

## THE EXTRACTION OF ZINC FROM WILLEMITE BY CALCIFIED-ROASTING AND AMMONIA-LEACHING PROCESS BASED ON PHASE RECONSTRUCTION

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### Abstract

Willemite is typically found in oxidized zinc ores and metallurgical secondary resources but without effective extraction method yet. Based on the ideas of zinc phase reconstruction in the willemite, the extraction of zinc from willemite by calcified-roasting using CaO as additive and ammonia-leaching process was studied in this paper. The influences of CaO dosage, roasting temperature, roasting time on the phase transformation and zinc leaching rate were studied, which were characterized by XRD. The results indicated that  $Zn_2SiO_4$  was transformed into ZnO or  $Zn_2CaSi_2O_7$ . After roasted with 1.4 times of theoretical CaO dosage at 1280 °C for 40 minutes, willemite was thoroughly transformed into ZnO. The zinc leaching rate of the roasted sample was 97.45% in  $NH_4Cl-NH_3 \cdot H_2O$  leaching system, which increased by 91.40 % compared with zinc leaching rate of 6.05% when willemite was directly leached in  $NH_4Cl-NH_3 \cdot H_2O$  system.

### Introduction

Several types of oxidized zinc ores have been found in nature so far, mainly include calamine ( $ZnCO_3$ ), willemite ( $Zn_2SiO_4$ ), hemimorphite ( $Zn_4(Si_2O_7)(OH)_2 \cdot H_2O$ ) and zincite ( $ZnO$ ) [1]. China has an abundant reserve of oxidized zinc ores (more than 40 million tons) which is mainly found in the southwest and northwest areas like a world-class mine: Yunnan Lanping zinc ore. Oxidized zinc resources usually contain much silicon and alkaline gangue, belonging to a low-grade and refractory zinc resource. Among the oxidized zinc resources, hemimorphite and willemite are most refractory because of their stable structures and high silicon contents [2].

There are also a lot of oxidized zinc resources in lead (Pb) and zinc metallurgical secondary slag. The smelting zinc slag exhausted from blast furnace or direct reduction furnace contains 10 wt. % to 20 wt. % zinc. And 66.28wt.% of Zn in a typical lead smelting slag exists in the form of  $Zn_2SiO_4$  and 31.63 wt.% in the form of  $ZnFe_2O_4$  [3]. In addition, many indigenous zinc smelting kilns had exhausted much smelting waste, in which zinc exists in the form of zinc metal and willemite [4].

Currently, the mainly processing methods of high-silicon contained oxidized zinc

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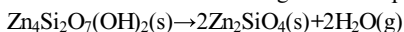
resource or smelting slag are: indirect smelting and direct smelting. Indirect smelting method enriches the zinc ores by floatation, followed by roasting, leaching and electrowinning (RLE) processes. Direct smelting method is processed without floatation and it includes two types: pyrometallurgical and hydrometallurgical method. Conventional floatation technique cannot effectively enrich the oxidized zinc resources because of the difficulty in separating zinc ores from gangue[5]. Direct pyrometallurgical method usually refers to high temperature reducing-evaporation method which has various shortcomings, such as the stricter reducing conditions required for willemite and hemimorphite than zincite, more investment and the generation of harmful greenhouse gases[6]. So the dominant method for extracting zinc at present is hydrometallurgical process. Sulfuric acid leaching process is typically used in zinc producing process with zinc sulfide ore as the raw material. However when the process is applied to the utilization of high-silicon contained zinc resources, a large number of silica gel is formed due to the silicon's dissolution, resulting in difficulties in liquid-solid separation. Therefore, some measures have been studied to control the polymerization of silica gel, such as rapid leaching and flocculation [7]. The easy-separating ore pulp can be gained by these methods, but the leaching requires strict control of conditions with great technical difficulty. In addition, the acid consumption is too high and it is difficult to purify the leaching solution because of the high content of alkaline gangue and impurity elements. Thus, many scientists have studied the alkali leaching for high-silicon contained oxidized zinc resources[8]. Z.W. Zhao [9] used mechanical activation method to leach hemimorphite in NaOH solution. The results showed that silicon was dissolved into solution in the form of  $\text{H}_2\text{SiO}_4^{2-}$  without the formation of silica gel while hemimorphite was dissolved in the form of  $\text{Zn}(\text{OH})_4^{2-}$ . A zinc leaching rate of 93% was obtained by alkali leaching with the disadvantages of poor selectivity, poor quality of products and increased difficulty to the subsequent solution purification, solution regeneration and zinc recycling process[10]. Ammonia leaching oxidized zinc resources has the comprehensive advantages of high selectivity, fewer impurities and easy-to-purify. But the zinc leaching rate of willemite by ammonia leaching is much lower than that of other oxidized zinc ore[10]. Z.Y.Liu [11,14] used hemimorphite and willemite pure minerals to study the leaching mechanism in ammonia system. 90% of zinc in hemimorphite could be leached under the condition of high liquid-solid ratio while only 10% of zinc in willemite could be leached because it was limited by the low solubility of silica and precipitation rate of silica gel. Willemite seems to be most difficult to leach in ammonia system among all types of oxidized zinc ores. Therefore, relying on previous studies, this paper proposed a calcified-roasting followed by ammonia leaching method to enhance the zinc leaching rate in ammonia system, based on the technical idea of reconstructing the existential form of zinc in willemite. Meanwhile, this paper takes examples of extracting vanadium by roasting and acid leaching process from vanadium slag[12], extracting vanadium by sodium-roasting or calcified-roasting process from stone coal[13] to study the willemite calcified-roasting and ammonia-leaching system. The mechanism of phase reconstruction during calcified-roasting process and the impact of reconstruction on

zinc leaching efficiency are studied as well.

## Experimental

### Raw Materials

Willemite samples used in this study is obtained by roasting natural hemimorphite from Lanning Oxidized Zinc Ore, in Yunnan Province(China). Hemimorphite is crushed and milled to no large than 74 $\mu\text{m}$ , and then it is roasted at temperature of 1100  $^{\circ}\text{C}$  for 3 h. The roasting reaction equation is:



The XRD pattern of willemite sample is shown in Fig.1.

The main chemical composition of willemite sample is listed in Table 1 .

Table 1 The main chemical composition of willemite sample

Zn	Fe	SiO <sub>2</sub>	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>
57.89	0.34	0.02	0.10	0.033	0.095

Results in Figure 1 and Table 1 show that hemimorphite sample has completely dehydrated and transformed into willemite (JCPDF NO 83-2270) after roasting. The zinc element content of willemite sample is 57.89wt.%, which is very close to theoretical content (58.34 wt.%) of willemite .

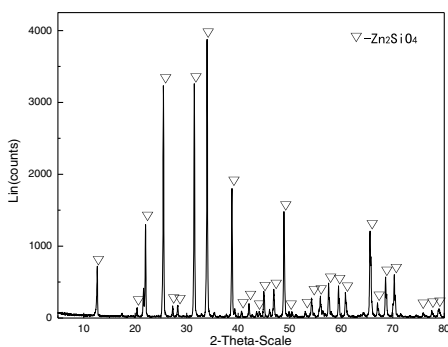


Fig.1 XRD pattern of willemite sample

### Experimental Method

(1) Roasting Experiment: Willemite sample powder and analytical CaO powder are mixed by a certain percentage then the mixture is loaded in a corundum boat and roasted in a horizontal tube furnace at a target reaction temperature.

(2) Leaching Experiment: The roasted ore samples are ground into the particle with size <74 $\mu\text{m}$ . Leaching experiments was conducted in a 250mL beaker heated in a water

bath at a target temperature. The leaching procedure initiated by pouring 100mL of required concentration ammonia leaching agent into a 250mL beaker with a plastic film covered. Then the leaching agent was heated to the experimental temperature with stirring. Time was counted when the willemite samples or calcified-roasting samples were added into the leaching beaker. When the required reaction time was up, the slurry was filtered, and then an appropriate dosage of dilution and leaching residue were taken for analysis. Each group of analysis is repeated for three times and the average value is taken as the final data.

### Analysis Methods

Zinc content: EDTA Complexometric Titration (GB/T 8151.1-2012) .

Chemical phase analysis: X-ray Diffraction (Rigaku-TTRJII, Cu target,  $K\alpha$ ,  $\lambda = 0.15406$  nm)

## **Results and Discussion**

The main affecting factors of the calcified-roasting process are the dosage of CaO additive, roasting temperature and roasting time were studied. Willemite samples and calcified-roasting samples were leached in  $\text{NH}_4\text{Cl}-\text{NH}_3\cdot\text{H}_2\text{O}$  leaching system. Leaching conditions: the total ammonia concentration was 6mol/L, the mole ratio of  $\text{NH}_4\text{Cl}$  to  $\text{NH}_3\cdot\text{H}_2\text{O}$  was 1:1, the leaching temperature was 40 °C, the solid-liquid ratio was 20g / L, the stirring speed was 350 r / min and the leaching time was 3h. A blank comparative experiment referring to Dr. Z.Y.Liu's thesis[14] under the above leaching conditions was conducted and the zinc leaching rate of willemite directly leached in  $\text{NH}_4\text{Cl} - \text{NH}_3\cdot\text{H}_2\text{O}$  leaching system was 6.02%.

### The Influence of the Dosage of CaO Additives on Zinc Leaching Rate

The influence of the dosage of CaO additive on zinc leaching rate is very significant as shown in Fig2. When the dosage of CaO additives increases from 0.5:1 (theoretical mole ratio) to 0.8:1, the zinc leaching rate increases from 69.19% to 98.22%. This is because willemite samples cannot fully contact with CaO when CaO is added in the theoretical amount. So since CaO dosage increases, willemite could become better contact with CaO which promotes the reaction and results in the increase of zinc leaching rate. Zinc leaching rate increases significantly, almost shows a linear relationship when the dosage of CaO additive increases from 0.5:1 to 0.7:1 (mole ratio). After that, a further increase of CaO dosage would not increase zinc leaching rate obviously, which indicates the CaO dosage has reached a sufficient dosage and it would no longer be a restriction factor of willemite roasting-transformation and leaching.

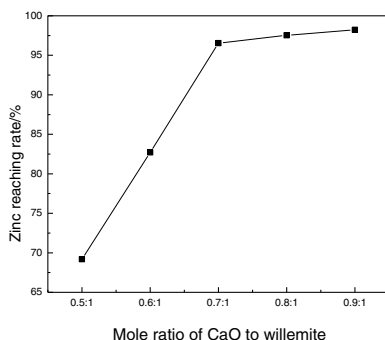


Fig. 2 Influence of CaO/ willemite(mole ratio) on zinc leaching rate

### The Influence of The Roasting Temperature on Zinc Leaching Rate

The fully mixed willemite and CaO samples (CaO: willemite=0.7: 1 mole ration) were roasted at the temperature from 1200 °C to 1300 °C for 40min. The influence of roasting time on zinc leaching rate is shown in Fig.3. As seen from Fig.3, the impact of temperature on zinc leaching rate is obvious. As the roasting temperature increases, zinc leaching rate increases as well. The zinc leaching rate continues to rise sharply from 64% (at 1200 °C) to 91.65% (at 1240°C) then the trend becomes slow. Zinc leaching rate almost does not continue to increase when the roasting temperature is above 1280 °C.

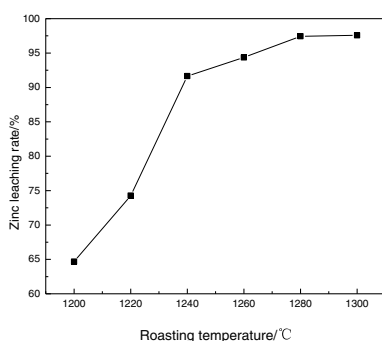


Fig.3 Influence of roasting temperature on zinc leaching rate

### Influence of roasting time on zinc leaching rate

Influence of roasting time on zinc leaching rate is shown in Fig. 4. The XRD patterns of calcified-roasting sample (roasted at 1280 °C for 10min or 40min) are shown in

Fig.5 and Fig.6.As shown in Fig.4, at lower temperatures, the influence of roasting time on zinc leaching rate is significant, when the temperature increases, roasting time has a weaker influence on the leaching rate. The appropriate roasting time at higher temperature is shorter than that of lower temperature. The appropriate roasting time at 1240°C is 40min while the appropriate roasting time at 1300°C is 30min with a higher zinc leaching rate. Zinc leaching rate does not increase obviously when continuing to prolong the roasting time longer than 40 min.

By analyzing Fig.5 and Fig.6,it can be seen that there are diffraction peaks of ZnO and  $Zn_2CaSi_2O_7$  in roasted ore sample (roasted at 1280 °C for 10min) while diffraction peaks of  $Zn_2CaSi_2O_7$  are not found in roasted ore sample(roasted at 1280 °C for 60min). It can be explained that most willemite has been transformed into ZnO after calcified-roasting for 60 min and that may account for the great increase of zinc leaching rate.

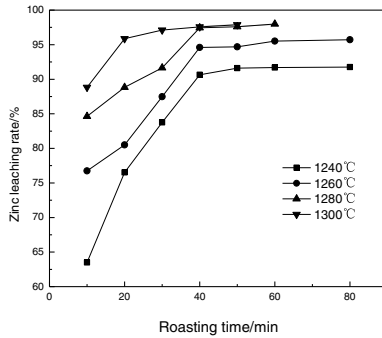


Fig. 4 Influence of roasting time on zinc leaching rate

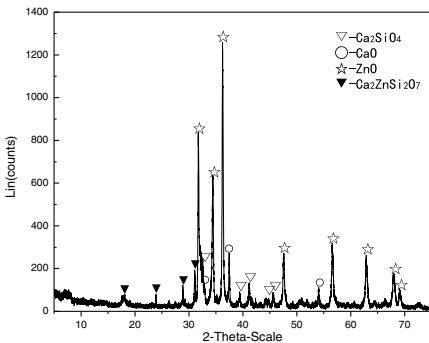


Fig. 5 XRD pattern of roasted sample (1280 °C for 10min)

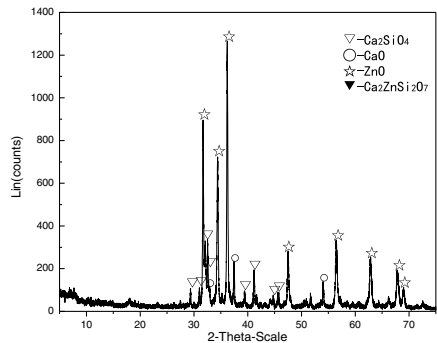


Fig. 6 XRD pattern of roasted sample (1280 °C for 60min)

The chemical phase composition of leaching residue( roasted at 1280 °C for 60min)

followed by leaching in  $\text{NH}_4\text{Cl} - \text{NH}_3 \cdot \text{H}_2\text{O}$  agent system) is shown in Fig.7 and only the diffraction peaks of  $\text{Ca}_2\text{SiO}_4$  can be found in the XRD pattern which proves that under adequate conditions, willemite can be fully transformed into  $\text{ZnO}$  during the calcified-roasting (phase-reconstruction) process and it means zinc element in reconstructed-roasting samples can be leached almost totally.

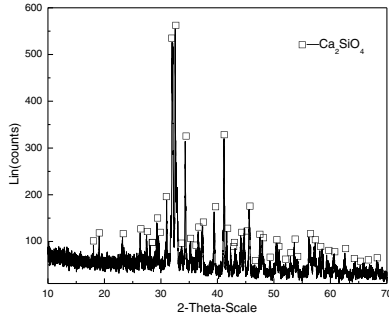


Fig.7 XRD pattern of leaching residue

### Conclusions

- (1) Within the roasting temperature range from  $1200^\circ\text{C}$  to  $1300^\circ\text{C}$ , willemite ( $\text{Zn}_2\text{SiO}_4$ ) can react with  $\text{CaO}$  and be transformed into  $\text{Zn}_2\text{CaSi}_2\text{O}_7$  (hardystonite) or  $\text{ZnO}$  due to different  $\text{CaO}$  dosage, roasting temperature and roasting time.
- (2) Compared with willemite, the calcified-roasted samples are much easier to leach in  $\text{NH}_4\text{Cl} - \text{NH}_3 \cdot \text{H}_2\text{O}$  leaching system. The zinc leaching rate of the roasted sample (roasted with  $\text{CaO}/$  willemite ratio at 0.7:1, the roasting temperature at  $1280^\circ\text{C}$  for 40 min) is 97.45% while the zinc leaching rate of willemite is only 6.02% under the same leaching conditions .
- (3) An appropriate increase of  $\text{CaO}$  dosage, roasting temperature or roasting time can promote the transformative reaction and lead to an obvious increase of zinc leaching rate.
- (4) Under optimal roasting conditions, the calcified-roasting (transformative) reaction could react thoroughly, and most of willemite is transformed into  $\text{ZnO}$ , correspondingly, the zinc leaching rate is higher than 95%.

### Acknowledgements

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