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ELECTROGENERATIVE-LEACHING OF MECHANICALLY ACTIVATED GALENA*

S. F. Wang[1**], *Z. Fang*[2] *and Y. F. Tai*[1]

[1]Department of Chemistry and Environmental Engineering, Changsha University of Science and Technology, Changsha 410077, China
[2]Institute of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China

The electrogenerative-leaching of galena activated mechanically in planetary centrifugal mill were studied. A dual cell system was introduced to investigate the leaching process. The experimental results indicated that the mechanical activation improved the galena's lattice constant, the lattice distortion and the degree of crystal defect, which resulted a decreasing of initial potential of galena electrode and an increasing of output voltage of the leaching cell.

Keywords: *electrogenerative-leaching, galena, mechanical activation*

Introduction

The basic principle and technique of electro-generative were introduced to hydrometallurgical process by Zhang *et al.* [1]. It has been confirmed experimentally that a certain quantity of electric energy together with the leached products could be obtained in the electrogenerative leaching process. Some influencing factors of the electrogenerative leaching, such as electrode structure, temperature and solution concentration, were studied [2–5]. In order to enhance the electrogenerative-leaching efficiency, the mechanical activation of mineral samples were applied to the electrogenerative leaching process. It is well known that the mechanical activation results in the formation of metastable solids, and is a means of accelerating the leaching process for sulfide minerals [6–8].

Experimental

Materials and apparatus

The galena electrodes were prepared with natural pure hand-sorted galena ore from a domestic mine, whose composition was presented as follows: Pb, 60.10 mass%; Zn, 14.17 mass%; S, 18.08 mass%; Cd, 0.28 mass%; Sb, 0.05 mass%; Bi, 0.01 mass%; In, 0.03 mass%. Chemical-grade MnO_2 (Mn, 54.82 mass%) was used as cathodic electrode material. Solutions used in the experiments were prepared using analytical-grade chemicals and distilled water.

Galena was mechanically activated in a planetary centrifugal mill for a certain period of time. Take the sample placed for 6 months after being mechanically activated in the mill for 60 min as non-activated sample.

The measurements of thermogravimetry analysis were performed using a thermal analyzer TGA/SDTA 851^e (Mettler Toledo, U.S.A. and Switzerland) with temperature range from 298.15 to 1273.15 K at the heating rate of 10 K min^{-1} under pure oxygen with flowing rate of 70 cm^3 min^{-1}. The sample mass was about 30.5 mg.

A dual cell system [2] was introduced to study the electrogenerative leaching process. Two mini-stirrers were used for agitating and water-bath thermostat for heating. Each of half-cell potentials (φ) and the output voltage (V) of the leaching cell were measured with digital voltmeter. The current (I) was measured with a low resistance milliammeter.

Preparation of electrodes

A mixture of 2.0 g galena activated mechanically and 0.12 g acetylene black was put into a columnar filter bag (φ2.35 cm), then a claviform graphite electrode (φ2.3 cm) was inserted as conductor. A mixture of 2.0 g MnO_2 and 0.06 g acetylene black was put into a columnar filter bag (φ2.35 cm), then a claviform graphite electrode (φ2.3 cm) was inserted as conductor.

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** Author for correspondence: wangsf711117@163.com

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Results and discussion

The TG curves of different galenas

The TG curves for different galenas are shown in Fig. 1. The corresponding mass increase rate (α) between 400 and 850 K in the TG curves for different galenas were presented in Table 1. The results show that the mass increase rate (α) between 400 and 850 K in the TG curves rises gradually with the increasing of grinding time. The state of the activated solids can be characterized as metastable [7–9].

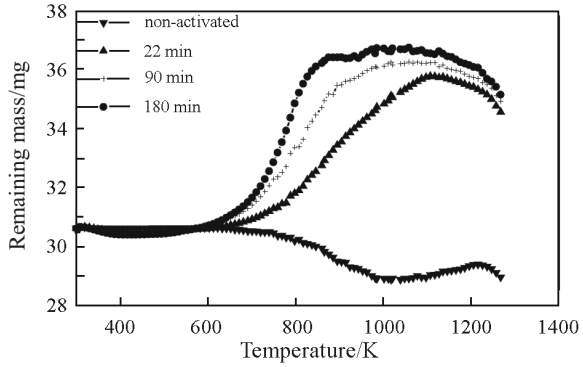

Fig. 1 TG curves of galena after grinding for different time

Table 1 The relationship between the mass increase rate (α) and grinding time (*t*)

t/min	0	22	90	180
α/mass%	–2.07*	7.42	13.29	21.29

*this minus number represents the mass loss of non-activated galena in the TG curve.

Non-activated galena transformed into metastable galena after mechanical activation. The metastable galena was more liable for anodic oxidation in the electrogenerative leaching process than non-activated galena.

The X-ray diffraction peaks (200) for different galenas

X-ray diffraction peaks corresponding to (200) plane for different galenas are shown in Fig. 2. By analyzing (200) diffraction peak of non-activated and mechanically activated galenas, the values of the crystallite sizes (*D*) and the deformations of crystal (ε) were obtained as shown in Table 2. The crystallite sizes (*D*) decreased and the deformations of the crystal (ε) increased gradually with grinding time.

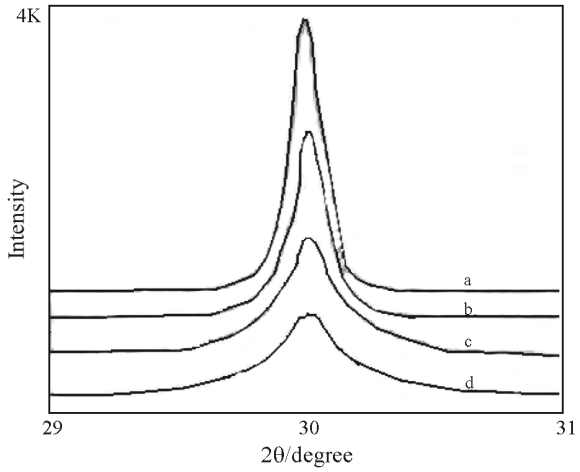

Fig. 2 Peaks (200) of X-ray diffraction patterns for different galenas after different grinding time, a – t=0 min; b – t=22 min; c – t=90 min; d – t=180 min

Table 2 The relationship between *D*, ε and grinding time (*t*)

t/min	0	22	90	180
D/Å	4040	2062	375	142
ε/%	0.01	0.06	0.19	0.34

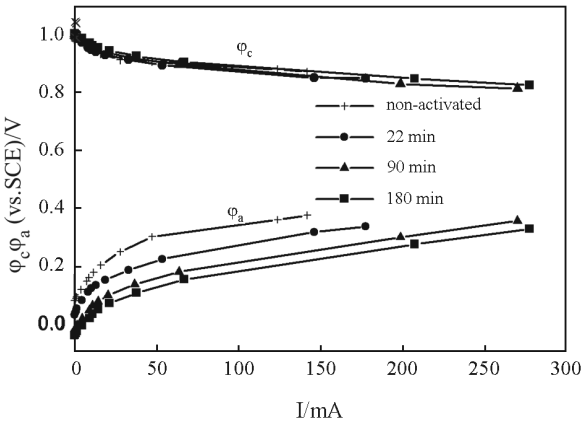

Fig. 3 Polarization curves of electrodes made of galena grinded for different time

The polarization curves of different electrodes

According to the literatures [6, 7], the mechanical grinding of mineral samples can increase their crystal lattice constant and lattice distortion as well as the degree of crystal defect, which cause the increase of Gibbs energy of formation ($\Delta_f G_m^\theta$) of mineral. The mineral in this state was so-called activated. Figure 3 shows the polarization curves of different leaching cells. The initial potential of galena electrode decreased with grinding time, and the electromotive force (*E*) was increasing. The leaching cell reaction is:

$$MnO_2(s)+4H^+(aq)+PbS(s)=$$
$$Mn^{2+}(aq)+Pb^{2+}(aq)+S(s)+2H_2O \quad (1)$$

The corresponding Gibbs free energy of leaching reaction ($\Delta_r G_m^\theta$) can be calculated via

$$\Delta_f G_m^\theta = \sum_B V_B \Delta_f G_m^\theta$$

and $\Delta_r G_m^\theta$ is decreased as $\Delta_f G_m^\theta$ of activated galena increasing. Based on the relation between $\Delta_r G$ and electromotive force (E), $\Delta_r G = -zFE$, where z is the number of electron in Eq. (1), F is Faraday constant, the electromotive force (E) of the cell increases with the decrease of $\Delta_r G$. In additional, according to $W'_{max} = \Delta_r G_{T,p}$, the energy stored in the mechanically activated process transform into electrical energy partially in electrogenerative leaching process.

The discharge process of different electrodes

The electrogenerative leaching was performed under a constant external resistance of 9.9 Ω for certain time and the discharge curves were listed in Fig. 4. It was indicated that the output current and potential increased with grinding time for different galena electrodes. The result of X-ray diffraction indicated that mechanical activation affected the surface fractal property [9], which resulted in the output current (I) of electrogenerative leaching process increase.

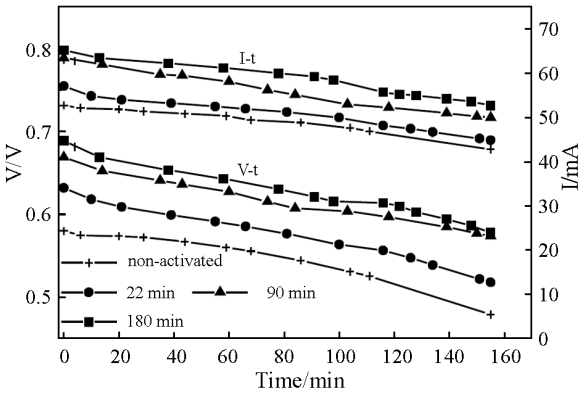

Fig. 4 Discharge curves of electrodes made of galena grinded for different time

Conclusions

Mechanical activation like grinding was favorable for elctrogenerative leaching of galena at certain extent. The activation of galena would cause more potential energy being liberated as electric work during the electrogenerative leaching process. Mechanical activation increased the lattice constant, lattice distortion as well as crystal defect degree of galena, which resulted in a decrease of initial potential of galena and an increase of output voltage. Mechanical activation affected the surface fractal property, which results an increase of the output current of electrogenerative leaching process.

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