

# Hydrometallurgy

## Efficiency and sustainable leaching process of manganese from pyrolusite-pyrite mixture in sulfuric acid systems enhanced by microwave heating --Manuscript Draft--

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<b>Abstract:</b>	<p>Recently, with the decrease in the quality of manganese resources, the efficient use of low-quality manganese ore resources has attracted widespread attention. At present, pyrite is often used as reducing agent to recover Mn(IV) in industrialization. However, the passivation of pyrite in the leaching reaction process will lead to a decreased reaction efficiency. Hence, in this study, microwave heating was applied in the reduction system in order to remove the inhibition of the passivation layer and accelerate the dissolution of pyrite, indicating an improvement in the corresponding Mn(IV) reduction efficiency. The results show that the leaching rate assisted by microwave heating was 95.07%, approximately 20% higher than that of conventional heating (75.08%), and the amount of sulfuric acid and pyrite was reduced by 14% and 20%, respectively. XPS analysis shows that there was an obvious sulfur elemental peak at 164.3 eV under traditional heating conditions, but it was absent when microwave heating was applied, and the elemental sulfur under conventional heating is 11.63%, which is higher than that under microwave heating (4.80%). Through scanning electron microscopy, it was noted that there are a large number of voids on the mineral surface under microwave heating, which can increase the solid-liquid contact area, effectively reducing the formation of the sulfur passivation layer and accelerating the dissolution of Mn (IV). In addition, the measurement of the dielectric constant of the solution mixture shows that the dielectric constant of the solution with mineral addition was increased from 36.533 (F/M) to 37.717 (F/M) and the loss tangent angle was increased from <math>8.61 \times 10^{-3}</math> to <math>9.21 \times 10^{-3}</math>. It can be inferred that microwaves act directly on the mineral itself through the solution. Thus, the application of pyrite and microwave heating in the recovery of Mn(IV) is expected to effectively reduce the use of sulfuric acid, and achieve green, environmentally friendly and efficient leaching of manganese.</p>
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Please, find below the referees' comments repeated in italics and our responses inserted after each comment.

Looking forward hearing from you soon.

Sincerely,

Guo Chen, Jin Chen and Lei Gao

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Editor:

1) Make sure that all of the reactions are balanced!

The authors want to express our apology for the unbalanced equations presented in the manuscript, and the typos are revised and highlighted in the updated manuscript.

Reviewer #2:

1) Do you have a reason for writing unbalanced reactions: 2, 6?

We appreciate this suggestion, and the authors want to express our apology for this mistake and has balanced Eq. (2), (6) in the revised manuscript. Moreover, we have checked the manuscript to make sure all the reactions are balanced, the revised and replenished places were highlighted. Thank you.

$2\text{FeS}_2 + 15\text{MnO}_2 + 28\text{H}^+ = 2\text{Fe}^{3+} + 15\text{Mn}^{2+} + 14\text{H}_2\text{O} + 4\text{SO}_4^{2-}$  (2)

$\text{FeS}_2 + 2\text{H}^+ = \text{Fe}^{2+} + \text{H}_2\text{S} + \text{S}$  (6)

- (1) A novel microwave leaching method is proposed for manganese selective recovery.
- (2) Microwave heating is proved to be more effective compared to conventional heating.
- (3) The passivation layer detected during normal leaching was suppressed by MW heating.

# Efficiency and sustainable leaching process of manganese from pyrolusite-pyrite mixture in sulfuric acid systems enhanced by microwave heating

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## Abstract

Recently, with the decrease in the quality of manganese resources, the efficient use of low-quality manganese ore resources has attracted widespread attention. At present, pyrite is often used as reducing agent to recover Mn(IV) in industrialization. However, the passivation of pyrite in the leaching reaction process will lead to a decreased reaction efficiency. Hence, in this study, microwave heating was applied in the reduction system in order to remove the inhibition of the passivation layer and accelerate the dissolution of pyrite, indicating an improvement in the corresponding Mn(IV) reduction efficiency. The results show that the leaching rate assisted by microwave heating was 95.07%, approximately 20% higher than that of conventional heating (75.08%), and the amount of sulfuric acid and pyrite was reduced by 14% and 20%, respectively. XPS analysis shows that there was an obvious sulfur elemental peak at 164.3 eV under traditional heating conditions, but it was absent when microwave heating was applied, and the elemental sulfur under conventional heating is 11.63%, which is higher than that under microwave heating (4.80%). Through scanning electron microscopy, it was noted that there are a large number of voids on the mineral surface under microwave heating, which can increase the solid-liquid contact area, effectively reducing the formation of the sulfur passivation layer and accelerating the dissolution of Mn (IV). In addition, the measurement of the dielectric constant of the solution mixture shows that the dielectric constant of the solution with mineral addition was increased from 36.533 (F/M) to 37.717 (F/M) and the loss tangent angle was increased from  $8.61 \times 10^{-3}$  to  $9.21 \times 10^{-3}$ . It can be inferred that microwaves act directly on the mineral itself through the solution. Thus, the application of pyrite and microwave heating in the recovery of Mn(IV) is expected to effectively reduce

the use of sulfuric acid, and achieve green, environmentally friendly and efficient leaching of manganese.

Keywords: pyrolusite-pyrite mixture; dielectric properties; leaching kinetics; reductive leaching; microwave heating; conventional heating.

## 1. Introduction

Manganese (Mn) usually exists in the form of  $\text{MnCO}_3$  and  $\text{MnO}_2$  in nature [1, 2].

Manganese is widely used in many aspects of human society; the most important application of manganese is as an additive in iron and steel production at approximately 90% of total consumption, with other applications in fireworks production, batteries, pharmaceutical manufacturing, fertilizer production and so on [3]. With the development of the iron and steel industry, the demand for high-quality and cheap manganese resources is continually increasing [4, 5].

Therefore, recovering manganese from the large number of low-grade manganese ores, which comprise approximately 93% of manganese resources, is particularly important [6]. It should be mentioned that two main methods are used to recover manganese resources: pyrometallurgy and hydrometallurgy [7]. Although pyrometallurgy has the advantage since it provides a decent recovery rate and is more efficient, it also has disadvantages such as high energy consumption and high pollution during the recovery process; thus, hydrometallurgy is focused on the aspect of environmental protection for the recovery of low-grade minerals [8,9]. Since the manganese in low-grade pyrolusite usually exists in the form of insoluble  $\text{Mn}^{4+}$ , it is necessary to add a reducing agent to assist the leaching process [10]. In addition,

the traditional hydrometallurgy process has a low leaching rate and poor economic benefits; hence, the development of an economical, clean and efficient process for the recovery process of manganese from low-grade ore is important for the sustainable development of the manganese industry.

Pyrite (cubic  $\text{FeS}_2$ ) is rich in the earth's crust, and has a strong reducibility [11]. Gan et al. used pyrite to reduce  $\text{Cr(VI)}$  to  $\text{Cr(III)}$  [12]. Thus, using pyrite as a reducing agent is beneficial for the recovery of manganese from manganese ore. Moreover, the anionic group ( $\text{S}_2^{2-}$ ) in pyrite is also an alternative source for sulfuric acid, used in many hydrometallurgical systems [13]. Hence, the addition of pyrite can reduce the use of sulfuric acid during the leaching process, which is beneficial for environment protection [14]. However, although pyrite has the advantages of strong reducibility and environmental protection, NAYAK et al. and Kholmogorovden et al. studied the redox reaction between  $\text{FeS}_2$  and  $\text{MnO}_2$  and found that  $\text{S}_2^{2-}$  produced sulfur ( $\text{S}^0$ ) in the redox reaction, and the hydrophobicity of the sulfur element hindered the contact of solid-liquid reaction, resulting in the interruption of the reaction [15,16]. Thus, it is of general significance to reduce the formation of a sulfur passivation layer during the reaction process to increase leaching efficiency [17]. Zhang et al. found that microwave heating is useful for reducing the encapsulation behaviour of pyrite [18], and Sabzezari et al. noticed that the formation of an ash layer (passivation layer) in sulphide ore was suppressed with the assistance of microwave energy [19]. Thus, microwave heating could be the solution for the formation of the passivation layer of pyrite.

Microwaves are an electromagnetic wave with a frequency of 0.3 GHz-300 GHz, and the microwave frequencies used in industrial heating are 2450 MHz and 915 MHz [20].

According to the electromagnetic radiation theory put forward by Maxwell, microwaves are composed of electric and magnetic fields that propagate in a straight line and are perpendicular to each other (Fig. 1a) [21]. The resulting electric and magnetic fields can directly act on the material itself. Thus, compared to traditional convection heating, microwave heating can directly heat the interior of the material, making it more efficient and faster (Fig. 1b) [22,23]. At present, microwave heating devices mainly include microwave generators, waveguides, heating chambers, water cooling systems, temperature measuring systems, and resonant cavities (single-mode or multi-mode) [24]. Of these, multi-mode microwave reactors are widely used in materials, chemical industry, metallurgy and other fields because of their large processing capacity [25]. It has applications in fields including materials, chemical engineering, metallurgical engineering and so on [26]; for example, Hou et al. used microwave hot pressing sintering to prepare diamond composites [27]. Zhi et al. used microwaves to recover V and Mo from waste catalyst, with recovery rates of 94.35% and 96.23%, respectively [28]. Moravvej et al. found that the leaching rate of copper under microwave radiation is 2.5 times higher than that of conventional heating [29]. Choi et al. found that obvious cracks appear on the surface of pyrite under microwave radiation, and the leaching rate can be largely improved [30]. Wen et al. found that microwaves can effectively reduce the passivation layer formed by the sulfur element in chalcopyrite [31]. Pyrite has similar chemical properties to chalcopyrite and has the problem of a passivation layer during the leaching process [12]. Hence, the use of microwave heating may reduce the energy and time consumed for the recovery process; meanwhile, it may inhibit the formation of a passivation layer in the process of pyrite reduction, which will increase the efficiency of the

leaching process of pyrolusite.

In the present study, a new auxiliary enhanced leaching method assisted by microwave heating was used for rapid recovery of manganese from low-grade pyrolusite. To show the advantages of microwave heating, the results of the conventional heating process were also provided for comparison. With the application of pyrite as a reducing agent, the influences of leaching parameters were studied to optimize the current manganese production process with a reducing leaching time and an improved leaching rate. In addition, the kinetic models under different heating processes are analysed to explain the advantages of microwave heating. Finally, the principle of microwave heating of the solution containing minerals is explained by the dielectric test.

## 2. Materials and methods

### 2.1. Materials

The as-received low-grade pyrolusite was from Nanning City, Guangxi Province, P.R. China, with an Mn of 26.389% ( $T_{Mn} < 35\%$ ); an Fe of 9.876%; an Si of 16.178%; and an Al of 2.037%. According to the classification standard of China's manganese ore industry, the as-received pyrolusite belongs to the third-grade iron-manganese ore since the mass ratio has the relationship of  $T_{Mn}\% + T_{Fe}\% \geq 30.000$  and  $T_{Mn}/T_{Fe} < 3.0$  [3, 32]. Fig. 2 shows that manganese in pyrolusite exists mainly in the form of  $MnO_2$ .

The as-received pyrite was from Wenshan Prefecture, Yunnan Province, China, with an  $FeS_2$  of 75.289%; an  $Fe_2O_3$  of 16.215%; and a ZnO of 2.64%. The as-received pyrolusite and pyrite were manually crushed with an agate mortar and screened from 180 mesh to 240 mesh,

respectively. The other reagents for the experimental use in this study were of analytical grade.

## 2.2. Characterization

### 2.2.1. X-ray diffraction (XRD)

XRD is one of the most commonly used methods to characterize the phases in the sample. To understand the characterize phases in the as-received pyrolusite, the X-ray diffraction pattern of pyrolusite was recorded at a scanning rate of 1.6 °/min in the range of 5 ° to 90 ° with a step of 0.026 ° at 40 mA and 40 kV. The duration of each step was approximately 135 s with an X'Pert3 powder X-ray diffractometer (Panaco) and a CuK $\alpha$  Radiation ( $\lambda=1.540598$  Å) as the anode target at room temperature.

### 2.2.2. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is usually used for investigating substances on mineral surfaces. In the present work, XPS was employed to understand the chemical composition on the surfaces of as-received pyrolusite samples and the leaching residues; the aim was to investigate the formation mechanism of the passivation layer.

The X-ray photoelectron spectra of pyrolusite samples were recorded with K-Alpha (Thermo Fisher Scientific, Waltham, MA, USA) at room temperature, equipped with Mono Al-K $\alpha$  as the light source and CAE scanning mode under the working conditions of 6 mA and 12 kV. The nonlinear least-squares curve-fitting program (Avantage software 5.976) was used to deconvolve the XPS data.

### 2.1.3. Scanning electron microscope (SEM).

Scanning electron microscopy (SEM) was used to understand the microstructure of as-

received pyrolusite samples and leaching residues. During the SEM analysis, the CeB6 filament with 2.5 eV escape power was used, the acceleration voltage of the instrument was 10 kV, and the backscatter electron detector with Phenom prox (PANalytical, Netherlands) was used to observe the surface morphology of the samples under different magnification. The instrument software package was used to record data.

### 2.3. Experimental step

In this experiment, first the as-received pyrolusite and pyrite were dried at 105 °C for 2 hours in a drying oven (Shanghai Yiheng Scientific Instrument Co., Ltd.) to remove the moisture that may be attached to the surface. In the sulfuric acid leaching experiment, 20.00 g  $\pm 0.01$  g pyrolusite and a certain amount of pyrite (2.00 g, 3.00 g, 4.00 g, 5.00 g and 6.00 g) were weighed using an analytical balance (OHAUS). Then, the required volume of sulfuric acid was added according to the liquid-solid ratio (10 ml/g). The solution was stirred by a mechanical agitator (IKA RW20) with a digital display. A DF-101S constant temperature water bath furnace was used to maintain a constant temperature for conventional heating. Microwave heating was undertaken using a microwave heating instrument developed by Kunming University of Science and Technology. All experiments used a K-type digital temperature controller to measure the temperature of the solution in the reactor [33], and the measuring range was 0 °C-300 °C with a temperature accuracy  $\pm 0.1$  °C. The reaction time was controlled by a digital chronograph. In the leaching process in the reactor, the sulfuric acid solution was stirred after the addition of a certain amount of prepared samples, and the digital timer was started at the same time. After the reaction occurred for a period of time, the mixer and the timer stopped working at the same time. The reaction solution was filtered

using a SHZ-D (III) vacuum pump. The manganese content in the filtrate was titrated with a solution of  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ . For the accuracy of the data, two repeated trials were done under the same conditions.

The leaching rate of manganese in manganese ore was calculated by the following equation [63]:

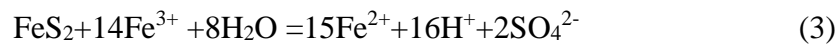
$$\eta_{\text{Mn}} = \frac{\rho \times V}{M_{(\text{ore})} \times W} \times 100\% \quad (1)$$

where  $\eta_{\text{Mn}}$  represents the leaching rate of manganese in pyrolusite,  $\rho$  represents the density of manganese in lixivium,  $M$  represents the mass of pyrolusite, and  $W$  represents the content of manganese in pyrolusite.

### 3. Results and discussion

#### 3.1. Thermodynamic analysis of leaching reaction

During the leaching process of low grade pyrolusite with the assistance of pyrite in sulfuric acid medium, the possible reactions Eq.(2)-Eq.(4) [15, 16, 34, 35] are listed as follows,



As shown in Fig. 3, the Gibbs free energies of the reaction in aqueous solution (Eq. 2-5, Fig. 3a) were preliminarily calculated by using thermodynamic software FactSage 7.2 (Germany). The Gibbs reaction free energy of 0 °C to 100 °C was calculated by using 10 °C

as the temperature interval. At the same time, the construction of the Eh-pH diagram was realized by using the chemical software HSC Chemical 6.0 [36] (Outokumpu, Helsinki, Finland), and the thermodynamic data all originated from the software itself (Fig. 3b).

The calculated results are shown in Fig. 3a. The Gibbs free energy ( $\Delta G$ ) is negative, indicating that the whole leaching process can happen spontaneously, and with the increase in the reaction temperature, the Gibbs free energy ( $\Delta G$ ) of the side reaction increases gradually, showing that temperature increases play a positive role in the occurrence of the reactions (2)-(5). In addition, Fig. 3b indicates a stable Eh-pH diagram of manganese dioxide ( $\text{MnO}_2$ ) at 90 °C. It can be seen from the diagram that the reduction of Mn(IV) to Mn(II) can be achieved by increasing the concentration of hydrogen ions resulting from the decrease in pH value, or by adding reductive ions ( $\text{Fe}^{2+}/\text{S}_2^{2-}$ ) to reduce the reduction potential in the solution. Therefore, the appropriate increase in hydrogen ion concentration and  $\text{Fe}^{2+}/\text{S}_2^{2-}$  can promote the occurrence of Eq. 4, which is beneficial to the reduction reaction of Mn (IV).

### 3.2 Studies of different leaching parameters

The intention of adding reducing agent pyrite during the recovery process is to provide assistance for the dissolving of manganese dioxide in acid. Thus, the effects of process parameters such as different mass ratios of pyrolusite to pyrite, different sulfuric acid concentration, different temperature and different stirring speed on microwave heating leaching were investigated for the optimum conditions.

#### 3.2.1. Effect of sulfuric acid concentration

Fig. 4 shows that the leaching rate of manganese metal has a positive relation with the concentration of the sulfuric acid, mainly because the increase in the concentration of sulfuric

acid leads to the decrease in pH of the solution. From the simulation data of Eh-PH (Fig. 3b), it is noticed that when the reduction potential is constant, the smaller the value of pH, the easier it is to convert into Mn (II). In addition, hydrogen ions can promote the decomposition of pyrite into  $\text{Fe}^{2+}$  and  $\text{S}_2^{2-}$  [12, 13]. Hence, in this experiment, different sulfuric acid concentrations (0.6 M-1.6 M) were used in microwave reactors and conventional reactors, respectively. It was found that when the concentration of the sulfuric acid varied between 0.6 M-1.2 M, the leaching rate of manganese by conventional heating increased from 57.02% to 75.08%, and the leaching rate of manganese by microwave heating increased from 69.52% to 95.07%. Olubambi et al. found that microwaves can increase solution convection, so that the leaching rate of microwave heating is much higher than that of conventional heating, and the utilization efficiency of sulfuric acid is also improved under the conditions of microwave heating. The amount of sulfuric acid used when the leaching rate of manganese is the highest (1.2 M) is 14% less than that for conventional heating (1.4 M) [61].

In the 0.8 M-1.0 M process, the leaching efficiency increases slowly under the two heating methods, which can be attributed to the competitive relationship between different reactions in the leaching process at this concentration. However, although a higher concentration of sulfuric acid is beneficial to improve the leaching of metals, too high a concentration of sulfuric acid will lead to difficulties in subsequent purification. In addition, NAYAK et al. found that too high a concentration of sulfuric acid concentration will lead to the dominant position of corrosion dissolution ( $\text{FeS}_2/\text{Fe}^{3+}$ ) of  $\text{FeS}_2$  and increase the rate of side reactions (3), (4), resulting in the formation of elemental sulfur [15]. Xiao et al. pointed out that too high a sulfuric acid concentration will lead to the formation of a sulfur film on the

mineral surface, decreasing the reaction rate [62]. Therefore, in order to improve the efficiency and save reagents, the feed solution with a sulfuric acid concentration of 1.2 mol/L was selected as the best choice for follow-up experiments to evaluate the influence of other factors. The above results show that it is feasible to extract manganese in a microwave reactor.

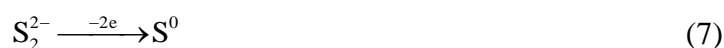
### 3.2.2. Effect of the amount of pyrite

Fig. 5 indicates the effect of the amount of reducing agent (pyrite) on the leaching rate of manganese under different heating methods at 90 °C. Since manganese dioxide ( $\text{MnO}_2$ ) is stable under acidic or alkaline conditions, acidic manganese extraction from pyrolusite needs to be carried out under reduction conditions. Therefore, the use of a reducing agent is essential [9]. Combined with the theoretical calculation of Fig. 3b, it can be found that the content of reducing agent can promote manganese leaching. Thence, in order to explore the relationship between the amount of reducing agent and the leaching efficiency of manganese, and to select the appropriate amount of reducing agent, the experiment was designed. It can be seen from Fig. 5 that when  $m(\text{pyrolusite}): m(\text{pyrite})=10:2.0$ , the leaching rate of manganese obtained by microwave heating is 95.07%, and when  $m(\text{pyrolusite}): m(\text{pyrite})=10:2.5$ , the leaching rate of manganese was obtained by conventional heating (75.08%). It can be seen that microwave heating can obviously reduce the amount of pyrite (at least 20%) and improve the leaching efficiency of manganese. The reason is that the strong convection of the solution induced by microwave electromagnetic fields increases the collision contact between magnetic ions or ion groups in the solution, which speeds up the occurrence of the reaction [37, 38]. However, it can be seen in the figure that when the amount of reducing agent is more than 10:2, the leaching rate under microwave radiation increases slowly, and the use of

reducing agent will also lead to increased cost and the production of sulfur element in the side reaction :



Excessive use of reducing agent will lead to the increase in reducing agent concentration in the solution and cause competition among reducing ions, which is less conducive to the further oxidation of sulfur [39].



Thence, the optimized ratio of pyrolusite to pyrite was 10:2 for the following experiments, and the follow-up experiments were carried out.

### 3.2.3. Effect of stirring speed

The leaching degree of Mn(II) under different stirring speeds and different heating methods is shown in Fig. 6. The stirring speed will affect the mass transfer process in the leaching process. Generally, the increase in stirring speed will usually reduce the thickness of the liquid film on the surface of the particles, and reduce the diffusion resistance in the liquid film, so the mass transfer efficiency can be improved [40]. Hence, in order to reduce the external diffusion resistance, in this experiment, the effect of stirring speed on the dissolution efficiency of manganese dioxide in pyrolusite was investigated in the range of 200 rpm-500 rpm (Fig. 6). The stirring speed has an effect on the dissolution of manganese from pyrolusite in both microwave reaction equipment and conventional reaction equipment.

In addition, Fig. 6 shows that the extraction efficiency of manganese has a strong positive relation with rotation, and when the stirring speed is higher than 400 revolutions, the

leaching efficiency of manganese in microwave devices decreases, which can be attributed to the fact that the fast rotation leads to the adhesion of solid particles to the surface of the container, thus reducing the acquisition of manganese in manganese ore. When the stirring speed was 400 rpm, the peak leaching rate was obtained, and the raw material loss was reduced because there are few solid particles adsorbed on the surface of the container. After comprehensive consideration of economic benefits, 400 rpm was selected for follow-up experiments to evaluate the impact of other factors on the leaching rate.

#### 3.2.4. Effect of temperature

Tanda et al pointed out that temperature is the most important factor affecting the leaching reaction, where a small increase in temperature will significantly increase the leaching rate [41]. Therefore, in order to explore the effect of temperature change on the leaching rate of manganese, and then determine the control steps of the leaching reaction, a temperature variable experiment was carried out (60 °C-90 °C). As the temperature increases from 60 °C to 90 °C (Fig. 7), the manganese leaching rate in the microwave reactor increases from 40% to 95% and the leaching rate of manganese in the conventional reactor increases from 25% to 75%. The results show that temperature plays an important role in the leaching ratio, and chemical reaction control is the most important controlling factor. In addition, the leaching rate of manganese increased under different heating methods, which can be attributed to the acceleration of the reaction rate of  $\text{MnO}_2$  and the reducing agent by high temperature [42]. Meanwhile, because the surface reaction rate has shown a positive relation with temperature, high temperature is encouraged for enhancing mass transfer process [43]. Considering the leaching cost and industrial production, 90 °C was selected as the reaction

temperature for the whole reaction process.

### 3.3. SEM-EDS analysis.

Scanning electron microscopy (SEM) is a common method to characterize the microstructure of minerals. Fig. 8 shows the surface topography of minerals under different experimental conditions, including (a) raw material; (b) leaching residue after conventional heating 150 min; and (c) leaching residue after microwave heating for 150 min. In Fig. 8(a), the surface of the raw material is relatively flat and smooth, indicating that pyrolusite is stable and difficult to reduce. Fig. 8(b) shows that small-scale voids appear on the ore surface under conventional heating methods, indicating that small-scale redox reactions can be carried out under acidic conditions and in the presence of reducing agents. However, slag surface erosion is more serious under microwave heating conditions (Fig. 8(c)), since many voids are formed on the surface. This porous structure can increase the contact area of the liquid-solid reaction, and reduce the external diffusion resistance of the leaching agent, which is beneficial to the leaching of manganese [44]. Therefore, microwave heating can promote the leaching of Mn from manganese ore.

### 3.4. XPS energy spectrum analysis.

X-ray photoelectron spectroscopy (XPS) is a very useful surface analysis tool, which can provide reliable data about the chemical state on the surface during the reduction [45]. Therefore, XPS was used to study the composition change on the surface of leaching residue. It should be noticed that the binding of elemental sulfur and the surface is rigid, which is slightly affected by the XPS measurement at room temperature [46]. The XPS results are shown in Fig. 9. First, the C1s charge correction for pyrolusite is carried out, and the

correction value is 284.8 eV [47]. Fig. 9(a) and Fig. 9(b) show the composition of pyrolusite. From the XPS full spectrum of the pyrolusite sample (Fig. 9(a)), it is shown that the pyrolusite is mainly composed of iron, manganese, oxygen, carbon, silicon and aluminium. Few sulfurs were found in pyrolusite, since there were few sulfur peaks. In addition, the narrow-band analysis of manganese was carried out and the XPS narrow-spectrum diagram of manganese is given (Fig. 9(b)); the manganese compound peak was calibrated by half-width at half-width (FWHM, 2.35 eV). It is reported that the characteristic peak Mn 2p<sub>3/2</sub> of MnO<sub>2</sub> is 642.4 eV [48], and the characteristic peak of Mn 2p<sub>1/2</sub> appears at 653 eV-654 eV [49,50]. Therefore, it can be determined that the manganese in pyrolusite mainly exists in the form of MnO<sub>2</sub>, and Mn(III) and Mn( II) were absent resulting from the narrow band of manganese. Then, the narrow-band analysis of manganese and sulfur was carried out for the leaching residue after conventional heating (Fig. 9(c) and Fig. 9(e)) and microwave heating (Fig. 9(d) and Fig. 9(f)), respectively. It is reported that the characteristic binding energy of manganese sulfate is 641.9 eV [51], and there is a characteristic peak near 169 eV in the narrow spectrum of sulfur, which is reported to be the characteristic peak of sulfate. Thus, it can be confirmed that the target product MnSO<sub>4</sub> is formed under both heating conditions [52]. In addition, there is a peak with the binding energy of 641.9 eV in the results from conventional heating, which is reported to be the characteristic peak of manganese. Combined with the sulfur peak and the binding energy of 162.5 eV in the corresponding narrow sulfur spectrum (the binding energy is reported to be MnS peak) [45], through XRD phase analysis (Fig. 10a) it can be seen that there are MnS crystals and a small amount of elemental S in the slag under conventional heating. It can be determined that MnS is formed in the reaction product. The source of MnS

is caused by the disproportionation of  $S_2^{2-}$  resulting in the formation of  $S^{2-}$  and  $S^0$ . In addition, the elemental sulfur peak with the binding energy of 164.3 eV appears in conventional heating [16]. It can be further concluded that there is the formation of sulfur element in conventional heating, and the sulfur element may have been closely combined with minerals. However, the peaks of MnS and S elements are absent in the minerals with microwave heating; therefore, it can be inferred that microwave heating can reduce the formation of S elements and increase the leaching rate. It is reported that the binding energy of disulfide is near 162.7 eV, thence 162.5 eV and 162.9 eV in the results indicate that there is disulfide in the leaching residue [52], and it is speculated that there may be pyrite in the leaching residue without complete reaction. Combined with Fig. 10, it can be seen that pyrite exists under conventional heating, while  $FeS_{1.92}$  appears under microwave heating, indicating that pyrite has surplus under both heating methods, but microwave heating can better accelerate the dissolution of pyrite. In addition, it can be seen from Fig. 9(e) that there is an obvious sulfur peak under conventional heating, indicating the content of sulfur element in the slag. The analysis results show that the sulfur content in the slag is as high as 11.63%, while the sulfur content under microwave heating is only 4.8%. It can be inferred that microwaves can promote the reaction and dissolution of sulfur.

### 3.7 Dielectric property analysis

In the microwave field, the dielectric properties are one of the most important factors for judging the microwave absorbing efficiency of the material [53]. Since there are few reports on the dielectric constant of the mixture, a dielectric constant detection experiment was carried out, which can be defined as [54]:

$$\varepsilon = \varepsilon' - \varepsilon'' \times j \quad (10)$$

where  $j$  is an imaginary number,  $j = \sqrt{-1}$ ;  $\varepsilon'$  represents the dielectric constant;  $\varepsilon''$  indicates the loss factor, and  $\varepsilon$  expresses the relative complex permittivity.

In addition, the loss tangent angle ( $\tan \delta$ ), as another parameter to characterize the microwave properties of materials, represents the efficiency of materials to convert microwave energy into thermal energy under certain conditions, which expressed as [55, 56]:

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \quad (11)$$

The loss tangent angle of the material has a positive relation with the microwave absorption properties of the material [32].

It can be seen from the single factor experiment that compared with conventional heating, a higher leaching rate (95.07%) can be obtained by microwave heating under the same conditions (1.2 M sulfuric acid, liquid/solid=10:1, pyrolusite:pyrite=0.2). Considering that the leaching rate of microwave heating is much higher than that of conventional heating, the dielectric testing device owned by the laboratory was used to detect the dielectric properties of minerals in order to further explore the principle of microwave action, and the measurement principle followed the simple resonant cavity disturbance method. The calculation principle is that the additional dielectric loss will be introduced according to the dielectric sample, which leads to a decrease in the inherent quality factor of the tested cylindrical cavity to  $Q_s$ . The relative permittivity  $\varepsilon$  and loss tangent  $\tan \delta$  of the dielectric sample can be calculated according to the change in resonant length  $S$  and quality factor before and after the test cavity is put into the dielectric sample. It is widely used because of its fast detection speed, simple operation and accurate results [57,58]. For this reason, two

groups of samples were prepared, 1.2 M sulfuric acid (control group) and 1.2 M sulfuric acid-mineral mixture (experimental group), and the dielectric properties in the temperature range of 50 °C-80 °C were tested with 10 °C as the temperature interval. The test results are shown in Fig. 11(a), indicating that the wave-absorbing strength of the test group (mixed ore powder and sulfuric acid) is higher than that of the control group (sulfuric acid), which is attributed to the improvement in the overall wave-absorbing properties caused by the addition of pyrolusite and pyrite. It is reported that both pyrolusite (214.5 °C/min) and pyrite ( $\text{FeS}_2$  20 °C/s) have excellent wave-absorbing properties [59, 60]. Hence, it is speculated that the microwave energy was partly absorbed by the solution and absorbed by the ore, as shown in Fig. 11(b). In addition, the microwave directly absorbed by the ore has different responses to the microwave, which leads to the temperature difference in the mineral and the thermal effect and producing the cracking of the orebody from the inside to the outside (Fig. 11(c)). Therefore, it can be seen from the SEM diagram that there are more mineral pores in the products under microwave heating than in the products under conventional heating. At the same time, the crack further expands the contact surface between the solution and the mineral and accelerates the reaction. The experimental results show that the microwave heating process was supported by the absorption of microwave energy both in the solution and in the materials.

#### 4. Conclusions

The effects of conventional heating and microwave heating on the recovery of manganese by acid leaching of pyrolusite-pyrite were studied, and the dielectric properties of

the mixed solution were tested. The main conclusions are as follows:

(1) Microwave heating is an environmentally friendly manganese recovery process that can enhance the recovery efficiency of pyrolusite and reduce the addition amount of sulfuric acid as well as the reducing agent.

(2) Microwave heating also has a significant effect on the phase transformation of manganese during the leaching process. Under the conditions of microwave heating, leaching in the solution at 90 °C for 2.5 h with a total acid concentration of 1.2 mol/L, 20% of additive pyrite, and a stirring rate of 400 rpm, the leaching rate of manganese was 95.07%. In conventional heating leaching, the leaching rate of manganese was only 75.08%, and sulfur element and MnS appeared in conventional heating, which can be avoided by microwave heating.

(3) The dielectric experiments have shown that when the leaching temperature was 80 °C, the dielectric constant of the mixture of sulfuric acid and ore was 37.787 (F/M). However, the dielectric constant of single sulfuric acid was 36.886 (F/M), indicating that the addition of minerals enhanced the microwave absorption properties.

The above results support that microwave heating technology is the solution for the suppression of the passivation layer in the process of pyrite leaching, and the application of microwave and pyrite in the leaching process can reduce sulfuric acid consumption, which is beneficial for the protection of the environment and reducing energy consumption. The proposed method has potential for practical and industrial production in the future.

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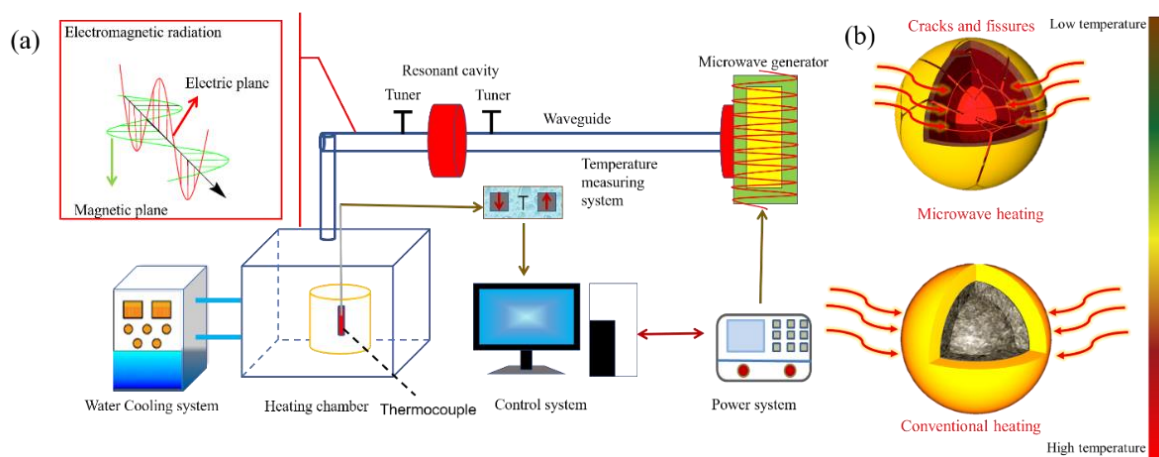


Fig. 1 a: Schematic diagram of microwave radiation and microwave heating system; b: conventional heating and microwave heating.

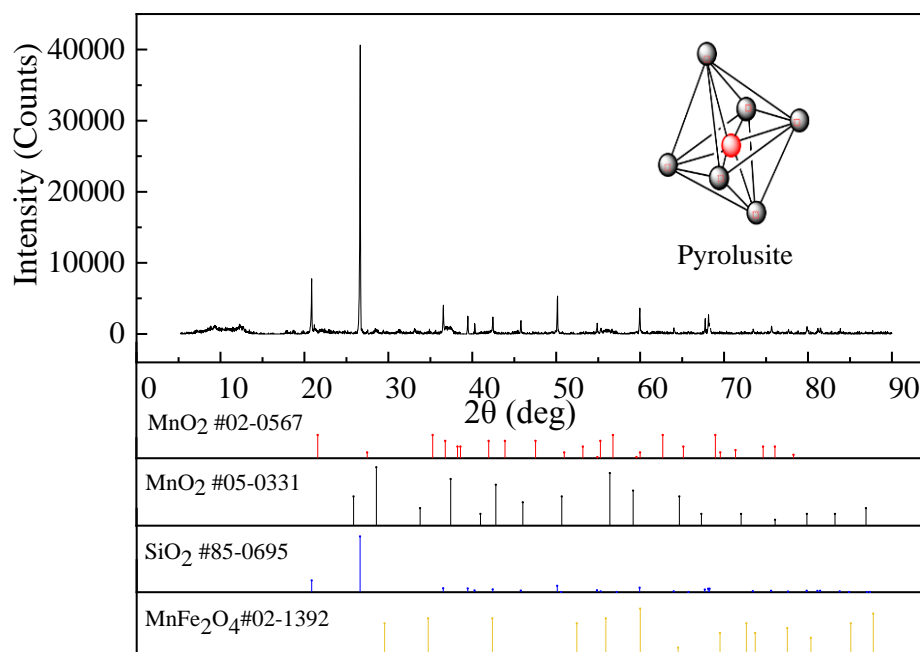


Fig. 2 The XRD patterns of pyrolusite.

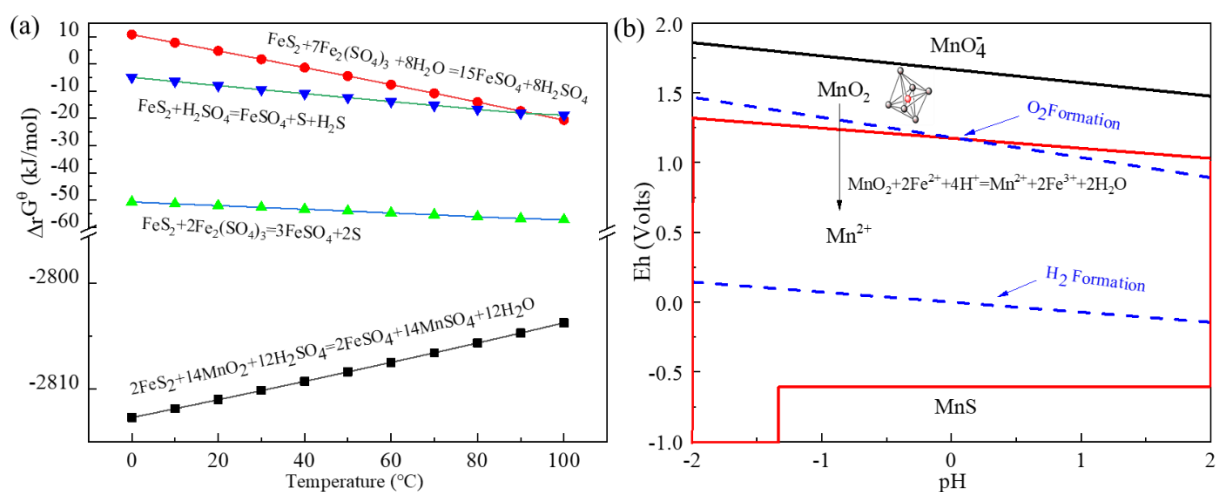


Fig. 3 Schematic diagram of reaction thermodynamics simulation (a) and Eh-pH stability diagram (b) at 90 °C.

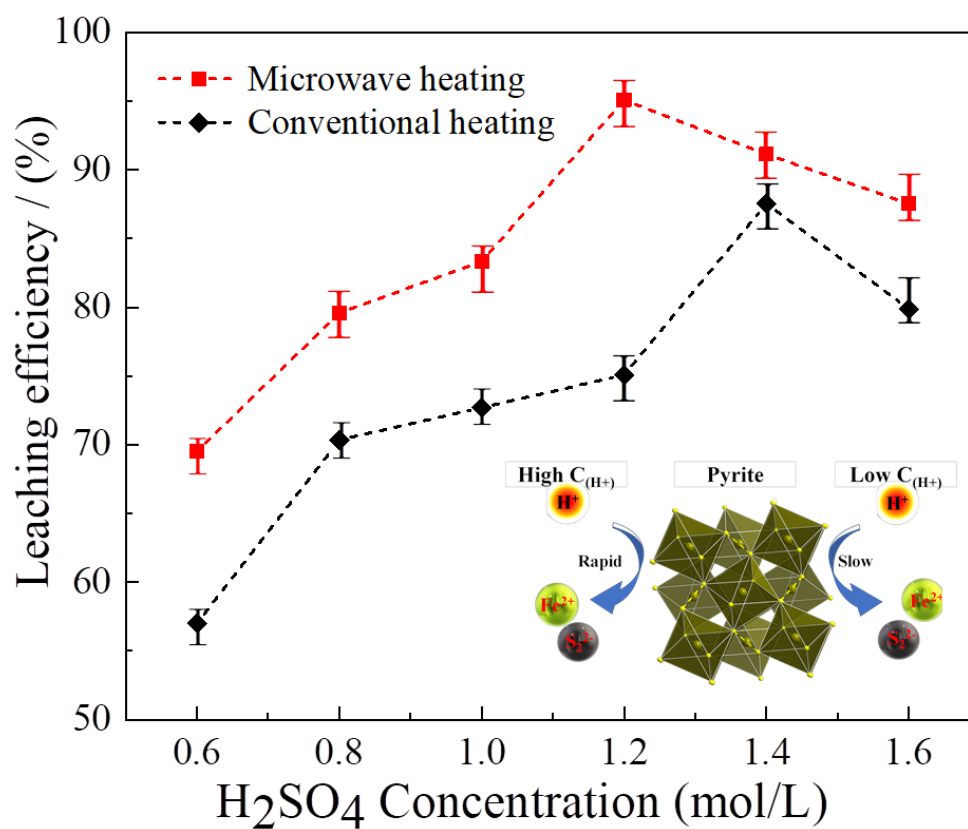


Fig. 4 Effect of the initial concentration of sulfuric acid on leaching efficiency.

(m(pyrolusite)/m(pyrite)=10:2.0, stirring speed=400 rpm, leach temperature=90 °C, leach time=150 min, 10 ml/g of liquid/solid).

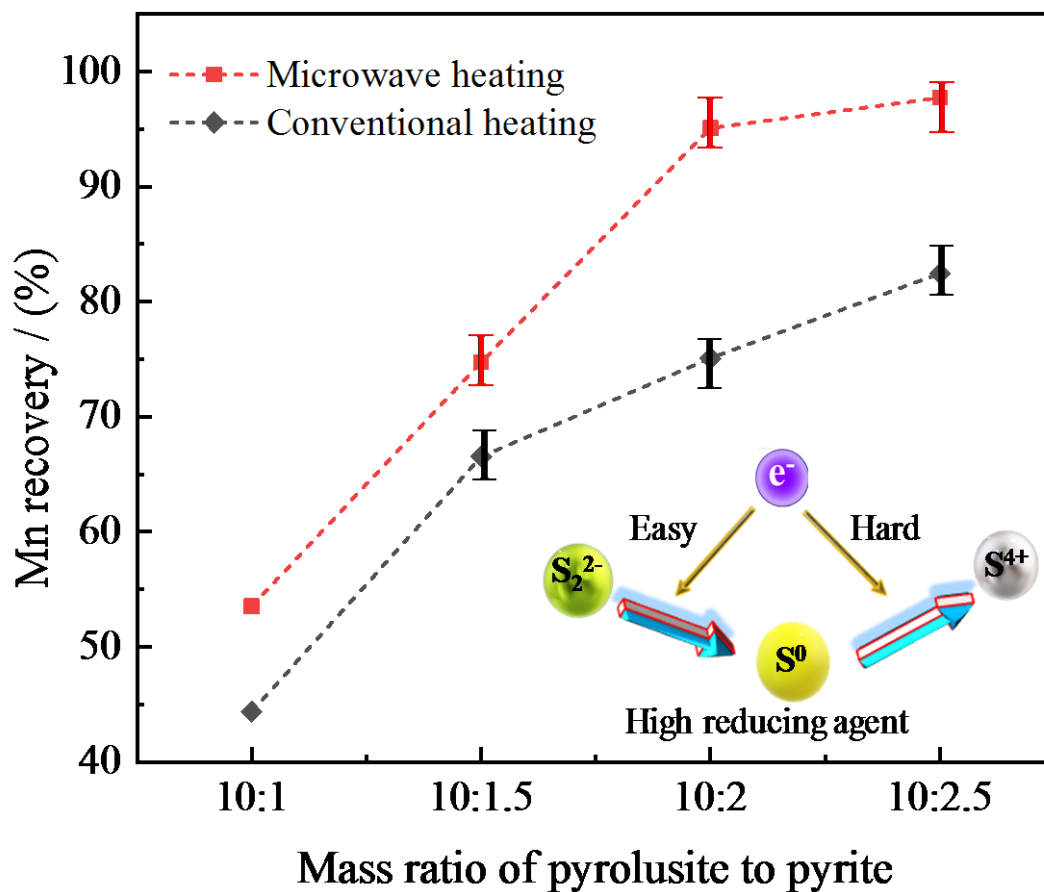


Fig. 5 Effect of the mass ratio of pyrolusite to pyrite on leaching efficiency. (Sulfuric acid concentration=1.2 M, stirring speed=400 rpm, leaching temperature=90 °C, leaching time=150 min, 10 ml/g of liquid/solid)

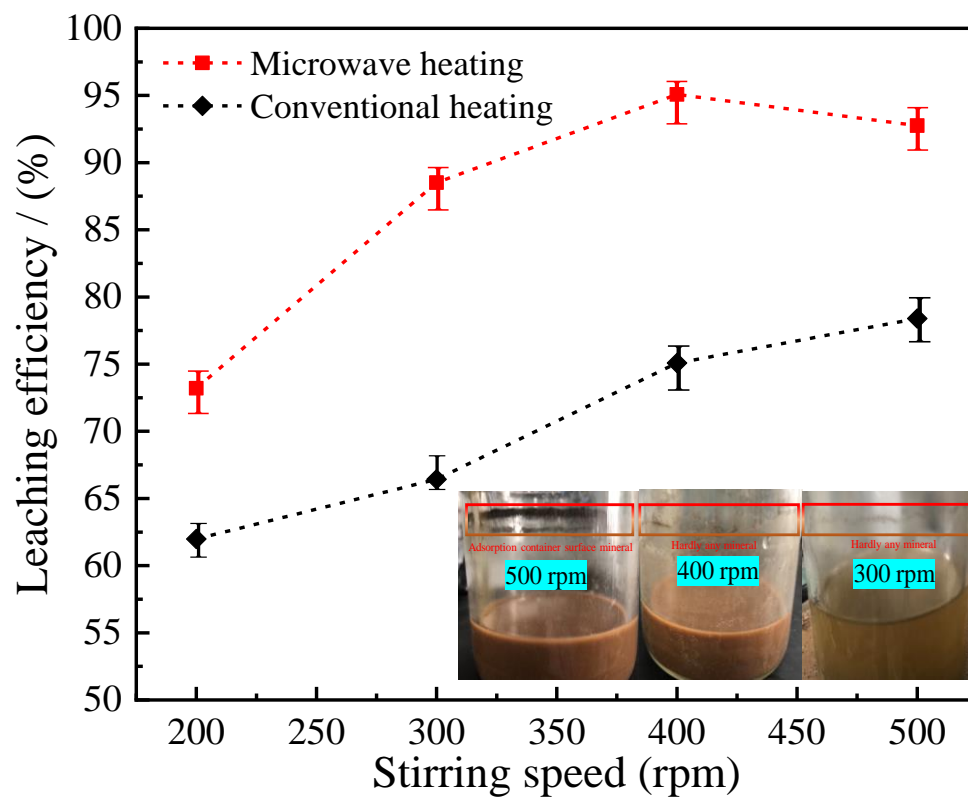


Fig. 6 Effect of stirring speed on leaching efficiency. (Sulfuric acid concentration=1.2 M,  $m(\text{pyrolusite})/m(\text{pyrite})=10:2.0$ , leaching temperature=90 °C, leaching time=150 min, 10 ml/g of liquid/solid).

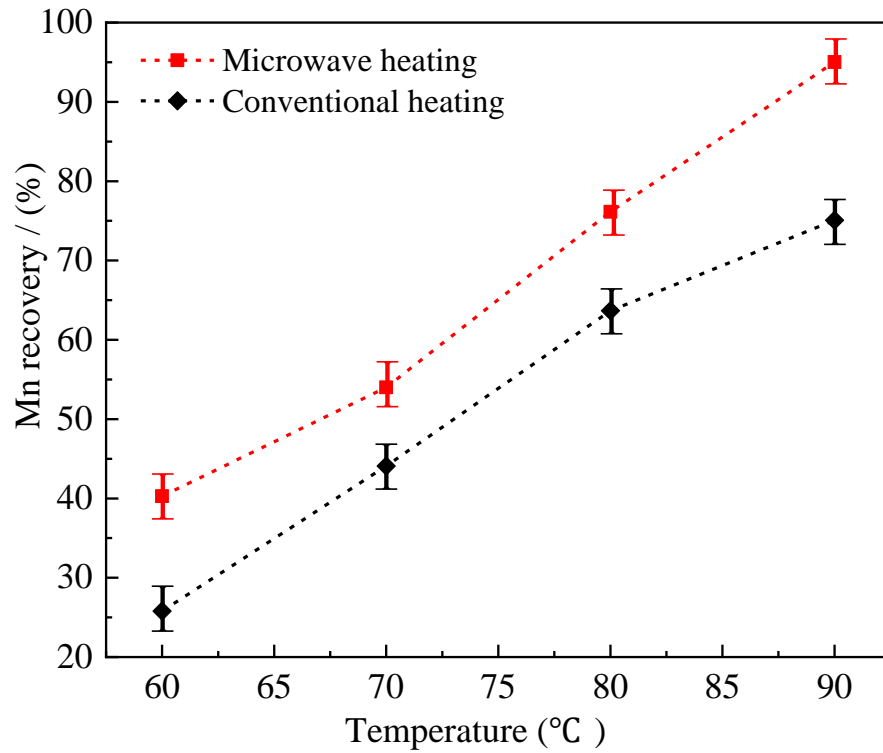


Fig. 7 Effect of temperature (60 °C, 70 °C, 80 °C, 90 °C) on leaching efficiency (Sulfuric acid concentration=1.2 M, m(pyrolusite)/m(pyrite)=10:2.0, stirring speed=400 rpm, leaching time=150 min, 10 ml/g of liquid/solid).

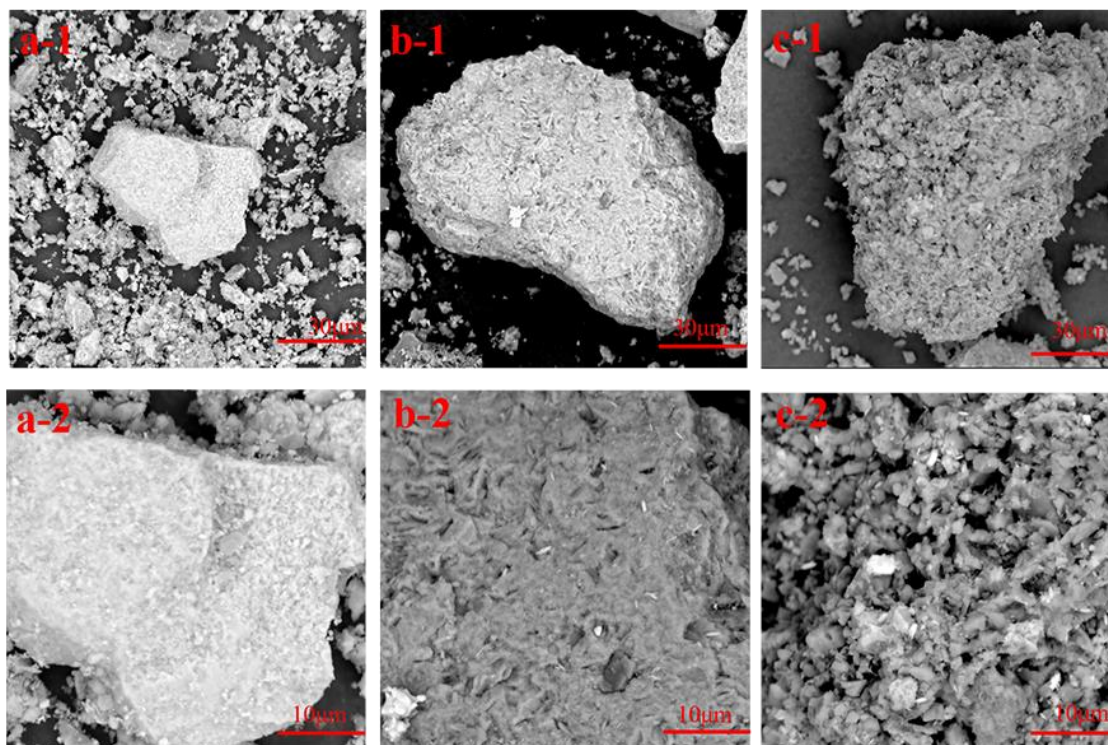


Fig. 8 SEM images of different samples: (a) raw pyrolusite, (b) slag in the conventional heating and (c) slag in the microwave heating leaching stage.

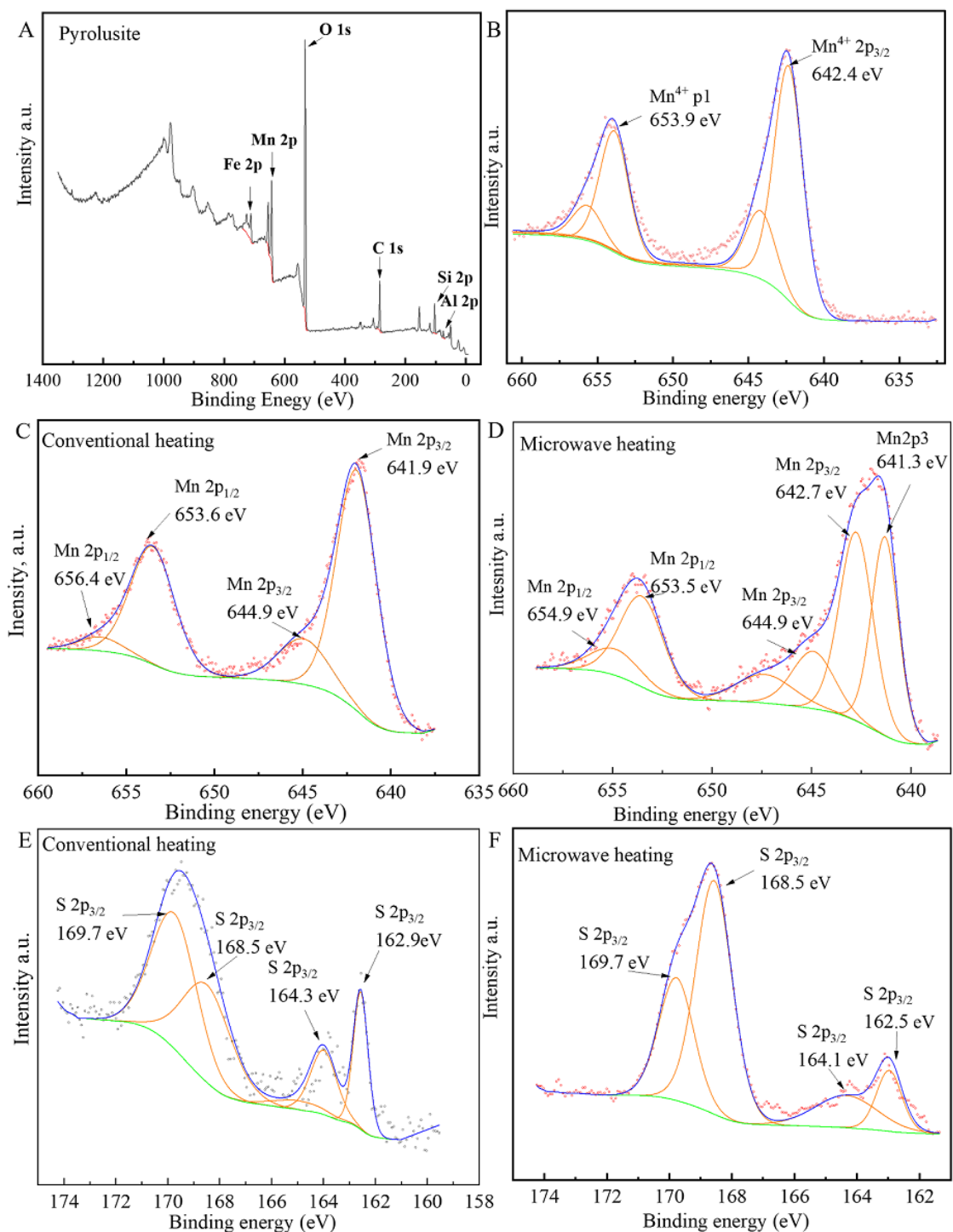


Fig. 9 a: XPS survey spectrum of pyrolusite, b: Mn2p XPS detail spectrum of pyrolusite, c: S2p detail spectrum of leaching residue under conventional conditions, d: S2p detail spectrum of leaching slag under microwave conditions, e: Mn2p detail spectrum of leaching residue under conventional conditions, f: Mn2p detail spectrum of leaching residue under microwave conditions.

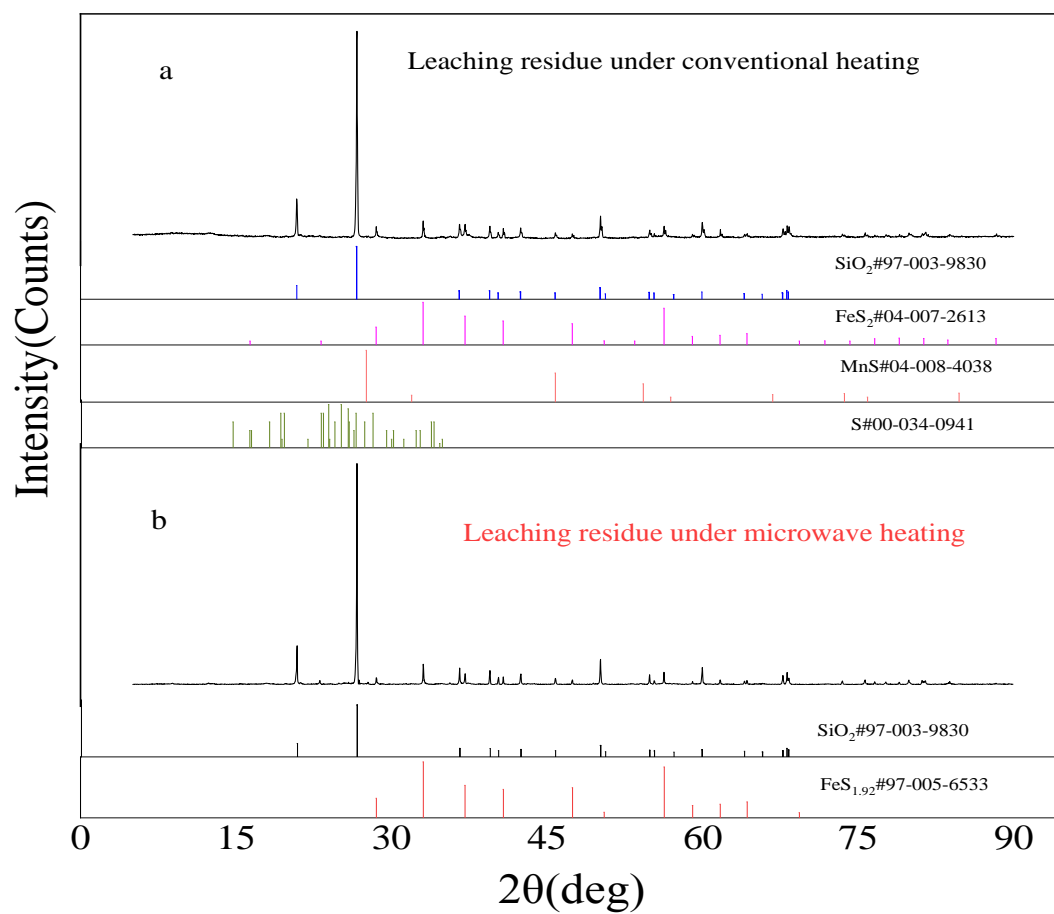
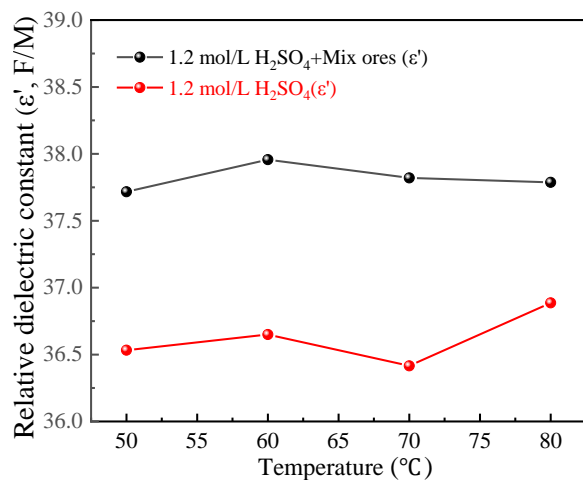
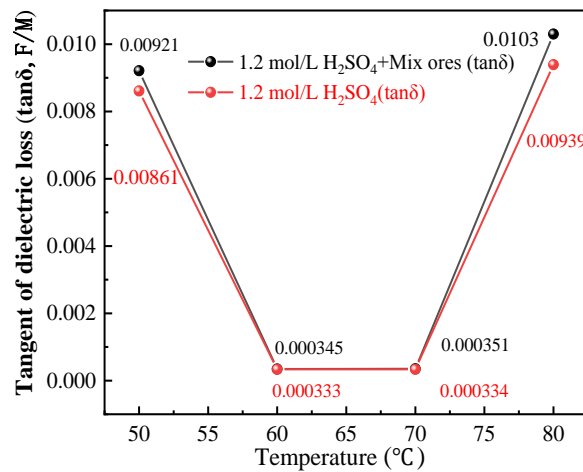


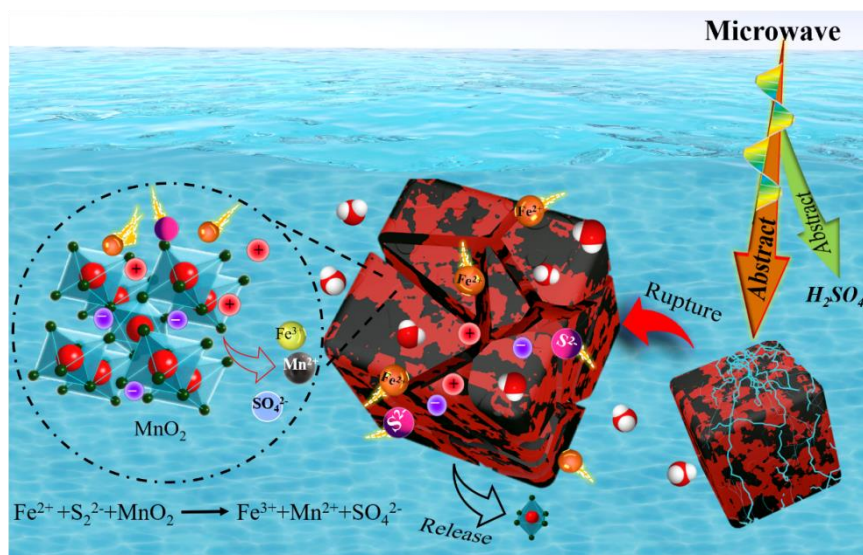
Fig. 10 a: XRD diagram of leaching residue under conventional heating, b: XRD diagram of leaching residue under microwave heating.



(a)

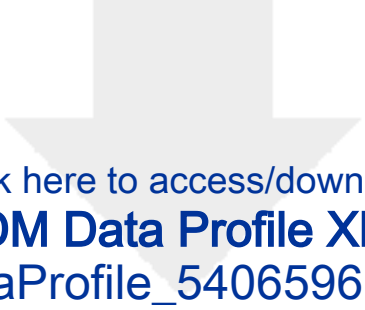


(b)

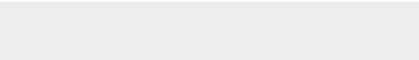
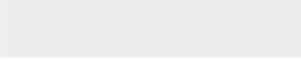


(c)

Fig. 11 a: Dielectric properties at different temperatures (50 °C, 60 °C, 70 °C, 80 °C), b: the values of tangent of dielectric loss at different temperatures (50 °C, 60 °C, 70 °C, 80 °C), c: reaction mechanism under microwave irradiation.



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**Declaration of interests**

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

## Credit Author Statement

Prof. Guo Chen, Prof. Jin Chen and Prof. Shenghui Guo conceived and designed the study. Mr. Shunda Lin, Mr. Yong Yang, Dr. Mamdouh Omran and Prof. Guo Chen performed the experiments. Prof. Guo Chen and Prof. Shenghui Guo provided the raw materials. Prof. Jin Chen, Prof. Guo Chen and Dr. Lei Gao provided the microwave high temperature furnace. Mr. Shunda Lin, Dr. Lei Gao and Prof. Jin Chen wrote the paper. Mr. Shunda Lin, Dr. Mamdouh Omran, Dr. Lei Gao and Prof. Guo Chen reviewed and edited the manuscript. All authors read and approved the manuscript.

