IRON OXIDE SYNERGISTIC VACUUM CARBOTHERMAL EXTRACTION OF ZINC FROM ZINC SULFIDE

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Abstract

To reduce the issues of high pollutant emissions and lengthy processes in extracting zinc from zinc sulfide ore, a new technical approach involving the synergistic use of iron oxide and vacuum carbothermal reduction to extract zinc from zinc sulfide ore is proposed. The iron oxide is sourced from high-iron-content metallurgical residue. Under vacuum conditions, carbon reduces the iron oxide to metallic iron, which then displaces the zinc in the sulfide and produces zinc vapor. The zinc vapor is finally condensed to obtain metallic zinc. This study investigates the extraction of zinc from zinc sulfide under vacuum conditions using iron powder, pure iron oxide powder, and iron oxide from roasted cyanide tailings as iron sources. The main factors examined were the reduction temperature and the holding time on the zinc volatilization rate. The results show that at a molar ratio of $n_{Fe}:n_{Zn}=1.1:1$, a temperature of 1000 °C, and an initial furnace pressure of 10 Pa, iron powder, pure iron oxide powder, and iron oxide from roasted cyanide tailings can all achieve a zinc volatilization rate of over 99% from zinc sulfide. Different iron sources react with zinc sulfide to form FeS, and no sulfur-containing gases are produced in the zinc extraction process.

Keywords: Vacuum carbothermal reduction; Iron oxide; Replacement; Zinc sulfide; Iron

1. Introduction

The extraction of metallic zinc from zinc sulfide concentrate generally employs the hydrometallurgical zinc production process. This process first involves roasting the zinc sulfide concentrate to convert it into zinc oxide. The zinc oxide is then acid-leached to obtain a zinc sulfate solution, which is purified and then subjected to electrolysis to produce metallic zinc. This process is lengthy and results in the emission of pollutants such as SO_2, metal-containing wastewater, purification residues, and leaching residues. These pollutants require harmless treatment, which incurs high management costs [1-4]. Therefore, there is a need to explore zinc extraction methods that produce fewer pollutants and have simpler processes. Under vacuum conditions at around 1100 °C, iron powder and ZnS can react through a displacement reaction to generate metallic zinc vapor. The zinc vapor can be condensed and collected to obtain metallic zinc crystals, combining iron with sulfur to form FeS [5]. Ferrous sulfide (FeS) can serve as a raw material for pyrometallurgical smelting of non-ferrous metals such as copper and lead. During the pyrometallurgical smelting process, FeS releases heat, serving as

supplementary heat for the smelting furnace, with iron aiding in residue formation, and sulfur being oxidized and collected in the smelting flue gas collection system. The of use of iron powder to displace ZnS under vacuum conditions is simple and can fix sulfur in the form of FeS in the residue, thereby reducing sulfur emissions during the zinc extraction process. However, since iron powder is expensive, its use as a displacement agent results in high production costs. Therefore, there is a need to explore other lower-cost iron sources as displacement agents for zinc in zinc sulfide, in order to reduce the cost of vacuum displacement zinc extraction. Many metals produce large amounts of high-iron residue during the smelting process, such as blast furnace dust, copper smelting residue, and gold smelting residue. Currently, the main resource utilization method for recovering iron from these high-iron residues is the high-temperature carbothermic reduction-magnetic separation method, which recovers iron to be used as a raw material for steelmaking [6-10]. However, the recovered iron has a high content of non-ferrous metals, which does not meet the requirements for ironmaking. Therefore, it is necessary to seek resource utilization methods for iron-containing

residue [8,11,12].

The displacement of zinc sulfide by iron powder and the carbothermic reduction of iron oxide both require high temperatures. The iron in smelting residue predominantly exists in the form of iron oxide, which can be reduced to metallic iron through high-temperature carbothermic reduction. The metallic iron can act as a source of iron for the displacement of zinc sulfide. Consequently, by mixing zinc sulfide ore with iron-containing residue and performing high-temperature carbothermic reduction under vacuum conditions, it is possible to achieve the reduction of iron in iron-containing residue and the displacement distillation of zinc in zinc sulfide to produce metallic zinc, with iron being converted to FeS. FeS can be used as an auxiliary material in copper smelting [13-17], thus enabling the utilization of both materials through a single reduction-distillation process. The schematic diagram of the technical approach for the synergistic extraction and utilization of iron-containing residue and zinc sulfide through the vacuum carbothermic method is shown in Figure 1. This technical approach allows for the short-process extraction of ZnS and the resource utilization of iron-containing smelting residue. Additionally, other non-ferrous metals in the iron-containing residue and the zinc sulfide ore may be carried into the ferrous sulfide, creating the conditions for the enrichment and extraction of other associated non-ferrous metals from both materials.

To verify the feasibility of this technical approach, studies were conducted on the vacuum extraction of zinc from ZnS using iron powder, iron oxide powder, and roasted cyanide tailings as iron sources, and semicoke powder as the carbonaceous reducing agent. The study focused on the effects of different heating temperatures and holding times on the zinc volatilization rate when using roasted cyanide tailings as the iron source. The results provide a reference for the short-process clean extraction of zinc sulfide and the comprehensive recovery and extraction of metals from iron-containing smelting residue.

2. Experimental Procedures
2.1. Raw materials

The ZnS sample used in this experiment is a zinc-containing waste desulfurization catalyst, with a zinc content of 62.2% (GB/T 8151.1-2012). The main phase of zinc in the waste catalyst is ZnS, and the phase detection results are shown in Figure 2. The iron powder and iron oxide powder used are commercially available analytical-grade reagents, with the phase of the iron oxide powder being Fe_2O_3. The iron-containing smelting residue is roasted cyanide tailings from a plant in Henan Province. The main components of the roasted cyanide tailings are shown in Table 1, where the primary phases are Fe_2O_3 and SiO_2. The phase detection results of the roasted cyanide tailings are shown in Figure 3. The reducing agent, carbon powder, is semicoke powder from Yulin, Shaanxi Province. The composition of the semicoke powder is shown in Table 2.

2.2. Experimental Procedures

The waste catalyst, iron-containing raw materials, and the semicoke powder were dried and then crushed to below 75 μm, and their main components were analyzed. The crushed samples were proportioned according to the experimental design and thoroughly mixed. The mixed materials were then pressed into cylindrical samples of Φ20×10 mm using a press at a pressure of 50 kN. The pressed samples were weighed
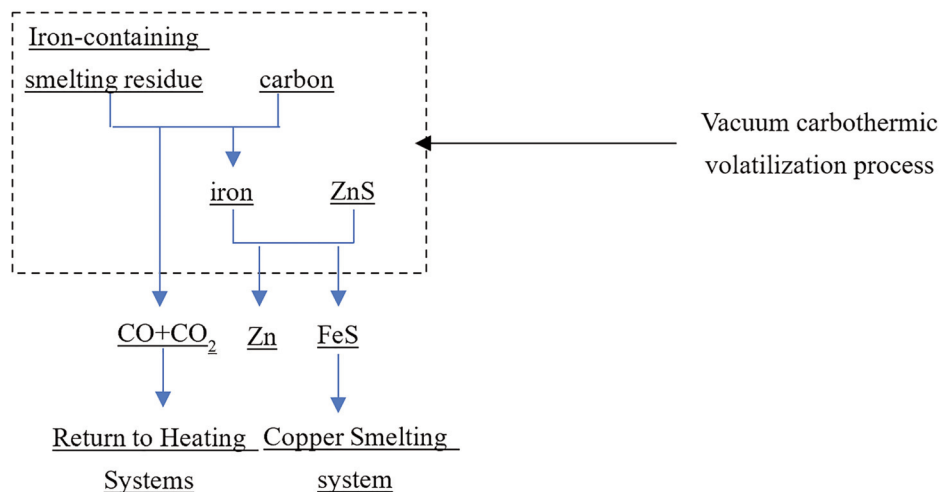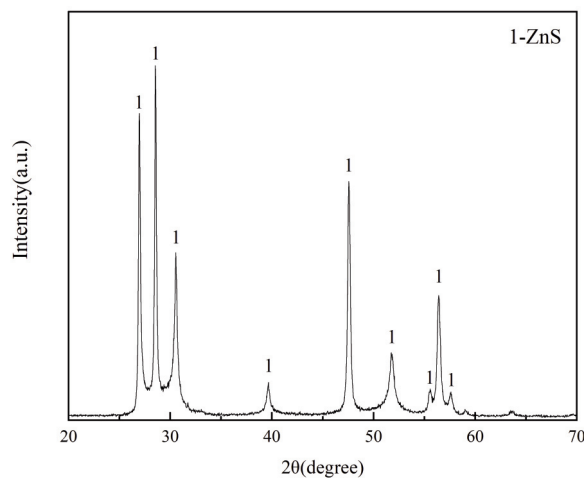

Figure 1. *Iron oxide synergistic vacuum carbothermal extraction of zinc in zinc sulfide technology idea*

Table 1. Content of major elements in residue

Components	S	Cu	Pb	Zn	SiO$_2$	Fe	Au*
Contents/%	1.4	1.4	0.27	0.009	35.92	33.9	1.14
Note: w(Au*)/(g·t^{-1})							

Table 2. Semi-coke composition/wt%

Aad	Vad	Fcad	Al$_2$O$_3$	CaO
7.6	3.73	75	2.18	2.29

*Figure 2. Main phases of zinc-containing waste desulfurization catalysts*

and then placed into a tubular vacuum furnace. The vacuum pump was turned on to reduce the pressure inside the furnace to below 10 Pa. Heating was initiated to raise the furnace temperature to the set value, and the temperature was maintained for a certain period. After the holding period, heating was stopped, and the samples were allowed to cool to room temperature inside the furnace. Once cooled, the vacuum was broken, and the samples were removed and weighed. The zinc content in the reduced samples was determined using Inductively Coupled Plasma (ICP) analysis, and the zinc volatilization rate was calculated. The main phases in the samples were analyzed using X-ray diffraction (XRD). The microstructure of the reduced residue and its micro-area composition were examined using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS).

2.3. Calculation of volatilization rate of zinc

The volatilization rate of zinc is calculated in equation (1).

$$\eta = \frac{m_1 s_1 - m_2 s_2}{m_1 s_1} \times 100\% \qquad (1)$$

In the formula: η- zinc volatilization rate, %; m_1-mass of the sample before heating, g; s_1-zinc content in the sample before heating, %; m_2-mass of the sample after heating, g; s_2-zinc content in the sample after heating, %.
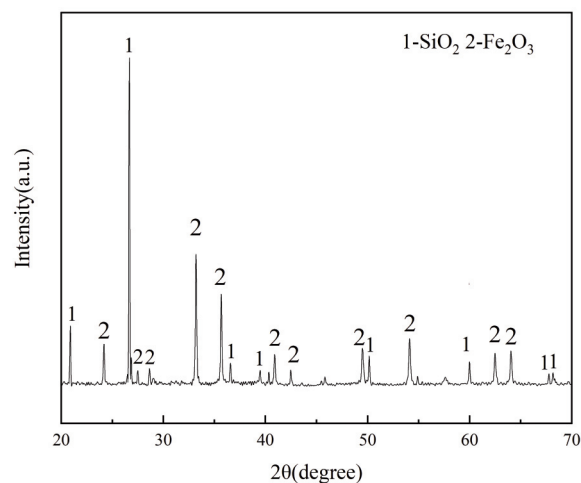
Figure 3. Main phases in roasted cyanide tailings

2.4. Reduction output tail gas composition testing

The composite material consisting of roasted cyanide tailings, zinc sulfide, and semicoke was pressed into a briquette, resulting in a sample weighing 6g. This sample, placed in a vacuum furnace with an initial pressure of 10 Pa, was heated to 1000 °C and held for 30 minutes. After the holding period, the sample was cooled down along with the furnace. Throughout the reduction and cooling process, a 1L gas collection bag was used to collect the exhaust gas from the vacuum pump's outlet. The composition of the exhaust gas, specifically the concentrations of CO, CO$_2$, SO$_2$, and COS, was analyzed using a Fourier Transform Infrared (FTIR) spectrometer.

3. Results and discussion
3.1. Theoretical analysis of iron oxide synergistic vacuum carbothermal extraction of zinc in zinc sulfide

The primary components in the mixture of roasted cyanide tailings, desulfurizer, and semicoke are Fe$_2$O$_3$, ZnS, and carbon. During the vacuum carbothermal reduction process, Fe$_2$O$_3$ is reduced by

carbon. This reduction can occur via direct or indirect mechanisms, producing CO and CO_2 as the byproducts of the carbon components. Fe_2O_3 is reduced to metallic iron, which subsequently undergoes a displacement reaction with ZnS, converting the zinc in ZnS to zinc (Zn). Due to the high vapor pressure of zinc at elevated temperatures, it transforms into gaseous zinc (Zn(g)), and iron combines with sulfur to form FeS. The potential reactions of the components in the mixture during the vacuum reduction process are shown in Equations (2) to (10). The initial reaction temperatures and ΔG^0_T values for Equations (2) to (10) under standard atmospheric pressure and a vacuum furnace pressure of 10 Pa were calculated using the Reaction Equation module of HSC Chemistry 6.0 software. The formula for ΔG^0_T values at a vacuum furnace pressure of 10 Pa is shown in Equation (11). The initial reaction temperatures under standard atmospheric pressure and a furnace pressure of 10 Pa are detailed in Table 3, and the relationship between Gibbs free energy and temperature for each reaction is illustrated in Figure 4.

In Table 3, Equations (2) to (5) as well as Equations (9) and (10) represent gas-generating expansion reactions, while Equations (6) to (8) are reactions where the amount of gas remains unchanged before and after the reaction. Comparing the initial reaction temperatures in Table 3 indicates that the initial reaction temperatures for gas-generating expansion reactions at a pressure of 10 Pa are lower than those at standard atmospheric pressure, while the initial reaction temperatures for reactions with no change in the amount of gas remain constant. This indicates that vacuum conditions can lower the initial reaction temperature of expansion reactions.

Based on the initial reaction temperatures, it can be deduced that during the vacuum reaction process, iron oxide can be reduced to metallic iron at lower temperatures (Equations (3) to (8)). The initial reaction temperature for the reaction of CO with ZnS to form COS gas and zinc vapor (Equation (9)) is

1200 °C, and for the reaction of FeO with ZnS to form SO_2 gas and zinc vapor (Equation (10)) is 900 °C. These temperatures are higher than the initial reaction temperature of 800 °C for the displacement reaction of metallic iron with ZnS to form FeS and zinc vapor (Equation (2)). This suggests that in the mixture, iron oxide is first reduced to metallic iron, which then reacts with ZnS to form FeS. Therefore, in the reaction system of the mixture, under conditions of sufficient iron, the sulfur in ZnS reacts with the metallic iron reduced from iron oxide to form FeS, which remains in the reaction residue and does not cause sulfur to be released.

$$\Delta G_T = \Delta G^0 + 2.303RT \lg K \tag{11}$$

$$K = \frac{p_1}{p^0} \times \frac{p_2}{p^0} \tag{12}$$

In the equation: ΔG^0 represents the standard Gibbs free energy of the reaction, kJ/mol; ΔG_T represents the Gibbs free energy of the reaction at the calculated temperature and pressure conditions, kJ/mol; p^1 and p^2 represent the partial pressures of various gas phases in the furnace during the vacuum reduction process, Pa; p^0 represents the standard atmospheric pressure, 101325 Pa; T represents the reaction temperature, K.

From Figure 4, it can be seen that with the increase in temperature, ∆G of reaction (8) increases, while the ∆G of other reactions decreases. The Gibbs free energy change (∆G) for the reduction of Fe_2O_3 with carbon is less than 0 at 400 °C, indicating that the reduction of Fe_2O_3 to metallic iron by carbon can occur at temperatures above 400 °C. The Gibbs free energy change (∆G) for the displacement of zinc sulfide by iron and the generation of zinc vapor is approximately 0 at 800 °C, indicating that the reaction can proceed at temperatures above 800 °C.

Table 3. Possible reactions and their reaction temperatures

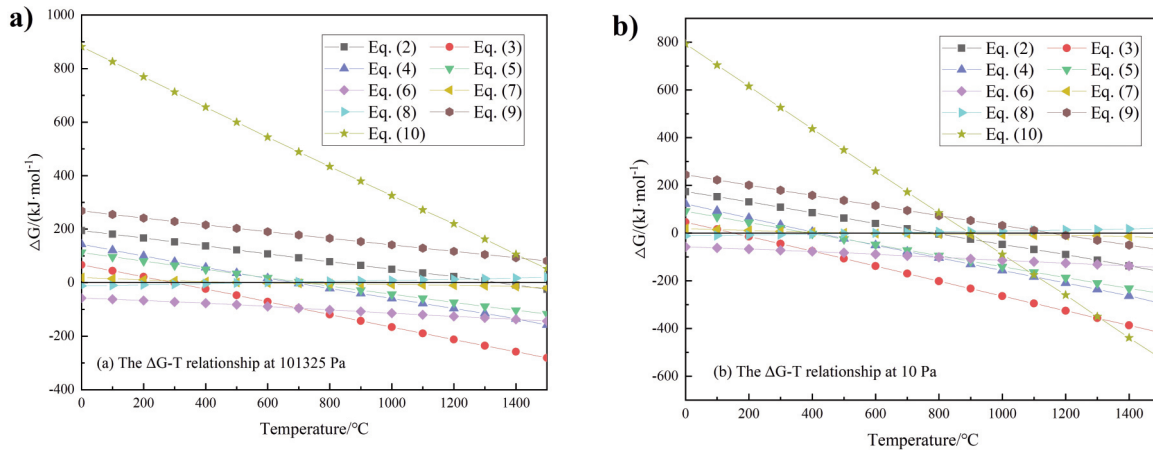| Serial number	Possible reactions	Initial reaction temperature at 101325 Pa / °C	Initial reaction temperature at 10 Pa / °C
(2)	Fe+ZnS=Zn(g)+FeS	1400	800
(3)	$C+3Fe_2O_3=2Fe_3O_4+CO$	300	200
(4)	$C+Fe_3O_4=3FeO+CO$	700	500
(5)	C+FeO=Fe+CO	800	400
(6)	$CO+3Fe_2O_3=2Fe_3O_4+CO_2$	0	0
(7)	$CO+Fe_3O_4=3FeO+CO_2$	600	600
(8)	$CO+FeO=Fe+CO_2$	≤500	≤500
(9)	CO+ZnS=COS(g)+Zn(g)	>1500	1200
(10)	$3ZnS+2FeO=SO_2(g)+3Zn(g)+2FeS$	>1500	900

Figure 4. *The ΔG-T relationship of each reaction under different pressure conditions: (a) the ΔG-T relationship at 101325 Pa; (b) the ΔG-T relationship at 10 Pa*

3.2. The test results of vacuum replacement of zinc in zinc sulfide with iron powder as iron source

The molar ratio of iron to zinc sulfide is 1.1:1, and the initial pressure inside the vacuum furnace is 10 Pa. The sample is heated to the experimentally set temperature and held for 30 minutes. The effect of the heating temperature on the zinc volatilization rate is shown in Figure 8.

From Figure 8, it can be seen that the zinc volatilization rate is 0 between 550~750 °C. Between 750~950 °C, the zinc volatilization rate increases rapidly with temperature, reaching 99.98% at 1000 °C, indicating that the zinc in the material is almost completely volatilized. There are two processes for the zinc volatilization from zinc sulfide: first, ZnS is displaced to form metallic zinc; then, the liquid metallic zinc changes to a gaseous state and volatilizes from the solid lumps into the gas phase. According to the theoretical calculation results for the iron displacement of zinc sulfide (Figure 4), the reaction initiation temperature for the iron displacing ZnS is about 800 °C. When the heating temperature is higher than 800 °C, the zinc volatilization rate gradually increases. As the temperature rises, zinc is displaced to form elemental zinc, and due to the high temperature in the furnace, the vapor pressure of zinc increases, promoting its volatilization. When the temperature is below 750 °C, the reaction of iron displacing ZnS cannot occur; hence, the zinc volatilization rate is 0.

3.3. The test results of vacuum carbothermal extraction of zinc from zinc sulfide with iron oxide as an iron source

To ensure that iron can fully displace zinc sulfide,

the amount of iron used in the experimental mixture is 1.1 times the theoretical amount needed for the displacement reaction, as calculated by reaction equation (2). To ensure that carbon can fully reduce iron oxide to metallic iron, the amount of carbon used is 1.1 times the theoretical amount needed for the reduction of iron oxide to metallic iron, as calculated by reaction equations (3) to (5). Based on the above mixing principles, the molar ratio of the three materials in the mixture is $(ZnS:Fe_2O_3:C) = 1:0.55:1.82$. The three raw materials were mixed according to the mixing requirements to make a sample, which was then placed in a furnace with an initial pressure of 10 Pa and heated to different temperatures, maintaining each temperature for 30 minutes. The relationship between the zinc volatilization rate and temperature is shown in Figure 8, and the phase changes of the reaction materials at different heating temperatures are shown in Figure 5.

From Figure 8, it can be seen that the zinc volatilization rate is 0 below 750 °C. Between 750 to
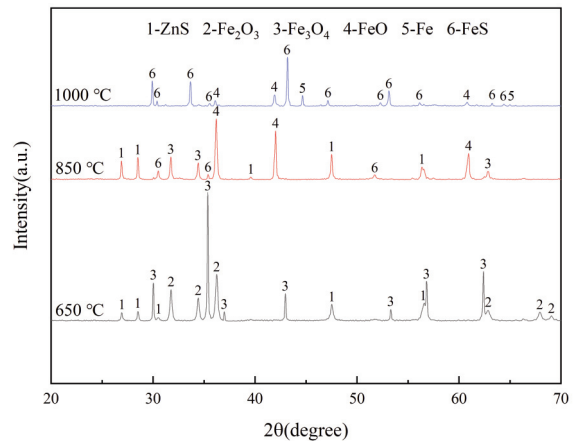

Figure 5. *Phase change of reaction materials at different heating temperatures*

950 °C, the zinc volatilization rate increases significantly with rising temperature, reaching 99.56% at 1000 °C. In Figure 5, the main phases at 650 °C are ZnS, Fe_2O_3, and Fe_3O_4, indicating that the phase of zinc sulfide in the reactants has not changed, while Fe_2O_3 begins to be reduced by carbon to Fe_3O_4. The main phases at 850 °C are ZnS, FeO, Fe_3O_4, and FeS. The formation of FeS begins, and there is no metallic zinc in the phase, indicating that at this temperature, the iron produced by the reduction of iron oxide starts to react with zinc sulfide, causing zinc to escape in the form of zinc vapor. The main phases at 1000 °C are FeS, FeO, and iron. There are no zinc or zinc compounds in the phase, indicating that all zinc has been displaced by the iron produced from the reduction of iron oxide and has left the reaction interface.

From the experimental results of iron powder displacing zinc sulfide, it can be concluded that above 750 °C, iron has already reacted with zinc sulfide in a displacement reaction. Based on this, it can be inferred that above 750 °C, the iron oxide in the mixed material, where iron oxide is the iron source, has been reduced by carbon to metallic iron, and the metallic iron produced by the reduction has reacted with zinc sulfide in a displacement reaction. The maximum heating temperature controlled in the experiment is 1000 °C, which is far below the melting point of zinc sulfide (1850 °C). Therefore, the reduction displacement reaction belongs to the solid-phase reaction category. The particle size of iron and zinc sulfide, as well as the degree of their contact, significantly affect the extent of the solid-phase reaction [19,20]. During the carbon reduction process, iron oxide first forms very small metallic iron particles, which then gradually grow and aggregate into larger metallic iron particles [12,18,19]. In Figure 8, the volatilization rate of zinc in the mixture of carbon, iron oxide, and zinc sulfide at 850 °C and 950 °C is significantly higher than that in the mixture of iron and zinc sulfide. This indicates that when iron oxide is used as the iron source to displace zinc sulfide, the initially formed small-diameter metallic iron particles produced by carbon reduction react with ZnS. The smaller diameter metallic iron particles have higher reactivity than pure iron powder and can promote the occurrence of the displacement reaction. On the other hand, at high temperatures, carbon in the compact reacts with iron oxide to form iron and CO or CO_2 gas. The consumption of carbon creates more pores in the compact. The increase in the number of pores in the lumps reduces the resistance for the zinc vapor generated by the displacement to diffuse from the inside to the outside of the lumps, which helps to increase the zinc volatilization rate.

3.4. The test results of vacuum carbothermal extraction of zinc from zinc sulfide with iron in roasted cyanide tailings as iron source

3.4.1. Effect of heating temperature on zinc volatilization rate

Using iron oxide as the iron source, efficient extraction of zinc from zinc sulfide can be achieved at 1000 °C. Referring to the experimental results of zinc extraction using iron oxide as the iron source, the ratio of the mixture of roasted cyanide tailings, semicoke, and zinc sulfide is kept consistent with the ratio using iron oxide as the iron source. The proportioning is $(ZnS:Fe_2O_3:C) = 1:0.55:1.82$, where the amount of Fe_2O_3 in the mixture is calculated based on the iron oxide content in the roasted cyanide tailings. The mixture samples were heated at different temperatures under an initial furnace pressure of 10 Pa and held for 30 minutes. The relationship between the zinc volatilization rate and temperature is shown in Figure 8, and the phase changes of the reaction materials at different heating temperatures are shown in Figure 6.
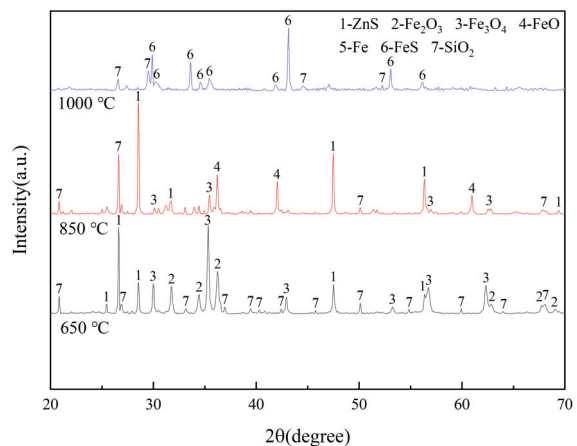

Figure 6. Phase change of reaction materials at different heating temperatures

From Figure 8, it can be seen that the zinc volatilization rate is 0 below 750 °C. Between 850 °C and 950 °C, the increase in zinc volatilization rate is significant, reaching 70.4% at 1000 °C. Figure 6 shows that under the same heating temperature conditions, the reaction residue using roasted cyanide tailings as the iron source contains more SiO_2 phase compared to the reaction residue using pure iron oxide as the iron source, while the reaction temperature and process remain unchanged.

In Figure 8, comparing the experimental results of using iron oxide as the iron source to displace zinc sulfide and using roasted cyanide tailings as the iron source to displace zinc sulfide, at the same temperature, the zinc volatilization rate is higher

when using iron oxide as the iron source compared to using roasted cyanide tailings as the iron source. The iron content in roasted cyanide tailings is 33.9%, whereas the iron content in pure Fe_2O_3 is about 70%. When displacing the same amount of ZnS, the amount of roasted cyanide tailings required in the mixture is be more than twice that of pure Fe_2O_3. Therefore, when using roasted cyanide tailings as the iron source, a large amount of other impurities will mix into the mixture, resulting in a lower zinc and iron grades in the mixture. The displacement reaction between iron and zinc sulfide is a solid-phase reaction. Microscopically, the zinc and iron grades in the lump material are reduced, and the distance between zinc sulfide and iron is relatively far. When the holding time is short, the metallic iron grains produced by the reduction of iron oxide are small. These smaller metallic iron grains cannot fully contact ZnS. Therefore, when using roasted cyanide tailings as the iron source, the zinc volatilization rate is lower compared to using pure iron oxide.

3.4.2. Effect of holding time on zinc volatilization rate

Samples were pressed from roasted cyanide tailings, semicoke, and zinc sulfide according to the ratio of (ZnS:Fe_2O_3:C) = 1:0.55:1.82. The samples were held at 1000 °C for different durations with an initial furnace pressure of 10 Pa. The relationship between holding time and zinc volatilization rate is shown in Figure 7.
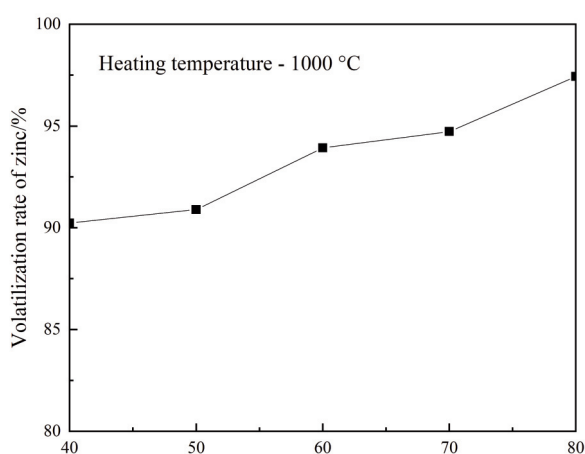

Figure 7. *Effect of different holding times on the volatilization rate of zinc with iron in roasted cyanide tailings as iron source*

From Figure 7, it can be seen that at 1000 °C, as the holding time increases, the zinc volatilization rate in the sample gradually increases, reaching 97.44% after holding for 80 minutes. As the holding time

increases, the iron oxide in the roasted cyanide tailings is reduced to metallic iron grains, which gradually grow larger [22]. Larger iron grains can fully contact ZnS, making the iron displacement reaction with ZnS more complete. The growth of the iron grains requires sufficient time. Compared to the displacement reaction using pure iron oxide as the iron source, using roasted cyanide tailings as the iron source for displacing zinc sulfide requires a longer reaction time. Longer holding times allow the iron grains to fully contact zinc sulfide, thereby increasing the zinc volatilization rate.

3.5. The difference of zinc volatilization rate by different iron sources

Figure 8 shows the effect of different iron sources on the zinc volatilization rate at the same heating temperature. In Figure 8, below 750 °C, none of the different iron sources cause the zinc in zinc sulfide to volatilize. Between 750 °C to 900 °C, the zinc volatilization rate is significantly higher when iron oxide is used as the iron source compared to using pure iron as the iron source. This indicates that when iron oxide is the iron source, the iron oxide can be reduced by carbon. The small particulate metallic iron produced during the initial reduction, having a smaller diameter, reacts with ZnS. The smaller diameter metallic iron particles are more reactive than pure iron powder, facilitating the displacement reaction. On the other hand, at high temperatures, the carbon in the briquettes reacts with the iron oxide to produce iron and CO or CO_2 gas, creating more pores within the briquettes. The increase in the number of pores reduces the diffusion resistance of the zinc vapor produced by the displacement reaction from the inside to the outside of the briquettes, helping to increase the zinc volatilization rate. Above 900 °C, according to the phase transformation rules of iron oxide during the vacuum carbothermal reduction process, iron oxide is no longer further reduced, so the volatilization rates are the same for both iron sources.

Between 750 °C and 850 °C, the iron oxide in the roasted cyanide tailings is not reduced to iron, and thus iron cannot displace the ZnS, resulting in a zinc volatilization rate of 0. Between 850 °C and 1000 °C, the zinc volatilization rate using iron powder as the iron source is greater than that using roasted cyanide tailings. When the heating temperature exceeds 750 °C, the zinc volatilization rate increases with the temperature. Zinc is displaced as elemental zinc, and the high temperature also increases the vapor pressure of the zinc, promoting its volatilization. When using roasted cyanide tailings to displace the same amount of ZnS, a large amount of other impurities are mixed
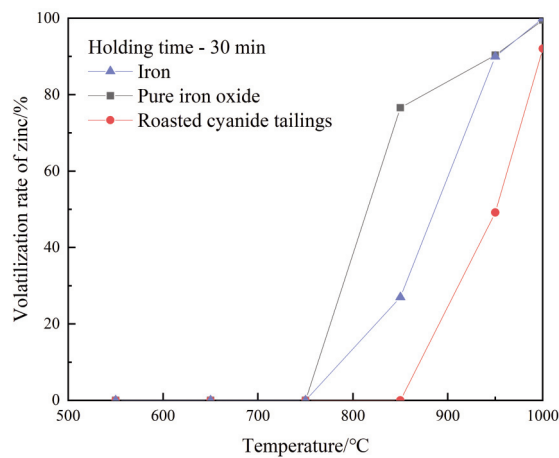
Figure 8. *Effect of different iron sources on zinc volatilization rate*

Table 4. *The composition of the gas generated by the reaction / ppm*

Iron Source Category	CO	CO_2	SO_2	COS
Pure iron oxide	7950	17630	0	0
Roasted cyanide tailings	5250	11080	0	0

larger iron particles, resulting in limited contact between iron and zinc sulfide, and thus the zinc volatilization rate is not high.

3.6. The exhaust gas composition and reducing residue phase in the process of vacuum carbothermal extraction of zinc sulfide with iron from roasted cyanide tailings as the iron source

The composition of the exhaust gas when using different iron sources is shown in Table 4. The
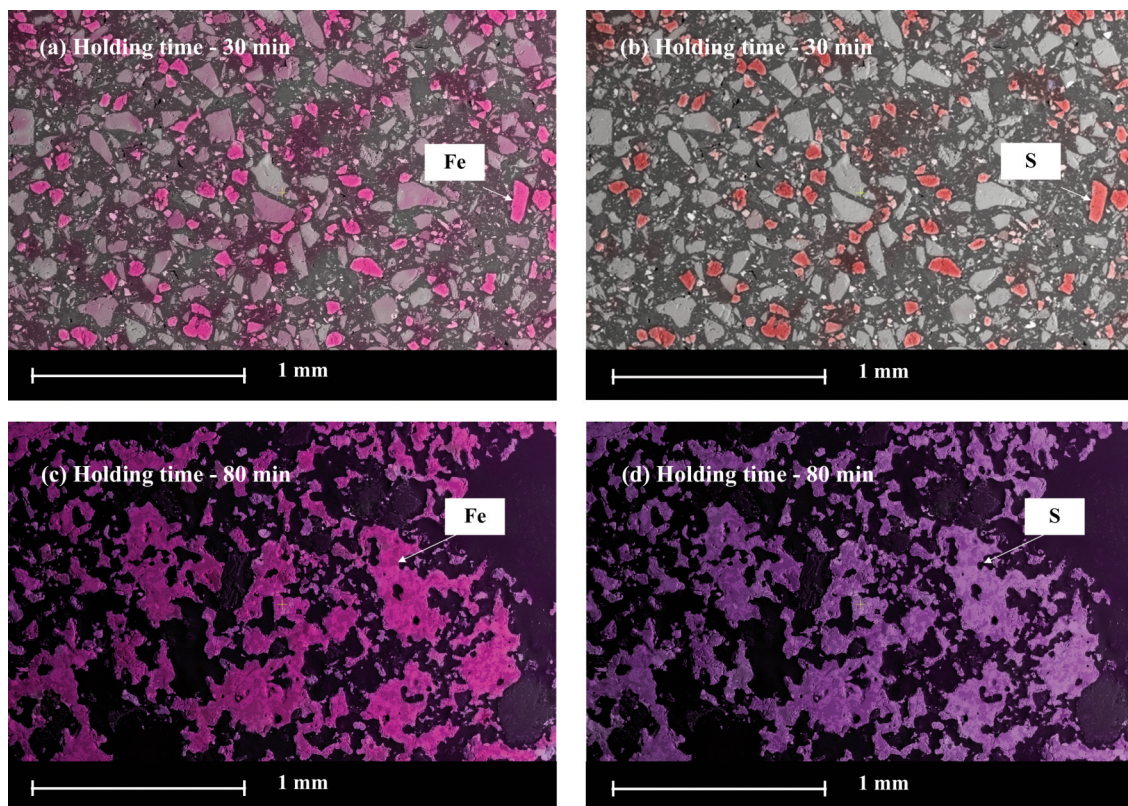

Figure 9. *Spectral analysis of reaction residue with roasted cyanide tailings as iron source for different holding time*

into the material, reducing the grades of zinc and iron in the mixture. The reaction between iron and zinc sulfide is a solid-phase displacement reaction. On a microscopic level, the grades of zinc and iron in the briquette material decrease, and the distance between zinc sulfide and iron increases. When the holding time is short, the metallic iron grains produced by the reduction of iron oxide are small. These small metallic iron grains do not have enough time to coalesce into

sectional EDS (Energy Dispersive Spectroscopy) analysis of the reaction residue using roasted cyanide tailings as the iron source, with a holding time of 30 minutes and 80 minutes, is shown in Figure 9. From Table 4, it can be seen that the exhaust gas from both iron oxide and roasted cyanide tailings contains mainly high levels of CO and CO_2, with no sulfur-containing gases like SO_2 and COS detected. The

concentration of CO_2 in the exhaust gas is higher than that of CO, indicating that in the process of reducing iron oxide in roasted cyanide tailings to metallic iron, both direct and indirect reduction reactions occur, with indirect reduction being predominant. The sulfur in the samples does not enter the gas phase. Combined with Figure 9, it can be determined that the sulfur in the samples is fixed in the residue in the form of FeS. In Figure 9, the FeS grain size in the reaction residue with a holding time of 80 minutes is significantly larger than with a holding time of 30 minutes. This indicates that the iron grains produced by the carbothermal reduction of iron oxide in roasted cyanide tailings continue to grow, and the resulting iron grains continuously react with ZnS, causing the FeS grain size in the reaction residue to increase as the holding time extends. Therefore, using iron-containing smelting residue as the iron source and vacuum carbothermal reduction for zinc extraction from ZnS, sulfur in ZnS will be fixed in the residue in the form of FeS, reducing the release of sulfur into the environment.

4. Conclusions

The extraction of zinc from zinc sulfide using the vacuum carbothermal reduction volatilization method with iron, iron oxide, and iron oxide in roasted cyanide tailings as the iron sources was studied, leading to the following conclusions:

(1) Using metallic iron powder, pure iron oxide powder, and iron oxide in roasted cyanide tailings as iron sources, the vacuum volatilization distillation method can effectively extract zinc from ZnS as metallic zinc and fix the sulfur in ZnS completely in the reduction residue in the form of FeS, thereby reducing sulfur emissions.

(2) At 1000 °C and an initial furnace pressure of 10 Pa, different iron sources can achieve zinc extraction from ZnS. Using iron powder as the iron source, with a material ratio of Fe:Zn = 1.1:1 and a holding time of 30 minutes, the zinc volatilization rate from ZnS is 99.98%. Using iron oxide as the iron source, with a material ratio of ($ZnS:Fe_2O_3:C$) = 1:0.55:1.82 and a holding time of 30 minutes, the zinc volatilization rate from ZnS is 99.56%. Using iron oxide in roasted cyanide tailings as the iron source, with a material ratio of ($ZnS:Fe_2O_3:C$) = 1:0.55:1.82 and a holding time of 80 minutes, the zinc volatilization rate from ZnS is 97.44%.

(3) Using iron oxide powder and iron oxide in roasted cyanide tailings as iron sources, the mechanism for extracting zinc from zinc sulfide is that the iron oxide is first reduced to metallic iron by carbon. The metallic iron then undergoes a displacement reaction with ZnS to form metallic zinc, which volatilizes in the form of zinc vapor. The metallic iron grains produced by the carbon reduction of iron oxide have higher reactivity compared to pure iron powder and can promote the displacement reaction. The process of reducing iron oxide by carbon is primarily dominated by indirect reduction.

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.

Author contributions

Hongzhou Ma: Writing - original draft, Methodology. Yubo Dang: Review & editing, Investigation. Yaoning Wang: Formal analysis. Jinyang Zeng: Review & editing. Minghua Guan: Supervision. Xiaojun Zhao: Formal analysis, Validation.

Acknowledgement

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SINERGIJSKA VAKUUMSKA KARBOTERMALNA EKSTRAKCIJA CINKA IZ CINK-SULFIDA KORIŠĆENJEM OKSIDA ŽELEZA

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Apstrakt

Kako bi se smanjili problemi visoke emisije zagađivača i dugih procesa u ekstrakciji cinka iz sulfidne rude cinka, predlaže se novi tehnički pristup koji uključuje sinergijsko korišćenje oksida železa i karbotermalne vakuumske redukcije za ekstrakciju cinka iz sulfidne rude cinka. Oksid železa se dobija iz metalurških ostataka sa visokim sadržajem železa. U vakuumskim uslovima, ugljenik redukuje oksid železa do metala železa, koje zatim zamenjuje cink u sulfidu i proizvodi cinkovu paru. Cinkova para se konačno kondenzuje kako bi se dobio metal cink. Ova studija istražuje ekstrakciju cinka iz cink-sulfida pod vakuumskim uslovima korišćenjem železnog praha, čistog praha oksida železa i oksida železa iz prženih cijanidnih ostataka kao izvora železa. Najvažniji faktori koji su istraživani su temperatura redukcije i vreme zadržavanja na stopu isparavanja cinka. Rezultati pokazuju da pri molarnom odnosu $n_{Fe}:n_{Zn}=1.1:1$, temperaturi od 1000 °C i početnom pritisku u peći od 10 Pa, prah železa, čisti prah oksida železa i oksid železa iz prženih cijanidnih ostataka mogu svi postići stopu isparavanja cinka od preko 99% iz cink-sulfida. Različiti izvori železa reaguju sa cink-sulfidom i formiraju FeS, a pri ekstrakciji cinka ne proizvode se gasovi koji sadrže sumpor.

Ključne reči: Vakuumska karbotermalna redukcija; Oksid železa; Zamena; Cink-sulfid; Železo