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Recovery of zinc and lead by simultaneously leaching from lead slag fuming dust with ammonium chloride solution

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Abstract: The effects of leaching temperature (60−105 °C), NH_4Cl concentration (3−7 mol/L), liquid/solid ratio (4:1−12:1 mL/g), stirring speed (150−750 r/min), and leaching time (5−90 min) on the leaching rates of Zn and Pb were investigated. The leaching kinetics of Zn- and Pb-rich fuming dust with a NH_4Cl solution was also studied. The leaching rates of Zn and Pb respectively reached 98.2% and 75.6% at leaching temperature of 100 °C, an NH_4Cl concentration of 7.0 mol/L, a liquid/solid ratio of 10:1 mL/g, a stirring speed of 450 r/min and leaching time of 60 min. The kinetics results indicate that the leaching of Zn and Pb conforms to the shrinking unreacted core model and is controlled by the internal diffusion of NH_4Cl through the reacted fuming dust layer and external diffusion of NH_4Cl through the leaching solution boundary layer, respectively. The apparent activation energies of Zn and Pb are 23.922 and 19.139 kJ/mol, respectively. This study demonstrates that the use of NH_4Cl solution, without ammonia, is an environmentally friendly method for simultaneous extracting Zn and Pb from the fuming dust of lead blast furnace slag.

Key words: lead blast furnace slag; fuming dust; ammonium chloride; simultaneous leaching; kinetics; shrinking unreacted core model

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1 Introduction

With the gradual depletion of zinc and lead ores, increasing attention has been paid to various secondary zinc−lead materials [1−5]. As a typical secondary zinc−lead material, fuming dust of lead blast furnace slag mainly contains zinc and lead oxides [6−8]. Sulfuric acid is the main acid leaching solvent used to treat secondary zinc−lead materials, and more than 90% of the lead and zinc contained in the materials can be recycled [9−12]. However, most impurity elements are dissolved in the solution together with lead and zinc, leading to difficulties in the subsequent purification process. Over 74% of zinc can be leached using sodium hydroxide solution to leach electric arc furnace dust (EAFD) and other waste smelting slags from zinc−lead smelting plants, but lead contained in them cannot be recycled [13−17]. In addition, ammonia−ammonium salt solutions, such as NH_3−$(NH_4)_2CO_3$ [18,19], NH_3−NH_4HCO_3 [20], NH_3−$(NH_4)_2SO_4$ [21], and NH_3−NH_4Cl [22,23], are adopted to leach secondary zinc−lead-bearing materials. The highest zinc leaching rate achieved is 96.7%, whereas impurity leaching is minimal, which indicates that ammonia−ammonium salt solutions have good selectivity for leaching zinc-bearing materials. However, ammonia−ammonium salt leaching method still suffers from ammonia volatilization, which degrades the operating environment.

To fully exploit the selective ability of ammonia and chloride with lead and zinc to form complexes [24−26] and solve the problem of ammonia volatilization, researchers have used ammonium chloride solution without ammonia to

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efficiently treat materials containing zinc produced in metallurgical processes [27,28]. For example, the "Engitec Zinc Extraction" (EZINEX®) process [29−31] developed by Italy Engitec Impianti S.p.A was used to leach zinc from electric arc furnace dust using ammonium chloride solution at 75 °C, then the leaching solution was purified and electro-deposited to obtain metal zinc. JU et al [32] reported that 91.2% of zinc in smithsonite ores was extracted using pure ammonium chloride at 90 °C.

Although a large number of studies have been carried out on the efficient leaching of zinc with ammonium chloride solution, there are few studies on the simultaneous extraction of lead and zinc and their kinetics from secondary resources. In this study, the effects of the ammonium chloride concentration, temperature, liquid/solid ratio (L/S), leaching time, and stirring speed on the leaching rates of zinc and lead were studied. The kinetics was also investigated to determine the control model and apparent activation energy of the leaching process.

2 Experimental

2.1 Materials

The raw material used in the leaching experiment was the zinc- and lead-containing dust produced from the fuming process of lead blast furnace slag in Guangdong Province, China. AR-grade ammonium chloride (99.8%) was purchased from Xilong Scientific Reagent Co. Ltd., China. The elemental contents of the fuming dust were analyzed using an inductively coupled plasma emission spectrometer (ICP–OES, Spectro Blus Sop), and the results are given in Table 1. The Zn and Pb contents were 44.27 and 27.92 wt.%, respectively, and the main impurities were As, Fe, S, Cl, etc. The phase composition and micromorphology of the fuming dust were determined using X-ray diffraction (XRD, TTR III, Rigaku) and scanning electron microscopy (SEM, JSM−7900F, JEOL), and the results are displayed in Fig. 1. The XRD pattern in Fig. 1(a) indicates that zinc oxide (ZnO, PDF#80−0075), lead sulfate ($PbSO_4$, PDF#82−1855), and a lead complex compound ($Pb_4(SO_4)(CO_3)_2(OH)_2$, PDF#85−1422) are the significant minerals present in the fuming dust. The SEM image in Fig. 1(b) shows that the particles are relatively uniform (5 μm) with a rough surface.

Table 1 Chemical elemental contents of fuming dust (wt.%)

Zn	Pb	S	Fe	As	SiO_2
44.27	27.92	3.02	0.43	0.35	0.43
Cl	Ga	Ge	In	Cd	Al_2O_3
0.24	0.0036	0.011	0.0098	0.041	0.26

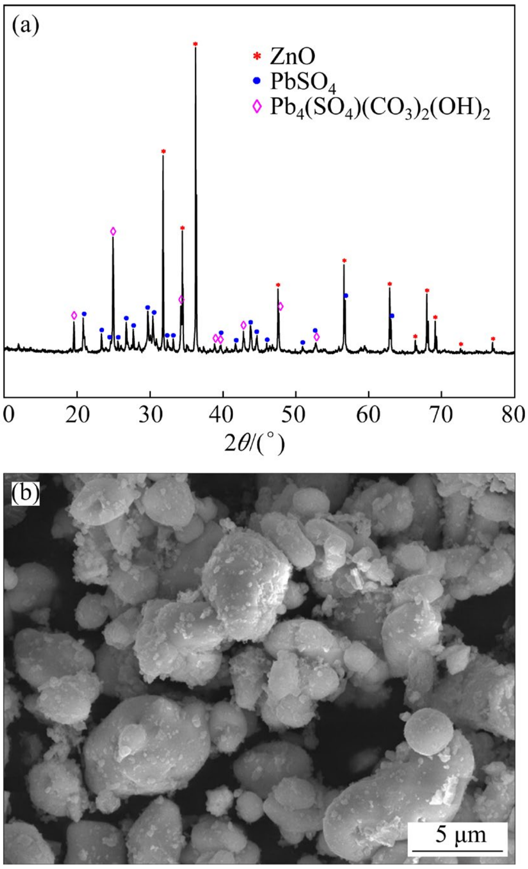

Fig. 1 XRD pattern (a) and SEM image (b) of fuming dust

2.2 Experimental procedure

The required concentrations of the prepared ammonium chloride solution varying from 3.0 to 7.0 mol/L were added to a 250 mL closed reactor with a constant temperature and continuous mechanical stirring function. The stirring speed and liquid/solid ratio were in the range of 150−750 r/min and 4:1−12:1 mL/g, respectively. The leaching temperature was in the range of 60−105 °C. When the desired temperature was reached and held steady, 10 g of fuming dust sample was added to the solution. The solution was stirred for a certain amount of time (5−90 min) and then separated by filtration. During filtration, the filter residue and flask were washed three to five times with approximately 20 mL of 10 wt.% HCl solution until the white solids disappeared. A sufficient amount of 8 wt.% H_2SO_4 solution was added to 1 mL leaching solution to precipitate Pb in the form of $PbSO_4$. Then, $PbSO_4$ was filtered and separated after standing for 30 min. The filtrate was used to analyze the content of zinc in the solution. The $PbSO_4$ precipitate obtained by filtration was fully dissolved with 20 wt.% of acetic acid−sodium acetate solution and the lead content was analyzed by titration.

The leaching rates of Zn and Pb are determined by

$$r=\frac{cVM}{m}\times 100\% \tag{1}$$

where r is the leaching rate of Zn and Pb (%), c is the concentration of Zn or Pb in the filtrate (mol/L), V is the total volume of the filtrate (L), M is the relative molar mass of Zn or Pb (g/mol), and m is the mass of Zn or Pb in the fuming dust (g).

3 Results and discussion

3.1 Leaching conditions

The optimal leaching parameters of zinc- and lead-bearing fuming dust using the ammonium chloride solution were studied. The results are shown in Fig. 2.

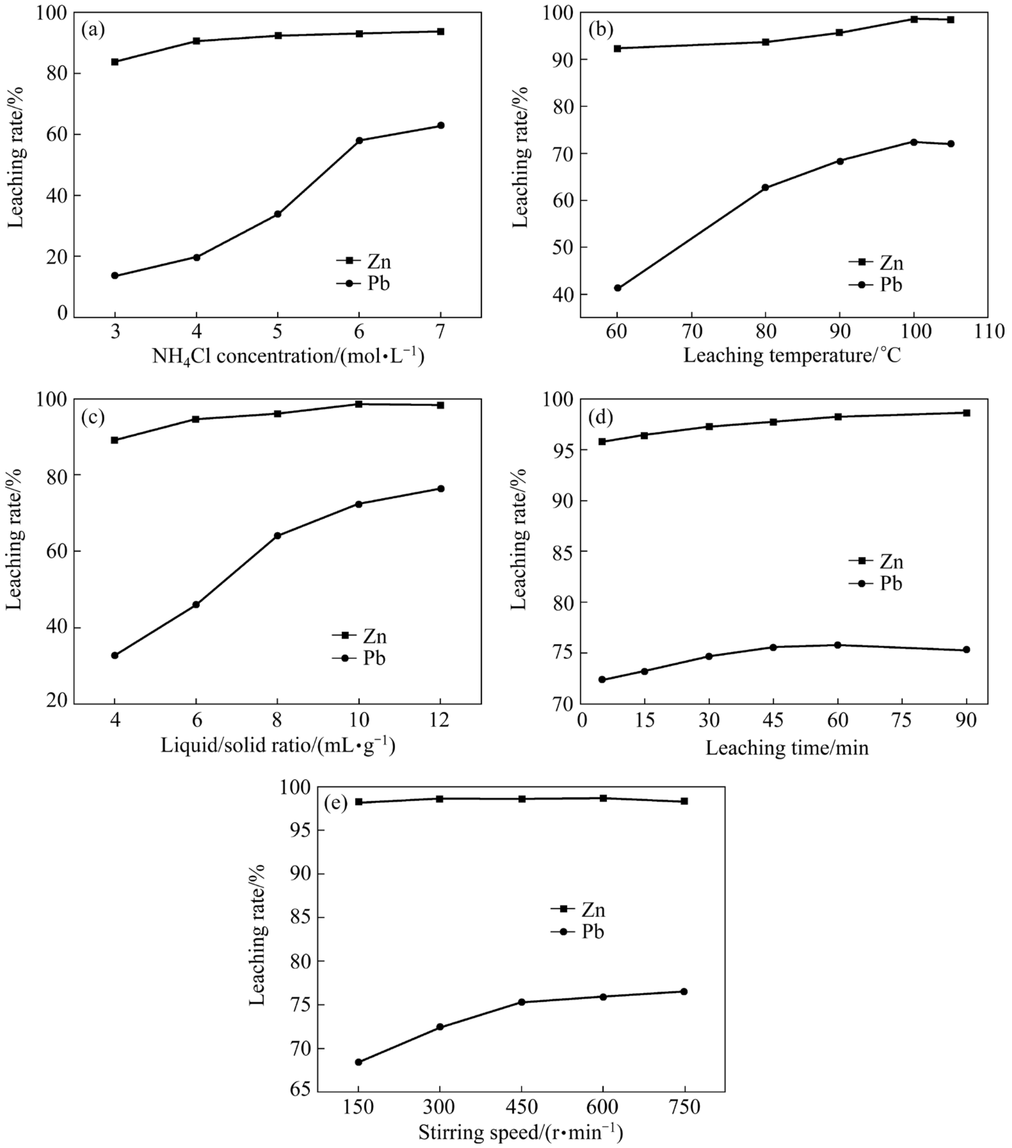

Fig. 2 Effects of leaching parameters on leaching rates of Zn and Pb: (a) NH_4Cl concentration; (b) Leaching temperature; (c) Liquid/solid ratio; (d) Leaching time; (e) Stirring speed

3.1.1 Effect of NH_4Cl concentration

The effects of the NH_4Cl concentration in the range of 3−7 mol/L on the leaching rates of Zn and Pb were studied at a leaching temperature of 80 °C, stirring speed of 300 r/min, liquid/solid ratio of 10:1 mL/g, and leaching time of 90 min. The results in Fig. 2(a) showed that the leaching rates of Zn and Pb increased with increasing NH_4Cl concentration; and the leaching rate of Zn was less affected by the NH_4Cl concentration than that of Pb. The NH_4Cl concentration of 3 mol/L was sufficient to achieve a Zn leaching rate of as high as 83.7%, and it increased to a maximum of 92.4% when the NH_4Cl concentration increased to 5 mol/L. As the NH_4Cl concentration increased from 3 to 6 mol/L, the leaching rate of Pb increased steeply from 13.6% to 58.04% and then increased slowly. This indicates that low NH_4Cl concentration can ensure the effective leaching of Zn, but the extraction of lead needs to control a higher concentration of NH_4Cl. This is mainly because NH_3 and Cl^- in the solution preferentially complex with Zn^{2+}; only when the concentration of Zn^{2+} in the solution decreases to a certain range does Cl^- begin to mainly complex with Pb^{2+}. To ensure the maximum leaching rates of Zn and Pb simultaneously, 7 mol/L was selected as the NH_4Cl concentration for subsequent experiments.

3.1.2 Effect of leaching temperature

The influence of leaching temperatures from 60 to 105 °C on the leaching rates of Zn and Pb was investigated at NH_4Cl concentration of 7 mol/L, stirring speed of 300 r/min, liquid/solid ratio of 10:1 mL/g, and leaching time of 90 min. The results in Fig. 2(b) reveal that the leaching temperature has a more significant effect on Pb than on Zn. The leaching rate of Pb increased from 41.2% to 72.4% as the temperature increased from 60 to 100 °C. In comparison, Zn leaching rate only increased from 92.3% to 98.6%. The Zn leaching rate reaches 92.3% at a low temperature in a short time, which indicates that Zn can easily form complexes with NH_3 and Cl^-. The change of Zn and Pb leaching rates with temperature means that the simultaneous leaching of Zn and Pb can be achieved by controlling the higher leaching temperature. But when the temperature is higher than 100 °C, the solution volatilizes seriously, and the leaching rate decreases. Thus, 100 °C was considered a suitable leaching temperature.

3.1.3 Effect of liquid/solid ratio

The influence of liquid/solid ratio from 4:1 to 10:1 mL/g on the leaching rates of Zn and Pb was investigated at NH_4Cl concentration of 7 mol/L, leaching temperature of 100 °C, stirring speed of 300 r/min, and leaching time of 90 min. Figure 2(c) showed that the Zn leaching rate increased slowly and the Pb leaching rate increased sharply as the liquid/solid ratio increased from 4:1 to 10:1 mL/g, and both changed little after a liquid/solid ratio of 10:1 mL/g. This indicates that high liquid/solid ratio is helpful for simultaneous leaching of Zn and Pb. Because increasing the liquid/solid ratio not only increases the initial NH_4Cl concentration but also increases the diffusion gradient between the particle surface and solution during the reaction process. A liquid/solid ratio of 10 mL/g is sufficient to ensure higher Zn and Pb leaching rates, and further increasing larger liquid/solid ratio will waste NH_4Cl. Thus, a liquid/solid ratio of 10:1 mL/g was used in subsequent experiments.

3.1.4 Effect of leaching time

The influence of leaching time from 5 to 90 min on the leaching rates of Zn and Pb was investigated at NH_4Cl concentration of 7 mol/L, leaching temperature of 100 °C, liquid/solid ratio of 10:1 mL/g, and stirring speed of 450 r/min. The results in Fig. 2(d) indicated that an increase in the leaching time had little influence on the Zn and Pb leaching rates. After a leaching time of 60 min, the leaching rates of Zn and Pb changed slightly. This indicated that 60 min was appropriate for subsequent experiments.

3.1.5 Effect of stirring speed

The influence of stirring speeds from 150 to 750 r/min on the leaching rates of Zn and Pb was investigated at NH_4Cl concentration of 7 mol/L, leaching temperature of 100 °C, liquid/solid ratio of 10:1 mL/g, and leaching time of 90 min. As shown in Fig. 2(e), the Zn leaching rate was less affected by the stirring speed, whereas the Pb leaching rate was significantly affected by it. When the stirring speed increased from 150 to 450 r/min, the leaching rate of Pb increased from 68.4% to 75.3% and then changed little with further increase in stirring speed. Increasing the stirring speed significantly improved the diffusion speed of the solute and strengthened the leaching process. Controlled by the diffusion, slight improvement in the Zn and Pb leaching rates was observed when the stirring speed exceeded 450 r/min; thus, 450 r/min was selected as the optimal stirring speed.

3.1.6 Comprehensive factor experiment

Three groups of comprehensive factor experiments were performed under the optimal leaching conditions based on the experimental results: NH_4Cl concentration of 7 mol/L, leaching temperature of 100 °C, liquid/solid ratio of 10:1 mL/g, stirring speed of 450 r/min, and leaching time of 60 min. The average leaching rates of Zn and Pb were 98.2% and 75.6%, respectively.

3.2 Kinetics analysis

The leaching process of Zn and Pb from fuming dust using the ammonium chloride solution mainly produces binary complexes of zinc and ammonia, zinc and chlorine, and lead and chlorine. In addition, zinc forms ternary complexes with ammonia and chlorine. Other impurity metals, such as Fe, As, and Ga, are not complexed with ammonia chloride and remain in the leaching residue. The possible complexation reactions are as follows:

$$ZnO+mNH_4^+=[Zn(NH_3)_m]^{2+}+(m-2)H^++H_2O \quad (2)$$

$$ZnO+H_2O+nCl^-=[ZnCl_n]^{2-n}+2OH^- \quad (3)$$

$$ZnO+2iNH_4^++jCl^-=[Zn(NH_3)_iCl_j]^{2-j}+H_2O+(2i-2)H^++iNH_{3(aq)} \quad (4)$$

$$PbSO_4+kCl^-=[PbCl_k]^{2-k}+SO_4^{2-} \quad (5)$$

where m, n, i, j, and k are coordination numbers.

These reactions are typical liquid/solid reactions occurring at two-phase interface of ammonium chloride solution and fuming dust, and the kinetics of this type of reaction is largely described by the shrinking unreacted core model, which consists of four steps: (1) external diffusion of NH_4Cl through the leaching solution boundary layer, (2) internal diffusion of NH_4Cl through the reacted fuming dust layer, (3) chemical reactions between ZnO and $PbSO_4$ with NH_4Cl, and (4) diffusion of the produced Zn and Pb complexes through the solid and liquid layers into the leaching solution. Therefore, three speed control steps are possible for the shrinking unreacted core model: internal diffusion control, external diffusion control, and chemical reaction control [33−35]. According to Fig. 2(e), the stirring speed has little effect on the leaching rate of Zn; therefore, internal diffusion, as shown in Eq. (6) [31,33−37], can be the dominant controlled step for leaching Zn from fuming dust using NH_4Cl:

$$1-2r/3-(1-r)^{2/3}=k_{in}t \quad (6)$$

In contrast, the leaching rate of Pb is evidently affected by the stirring speed, as shown in Fig. 2(e); therefore, external diffusion, as shown in Eq. (7) [38], can be the dominant controlled step for leaching Pb from fuming dust using NH_4Cl:

$$1-(1-r)^{2/3}=k_{ex}t \quad (7)$$

where r is the leaching rate of Zn or Pb (%), k_{in} and k_{ex} are the reaction rate constants for internal diffusion control process and external diffusion control process, respectively (min^{-1}), and t is the reaction time (min).

The effects of leaching temperatures from 60 to 105 °C on the leaching rates of Zn and Pb at liquid/solid ratio of 10:1 mL/g, stirring speed of 300 r/min, NH_4Cl concentration of 7 mol/L, and leaching time of 5−90 min are shown in Figs. 3(a) and (d), respectively. Figures 3(b) and (e) are obtained by plotting $1-2r/3-(1-r)^{2/3}$ and $1-(1-r)^{2/3}$ to leaching time with the experimental data presented in Figs. 3(a) and (d), respectively. A clear linear relationship between $1-2r/3-(1-r)^{2/3}$ and t for Zn and $1-(1-r)^{2/3}$ and t for Pb indicates that the leaching of Zn and Pb from fuming dust by a ammonium chloride solution is controlled by internal and external diffusion, respectively. The corresponding k_{in}, k_{ex}, and correlation coefficients for Zn and Pb are listed in Table 2.

After the reaction rate constants (k_{in} and k_{ex}) were obtained, the apparent activation energy of the relevant control process was calculated using the Arrhenius formula [38]:

$$\ln k=-\frac{E_a}{RT}+B \quad (8)$$

where k is the reaction rate constants (k_{in} and k_{ex}, min^{-1}), E_a is the apparent activation energy of the relevant control process (J/mol), R is the molar gas constant (8.314 J/(mol·K)), T is the reaction temperature (K), and B is the pre-exponential factor.

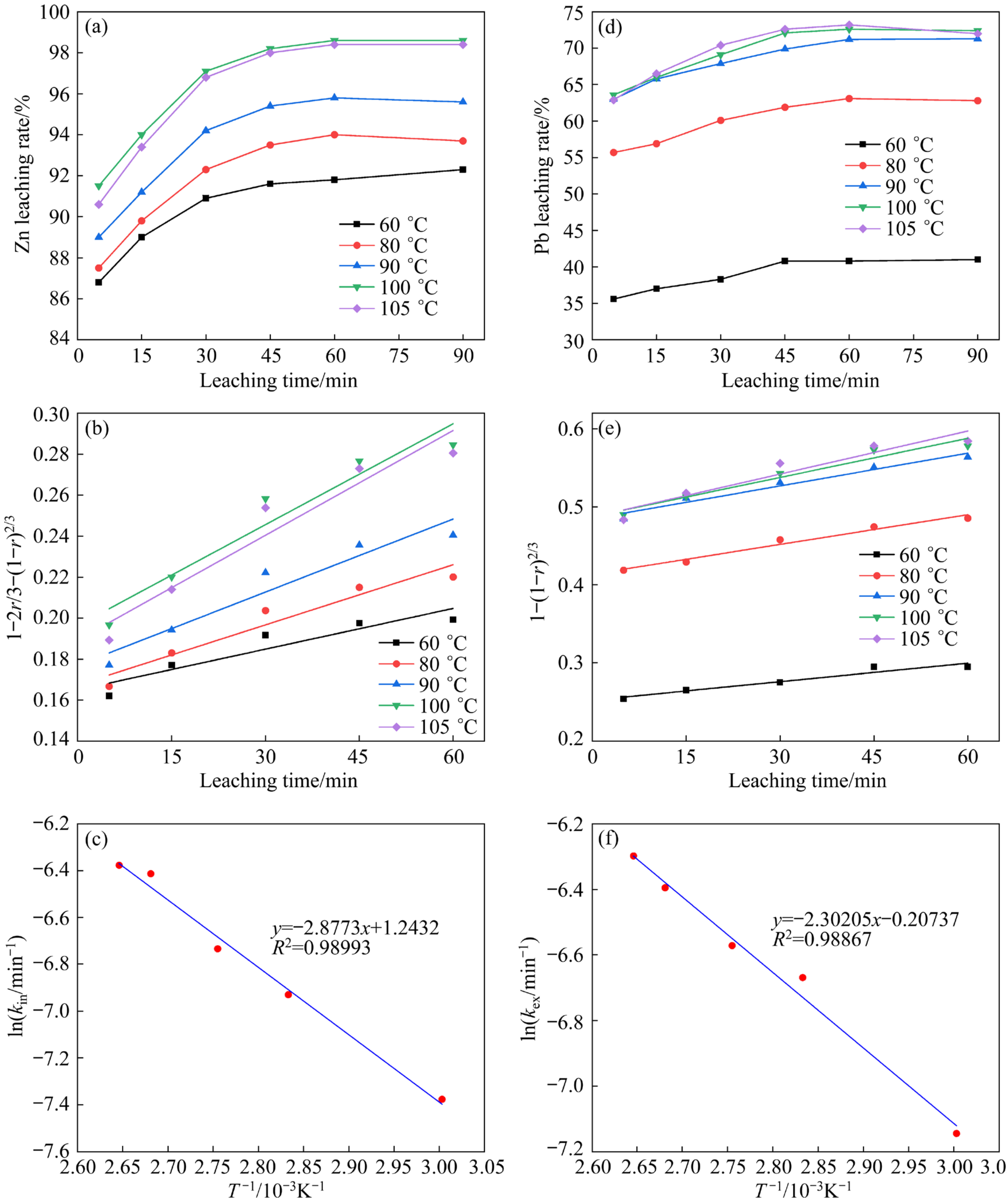

Fig. 3 Effects of temperature on leaching rates of Zn (a) and Pb (d), relationships between $1-2r/3-(1-r)^{2/3}$ and leaching time for Zn leaching process (b) and between $1-(1-r)^{2/3}$ and leaching time for Pb leaching process (e), and relationships between $\ln k$ and T^{-1} for Zn (c) and Pb (f) leaching processes

The $\ln k$ against T^{-1} plots of Zn and Pb are depicted in Figs. 3(c) and (f), respectively, and the E_a values are 23.922 and 19.139 kJ/mol as derived from the slope and intercept of the lines, also confirming that the leaching of Zn and Pb from fuming dust by ammonium chloride solution is controlled by internal and external diffusion, respectively. The kinetics equations for Zn and Pb are expressed by Eqs. (9) and (10), respectively:

$$1-2r/3-(1-r)^{2/3}=1.2432[\exp(-23922/(RT))]t \tag{9}$$

$$1-(1-r)^{2/3}=-0.20737[\exp(-19139/(RT))]t \tag{10}$$

The complexation constant of Zn with NH_3 can reach as much as 9.46, and Zn can also form a complex with Cl^-. Pb can only complex with Cl^-, with a maximum complexation constant of 3.23. At the beginning of the leaching, external diffusion is not the speed control step because of the high concentration of ammonium chloride in the solution. The complexation reaction of Zn is extremely fast, internal diffusion speed is slower than the complexation speed, and internal diffusion becomes the speed control step of Zn leaching. With the leaching of Zn, the concentration of ammonium chloride in the solution decreases, the complexation reaction of Pb^{2+} and Cl^- mainly occurs, and the external diffusion rate is slower than the complexation reaction rate; thus, external diffusion becomes the speed control step.

Table 2 k_{in}, k_{ex}, and correlation coefficients (R^2) of Zn and Pb

T/°C	$1-2r/3-(1-r)^{2/3}$ for Zn		$1-(1-r)^{2/3}$ for Pb	
	k_{in} /min^{-1}	R^2	k_{ex} /min^{-1}	R^2
60	0.000662183	0.87149	0.000789711	0.94001
80	0.000978018	0.93563	0.00127	0.97459
90	0.00119	0.92904	0.00140	0.96723
100	0.00164	0.93475	0.00167	0.95503
105	0.00170	0.93074	0.00184	0.91839

3.3 Characterization of leaching residue

XRD and SEM−EDS characterizations were performed to determine the mineralogical species and micromorphology of the leaching residue obtained in the comprehensive experiments. The XRD pattern of the leaching residue is shown in Fig. 4. The SEM image, main element surface distributions, and EDS patterns are shown in Fig. 5. Main elemental contents of leaching residue obtained from EDS patterns are listed in Table 3.

The XRD pattern shows that the main phase in the leaching residue is $PbCl_2$ (PDF#72−0440), and it also contains small amounts of ZnS (PDF#79−2204) and PbS (PDF#77−0244). Usually, Pb^{2+} and Cl^- can form three types of complex species, $PbCl^+$, $PbCl_{2(aq)}$, and $PbCl_3^-$, and their corresponding complexation constants are 1.42, 2.23, and 3.23, respectively [39]. Theoretically, $PbCl_3^-$ is preferentially generated in solution. However, the XRD results indicate that $PbCl_{2(aq)}$ is also generated in the leaching residue, causing some Pb loss, which may be the main reason for the low Pb leaching rate. In addition, small amounts of ZnS and PbS are precipitates formed by the trace sulfur contained in the raw material with Zn^{2+} and Pb^{2+} in the leaching solution; this also adversely affects the recovery rates of Zn and Pb.

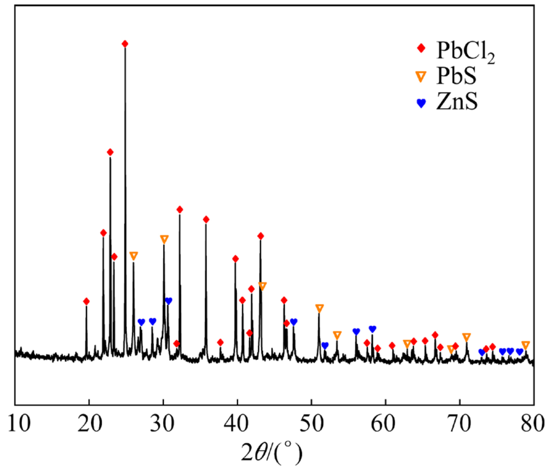

Fig. 4 XRD pattern of leaching residue

Table 3 Main elemental contents of leaching residue obtained from SEM−EDS

Element	Content/wt.%	Content/at.%
C	38.25	70.56
O	11.26	15.51
Al	0.37	0.30
Si	0.87	0.69
S	4.11	2.83
Cl	5.36	3.33
Fe	2.32	0.91
Zn	7.67	2.58
As	0.71	0.21
Pb	28.88	3.07

Figure 5 shows that Pb, Cl, and S are the main elements in the leaching residue, and the content of Zn in the residue is significantly lower than that of Pb, which is consistent with the XRD results. It also shows that Zn is leached prior to Pb in ammonium chloride solution. Trace impurity elements of As, Fe, and S in the raw material remaining in the leaching residue are not leached by ammonium chloride.

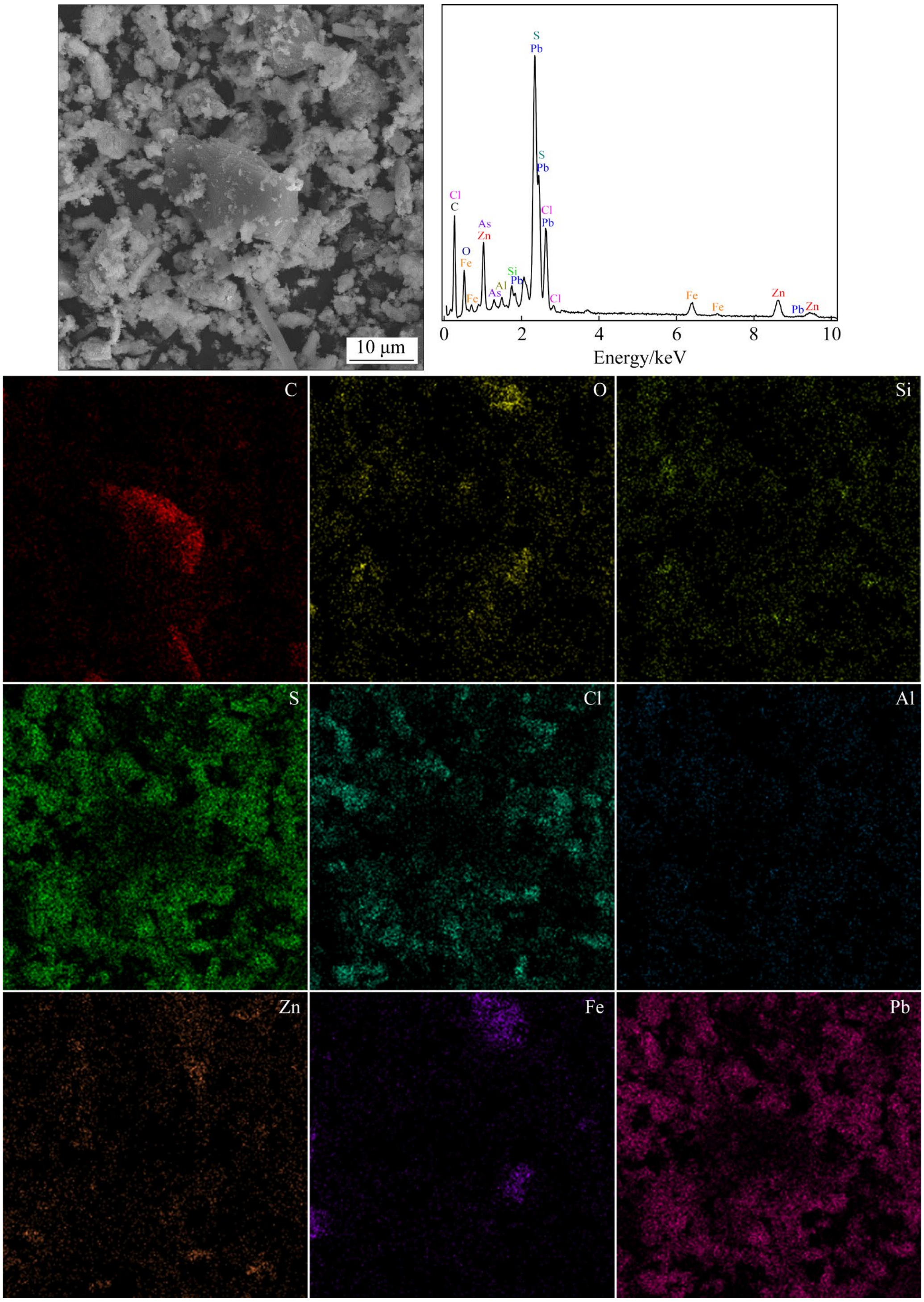

Fig. 5 SEM−EDS results of leaching residue

4 Conclusions

(1) The leaching rates of Zn and Pb reached 98.2% and 75.6% at 100 °C, an ammonium chloride concentration of 7.0 mol/L, a liquid/solid ratio of 10:1 mL/g, a stirring speed of 450 r/min, and leaching time of 60 min.

(2) The leaching of Zn and Pb conforms to the shrinking unreacted core model and is controlled by the internal diffusion of NH_4Cl through the reacted fuming dust layer and external diffusion of NH_4Cl through the leaching solution boundary layer, respectively. The apparent activation energies of Zn and Pb are 23.922 and 19.139 kJ/mol, respectively.

CRediT authorship contribution statement

Zhen-biao LI: Conceptualization, Methodology, Investigation, Formal analysis, Data curation, Visualization, Writing − Original draft; **Zhi-mei XIA:** Conceptualization, Methodology, Writing − Review & editing, Supervision, Project administration, Funding acquisition; **Shu-fen LIU** and **Long-gang YE:** Resources, Data curation, Supervision; **Jing-hao QI** and **Xiong-mei LI:** Data curation, Formal analysis, Visualization.

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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用氯化铵溶液同步提取铅渣烟化炉烟灰中的锌和铅

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摘　要：考察了浸出温度(60~105 ℃)、NH_4Cl 浓度(3~7 mol/L)、液固比(4:1–12:1 mL/g)、搅拌速度(150~750 r/min)和浸出时间(5~90 min)对锌和铅浸出率的影响。研究了 NH_4Cl 溶液浸出含铅、锌烟化烟灰的浸出动力学。在反应温度为 100 ℃、NH_4Cl 浓度为 7.0 mol/L、液固比为 10:1 mL/g、搅拌速度为 450 r/min 和反应时间为 60 min 的最佳工艺条件下，锌和铅的浸出率分别为 98.2%和 75.6%。动力学结果表明，锌和铅的浸出符合未反应收缩核模型，分别受 NH_4Cl 通过反应后烟化烟灰层的内扩散和 NH_4Cl 穿过浸出液边界层的外扩散控制。锌和铅的表观活化能分别为 23.922 和 19.139 kJ/mol。本研究证明了使用不含氨的 NH_4Cl 溶液从铅鼓风炉渣的烟化烟灰中同步提取锌和铅是一种环境友好的方法。

关键词：铅鼓风炉渣；烟化炉烟灰；氯化铵；同步提取；动力学；未反应收缩核模型

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