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## Selective recovery of zinc from zinc oxide dust using choline chloride based deep eutectic solvents

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Abstract: Deep eutectic solvents (DESs) are a kind of potential lixiviant for selective metal processing due to their versatile complexation properties. In this study, we investigated the recovery of zinc from zinc oxide dust using choline chloride–urea–ethylene glycol (ChCl–urea–EG) DESs. The zinc extraction efficiency can be up to 85.2% when the slurry concentration is 50 g/L, leaching temperature is 80 °C and stirring speed is 600 r/min. The leaching process is controlled by the diffusion and the corresponding activation energy is 32.1 kJ/mol. The resultant solution was directly used for the electrodeposition of zinc. The pure zinc deposit is obtained with a current efficiency of 82.6%. Furthermore, the ChCl–urea–EG DESs can be recycled. This approach is shown to be promising for the recycling of zinc from the zinc-containing dust.

Key words: deep eutectic solvent; selective leaching; zinc oxide dust; zinc; direct electrodeposition

## **1** Introduction

Zinc is an important nonferrous metal required for wide application in the alloy production and galvanization industries [1]. At present, zinc is mainly produced from zinc sulfide minerals. However, with the depletion of these sulfide ores, more and more attention has been paid to the recovery of zinc from various secondary resources, including flue dusts, dross, zinc ash and residue, which are generated in various metallurgical industries [2–5]. A significant amount of zinc oxide dusts are produced during the smelting of zinc, lead and copper. The zinc oxide dusts are of great recycling value because they contain high contents of zinc, lead, copper, etc [6-11]. Currently, sulfuric acid leaching has been the main process for the industrial recycling of zinc oxide dust [12]. However, this process has the disadvantages of high acid consumption and complicated purification procedures. In addition, the zinc oxide dust usually contains chloride and fluoride impurities. During the

leaching process, the chloride will enter solution and is seriously harmful to the subsequent zinc electrodeposition [6]. In general, chloride and fluoride must be removed before leaching. Therefore, it is particularly important to develop a simple and efficient method to recover zinc without complex purification steps and removal of chloride and fluoride.

Recently, deep eutectic solvents (DESs), which are a unique class of multicomponent solvent systems formed through hydrogen bond interactions, have been developed as a king of promising medium for replacing traditional solvents [13–15]. Due to their excellent properties such as low melting points, nontoxicity, high ion conductivity, distinct dissolution capability to metal oxides, low cost and easy to prepare, DESs have been applied in organic synthesis [16], electrochemistry [17], dissolution and extraction process [18–22]. Additionally, ABBOTT et al [23,24] found that DESs can dissolve valuable metal oxides, such as PbO, Cu<sub>2</sub>O and ZnO, but are unable to dissolve gangue ingredients including CaO, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, etc. On this basis, DESs have been used to

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selectively extract metals from oxide mixtures and complex compound [25], e.g. Zn from electric furnace dust [26], and gold from electrum ore [27]. The results show that DESs can selectively extract 35 wt.% of Zn present in the electric furnace dust at 60 °C, and dissolve electrum, galena, chalcopyrite and tellurobismuthite by oxidizing with iodine at low temperatures. But so far, there is no report on the recycling zinc oxide dust containing fluoride and chloride impurities with DESs. The phase composition of zinc oxide dust is different from that of electric furnace dust or electrum ore, resulting in their different dissolution behaviors in DESs. Besides, few studies involve the dissolution kinetics and influencing factors in the process of leaching the dust and ore with DESs.

In this study, a deep eutectic solvent choline chloride–urea–ethylene glycol (ChCl–urea–EG) was used to recover zinc from zinc oxide dust by selective leaching and direct electrowinning. The impact factors and the kinetic of leaching were investigated. The goal is to develop a simple method for the recovery of zinc from zinc oxide dust. The process effectively avoids complex purification processes and pretreatment for the removal of fluoride and chloride, which will significantly reduce the cost of utilizing or recycling zinc oxide dust.

#### **2** Experimental

#### 2.1 Zinc oxide dust samples

The zinc oxide dust used in this study was obtained from the zinc plant located at Qujing, Yunnan, China, and the contents of chloride and fluoride are high. The zinc oxide dust sample was dried in an oven at 105 °C to remove the moisture content. Table 1 shows the chemical compositions of zinc oxide dust and typical leaching residues.

 Table 1 Chemical compositions of zinc oxide dust and typical leaching residues (wt.%)

Sample	Zn	Pb	Fe	Al	Ca	Si	S	Cl	F
Zinc oxide dust	45.69	8.02	7.96	1.73	1.68	2.28	4.32	0.28	<0.01
Leaching residue	13.14	15.52	15.41	3.34	3.25	4.39	8.36	_	_

#### 2.2 Synthesis of deep eutectic solvent

The ChCl-urea-EG DESs were synthesized by mixing ChCl, urea and EG with a molar ratio of 2:4:1 at 353 K until a homogeneous, colorless liquid formed.

#### 2.3 Leaching tests

All leaching experiments were carried out in a conical flask using a magnetic stirrer with heating (RET Basic) to stir and heat the samples. The leaching

experiment was conducted under different stirring speeds (200-800 r/min) using the ChCl-urea-EG DESs (500 mL) as leaching agent with various slurry concentrations (25-200 g/L) in the temperature range of 60-90 °C.

The zinc contents of leaching solution and residues were analyzed quantitatively by EDTA titration method. The concentrations of lead, iron, aluminum and calcium in the leaching solution were determined by an inductively coupled plasma atomic emission spectrometry (ICP–AES, JY Ultima 2). Leaching residues were analyzed using an X-ray diffractometer (Rigaku Ultima+ D/MAX–2200). The contents of zinc, lead, iron, sulfur, aluminum, calcium and silicon in leaching residues were determined using an atomic absorption spectrometer (Hitachi Z–2310).

#### 2.4 Zinc electrowinning

Zinc electrowinning experiment was performed in a 500 mL plexiglass cell. A stainless steel sheet (4 cm  $\times$  5 cm) and a graphite sheet (4 cm  $\times$  5 cm) were used as the cathode and anode, respectively. The inter-electrode distance was 2.0 cm. The electrodeposition was conducted in leaching solution at a cell voltage of 2.0 V and a temperature of 343 K for different time. After electrodeposition, the cathode was removed from the electrolytic cell and thoroughly cleaned with ethanol. Zinc deposit was examined by SEM and EDS (XL 30 ESEM TMP model). Zinc concentration in the leach liquor was determined using EDTA complexometric titration and ICP–AES (JY Ultima 2).

#### **3** Results and discussion

#### 3.1 Chemistry mechanism of dust dissolution

The zinc oxide dust (25 mg) was added into the ChCl-urea-EG DESs (500 mL), and the suspension solution was stirred at 80 °C for 48 h. As a result, the concentration of zinc in the leaching solution is up to 19.4 g/L, while impurity metals (such as Fe, Ca, Al or Si) are in negligible concentrations (<10 mg/L). This indicates that the selective leaching of zinc from zinc oxide dust can be achieved.

ZnO is found to have the highest solubility and to put this into context, the solubility in a NaCl–KCl molten salt is about  $28 \times 10^{-6}$ . The high solubility of ZnO in DESs is due to its ability to complex with urea (or EG), thus increasing its size and interaction with the solvent. Such an interaction is absent in the hightemperature molten salts. For investigating the existence form of the ZnO in ChCl–urea–EG DESs, electrospray mass spectrometry (MS) measurement of leaching solution in the negative ion mode was performed, and the results are shown in Fig. 1. A group of signals at m/z values of 174, 176, and 178 with an isotope pattern are in accordance with the formula [ZnO·ureaCl]<sup>-</sup>, which is analogous to that of ZnO dissolved in ChCl–urea and BMIC–urea DESs [24,28]. No other zinc-containing clusters are observed using this technique. Hence, it can be concluded that the dissolution of zinc oxide in ChCl–urea–EG DESs is the result of the formation of [ZnO·ureaCl]<sup>-</sup> complexes between zinc oxide and ligand urea with chloride as well.

The primary mineral phases of zinc oxide dust are zinc oxide (ZnO), hematite (Fe<sub>2</sub>O<sub>3</sub>), zinc sulfide (ZnS) and galenite (PbS) (Fig. 2(a)).

The chemical composition of leaching residue was analyzed using atomic absorption spectroscopy and given in Table 1. As can be seen from Table 1, the leaching residue contains mainly Pb, Fe, Zn and S. The zinc content has been decreased from 45.69 wt.% to 13.14 wt.%. A calculated extraction efficiency of Zn is about 85.2%. In addition, the leaching residue was also analyzed by XRD, as shown in Fig. 2(b). Comparing with zinc oxide dust, the constituent phases of the leaching residue change significantly. The main phases of leaching residue are Fe<sub>2</sub>O<sub>3</sub>, PbS and ZnS. ZnO is



Fig. 1 Electrospray mass spectrum of leaching solution in negative ion mode



Fig. 2 XRD patterns of zinc oxide dust (a) and leaching residues (b)

almost completely leached. A large number of PbS and ZnS indicate that metal sulfides are essentially insoluble in ChCl–urea–EG DESs. Similar to SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, metal sulfides (PbS and ZnS) exhibit covalent character, indicating lack of ability to complex with urea [29]. That is, the interaction between metal sulfides and solvent is fragile. Thus, metal sulfides are almost insoluble in DESs. Based on the above analysis, it is reasonable to propose Eq. (1) as the primary dissolution reaction of zinc oxide dust in ChCl–urea–EG DESs.

$$ZnO+urea+Cl^{-} \rightarrow [ZnO-ureaCl]^{-}$$
(1)

#### 3.2 Effect of stirring speed

The effect of stirring speed on the dissolution of zinc from zinc oxide dust was studied. The results shown in Fig. 3 demonstrate that the zinc extraction efficiency increases with the increase of stirring speed from 200 to 600 r/min, but is independent of stirring speed beyond 600 r/min. Thus, 600 r/min is chosen as the optimal stirring speed, which is high enough to eliminate the influence of external diffusion. Besides, it is evident that the stirring speed affects the extraction efficiency, which indicates that external diffusion is the limiting step of the leaching process.



Fig. 3 Effect of stirring speed on zinc extraction efficiency at 80 °C and slurry concentration of 50 g/L

#### 3.3 Effect of slurry concentration

Figure 4 shows the variation of zinc extraction efficiency with the slurry concentration. It is found that the slurry concentration has a significant effect on zinc extraction efficiency. When the slurry concentration decreases from 200 to 50 g/L, zinc extraction increases from 32.3% to 85.2%.

A low slurry concentration is expected to reduce the viscosity of the slurry, which is conducive for reducing diffusional mass transfer resistance. Additionally, a decrease in slurry concentration increases the mole ratio of ligands (urea or Cl<sup>-</sup>) to ZnO, which promotes the formation of [ZnO-ureaCl]<sup>-</sup> complexes and improves the

zinc extraction efficiency. However, further reducing slurry concentration, the zinc extraction efficiency remains constant and does not exceed 87%. This may be due to the speciation of zinc. The XRD analysis result of the undissolved dust shows that zinc exists in two forms including zinc oxide and small quantities of zinc sulfide (Fig. 2(a)). These sulfides are extremely difficult to dissolve in ChCl-urea-based DESs (Fig. 2(b)). Thus, an appropriate slurry concentration is 50 g/L.



**Fig. 4** Effect of slurry concentration on zinc extraction efficiency at 80 °C and stirring speed of 600 r/min

#### 3.4 Effect of temperature

In order to investigate the effect of temperature, zinc oxide dust was leached at different temperatures  $(60-90 \ ^{\circ}C)$  and the results are shown in Fig. 5. As shown in Fig. 5, the zinc extraction efficiency increases from 48.6% to 85.2% with temperature increasing from 60 to  $80 \ ^{\circ}C$ , indicating that moderately high temperature is necessary. When the temperature increases beyond  $80 \ ^{\circ}C$ , the overall zinc extraction efficiency remains almost the same after 48 h. Therefore,  $80 \ ^{\circ}C$  is selected as an appropriate leaching temperature for subsequent experiments. With reaction temperature increasing, the

 $\begin{array}{c} 80 \\ 60 \\ 40 \\ 20 \\ 20 \\ 0 \\ 10 \\ 20 \\ 0 \\ 10 \\ 20 \\ 30 \\ 40 \\ 50 \\ t/h \end{array}$ 

Fig. 5 Influence of temperature on zinc extraction efficiency at slurry concentration of 50 g/L and stirring speed of 600 r/min

energy that is available for the activation of atom and molecule increases. Besides, the mass transfer coefficient and chemical reaction rate are improved with the increase of temperature.

#### 3.5 Kinetic analysis

The leaching behavior of zinc oxide dust in ChCl-urea-EG DESs is different from that of the traditional acid and alkaline leaching. The dissolution process of ZnO can be interpreted in terms of a complex reaction related to surface ligand (urea and Cl<sup>-</sup>) concentrations. During the DESs leaching, the free urea and Cl<sup>-</sup> are gradually consumed due to the formation of [ZnO·ureaCl]<sup>-</sup> complexes. However, the reduced amount of urea and Cl<sup>-</sup> is negligible compared to their high concentration. Thus, a shrinking core model is proposed to explain the dissolution kinetics of ZnO without the formation of a product layer. The leaching process of ZnO involves complexation reaction of ZnO with ligands (urea and Cl<sup>-</sup>) and diffusion of ligands or formed complex. Therefore, the integrated rate equation is shown below, assuming that the concentrations of the ligands are nearly constant [30]:

$$1 - (1 - x)^{1/3} = \frac{k' [\text{urea}]^m [\text{Cl}^-]^n}{\rho_{\text{ZnO}} r_0} t = kt$$
<sup>(2)</sup>

where x is the leaching efficiency of ZnO at time t; k' is the apparent rate constant; [urea] and [Cl<sup>-</sup>] are concentrations of urea and Cl<sup>-</sup> on the surface of unreacted ZnO core, respectively, both of which remain unchanged; m and n are the corresponding apparent reaction orders;  $\rho_{ZnO}$  is the molar density of ZnO;  $r_0$  is the initial radius of the solid particle; k is the kinetic constant calculated from Eq. (2).

Figure 6 shows the plots of  $1-(1-x)^{1/3}$  versus leaching time (*t*) at different temperatures. Obviously, the experimental data fit well for the shrinking core model. The higher viscosity of ChCl-urea-EG DESs leads to a slow diffusion rate of reactants (urea and Cl<sup>-</sup>).



**Fig. 6** Variation of  $1-(1-x)^{1/3}$  over time

Furthermore, the leaching efficiency is dependent on the stirring speed. Hence, it can be concluded that the leaching reaction is controlled by the diffusion through a liquid phase boundary layer.

Using the k value obtained by fitting, we can calculate the apparent activation energy of the leaching reaction based on the Arrhenius equation:

$$k = A \exp\left(\frac{E_{\rm a}}{RT}\right) \tag{3}$$

where A denotes a frequency factor,  $E_a$  denotes the apparent activation energy of the leaching reaction, R denotes a gas constant and T denotes the leaching temperature.

The logarithm of the kinetic rate constant  $(\ln k)$ versus 1/T shows a good linear relation (Fig. 7). According to the slope, the apparent activation energy is calculated to be 32.1 kJ/mol. This result further indicates that the leaching process is controlled by diffusion through a liquid phase boundary layer. The relatively high activation energy is contributed to the increased diffusion resistance caused by high viscosity of ChCl-urea-EG. It is worth mentioning that the results of kinetics analysis are different from those obtained in aqueous solution system. The leaching behavior of zinc-containing dust in ammonia solutions or sulfuric acid solution is a characteristic of a chemically controlled process [31]. The possible reason is that the viscosity of ChCl-urea-EG is higher than that of the aqueous solution [32].



Fig. 7 Arrhenius plot for dissolution of zinc oxide dust

#### **3.6 Zinc electrowinning**

After selective leaching of ZnO from zinc oxide dust, the DESs leaching solutions were used for direct electrodeposition of zinc. The electrodeposition of zinc was carried out at a cell voltage of 2.0 V and 80 °C for 4 h. The 2.0 V and 80 °C are the preferred conditions for Zn electrodeposition in DESs [33]. The current efficiency of the process is determined by weighing the cathode before and after electrodeposition. The current efficiency for the electrodeposition of zinc in this leaching solution is about 82.6%. The zinc deposits are light grey. The morphology and purity of zinc deposit are shown through a scanning electron microscopy (SEM) image and EDX spectrum of the surface in Fig. 8. The SEM image shows that the zinc deposit is composed of tightly packed irregular particles of 0.5–1.0  $\mu$ m in diameter. The EDX spectrum indicates peaks corresponding to Zn element. And no signal for impurity metals (such as Pb and Fe) and chloride is observed in the deposit. This confirms that the deposits are Zn with high purity.



Fig. 8 SEM image (a) and EDX spectrum (b) of zinc deposits

According to the above analysis,  $[ZnO\cdot ureaCl]^-$  is the dominant form of Zn(II) in leaching solution. The  $[ZnO\cdot ureaCl]^-$  can be electro-reduced at cathode by imposing a sufficient potential, generating metal zinc and releasing  $O^{2-}$  ions. Similar to high temperature molten salt, the released  $O^{2-}$  ions diffuse to the anode and discharge. The electrode reactions can be summarized as follows.

Cathode reaction:

$$[ZnO \cdot ureaCl]^{+}2e \rightarrow Zn+O^{2-}+Cl^{-}+urea \qquad (4)$$
  
Anode reaction:  
$$2O^{2-}\rightarrow O_{2}\uparrow +4e \qquad (5)$$

The concentration of Zn in DESs solution was determined using ICP–AES. After zinc electrodeposition for 4 h, the residual level of Zn in DESs is found to decrease to 7.48 g/L. When the electrolysis time is extended to 12 h, the residual Zn in DES solution is reduced to 56 mg/L.

#### 3.7 Recycling use of DESs

After zinc electrodeposition, the DESs were reused to extract zinc from zinc oxide dust. Figure 9 shows the zinc extraction efficiency as a function of time using different DES solutions. After electrolysis for 4 h, the DES solution is reused to leach zinc oxide dust, and the zinc extraction efficiency decreases to 61.4%. This is due to the residual of 7.48 g/L Zn in this solution. When the leaching experiment is carried out using the DES solution after electrolysis for 12 h, the zinc extraction efficiency can be up to 79.4%, which is close to that using newly prepared DESs (85.2%). These results demonstrate that DESs can be recycled.



**Fig. 9** Extraction of zinc from zinc oxide dust using ChClurea-EG solutions recycled: (a) Fresh ChCl-urea-EG DES solution; (b) ChCl-urea-EG leaching solution after electrolysis for 12 h; (c) ChCl-urea-EG leaching solution after electrolysis for 4 h

## **4** Conclusions

(1) The zinc present in zinc oxide dust can be recycled by selective dissolution and direct electrodeposition using ChCl-urea-EG DESs. The DES acts as a complexing agent and solvent during leaching of zinc oxide dust.

(2) The optimal conditions for leaching of zinc oxide dust in ChCl-urea-EG DESs are a leaching temperature of 80 °C, a slurry concentration of 50 g/L and a stirring speed of 600 r/min. Under this condition, the zinc extraction efficiency is 85.2%. The leaching process in the temperature range from 60 to 90 °C is

controlled by diffusion, and the apparent activation energy is 32.1 kJ/mol.

(3) The pure zinc can be directly electrodeposited from leaching solutions without purification. In addition, ChCl-urea-EG solution can be recycled. This develops a promising approach for the recovery of zinc from the zinc oxide dust, thereby the residues containing sulphides can be recycled in zinc-making processes.

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# 利用氯化胆碱基低共熔溶剂从氧化锌烟尘中选择性回收锌

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摘 要:低共熔溶剂(DESs)具有可调节的配位能力,是一种选择性回收金属的潜在浸出剂。本文作者采用氯化胆碱-尿素-乙二醇(ChCl-urea-EG)低共熔溶剂从氧化锌烟尘中选择性回收锌。当浆液浓度为 50 g/L、浸出温度为 80 °C、搅拌速度为 600 r/min 时,锌的浸出率达到 85.2%。该浸出过程受扩散控制,其活化能为 32.1 kJ/mol。将 浸出液直接用于电沉积锌,可得到纯锌镀层,电流效率达到 82.6%,且 ChCl-urea-EG 低共熔溶剂可循环使用。 该方法在处理含锌烟尘方面具有广阔的应用前景。

关键词:低共熔溶剂;选择性浸出;氧化锌烟尘;锌;直接电沉积

(Edited by Wei-ping CHEN)