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ATMOSPHERIC CURING OF ZINC SULFIDE CONCENTRATE BY SULFURIC ACID BELOW 300 °C

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Abstract

Because the traditional roasting-leaching-electrowinning zinc hydrometallurgy process has a small sulfuric acid sales radius and a high inventory pressure, the process of direct leaching zinc concentrate is gaining popularity, but the pressurized leaching process is a high-pressure condition, which requires strict equipment material and high safety requirements. Furthermore, the atmospheric leaching efficiency is low and generally introduces impurities and chloride ions, which increase the cost of subsequent decontamination. Therefore, a new environmentally friendly hydrometallurgy extraction method of zinc was proposed: an atmospheric pressure medium temperature sulfuric acid curing-leaching process. Under open-air conditions, zinc sulfide concentrate was cured with sulfuric acid at different acid-to-ore ratios and heated to 220 ℃~260 ℃ for a different time, then the cured product was leached. The effects of temperature, curing time, acid-to-ore ratio, and sulfuric acid concentration on the leaching ratio of zinc (η_{Zn}) were studied. The results demonstrated that η_{Zn} could reach as high as 98.23% under the optimized conditions of temperature 240 ℃, curing time 2.5 hours, acid-to-ore ratio 1.4:1, and sulfuric acid concentration 60 wt.%. The leaching residue ratio is 6%, with silicate accounting for the majority of it. The kinetic results support the shrinking core model, which is controlled by an interface chemical reaction with an apparent activation energy of 43.158 kJ/mol.

Keywords: *Zinc sulfide concentrate; Atmospheric curing; Kinetics; Shrinking core model*

1. Introduction

Zinc is an important and third widely used non-ferrous metal with good calendaring ability, wear resistance and corrosion resistance. It plays a principal role in industries such as steel, automobiles, machinery, aerospace, construction, ships, electronics, and daily chemicals [1, 2].

The conventional zinc production method is the conventional roasting-leaching-electrowinning-process (RLE process) [3, 4]. In RLE process, zinc concentrate is first roasted from zinc sulfide to zinc oxide calcine and SO_2 gas. After that, two-stepleaching of the calcine is carried out with sulfuric acid at room temperature and 60~80 ℃. The traditional zinc hydrometallurgy processes have always been associated with environmental pollution issues, such as soot and sulfur dioxide emissions [5]. It is mandatory to collect the SO_2 gas and convert it into sulfuric acid. Storage and sales of sulfuric acid are gradually becoming an economic obstacle [6]. Electrowinning is used to produce metallic zinc after the lixivium is carefully purified.

An alternative to the RLE process is direct leaching, where the zinc sulfide concentrates are directly leached without roasting and produces elemental sulfur or sulfate instead of gaseous SO_2. Hence, it is regarded as a more environmentally friendly process for zinc extraction [7-11], to a large extent for low grade and mineralogically complex concentrates [12-14].

Direct leaching processes can be divided into two categories: zinc pressure leaching (ZPL) processes, and atmospheric direct leaching (ADL) processes. Both processes have many industrial applications [15-19]. Sherritt Gordon Ltd. (Now Sheritt International) pioneered PL in the 1970s with its Sherritt Pressure Leach Process, which allows for quick concentrate dissolution [20]; the standard residence time of sphalerite pressure leaching process is 90 minutes, the leaching temperature is mostly higher than 120 °C, the pressure up to 1600 kpa, and autoclave equipment is

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required [21, 22]. The drawback of ZPL is large capital and maintenance requirements as well as high operational safety requirements. ADL is considered as an option to solve above-mentioned disadvantages, although ADL is carried out with slow reaction kinetics, resulting in approximately 24 hours of residence time paradoxically at near boiling temperature because of overly low solubility of oxygen in water and larger reactors are therefore needed compared to ZPL [15].

In ADL of zinc concentrate, besides oxygen, many other kinds of oxidizing agents have been applied such as Fe^{3+}, H_2O_2, HNO_3, O_3, MnO_2 or chlorate [1, 2, 23-26]. Notwithstanding, these oxidizing agent are costly or bring in metal impurities or chloride ions, which are tremendously harmful to the reaction system, and increase the difficulty and cost of subsequent impurity removal.

Concentrated sulfuric acid is both acidic and oxidizing. Nevertheless, there are few studies on the use of its first two properties simultaneously, and even fewer on atmospheric direct leaching of zinc sulfide concentrate adopting them [27]. Concentrated sulfuric acid was explored as a potential substitute oxidant in the atmospheric direct leaching process of zinc sulfide at medium temperature, which introduces no other impurity ions and improves the zinc extract efficiency.

2. Experimental

2.1. Materials

The zinc sulfide concentrate, from Yunnan province PRC, was dry ground in a ball mill and screened by 200 mesh with a particle size of less than 74 μm. The composition of zinc concentrate, determined by X-ray fluorescence analysis, is presented in Table 1. Sphalerite is the main mineral in the concentrate, in addition to sphalerite, zinc concentrate, as well as other sulfides such as pyrite and chalcopyrite, decided from the X-ray diffraction (XRD) pattern presented in Figure 1. A small quantity of galena and quartz are further observed through electron microscope as shown in Figure 2. Sphalerite particles vary in size, as shown in Figure 2. Pyrite and pyrrhotite mainly exist in a free form, while chalcopyrite mainly adheres to sphalerite and forms large symbiosis.

Table 1. *Chemical composition of zinc sulfide concentrate/wt.%*

Zn	Fe	Cu	S	Si	Pb	Others
56.50	7.14	2.13	23.16	4.33	0.14	6.60

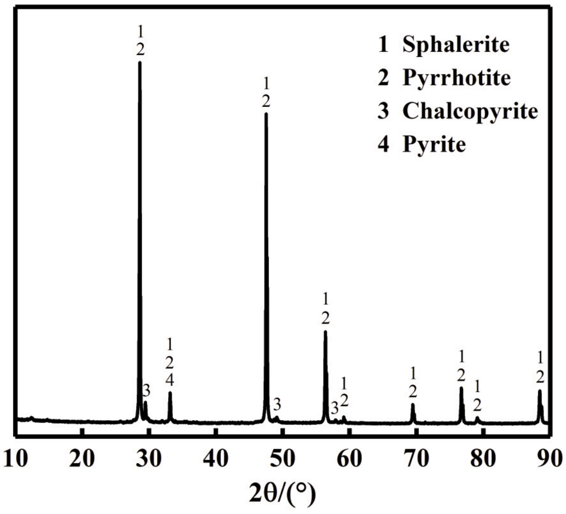

Figure 1. *XRD pattern of zinc sulfide concentrate*

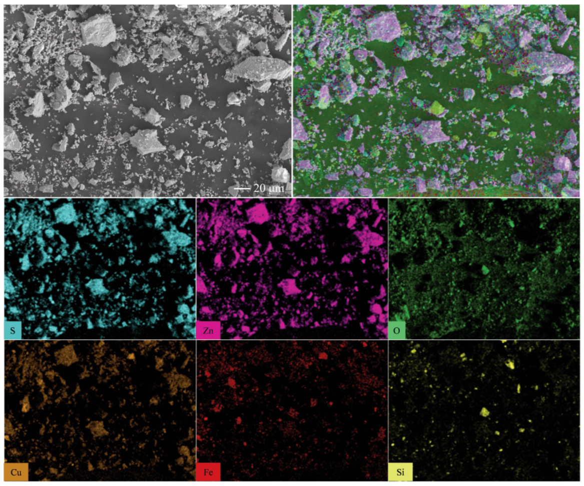

Figure 2. *Micrographs of zinc sulfide concentrate*

2.2. Equipment and procedures

The solutions adopted in the experiment were all prepared with deionized water produced in the laboratory with an electrical resistivity of 28.5 MΩ, and the chemical reagent used is concentrated sulfuric acid. Curing of 10 g zinc sulfide concentrate and dissimilar amount sulfuric acid were completed in an oil bath the temperature of which can be adjusted from room temperature to 300 °C. The pulp was made by adding a certain amount of water to the cooled cured mineral, stirring it at room temperature for a certain amount of time on a magnetic stirrer, then filtering and washing it for analysis.

The chemical composition of the zinc sulfide concentrates and leaching residue was determined by X-ray Fluorescence (ARLAdvantX Intellipower TM3600). Phase and structure analysis of the solid samples was regulated by X-ray diffractometer (D8 Advance powder diffractometer, Bruker) operated at an accelerating voltage of 40 kV, current of 40 mA and at a 2θ angle from 10° to 80° for Cu Kα radiation. Micro morphology of the samples was conducted by scanning electron microscope (Gemini 3 SEM, Carl Zeiss Microscopy GmbH). Moreover, solid samples were etched by ion beam etching system (AE4, ACME POLE Technology Co., Ltd). Inductively coupled plasma optical emission spectrometry (ICP-OES, Plasma 2000 ICP emission spectrometer, Ncs Testing Technology Co., Ltd) was employed to authenticate the concentrations of metal ions in solution samples.

3. Results and discussion

3.1. Effect of temperature and acid-to-ore ratio

The effects of acid-to-ore ratio ($R_{a/o}$) and temperature on zinc leaching rate (η_{Zn}) were investigated under the conditions of sulfuric acid concentration of 60 wt.% and curing time of 2.5 h. Figure 3 depicts the specific outcomes of the experiment.

As shown in Figure 3(a), the changes in temperature and acid-to-ore ratio have sensitive and intense effect on η_{Zn}. On the condition that the temperature is 160 °C, the η_{Zn} proved a trend of increasing first and then decreasing, and reached a maximum of 89.23% when the $R_{a/o}$ was 1.4. On the assumption the temperature is over 200 °C, η_{Zn} was raised with increasing the temperature untill the temperature reached 240 °C and began to decline. The highest η_{Zn} of 98.23% can be achieved at 240 °C. The optimum curing temperature is regarded as 240 °C.

$R_{a/o}$ also has a significant effect on η_{Zn} as presented in Figure 3(b). When the Ra/o is 1.2:1, η_{Zn} is relatively low, the highest leaching ratio of about 90.79% can be achieved when the temperature is 240 °C. Additionally η_{Zn} showed a trend of increasing first and then decreasing, and reached a maximum of 98.23% in the case that the $R_{a/o}$ was 1.4. As shown in Figure 3(b), η_{Zn} cannot be further enhanced by increasing the amount of sulfuric acid in the curing process. Excessive sulfuric acid increases the free residual acid in the leaching solution, increases the subsequent neutralization burden, and causes growing costs and environmental pollution. Hence, the optimum Ra/o is regarded as 1.4:1.

3.2. Effect of curing time

It is worth noting that the effect of curing time on η_{Zn} was explored under the conditions of curing temperature of 240 °C, $R_{a/o}$ of 1.4, and sulfuric acid concentration of 60 wt.%. Figure 4 depicts the specific experimental results.

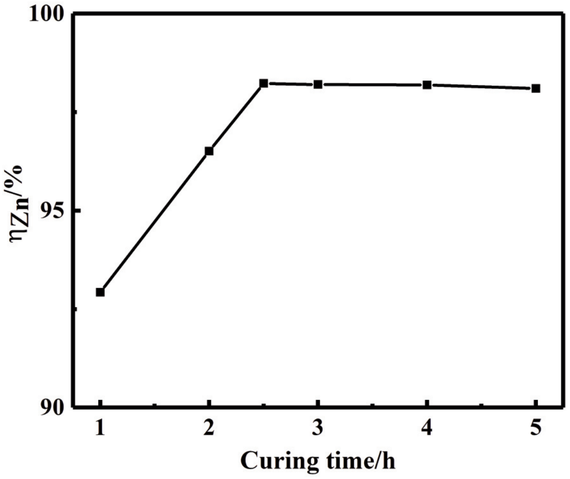

Figure 4. *Effect of curing time on η_{Zn}*

Figure 4 proves that the concentration of Zn increases significantly as the curing time increases. After 1 hour of curing, 92.93% of the zinc was converted from sulfide to soluble zinc sulfate. As the curing time extended, η_{Zn} reached the maximum value of 98.23% at 2.5h and then changed little. One

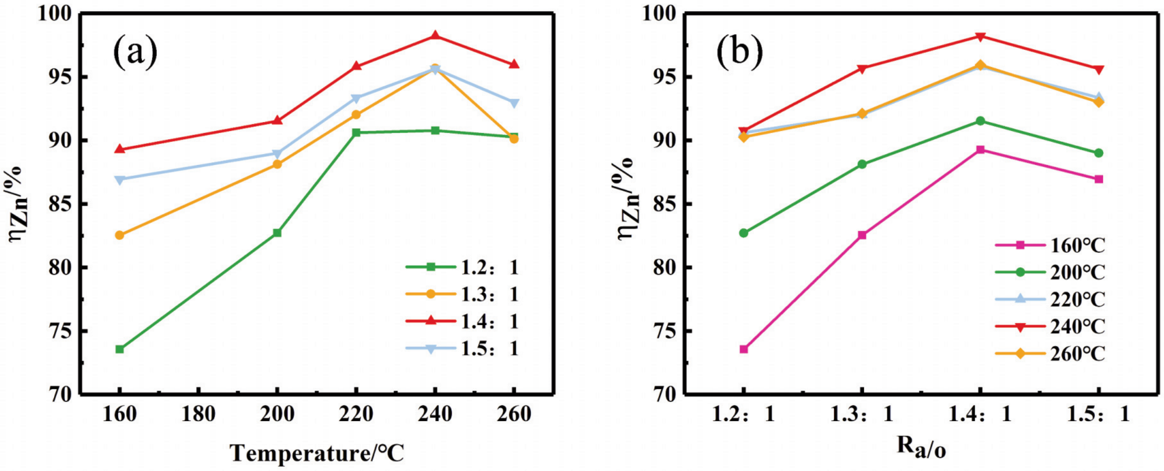

Figure 3. *Effect of curing temperature and $R_{a/o}$ on η_{Zn}*

explanation is that after 2.5 hours of curing, the samples were completely solidified, and no further zinc leaching was possible. Another possible explanation is that a small amount of elemental zinc was wrapped in silica and could not react with sulfuric acid, resulting in less fluctuation of η_{Zn} after 2.5 h.

XRD of the leaching residue at different curing times is shown in Figure 5. There are still some unreacted zinc sulfide components such as sulfide phase, sphalerite, and pyrite which remained in the leaching residue after 1 h and 2 h of curing. When the curing time is extended to 2.5 hours, the sulfide phase in the leaching residue disappears completely, and the leaching residue contains at most some difficult-to-react components such as silica, silicate, and a small part of $CuFeS_2$. It is observable from Figure 5 that the components in the leaching residue are only silica and silicate when the curing time is further extended to 5 hours.

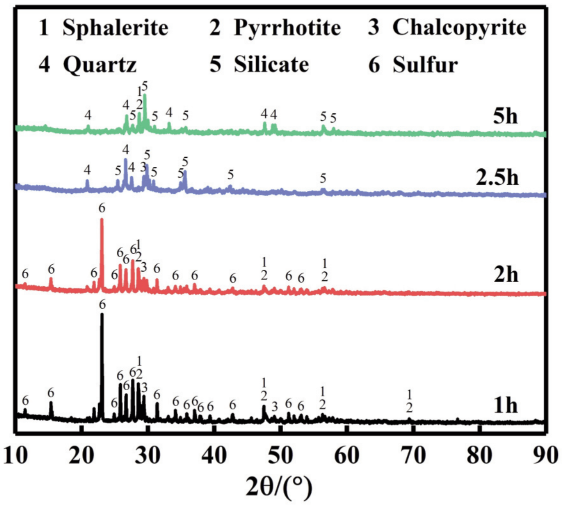

Figure 5. XRD patterns of leaching residues at contrasting curing times

It is obvious from Figure 5 that the leaching residue contains a large amount of sulfur when the curing time is less than 2.5 hours. The source of elemental sulfur should be attributed to the result of the acidity of sulfuric acid, as indicated in the reaction Equations (1) and (2), or to the result of the oxidizing ability of concentrated sulfuric acid, as proved in the reaction Equation (3).

$$ZnS + H_2SO_4 = ZnSO_4 + H_2S\uparrow \tag{1}$$

$$H_2S + H_2SO_4 = S\downarrow + SO_2 + 2H_2O \tag{2}$$

$$ZnS + 2H_2SO_4 = ZnSO_4 + S + SO_2\uparrow + 2H_2O \tag{3}$$

With the passage of time, the amount of elemental sulfur in the leaching residue gradually decreases. It should be attributed to the high vapor pressure of elemental sulfur at temperatures over 200 °C and the open-end condition turns elemental sulfur into gas overflow. This also explains why elemental sulfur in the leaching residue vanishes after 2.5 hours of curing.

When the curing time is increased to 5 hours, the zinc sulfide phase, which had previously vanished from the leaching residue, reappears. The reappearance of zinc sulfide phase should be ascribed to a small amount of $ZnSO_4$ product in the system which is transformed into ZnS with increasing curing time. This result is similar with Zhang et al [28], resulting in the decrease of η_{Zn}. Therefore, the optimum curing time is 2.5 hours

Table 2. *Chemical composition of leaching residue at contrasting curing times/wt.%*

Sample	Zn	S	Si	Ca	Mg	Pb
1 h-Leaching residue	1.02	32.24	5.14	0.63	0.38	0.06
2.5 h-Leaching residue	0.23	3.47	31.14	7.03	1.99	0.17
5 h-Leaching residue	1.80	5.25	27.18	4.20	1.72	0.28

3.3. *Effect of acid concentration*

The effects of sulfuric acid concentrations on η_{Zn} were explored under the conditions of curing temperature of 240 °C, $R_{a/o}$ of 1.4, and curing time of 2.5 hours. The results are shown in Figure 6. The XRD patterns of the leaching residue with contrasting sulfuric acid concentrations are presented in Figure 7.

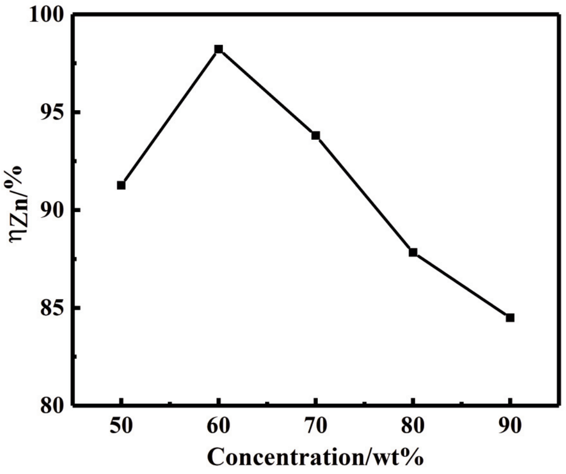

Figure 6. Effect of sulfuric acid concentration on η_{Zn}

As proved in Figure 6, when the concentration of sulfuric acid was 50 wt.%, the η_{Zn} was 91.27%. As the concentration of sulfuric acid increased to 60 wt.%, η_{Zn} raised to 98.23%. If the concentration of sulfuric acid increased further, the η_{Zn} began to decrease gradually, and when the concentration of sulfuric acid was 90 wt.%, the η_{Zn} was only 84.5%.

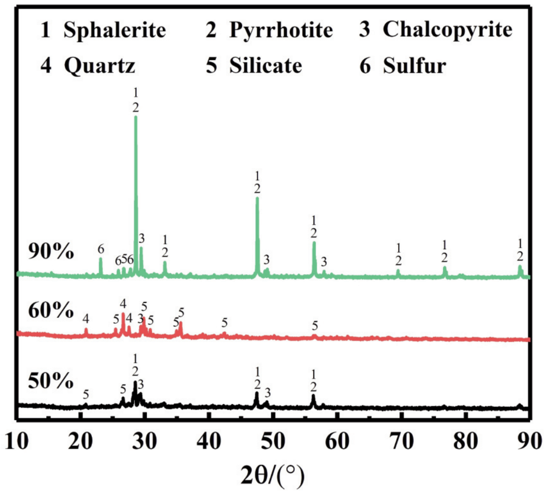

Figure 7. *XRD patterns of leaching residues with different acid concentrations*

Figure 7 and Table 3 depict the XRD patterns and chemical composition of leaching residues with different sulfuric acid concentrations. It can be concluded from Figure 7 that the leaching residue contains some unreacted zinc sulfide and higher sulfide elements when the sulfuric acid concentration is too low or too high, which is the reason for the low zinc leaching rate. Besides micromorphology of leaching residue with 90 wt.%, sulfuric acid concentrations were employed to clarify the reason for lower η_{Zn} with higher sulfuric acid concentration. Following the etched with ion beam etching system for 60 minutes, SEM of the leaching residue showed that there were some annular inclusions in the leaching residue, as presented in Figure 8. From Figure 8 (a), the profile of zinc sulfide particles in the leaching residue after reaction is annular, and the internal particles are wrapped by a layer of elemental sulfur deduced from the line scanning results in Figure 8(b).

Table 3. *Composition of leaching residue with different H_2SO_4 concentration/wt.%*

Sample	Zn	S	Si	Ca	Mg	Pb
50 wt.%-H_2SO_4	4.85	7.38	23.69	3.22	0.98	0.28
60 wt.%-H_2SO_4	0.23	3.47	31.14	7.03	1.99	0.17
90 wt.%-H_2SO_4	10.16	20.38	9.65	1.52	0.79	0.09

It is apparent from Table 3 that there is a large amount of sulfur in the leaching residue when the concentration of sulfuric acid is 90 wt.%. The results of the electron microscope revealed that the leaching residue contained more sulfur ring inclusions. It can be inferred that the wrapping of sulfur hinders the reaction between zinc sulfide concentrate and sulfuric acid. When the concentration of sulfuric acid is excessively high, its oxidizability is excessively strong, resulting in the direct oxidation of zinc sulfide concentrate as depicted by the formula (3). The sulfur in zinc sulfide is directly oxidized to elemental sulfur, resulting in the zinc sulfide particles being wrapped by in-situ product of elemental sulfur, which hinders the reaction of zinc sulfide and reduces the leaching ratio of zinc. Furthermore, the lower the concentration of sulfuric acid is, the lower its oxidation is, and indirect oxidation reaction occurs in zinc sulfide concentrate. Zinc sulfide reacts with sulfuric acid solution to produce H_2S gas, and then a part of H_2S reacts with sulfuric acid solution to produce elemental sulfur. Elemental sulfur is not rapped on sulfide during the indirect oxidation reaction.

4. Leaching residue

After curing and leaching of 10 g zinc sulfide concentrate for 2.5 hours at 240 °C with 60 wt.% sulfuric acid, 0.6 g leaching residue can be obtained. The morphology and chemical composition of the leaching residue is presented in Figure 9, Figure 10, and Table 3. The main components of the leaching residue are silica, silicate, and some sulfur. Any zinc-

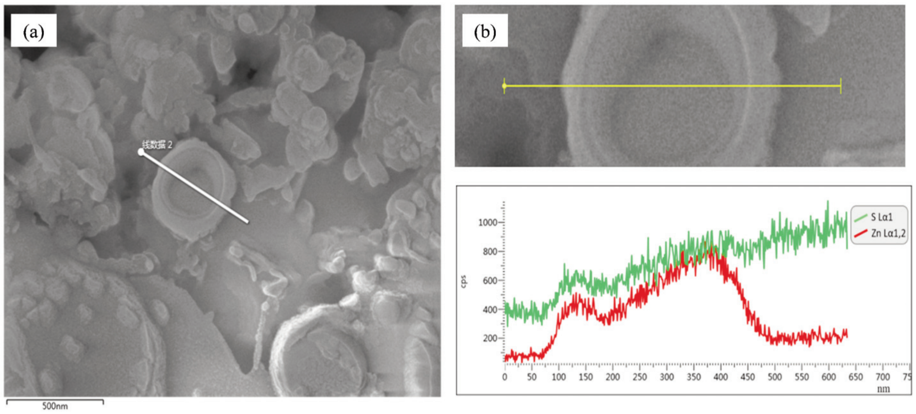

Figure 8. *SEM of leaching residue with curing sulfuric acid concentration of 90 wt.%*

containing phase did not appear in the leaching residue. The results make it clear that there is no obvious impediment to the zinc leaching process under open-air conditions when the zinc sulfide concentrate is solidified at high temperature and concentrated sulfuric acid. Other oxidants that cause this include the ferric system [9, 29], persulfates [22], nitric acid [23] or hydrogen peroxide [14, 30].

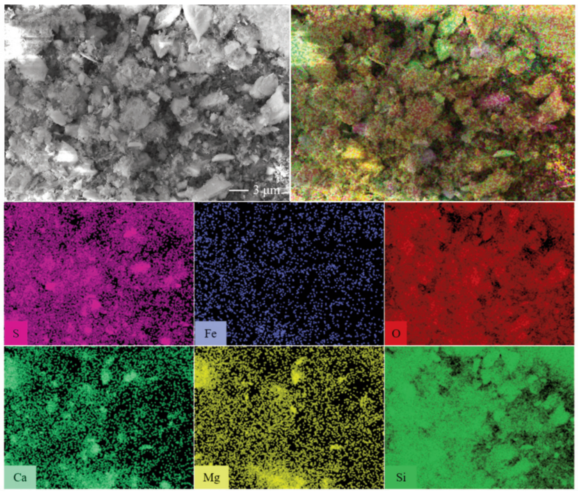

Figure 9. *Micrographs of optimum conditions for leaching residue*

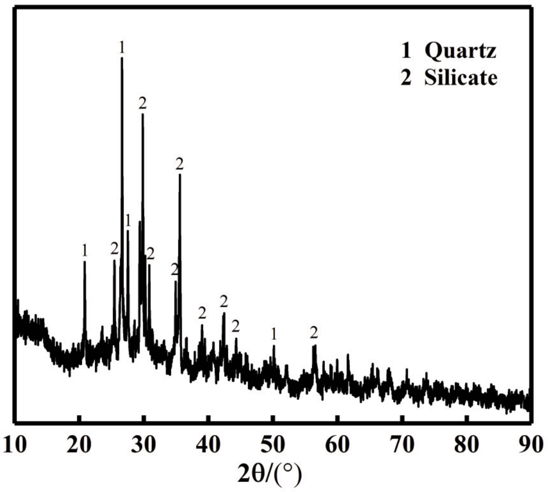

Figure 10. *XRD patterns of leaching residue*

5. Kinetics

The overall reaction process is controlled by a surface reaction, according to the best result from data-fit of the used kinetic models obtained through Equation (4):

$$1-(1-x)^{(1/3)}=k_r t \qquad (4)$$

where x is the conversion fraction of the zinc sulfide concentrate, calculated on the basis of the fraction of zinc dissolved; k_r is the rate constant; t is the curing time.

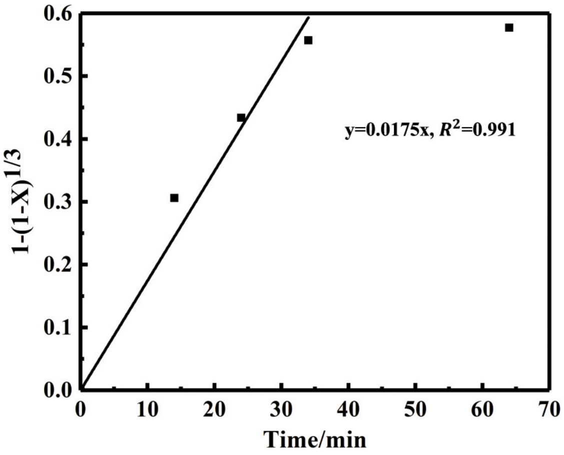

Figure 11. *$(1-x)^{(1/3)}$ vs t under the optimized condition*

Figure 11 shows that the chemical reaction at the interface controls the zinc leaching at the beginning of the process, following the kinetic law controlling the chemical reaction at the interface of the shrink core model [24]. As the reaction progresses, the data dispersion increases, indicating diffusion through the product layer. In addition s, the hindering effect on mineral dissolution gradually increases, which is consistent with the phenomenon that the zinc leaching rate increases sharply in the initial phaseand slows steadily in the laterphase.

Figure 12 is the plot of $1-(1-X)^{1/3}$ versus time for the dissolution of zinc at the moment that the zinc sulfide concentrate (75 µm) was curing in 60 wt.% sulfuric acid solution at various temperatures (160 °C, 180 °C, 200 °C, 220 °C, and 240 °C). At 160 °C-240 °C, the curves are essentially linear, and the rate

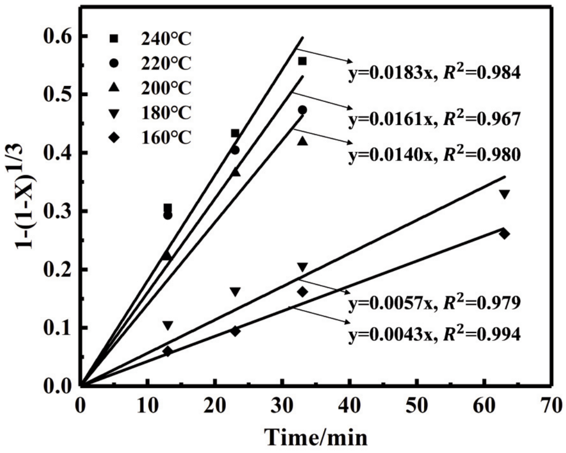

Figure 12. *$(1-x)^{(1/3)}$ vs t at different curing temperature*

constants, k_r, were calculated from the slopes of the straight lines and displayed in Figure 12. Nevertheless, Figure 12 indicates that the faster the chemical reaction is, the faster the data enter the discrete state as the temperature increases.

By plotting the natural logarithm of the rate constant (ln k *vs* 1/T), the Arrhenius plot is presented in Figure 13. The slope of this plot (−E/R) is −5.191. The activation energy was calculated as 43.158 kJ/mol, in the range of 40~300 kJ/mol, indicating extremely temperature-sensitive and such high activation energies fit for a surface chemical reaction controlled process. The activation energies for sphalerite leaching reported by various authors are similar to this value (Table 4).

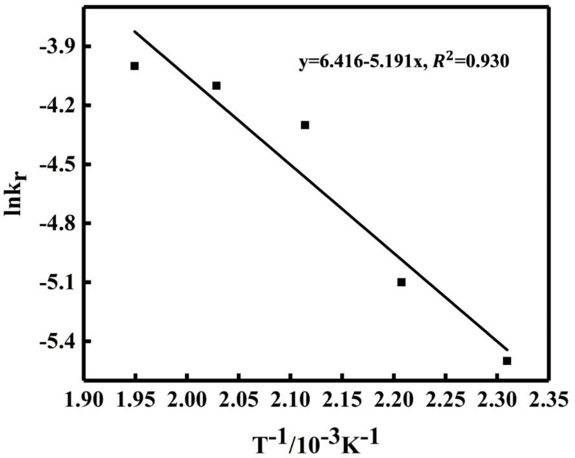

Figure 13. *Arrhenius plot of reaction rate versus curing temperature*

Table 4. *Reported activation energies for leaching of zinc concentrate with different leaching*

Leaching reagent	Activation energy/(kJ/mol)	Reference
Sodium chlorate in hydrochloric acid	41.1	[31]
Ferric sulfate	44.0	[32]
Acid ferric sulphate	49.7	[16]
Ferric chloride in hydrochloric acid	45.3	[25]
Ferric chloride	46.9	[33]
Hydrogen peroxide in sulphuric acid	43.0	[14]

6. Conclusions

The results of the experiment showed that 60 wt.% sulfuric acid was effective as an oxidant and leaching agent in the direct leaching of sphalerite concentrate in the openair at high temperature. Under the optimized conditions of 240 °C temperature, 2.5 hours curing time, acid-ore ratio of 1.4:1, and sulfuric acid concentration of 60 wt.%, a zinc leaching efficiency of 98.23% was achieved. The reaction is consistent with the to the shrinking core model. In the initial phase, the reaction is controlled by the surface chemical reaction, whose calculated activation energy is 43.158 kJ/mol.

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Author contributions

Writing-original draft, Investigation, Data curation: Fanlei Deng. Conceptualization, Funding acquisition, Writing-review & editing: Ruixin Ma. Supervision: Shina Li. Investigation: Guixiao Xu. Validation: Wenwen Fan.

Data availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflict of 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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ATMOSFERSKO TRETIRANJE KONCENTRATA CINK SULFIDA SUMPORNOM KISELINOM ISPOD 300 °C

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Apstrakt

Pošto tradicionalni proces hidrometalurgije cinka koji uključuje prženje, luženje i elektrolitičku ekstrakciju ima mali radijus prodaje sumporne kiseline i dolazi do gomilanja zaliha, proces direktnog luženja koncentrata cinka je sve popularniji. Međutim, proces luženja pod pritiskom zahteva uslove visokog pritiska za koji su potrebni kako striktna oprema tako i visoki sigurnosni zahtevi. Štaviše, efikasnost atmosferskog luženja je niska i obično uvodi nečistoće i hloridne jone, što povećava troškove naknadne dekontaminacije. Stoga je predložena nova, ekološki prihvatljiva hidrometalurška metoda ekstrakcije cinka: proces tretiranja-luženja sumpornom kiselinom pri atmosferskom pritisku na srednjoj temperaturi. U uslovima na otvorenom, koncentrat cink sulfida se tretira sumpornom kiselinom u različitim odnosima kiseline i rude, i zagreva na 220 °C ~ 260 °C tokom različitih vremenskih perioda, a zatim se tretirani proizvod luži. Proučavani su uticaji temperature, vremena tretiranja, odnosa kiseline i rude i koncentracije sumporne kiseline na odnos luženja cinka (η_{Zn}). Rezultati su pokazali da η_{Zn} može dostići čak 98,23% pod optimizovanim uslovima temperature 240 °C, vremena tretiranja 2,5 sata, odnosa kiseline i rude 1,4:1 i koncentracije sumporne kiseline 60 wt.%. Udeo ostatka luženja je 6%, pri čemu najveći deo čini silikat. Kinetički rezultati podržavaju model kontrakcije jezgra, koji je kontrolisan hemijskom reakcijom na međufaznoj površini sa energijom aktivacije od 43,158 kJ/mol.

Ključne reči: *Koncentrat cink sulfida; Atmosfersko tretiranje; Kinetika; Model kontrakcije jezgra*