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Calorimetric investigation on mechanically activated storage energy mechanism of sphalerite and pyrite

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Abstract

The structural changes of mechanically activated sphalerite and pyrite under different grinding conditions were determined by X-ray powder diffraction (XRD), laser particle size analyzer and elemental analysis. The storage energy of mechanically activated sphalerite and pyrite was measured by a calorimetric method. A thermochemical cycle was designed so that mechanically activated and non-activated minerals reached the same final state when dissolved in the same oxidizing solvent. The results show that the storage energy of mechanically activated sphalerite and pyrite rises with increased in grinding time, and reaches a maximum after a certain grinding period. The storage energy of mechanically activated pyrite decreases when heated under inert atmosphere. The storage energy of mechanically activated sphalerite and pyrite remains constant when treated below 573 K under inert atmosphere. The percentage of the storage energy caused by surface area increase during mechanical activation decreases with increasing grinding time. These results support our opinion that the mechanically activated storage energy of sphalerite is closely related to lattice distortions, and the mechanically activated storage energy of pyrite is mainly caused by the formation of reactive sites on the surface.

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Keywords: Calorimetry; Storage energy; Mechanical activation; Sulfide ore; Structural change

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1. Introduction

Mechanical activation is one of the most important methods to enhance hydrometallurgical processes. Dislocations and various structural defects produced in crystals as a result of mechanical activation cause accumulation of energy, i.e. mechanically activated storage energy [1]. Schellinger [2] reported that mechanically activated storage energy in minerals was between 10% and 20% of the input energy during mechanical activation. Calorimetry [3–5] can be applied to determine energy change, but application in determination of mechanically activated storage energy has not been reported.

In this work, the energy changes of mechanically activated sulfide ores were measured by a calorimetric method to determine the relationship between mechanically activated storage energy and structural changes.

2. Experimental

2.1. Materials

Natural pyrite and sphalerite minerals were purchased from a geological museum, and their chemical compositions are presented in Table 1. X-ray diffraction analysis showed that the natural pyrite and sphalerite contained cubic pyrite and cubic sphalerite as a predominant component, respectively. The non-activated pyrite or sphalerite was prepared by crushing respective minerals in a jaw crusher to a certain particle size, then exposed to ambient air for more than 1 year, then sieved to obtain −1 or +1 mm and −1.5 mm (abbreviated as +1 mm) pyrite or sphalerite.

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Table 1
The chemical analyses of the natural sphalerite and pyrite

Elements	Content (in sphalerite) (wt.%)	Content (in pyrite) (wt.%)
Zn	61.39	0.05
Fe	2.38	45.63
S	32.11	52.38
Sb	0.05	0.01
Pb	1.92	–
Cd	0.28	–
Bi	0.01	–
In	0.03	–
Si	–	0.1
Ca	–	0.01
Sn	–	0.01
As	–	0.03
Co	–	0.005
Ni	–	0.001

To obtain mechanically activated pyrite or sphalerite, the non-activated pyrite or sphalerite (10 g) was added into a stainless vessel with 6 stainless steel balls of 18 mm diameter and 12 stainless steel balls of 8 mm diameter (powder-to-ball mass ratio of 1:25). The vessel was twice evacuated and purged with high purity nitrogen for half an hour, and then mechanically activated for a certain period in a planetary ball mill (QM-ISP planetary ball mill, PR China) at 200 rpm.

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

Sphalerite or pyrite mechanically activated for 120 min was placed in with a porcelain boat reactor in an electric tube furnace which was evacuated, followed by sweeping pure argon into it. The vacuum pumping and pure argon gassing operations were done for three times. Then the tube furnace was maintained at 323, 423, 573, 623, 673, or 773 K for 2 h.

2.3. *Calorimetric experiments*

Since the mechanically activated storage energy of sulfide ores is not released completely during heat treatment [5,6], the mechanically activated storage energy was obtained from the difference between the reaction enthalpy of mechanically activated and non-activated minerals $Ce(SO_4)_2 + H_2SO_4$ solution or $FeCl_3$ solution were selected as a suitable oxidizing solvent for pyrite or sphalerite dissolution, respectively. In accordance with the E-pH stability diagrams [7], the dissolution reaction can be represented as

$$\begin{aligned} &17Ce^{4+} + FeS_2 + 8H_2O \\ &= 17Ce^{3+} + Fe^{3+} + 2SO_4{}^{2-} + 16H^+ \end{aligned} \tag{1}$$

and [8,9]

$$2Fe^{3+} + ZnS = Zn^{2+} + 2Fe^{2+} + S^0 \tag{2}$$

The reaction enthalpies of pyrite and sphalerite in the respective oxidizing solvents were measured by calorimetry. An HT-1000 heat conduction calorimeter (SETARAM, France) was used for heat measurements at 298 K. 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, 17.24 ± 0.05 kJ mol^{-1} agrees with the literature [10] 17.241 ± 0.018 kJ mol^{-1}.

Samples of sphalerite or pyrite were weighed (0.15 ± 0.0001 g) with BP190S electronic balance (Sartorius, Germany) and sealed into a 3 mL glass ampoule. The ampoule was broken in the calorimeter to allow the sample to reacted with 10.00 mL of 1.0 mol L^{-1} $FeCl_3$ solution or with 10.00 mL of 0.451 mol L^{-1} $Ce(SO_4)_2$ solution. After 4 h the calorimeter returned to baseline, heat rate data were recorded in a personal computer. After the experiment, the concentration of dissolved zinc or iron was determined by PS-6 ICP atomic emission spectrometer (Baird, USA).

The storage energy of mechanically activated sulfide ores can be given as

$$E = \Delta_r H_{m1} - \Delta_r H_{m2} = \Delta_r H_{m1} - \Delta_r H'_{m2} - \Delta_r H''_{m2} \tag{3}$$

where E is the mechanically activated storage energy of sulfide ores, $\Delta_r H_{m1}$ the reaction enthalpy of non-activated ores, $\Delta_r H'_{m2}$ the reaction enthalpy of mechanically activated ores and $\Delta_r H''_{m2}$ is the enthalpy of dilution of the solvent by calorimetry.

The specific surface energy of sphalerite or pyrite from our previous work [6] is 0.65 and 4.21 J m^{-2}, respectively. The storage energy caused by the increased surface area (E_s) can be calculated according to

$$E_s = \gamma \Delta S_G M \tag{4}$$

where γ (J m^{-2}) is the specific surface energy, ΔS_G (m^2 g^{-1}) the increased surface area and M (g mol^{-1}) is the mole mass (M).

2.4. *Structural characteristics*

The structural disorder of mechanically activated sphalerite or pyrite 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 s^{-1}, step size 0.03 and collection time 3 s/step (no internal standard). The recorded XRD spectra were used to calculate the degree of structural disorder, i.e. 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. As the diffraction line broadening depends mainly on the increase in ε and the decrease in D, ε and D can be calculated by a Gaussian function [11,12]. In this experiment, ε and D were obtained from the integral width of diffraction peaks (1 1 1) and (3 3 1) of sphalerite or (2 2 0) and (5 5 1) of pyrite.

Table 2
The values of $\Delta_r H'_{m2}$, $\Delta_r H''_{m2}$, E, S_G, D, ε and E_s for non-activated sphalerite and sphalerite mechanically activated for different times

	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
E_s (kJ mol^{-1})		0.382	0.612	0.830	0.918	0.971
E_s/E (%)		20.1	8.24	7.92	5.84	5.73

Note: E_s is the storage energy caused by the increased surface area during mechanical activation.

The specific granulometric surface area (S_G) was calculated from the corresponding average particle size measured with Mastersizer 2000 Laser Diffraction Particle Size Analyzer (Malvern, UK). Where distilled water was used as a dispersing agent.

The elemental sulfur contents of unactivated and mechanically activated pyrite or sphalerite were determined by using a gravimetric method. A typical operation was performed as follows: 2.000 g mechanically activated pyrite or sphalerite and 20 mL CCl_4 were added into a 50 mL flask, refluxed for 72 h, and finally filtered. CCl_4 was then evaporated at ambient temperature to yield elemental sulfur, which was then weighed to determine the elemental sulfur content.

3. Results

The enthalpy of reaction ($\Delta_r H_{m1}$) of non-activated sulfide ores was obtained from five measurement, $\Delta_r H_{m1}$ for non-activated sphalerite is -11.50 ± 0.04 kJ mol^{-1} and for pyrite -33.83 ± 0.02 kJ mol^{-1}.

3.1. The mechanically activated storage energy of sphalerites and pyrites for different grinding time

The mechanically activated storage energy, crystallite sizes, the deformations of the lattice and specific granulometric surface area of non-activated sphalerite and sphalerite mechanically activated for different times are listed in Tables 2 and 3.

Table 2 indicates that the mechanically activated storage energy of sphalerite increases with increased grinding time, the crystallite sizes decrease, and the deformations of the lattice increase with increased grinding time. Similar mechanically activated chalcopyrite [13]. The increase in specific surface area during mechanical activation is not a major factor responsible for the increase in E. This is supported by above experimental results. Chen et al. [13] reported that no elemental sulphur was produced during the mechanical activation of sphalerite. And the mechanical activation was performed under inert atmosphere. So the chemical reaction of this mechanical activation for sphalerite can be neglected.

Non-activated sphalerite undergoes structural distortion during the mechanical activation under inert atmosphere, which leads to the formation of metastable sphalerite that contains accumulated excess energy. The mechanically activated storage energy of sphalerite is closely related to the lattice distortion.

Table 3 shows that the mechanically activated storage energy of pyrite increases with increased grinding time. The specific granulometric surface area of mechanically activated pyrite rises with the increase in grinding time, but remains almost constant after a certain time, which indicates that the increase in the specific surface area during mechanical activation is not a major factor for the increase in the mechanically activated storage energy of pyrite. The change of the deformation of the lattice is very small, but the crystallite sizes decrease gradually with the increase in grinding time. Elemental sulfur was found to be produced during mechanical

Table 3
$\Delta_r H_{m2}$, E, S_G, D, ε and E_s for non-activated pyrite and pyrite mechanically activated for different times

	Grinding time (min)				
	20	40	60	120	260
$\Delta_r H_{m2}$ (kJ mol^{-1})	−36.11	−46.93		−49.22	−50.30
E (kJ mol^{-1})	2.28	13.11		15.39	16.47
S_G (m^2 g^{-1})	2.60	3.38		5.34	5.15
D (Å)	2988	675		564	544
ε (%)	0.03	0.05		0.06	0.07
The content of elemental sulfur (mg g^{-1})	4.1	8.3		10.1	16.1
E_s (kJ mol^{-1})	1.01	1.40	1.83	2.39	2.30
E_s/E (%)	43.0	10.7	11.1	15.5	14.0

activation of pyrite, and increased with increased grinding time.

On the other hand, pyrite has incomplete cleavage planes, and sphalerite has complete cleavage planes, which shows that pyrite has much more bond linkages between two cleavage planes than sphalerite [16]. When these sulfide ores were broken into small particles during mechanical activation for the same grinding time, the reactive sites produced on the surface of mechanically activated pyrite are much more than that on the surface of mechanically activated sphalerite. Therefore, the increase in the mechanically activated storage energy of pyrite mainly results from the formation of reactive sites on the surface of pyrite during mechanical activation.

The storage energy (E_s) caused by the increased surface area during mechanical activation is shown in Tables 2 and 3 [6]. The results indicate that the contribution of E_s to the mechanically activated storage energy (E) decreases from 20.1% to 5.7% for sphalerite and from 43% to 14% for pyrite with the increase in grinding time from 20 to 260 min, respectively. This is further evidence that the decrease in particle size of mechanically activated sulfide ore is not the major cause of increase mechanically activated storage energy.

3.2. The mechanically activated storage energy of the products from 2 h treatment of mechanically activated sphalerite and pyrite under inert atmosphere

Table 4 shows that the storage energy of the products remains almost constant with the increase in treating temperature [15]. The specific granulometric surface area of mechanically activated sphalerite decreases with the 2 h treatment but the lattice structure does not. This is further evidence that the decrease in particle size of mechanically activated sphalerite is not the major cause of the increase in mechanically activated storage energy.

Table 5 shows that the storage energy remains almost constant with the increase in treating temperature between 373 and 573 K, while the average surface area changes from 5.34 to 3.14 $m^2 g^{-1}$. This is further evidence that the decrease in particle size of mechanically activated pyrite is not the major factor for the increase in the storage energy of mechanically activated pyrite.

The XRD results from literature [14,15] of the products of the mechanically activated pyrite treated at 573 K for 2 h indicate that the structure maintains constant, and the products treated above 573 K decompose.

Table 4
The storage energy of the products from the 2 h treatment of mechanically activated sphalerite under inert atmosphere

Treating temperature (K)	$\Delta_r H_{m2}$ (kJ mol^{-1})	E (kJ mol^{-1})	S_G (m^2 g^{-1})
Without treatment	−27.21	15.71	16.64
323	−25.84	14.42	9.123
423	−25.83	14.41	8.612
573	−25.36	13.94	6.404

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

Treatment temperature (K)	$\Delta_r H_{m2}$ (kJ mol^{-1})	E (kJ mol^{-1})	S_G (m^2 g^{-1})
Without treatment	−49.22	15.39	5.34
373	−49.30	15.47	
523	−49.18	15.35	
573	−49.07	15.24	3.14
623	−43.40	9.57	
673	−36.86	3.03	2.03
773	−33.68	−0.15	

4. Conclusions

(1) The mechanically activated storage energy of sphalerite and pyrite increases with the increase in grinding time.
(2) The surface area increase during mechanical activation is not a major factor for the increase in the mechanically activated storage energy of sphalerite and pyrite.
(3) The mechanically activated storage energy of sphalerite is mainly resulted from the structural disorder during the mechanical activation of sphalerite.
(4) Mechanically activated storage energy of pyrite is mainly caused by the formation of reactive sites on the surface of pyrite during mechanical activation.

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