Metallurgical Wastes as Resources for Sustainability of the Steel Industry. *Sustainability* **2022**, *14*, 5488. [\[CrossRef\]](#)
24. Sarfo, P.; Das, A.; Wyss, G.; Young, C. Recovery of metal values from copper slag and reuse of residual secondary slag. *Waste Manag.* **2017**, *70*, 272–281. [\[CrossRef\]](#) [\[PubMed\]](#)
25. Zhao, Q.; Ma, S.; Ho, W.; Wang, Y.; Ho, J.Y.T.; Shih, K. Simple and environmentally friendly metal recovery from waste printed circuit boards by using deep eutectic solvents. *J. Clean. Prod.* **2023**, *421*, 138508. [\[CrossRef\]](#)
26. Rashid, S.N.; Hizaddin, H.F.; Hayyan, A.; Hasikin, K.; Abdul Razak, S.; Mokhtar, M.I.; Azizan, M.M. Deep eutectic solvents for the removal of lead contaminants in mangrove soil. *J. Environ. Chem. Eng.* **2022**, *10*, 107264. [\[CrossRef\]](#)
27. Huang, K.; Shen, Y.; Wang, X.; Song, X.; Yuan, W.; Xie, J.; Wang, S.; Bai, J.; Wang, J. Choline-based deep eutectic solvent combined with EDTA-2Na as novel soil washing agent for lead removal in contaminated soil. *Chemosphere* **2021**, *279*, 130568. [\[CrossRef\]](#) [\[PubMed\]](#)
28. Wu, J.D.; Ding, Y.; Zhu, F.; Gu, Y.; Wang, W.W.; Sun, L.; Mao, B.W.; Yan, J.W. The Role of Water Content of Deep Eutectic Solvent Ethaline in the Anodic Process of Gold Electrode. *Molecules* **2023**, *28*, 2300. [\[CrossRef\]](#) [\[PubMed\]](#)
29. Vilková, M.; Płotka-Wasyłka, J.; Andruch, V. The role of water in deep eutectic solvent-base extraction. *J. Mol. Liq.* **2020**, *304*, 112747. [\[CrossRef\]](#)
30. Smith, E.L.; Abbott, A.P.; Ryder, K.S. Deep Eutectic Solvents (DESs) and Their Applications. *Chem. Rev.* **2014**, *114*, 11060–11082. [\[CrossRef\]](#) [\[PubMed\]](#)
31. Heathcote, R.; Nash, W.; Graf, A.; Hudson-Edwards, K.A.; Crane, R. Selective leaching of Cu and Co from stratiform sediment-hosted copper ore using deep eutectic solvents. *Miner. Eng.* **2026**, *237*, 109990. [\[CrossRef\]](#)

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