Influence of microwave irradiation on boron concentrate activation with an emphasis on surface properties

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Abstract: In this study, we employed microwave irradiation for activating boron concentrate, an abundant but low-grade boron mineral resource in China. The boron concentrate was pretreated by microwave irradiation based on TG-DTG-DSC analysis, and the influence of each parameter on processing efficiency was characterized using chemical analysis, XRD, SEM, FTIR and particle distribution analysis. Subsequently, the surface properties of boron concentrate and the mechanism of microwave irradiation was analyzed. Our results indicate that microwave irradiation decreased the processing temperature and shortened the roasting time by accelerating dehydroxylation and oxidation reactions in the boron concentrate, reducing the particle diameter and damaging the microstructure of the minerals, and it increased the B₂O₃ activity of boron from 64.68% to 86.73%, greater than the optimal conventional treatment. Compared with the simple thermal field, microwave roasting obviously increased ability of the boron concentrate to absorb OH⁻ in the leachant and promoted boron leaching by expanding the contact area of the mineral exposed to leachant, boosting the amount of Mg²⁺ and Fe³⁺ on mineral surfaces, and increasing the hydrophilicity of the boron concentrate respectively. It enhanced the γ_{SV}^{LW} and γ_{SV}^{-} of boron concentrate from 29.15 mJ/m² and 5.07 mJ/m² to 37.07 mJ/m² and 12.41 mJ/m².

Keywords: Boron concentrate; Microwave irradiation; Activation roasting; Contact angle;
Surface free energy

1. Introduction

Boron is an important element, forming compounds that are important materials in industrial production and national defense construction; it also plays an essential role throughout scientific and technological fields [1,2]. Boron concentrate is a product of the combined magnetic and gravity separation of ludwigite and contains only approximately 12% B_2O_3 . The resulting B_2O_3 accounts for almost 58% of China's boron resources, though it has not yet been exploited on a large scale because of its complicated mineralogical structure and composition [3]. Facing an increasing need for boron-containing products and the imminent exhaustion of ascarite reserves, boron concentrate has begun to replace ascarite as the most important source of raw material for the Chinese boron industry [4,5]. However, the roasting process for ascarite cannot achieve the expected activation efficiency for boron concentrate and usually fails to enhance its B_2O_3 activity over 80%. Moreover, most current roasting methods require temperatures above $800^{\circ}C$ and long processing times, and the crude and inefficient equipment currently used by the boron industry is costly in terms of fossil fuel resources [6] and generates a considerable amount of dust and harmful waste gas (such as SO_2) [7]. Hence, in addition to exploration for new high-grade boron mineral resources, it has become increasingly important to improve the technology and equipment used in processing boron concentrate.

Microwaves are a relatively new energy resource; they are non-ionizing electromagnetic waves with a frequency ranging from 300MHz to 300GHz and free space wavelength ranging from 1×10^5 mm to 1 mm [8-10]. Microwave heating differs from conventional heating methods in which samples are heated from the surface to the interior via standard heat transfer mechanisms such as convection, conduction and radiation. In microwave heating, energy rather than heat is directly transferred through the heating cavity and rapidly delivered into samples [11,12]. In other words, microwave irradiation penetrates the sample,

interacts with sample molecules and is transformed into heat, thus heating the sample holistically and evenly [13,14]. Compared with conventional heating techniques, heating by microwave irradiation can heat the sample rapidly and selectively heat different phase compositions of the sample based on their different microwave absorbing properties; thus, it can produce temperature gradients and thermal stresses along the interface between these phases. Therefore, applying microwave irradiation during mineral processing promotes the development of cracks and micro-cracks in the sample, rapidly and efficiently damaging its mineralogical structure [15]. This can reduce the processing time and enhance the roasting efficiency and the roasting effect, considerably decreasing energy consumption [8,13]. Consequently, microwave irradiation has begun to play an increasingly important role in mineral processing, and it has been the subject of many studies. In recent years, although many researchers have examined the use of microwave irradiation in mineral processing, few have focused on the mechanism of microwave roasting.

In this study, we applied microwave irradiation to the activation roasting process of boron concentrate using TG-DTG-DSC analysis. We studied the influence of each processing parameter on the activation roasting; these included roasting temperature, output power and sample mass. Finally, we investigated the mechanism of microwave irradiation by analyzing surface properties such as hydrophilicity and surface free energy.

2. Experimental

2.1 Materials

The raw boron concentrate used in this research was provided by the Fengcheng Chemical Group Co., Ltd., China. After crushing, grinding to 150 μm and drying, the boron concentrate was stored in dry conditions. The chemical composition of the raw material is listed in **Table 1**. The boron concentrate used in this research contained 11.57 wt.% of B_2O_3 ; the lithogenous components included 24.98 wt.% SiO_2 and 39.93 wt.% MgO ; there was a small amount of components that efficiently absorbed microwaves, mainly iron oxides with 4.98 wt.%

TFe.

Insert Table 1

Figs. 1-4 show the XRD pattern, FTIR spectrum, SEM micrograph and particle size distribution of the initial boron concentrate samples. As shown in **Fig. 1**, the major phases in the boron concentrate are szaibelyite ($\text{MgBO}_2(\text{OH})$), biotite ($\text{K}[\text{Mg,Fe}]_3[\text{Al,Fe}]\text{Si}_3\text{O}_{10}(\text{OH,F})_2$), magnetite (Fe_3O_4), serpentine ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$), forsterite (Mg_2SiO_4), and quartz (SiO_2).

Insert Fig. 1

Fig. 2 shows absorption peaks in the FTIR spectrum at 3691.0 cm^{-1} and 3558 cm^{-1} and weak absorption peaks at 1631.3 cm^{-1} and 1087.7 cm^{-1} ; these can be attributed to the asymmetric and symmetric stretching vibrations of hydroxyl groups, indicating the presence of hydroxyl in the initial sample [16,17]. And according to Infrared spectra of mineral edited by Peng et al. [18], the broad band at 2530.1 cm^{-1} corresponds to carbonate groups, likely because of a small amount of MgCO_3 in the sample, stretching vibration bands at 1457.7 cm^{-1} , 1384.6 cm^{-1} , 836.9 cm^{-1} and 711.6 cm^{-1} can be attributed to M-OH functional groups, in which M represents Fe or Mg, absorption at 617.1 cm^{-1} and 574.7 cm^{-1} comes from the bending vibration bands of O-H, stretching vibration bands at 1297.8 cm^{-1} and 1228.8 cm^{-1} can be attributed to B-O and bands at 1006.7 cm^{-1} and 435.4 cm^{-1} to Si-O.

Insert Fig. 2

The SEM micrograph of the initial material presented in **Fig. 3** demonstrates banding, granular, needle-shape, and fibriform patterns in the boron concentrate. The figure also shows that particles of the untreated sample are relatively large, with a median diameter of $19.44\text{ }\mu\text{m}$.

Insert Fig. 3 and Fig. 4

All chemical reagents used in this research were analytically pure and were produced by Sinopharm Chemical Reagent Co., Ltd. The water used in this research was ultrapure.

2.2 Methods and characterization

2.2.1 Experimental procedure

In this paper, microwave irradiation parameters including roasting temperature, microwave power and sample mass were optimized using a single-factor analysis method. The effect of each variable was studied and the best conventional roasting activation effect was determined. Next, the influence of microwave irradiation was studied by comparing the changes in phase composition, particle size distribution and surface free energy of the microwave-irradiated products and products roasted without microwaves under similar thermal conditions. A flow chart of the experimental method is shown in **Fig. 5**.

Insert Fig. 5

2.2.2 Material characterization

All components in the sample were analyzed using the recommended methods from the National Standard of the People's Republic of China (GB/T). The phase compositions of the samples were characterized using an X-ray diffractometer (X'PERT PRO MPD/PW3040, PANalytical B.V. Corporation, Netherlands) at a scanning rate of 8°/min using Cu K α radiation with a 2 θ angle ranging from 5-75°. The surface functional groups of the samples were analyzed using Fourier transform infrared (FT-IR) spectroscopy; we used an FT-IR analyzer (Nicolet-380, Thermo Corporation, USA) with a spectrum range from 400 cm⁻¹ to 4000 cm⁻¹. The microstructures of boron concentrate and its products were analyzed using a scanning electron microscope (SEM) (S3400N, Hitachi Ltd, Japan). The particle size distribution of the samples was analyzed with a laser diffraction size analyzer (BT-9300H, Dandong Bettersize Instruments Ltd., China).

The thermal behavior of the raw material was examined with thermogravimetry analysis (TG-DTG-DSC), which was performed in simultaneous thermal analyzer (STA 449 C, NETZSCH Instrument Trading, Ltd. Germany) under an air atmosphere. Approximately 9.655 mg of boron concentrate was placed in a corundum crucible in a microbalance pan at a heating

rate of 10°C/min with temperatures ranging from 30°C to 1000°C. Differential thermal gravity (DTG) was applied during this analysis to differentiate the mass loss in the TG curve.

2.2.3 Microwave irradiation roasting

Microwave roasting was carried out in a 2.45 GHz microwave oven with a discontinuous output power range of 1 kW, 2 kW, and 3 kW and a maximum of 4 kW (Mobilelab workstation mode, Tangshan Nano Source Thermal Instrument Manufacturing Co., Ltd, with a cavity dimension of 410×410×540 mm). Prepared samples with a mass from 75 g to 175 g were placed in a 200 mL microwave-transparent crucible and heated to a planned holding temperature that varied from 500°C to 800°C. The microwave power was altered from 1 kW to 4 kW for certain holding times; this significantly affected B₂O₃ activity when the time was less than 10 min but the effect was marginal from 10 min to 25 min. The times were set according to specific conditions. A thermal insulation sleeve with auxiliary heating material coating on the inner surface was used to accelerate the heating rate of the boron concentrate during the initial stage of microwave heating. This was used because direct microwave heating tests failed to heat the sample due to the low microwave-absorption ability of the boron concentrate at relatively low temperatures. To minimize the effect of the field pattern variation in the oven, all samples were placed at the center of the thermal insulation sleeve and the microwave-reflecting cavity. To ensure heating efficiency, a structure was used to adjust the height of the thermal insulation sleeve and ensure that the sample was in the range of the microwave emissions. The temperature of the test sample in the oven was measured continuously using a stainless steel-sheathed, K type thermocouple that was inserted into the sample; the tip was positioned 5 mm from the bottom of the crucible (the sample thickness was greater than 10 mm). The temperature measurements in this study did not affect the even heating of the sample in the microwave heating system with an auxiliary heater. The variables of roasting temperature, output microwave power, processing time and sample mass were studied using a single-factor analysis method. A schematic illustration of the microwave roasting system is shown in Fig. 6.

Insert Fig. 6

2.2.4 Conventional roasting

All conventional roasting was conducted in a laboratory muffle oven. To begin with, according to a previous study by Liu [19], the conventional activation efficiency in this study was optimized using single-factor analysis method based on TG-DTG-DSC. And the optimal conventional roasting conditions and activation efficiency will be used as a reference to evaluate the activation efficiency of subsequent microwave roasting.

Furthermore, after the optimal microwave processing conditions are determined, a mineral sample with certain optimal sample mass was roasted under simulated conventional thermal field without microwave irradiation to investigate the influence of microwave irradiation on roasting and compare the effects of a microwave field versus a thermal field.

2.2.5 B₂O₃ activity

According to enterprise standards provided by the Fengcheng Chemical Group Co., Ltd., China, the B₂O₃ activity of the boron concentrate and the roasted products was characterized based on the alkali leaching rate of 5.00 g of B₂O₃ sample by a 20% NaOH solution with a solid-liquid ratio of 1:10 at 105 °C (±0.5 °C) for 2 h. This is representative of the leaching rate of B₂O₃ from boron-containing material during the carbonate alkaline leaching process used in the borax industry. The B₂O₃ activity of the boron concentrate was calculated using the following equation:

$$B_2O_3 \text{ activity} = \left(1 - \frac{\text{Mass of } B_2O_3 \text{ in leaching residue}}{\text{Mass of } B_2O_3 \text{ in sample}}\right) \times 100\% \quad (1)$$

2.2.6 Contact angle, surface free energy and interactions

Although the surface free energy of solids cannot be measured directly, it can be calculated based on the results of contact angle measurements with appropriate liquids. The contact angles of boron concentrate and treated products were measured using surface tension and contact angle measuring instruments (DCAT21, Dataphysics Corporation, Germany) according to the Washburn theory. The following equation was used [20-24]:

$$w^2 = \frac{C_g \rho^2 \gamma_{LV} \cos \theta}{\eta} \times t \quad (2)$$

where w is the wetting mass of the probe liquid in g; C_g is the geometric factor, which is a dimensionless quantity; ρ is the liquid density in g/cm³; γ_{LV} is the surface tension of this probe liquid in mJ/m²; θ is the contact angle of the probe liquid to boron concentrate in °; η is the viscosity of the probe liquid in cP; and t is the wetting time in s.

The influence of microwave irradiation on the absolute value and interactions of the surface free energy of the boron concentrate was analyzed according to Young's function (Eq. 3) and the Oss-Chaudry-Good equations [25]. These equations introduce Lewis acid-base theory into the surface free energy calculation and take into consideration all three intermolecular forces (Born, Van der Waals and exceptional forces). As a result, there is diminished experimental error induced by exceptional forces including the forces of hydrogen bonds and metallic bonds, as well as electronic and ionic interactive forces [20]. Eq. 4 and Eq. 5 show the Oss-Chaudry-Good equations applicable to liquids and solids, respectively.

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad (3)$$

where γ_{SV} is the solid-vaporization interface free energy per unit area in mJ/m²; γ_{SL} is the solid-liquid interface free energy per unit area in mJ/m²; γ_{LV} is the liquid-vaporization interface free energy per unit area in mJ/m²; and θ is the contact angle of liquid to solid in °.

$$\gamma_{LV} = \gamma_{LV}^{LW} + \gamma_{LV}^{AB} = \gamma_{LV}^{LW} + 2\sqrt{\gamma_{LV}^+ \gamma_{LV}^-} \quad (4)$$

$$\gamma_{SV} = \gamma_{SV}^{LW} + \gamma_{SV}^{AB} = \gamma_{SV}^{LW} + 2\sqrt{\gamma_{SV}^+ \gamma_{SV}^-} \quad (5)$$

In Eq. 4, the surface free energy of liquid samples, γ_{LV} (mJ/m²), includes Lifshitz-Van der Waals interactions, γ_{LV}^{LW} (mJ/m²), and polar interactions, γ_{LV}^{AB} (mJ/m²). These are comprised of Lewis acid interactions, γ_{LV}^+ (mJ/m²), and Lewis base interactions, γ_{LV}^- (mJ/m²). As shown in Eq. 5, the surface free energy of solid samples, γ_{SV} (mJ/m²), includes Lifshitz-Van der Waals interactions, γ_{SV}^{LW} (mJ/m²), and polar interactions, γ_{SV}^{AB} (mJ/m²), which are comprised of Lewis acid interactions, γ_{SV}^+ (mJ/m²), and Lewis base interactions, γ_{SV}^- (mJ/m²).

The relationship of surface free energy between the solid and each probe liquid can be calculated using **Eq. 6**. Applying Young's function to **Eq. 6** gives **Eq. 7**, which was used to calculate the surface free energy and interactions for each sample.

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2 \left(\sqrt{\gamma_{SV}^{LW} \gamma_{LV}^{LW}} + \sqrt{\gamma_{SV}^{+} \gamma_{LV}^{-}} + \sqrt{\gamma_{SV}^{-} \gamma_{LV}^{+}} \right) \quad (6)$$

$$(1 + \cos\theta) \gamma_{LV} = 2 \left(\sqrt{\gamma_{SV}^{LW} \gamma_{LV}^{LW}} + \sqrt{\gamma_{SV}^{+} \gamma_{LV}^{-}} + \sqrt{\gamma_{SV}^{-} \gamma_{LV}^{+}} \right) \quad (7)$$

To ensure measurement accuracy, n-Hexane, diiodomethane, ultrapure water, and ethylene glycol were used as probe liquids. Of those liquids, n-Hexane was used to calculate the C_g and to adjust the contact measurements of the other probe liquids. All parameters of these probe liquids were provided by the Dataphysics Corporation and are listed in **Table 2**.

Insert Table 2

3. Results and discussion

3.1 Thermogravimetry analysis (TG-DTG-DSC) of material

The TG-DTG-DSC curve of boron concentrate is shown in **Fig. 7**. The mass of boron concentrate gradually increased during initial heating, likely because the dried sample absorbed H₂O from the flow of atmospheric air at relatively low temperatures. After this initial stage, the reaction process can be divided into four stages of mass loss based on the TG-DTG curve of the raw material. The first stage occurs from 38.76°C to 253.60°C and is associated with a mass loss of 0.12% due to the removal of free moisture from the sample surface. In the second stage, from 253.60°C to 463.90°C, there is a mass loss of 1.08% caused by the dehydroxylation of a small amount of impurities in the sample including diaspore, brucite and ferric hydroxide [19,26][26]. The third stage begins at 439.60°C, and a mass loss of 9.01% was observed; the mass loss rate increased until 845.50°C. During this time, the magnetite component in the boron concentrate was oxidized to hematite (Fe₂O₃), and the major target phases szaibelyite and lithogenous phase serpentine were dehydroxylated and transformed into suanite (Mg₂B₂O₅),

which has higher B_2O_3 activity than szaibelyite. In addition, forsterite was recrystallized during heating until 747.10°C , after which there is a remarkable endothermic peak on the DSC curve corresponding to an oxidation reaction and two decomposition reactions, shown in **Eq. 7**, **Eq. 8** and **Eq. 9**, respectively. Subsequently, the Fe-OH chemical bond of biotite was broken in the final mass loss stage [27].

Insert Fig. 7.

3.2 Microwave roasting

To better evaluate the activation efficiency, the optimal activation efficiency and processing parameters of conventional roasting were determined firstly. The B_2O_3 activity of untreated raw material is only 64.48%. Treated by conventional roasting, with a sample mass of 150 g, the B_2O_3 activity of boron concentrate increased to 83.00% under the optimal processing conditions of roasting at 700°C for 2 h, which is consistent with Liu's study [19].

3.2.1 Effect of roasting temperature

To optimize the microwave processing temperature, 100 g of boron concentrate was roasted at different temperatures using microwave irradiation; each sample was held for 10 min with an output power of 4 kW. As shown in **Fig. 8**, the B_2O_3 activity of the roasted products initially increased with roasting temperature but decreased at temperatures greater than 600°C , at which B_2O_3 activity increased to 80.20%.

Insert Fig. 8

During the roasting process, both the rate and equilibrium of the reaction were closely related to the roasting temperature. Increasing the temperature promoted chemical reactions during the roasting process. According to the Arrhenius equation, it also enhanced the rate of the

chemical reaction and the diffusion of both the reactants and the products. This increased the activation effect of processing at a certain temperature range.

The XRD patterns of products roasted at different temperatures shown in **Fig. 9** indicate that for roasting at 500°C, the phase composition of the sample changed little. A small amount of magnetite was oxidized to hematite, and szaibelyite and serpentine in the sample underwent partial dehydroxylation when the temperature was increased to 600°C, at which the magnetite was oxidized to hematite. The newly formed phase (suanite) markedly lowered the activation energy of the alkali leaching reaction and hence increased the B₂O₃ activity of the sample. In addition, the oxidation of Fe²⁺ to Fe³⁺ raised the percentage of positive electric charge in the sample, which increased the sample's ability to absorb OH⁻. With the increase in temperature, more of these reactions went to completion. However, when the holding temperature was increased to 800°C, the szaibelyite in the sample was almost completely dehydroxylated and transformed into suanite, forsterite and then quartz. This caused the B₂O₃ activity of the sample to decrease because the higher temperature induced a reaction between iron oxide and suanite to form Mg-Fe-B-O eutectic [28].

Insert Fig. 9

The result of FTIR analysis in **Fig. 10** is consistent with the XRD patterns. The major absorption peaks of the hydrophilic oxygen functional group and the carbonate group in the FTIR spectra gradually decrease or disappear as the roasting temperature increases, which suggests that the dehydroxylation and decarbonation of the sample increased with processing temperature. Furthermore, when the holding temperature reached 800°C, the Si-O and B-O vibration bands increased both in number and in absorption, which indicates the relatively complete decomposition of szaibelyite and serpentine.

Insert Fig. 10

Particle size distribution analysis of the roasted products at 600°C and 800°C is shown in **Fig. 11**. The particle size distribution of the roasted products was noticeably smaller at 600°C and the D₅₀ decreased to 11.67 μm. In contrast, at 800°C, the particle size distribution

was greater, and the D_{50} increased to 16.87 μm .

Insert Fig. 11

SEM micrographs of the roasted products processed at 600°C and 800°C are shown in **Figs. 12(a) and (b)**. **Fig. 12(a)** shows that the crystal grains in the product processed at 600°C were incompletely grown and loosely agglomerated in a granular form; their diameters were relatively small and the surface of the mineral microstructure was extremely rough, which is conducive to alkali leaching. In contrast, **Fig. 12(b)** shows that material roasted at 800°C had fully grown grains that were columnar and rod-like, with a smooth surface and compact structure; the grains had a larger average diameter.

Insert Fig. 12

Boron concentrate is a multi-composite mineral with complicated paragenesis and structure. It has various complex crystal forms and numerous mineral phases. When boron concentrate was treated with microwave irradiation, magnetite was heated and rapidly oxidized due to its high absorption of microwaves and high heating rate [29]. Differences in the permittivity and dielectric loss of different mineral compositions within the sample lead to variations in heating rate, which can result in mechanical and thermal stresses within the grain boundaries because of differential expansion between phases. Thus, microwave irradiation introduced more intergranular and transgranular cracks and micro-cracks than conventional roasting. Furthermore, microwave irradiation markedly increased the integral heating rate of the sample and promoted rapid dehydroxylation of szaibelyite and serpentine. This generated H_2O within the sample, further increasing the stresses inside the mineral and forming cracks and micro-cracks [30,31]. Thus, roasting by microwave irradiation at a proper temperature efficiently destroyed the mineral structure of boron concentrate, and the resulting breakages in the structure of the boron concentrate increased the area of the sample that could be exposed to leachant. This enhanced the reaction rate and improved the efficiency of the alkali leaching process, improving the B_2O_3 activity. Hence, roasting by microwave irradiation was more efficient at a lower roasting temperature of 600°C.

3.2.2 Effect of output power

Material can be rapidly heated in a microwave because the orientation polarization and interfacial polarization can be induced by microwave irradiation; the relaxation times in the material have the same order of magnitude as the period of microwaves [28]. The orientation polarization mainly depends on the permittivity of the material, and the interfacial orientation depends on both the permittivity and conductivity. The microwave field causes the rotation of dipoles and the discharge of electrons agglomerated to the interfaces of different mineral phases, efficiently transforming microwave energy to heat energy and causing dielectric loss [32].

To study the effect of microwave power on roasting efficiency, 100 g boron concentrate was roasted to 600°C by microwave irradiation at 1 kW, 2 kW, 3 kW and 4 kW. The heating curve was recorded to investigate the heating characteristics of boron concentrate at each output power. **Fig. 13** shows that as output power increased, so did the heating rate of the boron concentrate. The concentrate needed less than 6 min reach 600°C at an output power of 4 kW, but needed 17 min at 1 kW. Thus, to minimize the influence of different heating rate on the total treatment time when irradiating samples at different output powers, all of the samples were held at 600°C for 20 min. This time was chosen because the holding time only induced a small fluctuation ($\leq \pm 1.40\%$) in the B_2O_3 activity; it did not change the phase composition after 10 min but had an unwanted influence on the microstructure of the mineral after 25 min.

Insert Fig. 13

Fig. 14 shows that the product heated at 1 kW had a relatively high B_2O_3 activity because of its long treatment time. Otherwise, the B_2O_3 activity of the roasted boron concentrate increased with microwave power and reached 82.92% at 4 kW, the maximum power of the Mobilelab microwave oven. As reported by C.A. Pickles [10], applying greater power during microwave irradiation increases the utilization rate and integral distribution density of microwaves in the material. This improves both the local and integral heating rate in the sample, accelerating dehydroxylation and oxidation reactions, enlarging the temperature gradient at heterogeneous interfaces, and further promoting damage in the mineral microstructure. It also

liberates minerals [33] and enhances the activation effect of minerals.

Insert Fig. 14

3.2.3 Effect of sample mass

As reported in previous studies, the utilization efficiency of microwave irradiation is significantly impacted by the sample mass during mineral processing [34]. To investigate the influence of sample mass on the activation efficiency of B_2O_3 in boron concentrate, boron concentrate of various masses was roasted to $600^\circ C$ by microwave irradiation and held for 10 min at an output power of 4 kW. The mass of material was changed from 75 g to 150 g, but the heating rate of all samples was maintained at a similar level. The B_2O_3 activity as a function of sample mass is shown in **Fig. 15**. The B_2O_3 activity of the roasted product increases with sample mass until 150 g, when it reached 86.73% and then remained constant.

Insert Fig. 15

The phase compositions of the roasted products were analyzed to understand the influence of sample mass on microwave heating. The XRD patterns of these products are shown in **Fig. 16**. These roasted products had multiple phases including szaibelyite, serpentine, suanite, forsterite, quartz and biotite. Except for a small amount of magnetite in the roasted product with an initial mass of 75 g, the magnetite in the boron concentrate was completely oxidized and converted to hematite after the sample mass reached 100 g. As the initial sample mass increased, so did the dehydroxylation and decomposition of szaibelyite and serpentine; this remained stable after the sample mass reached 150 g.

Insert Fig. 16

According to previous research [10], the heating mechanism of microwave roasting is characteristic of volumetric heating. When minerals are roasted by microwave irradiation, the heat generated inside the material due to dielectric loss is diffused from the material's surface and heated directly; this is in contrast to conventional heating, in which the material is heated from the outside and heat is conducted to the inner material. Thus, increasing the sample mass influenced the roasting effect in two ways. First, it increased the sample volume that could

absorb microwaves, thus raising the gross microwave absorption of the sample and the utilization rate of microwave energy [11,34,35]. Second, it decreased the specific surface area of the sample, which reduced the heat release per unit volume and increased the sample's heat storage capacity. Consequently, increasing the quantity of material enhanced the activation efficiency of boron concentrate when roasted by microwave irradiation.

3.3 Mechanism of microwave irradiation roasting

The B_2O_3 activity of the microwave roasted product reached 86.73%, while the product roasted with conventional thermal methods had a B_2O_3 activity of 67.88%. The XRD pattern of the sample treated in a thermal field is shown in **Fig. 17**, which indicates that the magnetite in the boron concentrate was barely oxidized, and there was no obvious dehydroxylation of szaibelyite and serpentine.

Insert Fig. 17

Fig. 18 shows the particle distribution of the products roasted in a microwave versus a thermal field. After microwave treatment, the particle diameter distribution of the boron concentrate was smaller, while the thermal field had a lesser influence on the particle size at the same temperature.

Insert Fig. 18

We calculated the contact angles of the three probe liquids and the surface free energy for the two roasted products; the results are shown in **Tables 3** and **4**.

Insert Table 3 and Table 4

Table 3 demonstrates that there was a decrease in the contact angles of the probe liquids for the microwave treated products. The contact angle to diiodomethane decreased from 64.75° to 44.90° ; the angle to ethylene glycol decreased from 71.92° to 55.29° ; and the angle to ultrapure water decreased from 86.58° to 74.36° . The contact angles of the product treated in a thermal field did not change as dramatically. The angle to ethylene glycol decreased 13.03° and the angle to water decreased 2.02° , while the angle to diiodomethane increased 2.92° . Thus, treatment with microwave irradiation noticeably enhanced the hydrophilicity of boron

concentrate. **Table 4** shows that the γ_{SV} of the untreated boron concentrate was 29.15 mJ/m², and the γ_{SV}^{LW} , γ_{SV}^{+} and γ_{SV}^{-} were 29.15 mJ/m², 0 mJ/m² and 5.07 mJ/m², respectively. Microwave roasting significantly increased γ_{SV} to 37.07 mJ/m² and increased γ_{SV}^{LW} and γ_{SV}^{-} , respectively, to 37.07 mJ/m² and 12.41 mJ/m². These changes were likely due to damage to the mineral microstructure and the promotion of surface absorption of OH⁻ as a result of the complete oxidation of Fe²⁺ to Fe³⁺ and the exposure of Mg²⁺ on the surface of the mineral particles caused by rapid dehydroxylation. In contrast, the surface free energy and interaction of the thermally treated boron concentrate showed only small changes. Thus, in contrast to treatment with a simple thermal field, microwave irradiation efficiently enhances the hydrophilicity of boron concentrate, as well as its OH⁻ absorption capability in the leachant, which is beneficial for alkali leaching of the mineral.

The high activation efficiency caused by microwave roasting can be explained by the heating mechanism of microwave irradiation, which is conducive to chemical reactions and produces cracks and micro-cracks in the boron concentrate. The mechanisms of microwave irradiation and thermal field treatment are shown schematically in **Fig. 19**.

Insert Fig. 19

In a simple thermal field, material is heated from the surface to the interior and there is little temperature difference among neighboring phases. Microwave irradiation enters a sample as an electromagnetic wave and is absorbed and converted into heat to varying degrees by different minerals in the sample. This creates a large temperature gradient and induces cracks at mineral boundaries, damages the microstructure of the sample, and accelerates chemical reactions such as dehydroxylation and oxidation. Consequently, microwave irradiation exposes more mineral surfaces to the alkali leachant, allowing more OH⁻ in the leachant to be absorbed onto the Fe³⁺ and Mg²⁺ exposed on the surface of the mineral particles. This promotes leaching of B₂O₃ and increases the activity of B₂O₃ in the boron concentrate.

4. Conclusion

This study uses microwave irradiation as a novel roasting method to efficiently activate boron concentrate. We analyzed the effect of each parameter on activation efficiency and investigated the mechanism by which microwave irradiation achieves activation roasting with an emphasis on surface properties and found that microwave irradiation roasting eases processing conditions and reduces the roasting time of boron concentrate.

The activation effect during microwave processing can be greatly influenced by roasting temperature, output power and sample mass. The B_2O_3 activity of the boron concentrate increased from 64.68% to 86.73% under optimal processing conditions at 4 kW and 600°C for 10 min for a sample mass of 150 g. This is 3.73% higher than the highest B_2O_3 activity that results from conventional roasting at 700°C for 2 h for a same sample mass.

The rapid and relatively complete oxidation and dehydroxylation reactions in boron concentrate induced by microwave irradiation promoted the generation of temperature gradients and thermal stresses within the mineral, and accelerated the generation of gaseous H_2O and highly active suanite. This increased cracks and micro-cracks in the minerals, significantly decreased the average diameter of mineral particles, and efficiently enhanced the exposure of Fe^{3+} and Mg^{2+} during microwave processing. In contrast to conventional thermal treating, microwave irradiation greatly improved hydrophilicity as well as surface free energy of boron concentrate; it increased the γ_{SV}^{LW} and γ_{SV}^- of the boron concentrate from 19.15 mJ/m² and 5.07 mJ/m² to 37.07 mJ/m² and 12.41 mJ/m², respectively. Consequently, microwave irradiation could further promote the reaction of the suanite with the leachant and enhance the B_2O_3 activity by enhancing the capability of boron concentrate to absorb OH^- in the alkali leachant.

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Captions

Table 1. Chemical compositions of boron concentrate (wt.%)

Table 2. Parameters of probe liquids

- Table 3.** Contact angles of probe liquids to boron concentrate treated under different conditions
- Table 4.** Surface energy and distribution of boron concentrate treated under different conditions
- Fig. 1.** XRD pattern of boron concentrate
- Fig. 2.** FTIR spectrum of boron concentrate
- Fig. 3.** SEM image of boron concentrate
- Fig. 4.** Particle distribution of boron concentrate
- Fig. 5.** Flow chart of experimental method
- Fig. 6.** Schematic illustration of microwave oven
- Fig. 7.** TG-DTG-DSC curve of boron concentrate
- Fig. 8.** Influence of roasting temperature on the microwave activation of boron concentrate
- Fig. 9.** XRD patterns of boron concentrate roasted by microwave irradiation at different temperatures
- Fig. 10.** Infrared spectra of boron concentrate roasted by microwave irradiation at different temperatures
- Fig. 11.** Particle distribution of boron concentrate roasted by microwave irradiation at 600°C and 800°C
- Fig. 12.** (a) SEM image of boron concentrate roasted by microwave irradiation at 600°C; (b) SEM image of boron concentrate roasted by microwave irradiation at 800°C
- Fig. 13.** Temperature curves of boron concentrate roasted at different microwave powers
- Fig. 14.** Influence of microwave power on activation of boron concentrate
- Fig. 15.** Influence of sample mass on microwave activation of boron concentrate
- Fig. 16.** XRD patterns of boron concentrate roasted by microwave irradiation for different sample masses
- Fig. 17.** XRD pattern of boron concentrate roasted by a thermal field
- Fig. 18.** Particle distribution of boron concentrate roasted by microwave irradiation and a thermal field
- Fig. 19.** Schematic representation of the mechanisms of roasting boron concentrate by

microwave irradiation and a thermal field

Figure and Chart

Table 1. Chemical compositions of boron concentrate (wt.%)

Component	B ₂ O ₃	MgO	SiO ₂	Fe ₂ O ₃	TFe	Al ₂ O ₃	CaO	Loss on ignition	Total
Content (wt.%)	11.57	39.93	24.98	4.28	4.98	1.35	1.14	12.11	97.92

Table 2. Parameters of probe liquids

Probe Liquid	η Viscosity (cP)	ρ Density (g/cm ³)	γ Surface tension (mJ/m ²)			
			γ_{LV}	γ_{LV}^{LW}	γ_{LV}^{+}	γ_{LV}^{-}
n-Hexane	0.3080	0.6603	18.43	18.43	0	0
Diiodomethane	2.7600	3.3254	50.80	50.8	0	0
Ethylene glycol	21.8000	1.1080	48.00	29.00	1.92	47.00
Ultrapure water	1.0020	0.9982	72.50	21.5	25.50	25.50

Table 3. Contact angles of probe liquids to boron concentrate treated under different conditions

Sample	Contact angle $\theta(^{\circ})$		
	Diiodomethane	Ethylene glycol	Ultrapure water
Untreated	64.75	71.92	86.58
Thermal field	67.67	58.89	84.56
Microwave field	44.90	55.29	74.36

Table 4. Surface energy and distribution of boron concentrate treated under different conditions

Sample	γ (mJ/m ²)			
	γ_{LV}	γ_{LV}^{LW}	γ_{LV}^{+}	γ_{LV}^{-}
Untreated	29.15	29.15	0	5.07
Thermal field	29.21	29.21	0	8.37

Microwave field

37.07

37.07

0

12.41

Fig. 1. XRD pattern of boron concentrate

Fig. 2. FTIR spectrum of boron concentrate

Fig. 3. SEM image of boron concentrate

Fig. 4. Particle distribution of boron concentrate

Fig. 5. Flow chart of experimental method

Fig. 6. Schematic illustration of microwave oven

Fig. 7. TG-DTG-DSC curve of boron concentrate

Fig. 8. Influence of roasting temperature on the microwave activation of boron concentrate

Fig. 9. XRD patterns of boron concentrate roasted by microwave irradiation at different temperatures

Fig. 10. Infrared spectra of boron concentrate roasted by microwave irradiation at different temperatures

Fig. 11. Particle distribution of boron concentrate roasted by microwave irradiation at 600°C and 800°C

(a)

(b)

Fig. 12. (a) SEM image of boron concentrate roasted by microwave irradiation at 600°C;

(b) SEM image of boron concentrate roasted by microwave irradiation at 800°C

Fig. 13. Temperature curves of boron concentrate roasted at different microwave powers

Fig. 14. Influence of microwave power on activation of boron concentrate

Fig. 15. Influence of sample mass on microwave activation of boron concentrate

Fig. 16. XRD patterns of boron concentrate roasted by microwave irradiation for different sample masses

Fig. 17. XRD pattern of boron concentrate roasted by a thermal field

Fig. 18. Particle distribution of boron concentrate roasted by microwave irradiation and a thermal field

Fig. 19. Schematic representation of the mechanisms of roasting boron concentrate by microwave irradiation and a thermal field