

Correlations among factors of sulfide ores in oxidation process at ambient temperature^①

WU Chao(吴超), LI Zhi-jun(李孜军), ZHOU Bo(周勃)

(School of Resources and Safety Engineering, Central South University, Changsha 410083, China)

Abstract: Spontaneous combustion is one of the serious problems in the mining of sulfide ore deposits. The relevant factors, e. g. oxygen absorption quantity, mass increase, contents of water soluble iron ions and sulfate ion of sulfide ore samples in the oxidation process were investigated both in theory and experiment. The results from the investigation show that there is no general interpretation relation among the oxygen absorption quantity, the contents of sulfate ion and water soluble iron ions during the oxidation process of sulfide ores at ambient temperature. However, there is a linear relationship between the mass increase of the sulfide ore samples in the oxidation process at ambient temperature and the quantity of oxygen absorption. Therefore, the simple and cheap mass scaling method is suitable for predicting the oxygen absorption performance of sulfide ores at ambient temperature in place of the expensive and complicated chemical method used hitherto. Furthermore, combined with other items of breeding-fire test, the mass increase potential can also be used to predict the spontaneous combustion tendency of sulfide ores.

Key words: sulfide ore; oxidation absorption; oxidization products; spontaneous combustion; mass increase scaling method; combustion prediction

CLC number: TD 75

Document code: A

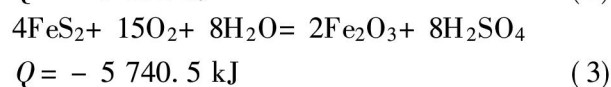
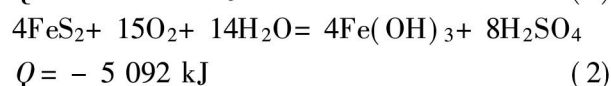
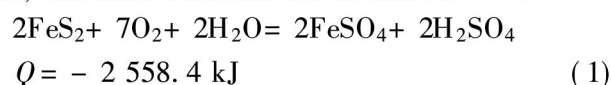
1 INTRODUCTION

It is well known that spontaneous combustion, premature detonation and dust explosion are serious problems when mining sulfide ore deposits^[1-6]. For example, outbreak of fire from the spontaneous combustion of sulfide ores in a mine can produce large quantities of toxic gases and intense heat, which pollutes the working environment, and may lead to big economic losses as well as loss of life. Therefore, it is very important to evaluate the potential for spontaneous combustion of sulfide ores before designing and mining the ore deposits. At present, the mechanism of spontaneous combustion commonly accepted is that sulfide ores undergo a slow oxidation process when exposed to moist air at ambient temperature, with emission of heat, gases and moisture. If the heat generated does not dissipate, it will increase the temperature of sulfide ores, and as the result the rate of oxidation will increase. If it proceeds unchecked, it can eventually result in the ignition of sulfide ores^[7]. Hence, it is very significant to estimate the oxidation potential of sulfide ores and to invent the effective controlling ways. There are several methods which are applicable for this purpose^[7-19]. However, all these methods are complicated and involve costly chemical analysis. For example, Ref. [7] described a complex assessing method, which includes: 1) geo-

logical investigation; 2) ore sampling; 3) mineralogy and chemical analysis; 4) ore sample crushing and physical parameter test; 5) measurements of mass increase, water soluble iron ions, sulfate ion, pH value, rate of oxygen absorption, critical temperature of accelerating self-heating, ignition point; 6) in-situ investigation of sulfide ore type distribution, mining condition analysis; 7) risk assessment; 8) control examination if necessary. Among the investigation items of this schedule, some complicated and costly chemical analysis methods are required, particularly the testing of oxygen absorption. From an economic stand point, it will be very significant if a simple and cheap test method can be devised in lieu of the chemical one.

2 THEORETICAL ANALYSIS

At ambient temperature, sulfide ores can react with oxygen and water in a given environment. For pyrite, the main reactions are as follows^[1, 19]:

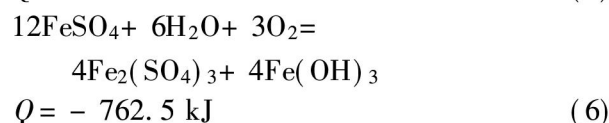
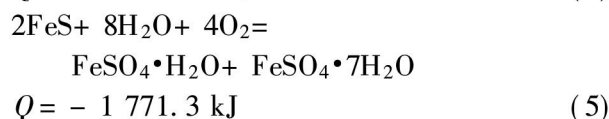
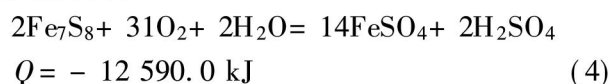


① **Foundation item:** Project(95-116-01-03-03) supported by the Ministry of Science and Technology, China

Received date: 2003 - 02 - 26; **Accepted date:** 2003 - 07 - 08

Correspondence: WU Chao, Professor, PhD; Tel: + 86-731-8876524; E-mail: wuchao@mail.csu.edu.cn

For sulfur-rich pyrite, the important reactions are as follows:



From Eqns. (1)–(6), it can be seen that at ambient temperature, no SO_2 gas or other volatile matter is released, and therefore, the mass of the sulfide ores will increase with increasing oxidation time. The more active the sample is, the larger the mass increase in the ore sample will be. A large scale field experiment, piling ore dumps in a stope, described in Ref. [15] has proved that almost no SO_2 gas is released during the oxidation process of sulfide ores at ambient temperature (usually below 40°C). However, can the mass scaling method be used to determine the oxidation speed of sulfide ore samples? What factors can be interpreted from the mass increase? These questions should be investigated in more detail by experimentation. If positive conclusions to these questions are obtained, it will be much simpler and more economical to predict the oxidation potential of sulfide ores during oxidization process at ambient temperature.

3 EXPERIMENTAL

3.1 Ore sampling

To investigate the relationship among the relevant factors of sulfide ores during oxidation process at ambient temperature and to solve the questions pointed out above, two groups of sulfide ore samples were collected from two mines (Tongguang-shan Copper Mine and Dongguashan Copper Mine in Anhui province, China, simply described by MINE1 and MINE2 below). In MINE1, out of six sulfide ore samples collected, one (No. 3) has no spontaneous combustion potential (established subsequently through tests). In MINE2, out of thirteen sulfide ore samples collected, six (samples No. 5, 8, 9, 10, 11 and 12) have no spontaneous combustion potential (established subsequently through tests also). The main chemical compositions and some significant properties of these ore samples by mineralography and chemical analysis are shown in Tables 1 and 2.

3.2 Test method

3.2.1 Measurement of mass increase, water soluble iron ions and sulfate ion of ore samples

Table 1 Chemical composition of selected sulfide ores in MINE1* (mass fraction, %)

Sample No.	Main sulfide minerals	Other sulfide minerals	Total sulfur content	Total iron content
1	FeS 95%	CuFeS ₂ 1%	35.34	56.74
2	FeS ₂ 45%, FeS 38%	CuFeS ₂ 1%	44.01	45.37
4	FeS 96.5%	CuFeS ₂ 0.5%	36.03	56.89
5	FeS ₂ 20%, FeS 72%	CuFeS ₂ 1%	38.31	49.54
6	FeS ₂ 66%, FeS 3%	CuFeS ₂ 3%, FeAsS 15%	28.22	43.57

* —Crystal size: FeS 0.15–1.0 mm; FeS₂ 0.2–0.5 mm; CuFeS₂ 0.03–0.2 mm

Table 2 Chemical composition of selected sulfide ores in MINE2* (mass fraction, %)

Sample No.	Main sulfide minerals	Other sulfide minerals	Total sulfur content/ %	Total iron content/ %
1	FeS ₂ , FeS	CuFeS ₂	31.59	54.51
2	FeS ₂ , FeS	CuFeS ₂	30.30	55.63
3	FeS ₂ , FeS	CuFeS ₂ , ZnS	32.26	56.63
4	FeS ₂ , FeS	CuFeS ₂	34.48	58.27
6	FeS ₂ , FeS	CuFeS ₂	28.23	48.95
7	FeS ₂ , FeS	CuFeS ₂	33.09	57.00
13	FeS ₂ , FeS	CuFeS ₂	27.20	47.71

* —Crystal size: FeS 0.05–0.8 mm; FeS₂ 0.05–0.6 mm; CuFeS₂ 0.02–0.3 mm; Average sulfide content: FeS 41.67%; FeS₂ 9.25%; CuFeS₂ 3.21%

The selected ore samples were reduced in size to less than $450 \mu\text{m}$ and were placed in sealed bottles. During the experiment, an ore sample weighing 40 g was placed on an evaporation glass pan with diameter of 50 mm. A group of similar ore samples were prepared and these test samples were placed in a constant humidity chamber. The temperature and relative humidity were then adjusted to approximately 40°C and 90%, respectively. Over 4 to 10 d, all the tested samples were weighed on an electronic scale with an accuracy of 0.1 mg. At the same time, the contents of the sulfate ion and the water soluble iron ions in the ore sample were also analyzed by chemical apparatus^[7, 19].

3.2.2 Measurement of oxygen absorption of ore samples

In the investigation, a given mass of sulfide ore sample weighing 100 g was placed in a sealed container which had enough space to fill a known volume of air. The container was put in an isothermal water

trough. Over a period of time, the amount of oxygen absorbed by the ore sample in the bottle was tested by an apparatus, and the total quantity of oxygen absorbed was calculated by the relevant formula. Refs. [7, 19] had given a detailed description of the experiment and the device.

3.3 Test results

The test results of the relationships between the oxygen absorption quantity, mass increase, content of water soluble iron ions, content of sulfate ion, and oxidizing time of the ore samples from MINE1 and MINE2 are shown in Figs. 1 to 10.

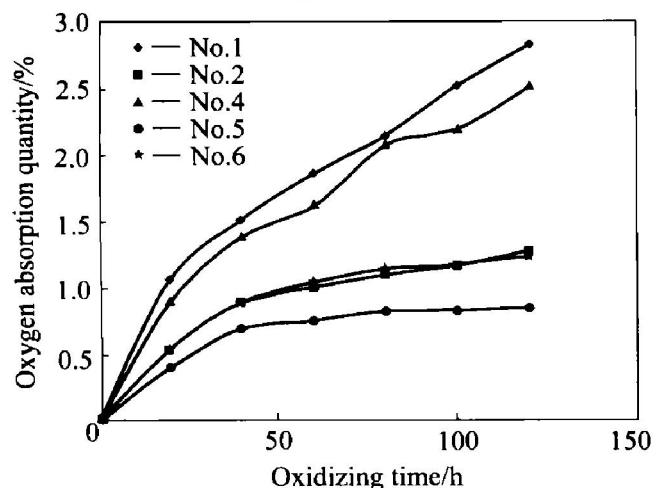


Fig. 1 Quantity of oxygen absorption by ore samples from MINE1 versus oxidizing time

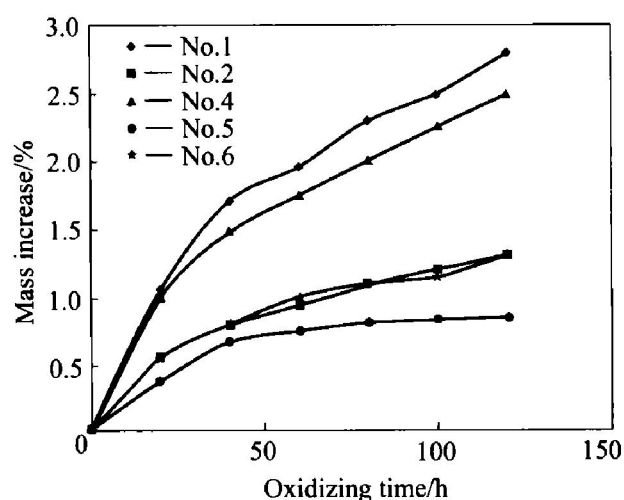


Fig. 2 Mass increase of ore samples from MINE1 versus oxidizing time

4 DISCUSSION

1) The variable tendency of the quantity of oxygen absorption vs the oxidizing time of all samples from MINE1 and MINE2 in Figs. 1 and 6 has an obvious correlation with that of the mass increase vs the oxidizing time shown in Figs. 2 and 7, respectively. The coincidence between the oxygen absorption quantity and the mass increase shows a very good linear

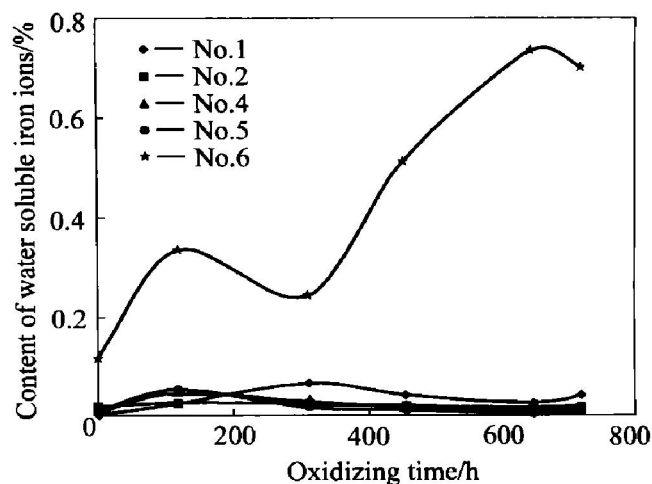


Fig. 3 Content of water soluble iron ions of ore samples from MINE1 versus oxidizing time

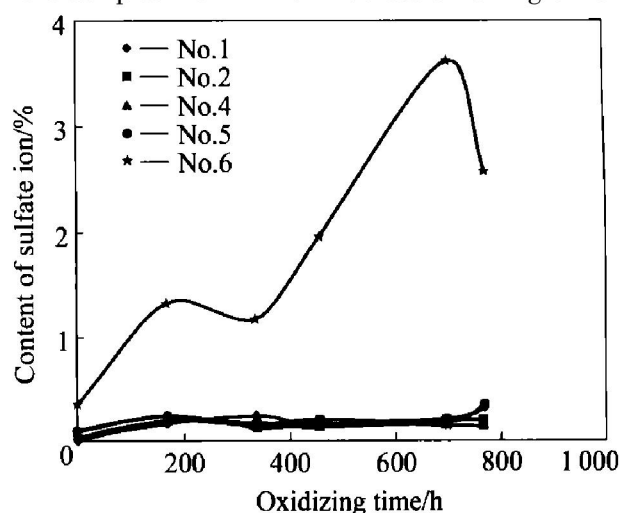


Fig. 4 Content of sulfate ion of ore samples from MINE1 versus oxidizing time

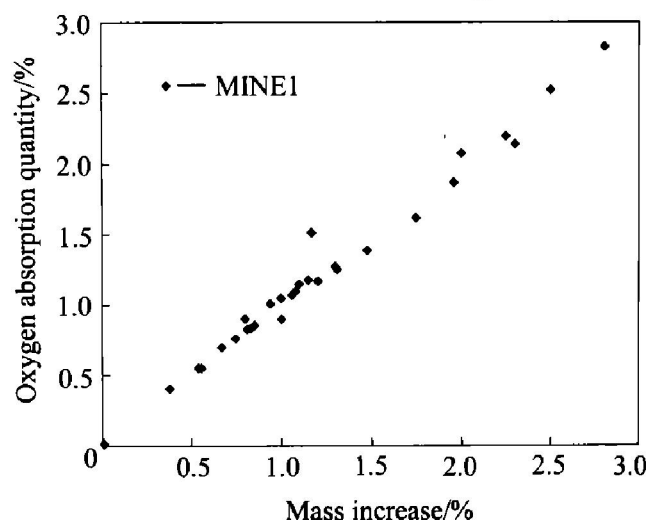


Fig. 5 Coincidence between quantity of oxygen absorption and mass increase of ore samples from MINE1

pattern of all samples from MINE1 and MINE2 (Figs. 5 and 10). The coherent coefficient reaches 0.9 by computation. These test results verify that the theoretical analysis and prediction are correct. The mass increase of the ore samples mainly depends on

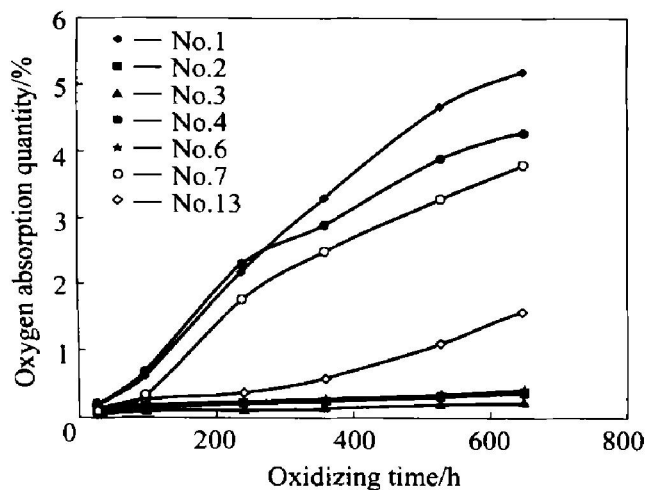


Fig. 6 Quantity of oxygen absorption by ore samples from MINE2 versus oxidizing time

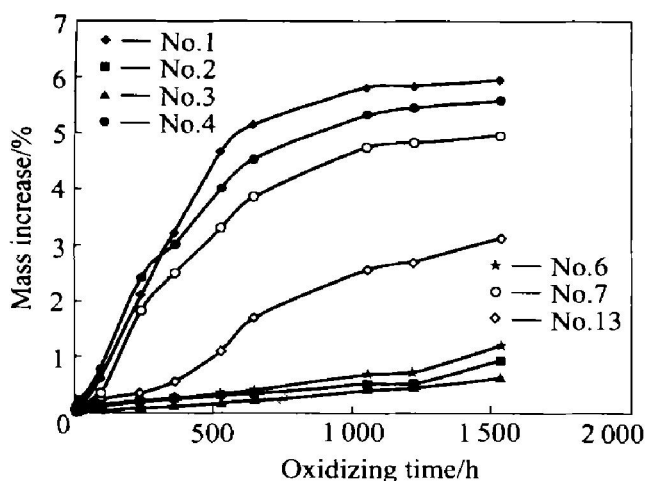


Fig. 7 Mass increase of ore samples from MINE2 versus oxidizing time

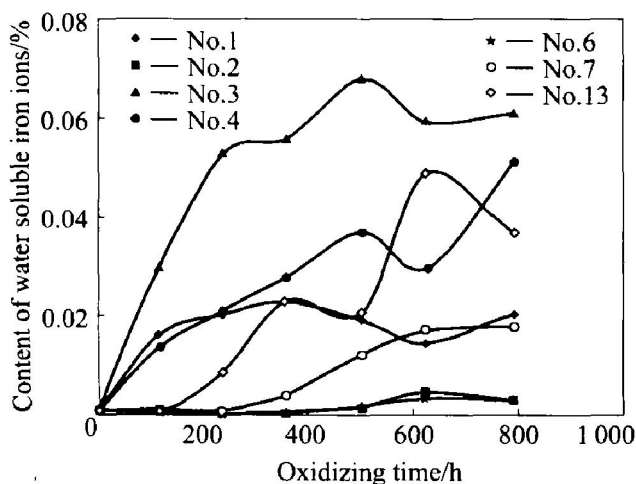


Fig. 8 Content of water soluble iron ions of ore samples from MINE2 versus oxidizing time

absorbing oxygen from the air at ambient temperature. It indicates that the mass scaling method of the oxygen absorption quantity of sulfide ore samples at ambient temperature can be used in place of the chemical test method.

2) The curves in Figs. 1 and 2 can be divided into two sections according to the oxidizing time. In

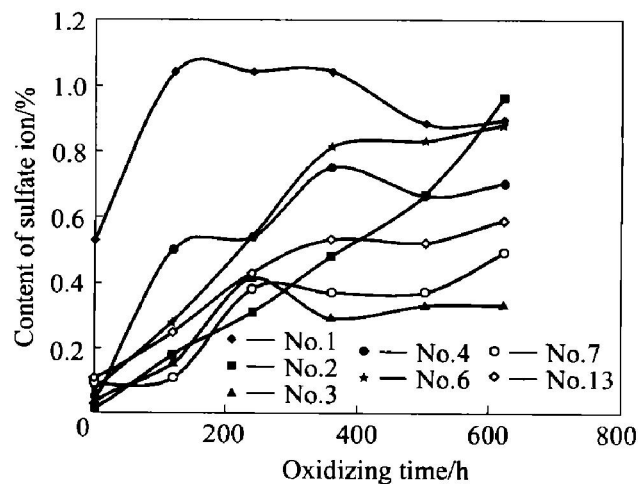


Fig. 9 Content of sulfate ion of ore samples from MINE2 versus oxidizing time

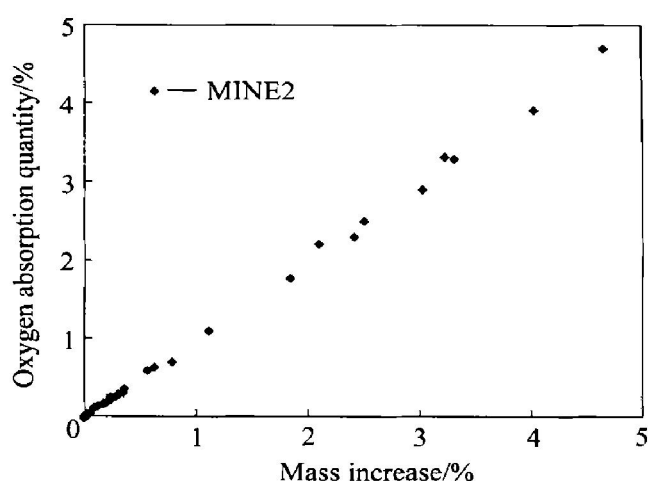


Fig. 10 Coincidence between quantity of oxygen absorption and mass increase of ore samples from MINE2

the initial period of oxidation, the oxygen absorption quantity and the mass increase increase with increasing oxidizing time in linear pattern. When the oxidizing time increases further, the slope of the linear curves decreases. The possible reason for this is that a thin layer of formed products coats the surface of the ore sample. This anti-reacts the oxidation in some way, and at the same time, the effective specific area of the ore sample is reduced. In Figs. 6 and 7, the variation of the oxygen absorption quantity vs the oxidizing time is somewhat different from that shown in Figs. 1 and 2. In the initial stage, the rate of oxygen absorption and the mass increase of the ore samples are both very slow. The possible reason is that the ore samples from MINE2 are original ores, and they need to be pre-oxidized for a period of time. During this period of pre-oxidation, some formed products are created and can accelerate the oxidation speed. For the samples No. 2, 3, 6 and 13 of MINE2, the pre-oxidized period is longer than for that of the samples No. 1, 4, 7 of MINE2. With the increasing of the oxidizing time, the rate of oxygen absorption increases quickly. However, with a further increasing of ox-

idizing time, the rate decreases as demonstrated by the curves in Figs. 1 and 2.

3) The variation tendency of all curves in Figs. 3, 4, 8 and 9 bears no regular pattern. There is no coincidence among the water soluble iron ions content, sulfate ion content and oxygen absorption quantity (or mass increase) of all ore samples. The possible reason is that some formed products during the oxidation of ore samples are almost water insoluble according to Eqns. (1) to (6), e. g. Fe^{3+} in $\text{Fe}_2(\text{SO}_4)_3$, $\text{Fe}(\text{OH})_3$, Fe_2O_3 .

5 CONCLUSIONS

At ambient temperature, the quantity of oxygen absorption of sulfide ore samples during oxidation process can be tested by mass scaling method because the coincidence between these factors is in linear pattern with good inherent coefficient. However, the water soluble iron ions content, sulfate ion content and oxygen absorption quantity (or mass increase) have no inherent correspondence with each other.

ACKNOWLEDGEMENT

The authors are greatly indebted to Professor Gour Sen of Wollongong University in Australia for editing this paper.

REFERENCES

- [1] Ninteman D J. Spontaneous oxidation and combustion of sulfide ores in underground mines[R]. Information Circular 8775. USA: Bureau of Mines, 1978. 1 - 40.
- [2] Byberg K G, Wheeland K G. Sulfide ore dust explosions —an overview[A]. Proceedings of the Special Session held at the CIM Annual General Meeting[C]. Edmonton: CIMM, 1988. 1 - 16.
- [3] Mohan S. Genesis of mine fires[J]. Journal of Mines, Metals & Fuels, 1996, 44(6): 195 - 198.
- [4] McKenzie J B. Sulfide ignition experiences at Ruttan[A]. Proceedings of the Special Session held at the CIM Annual General Meeting[C]. Edmonton: CIMM, 1988. 81 - 98.
- [5] Miron Y. Blasting hazards of gold mining in sulfide-bearing ore bodies[R]. Information Circular 9335, USA: Bureau of Mines, 1992. 1 - 10.
- [6] Miron Y, Ruhe T C, Watson R W. Reactivity of ANFO with pyrite containing weathering products[R]. Report of Investigation 8373, USA: Bureau of Mines, 1979. 1 - 24.
- [7] MENG Ting-rang, WU Chao, WANG Ping-long. Study of mine spontaneous combustion of sulphide ores[A]. Ragula B ed. Proceedings of the US Mine Ventilation Symposium[C]. Salt Lake City, UT: SME, 1993. 203 - 207.
- [8] Cranney D H. Assessing the hazards of blasting in reactive sulfide ores and the application of products to mitigate these hazards[A]. Proceedings of 28th Annual Institute on Mining Health, Safety and Research[C]. Salt Lake City: IMHSR, 1997. 111 - 117.
- [9] Pahlman J E, Reimers G W. Thermal gravimetric analysis of pyrite oxidation at low temperature[R]. Report of Investigations 9059, USA: Bureau of Mines, 1986. 1 - 15.
- [10] Rosenblum F, Spira P. Evaluation of hazard from self heating of sulfide rock[J]. CIM Bull, 1995, 88(989): 44 - 49.
- [11] Steis T E W. Sulfide ore/explosives exothermic reactions[J]. CIM Bull, 1995, 87(987): 54 - 57.
- [12] William H. Spontaneous combustion fire detection for metal mines[R]. Information Circular 9144, USA: Bureau of Mines, 1987. 1 - 25.
- [13] WU Chao. Fault tree analysis of spontaneous combustion of sulphide ores and its risk assessment[J]. Journal of Central South University of Technology, 1995, 2(2): 77 - 80.
- [14] WU Chao, MENG Ting-rang. Safety assessment technique for the spontaneous detonation of explosives in the mining of sulphide ore deposits[J]. Mining Technology, 1996, 78(902): 285 - 288.
- [15] WU Chao, WANG Ping-long, MENG Ting-rang. In situ measurement of breeding-fire of sulphide ore dumps[J]. Trans Nonferrous Met Soc China, 1997, 7(1): 33 - 37.
- [16] Pomroy W H. Spontaneous combustion fire detection for deep metal mines[R]. Information Circular 9144, USA: Bureau of Mines, 1987, 1 - 25.
- [17] Johnson G A. Spontaneous combustion fire warning systems for non-coal mines[A]. Proceedings of the US Bureau of Mines Technology[C]. Denver, Colorado, 1981. 17 - 27.
- [18] WU Chao, LI Zi-jun, ZHOU Bo, et al. Investigation of chemical suppressants for inactivation of sulfide ores[J]. Journal of Central South University of Technology, 2001, 8(3): 180 - 184.
- [19] WU Chao, MENG Ting-rang, WANG Ping-long, et al. Research on the chemical thermodynamics mechanism for the spontaneous combustion of sulphide ores[J]. Journal of Central South Institute of Mining and Metallurgy, 1994, 25(2): 161 - 167. (in Chinese)

(Edited by YANG Bing)