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ORIGINAL ARTICLE

Leaching of zinc and germanium from zinc oxide dust in sulfuric acid-ozone media

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KEYWORDS

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Leaching rate

Abstract A new process of leaching zinc oxide dust by ozone oxidation in a sulfuric acid system was studied. The main factors affecting the leaching rate, such as ozone time, leaching temperature, initial acidity, leaching time, and liquid/solid mass ratio, were comprehensively investigated. The results show that leaching efficiency depends on all the above factors. The optimum conditions for leaching Zn and Ge from zinc oxide dust are as follows: ozone time 10 min, leaching temperature 90 ℃, initial acidity 160 g/L, leaching time 60 min, and liquid/solid mass ratio 7:1. Under the optimum conditions, the leaching rates of Zn and Ge are 95.79% and 93.65%, respectively. The leaching rates of zinc and germanium in the ozone leaching are 4.05% and 10.49% higher than those of the atmospheric leaching, respectively. Therefore, it is determined that ozone in solution plays a key role in rapidly oxidizing sulfide and releasing encapsulated germanium. Sulfuric acid-ozone media can efficiently extract Zn and Ge from zinc oxide dust.

1. Introduction

The two main sources of germanium for industrial production are smelting residues from lead-zinc mines and coal flue ash (Depuydt et al., 2007; Nusen et al., 2015). Zinc oxide dust with high germanium content is obtained by pyrometallurgical enrichment of lead-zinc ore residue containing germanium, that is, zinc oxide dust is prepared by pyrometallurgical roasting of zinc leaching residue or lead smelting slag at high temperature (Chen et al., 2017; Liu et al., 2016). At present, the most extensive method for recovering metallic germanium

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from zinc oxide dust is: using sulfuric acid as a leaching agent to directly leach zinc oxide fume under normal pressure. The leaching residue contains a high lead content and can be used as a raw material for lead smelting. The leachate contains not only germanium but also a high concentration of zinc. First, the germanium in the solution is separated from other metals (such as Zn, As, Fe, Cd, and Si) by the tannin precipitation method, and then obtain germanium concentrate by roasting the tannin precipitate (Di et al., 2021; Patel and Karamalidis, 2021; Jiang et al., 2021; Jha et al., 2001; Liang et al., 2008a, 2008b; Rudnik et al., 2019a, 2019b; Rutledge and Anderson, 2015). Finally, the germanium-free leaching solution is sent to the electrowinning process to recover zinc (Jha et al., 2001; Rudnik et al., 2019a, 2019b). The data of enterprises and laboratories show that the leaching rates of Zn and Ge are only 80–90% and 60–85%, respectively, and the recovery efficiency is low (Fu et al., 2018; Li et al., 2011; Yang et al., 2014). Existing studies have shown that in different geochemical environments, germanium exhibits different geochemical properties, including lithophile affinity, siderophile, and sulfur affinity (Arbuzov et al., 2021; Benites et al., 2021; Höll et al., 2007; Patel and Karamalidis, 2021). Germanium in ores is usually associated with zinc, lead, iron or silicon. The complexity of germanium-bearing minerals is the main problem in extracting germanium from zinc oxide dust.

The sulfur affinity of germanium makes it enriched in some sulfides of lead–zinc ores, such as sphalerite (ZnS) and galena (PbS). Germanium enters the sphalerite lattice as isomorphism, which is the biggest feature of germanium enrichment in sulfide (Frenzel et al., 2014; Zhao et al., 2019). Cook et al. (2015) results show that germanium is preferred to be mixed in iron-rich sphalerite or in sphalerite which is associated with wurtzite. The results of Jiang et al. (2019) showed that the germanium in zinc oxide dust is mainly enriched in galena (PbS), zinc, and lead oxide. The leaching solution without the presence of oxidant cannot leached sphalerite and galena, which may be an important cause of the loss of Zn and Ge. Zhu et al. (2021) studied the recovery of zinc and germanium from zinc oxide dust containing germanium by atmospheric oxygen enrichment leaching. The results showed that the leaching rates of zinc and germanium were 92.51% and 90.67%, respectively. This study proved that oxidants can increase the leaching rate of zinc and germanium. However, oxygen has low oxidability, and it takes a long time to oxidize and dissolve the sulfide, resulting in a part of the loss of zinc and germanium. Therefore, it is necessary to find a new method that has a strong oxidizing ability under normal pressure and can quickly oxidize and leach zinc oxide dust containing sulfide. To speed up the leaching reaction, save time, and have a higher leaching rate. This new method is to use ozone to oxidize sulfide in the leaching process. The application of ozone in leaching zinc oxide dust has not been reported so far, but many researchers have proved that it is suitable for the oxidation of refractory sulfide ore (Guo et al., 2017; Helbig et al., 2018; Jing et al., 2014; Lv et al., 2021; Mubarok et al., 2018; Zhang et al., 2020). (Carrillo-Pedroza et al., 2010, 2012) and (Havlik et al., 1999; Havlik and Skrobian, 1990) reported that ozone can improve the solubility of copper in chalcopyrite, which is the most difficult copper in water treatment. There are also some reports that the cyanidation of gold in refractory concentrate can be improved by using ozone for pre-oxidation, indicating that it can effectively leach gold from sulfide minerals (especially pyrite and pyrargyrite) (Cao et al., 2021; González-Anaya et al.,2011; Wu et al., 2021). The highest reduction potential of ozone is 2.08 V, that of persulfate is 2.01 V and that of hydrogen peroxide is 1.77 V. Adding ozone into the leaching system will not introduce new ions that pollute the downstream process. For example, in the process of zinc electrowinning, nitrate will be reduced at the cathode, thus reducing the current efficiency (Sinclair, 2005). The advantage of using ozone is that the product oxygen has no pollution to the environment, increasing the possibility of leaching process operating at room temperature and atmospheric pressure (Roca et al., 2000). It can oxidize sulfide in zinc oxide dust to soluble sulfate according to the following reaction (Eqs. (1)-(4)) (Heidel et al., 2013; Markus et al., 2004; Melashvili et al., 2016; Mubarok et al., 2018; Zarate-Gutierrez et al., 2010):

$$3ZnS_{(s)} + 3H_2SO_{4(aq)} + O_{3(g)} = 3ZnSO_{4(aq)} + 3H_2O_{(l)} + 3S_{(s)} \tag{1}$$

$$2FeS_{2(s)} + H_2SO_{4(aq)} + 3O_{3(g)} = Fe_2(SO_4)_{3(aq)} + H_2O_{(l)} + 2S_{(s)} \tag{2}$$

$$ZnS_{(s)} + Fe_2(SO_4)_{3(aq)} = ZnSO_4 + 2FeSO_{4(aq)} + S_{(s)} \tag{3}$$

$$3PbS_{(s)} + O_{3(g)} + 3H_2SO_{4(aq)} = 3PbSO_{4(s)} + 3H_2O_{(l)} + 3S_{(s)} \tag{4}$$

The purpose of this study is to study the optimum conditions for leaching zinc oxide dust by adding ozone into the sulfuric acid solution, To improve the dissolution of Zn and Ge to the maximum extent. The effects of initial acidity, leaching temperature, leaching time, liquid/solid mass ratio, and ozone time on the leaching rate of Zn and Ge were verified, and the role of ozone in the leaching process was discussed.

2. Materials and methods

2.1. Materials and characterization

The mineral sample used in this study is zinc oxide dust obtained from a lead zinc smelting company in Yunnan Province, China. Table 1 and Table 2 respectively list the XRF quantitative analysis results and the chemical phase analysis results of zinc oxide dust. The zinc oxide dust sample was prepared at 105℃ to remove moisture and grind to 200 μm. In addition, all other reagents used for leaching experiments and chemical analysis are analytically pure (purity greater than 99.9%). Deionized water was used in all experiments. The volume flow of ozone is controlled at 2 L/min by the ozone generator.

X-ray fluorescence (XRF) spectrometry was used to analyze the chemical compositions of the concentrate. The phases and contents of Zn, Pb, and Fe in zinc oxide dust were analyzed. The main mineral phases were identified by X-ray diffraction (XRD, Philips pw1825). The results of the analysis are shown in Fig. 1, which shows that the main phases in the dust are ZnO, $PbSO_4$, PbS, and ZnS. The surface microstructure of leaching residue was analyzed using a scanning electron microscope and an energy spectrometer (SEM-EDS) with the equipment model Nova-NanoSEM-450. EPMA-1720 series

Table 1 Main chemical composition of zinc oxide dust.

Element	Zn	Pb	S	Fe	As	Ge	Si
Content, wt.%	49. 65	15.92	4.70	3.02	0.99	620.4 g/t	0.576

Table 2 Mineralogical composition of the zinc oxide dust.

Constituent	ZnO	$ZnSO_4$	ZnS	$ZnFe_2O_4$	$PbSO_4$	$PbCO_3$
Wt.%	42.66	0.92	5.31	0.76	4.14	8.97
Constituent	PbS	Fe_3O_4	$Fe_2(CO_3)_3$	$Fe_2(SiO_3)_3$	FeS_2	Fe_2O_3
Wt.%	2.6	0.86	0.22	0.28	0.29	0.41

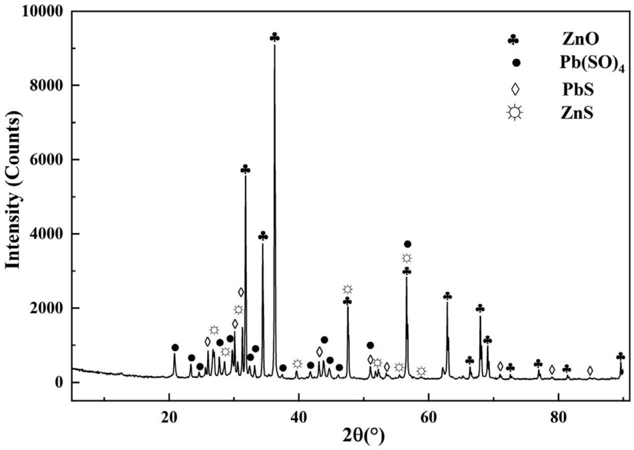


Fig. 1 XRD pattern of Characterization of the zinc oxide dust.

electron microprobes (15 kV and 10na) were used to determine the distribution of main elements in leaching residue. Further, the contents of Zn and Ge in minerals and solutions were determined by inductively coupled plasma atomic emission spectrometry (ICP).

The leaching rate of metal was calculated with Eq. (5):

$$\lambda_{Me} = \frac{\theta_{Me} \times V}{\theta^0_{Me} \times m} \tag{5}$$

where λ_{Me}(%) is the leaching rate of the metal, θ_{Me}(g/L) is the concentration of a metal ion in the leaching solution, V(L) is the volume of the leaching solution, θ^0_{Me} is the metal content of the zinc oxide dust, and m(g) is the mass of the zinc oxide dust.

2.2. Leaching procedure

The experimental setup is shown in Fig. 2. All leaching experiments were carried out in a 250 mL flask equipped with a condenser and a thermometer in a constant temperature water bath. All experiments were carried out at 400 rpm. When the solution temperature reaches the set value, ozone is introduced from the ozone generator to start stirring and leaching. After the experiment, the precipitate and filtrate were separated. The concentration of Zn and Ge infiltrate was determined by ICP. The residue was analyzed by XRF, XRD, SEM-EDS, and EPMA. All experiments in this study were repeated at least 3 times, and the final result was the average of the three experimental results.

3. Results and discussion

The effects of ozone time, initial acidity, liquid/solid mass ratio, leaching time, and temperature on the leaching efficiency of Zn and Ge were studied. The optimum conditions were explored to maximize the dissolution of Zn and Ge, and the role of ozone in the leaching process was discussed.

3.1. The factorial experiments

3.1.1. Effect of ozone time

Under the conditions of temperature 90℃, leaching time 60 min, initial acidity 160 g/L, and liquid/solid mass ratio 5:1, the effect of ozone time (5–60 min) on the dissolution of Zn and Ge was studied. Fig. 3 shows the curve of the leaching rate of Zn and Ge with the time of ozone. The leaching rate of Zn and Ge began to increase when ozone was introduced for 5 min, and the leaching rate of Zn and Ge reached the maximum value of 91.10% and 82.14% when ozone was introduced for 10 min. The terminal pH of the extract is 1.5–2.5. The leaching rate of Zn and Ge begins to decrease with the increase of ozone time. The reason may be that as the ozone time increases, the leaching time also increases, and iron is continuously leached (Wang et al.,2021). As the ozone time increases, the ozone in the solution is excessive, causing Fe^{2+} to be oxidized to Fe^{3+} by the excess ozone. When there is a large amount of Fe^{3+} in the solution, Fe^{3+} will start to form Fe $(OH)_3$ colloids at a pH of about 1.6, which will precipitate the zinc and germanium that have been leached in the solution into the slag, causing the loss of zinc and germanium, resulting in The actual leaching rate of zinc and germanium has decreased (Coetzee et al., 2018; Deng et al., 2020). Therefore, the ozone injection time cannot be too long, and 10 min is the most appropriate.

3.1.2. Effect of leaching time

Fig. 4 shows the curve of the leaching rate of Zn and Ge with leaching time. The experiment was carried out under the following conditions: ozone time 10 min, initial acidity 160 g/L, leaching temperature 90℃, liquid/solid mass ratio 5:1, leaching time 30–240 min varied. The maximum leaching rate of Zn was 91.10% and that of Ge was 82.14% at 60 min. The terminal pH of the extract is 1.5–2.5. After more than 60 min, the Zn leaching rate began to decrease, while the Ge leaching rate rose slowly, reaching a maximum of 82.42% at 120 min, which was not much different from that at 60 min. Because the amount of soluble reactants is constant, that is, the consumption of acid is also constant. When it reaches 60 min, the soluble Zn and Ge are completely leached. Therefore, leaching for 60 min is sufficient to completely leaching the soluble Zn and Ge in the zinc oxide dust. The leaching rates of Fe, Pb, Si, and Al are shown in Fig. 5. As the leaching time increases, Fe, Pb, Si, and Al are continuously leached, resulting in the formation of $PbSO_4$, Fe $(OH)_3$, and Silica gel (Liu et al., 2016; Patel and Karamalidis, 2021). $PbSO_4$ can form Pb-based spheres, wrap Zn and Ge,

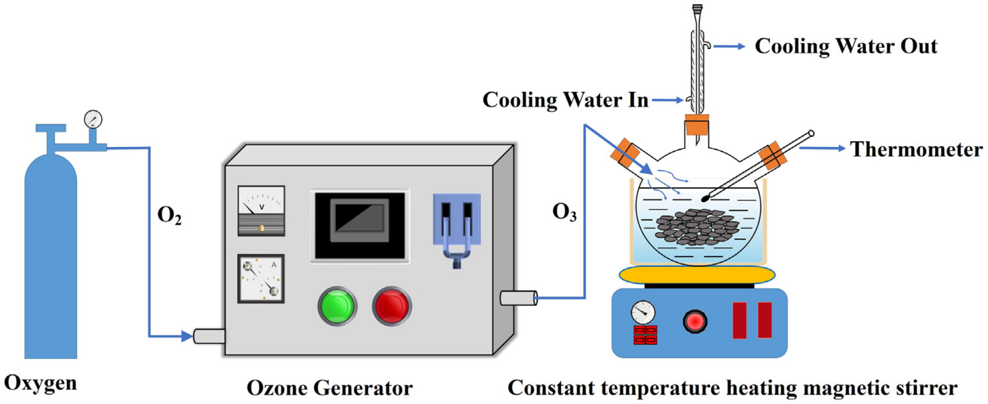


Fig. 2 Schematic diagram of the leaching experimental setup.

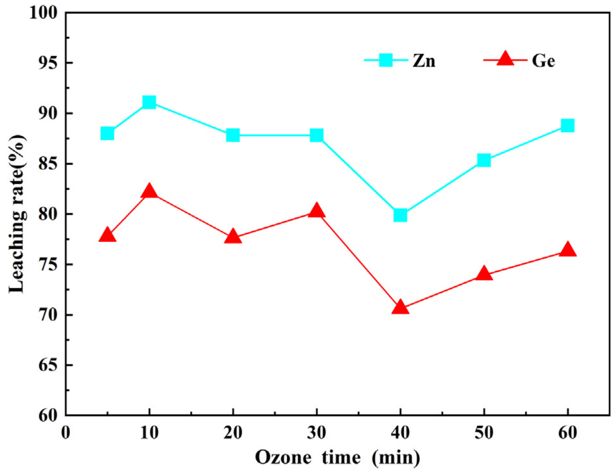


Fig. 3 Effect of ozone time on metal leaching rate.

make sulfuric acid and ozone unable to contact them, and lead to the decrease of leaching rate (Jiang et al., 2020). When the leaching continues, the excess acid will be combined with iron-containing minerals and silicates The reaction of other compounds causes the Zn and Ge in the solution to enter the slag due to iron hydrolysis and impurity ion adsorption, causing the apparent leaching rate to decrease. Among them, germanium and silicon have similar covalent radii and ionic radii, and it is easy to form co-iron, silicon–germanium colloidal precipitation with iron and cause germanium loss (Zhang et al., 2003). Dutrize et al. (1996) confirmed that most germanium in weak acid slag is iron-silicon Germanium exists in colloidal form. The optimal leaching time is 60 min. Liang et al. (2009) confirmed that as the leaching time increases, the amount of silica leached gradually increases, and a large amount of silica in the residue is leached to form silica gel. The zinc and germanium are adsorbed by the silica gel into the slag, causing the loss of zinc and germanium to increase.

3.1.3. Effect of initial acidity

The effect of initial acidity on the dissolution of Zn and Ge is shown in Fig. 6. The experiment was carried out under the following conditions: ozone time 10 min, leaching temperature 90℃, liquid/solid mass ratio 5:1, leaching time 60 min, and initial acidity was varied between 100 and 200 g/L. Although the extraction of Zn and Ge from zinc oxide dust is strongly dependent on initial acidity. However, when the concentration increased to 160 g/L, the leaching rates of Zn and Ge reached the maximum, which were 90.60% and 81.48%, respectively.

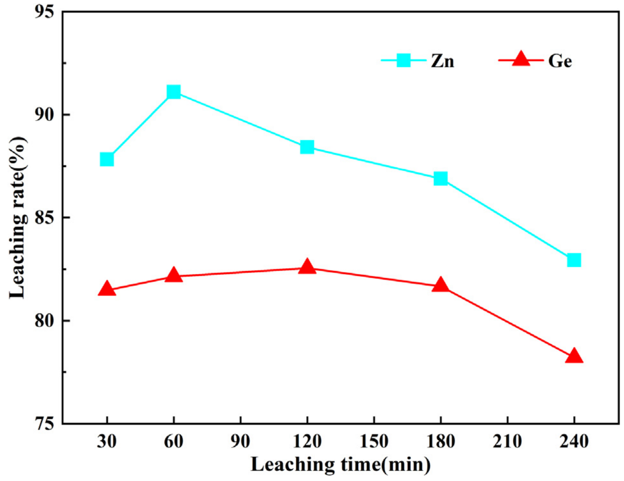


Fig. 4 Effect of leaching time on metal leaching rate.

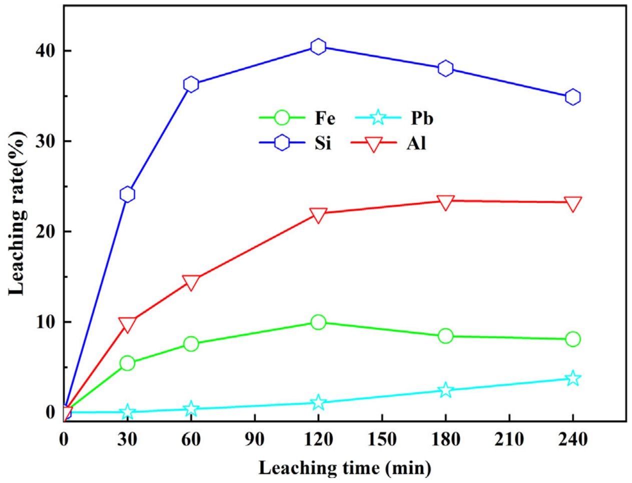


Fig. 5 Effect of leaching time on impurity metal leaching rate.

When the concentration of sulfuric acid continues to increase, the leaching rate begins to decrease. The leaching rate of Zn and Ge decreased at higher initial acidity, which was related to the solubility of ozone. Levanov et al. (2008) and Mubarok et al. (2018) showed that the amount of dissolved ozone decreased with the increase of initial acidity, which they attributed to the salting-out effect. Both sulfuric acid and ozone play an important role in the dissolution of metals. The best balance between initial acidity and ozone solubility is the key to achieve the maximum leaching rate. Therefore, when the highest leaching rate of Zn and Ge is obtained, and enough ozone is obtained in the system, the optimal initial acidity is 160 g/L.

3.1.4. Effect of liquid/solid mass ratio

When the amount of mineral is constant, the increase of liquid/solid mass ratio will increase the concentration of sulfuric acid, which is helpful to improve the dissolution rate of metal in a certain leaching time. Fig. 7 shows the effect of the liquid/solid mass ratio on the leaching rate of Zn and Ge. The experiment was carried out under the following conditions: ozone time 10 min, leaching temperature 90℃, leaching time 60 min, initial acidity 160 g/L, liquid/solid mass ratio between 4:1 and 8:1. With the increase of liquid/solid ratio from 4:1 to 7:1, the leaching rates of Zn and Ge increased significantly, and then decreased with the further increase of liquid/solid ratio, reaching the maximum of 95.79% and 93.65%, respectively, when the liquid/solid ratio was 7:1. Some studies have shown that increasing the liquid/solid mass ratio properly can promote the mass transfer process at the solid–liquid interface (Aydogan et al., 2005; Zhang et al., 2005). However, the higher the liquid/solid mass ratio is, the higher the final acidity of the leaching solution is, and a large amount of Fe will be leached into the solution. The high concentration of Fe ion in the leaching solution will have a great impact on the recovery of Ge in the subsequent process, and the high liquid/solid mass ratio will lead to low utilization of the equipment. Therefore, considering the factors of economy and recovery rate of Zn and Ge, the liquid/solid mass ratio of 7:1 is considered as the best condition.

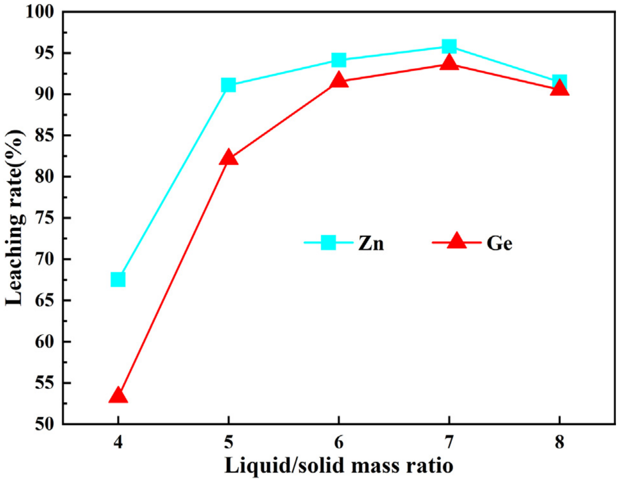


Fig. 7 Effect of liquid/solid mass ratio on metal leaching rate.

3.1.5. Effect of leaching temperature

Fig. 8 shows the effect of leaching temperature on the leaching rates of Zn and Ge. The experiment was carried out under the following conditions: ozone time 10 min, leaching time 60 min, initial acidity 160 g/L, liquid/solid mass ratio 7:1, leaching temperature between 50℃ and 90℃. The results show that the leaching rates of Zn and Ge increase with the increase of temperature. When the temperature rises to 90℃, the leaching rates of Zn and Ge can reach the maximum of 95.79% and 93.65%, which may be because with the increase of temperature, the mass transfer among ore, ozone gas, and leaching solution is promoted, and the reaction is easier to occur at high temperature. The standard hydrogen electrode potential of ozone is 2.07 V. The decomposition of ozone in water is accelerated with the increase of temperature, and hydroxyl radical (•OH) with a standard hydrogen electrode potential of 2.80 V is produced. This indicates that hydroxyl radical (•OH) with stronger oxidation ability than ozone can be obtained after ozone is introduced into the solution, which is more conducive to improving the ability of sulfide oxidation in the leaching process (Guedes et al., 2003; Knud et al., 1991;). Therefore, the optimum leaching temperature is 90 ℃.

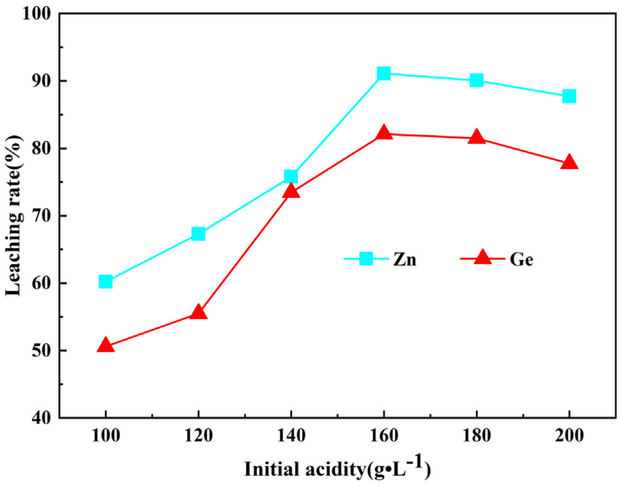


Fig. 6 Effect of initial acidity on metal leaching rate.

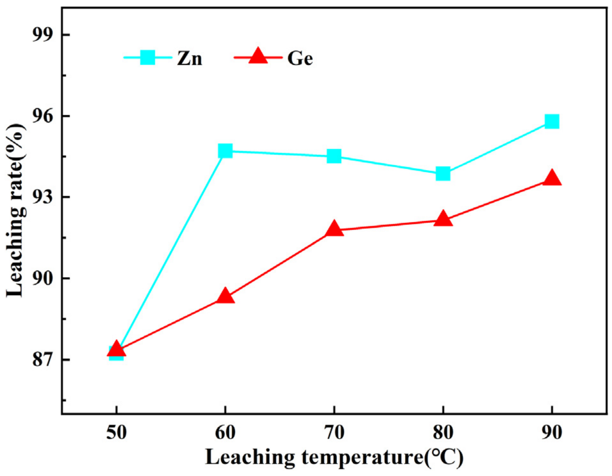


Fig. 8 Effect of leaching temperature on metal leaching rate.

3.1.6. *Effect of different oxidants*

According to the above experiments, the optimum leaching conditions of ozone are as follows: ozone time 10 min, leaching temperature 90℃, initial acidity 160 g/L, leaching time 60 min, and liquid/solid mass ratio 7:1. The leaching rates of Zn and Ge are 95.79% and 93.65%, respectively. To compare the difference between ozone and other oxidants on the leaching of zinc and germanium from zinc oxide dust, the same basic conditions (initial acidity 160 g/L, liquid/solid mass ratio 7:1, leaching time 60 min, leaching temperature 90 ℃) were studied. Experiment with oxygen, 30% H_2O_2, and no oxidant. The experimental results are shown in Table 3. The results showed that the leaching rates of Zn and Ge were 91.74% and 83.16% in the atmospheric leaching experiment without an oxidant. After adding various oxidants, the leaching rates of Zn and Ge are improved. The time of introduction of oxygen has a great influence on germanium. As the time of introducing oxygen increases, the leaching rate of germanium decreases. Zhu et al. (2021) studied the recovery of zinc and germanium by leaching germanium-containing zinc oxide dust under oxygen-rich conditions. The results show that the leaching rates of zinc and germanium are 92.51% and 90.67%, respectively, which are consistent with the results of this study. The addition of H_2O_2 can effectively increase the leaching rate of zinc, but has little effect on germanium. The best effect is ozone leaching. The leaching rate of germanium after passing ozone is more than 6% higher than other oxidants. This shows that ozone plays a key role in the dissolution of zinc and germanium in zinc oxide dust. This is consistent with the results previously reported (Ichlas et al., 2020; Li et al., 2021; Oruê et al., 2020).

3.2. *Characterization analysis*

Atmospheric leaching residue was obtained under the conditions of leaching temperature 90℃, initial acidity 160 g/L, liquid/solid mass ratio 7:1, leaching time 60 min. The leaching rates of Zn and Ge were 91.74% and 83.16%, respectively. Based on the optimal leaching conditions of atmospheric leaching, 10 min ozone was injected to obtain ozone leaching residue. The leaching rates of Zn and Ge were 95.79% and 93.65%, respectively.

3.2.1. *XRF characterization analysis*

Table 4 lists the chemical composition of ozone leaching residue. The ozone leaching residue is mainly composed of 44.08 wt% Pb, 5.55 wt% Zn, 14.07 wt% S, 1.63 wt% Fe, 0.50 wt% As, 0.46 wt% K, 1.63 wt% Si and 1.05 wt% Al. Comparing and observing the chemical composition of zinc oxide dust in Table 1, the zinc content of the ozone leaching residue was significantly reduced, and the lead content was significantly increased, indicating that most of the zinc was leached and lead was enriched. Because XRF cannot detect low-content elements. Therefore, after chemically dissolving the leaching residue, inductively coupled plasma-optical emission spectrometry (ICP-OES) is used to determine the content of germanium in the leaching residue. The Ge content is 104.61 g/t. The ozone leaching residue is mainly lead-based lead-silver slag with a Pb content of as high as 44.08%, which can be returned to lead smelting enterprises as raw materials for lead smelting.

3.2.2. *XRD characterization analysis*

The XRD results of leaching residue are shown in Fig. 9. The two kinds of leaching slag are the same in composition, mainly composed of $PbSO_4$ and a small amount of PbS and ZnS. Compared with the zinc oxide dust in Fig. 1, it can be found that there is no ZnO diffraction peak in the leaching residue, indicating that ZnO can be completely leached by atmospheric leaching. By observing the diffraction peaks of the three phases, it can be found that the intensity of the diffraction peaks of PbSO4, ZnS, and PbS in the ozone leaching residue is significantly lower than that of the atmospheric leaching residue. The weakening of the intensity of the characteristic diffraction peaks indicates that the introduction of ozone during the leaching process causes the intensity of the diffraction peaks of the PbSO4, ZnS, and PbS crystal planes to decrease significantly. This is because the continuous oxidation of minerals by ozone in the leaching process reduces the crystallinity of minerals, destroys the crystal structure of minerals, and causes some ore components to dissolve (Cao et al., 2019; Xiong et al., 2015). Combining Eqs (1)-(4), explain the leaching effect of ozone on ZnS and PbS. It is proved that ozone can quickly leaching sulfide that cannot be leach by the normal pressure process, To achieve the purpose of improving the metal leaching rate.

3.2.3. *SEM-EDS characterization analysis*

Fig. 10 shows zinc oxide dust, atmospheric leaching residue, and ozone leaching residue. Fig. 10a shows that the particles are agglomerated, while Fig. 10b and c show the bulky agglomerates produced by the reaction of atmospheric pressure and ozone. Fig. 10d is an EDS analysis, showing the difference in mass percentage composition of the entire area in Fig. 10(a-c). Zinc oxide dust showed a high zinc content of 48.53%. The content of zinc decreased in turn from zinc oxide dust, atmospheric leaching residue, and ozone leaching residue, while the content of lead increased in turn, indicating that a large amount of zinc was leached. $PbSO_4$ is enriched to form a Pb-based sphere, which will encapsulate Zn and Ge, which

Table 3 Experimental results of leaching zinc oxide dust with different oxidants.

No.	Oxidant	Addition amount	Leaching rate of Zn/ (%)	Leaching rate of Ge/ (%)
1	No oxidant	0	91.74	83.16
2	O_2	10 min O_2	93.03	87.54
3	O_2	30 min O_2	93.68	84.59
4	H_2O_2	6 mL	93.22	83.76
5	H_2O_2	14.8 mL	95.65	85.90
6	O_3	10 min O_3	95.79	93.65

Table 4 Main chemical composition of ozone leaching residue.

Element	Pb	Zn	S	Fe	As	K	Si	Al
Content, wt.%	44.08	5.55	14.07	1.63	0.50	0.46	1.63	1.05

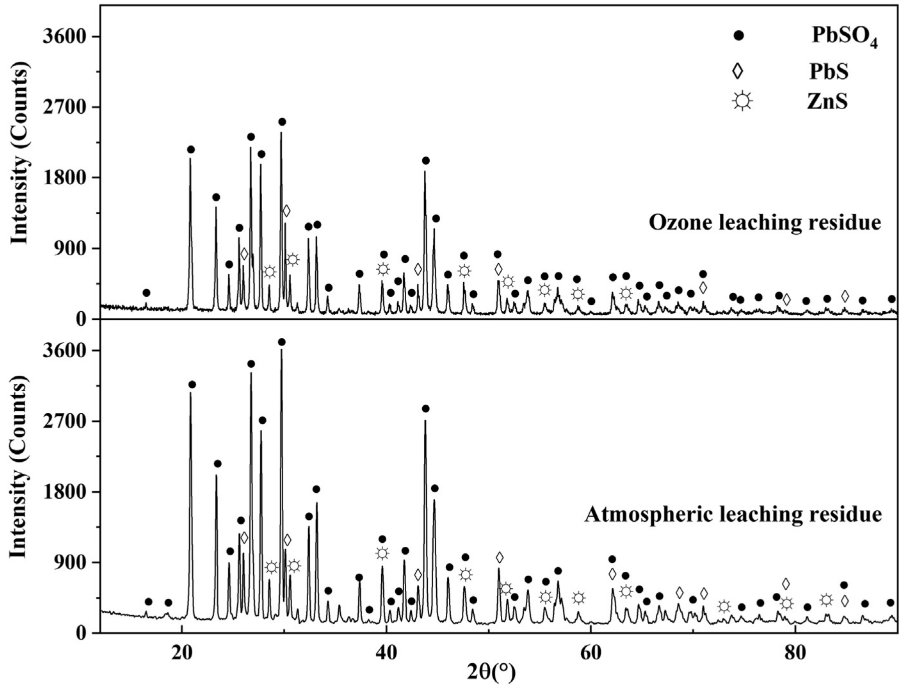
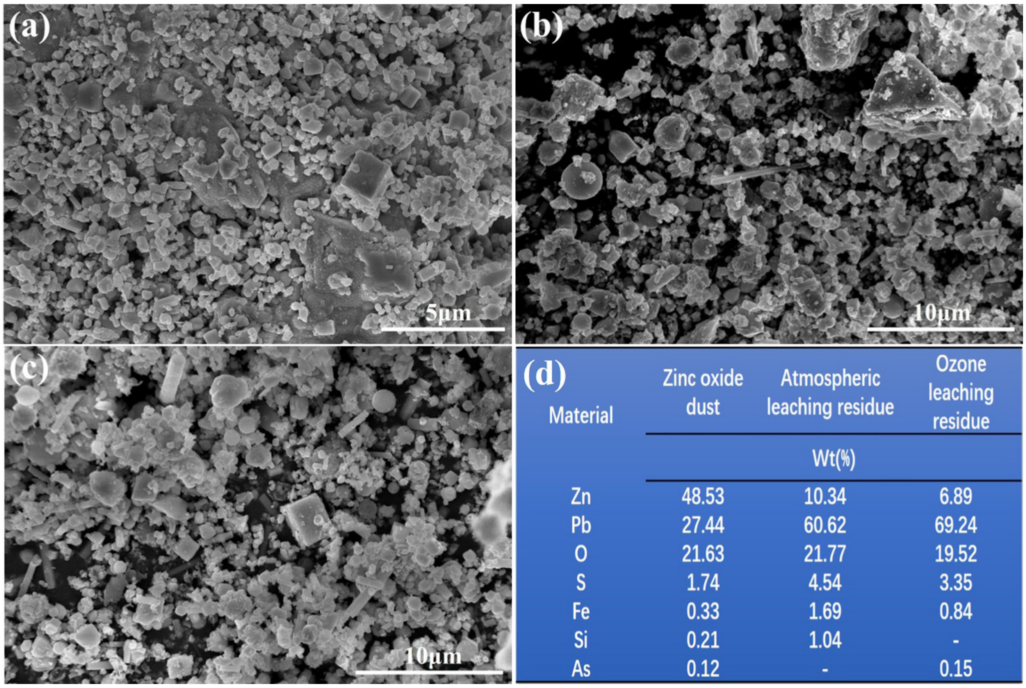


Fig. 9 XRD pattern of Characterization of the leaching residue.



Material	Zinc oxide dust	Atmospheric leaching residue	Ozone leaching residue
	Wt(%)		
Zn	48.53	10.34	6.89
Pb	27.44	60.62	69.24
O	21.63	21.77	19.52
S	1.74	4.54	3.35
Fe	0.33	1.69	0.84
Si	0.21	1.04	-
As	0.12	-	0.15

Fig. 10 SEM images of zinc oxide dust (a), atmospheric leaching residue (b) and ozone leaching residue (c) and EDS analysis (d).

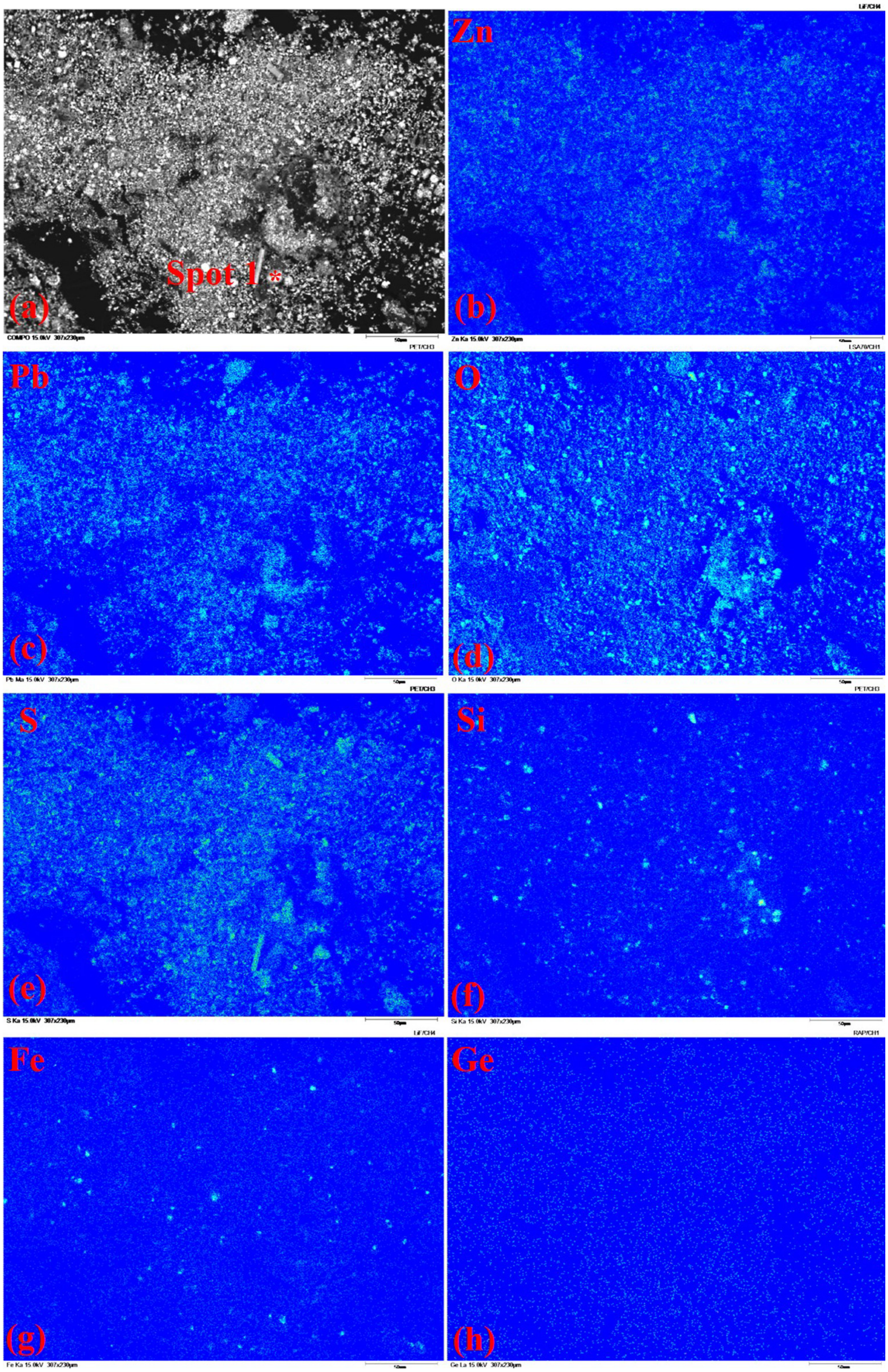


Fig. 11 BSE image (a) and EPMA element image (g-h) of ozone leaching residue.

may be the cause of partial loss of Zn and Ge (Jiang et al., 2020).

The content of sulfur increased from 1.74% in zinc oxide dust to 4.54% in atmospheric leaching residue, indicating that sulfur is further enriched and it is difficult to leach sulfide in atmospheric leaching. However, the sulfur content decreased to 3.35% after ozonation, which indicates that ozone can effectively leach sulfide. The iron-bearing phase is similar sulfide leaching, and iron is leached in large quantities after ozone is introduced. EDS analysis as expected, and combined with XRD analysis results was further confirmed.

Table 5 EDS analysis of ozone leaching residue in Fig. 11 (a).

Item	Spot 1
	wt. %
Zn	1.857
Pb	82.57
O	8.459
S	7.069
Ge	0.045
Assumed phase	$PbSO_4$, PbS, ZnS, Ge-containing minerals

3.2.4. EPMA characterization and analysis

Fig. 11a is the BSE image of ozone leaching residue, and Fig. 11 (b-h) is the EPMA image of Zn, Pb, O, S, Si, Fe, and Ge, respectively. It can be seen from the element distribution that the main phases are PbS, $PbSO_4$, ZnS, SiO_2, iron compounds, and Ge compounds. According to Fig. 11*h*, Ge is dispersed in phases containing Zn, Pb, Si, and Fe, which is consistent with the results of Jiang et al (2020) and Zheng et al (2012). The morphology of some spherical or near-spherical particles can be found in Fig. 11a. The EDS analysis results in Table 5 show that the spherical structure is mainly composed of lead, but contains a small amount of zinc, sulfur, germanium, and other elements, so it can be named Pb-based spheres, indicating that some of them (Ge compounds or Ge containing lead and zinc substances) is coated or trapped by Pb-based spheres (Jiang et al., 2020). During the leaching process, PbO (or Pb) on the surface of these particles is converted to $PbSO_4$, which forms a shielding layer to cut off the reaction between sulfuric acid and the substances in the particles, thus forming spherical particles in the residue (Jiang et al., 2020). These particles prevent some Zn and Ge from contacting with ozone, resulting in a small amount of Zn and Ge loss.

4. Conclusion

1) The results show that the optimum conditions of ozone leaching are as follows: the flow rate of ozone is 2 L/min, ozone time 10 min, initial acidity 160 g/L, liquid/solid mass ratio 7:1, leaching time 60 min, and leaching temperature 90℃. Under these conditions, the leaching rates of Zn and Ge are 95.79% and 93.65%, respectively. The leaching efficiency of Zn and Ge by ozone is 4.05% and 10.49% higher than that by atmospheric pressure, respectively.
2) Through leaching experiments combined with characterization analysis methods (XRD, SEM-EDS, and EPMA), it is proved that ozone can effectively leach ZnS and realize the efficient leaching of Zn and Ge.
3) The process is simple, the ozonation product is oxygen, clean, and pollution-free, and no new impurity ions will be introduced, which avoids the pollution caused by the traditional oxidant. At the same time, when the gas enters the solution system, it will play a stirring role and increase the contact efficiency between the material and the solution. Ozone is an easily available conventional raw material, which is easy to industrialize and implement.
4) The ozone leaching residue is mainly lead-based lead-silver slag, with a Pb content of 44.08%, which has great application value and can be returned to lead smelting enterprises as raw materials for lead smelting.

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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