

Thermodynamics and phase transformations in the recovery of zinc from willemite

Feng Chen, Wei Chen, Yu-feng Guo, Shuai Wang, Fu-qiang Zheng, Tao Jiang, Ze-qiang Xie, and Ling-zhi Yang

School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China
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Abstract: Willemite is a common component of zinc and lead metallurgical slags that, in the absence of effective utilization methods, cause serious environmental problems. To solve this problem and increase zinc recovery, we proposed a novel extraction method of zinc from willemite by calcified roasting followed by leaching in $\text{NH}_4\text{Cl}\text{--}\text{NH}_3\text{--}\text{H}_2\text{O}$ solution. The thermodynamics and phase conversion of Zn_2SiO_4 to zinc oxide (ZnO) during calcified roasting with CaO were investigated. The mechanism of mineralogical phase conversion and the effects of the CaO -to- Zn_2SiO_4 mole ratio ($n(\text{CaO})/n(\text{Zn}_2\text{SiO}_4)$), roasting temperature, and the roasting time on zinc-bearing phase conversion were experimentally investigated. The results show that Zn_2SiO_4 was first converted to $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ and then to ZnO . The critical step in extracting zinc from willemite is the conversion of Zn_2SiO_4 to ZnO . The zinc percent leached in the ammonia leaching system rapidly increased because of the gradual complete phase conversion from willemite to ZnO via the calcified roasting process.

Keywords: willemite; zinc residues; calcified-roasting; thermodynamics; mineralogical phase conversion

1. Introduction

Zinc is a valuable metal that is widely used in many fields [1], and economic and societal development drive increasing demand for zinc. Given that modern industry is depleting high-quality zinc sulfide resources, the exploitation of other zinc-containing minerals such as willemite, zincite, and smithsonite is becoming imperative. Hydrometallurgical leaching has achieved satisfactory results in recovering zinc from zincite and smithsonite; however, the zinc percent leached from willemite is much lower [2–3]. Large amounts of zinc smelting slag have been generated through direct carbon reduction of zinc oxides (ZnO), in which zinc exists primarily as willemite and zinc ferrite. Moreover, in typical lead smelting slag, the main zinc-bearing minerals are willemite, hardystonite, and franklinite, with willemite representing approximately 66wt% of the total zinc content [4–7]. In addition, untreated stacked willemite-bearing slags or residues are considered a waste of zinc resources; they also occupy

land if they are directly stockpiled. Therefore, the ability to extract zinc from the willemite-bearing residues in the zinc industry is essential for resource recycling and environmental protection [8–10].

Numerous methods to recover zinc from willemite ores or willemite-bearing residues have been developed, including pyrometallurgical reduction and hydrometallurgical leaching. The common pyrometallurgical reduction methods for processing zinc metallurgy residues include the Waelz and Ausmelt methods. However, willemite is much more stable and resistant to leaching and cannot be effectively utilized in the aforementioned conventional methods. Furthermore, the disadvantages of the reduction–evaporation method, including reliance on reduction coal, high energy consumption, high equipment cost, low extraction efficiency, and low product quality, cannot be neglected [11–12]. In addition, acid leaching and alkaline leaching are the general hydrometallurgical leaching methods for zinc recovery [13–15]. Zinc is easily leached into acid leachate or alkaline leachate when in the form of

Corresponding author: Yu-feng Guo E-mail: yfguo@csu.edu.cn

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ZnO or zinc carbonate (ZnCO_3) in a residue. However, the yield of zinc leached from willemite-bearing residues is low because willemite is stable and resistant to dissolution in alkaline or acid solutions under moderate conditions [16–17]. Moreover, because the silicon in willemite also dissolves, a large amount of silica gel forms, which makes liquid–solid separation and the subsequent purification process difficult when common acid leaching methods are used [18]. The ammonia leaching method has been widely studied in recent years, and satisfactory results have been achieved because the process is highly selective toward zinc and requires a short purification procedure, among other advantages. However, the percentage of zinc leached from willemite into ammonia solution is only approximately 5wt%, whereas the zinc percent leached from ZnO can exceed 95wt% [19]. Compared with willemite, ZnO is much easier to process by either pyrometallurgy or hydrometallurgy methods. Thus, the transformation of zinc in willemite to ZnO might be an effective approach to improving the recovery of zinc.

Chen *et al.* [20] have investigated the feasibility of extracting zinc from willemite according to the aforementioned method of the transformation of zinc in willemite to ZnO. They conducted primary experiments on zinc leaching of calcified roasting samples in $\text{NH}_4\text{Cl}-\text{NH}_3\cdot\text{H}_2\text{O}$ solution to verify this method's validity. However, numerous mechanisms involved in this process have not yet been elucidated, including the mechanism of the mineralogical phase conversion from Zn_2SiO_4 to ZnO. Likewise, the relationship between the ZnO conversion of calcified roasting samples and the zinc percent leached in an ammonia system is not well understood.

In the present work, we investigated the thermodynamics and mechanism of zinc extraction from willemite by roasting with CaO. The phase conversion and its influence on the zinc percent leached were analyzed. The factors that affect the calcified roasting process, including the effects of $n(\text{CaO})/n(\text{Zn}_2\text{SiO}_4)$ ratio, roasting temperature, and the roasting time on the phase conversion, were systematically investigated. The experimental material used in this research was pure willemite samples to avoid interference from other elements in willemite-bearing residues. Our findings provide a technical basis for the extraction of zinc from willemite.

2. Experimental

2.1. Raw materials

The chemical composition of the willemite sample used

in this study is shown in Table 1. The zinc content of the willemite sample was 57.89wt%, which is very similar to the theoretical zinc content (58.34wt%) of pure willemite. The chemicals used in this study were all of analytical grade. Distilled water was used in the leaching experiments.

Table 1. Main chemical composition of the willemite sample wt%

TZn	TFe	SiO_2	CaO	MgO	Al_2O_3
57.89	0.34	26.57	0.10	0.033	0.095

Note: TZn is total zinc content; TFe is total iron content.

2.2. Experimental procedure

2.2.1. Roasting with CaO

A willemite sample was thoroughly mixed with CaO powder at a designed mole ratio. The mixture (20 g) was placed in an alumina boat and roasted in a horizontal tube furnace with silicon carbide heating elements. The isothermal section in the middle was approximately 9 cm long and the temperature variation was within ± 5 K. The roasted samples were subjected to dry-grinding and were subsequently dry-sieved to yield a particle size distribution finer than 0.074 mm prior to leaching experiments or phases analysis.

2.2.2. Leaching in $\text{NH}_4\text{Cl}-\text{NH}_3\cdot\text{H}_2\text{O}$

$\text{NH}_4\text{Cl}-\text{NH}_3\cdot\text{H}_2\text{O}$ solution was chosen as the leaching system for the calcified roasted samples. Details of the experimental leaching methods have been reported elsewhere [20].

2.3. Definition of parameters

The zinc contents in the calcified roasting samples and filtrates were analyzed by ethylene diamine tetraacetic acid (EDTA) complexometric titration methods according to Chinese standard GB/T 8151.1-2012. The percent of leached zinc was calculated using Eq. (1):

$$R = (C \times V) / (G \times W) \times 100\% \quad (1)$$

where R is the percent of leached zinc (wt%), C is the concentration of zinc in the filtrate (g/L); V is the volume of the filtrate (L); G is the mass of the roasted sample (g); and W is zinc content in the calcified roasted sample (wt%).

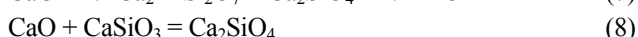
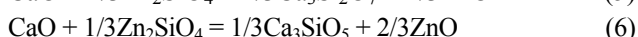
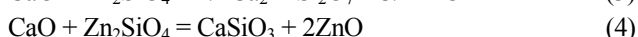
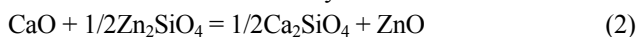
2.4. Analysis and characterization

The mineralogical phases of the willemite sample, calcified roasting samples, and leaching residues were analyzed by X-ray diffraction (Rigaku, TTR-III, D8 Advance) on a 2θ scale with Cu K_α radiation ($\lambda = 0.15406$ nm, 50 kV, 100 mA). A JEOL JSM-6360LV scanning electron mi-

croscope equipped with an energy-dispersive spectrometer (Genesis 60S) was used to analyze the morphology and elemental composition of the samples. The thermodynamic calculations of the reactions (standard state) in this study were performed with FactSage 7.1 [21] using the Reaction module. The databases chosen for the present study were FToxid and FactPS.

3. Thermodynamic analysis

The reactions possibly occurring during the willemite roasting process in the presence of CaO are given in Eqs. (2)–(10). The calculations were performed for 1 mol of CaO with different reactants in the temperature range 273–1673 K at the standard state; the standard Gibbs free energy ($\Delta_r G^\ominus$) values were calculated by FactSage 7.1 to assess the reactions' feasibility.



The thermodynamic calculations (Fig. 1) show that the $\Delta_r G^\ominus$ for Eqs. (2)–(10) occurring in the process of willemite roasting with CaO are negative over the temperature range 298–1673 K, which indicates that these reactions are thermodynamically feasible. The $\Delta_r G^\ominus$ for the formation of $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ (Eq. (3)) is the most negative, indicating that this reaction is the easiest to occur ($T > 700$ K). The $\Delta_r G^\ominus$ values for Eqs. (4) and (5) are more negative than those for Eqs. (2) and (6) but more positive than that for Eq. (3); thus, CaSiO_3 and $\text{Ca}_3\text{Si}_2\text{O}_7$ form more easily than Ca_2SiO_4 and Ca_3SiO_5 but less easily than $\text{Ca}_2\text{ZnSi}_2\text{O}_7$. The $\Delta_r G^\ominus$ value for Eq. (3) is the most negative among the $\Delta_r G^\ominus$ values for Eqs. (2)–(10), indicating that the reaction of willemite with CaO and subsequent conversion to $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ is the most thermodynamically favored process. The $\Delta_r G^\ominus$ value for Eq. (7) is negative, which means that $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ converted from Zn_2SiO_4 via Eq. (3) continues to react with CaO and is eventually converted to ZnO.

The values of $\Delta_r G^\ominus$ for Eqs. (7)–(9) are negative and decrease with increasing temperature in the temperature range from 1120 to 1700 K, indicating that CaSiO_3 , $\text{Ca}_3\text{Si}_2\text{O}_7$, and $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ will eventually be converted to Ca_2SiO_4 .

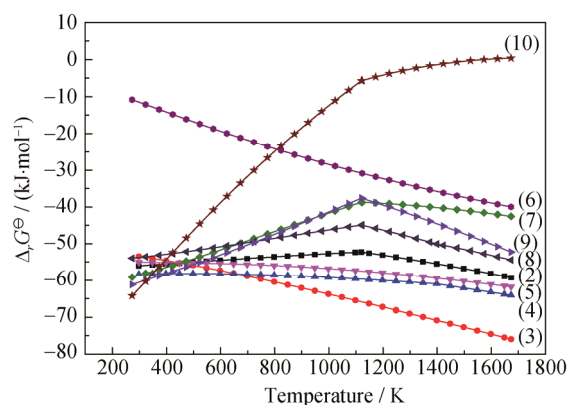


Fig. 1. The standard Gibbs free energy ($\Delta_r G^\ominus$) values of Eqs. (2)–(10) in the roasting temperature range from 200 K to 1800 K.

In summary, Eq. (3) is the most thermodynamically favored reaction among Eqs. (2)–(10) because of its most negative $\Delta_r G^\ominus$. Thus, Zn_2SiO_4 might undergo two reaction stages: the conversion of Zn_2SiO_4 to $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ via Eq. (3), followed by the further conversion of the generated $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ to ZnO via Eq. (7). The overall reaction is shown as Eq. (2). The most likely phase conversion process for willemite in the calcified roasting process is $\text{Zn}_2\text{SiO}_4 \rightarrow \text{Ca}_2\text{ZnSi}_2\text{O}_7 \rightarrow \text{ZnO}$ when sufficient CaO is provided.

According to the thermodynamic calculations, willemite can be thoroughly converted to ZnO during the roasting process with the addition of sufficient CaO.

4. Results and discussion

4.1. Effects of the CaO-to- Zn_2SiO_4 mole ratio

4.1.1. Phase conversion

The critical point of the calcified roasting is to implement the thorough conversion from Zn_2SiO_4 to ZnO. As illustrated in the overall objective Eq. (2), the $n(\text{CaO})/n(\text{Zn}_2\text{SiO}_4)$ mole ratio is 2:1. To completely convert Zn_2SiO_4 to ZnO, an excess of CaO was added during the roasting process and carried out the roasting at 1553 K for 40 min.

The phases of the calcified roasting samples with various $n(\text{CaO})/n(\text{Zn}_2\text{SiO}_4)$ ratios were analyzed by XRD; the results are shown in Fig. 2. ZnO and $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ peaks appeared, and the intensity of the Zn_2SiO_4 peaks decreased in the XRD pattern of the sample with a $n(\text{CaO})/n(\text{Zn}_2\text{SiO}_4)$ ratio of 2:1. The intensity of the ZnO peaks increased when the $n(\text{CaO})/n(\text{Zn}_2\text{SiO}_4)$ ratio was increased from 2.4:1 to 3.2:1, whereas the intensity of the $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ peaks decreased and the peaks eventually disappeared at a $n(\text{CaO})/n(\text{Zn}_2\text{SiO}_4)$ ratio of 2.8:1. No peaks of a

zinc-bearing phase other than ZnO were observed, suggesting that the final calcified roasting samples were mainly composed of ZnO and Ca_2SiO_4 .

The XRD results indicate that the zinc-bearing phase conversion during the calcified roasting of willemite is from Zn_2SiO_4 to ZnO with $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ as the intermediate, which confirms the results of the thermodynamics analysis. The transformation relationship of zinc-bearing phases during calcified roasting of willemite is shown in Fig. 3, which leads to the conclusion that Ca^{2+} ions gradually replace Zn^{2+} ions in Zn_2SiO_4 (Figs. 3(a)–3(b)) and that Zn^{2+} ions are liberated from Si^{4+} ions to form ZnO (Figs. 3(b)–3(c)).

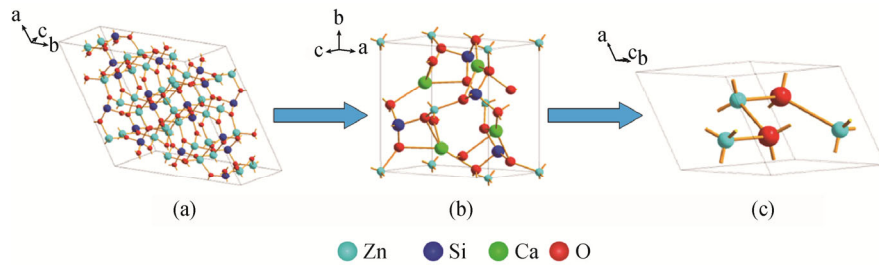


Fig. 3. Conversion of the zinc-bearing phases during the calcified roasting of willemite: (a) Zn_2SiO_4 ; (b) $\text{Ca}_2\text{ZnSi}_2\text{O}_7$; (c) CaO.

4.1.2. Microscopic structure

As shown in Fig. 4(a), the main components in the calcified roasted samples with a $n(\text{CaO})/n(\text{Zn}_2\text{SiO}_4)$ ratio of 2:1 are ZnO, Ca_2SiO_4 , a solid solution of CaO-ZnO-SiO_2 and impurities of Mg and Fe oxides. The Zn-to-Si mole ratio in the solid solution of CaO-ZnO-SiO_2 is less than 2:1 (i.e., the Zn-to-Si mole ratio in Zn_2SiO_4), which sug-

gests that zinc is gradually separated from silicon and that Zn_2SiO_4 is transferred to $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ and ZnO. Under a $n(\text{CaO})/n(\text{Zn}_2\text{SiO}_4)$ ratio of 2:1, the edge parts of Zn_2SiO_4 particles fully reacted with CaO, forming ZnO and Ca_2SiO_4 , whereas the center part did not thoroughly react, which led to formation of the CaO-ZnO-SiO_2 solid solution.

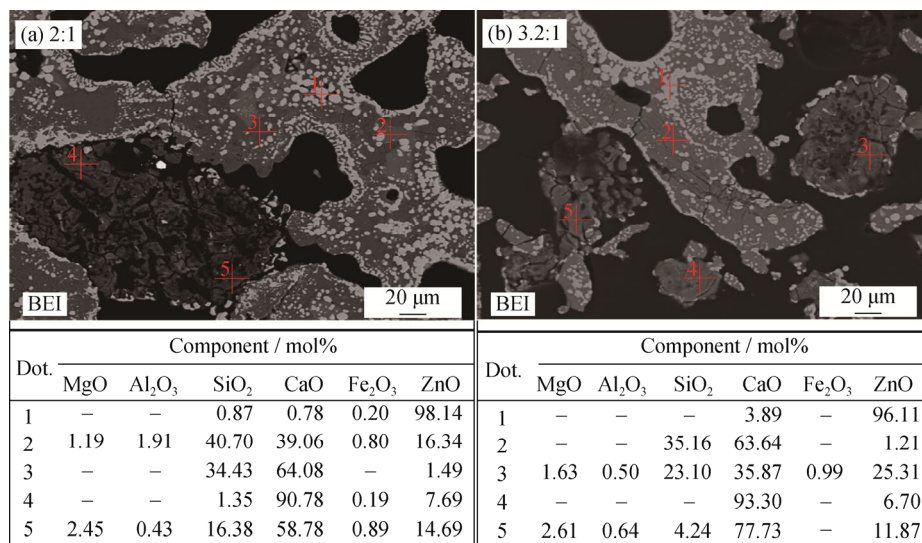


Fig. 4. Backscattered electron images and EDS analysis results of calcified roasted samples with $n(\text{CaO})/n(\text{Zn}_2\text{SiO}_4)$ ratios of (a) 2:1 and (b) 3.2:1.

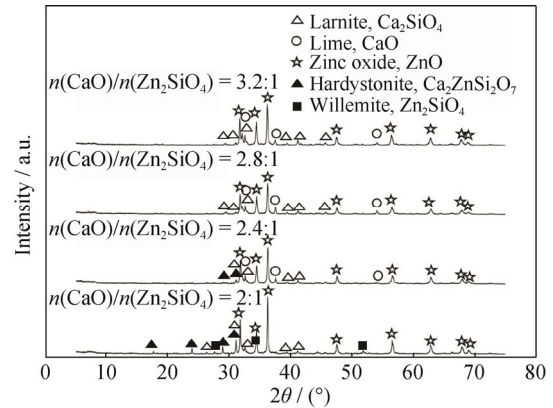


Fig. 2. XRD pattern of samples after calcified roasting at 1553 K for 40 min with different $n(\text{CaO})/n(\text{Zn}_2\text{SiO}_4)$ ratios.

As shown in Fig. 4(b), when excess CaO was provided ($n(\text{CaO})/n(\text{Zn}_2\text{SiO}_4)$ ratio of 3.2:1), both the edge and center parts of Zn_2SiO_4 particles reacted with CaO and the main zinc-containing component in the calcified product was ZnO. Because of the influence of Mg and Fe oxide impurities on the conversion from Zn_2SiO_4 to ZnO, the roasted sample contained a small amount of CaO–ZnO– SiO_2 solid solution. The Zn-to-Si mole ratio in the solid solution was lower than that in the roasted sample with an $n(\text{CaO})/n(\text{Zn}_2\text{SiO}_4)$ ratio of 2:1, indicating that more zinc was separated from Zn_2SiO_4 to generate ZnO. Combined with the XRD phase analysis, these results indicate that Zn_2SiO_4 was almost fully converted to ZnO through calcified roasting with excess CaO.

4.1.3. Ammonia leaching

The ammonia leaching results for calcified roasting samples in $\text{NH}_4\text{Cl-NH}_3\cdot\text{H}_2\text{O}$ solution were presented in the discussion of the feasibility research. They showed that the calcified roasting plays an important role in the extraction of zinc from willemite during ammonia leaching.

The zinc percent leached from willemite was 6.02wt% in the direct leaching experiment for a willemite sample not subjected to calcified roasting. However, the zinc percent leached increased rapidly to 69.19wt% when the $n(\text{CaO})/n(\text{Zn}_2\text{SiO}_4)$ ratio was increased to 2:1 and reached 96.54wt% when the $n(\text{CaO})/n(\text{Zn}_2\text{SiO}_4)$ ratio was further increased to 2.8:1 [20].

Combined with the XRD analysis of the calcified

roasting samples in Fig. 2, it can be implied that the zinc percent leached in $\text{NH}_4\text{Cl-NH}_3\cdot\text{H}_2\text{O}$ solution is greatly enhanced due to the phase conversion of ZnO from willemite during calcified roasting. Thus, the results indicate that the critical step in extracting zinc from willemite is the conversion of Zn_2SiO_4 to ZnO, a simple zinc-containing mineral that is easily leached in an ammonia leaching system.

4.2. Effects of the roasting temperature and time on phase conversion

While maintaining the $n(\text{CaO})/n(\text{Zn}_2\text{SiO}_4)$ ratio at 2.8:1 and the roasting time at 40 min, the effects of roasting temperature on the phase conversion of the calcified roasting sample were analyzed by XRD. The results in Fig. 5(a) show that the phase-change pattern of the willemite subjected to calcified roasting under different roasting temperatures is similar to that of the willemite subjected to calcified roasting under different $n(\text{CaO})/n(\text{Zn}_2\text{SiO}_4)$ ratios. When the roasting temperature was 1473 K, a portion of the willemite was converted to ZnO and $\text{Ca}_2\text{ZnSi}_2\text{O}_7$, whereas the rest of the willemite remained unconverted. With increasing roasting temperature, willemite was gradually completely converted to ZnO. Because of the complete conversion of the zinc-bearing phase from Zn_2SiO_4 to ZnO, the zinc percent leached increased rapidly from 64.67wt% to 97.45wt% when the roasting temperature increased from 1473 to 1553 K, as shown in the feasibility research [20].

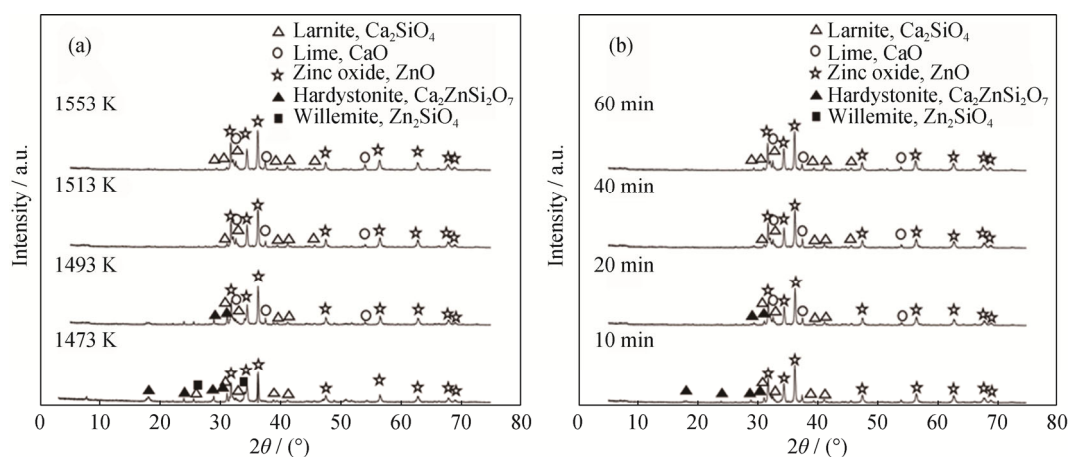


Fig. 5. XRD patterns of samples with a $n(\text{CaO})/n(\text{Zn}_2\text{SiO}_4)$ ratio of 2.8:1 after calcified roasting (a) at different temperatures for 40 min and (b) at 1553 K for different times.

As shown in Fig. 5(b), the phase conversion of willemite calcified roasting samples roasted for different times ($n(\text{CaO})/n(\text{Zn}_2\text{SiO}_4)$ of 2.8:1, roasting temperature of 1553 K) is similar to the phase conversion of willemite during

calcified roasting under different $n(\text{CaO})/n(\text{Zn}_2\text{SiO}_4)$ ratios. When the roasting time was 10 min, some willemite was converted to ZnO and $\text{Ca}_2\text{ZnSi}_2\text{O}_7$, whereas other willemite was unreacted. With increasing roasting time,

willemite was gradually converted to ZnO completely and the zinc percent leached increased from 84.63wt% to 97.99wt% when the roasting time was increased from 10 to 60 min, consistent with the completion of the ZnO conversion reported in the previous feasibility research [20].

4.3. Analysis of the leaching residue of the calcified roasting sample

The phase of the leaching residue of the calcified roasting sample under optimized roasting and leaching conditions ($n(\text{CaO})/n(\text{Zn}_2\text{SiO}_4)$ ratio of 2.8:1, roasting at 1553 K for 40 min, leaching in $\text{NH}_4\text{Cl}-\text{NH}_3\cdot\text{H}_2\text{O}$ system) was analyzed by XRD, as shown in Fig. 6(a), and the results were compared with the XRD analysis of the raw willemite.

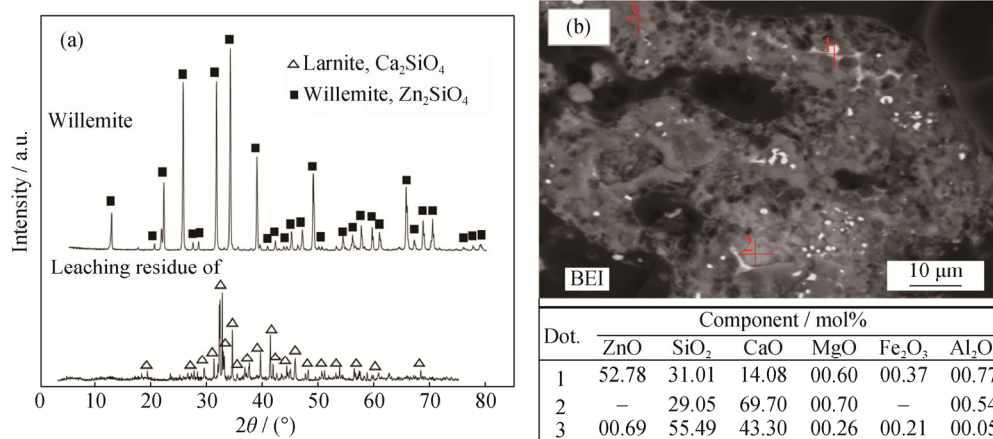


Fig. 6. Comparison of the XRD patterns of willemite and the leaching residue of a calcified roasting sample (a) and SEM-EDS analysis of the leaching residue (b).

5. Conclusions

(1) The conversion of willemite (Zn_2SiO_4) to ZnO by calcified roasting with CaO is thermodynamically feasible. The zinc-bearing phases in willemite undergo a two-stage conversion of Zn_2SiO_4 to $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ in the first stage and $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ to ZnO in the second stage.

(2) The zinc-bearing phase conversion is affected by the CaO-to- Zn_2SiO_4 mole ratio, roasting temperature, and the roasting time. Zn_2SiO_4 is thoroughly converted to ZnO under a roasting temperature of 1553 K for 40 min with a $n(\text{CaO})/n(\text{Zn}_2\text{SiO}_4)$ ratio of 2.8:1.

(3) Compared with the raw willemite, the calcified roasted samples leached much easier into $\text{NH}_4\text{Cl}-\text{NH}_3\cdot\text{H}_2\text{O}$ solution. The phase conversion from Zn_2SiO_4 to ZnO plays a significant role in the intensified extraction of zinc from willemite.

No diffraction peaks of other minerals are observed in the XRD pattern in Fig. 6(a), indicating that willemite was almost fully converted to ZnO after calcified roasting at 1553 K for 40 min with a $n(\text{CaO})/n(\text{Zn}_2\text{SiO}_4)$ ratio of 2.8:1, leaving a small amount of ZnO remaining in the CaO-ZnO-SiO₂ solid solution. Fig. 6(b) shows that the main component in leached residues, as determined by scanning electron microscopy-energy-dispersive spectroscopy (SEM-EDS), was calcium silicate or dicalcium silicate (gray) and ZnO (bright white). The tiny size of the ZnO (bright white) regions may lead to poor focus and low accuracy of the EDS results. A small number of tiny ZnO particles (bright white) were embedded in the middle of the calcified product particles, which might result in the incomplete leaching of ZnO.

Acknowledgements

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