Research Article

Nonlinear Determination Method for Self-Heating Initiative Temperature of Sulfide Ores

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Abstract

The purpose of this article is to explore a new method to determine the self-heating initiative temperature of sulfide ores for preventing spontaneous combustion of sulfide ores. Two typical ore samples with self-heating characteristics are studied by wavelet transform, recursive graph analysis, Hurst index extraction, and approximate entropy detection. On this basis, self-heating initiative temperature of sulfide ores was measured. The results indicate that the Hurst index of both ore samples in the experiment is greater than 0.5; moreover, the Hurst index in the later period of the experiment is greater than that of the earlier period. The self-heating of sulfide ores is an unsteady process with positive persistence and obvious mutation, so the possibility of self-heating of sulfide ores can be determined according to the change characteristics of Hurst index. The mutation times of the two samples are 864 min and 819 min, respectively, reference values of self-heating initiative temperature are 219.4°C and 232.3°C, and the average relative error is only 1.49%, which are in good agreement with the measured values, and therefore, it provides basis for safety production of high-sulfur ore mine.

1. Introduction

Moist sulfide ores are usually easy to oxidize when there is oxygen in the air; the oxidation reaction is exothermic; if the reaction heat is not dissipated to the external environment completely, the temperature of the sulfide materials will increase; that is called self-heating [1–3]. Sulfide ores are always exposed to oxygen in the air rather than to any external heating during mining, mineral processing, storage, and transportation of related sulfide materials; this will eventually lead to serious potential hazards [3–8]. For example, when pyrite (FeS2) is in contact with air and water, the following reactions will occur:

\[
\begin{align*}
2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} & = 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 - 2558.4\text{kJ} \\
4\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 + \text{O}_2 & = 2\text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O} - 393.3\text{kJ} \\
12\text{FeSO}_4 + 3\text{O}_2 + 6\text{H}_2\text{O} & = 4\text{Fe}_2(\text{SO}_4)_3 + 4\text{Fe} (\text{OH})_3 - 762.5\text{kJ}
\end{align*}
\]

(1)

The self-heating initial temperature of sulfide ores is a comprehensive evaluation index of spontaneous combustion tendency of sulfide ores [9]. Once the self-heating of sulfide ores occurs, the spontaneous combustion fire will occur when the temperature of ore heap reaches the ignition point of ore. The prevention and control on spontaneous combustion of sulfide ores are always the main safety problem for sulfide ore deposits. It is very important to exactly measure the spontaneous combustion tendency of sulfide ores in order to protect the safety of miners’ life, maintain the normal production of mine, and make good utilization of the natural resources [10–14].

According to the existing research literature about spontaneous combustion of sulfide ores, it can be found that spontaneous combustion tendency evaluation is a research hotspot. Thus, researchers have done a lot of studies on the self-heating characteristics of sulfide ores. Methods to identify the potential for self-heating of sulphides have been proposed [15–21], such as evaluation model based on entropy and set pair analysis theory [22], matter-element
model [23], apparent activation energy method [24], uncertainty measurement model [25], and fisher discriminant analysis method [26]. In addition, Payant et al. [27] verified the hypothesis that galvanic interaction between some sulfide ores could accelerate self-heating effect; Somot and Finch [28] confirmed that a high pyrrhotite content could provide a more reducing environment favouring formation of hydrogen sulfide; Yang and Wu [29] found that exothermic reaction activity of sulfide ores is enhanced by all kinds of mechanical forces through the mechanical activation experiment.

Regrettably, as the self-heating experiment in laboratory is affected by multiple factors, such as ores particle size, ores moisture content, especially the heating rate of automatic heating incubator, the accuracy of self-heating initiative temperature measurement results needs to be validated. Therefore, self-heating initiative temperature becomes an important index for the evaluation of spontaneous combustion possibility of sulfide ores. Because of that need, it is worth studying to identify the mutation point in the process of self-heating and determine the reference value of the initiative temperature of self-heating by using the non-linear theory. Previous studies have shown that the self-heating of sulfide ores is a non-linear and unsteady evolution process. Li et al. [30] put forward a rheology and mutation model for spontaneous combustion of sulfide ore; Pan et al. [31] concluded that the self-heating process of sulfide ores can be divided into two stages, slow oxidation stage and rapid oxidation stage, and verified the conclusion through experiment.

In this study, we measured two typical sulfide ore samples; after extracting information from the measured temperature series based on wavelet analysis, the research series of ore samples are analyzed by using recurrence plot analysis, Hurst exponent extraction, and approximate entropy detection methods. Consequently, we proposed a new determination method for self-heating initiative temperature of sulfide ores based on non-linear theory and repeated the experiments to verify the accuracy of the conclusions in this paper.

2. Self-Heating Experiment

2.1. Experimental Materials. We used the multi-point sampling method to collect sulfide ore samples from a mine in China. According to the statistics in recent years, many spontaneous combustion cases have occurred: in 2004, when mining in the 910 layer, spontaneous combustion phenomenon is observed in the ores; in September 2007, fire areas expanded significantly. Consequently, the mine is forced to stop mining the orebody II.

In this experiment, two kinds of typical samples with self-heating tendency, named sample A and sample B, are selected as experimental materials; Figure 1 illustrates the typical micrograph of sulfide ores. Mineralogical analysis results indicate that the typical metal mineral of the ore samples is pyrite. The pyrite crystals are subhedral, euhedral, or cube-like, the maximum particle size of pyrite is about 3 mm, and the average particle size is about 1 mm. There are also a small amount of quartz and other gangue minerals found in the micrograph of the ore samples.

By means of chemical composition analysis, it is found that average sulfur content of the two samples is 41.77%, greater than the average value of the mine (29.41%). Sulfur content in sulfide ore is the decisive factor of spontaneous combustion of sulfide ore [32, 33]. Therefore, both of sample A and sample B belong to the ore prone to spontaneous combustion.

2.2. Experimental Scheme. At room temperature, sulfide ores could slightly oxidize; in order to speed up the oxidation process, ore samples are put into the reactor in the automatic heating incubator. Self-heating initiative temperature of sulfide ores is defined as the minimum ambient temperature that can lead to rapid oxidation of sulfide ore [34]. If there is an obvious self-heating tendency in the ore samples, the temperature of the ore sample can increase rapidly and eventually exceed the ambient temperature of the automatic heating incubator. The crossing point temperature is determined as self-heating initiative temperature of ore sample, the main experimental parameters are listed in Table 1, and the experimental device is shown in Figure 2.

2.3. Experimental Results. It can be found from Figure 3 that the self-heating initiative temperatures of the two samples are 219.7°C and 239.1°C, respectively. According to the definition of self-heating initiative temperature and the measured self-heating curves of the two samples, we can find that both samples have obvious self-heating phenomenon and the corresponding self-heating initiation time is 855 min and 867 min, respectively.

3. Research Methods

Four main research methods, including wavelet transform [35], recurrence plot analysis [36], Hurst exponent extraction [37], and approximate entropy detection [38], are adopted in this work. Wavelet transform is used to remove the influence of automatic heating incubator on self-heating process of sulfide ores. Through recurrence plot analysis, mutation characteristics of self-heating of ore samples are identified qualitatively. By comparing the Hurst exponent of the earlier period and the later period during self-heating
experiment, mutation characteristics of self-heating are quantitatively identified. With the approximate entropy detection method, the mutation points and reference values of self-heating initiative temperature are determined. \( x_{Z_{he}} \) is the key of wavelet analysis to select the appropriate wavelet function. Firstly, different wavelet functions are used to decompose the corresponding sequence of each measuring point into two parts: low frequency and high frequency. Then, the eigenvalues \( (C_v, r_1) \) of the low-frequency reconstruction sequence and the original sequence are compared, and if the selected wavelet function is appropriate, the eigenvalues between the low-frequency reconstruction sequence and the original sequence should conform to the following criteria:

1. Because the complex information in the self-heating process of ore heap is removed, the \( C_v \) value of low-frequency reconstruction sequence should be reduced compared with the original sequence.

2. The interference of complex information in the self-heating process of ore heap will weaken the correlation of the original sequence. After eliminating these interferences, the \( r_1 \) value of low-frequency reconstruction sequence should be increased.

According to the main characteristic values of the corresponding series in Figure 5, it can be seen from the results of wavelet function optimization that the wavelet function bior3.1 is suitable for samples temperature measurement series. Obviously, both for the two samples, the autocorrelation coefficient \( r_1 \) of low-frequency reconstructed series is greater than that of the original series, but the variation coefficient \( C_v \), of low-frequency reconstructed series is less than that of the original series (because interference of the complicated self-heating information will weaken the correlation of the original series, resulting in the increase of degree of change).

Through wavelet decomposition and reconstruction with bior3.1, research series of the two samples are obtained. Wavelet transform for the measured temperature increment series of the two samples is displayed in Figure 6. It is found that, compared with the original series, research series have more complex details and show sharp fluctuations.

### 4. Calculation Results Analysis

#### 4.1. Wavelet Transform of the Measured Temperature Series

Wavelet analysis is derived from the expansion and translation of functions; it is the direct result of the development of Fourier analysis, Gabor analysis, and short-term Fourier analysis. For any signal function of Fourier analysis, Gabor analysis, and short-term Fourier analysis of functions; it is the direct result of the development of wavelet analysis is derived from the expansion and translation of functions. Wavelet analysis is developed from wavelet functions.

#### 4.2. Recurrence Plot Analysis

The reconstruction of phase space is the basis for the analysis of recurrence plot for nonlinear time series. According to the embedding theorem proposed by Takens [40], the phase space of non-linear time series \( X_i \) is reconstructed by selecting appropriate time delay \( \tau \) and embedding dimension \( m \). At this time, the reconstructed phase space is equivalent to the original dynamic system and has the same topological structure.

Taking any sequence \( \{x_i\} \) as an example, the reconstructed phase space elements are as follows:

\[
X_i = \{x_i, x_{i+\tau}, \ldots, x_{i+(m-1)\tau}\}, \quad i = 1, 2, \ldots, N.
\] (3)

In this formula, \( m \) is the embedding dimension; \( \tau \) is the delay time; \( N = n - (m - 1) \) is the reconstructed phase number; and \( n \) is the sequence length.

From the equation, the trajectory of the dynamic system in the reconstructed phase space is obtained as follows:

\[
X_1 = (x_1, x_1+\tau, \ldots, x_{1+(m-1)\tau}),
X_2 = (x_2, x_{2+\tau}, \ldots, x_{2+(m-1)\tau}),
X_3 = (x_3, x_{3+\tau}, \ldots, x_{3+(m-1)\tau}),
\]

\[
X_N = (x_N, x_{N+\tau}, \ldots, x_{N+(m-1)\tau}).
\] (4)
When reconstructing the phase space, the complex autocorrelation method is used to determine the delay time. The \( m \)-dimensional depolarization complex autocorrelation method is defined as follows [41]:

\[
C_{xx}^{m}(\tau) = \frac{1}{n}\sum_{i=1}^{n}\sum_{j=1}^{m-1}\left\{ [x_i - \bar{x}][x_{i+j\tau} - \bar{x}] \right\}
\]

(5)

\[
= \frac{1}{n}\sum_{i=1}^{n}\sum_{j=1}^{m-1}x_i x_{i+j\tau}. \quad \text{The first zero of } C_{xx}^{m}(\tau) \text{ is selected as the delay time } \tau.
\]

The analysis steps of recurrence plot analysis are as follows [42]:

1. Let the reconstructed phase space elements be

\[
X_i = \{x_i, x_{i+\tau}, \ldots, x_{i+(m-1)\tau} \}, \quad i = 1, 2, \ldots, N,
\]

(6)

where \( m \) is the embedding dimension; \( \tau \) is the delay time; \( N = n - (m - 1)\tau \) is the reconstructed phase number; and \( n \) is the sequence length.

2. Calculate the distance between \( X_i \) and \( X_j \): \( \delta_{ij} = X_i - X_j \).

3. Given a distance \( r \), when \( \delta_{ij} < r \), make a point at \( (i, j) \), and the resulting graph is called recurrence plot.

According to the definition of recurrence plot, it describes how the reconstructed trajectory recurses or repeats itself, and reveals the time related information of the system. Based on the complex autocorrelation method, the delay time \( \tau \) of the standardized sequence is calculated. According to the theory of phase space reconstruction, the dimensional phase space \( m \) of the sequence is reconstructed. The basic idea of estimating the optimal delay time \( \tau \) is to make the reconstructed phase space vector component \( x_i, x_{i+\tau} \) independent of each other and not completely unrelated, so that they can become independent coordinates in phase space.
Appropriate delay time is critical to recurrence plot analysis. In this research, delay time of the two samples is determined based on the modified autocorrelation function method [43]. The calculation results of delay time are shown in Figure 7. It can be found that autocorrelation function values of the two samples change from positive to negative when delay time increases from 3 min to 6 min, which indicates that their correlation trends have changed during this period. According to the determination criterion, the optimal delay time of the two samples is equal to 3 min.

The recurrence plots of the two samples are demonstrated in Figure 8. It is clear that self-heating process of sulfide ores contains mutation structures because there are large areas of white blocks or bands in recurrence plots. Compared with sample B, mutation structure of sample A is more complicated. The possible reason is that self-heating initiative temperature of the sample A is relatively low. Under the same experimental conditions, complexity of the self-heating process of sample A is more than that of sample B.

4.3. Hurst Exponent Analysis. Hurst exponent is an indicator of temporal sequential correlation and trend intensity. By comparing Hurst exponents of different periods, the unsteady self-heating process of sulfide ores can be quantitatively identified.

The Hurst exponent calculation results of the two samples in some periods are shown in Figure 9, where R/S and n are separately average rescaled range and subinterval length. The slope of the fitting line in the figure is the calculation value of Hurst exponent. It is found that all the Hurst exponents are more than 0.5. According to the definition of Hurst exponent [44] ($H < 0.5$ refers to the time series which can be described by random walk “Brownian motion”; $0 < H < 0.5$ refers to the weakening of memory/anti-persistence, that is, the process of mean reversion; $0.5 < H < 1$ refers to memory enhancement/persistence, that is, the time series of long-term memory), it can be concluded that self-heating process of sulfide ores has a positive continuity, which accords with the positive acceleration.
characteristics of self-heating reaction. It is also found that Hurst exponent of the later period is generally greater than that of the earlier period, especially in 750–897 min; the Hurst exponent increases of the two samples are 20.86% and 5.31%, respectively. This is because ores temperature increases with time in self-heating experiment, which accelerates the self-heating and leads to the increase of positive correlation. Thus, the self-heating possibility of sulfide ores can be determined based on the variation characteristics of Hurst exponent. If Hurst exponent increases with time during the self-heating experiment, it means that the oxidation rate of sulfide ores can be accelerated and finally ores can produce obvious self-heating under the heating condition; otherwise, it means that ores cannot show obvious self-heating tendency.

4.4. Approximate Entropy Detection. To obtain the mutation point and reference value of self-heating initiative temperature of each sample with approximate entropy detection method, the sliding window width and sliding step length are set as 297 min and 3 min, respectively.

Figure 10 illustrates mutation detection results of the two samples. It is clear that there are obvious mutation points on the approximate entropy curves. It is also found that approximate entropy changes irregularly at slow oxidation stage. The reason is that ambient temperature of the automatic heating incubator at this stage is not enough to induce sulfide ores to produce rapid self-heating. Ores self-heating effect is not significant so that the complexity change shows the sign of fluctuation. At rapid oxidation stage, the reason why the approximate entropy increases first and then decreases is that, in the early stage of rapid oxidation, the oxidation rate of sulfide ore increases rapidly due to the energy accumulation and activation. Ores temperature reaches the critical value of rapid self-heating. Therefore, the system complexity increases gradually at the later stage of rapid oxidation; as the surface of ore particles has been oxidized, the system complexity reduces gradually. So, it can be inferred that the complexity trend of oxidation process of sulfide ores includes three stages: relatively stable stage, gradually increasing stage, and gradually decreasing stage. At the gradually increasing stage, sulfide ores generate obvious self-heating.

For each sample, ambient temperature of the automatic heating incubator at mutation time is taken as the reference value of self-heating initiative temperature. Comparisons of the reference and measured values of self-heating initiative temperature are listed in Table 2. It is found that the reference values are consistent with measured values, and the average relative error is only 1.49%. Therefore, it is feasible to use the method based on non-linear theory to determine the self-heating initiative temperature.

5. Discussion

Finding the crossing point accurately is the key to determine self-heating initiative temperature of sulfide ores. But actually ores temperature usually cannot exceed the ambient temperature in the experiment because of the low heat liberation and other influencing factors. In this case, self-heating experiments will be carried out several times under fine-tuned experimental conditions. For those sulfide ores without self-heating tendency, repeated experiments will result in a great deal of waste of manpower and material. Moreover, the difference of heating rate has certain effect on the measured results. For instance, when the heating rate is overtrop, the ore temperature is usually lower than the ambient temperature. Consequently, the measured self-heating curves often have no crossing point even if the self-heating initiative temperature could be measured; it is usually greater than the actual value. When the heating rate is too low, the samples might be completely oxidized at slow oxidation stage. Under the circumstances, obvious self-heating phenomenon usually cannot appear in the sulfide ores. For example, when the average heating rate is 0.3°C·min⁻¹, 0.5°C·min⁻¹, 0.8°C·min⁻¹, and 1.3°C·min⁻¹ in this experiment, there are no crossing points on the measured self-heating curves of the two samples. Thus, self-heating initiative temperature of the two samples could not be measured in this case.

From the view of complexity variation in self-eating process, the non-linear method to determine the reference value of self-heating initiative temperature of sulfide ores is put forward in this work. This method includes three steps: first, preprocessing of the measured temperature series based on wavelet technology, which could eliminate the influence of automatic heating incubator on self-heating process of sulfide ores to a certain extent; second, mutation identification of self-heating process with recurrence plot method and Hurst exponent method, which could identify the ore samples without self-heating tendency and reduce workload of repeated experiments; third, mutation detection of self-heating process using approximate entropy method, which could obtain the mutation time and reference value of self-heating initiative temperature. The practical application
Figure 8: Recurrence plots of ore samples: (a) sample A; (b) sample B.

Figure 9: Continued.
\[
\ln \left( \frac{R}{S} \right) = 0.6535 \ln n - 0.3568 \\
(R^2 = 0.9536)
\]

\[
\ln \left( \frac{R}{S} \right) = 0.7190 \ln n - 0.5385 \\
(R^2 = 0.9706)
\]

- **Figure 9:** Hurst exponent calculation results of ore samples in some periods: (a) 0~147 min; (b) 150~297 min; (c) 300~447 min; (d) 450~597 min; (e) 600~747 min; (f) 750~897 min.

- **Figure 10:** Continued.
indicates that the non-linear determination method has a higher determination precision and can be used to validate the reliability of the measured results. Furthermore, so far as we know, this is a new determination method for self-heating initiative temperature of sulfide ores.

However, it should be noted that self-heating process of sulfide ores is influenced by many factors. To verify the universality of the results of this work, multi-sample experiments study under different experimental conditions will be our next tasks.

6. Conclusions

(1) Qualitative and quantitative identification of mutation indicate that self-heating of sulfide ores is an unsteady process. For sample A and sample B, all the Hurst exponents of different periods are more than 0.5, which indicates that self-heating process of sulfide ores has a positive continuity. Hurst exponent of the later period is greater than that of the earlier period during the experiment. Thus, the self-heating possibility of sulfide ores can be determined according to the variation characteristics of Hurst exponent.

(2) Mutation detection results show that the mutation times of sample A and sample B are 864 min and 819 min, respectively. Correspondingly, reference values of self-heating initiative temperature of the two samples are 219.4°C and 232.3°C, which are in good agreement with the measured values with the average relative error of 1.49%. Thus, the new determination method for self-heating initiative temperature of sulfide ores based on non-linear theory can be used to verify the reliability of the measured results.

(3) The non-linear determination method is applied to the measurement of the self-heating initiative temperature of sulfide ores, which can accurately and intuitively reflect the three stages of the self-heating of sulfide ores. It shows that the practicability and reliability of this method is of great significance to improve the theoretical and practical level of the early prevention of spontaneous combustion of sulfide ores and even to achieve the prevention and control of spontaneous combustion of sulfide ores.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare no conflicts of interest.
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