Prediction and Forecast of Spontaneous Combustion of Sulfide Minerals — Theory and Technology

硫化矿自燃预测预报理论与技术

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内 容 提 要

本书在阐述硫化矿自然发火本质特征的基础上，以预测预报金属矿山硫化矿自燃火灾为出发点，详细介绍了硫化矿常温氧化的行为及影响因素、自然发火机理、自燃倾向性测试技术、自燃预测数学模型、数值模拟技术、自燃危险性评价方法、自燃火灾的非接触式检测技术等方面的最新研究成果。

本书可供有关矿山设计、研究、开发和管理的科研人员、工程技术人员和现场施工管理人员等参阅，也可供高校采矿工程和安全工程等专业的研究生参考学习。

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前　言

硫化矿自然发火是金属矿山和化工矿山开采过程中可能遇到的重大灾害之一，火灾的发生将引发一系列的安全与环境问题，并且造成矿物资源的巨大浪费。硫化矿石被崩落以后，其比表面积骤然增大，矿石与潮湿空气发生氧化反应而放出热量；若反应生成的热量大于其向周围环境散发的热量，矿石温度将不断上升，直到达到自燃点，从而导致自燃火灾。随着全球矿产资源日益贫乏，矿山开采的深度必将加大，深部开采的高温问题又将加剧高硫矿山自燃火灾事故的高发。因此，开展硫化矿自燃预测预报技术研究，是有关新建矿山和延深矿山实现有效安全开采的重要工作，其研究结果可以使矿山达到避免盲目设计、节省投资、保障矿井安全生产、减少国家资源损失的目的。

作者在系统检索及深入分析前人已取得研究成果的基础上，采取理论分析与实践应用相结合的研究手段，在硫化矿石的常温氧化行为、自然发火机理、自燃倾向性测试技术、自燃预测的数学模型、数值模拟、非接触式检测技术等方面做了数年的深入研究工作。本书是在完成上述研究工作的基础上写成的。全书主要内容如下：

(1) 借助著名数据库，统计分析了国内外有关矿山自燃火灾研究的文献共计300余篇。阐述了现有解释硫化矿石自然发火的各种理论，包括物理吸附氧机理、化学热力学机理、电化学机理以及微生物氧化机理。综述了硫化矿石自燃倾向性测试技术的研究成果，着重评述了硫化矿石自燃倾向性测试的吸氧速度法、传统的交叉点温度法、动态自热率测试法、绝热氧化法、金属网篮交叉点法、综合指标测试法、程序升温氧化法等，并将各种测试方法加以分类。

(2) 从典型金属矿山采集了多个具有代表性的硫化矿石矿样，在实验室环境中模拟了各个矿样的常温氧化反应过程。综合运用X射线衍射（XRD）、电镜扫描（SEM）、能谱分析（EDAX）、傅里叶变换红外光谱（FTIR）等先进测试技术获得矿样的特征图谱，并对每一个矿样在发生氧化作用前后，宏观与微观特征的差异进行了分析。测得各个矿样在经历不同反应时间后，其氧化增重率及内部水溶性铁离子、硫酸根离子等含量的变化。系统分析了影响硫化矿石常温氧化行为的矿物晶体结构、化学成分、痕量元素的含量、环境温度、铁离

子含量、氧气浓度、空气湿度、矿样的粒度分布、环境的 pH 值、微生物以及地质条件等诸多因素。

(3) 提出了一种新的解释硫化矿石自燃的机械活化理论，认为矿山开采中施加于矿体上的各种机械力使得硫化矿石经历了机械活化作用，相应的化学反应活性得到提高，在一定的环境条件下容易发生氧化自热，最终引发自燃火灾。表征了硫化矿石在经历不同机械活化时间后，各种矿样的表观形貌、微观结构、粒度分布、比表面积、热行为等物理化学性质的差异。结果发现，硫化矿石在经历机械活化作用以后，粒度变小、比表面积增大、出现团聚效应、产生晶格畸变与晶格缺陷，且初始放热点及最大反应速率所对应的温度均有所下降；暴露在自然环境中，经历机械活化后的矿样更容易发生氧化作用。

(4) 提出了硫化矿石自燃倾向性测试的氧化动力学研究方法，自行组装了一套实验系统。基于金属网篮交叉点温度法，测试了不同类型矿样的氧化自热性质，并得到相应的氧化动力学参数。运用 TG-DSC 联合法测试了多个硫化矿石矿样的热行为，获得不同升温速率下的 TG-DTG-DSC 曲线，并找出相应的特征温度值，基于 Ozawa-Flynn-Wall 方法求得相应区间内的表观活化能值。提出运用 TG-DSC 联合法测试硫化矿石的自燃倾向性，并以获得的反应动力学参数（活化能）作为划分矿石自燃倾向性的鉴定指标。在获得多个样本的活化能值以后，新建立了硫化矿石自燃倾向性的鉴定标准，将硫化矿石的自燃倾向性等级划分为三大类，并规范了矿样的具体测试程序。

(5) 将采场硫化矿石爆堆视为多孔介质，基于传热传质学理论、达西定律、质量守恒定律、能量守恒方程等，建立了描述硫化矿石自然发火的数学模型，包括矿堆内部的风流场、氧气浓度场、温度场。基于电化学与传热学理论，推算出硫化矿石自然发火期的数学模型，并予以修正。提出了矿仓硫精矿自燃临界堆积厚度的概念，基于 Frank-Kamenetskii 自燃模型解算出高硫精矿与硫铁精矿在不同环境中的自燃临界堆积厚度。综合考虑了影响硫化矿石爆堆自燃的各种因素，将未确知测度理论应用于矿石爆堆的自燃危险性评价中，该方法解决了硫化矿石爆堆自燃危险性评价中诸多因素的不确定性问题，并能进行定量分析。

(6) 采用室内测试与理论分析相结合的研究方法确定了硫化矿石自燃数学模型中的重要参数，包括矿石的放热强度、导热系数、耗氧速率、矿石堆的孔隙率、渗透系数等。运用 ANSYS 与 FLUENT 等数值分析软件对硫化矿自然发火的数学模型进行解算，揭示出不同矿样的动态自热规律、采场硫化矿

石爆堆（硫精矿堆）在某个时刻的风流场、氧气浓度场、二氧化硫浓度场，以及温度场的分布规律，可以指导有自燃倾向性的硫化矿矿山的现场防灭火工作。

（7）运用 Raytek 红外测温仪与 Center 接触式测温表同时测定了三种不同类型矿样（粉状、小块、大块）的表面温度；找出了红外测温仪在不同感温距离、不同感温角度、不同环境条件、不同类型矿堆等参数条件下，感温读数与矿堆实际温度之间的变化规律；揭示了硫化矿堆自燃非接触式检测中各种测量误差的产生机理。开展了实验仪器配套装置的改进研究，并应用于典型金属矿山自燃火灾的检测中，验证了所选仪器的适用性。

作者在开展本项目研究和撰写本书过程中得到了许多人的帮助，在此首先要特别感谢中南大学安全与环保研究所的有关老师和研究生，感谢李孜军副教授、胡汉华教授等的关心与指导，感谢毛丹硕士、汪发松硕士、郄军芳硕士等参与了部分实验工作。书中引用了大量国内外有关矿山自燃研究的专业文献，谨此向所有参考文献的作者们表示感谢！本书的部分研究背景源于国内冬瓜山铜矿、银家沟硫铁矿等矿山，感谢这些单位及相关工作人员的大力支持。最后，还要感谢国家科技支撑计划课题资助（2006BAK04B03）、国家自然科学基金项目资助（51074181）、教育部博士生学术新人奖专项资助（1343-71134001011）、中南大学优秀博士学位论文扶植项目资助（2009yb047）等为本项目的研究和本书的出版提供的经费支持。

由于作者水平所限，书中的某些内容与观点还有待进一步研究和完善，不足之处在所难免，敬请各位读者批评指正！

作　者

2011 年 10 月

Foreword

Spontaneous combustion of sulfide minerals is one of the most serious disasters in the mining of metal and chemical mines. Once a fire is initiated in stored sulfide ores or concentrates, the disaster will lead to a series of environmental and safety problems, and losing large quantities of mineral resources. When sulfide ore deposit exploited and exposed to air for a period of time, sulfide minerals will begin chemisorbing oxygen and oxidizing, releasing lots of heat. If the rate of heat generation in sulfide mineral stockpiles exceeds that of heat removal from the boundaries, the heat accumulates and their temperature rises gradually, and the oxidizing reaction will accelerate, up to the auto-ignition point. With the mineral resources becoming poorer over the world, the mining depth will be increased. The high environmental temperature in deep mines will aggravate spontaneous combustion of sulfide ores. Therefore, predicting and forecasting spontaneous combustion of sulfide minerals are the prerequisits for new mines to avoid blind design, save investment, keep safe mining, and reduce resource loss.

By referring to and analyzing many former research fruits about spontaneous combustion hazard in mines, a lot of study work has been made by combining theoretical analysis with practical application, aiming at the oxidation behavior of sulfide ores under ambient environment, the mechanism of spontaneous combustion, the test method and standard for evaluating spontaneous combustion tendency of sulfide minerals, mathematical models and simulations, non-contact measuring of temperature in metal mines. The main study contents and conclusions of the book are as follows:

(1) Based on several famous databases over the world, about 300 papers toward spontaneous combustion in mines were consulted and analyzed. The current mechanisms on spontaneous combustion of sulfide minerals were discussed systematically, including the physical oxygen adsorption theory, chemical thermodynamics mechanism, electrochemistry mechanism, and bio-oxidation theory. Also, the test methods for spontaneous combustion tendency appraisal of sulfide minerals were set forth, including oxygen-adsorption velocity test, traditional crossing-point temperature test,

adiabatic oxidation test, comprehensive test, new wire-mesh basket method, temperature programmed oxidation method, etc.; these methods were classified by their intrinsic characteristics.

(2) Several representative sulfide ore samples were obtained from typical metal mines. The oxidation process of each sample at ambient temperature was simulated in the laboratory. The colors, agglomeration properties, microstructures, chemical compositions, and mineralogical analysis of each sample before and after the oxidation were compared by scanning electron microscope (SEM), Energy Dispersive Spectrometry (EDAX), X-ray diffraction analysis (XRD), and Fourier Transform Infrared Spectroscopy (FTIR). The weight increment rate of each sample and the contents of water soluble iron and sulfate ions at different time were also measured. Furthermore, the main factors affecting the oxidation of sulfide ores were identified, including the crystal structure, chemical compositions, trace metal content, environmental temperature, oxygen concentration, air moisture, particle size, environmental pH value, ferric iron ion, bacteria, geological conditions, etc.

(3) A new theory of mechanical activation for explaining spontaneous combustion of sulfide minerals was put forward, in which the chemical reaction activation of sulfide ores was considered to be heightened by all kinds of mechanical forces during the mining. The apparent appearances, microstructures, particle sizes, specific surface areas, and heat behaviors of activated samples were characterized by advanced apparatuses. It is found that sulfide ores after mechanical activation show many evident changes with decreased particle sizes, increased specific surface areas, agglomeration phenomenon, defect and deformation of lattice structure, and lower temperatures for the initial heat release and self-ignition points. At ambient environment, the activated samples are more susceptible to being oxidized.

(4) The oxidation kinetics test method for spontaneous combustion tendency of sulfide minerals was advanced. Based on the new wire-mesh basket crossing-point temperature (CPT) method, an experimental system was assembled to gain oxidation and self-heating properties of three different sulfide minerals, and corresponding oxidation kinetics parameters were calculated. The combination of thermogravimetry (TG) with differential scanning calorimeter (DSC) was applied to test sulfide ores, and the TG-DTG-DSC curves for each sample at different heating rates were gained. By the peak temperatures on DTG curves, the whole reaction process of each

sample was divided into different stages, and the corresponding apparent activation energies were calculated using the Ozawa-Flynn-Wall method. Furthermore, activation energy value was considered to be used as the index for evaluating spontaneous combustion tendency. A new appraisal system for assessing spontaneous combustion tendency of sulfide minerals was built, and the concrete test procedure was also regulated.

(5) Sulfide ore stockpile in stope was seen as porous media, and the mathematical models for describing the dynamic process of spontaneous combustion of sulfide minerals were deduced by the theories of heat and mass transfer theory, Darcy Law, conservation of mass and energy laws, etc. Also, the mathematical formulas for calculating spontaneous combustion period of sulfide minerals were improved. The concept of critical accumulative thickness for spontaneous combustion of sulfide concentrates in storage was put forward; the corresponding critical values for each sample under different environmental temperatures were gained by Frank-Kamenetskii model of spontaneous combustion. Furthermore, considering the main factors that influence spontaneous combustion of sulfide ores in stope, the uncertainty measurement theory was applied to evaluate the spontaneous combustion hazard, which can solve the uncertainty problems in spontaneous combustion assessment of sulfide ores and can analyze the problems quantitatively.

(6) The combination of experimental test and theoretical analysis was used to obtain several important parameters in the mathematical models of spontaneous combustion, including the heat release intensity, heat conductivity coefficient, oxygen consumption rate, porosity of ore piles, osmosis coefficient, etc. Combining with the locale boundary and initial conditions in stope, FLUENT and ANSYS softwares were applied to simulate the air flow field, SO_2 and O_2 concentration fields, and dynamic temperature fields of typical metal mines that had serious spontaneous combustion phenomenon, and the simulation results were used to direct the fire control work effectively.

(7) The surface temperatures of diverse sulfide minerals samples were measured simultaneously by Raytek infrared thermometer and Center tangent thermometer. The relationship between the sensing data of the infrared thermometer and the actual surface temperature with various measuring distances, measuring angles, mineral types, and environmental conditions were investigated. Also, how the measuring errors come

in bad conditions during practical applications were analyzed systematically. The improved instruments adopted in the laboratory were utilized to measure the temperature of sulfide ores and concentrates on locale, and had good effects.

The research work in this book has been supported financially by several important projects, such as the National Science and Technology Pillar Program during the 11th Five-Year Plan Period of China (2006BAK04B03), the National Natural Science Foundation of China (51074181), and the Scholarship Award for Excellent Doctoral Student Granted by Ministry of Education of China (1343-71134001011), etc. The authors greatly appreciated much help of the other relevant researchers of the project group and would like to acknowledge Associate Professor Li Zi-jun, Professor Hu Han-hua, and graduate students Mao Dan, Wang Fa-song and Qie Jun-fang for a part of experimental work. At the same time, lots of references on spontaneous combustion in mines are cited in this book, so the authors would like to aoknowledge all the references' authors. Moreover, the authors would like to acknowledge some workers in Anhui Tongling Dongguashan Copper Mine and Henan Lingbao Yinjiagou Iron Sulfide Mine for their support in the locale work.

Since some contents and viewpoints maybe need to be furtherly studied and complemented, corrections and suggestions are warmly welcomed.

The Authors
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