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Calorimetric studies on leaching of mechanically activated sphalerite in $FeCl_3$ solution

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Abstract

The thermal behaviors of the leaching of mechanically activated sphalerite were investigated for the first time by calorimetry. The specific granulometric surface area and the structural disorder sphalerite were also analyzed by X-ray diffraction laser particle size analyzer and X-ray powder diffraction (XRD) analysis, respectively. A new method to measure the mechanically activated storage energy of minerals was proposed by designing a thermochemical cycle that made mechanically activated and non-activated mineral reaching the same final state while leaching in $FeCl_3$ solution. The results indicate that the mechanically activated storage energy of sphalerite rises with the increased grinding time and is closely related to the lattice distortions and crystallite sizes. The calorimetric results of the products from sieved in water or ethanol medium and the products from 2 h treatment of mechanically activated sphalerite under pure argon (99.99 vol.%) at different temperatures indicate that the mechanically activated storage energy of sphalerite is caused mainly by changes of the crystal structure, and the reactivity of mechanically activated sphalerite is difficult to lose.

Keywords: Calorimetric method; Mechanical activation; Sphalerite; Leaching; Structural disorder

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1. Introduction

Dislocations and various structural defects produced in crystals as a result of mechanical treatment cause accumulation of large excess of energy. The excess energy is named as mechanically activated storage energy [1], which has been given considerable attention recently. Schellinger [2] reported that the mechanical activated storage energy in the minerals were between 10 and 20% of the total energy after mechanical activation. De Lima and Kim et al. [3,4] investigated the thermal properties of ball-milled amorphous solid using differential scanning calorimetry (DSC). By the described precision of the DSC method, it is hard to obtain the accurate mechanically activated storage energy data. Microcalorimetry has been shown as an important tool in the study on energy change and its use is increasing nowadays [5–7]. But applications of microcalorimetry to determine mechanically activated storage energy has not been reported due to the complexity of the releasing of mechanically activated storage energy.

In this paper, the storage energy behaviors of mechanically activated sphalerite samples prepared by various treatment methods were investigated by calorimetric experiments to get the essence of mechanically activated storage energy.

2. Experimental

Since the mechanically activated storage energy of sphalerite cannot be released completely in the course of heating, a suitable leaching agent was selected to release all storage energy by a leaching procedure. A thermochemical cycle was designed to make mechanically activated and non-activated mineral reaching the definite final state. Thus the mechanically activated storage energy can be acquired by calculating the difference of the reaction enthalpy of mechanically activated and non-activated minerals in each process.

The selection of a suitable leaching system is very important for the calorimetric experiment of sphalerite, which has been summarized in many publications [8,9]. Although various acids (H_2SO_4, HCl) and bases (ammonia) solutions have been tested, they did not fit the calorimetry experiment

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Table 1
The chemical analyses of the natural sphalerite

	Elements							
	Zn	S	Fe	Pb	Cd	Sb	Bi	In
Content (wt.%)	61.39	32.11	2.38	1.92	0.28	0.05	0.01	0.03

due to gas releasing. $FeCl_3$ solution was selected as a suitable lixiviant for sphalerite leaching in our experiments. Dutrizac, MacDonald and Maurice [10,11,14] stated in their study of oxidative leaching of sphalerite by $FeCl_3$. In accordance with the literature data the leaching reaction can be represented as:

$$2Fe^{3+} + ZnS = Zn^{2+} + 2Fe^{2+} + S^0 \quad (1)$$

The reaction enthalpy of sphalerite samples in $FeCl_3$ solution was measured by batch experiments.

2.1. *Preparation of the samples*

2.1.1. *Preparation of mechanically activated sphalerite*

Natural pure hand-sorted sphalerite ore was purchased from a domestic mine, and its chemical compositions are summarized in Table 1. It was found by X-ray diffraction analysis that the natural sphalerite contained cubic sphalerite as a predominant component (shown in Fig. 1). The non-activated sphalerite was prepared by crushing the natural sphalerite in a jaw crusher to a particle size of ≤1 mm, then stored for more than 6 months. The non-activated sphalerite (10 g) was added into a stainless vessel with six stainless steel balls of 18 mm in diameter and 12 balls of 8 mm in diameter, then kept in higher vacuum (the residue pressure $\leq$ 1 Pa), followed by pouring pure nitrogen into this vessel for 0.5 h (these operations were performed once again), i.e., non-activated sphalerite was kept under an inert atmosphere, and then mechanically activated in a planetary ball mill (QM-ISP planetary ball mill, PR China) under a rotation rate of 200 rpm, and a powder-to-ball mass ratio of 1:25. Mechanically activated sphalerites were obtained after grinding for $t_G = 20$, 40, 120, 180 and 260 min, respectively.

2.1.2. *Mechanically activated sphalerite sieved in water or ethanol medium*

The sieving experiment was completed in a 500 ml beaker to which 100 ml of distilled water or ethanol and 5 g mechanically activated sphalerite samples were added. The mixture was introduced sequentially to 60, 100, 120, 140, 160, 180 and 200 mesh sieves to obtain the samples with different particle size. The samples were then dried in a thermostatically controlled furnace at 343.15 K.

2.1.3. *Products from 2 h treatment under an inert atmosphere at different temperatures*

Mechanically activated sphalerite grinding for 120 min was loaded with a porcelain boat reactor in a electric tube furnace which was kept in higher vacuum (the residue pressure $\leq$ 3 Pa), followed by pouring highly pure argon into it. The vacuum pumping and pure argon gassing operations were repeated for three times, then the electric tube furnace was maintained at 323.15, 423.15 and 573.15 K for 2 h, respectively, to obtain the products from 2 h treatment under an inert atmosphere at different temperatures.

2.2. *Calorimetric experiments*

A HT-1000 heat flow calorimeter (SETRAM, France) was used for isothermal heat measurements at 298.15 K. The sensitivity and temperature scales of the calorimeter were calibrated carefully [7] before experiments. The enthalpy of solution of KCl(s) in water (10.00 cm^3) to form about $KCl{\cdot}1120H_2O$ was measured at $T = (298.15 \pm 0.05)$ K to check the accuracy of the calorimetric method. The results was (17.49 ± 0.13) kJ mol^{-1}, which was in good agreement with the value 17.503 kJ mol^{-1} from the literature [18].

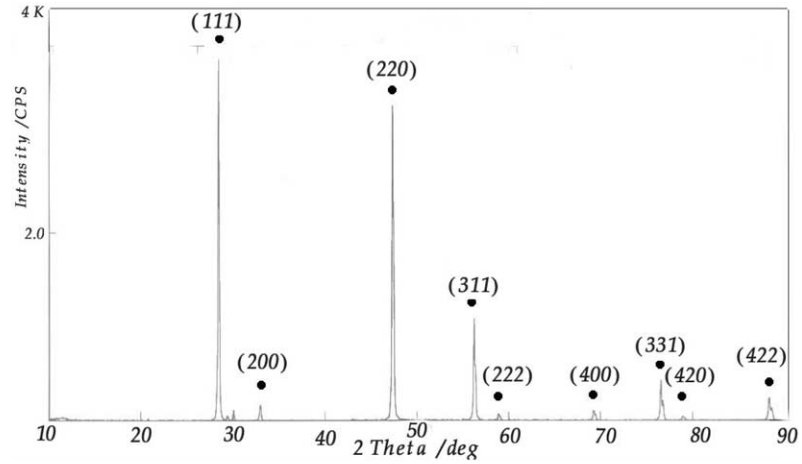

Fig. 1. XRD pattern of natural sphalerite.

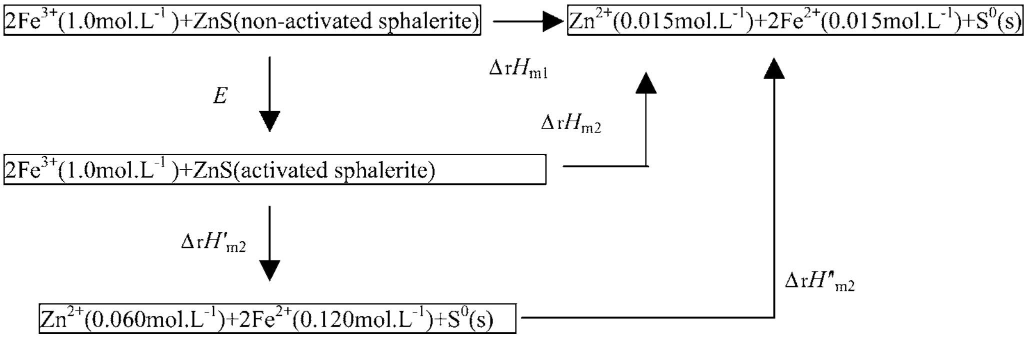

Fig. 2. Thermochemical cycle for the leaching of the activated sphalerite.

Sphalerite sample of 0.15 g (±0.0001 g) weighed with BP190S electronic balance (Sartorius, Germany) in a sealed glass ampoule of 3 ml in volume was broken and reacted with 10.00 ml 1.0 mol l^{-1} $FeCl_3$ solution for 4 h after the baseline of the calorimeter reached a stable state. The heat flow data were recorded by a data acquisition computer until the system reached thermal equilibrium. At the end of the experiment, the sample was removed from the calorimeter and frozen at once. The amount of solubilized zinc ion was determined by PS-6 ICP atomic emission spectrometer (Baird, USA). Then the reaction enthalpy for 1 mol zinc leached from sphalerite was obtained by data treatment as follows:

$$Q_p = \Delta_r H_m = \frac{\int_0^t h\,dt}{c_{Zn^{2+}} V}$$

where $\Delta_r H_m$ (kJ mol^{-1}), h (W), t (s), $c_{Zn^{2+}}$ (mol l^{-1}) and V (l) are the reaction enthalpy of 1 mol zinc leached, the heat flow, the reaction time, the zinc ion concentration of leaching solution and solution volume, respectively.

In accordance with Eq. (1), a thermochemical cycle was designed (shown in Fig. 2). The storage energy of the activated sphalerite can be given by

$$E = \Delta_r H_{m1} - \Delta_r H_{m2} = \Delta_r H_{m1} - \Delta_r H'_{m2} - \Delta_r H''_{m2}$$

where E, $\Delta_r H_{m1}$, $\Delta_r H'_{m2}$, and $\Delta_r H''_{m2}$ are the mechanically activated storage energy of sphalerite, the reaction enthalpy of non-activated sphalerite in leaching, the reaction enthalpy of mechanically activated sphalerite in leaching and the enthalpy of dilution, respectively.

The mean of the enthalpy of non-activated sphalerite in leaching obtained from data in Table 2 ($\Delta_r H_{m1}$: −11.50 kJ mol^{-1}).

2.3. *Surface structural characteristics*

The structural disorder of mechanically activated sphalerites was characterized by X-ray diffraction analysis on a diffractometer (Rigaku, Japan) using Cu Kα radiation ($\lambda = 1.54$ Å, voltage: 40 kV, current: 20 mA) with time constant 0.5 s, limit of measurement 10 impulses per second, step size 0.03 and collection time 3 s per step (no internal standard). The recorded X-ray powder diffraction (XRD) spectra were used for calculation of the degree of structural disorder—the distortion (ε) of crystal lattice (presented as a percentage) and the crystallite size (D), which were determined from the changes in profile of the diffraction peaks, such as (1 1 1) and (3 3 1) of sphalerite. As the diffraction line broadening depends mainly on the increase of ε and the decrease of D, ε and D can be calculated by using the model of Gaussian function [12,13]. In this experiment, ε and D were obtained by dealing with the integral width of diffraction peaks (1 1 1) and (3 3 1) of non-activated or mechanically activated sphalerites at different grinding time.

The specific granulometric surface area (S_G) of mechanically activated sphalerites was calculated from the corresponding average particle size measured using Mastersizer 2000 Laser Diffraction Particle Size Analyzer (Malvern, Great Britain), where distilled water was used as a dispersing agent.

3. Results and discussion

3.1. *Mechanically activated storage energy of non-activated sphalerite and sphalerite mechanically activated for different time*

The mechanically activated storage energy, crystallite sizes, the deformations of the crystal and specific

Table 2
The reaction enthalpy of non-activated sphalerite

	No.					Mean
	1	2	3	4	5	
$\Delta_r H_{m1}$ (kJ mol^{-1})	−11.46	−11.52	−11.54	−11.48	−11.50	−11.50 ± 0.04

Table 3
The values of $\Delta_r H'_{m2}$, $\Delta_r H''_{m2}$, E, S_G, D and ε for non-activated sphalerite and sphalerites mechanically activated for different time leaching condition: C_{FeCl_3}, 1 mol l^{-1}; temperature, 298.15 K; reaction time, 4 h

	Grinding time (min)					
	0	20	40	60	120	260
$\Delta_r H'_{m2}$ (kJ mol^{-1})	−11.50	−14.50	−18.93	−21.98	−27.21	−28.46
$\Delta_r H''_{m2}$ (kJ mol^{-1})	0	−0.0032	−0.0092	−0.0086	−0.0106	−0.0113
E (kJ mol^{-1})	0	1.90	7.43	10.48	15.71	16.96
S_G (m^2 g^{-1})	3.15	4.94	6.02	7.04	7.45	7.70
D (Å)	964	615	472	339	230	163
ε (%)	0	0.32	0.45	0.92	0.99	1.15

granulometric surface area of non-activated sphalerite and sphalerites mechanically activated for different time were listed in Table 3. Chen and Xiao et al. [9,17] reported that no elemental sulfur was produced during mechanical activation of sphalerite and this mechanical activation was performed under inert atmosphere, therefore, the chemical reaction of this mechanical activation for sphalerite can be neglected.

Table 3 indicates that the mechanically activated storage energy of sphalerite increases with the increased grinding time, and the crystallite sizes decrease and the deformations of the crystal increase gradually with the increased grinding time, which is similar with the study of mechanically activated chalcopyrite and pyrite [15,16]. Therefore, it can be deduced that non-activated sphalerite undergoes the structural distortion during the mechanical activation under an inert atmosphere, which leads to the formation of metastable sphalerites. The metastable sphalerites containing accumulated excess energy, so the mechanically activated storage energy of sphalerite is closely related to the structural differences between non-activated and mechanically activated sphalerites.

3.2. *Mechanically activated storage energy of mechanically activated sphalerite sieved in water or ethanol medium*

The mechanically activated storage energy of sphalerite sieved in water or ethanol medium is shown in Table 4.

Table 4 shows that the mechanically activated storage energy of the samples is almost independent of the sieving medium and the particle size of mechanically activated sphalerite. It indicates that the decrease of the particle size of mechanically activated sphalerite is not the major factor of the increase of the storage energy of mechanically activated sphalerite.

Table 5
The storage energy of the products from the 2 h treatment of mechanically activated sphalerite under inert atmosphere

	Without the treatment	Treating temperature		
		323.15 K	423.15 K	573.15 K
$\Delta_r H_{m2}$ (kJ mol^{-1})	−27.21	−25.84	−25.83	−25.36
E (kJ mol^{-1})	15.71	14.42	14.41	13.94
S_G (m^2 g^{-1})	16.64	9.123	8.612	6.404

3.3. *Mechanically activated storage energy of the products from 2 h treatment of mechanically activated sphalerite under an inert atmosphere*

The storage energy of the products from the 2 h treatment of mechanically activated sphalerite under an inert atmosphere at different temperatures is listed in Table 5. The products were also characterized by XRD analysis (shown in Fig. 3).

Table 5 shows that the storage energy of the products remains almost constant with increased treating temperature. Fig. 3 and Table 5 indicate that the average surface area of mechanically activated sphalerite changes with the 2 h treatment but does not change the lattice structure of

Table 4
Storage energy of mechanically activated sphalerites sieved in different medium[a]

	Particle size (mesh)			
	60–100	120–140	160–180	180–200
$\Delta_r H_{m2}$, sieved in H_2O (kJ mol^{-1})	−22.89	−23.10	−23.05	−22.87
E, sieved in H_2O (kJ mol^{-1})	11.39	11.60	11.55	11.37
$\Delta_r H_{m2}$, sieved in C_2H_5OH (kJ mol^{-1})	−23.81	−23.77	−23.99	−24.34
E, sieved in C_2H_5OH (kJ mol^{-1})	12.31	12.27	12.49	11.84

[a] $\Delta_r H_{m2} = \Delta_r H'_{m2} + \Delta_r H''_{m2}$.

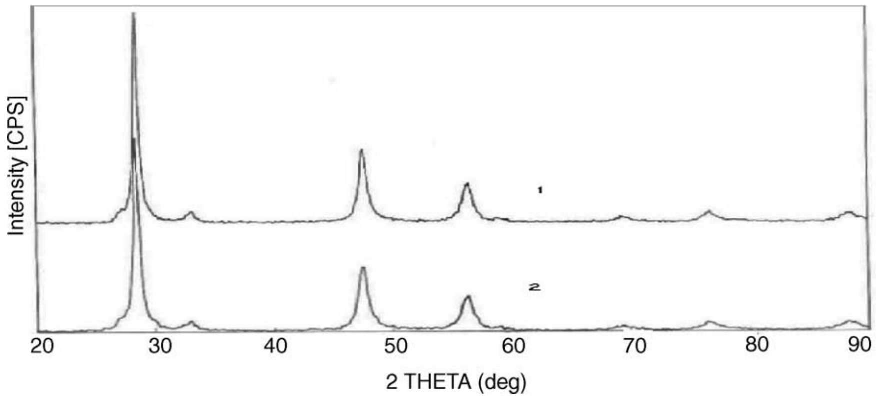

Fig. 3. XRD patterns of mechanically activated sphalerite (1) and its treated product (2): (1) mechanically activated sphalerite without the 2 h treatment; (2) the product obtained from the 2 h treatment under inert atmosphere at 573.15 K.

mechanically activated sphalerite. This is another support for the opinion that the decrease of particle size of mechanically activated sphalerite is not the major factor of resulting in the increase of the storage energy of mechanically activated sphalerite.

4. Conclusions

1. The mechanically activated storage energy of sphalerite increases with the increased grinding time, and is independent of the particle size of mechanically activated sphalerite and the sieving medium, i.e. water and ethanol.
2. The storage energy of mechanically activated sphalerite is mainly resulted from the structural disorder during the mechanical activation of sphalerites in inert atmosphere.
3. The reactivity of mechanically activated sphalerite maintains stable.

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