

## Article

# Application of the Microwave and Ultrasonic Combined Technique in the Extraction of Refractory Complex Zinc Ore

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**Abstract:** This paper proposes a combined microwave and ultrasonic technique that aims to extract the refractory mineralogical properties of complex zinc ore. This technique consists of two steps: microwave-assisted phase transformation and ultrasonic-assisted complexation leaching. During the microwave-assisted phase transformation step, the refractory zinc phases transform into manageable phases using doping oxidation agents. In the ultrasonic-assisted complexation leaching step, the effect of NTA<sup>3-</sup> on Zn<sup>2+</sup> species distribution is explored. The results show that microwave roasting with 20% Na<sub>2</sub>O<sub>2</sub> at 600 °C for 15 min adequately transforms ZnS, ZnCO<sub>3</sub> and Zn<sub>2</sub>SiO<sub>4</sub> into ZnO and avoids the generation of Zn<sub>2</sub>SiO<sub>4</sub>. Further, 0.5 mol/L NTA<sup>3-</sup> (nitrilotriacetic acid) is especially effective as a complex additive for complexes with Zn<sup>2+</sup> as Zn(NTA)<sub>2</sub><sup>4-</sup>. The ultrasonic technique can reduce the diffusion resistance and open the products in the leaching process, improving zinc leaching by 4.7%. The degree of zinc recovered from zinc ore can reach 91.4% when leach is assisted with 225 W ultrasonic force at 80 °C for 75 min. This paper shows great potential for the green extraction of non-traditional zinc-containing resources.

**Keywords:** complex zinc ore; microwave; Na<sub>2</sub>O<sub>2</sub>; ultrasonic; NTA<sup>3-</sup>



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## 1. Introduction

With increasingly scarce supplies of non-ferrous metal resources, research into the green extraction of non-traditional zinc-containing resources is urgent, as it has the potential to effectively alleviate the dependence on foreign resources and provide protection to domestic economic sustainable development and national security. There are a million tons of the discovered complex zinc ore, and it is characterized as a complicated component because it has a high content of alkaline gangue, is multi-metal associated and has one metal existing in a multiphase [1], and thus cannot be impressively processed by existing technologies [2]. Many researchers have proven that complexation leaching is an attractive way to recover multi-metal ores, as this technique shows great potential in separation and extraction [3,4].

Nowadays, microwave heating has evolved into a frequently used tool for chemists, based on its numerous advantages over conventional conductive heating, which applies efficient internal heating via direct coupling of microwave energy with the molecules that are present in the reaction mixture [5,6]. The popularity of microwave irradiation for chemistry is based on the observed higher yields, faster reactions, reduced side-product formation and even changed selectivity [7]. Taking into account these advantages of microwave irradiation in chemistry, a variety of reports discuss the microwave-assisted phase transformation of refractory zinc minerals [8–10]. Al-harashsheh et al. [11] investigated the microwave treatment of electric arc furnace dust (EAFD) mixed with tetrabromobisphenol A (TBBPA) and demonstrated great selectivity in the leachability of both zinc and iron,

with iron being left in the solid residue. Yang et al. [12] proposed a novel combination of phase transformation and leaching to recover zinc from an oxide–sulphide zinc ore, and suggested that both microwave heating and the  $\text{Na}_2\text{O}_2$  level have significant effects on phase transformation and zinc leaching. Vereš et al. [13] presented the characterization of blast furnace sludge and the removal of zinc through microwave-assisted extraction, in an attempt to allow for the reuse of sludge with relatively high iron content in the subsequent production steps.

Ultrasound is characterized as being high frequency and high power, with a short wavelength, small diffraction and high energy and orientation [14]. In the process of propagation, ultrasound will interact with the available material, resulting in the cavitation effect; there is a change in the composition, structure, nature, state and function, with a change in its own phase and amplitude [15]. In recent years, many domestic and foreign researchers have introduced ultrasonic technology into their specific research, hoping to improve the reaction process or to create some strange reactions. Slaczka [16] investigated the effect of ultrasound on the ammonium leaching of zinc from galmei and found that the use of ultrasound can decrease the surface diffusion layer thickness and, thus, shorten the leaching time. Bese [17] presented the optimum conditions for the dissolution of copper converter slag in the presence and absence of ultrasound and showed that under the same conditions, the extraction efficiency of zinc from the slag was 51.32% in the presence of ultrasound, while it was 48.28% in the absence of ultrasound.

In the present study, the efficacy of a combined microwave-roasting and ultrasonic-leaching technology for the recovery of  $\text{Zn}^{2+}$  from complex zinc ore is investigated. The main influencing factors, such as the  $\text{Na}_2\text{O}_2$  additive, microwave-assisted heating, complexing agents and ultrasonic-assisted leaching, are examined, with the  $\text{Na}_2\text{O}_2$  additive being chosen in reference to our previous research [12]. The thermodynamic mechanisms involved in the processes of phase transformation and coordination leaching are calculated using Factsage and HYDRA/MEDUSA, respectively.

## 2. Materials and Methods

### 2.1. Materials

The main component of complex zinc ore is given in Table 1, which indicates that this complex zinc ore is a high-grade sample and has high alkalinity, with a content of  $(\text{CaO} + \text{MgO}) > 12\%$ ; thus, it is not suited for acid hydrometallurgy treatment. The mass fractions of Fe and  $\text{SiO}_2$  are relatively high, providing further evidence against the use of the acid processing procedure.

**Table 1.** The main chemical components of complex zinc ore (mass fraction, wt-%).

ZnT	CaO	$\text{SiO}_2$	S	Fe	Pb	$\text{Al}_2\text{O}_3$	MgO
24.91	11.96	10.30	10.20	7.70	4.80	1.27	0.22

Zn<sub>T</sub>-total zinc.

Deduced from the distribution of the zinc phases in complex zinc ore (Table 2), the content of zinc sulphide and zinc oxide is basically equivalent, as the mass fraction of zinc existing in sulfide is 11.06% and in the form of zinc oxides (zinc carbonate and zinc silicate) is 13.68%. This ore has representative oxide–sulphide sample characteristics, implying that it existed in the oxidized zone of the sulfide deposit.

**Table 2.** The distribution of zinc phases in complex zinc ore.

Zinc Phases	Sulphide	Carbonate	Silicate	Franklinite et al.	Zn <sub>T</sub>
Mass fraction/wt-%	11.06	9.68	4.00	0.052	24.91
Distribution/wt-%	44.61	39.04	16.13	0.21	100

## 2.2. Analytical Techniques

Modern analysis techniques are employed throughout this paper to provide evidence for the technological mineralogy of complex zinc ore and the reaction mechanism of the complex recovery process, wherein XRD patterns of raw ore and zinc calcines provide information about the phase compositions, which can directly reflect the phase transformation. The phase compositions of the samples are identified by a Japanese D/MAX-3B-type target X-ray diffractometer. The conditions are as follows: 20~80°, CuK $\alpha$  radiation ( $\lambda = 0.15406$  nm), graphite monochromator, 40 kV tube pressure, tube flow 200 mA, and continuous scanning speed 4 deg/min. The surface morphology and elemental distribution of the samples are observed using a Quanta 200 scanning electron microscope manufactured by FEI. The test conditions are as follows: 30 kV acceleration voltage, 3.5 nm resolution and use of the accompanying EDAX for sample elemental analysis. Photoelectron spectroscopy of the samples is recorded in a ULVAC PHI-5000 Versa Probe II spectrometer with an Al K $\alpha$  X-ray source ( $h\nu = 1486.6$  eV). The vacuum pressure in the chamber is  $10^{-7}$  Torr, the X-ray is non-monochromatic and all the binding energy is calibrated with a C1s peak binding energy at 284.8 eV [18].

## 2.3. Experimental Method

The improved complex recovery technology for complex zinc ore is comprised of two procedures: microwave-assisted phase transformation and ultrasonic-assisted complexation leaching. Several detailed steps, as presented in Figure 1, occur, including mixing specific concentrations of the complex zinc ore and Na<sub>2</sub>O<sub>2</sub>, roasting the mixture using a self-made high-temperature microwave reactor (2450 GHz, 3 kW), which has the advantage of high power, being operation stable, having good efficiency, and being smart and then leaching the zinc calcines in a NH<sub>3</sub><sup>-</sup>-NH<sub>4</sub>Cl<sup>-</sup> NTA<sup>3-</sup>-H<sub>2</sub>O complexation system. The concentration of (NH<sub>3</sub>)T (c(NH<sub>4</sub>Cl) + c(NH<sub>3</sub>·H<sub>2</sub>O)) is 7.5 mol/L, the molar ratio of NH<sub>4</sub><sup>+</sup> (NH<sub>4</sub>Cl) and NH<sub>3</sub> (NH<sub>3</sub>·H<sub>2</sub>O) is 1:1, the agitation speed is 300 rpm and the ratio of solid: liquid is 1:5. Furthermore, the complexation leaching is assisted by ultrasound, using self-made plug-in ultrasonic equipment in the laboratory (Figure 2), with a frequency of 20 kHz, a power of 0–1 kW and a probe diameter of 1 cm.

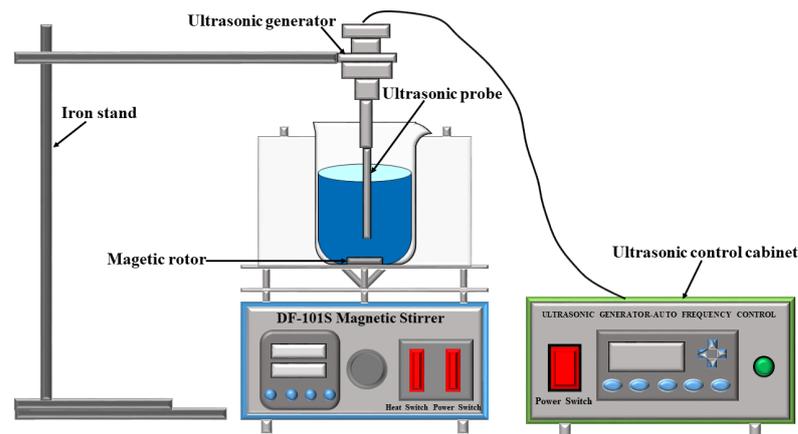
The zinc leaching rate is calculated by using the following formula:

$$x = \frac{w \times m - w_0 \times m_0}{w \times m} \times 100\%$$

where  $x$  is the leaching rate of Zn (%);  $w$  and  $w_0$  represent the content of Zn (%) in the raw ore and the leaching slag;  $m$  and  $m_0$  represent the weight of raw ore and the leaching slag(g), respectively.



Figure 1. A flow diagram of the experiment.



**Figure 2.** The experimental ultrasonic equipment is shown in the diagram.

#### 2.4. Thermodynamic Simulation Method

Factsage 7.1 software is used to study the thermodynamic process of phase transformation. The Factsage database is rich in content and powerful in calculations, so can simulate and calculate complex industrial processes. The calculation modules include balance and phase diagrams. The Equilib module applies the Gibbs energy minimization method, calculating specific elements or compounds or part of a reaction to the state of equilibrium, the whole system and the chemical composition of the equilibrium concentration [19].

In this paper, the thermodynamics of the leaching system were calculated using HYDRA/MEDUSA software. The HYDRA/MEDUSA software was developed by Ignasi Puigdomenech, an inorganic chemistry expert at the Royal Swedish Institute of Technology (KTH), and consists of two basic building blocks, HYDRA and MEDUSA. The HYDRA module is the constant that balances many basic chemical reactions in water chemistry. MEDUSA (Make Equilibrium Diagrams Using Sophisticated Algorithms) module is a module for calculating and charting chemical equilibrium systems determined by HYDRA [20].

### 3. Results and Discussion

#### 3.1. The Mineralogical Characteristics of Complex Zinc Ore

The XRD pattern of complex zinc ore is presented in Figure 3, from which it can be inferred that the main phases of this zinc ore include zinc sulfide (ZnS), ferrous disulfide (FeS<sub>2</sub>), lead sulfide (PbS), zinc carbonate (ZnCO<sub>3</sub>), silicon dioxide (SiO<sub>2</sub>) and calcium carbonate (CaCO<sub>3</sub>). The zinc is distributed between three phases: ZnS, ZnCO<sub>3</sub> and (zinc Silicate) Zn<sub>2</sub>SiO<sub>4</sub>, with the content decreasing gradually.

Figure 4 gives the EDAX spectra of the complex zinc ore and the relative elemental weight percentage values, displayed in Table 3. Point A is deemed to be galena and smithsonite. Point B represents sulphides of zinc, lead and iron, namely sphalerite, galena and pyrite, and obviously contains sphalerite domains. Point C is the independent galena. Point D consists of SiO<sub>2</sub>. Combining the analyses of chemical composition, using the XRD pattern and EDAX spectra, it can be deduced that this complex zinc ore comprises sphalerite, willemite, smithsonite, galena, quartz, pyrite and calcium carbonate, etc., and possesses refractory mineralogical properties.

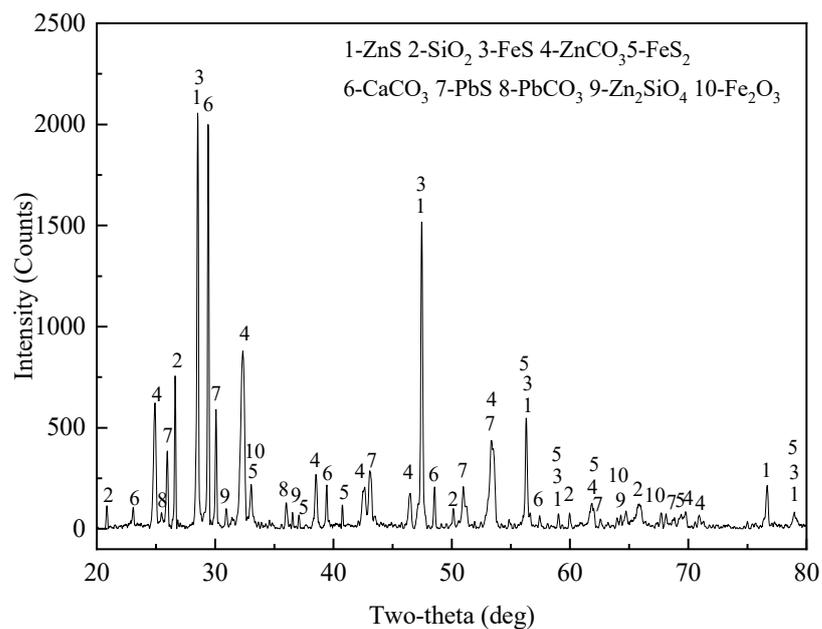


Figure 3. The XRD pattern of complex zinc ore.

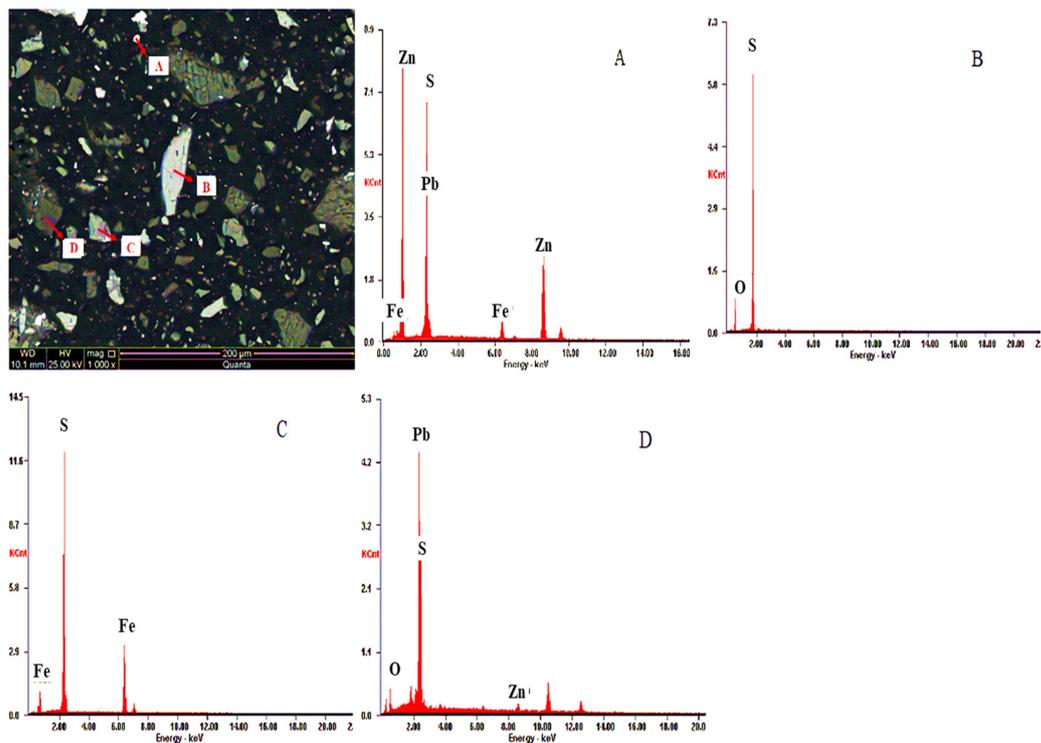


Figure 4. The EDAX spectra of the complex zinc ore.

Table 3. The distribution of the zinc phases in the complex zinc ore.

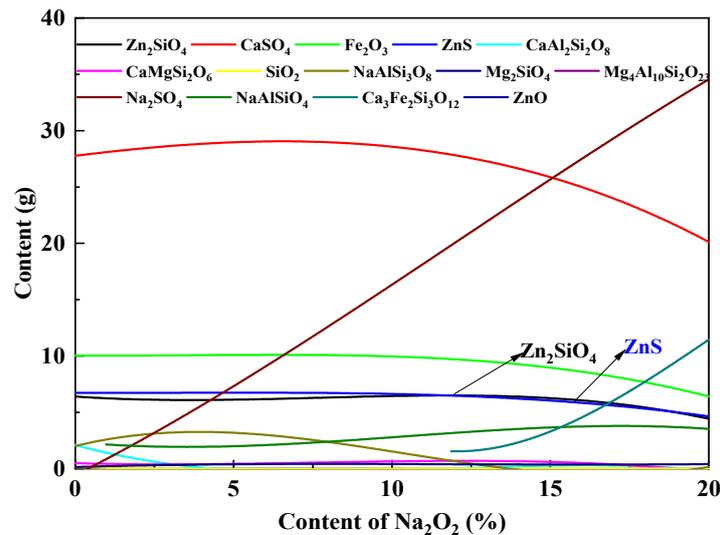
Elements	S	Pb	Fe	Zn	O	Si
A/wt%	1.85	84.56	–	4.95	8.64	–
B/wt%	33.89	4.73	6.61	54.76	–	–
C/wt%	54.20	45.80	–	–	–	–
D/wt%	–	–	–	–	35.51	64.49

### 3.2. Microwave-Assisted Phase Transformation

Based on our previous study,  $\text{Na}_2\text{O}_2$  is the ideal addition for the phase transformation of complex zinc ore [12], so we directly investigated the influence mechanism of adding  $\text{Na}_2\text{O}_2$  and microwave roasting on the phase transformation in this paper.

#### 3.2.1. Effect of $\text{Na}_2\text{O}_2$ Additive Doping on Phase Transformation

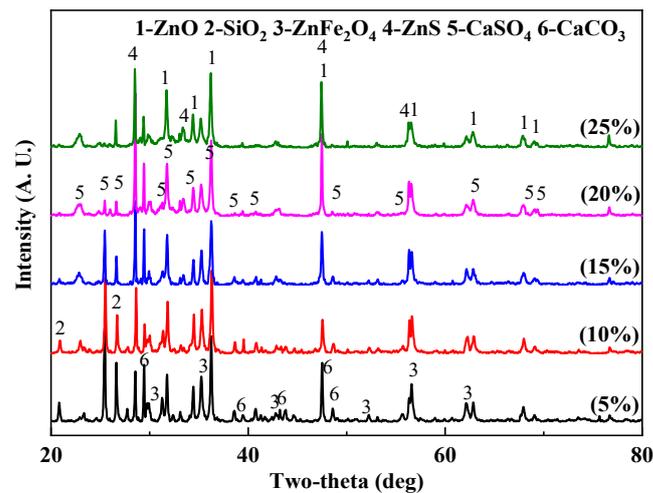
The effect of the  $\text{Na}_2\text{O}_2$  doping concentration on the equilibrium composition of the products is calculated by the Equilib module in Factsage, and the results are shown in Figure 5. The calculation procedure takes references from Yang et al. [21].



**Figure 5.** The effects of the  $\text{Na}_2\text{O}_2$  doping concentration on the equilibrium composition of productions.

The reactants have the following proportions: 21.17%  $\text{ZnCO}_3$  + 18.79%  $\text{ZnS}$  + 7.78%  $\text{Zn}_2\text{SiO}_4$  + 18.86%  $\text{FeS}_2$  + 6.32%  $\text{PbS}$  + 11.75%  $\text{SiO}_2$  + 13.64%  $\text{CaO}$  + 0.25%  $\text{MgO}$  + 1.45%  $\text{Al}_2\text{O}_3$  +  $\text{O}_2$  +  $\langle A \rangle$  %  $\text{Na}_2\text{O}_2$ . These are deduced from the contents and mineralogical characteristics of the complex zinc ore. Other conditions are set as 700 °C (conventional condition) and 1 atm. There is a range of  $\langle A \rangle$  limits at 0~20%. The results are displayed in a transition mode. From the equilibrium calculation results in Figure 3, it is seen that when the addition content of  $\text{Na}_2\text{O}_2$  is 0~15%, the main components of the complex zinc ore include  $\text{CaSO}_4$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Zn}_2\text{SiO}_4$ ,  $\text{ZnS}$  and  $\text{Na}_2\text{SO}_4$ , and their contents all increase with doping  $\text{Na}_2\text{O}_2$ . However, the effect of sodium peroxide on the equilibrium content of  $\text{Zn}_2\text{SiO}_4$  and  $\text{ZnS}$  is insignificant in this range. After the addition of  $\text{Na}_2\text{O}_2$ , the equilibrium contents of  $\text{Zn}_2\text{SiO}_4$ ,  $\text{ZnS}$ ,  $\text{CaSO}_4$  and  $\text{Fe}_2\text{O}_3$  began to decrease, with a large quantity of  $\text{ZnO}$  and  $\text{NaAlSiO}_4$  being produced, which are beneficial for the recovery of complex zinc ore. Thus, conclusions can be drawn that low doping concentrations of  $\text{Na}_2\text{O}_2$  have little effect on the phase transformation of complex zinc ore, yet once the concentration is beyond 15%, the oxidation degree of  $\text{ZnS}$  rapidly improves and the generation of  $\text{Zn}_2\text{SiO}_4$  will be suppressed. Taking into account the cost of the additives, it is reasonable to choose 20% sodium peroxide for the phase transformation process of complex zinc ore.

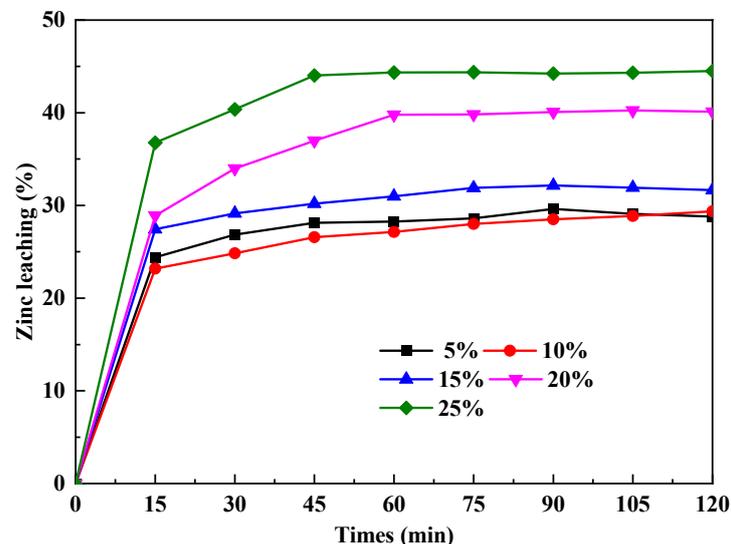
The calculation results seen in Figure 6 were verified by detecting the XRD patterns of zinc calcines, which are obtained by roasting at 700 °C for 15 min in a traditional heating furnace, with different levels of  $\text{Na}_2\text{O}_2$  added. The results are shown in Figure 6, and the added levels of  $\text{Na}_2\text{O}_2$  are 5%, 10%, 15%, 20% and 25%, respectively. It is shown that the main phases in these zinc calcines include  $\text{ZnO}$ ,  $\text{ZnS}$ ,  $\text{ZnFe}_2\text{O}_4$ ,  $\text{SiO}_2$ ,  $\text{CaSO}_4$  and  $\text{CaCO}_3$ . With an increasing concentration of sodium peroxide, the contents of  $\text{ZnFe}_2\text{O}_4$  and  $\text{ZnS}$  gradually decrease while the diffraction intensity of  $\text{ZnO}$  is enhanced, which is in accordance with the thermodynamic analysis results (Figure 5) and proves the feasibility of applying the Equilib module in FactSage to calculate the phase transformation process.



**Figure 6.** The effects of different doping concentrations of  $\text{Na}_2\text{O}_2$  on the XRD patterns of zinc calcines.

Figure 6 also strongly supports that sodium peroxide is an ideal assisted flux for the oxidation roasting of the complex zinc ore, which can improve the transformation and recovery of the complex zinc ore.

Figure 7 shows the effects of the  $\text{Na}_2\text{O}_2$  doping concentration on zinc leaching under conventional conditions. The calcines are obtained by roasting at  $700\text{ }^\circ\text{C}$  for 15 min in a traditional electro-thermal furnace. The leaching experiments are carried out under specific conditions: the total ammonia concentration is  $7.5\text{ mol/L}$ , the molar ratio of ammonia and ammonium chloride is 1:1, the leaching occurs at room temperature, the liquid:solid ratio is 10:1 and the stirring rate is 300 rpm.



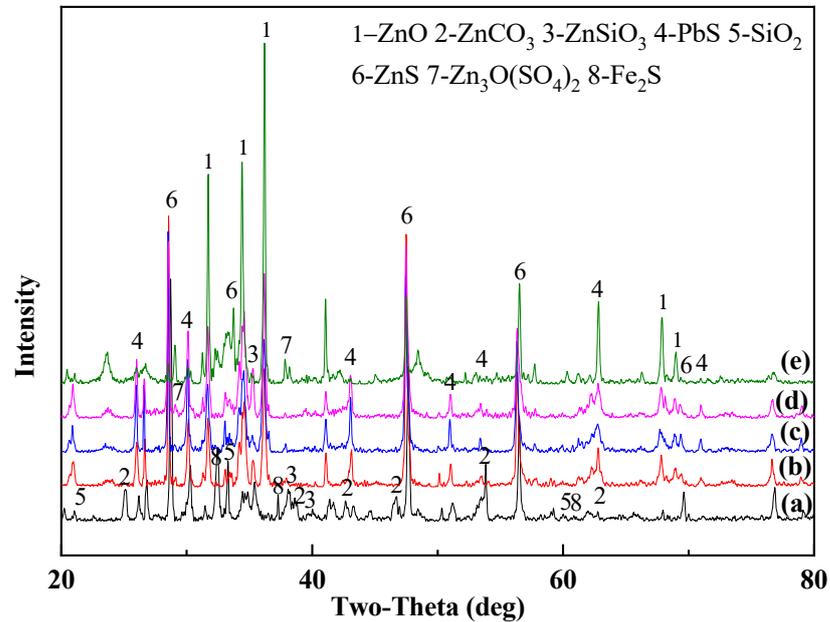
**Figure 7.** The effects of the  $\text{Na}_2\text{O}_2$  doping concentration on zinc leaching under conventional conditions.

From Figure 7, it is observed that, with the addition of sodium peroxide, the leaching of complex zinc ore gradually increases, and when the doping concentration is 20%, zinc leaching reaches about 40%. Combining the thermodynamic calculation results and the XRD and XPS analyses, it can be deduced that, when using traditional heating, there is still a large part of sphalerite not transforming, which may be caused by a short holding time.

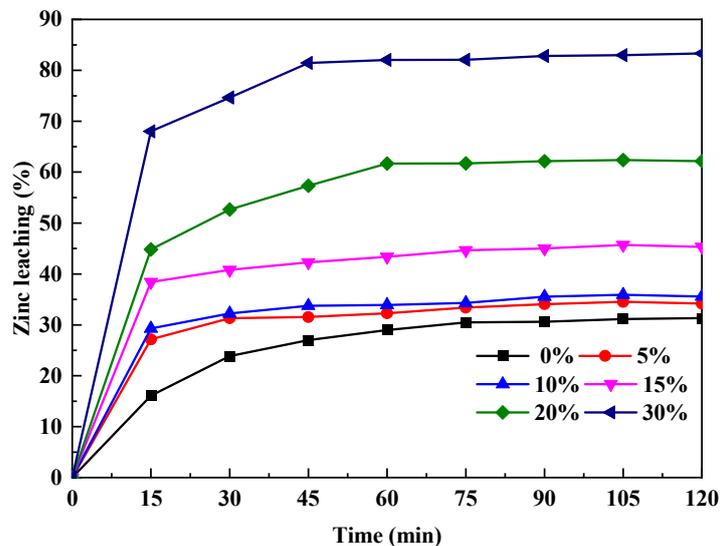
### 3.2.2. Effect of Microwave-Assisted Heating on Phase Transformation

When using a conventional heating process, the heat is transferred from the surface to the inside, leading to low heating efficiency [22]. To considerably improve the heating

reaction and reduce processing time, microwave-assisted heating is adopted, and the results are shown in Figures 8 and 9.



**Figure 8.** The effects of different roasting temperatures on the XRD patterns of zinc calcines under the microwave roasting condition. (a) 200 °C; (b) 300 °C; (c) 400 °C; (d) 500 °C; (e) 600 °C.



**Figure 9.** The leaching degrees of zinc calcines under microwave-assisted heating conditions.

The advantage of microwave-assisted heating on phase transformation is determined by detecting the phase compositions of the zinc calcines at different temperatures. The selected study roasting temperatures are 200 °C, 300 °C, 400 °C, 500 °C and 600 °C, the mass ratio of sodium peroxide is 20%, the holding time is 15 min and the microwave roasting power is 800 W. The results are shown in Figure 8.

As can be seen, the zinc calcine obtained using microwave roasting at 200 °C is mainly composed of ZnS, and some ZnCO<sub>3</sub>, FeS<sub>2</sub> and ZnSiO<sub>3</sub>. Compared with the raw complex zinc ore, the diffraction peaks of ZnCO<sub>3</sub> and ZnS have little or no change, indicating that the decomposition or oxidation of ZnCO<sub>3</sub> or ZnS requires higher energy. This is consistent with the physicochemical properties of ZnCO<sub>3</sub> and ZnS. When the microwave heating temperature reaches 300 °C, the diffraction peaks of ZnSiO<sub>3</sub> and ZnCO<sub>3</sub> almost completely

disappear and the ZnO phase appears.  $\text{Zn}_3\text{O}(\text{SO}_4)_2$  appeared using microwave heating at 400 °C, which is much lower than the reported oxidation calcination temperature. This was attributed to the combined action of microwave roasting and sodium peroxide. With a further increase in temperature, the diffraction peak of ZnS decreases. When the roasting temperature is 600 °C, the zinc-containing phase is mainly ZnO, which is a better outcome than conventional roasting at 700 °C. The lowered roasting temperature is due to the “non-thermal microwave effects” [23], and the phase transformation temperature of complex zinc ore assisted by microwave heating is, thus, chosen at 600 °C.

The effect of microwave-assisted phase transformation on the leaching degree of zinc is shown in Figure 8, and the leaching conditions are essentially the same as in the above section. It can be seen that, under microwave-assisted heating conditions, increasing the  $\text{Na}_2\text{O}_2$  doping concentration causes a gradual improvement in zinc leaching, which is the same as in traditional heating. Considering that the cost of adding 30% sodium peroxide is too high, a 20%  $\text{Na}_2\text{O}_2$  doping concentration is more suitable, as with this concentration, the recovery of zinc can reach 62.17%, which is an acceptable value and a big leap in contrast to the recovery achieved by conventional heating. Namely, phase transformation with the assistance of 20%  $\text{Na}_2\text{O}_2$  doping and microwave roasting at 600 °C leaches 22.17% more zinc than conventional roasting.

Given that the recovery value is still not optimal, techniques for complex leaching and ultrasonic strengthening are considered.

### 3.3. Ultrasonic-Assisted Complexation Leaching

#### 3.3.1. The Complexation Leaching Equilibrium under $\text{Zn}(\text{II})\text{-NH}_4^+\text{-NH}_3\text{-NTA}^{3-}\text{-H}_2\text{O}$ System

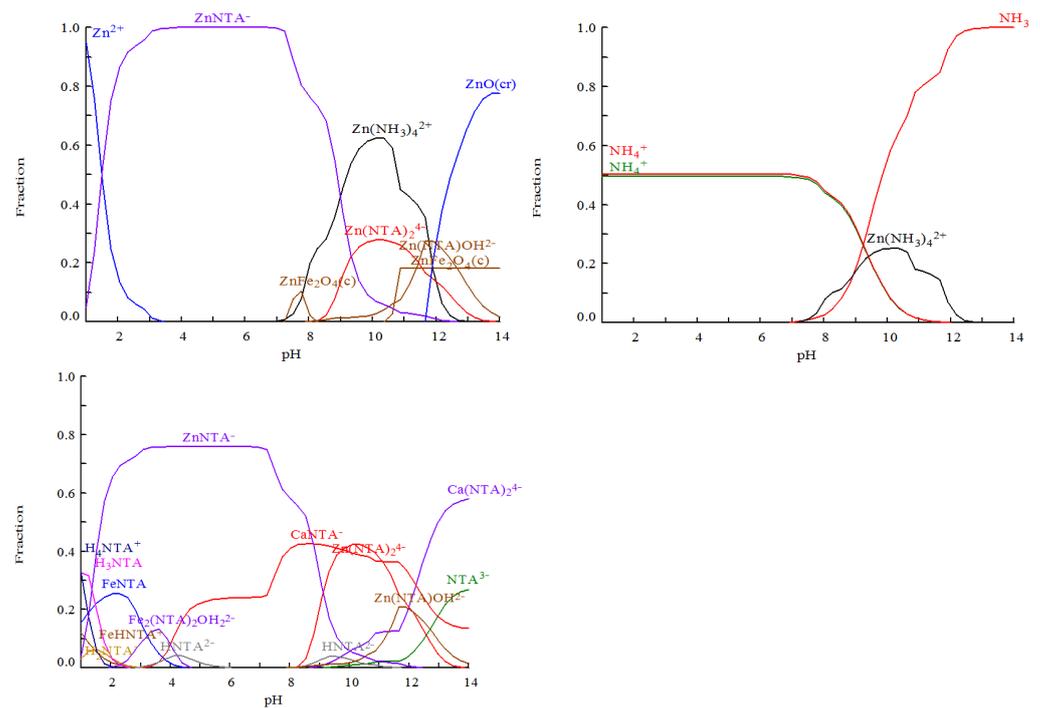
In this section, commonly used complexing agents are analyzed for strengthening the leaching of zinc calcines, and the cumulative formation constants for zinc complexes are shown in Table 4.

**Table 4.** The cumulative formation constants for zinc complexes.

	LogK <sub>1</sub>	LogK <sub>2</sub>	LogK <sub>3</sub>	LogK <sub>4</sub>
Ammonia–zinc	2.37	4.81	7.31	9.46
Hydroxide–zinc	4.40	11.30	14.14	17.66
Chloride–zinc	0.43	0.61	0.43	0.20
Nitrilotriacetic–zinc	10.45	13.45	-	-

The equilibrium constants for the complexation equilibrium reaction are generally checked using Lange’s handbook of chemistry [24] and the critical stability constants [25]. The equilibrium constants are also called cumulative formation constants for the complexes, expressed by a value of K. The stability of zinc complexes can be expressed by the equilibrium constants of the complexes formed. A greater value of K means a greater tendency to form complex ions and, therefore, a more stable complex forming.

Information can be obtained from Table 3 to support that the tetra–zinc–ammonia complex is the most stable. It is feasible to dope a small concentration of nitrilotriacetic acid ( $\text{NTA}^{3-}$ ) in the ammonia leaching solution, which is simple and has a slightly larger complexation equilibrium constant with zinc. The distribution of zinc and complexing agents in ammonia solutions is studied by HYDRA/MEDUSA [26,27]. For the convenience of the investigation, the molar mixing ratio of ammonia to ammonium salt is 1:1, both being 3.75 mol/L, the pH value of the solution is 9.3 and the liquid:solid ratio is 10:1, in which all elements are assumed to present in an ionic state. The concentration of complexing agents is 0.5 mol/L, and the results are shown in Figure 10.



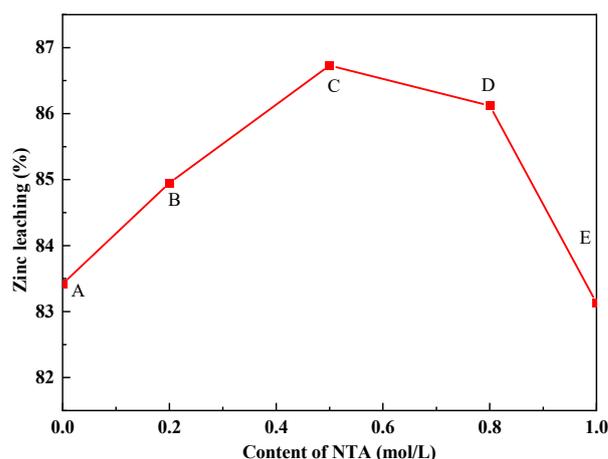
**Figure 10.** The effect of  $\text{NTA}^{3-}$  on Zn (II) species,  $\text{NTA}^{3-}$  species and  $\text{NH}_3$  species distribution diagrams in the solution. The diagram is made by the authors in Medusa software version 2010.

It can be seen that  $\text{Zn}^{2+}$  presents in phases of  $\text{Zn}(\text{NTA})^-$ ,  $\text{Zn}(\text{NTA})_2^{4-}$  and  $\text{Zn}(\text{NH}_3)_4^{2+}$  complexation compounds at a pH of 9.3. The promoting effect of  $\text{NTA}^{3-}$  on zinc leaching is mainly due to the formation of  $\text{Zn}(\text{NTA})_2^{4-}$ , which is more stable than  $\text{Zn}(\text{NH}_3)_4^{2+}$ . However,  $\text{NTA}^{3-}$  also complexes with  $\text{Ca}^{2+}$  to form  $\text{CaNTA}^-$ , which is disadvantageous for the utilization of  $\text{NTA}^{3-}$ . To improve the efficiency of  $\text{NTA}^{3-}$ , it is preferable to add a calcium inhibitor before the complexation leaching of the zinc ore in the  $\text{NH}_4^+$ - $\text{NH}_3$ - $\text{NTA}^{3-}$ - $\text{H}_2\text{O}$  system. In general, it is advantageous to add nitrilotriacetic acid in the ammonia leaching of zinc ore.

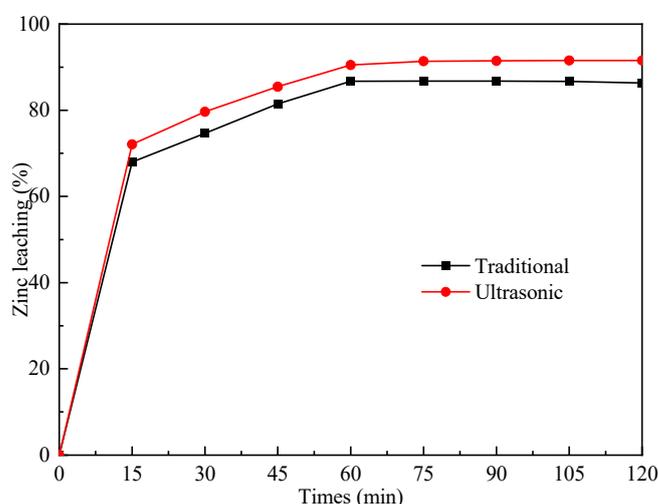
The effects of different addition concentrations of  $\text{NTA}^{3-}$  on zinc leaching are studied (Figure 11). The leaching is carried out under conditions of 20% sodium peroxide doping, microwave-assisted calcining at 600 °C for 15 min, mechanical stirring, 80 °C leaching for 1 h, and the concentration of  $\text{NTA}^{3-}$  being 0~1 mol/L. The results are shown in Figure 10. When the addition concentration of  $\text{NTA}^{3-}$  is 0.5 mol/L, the leaching degree of zinc is the greatest, at 86.73%. The strengthened effect of ultrasound on the leaching degree of complex zinc ore is shown in Figure 12. The other operating conditions are kept unchanged.

### 3.3.2. The Effect of Ultrasonic-Assisted Complexation Leaching

From the effect of ultrasonic-assisted complexation leaching on the extraction of zinc calcines in Figure 11, it can be seen that ultrasound can gradually improve zinc leaching, with initially no disparity to 4.7% at 75 min. Introducing ultrasound during complexation leaching greatly promotes the recovery of zinc, reaching 91.4%, in contrast to traditional leaching, achieving only 86.7%. Thus, the potential of ultrasound in the leaching process of complex zinc ore is illustrated.



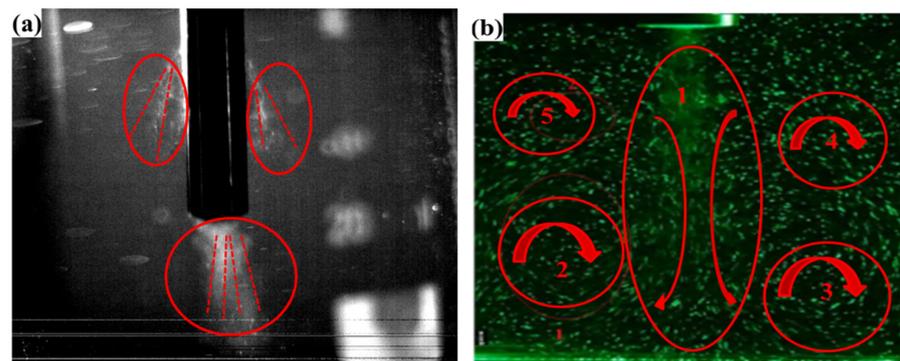
**Figure 11.** The effect of  $\text{NTA}^{3-}$  concentrations on the leaching of complex zinc ore.



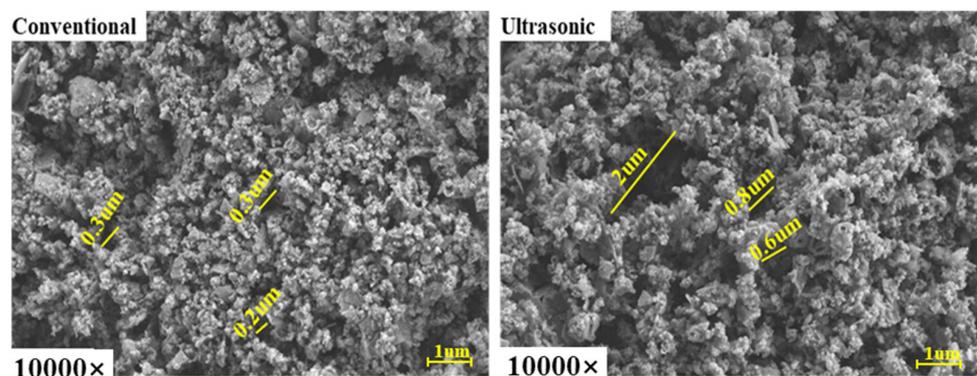
**Figure 12.** The effect of ultrasound on the leaching of complex zinc ore.

The strengthening principle of ultrasound is confirmed by the high-speed image in Figure 12 and the SEM images of the leaching slag in Figure 13. The cavitation caused by ultrasound (Figure 13a) produces a powerful high-pressure heterogeneous jet, which makes the complex zinc ore particles move in a variety of vortices and subjects them to multi-strength impact forces in different directions (Figure 13b). Thus, ultrasound can reduce the diffusion resistance so that the NTA can have better contact with the zinc minerals and reduces the activation energy of the reaction.

The SEM images of the leaching slag under traditional and ultrasonic conditions are shown in Figure 14. It can be seen that the pore size of the leached slag under ultrasonic conditions is 0.6–2  $\mu\text{m}$ , which is 100%–900% larger than that seen under traditional conditions (0.2–0.3  $\mu\text{m}$ ). In other words, ultrasonic leaching helps to open the packaging of the products in the leaching process, therefore helping the reaction reagent to enter into the particle and make contact with the unreacted layer, strengthening the complex reaction of the unreacted layer, thus, strengthening zinc leaching.



**Figure 13.** A high-speed image of ultrasonic leaching: ultrasonic cavitation (a); particle motion in the ultrasonic field (b).



**Figure 14.** The SEM images of the leaching slag under traditional and ultrasonic conditions.

#### 4. Conclusions

In this research, effectively extracting  $Zn^{2+}$  from refractory complex zinc ore is realized through microwave- and ultrasonic-combined technology. The recovery process consists of two procedures, microwave-assisted phase transformation and ultrasonic-assisted complexation leaching. The thermodynamic mechanisms of phase transformation and complexation leaching are calculated by Factsage and HYDRA/MEDUSA, respectively. The results show that the addition of sodium peroxide and microwave-assisted leaching can promote the transformation of the refractory zinc phase to  $ZnO$  and inhibit the formation of  $Zn_2SiO_4$ . The species distribution in the leaching solution was analyzed by HYDRA/MEDUSA. The results showed that  $Zn^{2+}$  mainly exists in a form of  $Zn(NH_3)_4^{2+}$  tetrahedral complex in the  $Zn-NH_3-NH_4^+-H_2O$  system and that the addition of the complexing agent, citric acid, can inhibit the generation of low-coordination  $Zn(NH_3)_3^{2+}$ . It was also found that the promoting effect of  $NTA^{3-}$  on zinc leaching is mainly due to the formation of  $Zn(NTA)_2^{4-}$ . The ultrasonic technique can reduce the diffusion resistance by generating a high-pressure heterogeneous jet and open the products by generating a bigger pore size, which improves zinc leaching by 4.7%. Under set conditions, microwave heating at  $600\text{ }^\circ\text{C}$  for 15 min, the doping concentration of  $Na_2O_2$  being 20% and leaching assistance with 225 W ultrasonic, zinc leaching can reach 91.4%, with 0.5 mol/L  $NTA^{3-}$  adding and  $80\text{ }^\circ\text{C}$  leaching taking 75 min. This paper shows great potential for the green extraction of non-traditional zinc-containing resources.

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