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Risk Assessment Method for Spontaneous Combustion of Pyrophoric Iron Sulfides

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Abstract: Pyrophoric iron sulfides (PISs) can spontaneously oxidize and release heat when they come into contact with air, resulting in fire and explosion accidents. In order to reduce the risk of spontaneous combustion, risk assessment methods need to be developed. In this paper, the preparation experiment and oxidation experiment of PISs are carried out to obtain the data of solid phase temperature and time, and the temperature–time curve is drawn. Based on the risk assessment method of thermal runaway and the oxidation experiment law of PISs, the risk assessment index system of spontaneous combustion is established, and the possibility and consequence severity of spontaneous combustion are classified. On this basis, the risk assessment matrix is used to determine the risk level of spontaneous combustion, and the risk assessment method of spontaneous combustion of PISs is established. Finally, nine groups of different oxidation processes of PISs are used to verify that the method is reasonable and effective.

Keywords: pyrophoric material; spontaneous combustion; risk assessment matrix

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1. Introduction

Pyrophoric iron sulfides (PISs) are widely distributed in oil and gas exploitation, transportation, storage, and refining equipment. When it comes into contact with air, it can spontaneously oxidize and release heat, ignite the surrounding flammable substances, cause fire and explosion accidents, and seriously threaten the safe production of fossil energy industry. Risk assessment of spontaneous combustion of PISs is the critical way to better prevent accidents in the industrial field and provide a solid scientific basis and technological support for global and regional sustainable safety [1]. At present, there are few studies on the risk assessment of oxidation and spontaneous combustion of PISs, and related risk assessment methods are even fewer. Therefore, it is the top priority of current research to propose an effective risk assessment method for the spontaneous combustion characteristics of PISs.

Metal corrosion usually occurs on the inner walls of crude oil tanks, transportation equipment, and refining equipment, and ferrite compounds are thereby generated. These substances can react with active sulfur, such as H_2S in crude oil to form PISs that are insoluble in water [2], and the main components are FeS, FeS_2, Fe_2S_3, Fe_3S_4, and Fe_7S_8. Regardless of whether or not formed under high temperature and high pressure or normal temperature and pressure, PISs would spontaneously ignite when exposed to wet oxygen [3]. Generally, the content of FeS_x ($0 < x < 2$) is determined by equipment material, inner wall coating, operation processes, etc., and most of them are dense, loose porous, or granular [4,5]. Dou et al. [6] analyzed PISs using X-ray energy dispersive spectrometry (EDS). They concluded that the main components were FeS and FeS_2. These components are readily spontaneously combustible. Gao et al. [7] synthesized FeS samples with high spontaneous combustion activity in the laboratory. Beilin et al. [8] found that the composition of PISs changed with the thickness of the corrosion layer. The near metal layer

was composed of almost pure sulfur, and the middle layer was pyrite (0.5–1.0 mm thick FeS). The outer layer was pyrite and crystalline sulfur. Dou et al. [3] found that PISs were short, rhombic, and large in nuclear size and contained S, Fe_3S_4, and FeS_2. Furthermore, FeS was contained in wet PISs. Depending on the different compositions and structures of PIS film, the metal corrosion rate will be different. When exposed to oxygen, dense PIS films rarely get oxidized. On the contrary, loose porous and granular PIS films tend to have high oxidation activity, and the larger the specific surface area is, the easier it is to be oxidized [9]. For example, the PIS film in the gas phase space of oil tanks is loose with a large specific surface area, and this can readily cause spontaneous combustion to occur. Usually, the sequence of PISs on the metal surface is $Fe_{1+x}S$, $Fe_{1-x}S$, and FeS_2. Regarding the protection of performance, the dissolution rate of Fe_9S_8 is 10-fold faster than that of FeS_2, and the corrosion resistance of $Fe_{1+x}S$ is similar to that of Fe_9S_8 [10].

In recent decades, the research into the possibility of the spontaneous combustion of PISs have mainly been divided into two principal aspects [11]: (1) in terms of the concentration of SO_2 and temperature of PISs as monitoring indicators to determine the possibility of the spontaneous combustion of PISs; (2) the apparent activation energy of the oxidation reaction obtained through thermal analysis experiments is employed to determine the possibility of the spontaneous combustion of PISs.

Mao et al. [12] observed in the experiment that when SO_2 was detected, the heating rate of the oxidation would increase; Wang et al. [13] verified that the mass concentration of SO_2 gas can be used to follow the degree of oxidation in FeS and iron polysulfide in the equipment, so they both believed that SO_2 could be used as a monitoring and early warning indicator in the oxidation process. Zhao et al. [14] applied Fe_2O_3, Fe_3O_4, and $Fe(OH)_3$ to prepare PISs, respectively. The temperature of PISs and the SO_2 gas concentration were used as detection indicators to predict the possibility of spontaneous combustion. Dou et al. [15] proposed monitoring and warning indicators for oxidation and spontaneous combustion of PISs based on specimen temperature and SO_2 concentration.

Up to now, a large portion of the research has been conducted on the activation energy of the oxidation and spontaneous combustion of PISs. For instance, Zhao [16] calculated the apparent activation energy for the spontaneous combustion of FeS. Cai [17] figured out the apparent activation energy for the spontaneous combustion of PISs in equipment and laboratory-made PISs. Man [18] projected the apparent activation energy of laboratory-made PISs under different oxygen volume concentration conditions. The apparent activation energy for the spontaneous combustion of ferro sulfides was determined by Li et al. [19] and Liu et al. [20]. Although apparent activation energy is often regarded as the main basis for the possibility of spontaneous combustion, it is not a decisive factor. The evaluation of the spontaneous combustion possibility of PISs should comprehensively take various indexes representing spontaneous combustion characteristics into account.

In addition to the abovementioned research, the point of view that the spontaneous combustion point and the maximum temperature rise rate time TMR_{ad} under adiabatic conditions should be considered the discriminant parameters of the possibility of the spontaneous combustion of PISs is proposed by Zhang et al. [21]. Dou et al. [22] established a prediction model using the Support Vector Machine algorithm to predict the maximum temperature of the PISs during oxidation and spontaneous combustion based on a large amount of experimental data.

According to the literature, there is little research on the severity of the spontaneous combustion of PISs, and only a few scholars directly study the risk of spontaneous combustion of PISs. Xu et al. [23] adopted the fault tree analysis method to evaluate the risk of spontaneous combustion of PISs in naphtha storage tanks. Based on comprehensive consideration of equipment operation and maintenance, combined with fluid properties, the structural characteristics of different pieces of equipment, material characteristics, and anticorrosion measures, Deng [24] divided the equipment risk in the LD32-2 oilfield process into four grades, and determined the key points of spontaneous combustion risk prevention and control of PISs.

In the above studies, the number of studies on the risk assessment of oxidation and spontaneous combustion of PISs is small, and most of them are indirect judgments of risk, which cannot be applied in practice. In this paper, combined with the oxidation characteristics of PISs, a risk assessment index system is established, and the classification criteria for the possibility of spontaneous combustion of PISs and the severity of consequences are determined. Finally, the risk matrix is drawn to evaluate the semi-quantitative risk of spontaneous combustion of PISs, and the feasibility of the evaluation method is tested using the oxidation process of PISs. The context of this article is shown in Figure 1.

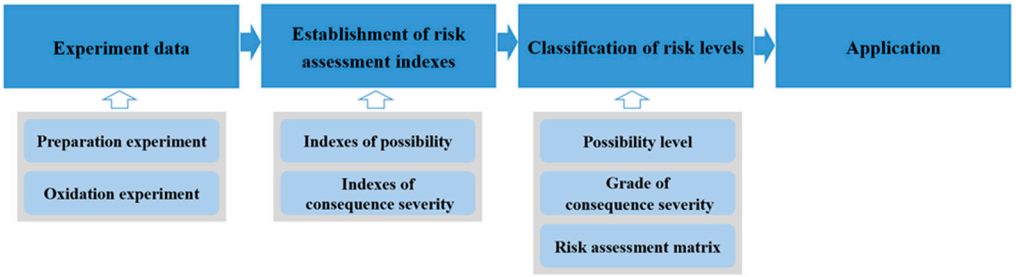


Figure 1. Context structure of this paper.

2. Experiments

The preparation experiment and oxidation experiment of PISs are the bases for determining its spontaneous combustion risk assessment. In this chapter, a self-built experimental device was used to prepare PISs using a reaction with rust and hydrogen sulfide gas as raw materials. The obtained products were exposed to an oxygen environment to simulate the oxidation and spontaneous combustion process of PISs. The oxidation process of typical PISs was observed, analyzed, and summarized, which laid a foundation for the risk assessment and follow-up study of the spontaneous combustion of PISs.

2.1. Oxidation of PISs

The PIS oxidation experiment is divided into two stages: the first stage is the sulfide experiment of rust, using wet H_2S gas to react with rust to generate PISs to provide raw materials for the second stage of the experiment; the second stage is the oxidation experiment of PISs, in which air is passed into a quartz glass tube to react with the PISs to simulate the oxidation process, and the temperature change in the PISs over time during the process is recorded.

2.1.1. Sample Preparation

Rust was used for the preparation of PISs collected from the inner wall of the manhole of the depressurization tower of a petrochemical company in Guangzhou. The experimental device is shown in Figure 2 and is divided into four parts: the first part is the gas supply area, corresponding to a hydrogen sulfide gas cylinder, a nitrogen cylinder, an air cylinder, and a gas buffer and flow controller. The second part is the gas wetting and flow measurement area, which corresponds to two conical cylinders filled with water (to ensure that the hydrogen sulfide gas is wetted, the volume of water is one-fourth of the capacity of the conical cylinders) and a gas flow meter. The third part is the reaction zone, which corresponds to a quartz glass tube (quartz glass tube with heat-resistant tape wrapped around the outer wall) with an armored thermocouple. The fourth part is the tail gas absorption zone, consisting of a conical flask with a sodium hydroxide solution.

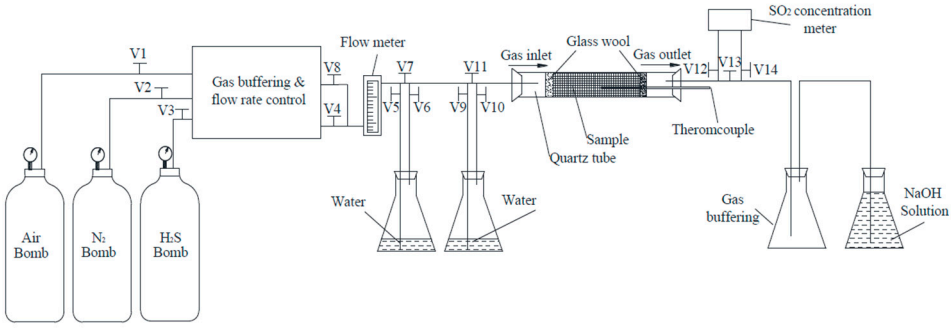


Figure 2. Test device.

In order to reduce the duration of the experiment, the collected rust was ground to a particle size of less than 250 μm. Before the experiment, the rust samples of different qualities were placed in the middle of the quartz glass tube, and glass fiber cotton was plugged at both ends of the sample. The quartz glass tube containing the rust sample was connected to each part of the experimental system, and the airtightness of the experimental system was checked. First, nitrogen was used to replace the air in the experimental system. Then, the resistance heating belt was wound on the quartz glass tube, and the temperature regulator was controlled to heat the rust sample to a certain temperature. Finally, hydrogen sulfide gas and air were introduced, and the gas flow rate was controlled by adjusting the gas buffer and flow control device, so that the rust sample in the quartz glass tube was vulcanized. The remaining hydrogen sulfide gas in the experiment was passed into the tail gas absorption zone and absorbed by an aqueous sodium hydroxide solution. This experiment was carried out for 6 h. When the PISs in the quartz tube were cooled to room temperature, the wet PISs could be obtained.

2.1.2. Oxidation of Samples

To avoid the deterioration of the PISs, the oxidation experiment was continued in the device after the wet PISs were obtained, and the PISs were not removed from the device. Air with different concentrations and flow rates was introduced into the experimental device to carry out the PIS oxidation experiment. After obtaining the PISs at room temperature, the airtightness of the experimental system was checked first. Then, the nitrogen cylinder valve was opened, and the valves V2, V8, V7, V9, V10 and V13 were opened for 15 min. Next, the valve V11 was opened for 15 min to fill the experimental system with nitrogen. After that, the valves in the system were closed. Finally, the air cylinder valve and valves V1, V8, V7, V9, V10 and V13 were opened, and temperature changes during the oxidation of PISs were recorded.

In the PIS generation experiment, different water contents of the PISs were obtained by adjusting the level of water in the conical flask; the mass of PISs per unit area was determined by the mass of the rust sample used in the experiment. In the natural oxidation experiment, the air flow rate through the PISs was obtained by air flow conversion; different oxygen concentrations were achieved by adjusting the gas buffer and flow control device in the gas supply area to change the ratio of air to nitrogen flow. According to the experimental requirements, the heating power of the resistance heating band (wrapped around the quartz glass tube) was adjusted to obtain different ambient temperatures. In order to improve the accuracy of the experimental results, three repetitions of the experiment were required for each set of data.

2.2. Results and Preliminary Analysis

In the experiment, 111 groups of data of solid phase temperature over time in the oxidation process of PISs under different conditions of water content F_{wat} (%), mass M_{irs} (g), ambient temperature T_{env} (°C), air flow rate V_{air} (ml/min) and oxygen concentration C_{oxy} (%) were obtained. Five groups of typical data were selected to draw the temperature–time

curve of PISs, as shown in Figure 3. Considering the complexity of the oxidation and spontaneous combustion process of PISs and the influence of the experimental conditions, the critical temperatures of the oxidation and spontaneous combustion of PISs given in different works of literature are 70 °C, 150 °C, and 230 °C [25–27]. Once the temperature of the PISs is higher than the critical temperature of spontaneous combustion, the risk of fire and explosion accidents will be greatly improved. Therefore, this paper defines 70 °C, 150 °C, and 230 °C as the first, second, and third critical temperatures, respectively, in judging whether the oxidation and spontaneous combustion of PISs will cause fire and explosion accidents [8]. The three critical temperature lines are marked in Figure 3.

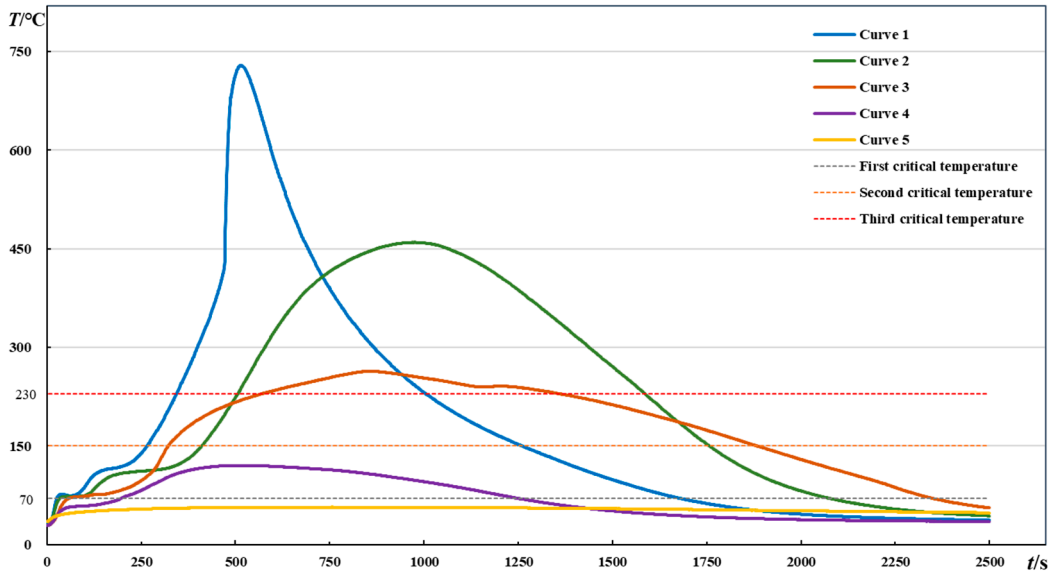


Figure 3. Temperature–time curve of oxidation process of PISs.

As shown in Figure 3, curves 1 and 2 enter a short, rapid temperature rise in the initial phase of the reaction, reaching 75.81 °C and 72.81 °C for 32 s and 42 s, respectively. Then, both curves enter a plateau with a temperature change of less than 1 °C. Immediately afterwards, both curves enter the second temperature rise phase, with curve 1 increasing from 74 °C to 112 °C in 70 s and curve 2 increasing by nearly 30 °C in 90 s. Subsequently, the two curves enter the second plateau with a temperature increase of about 9 °C in 60 s and 140 s, respectively. Finally, the two curves enter a third temperature rise phase, which takes the longest time and has the largest temperature increase, and the reaction temperature reaches the highest temperature of the whole oxidation process, 728.94 °C and 459.75 °C, respectively. After that, the oxidation and spontaneous combustion process of PISs end, and the temperature gradually decreases to room temperature.

Curves 3 and 4 experience rapid temperature rise in the initial stage of the reaction, and the fastest instantaneous temperature rise rates of two curves appear in this stage, which are 2 °C/s and 1.44 °C/s. Afterwards, the temperature changes enter a plateau period of 100 s and 80 s, respectively, and the temperature rise is lower than 7 °C. Finally, the second temperature rise stage is entered, and the reaction temperatures reach the peaks of 263.81 °C and 120.38 °C, respectively. Finally, the temperature gradually decreases to room temperature. In curve 5, there is only one ramp-up phase, which starts slowly after a rapid warming of about 30 s. The temperature starts to decrease slowly to room temperature when it reaches a maximum value of 57 °C.

Through the description of the curves, it was found that the oxidation temperature of the PISs varied under different conditions, and the number of warming stages experienced was also different. For example, the highest oxidation temperature of PISs can reach up to 728 °C (curve 1), but the lowest is only 57 °C (curve 5). Curves 1 and 2 experienced three warming stages in the oxidation process, while curves 3 and 4 experienced two warming

stages in the oxidation process, and curve 5 only had one warming stage. There are also significant differences in the time before reaching different critical temperatures under different conditions and the duration when the oxidation temperature of PISs is higher than different critical temperatures. These parameter values may affect the possibility and consequence severity of the spontaneous combustion of PISs [28]. In addition, it is observed that the oxidative spontaneous combustion process of PISs has something in common with the thermal runaway process of chemical processes due to cooling failure [29].

The oxidation process of PISs is analyzed with a typical curve 2, as is shown in Figure 4. This process is divided into three stages, which are the green part, the yellow part, and the blue part. Figure 5 is the temperature change curve of the thermal runaway process. From the diagram, it can be seen that the oxidation process and the thermal runaway process both undergo three heating stages, and the temperature change trends of the three stages are the same. That is, the temperature change trends of the green area, yellow area, and blue area in Figure 4 are the same as the temperature change trends of the normal process state, cooling failure, and secondary reaction in Figure 5. Thus, the study of the oxidative spontaneous combustion of the PIS process can be referred to the chemical process due to the cooling failure caused by the thermal runaway-related research methods.

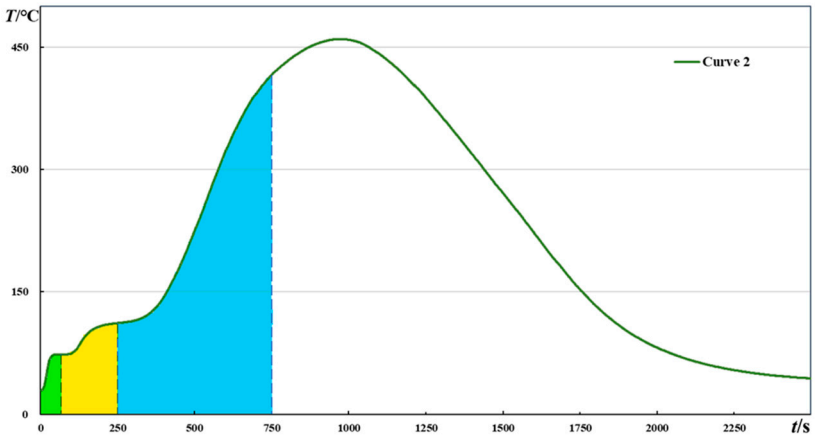


Figure 4. Curve 2 representing oxidation heating process.

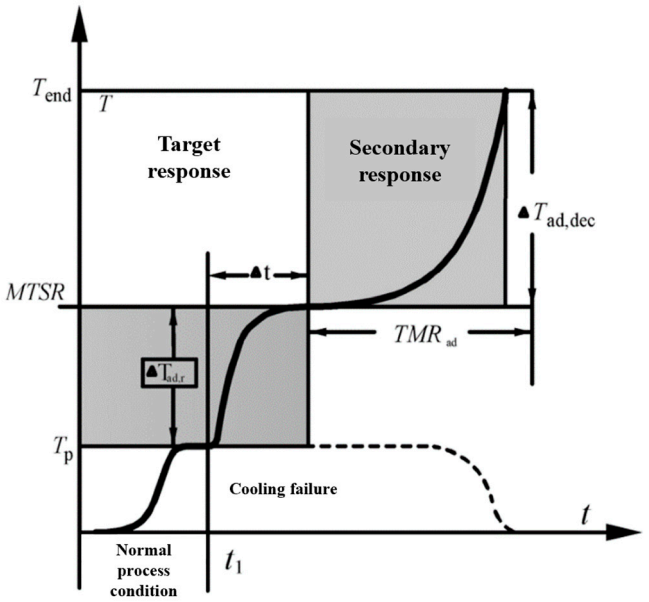


Figure 5. Temperature curve of thermal runaway process. 0–t_1: Normal process condition; t_1 + Δt: Target response; TMR_{ad}: Secondary response; Δt + TMR_{ad}: Cooling failure.

The oxidation process of curves 4 and 5 in Figure 3 only undergoes one or two heating stages, corresponding to the first or first two stages of the thermal runaway process. Since there is no rapid temperature rise similar to the "secondary reaction" stage, it is assumed that the probability of spontaneous combustion is low for these curves, so the risk is also low [30].

3. Establishment of Risk Assessment Indexes

Risk is a combination of the likelihood of a potential accident occurring and the severity of its consequences [31]. Therefore, the assessment of the risk of spontaneous combustion of PISs must assess both the likelihood of its occurrence and the severity of its consequences. Based on the experiments of oxidation and spontaneous combustion and analysis of the obtained data, combined with the field application needs and the current common indexes in the assessment of thermal runaway risk, the assessment indexes of the probability of occurrence and the severity of consequences of spontaneous combustion will be proposed in this section, and the risk assessment index system of the spontaneous combustion of PISs will be established.

3.1. Basic Principles

The oxidation and spontaneous combustion of PISs is a complex physicochemical process, which is affected by various factors. The construction of a risk assessment index system for PISs is the first step in conducting a risk assessment, and the following two basic principles should be followed when establishing the index system [32]:

1. Scientific feasibility

Scientific feasibility is the basis for the establishment of the risk assessment index system for the oxidation and spontaneous combustion of PISs. This system is a summary and explanation of the whole process of spontaneous combustion of pyrophoric iron sulfide. It should be able to truly evaluate the possibility and severity of spontaneous combustion. Therefore, the selected indicators should be scientific, reasonable, objective and fair, and in line with the basic knowledge and basic logic of spontaneous combustion and other related disciplines.

At the same time, the establishment of the index system is to assess the risk of oxidative spontaneous combustion of PISs in practice and to provide technical assurance for safe production, so the index should be available, easy to obtain, and accurate and reliable.

2. Simplicity and independence

An evaluation index is not the larger, the better. On the basis of ensuring scientific and objective evaluation, representative and appropriate evaluation indicators should be selected. In addition, the proposed evaluation indicators should be interrelated but independent of each other to minimize the intersection of indicators.

3.2. Possibility of Spontaneous Combustion

Generally, to assess the thermal runaway risk of a chemical reaction, the maximum reaction rate arrival time (TMRad) is often adopted to characterize the possibility of thermal runaway. However, for the spontaneous combustion of PISs, its oxidation process is affected by both internal and external factors, and the corresponding mechanism are still unclear [5]. Therefore, considering the actual experiment circumstances of PISs spontaneous combustion, the following assessment indexes involving the possibility of spontaneous combustion occurrence are proposed.

3.2.1. Maximum Temperature Rise Rate v_1

The maximum temperature rise rate of the five curves before reaching the maximum critical temperature during the oxidation process and the corresponding temperature and time are shown in Table 1.

Table 1. Maximum heating rate of different curves before reaching the third critical temperature.

Indexes	Curve 1	Curve 2	Curve 3	Curve 4	Curve 5
Maximum temperature rise rate before reaching the third critical temperature (°C/s)	4.50	3.56	2.00	1.44	0.81
Temperature (°C)	58.65	52.38	52.56	40.06	37.19
Time (s)	20	20	32	21	5
Maximum temperature (°C)	728.94	459.75	263.81	120.38	57.00

From the above table, it can be seen that temperature rise rate of PISs before oxidation temperature reaches the third critical temperature is positively correlated with the highest temperature of oxidation. That is, the higher the temperature rise rate before reaching the third-order critical temperature, the higher the highest temperature of oxidation. In addition, it can also be observed that the maximum temperature rise rate of each curve occurs in the early stage of the reaction, which takes a short time, and the corresponding temperature is lower than the first critical temperature (70 °C). In other words, the maximum temperature rise rate before reaching the third critical temperature is the same as that before reaching the first critical temperature. Considering that the time to reach the first critical temperature is earlier than the third critical temperature, and this value is positively correlated with the maximum temperature of PIS oxidation within a certain range, the maximum temperature of oxidation can be speculated earlier, which is conducive to early spontaneous combustion warning and prevention. Therefore, the maximum temperature rise rate v_1 before reaching the first critical temperature is used as an evaluation index to judge the possibility of spontaneous combustion consequences of PISs.

3.2.2. Maximum Oxidation Temperature T_{max}

When the maximum temperature of the oxidation process of PISs is lower than the critical temperature, even if v_1 is large, the PISs will not combust spontaneously. At this time, the possibility of spontaneous combustion is 0, and the PISs are exposed to the air without the risk of spontaneous combustion. According to the literature, sulfur will be produced in the formation of PISs [33] and in the early stage of oxidation reaction [25]. Once the temperature of the oxidation reaction reaches the spontaneous combustion point of sulfur 232 °C, it will spontaneously combust, which provides the heat source for the oxidation of PISs [4] and increases the risk of the spontaneous combustion of PISs. Therefore, when the maximum oxidation temperature is lower than the third critical temperature, it is considered that there is no possibility of spontaneous combustion in the contact between PISs and air. Otherwise, v_1 is used to qualitatively judge the possibility of spontaneous combustion, and then the severity of the consequences is further evaluated. Therefore, the maximum oxidation temperature T_{max} is one of the evaluation indexes for the possibility of the spontaneous combustion of PISs.

3.3. Severity of Oxidation to Spontaneous Combustion

The severity is the damage caused by the release of uncontrolled energy in the process of an uncontrolled reaction. The consequence severity of the uncontrolled reaction is related to the amount and speed of the energy released. The more heat that is released from the reaction, the faster the temperature of the reaction system rises, which can easily lead to the temperature of the reaction system exceeding the spontaneous combustion point of some components, triggering spontaneous combustion and producing toxic and harmful gases. The assessment of the thermal runaway risk in the fine chemical industry is usually based on the decomposition reaction's adiabatic temperature rise ΔT_{ad} and the

amount of heat released Q to evaluate the severity of the runaway reaction [34]. Since the oxidation process of PISs is not an adiabatic process, coupled with the fact that the severity of accident consequences is related to the speed of energy release, this paper combines the temperature–time diagram of the oxidative spontaneous combustion process of PISs and proposes to measure the amount of heat release by the duration τ above the tertiary critical temperature as an indicator, and the instantaneous temperature rise rate v_2 when reaching the tertiary critical temperature as an indicator to measure the speed of heat release.

3.3.1. Characteristic Duration τ

A fire occurring in chemical equipment will cause a certain degree of damage to the equipment body. The duration of a fire has a great influence on the corrosion resistance and burned area of the burned material [35]. It will cause different degrees of local or overall permanent deformation and material damage to the equipment, affecting the safety and service life of the equipment [36]. In addition, it will produce toxic gas SO_2 during oxidation and spontaneous combustion. The longer the spontaneous combustion time, the more harmful gas may be produced, and the greater the risk to plants and people in the surrounding environment [27].

It can be seen that the duration of the fire is positively correlated with the severity of the consequences caused by the fire. In light of the previous view that when the maximum oxidation temperature is higher than the third critical temperature, it is considered that there is a possibility of spontaneous combustion of PISs in contact with air, and that this severity index should be consistent with the previous content to better carry out risk assessment, then the characteristic duration τ higher than the third critical temperature is used as a parameter to characterize the severity of the consequences.

3.3.2. Third Instantaneous Heating Rate v_2

The instantaneous heating rate indicates the speed of heat release. The faster the heat release, the more serious the consequences. Compared with combustion and explosion, the main difference between the two is the burning rate of the material. For example, the combustion heat of 1 kg of wood is 16,700 kJ, and complete combustion takes 10 min. The explosion heat of 1 kg of TNT explosive is only 4200 kJ, and its explosion reaction takes only tens of microseconds. The time required for the two is tens of millions of times, and the severity of the consequences is also far from each other [37]. Similarly, if PISs produce a large amount of reaction heat in a short time, and it is too late to transfer it to the outside world, then the heat will be used for its own temperature rise, which will further increase the risk of spontaneous combustion. At present, the use of low-concentration oxygen to passivate PISs is the best practical case of this principle.

According to the experimental data, the instantaneous heating rate at the third critical temperature and the maximum heating rate between the third critical temperature and the maximum temperature can be calculated, as shown in Table 2. From the point of view of simplifying the problem as much as possible [38], combined with the actual inspection and maintenance process of the industry, it is considered that the time to reach the maximum heating rate is not easy to determine. Moreover, if the time is very close to the maximum temperature, it is of little significance for accident prevention, which also violates the real purpose of risk assessment: to minimize the risk before spontaneous combustion occurs. However, if the instantaneous heating rate corresponding to 230 °C is used as an indicator, once the target temperature is reached, the instantaneous heating rate can be obtained immediately to determine the severity of the consequences, and then appropriate interventions can be taken based on the results. In addition, it can be seen from Table 2 that the maximum temperature rise rate corresponding to the heating rate of curves 2 and 3 at 230 °C is very close. Therefore, for these two curves, any temperature rise rate can be selected. However, curve 1 has a larger heating rate after 230 °C, so if the temperature reaches 230 °C, preventive measures can be taken to prevent the emergence of a higher heating rate and to reduce the risk of spontaneous combustion. Hence, the instantaneous

heating rate corresponding to the third critical temperature v_2 is one of the evaluation indexes of the severity of the oxidation and spontaneous combustion of PISs.

Table 2. Different instantaneous temperature rise rates of different curves.

Curves	Instantaneous Heating Rate Corresponding to the Third Critical Temperature (°C/s)	Temperature (°C)	Time (s)	Maximum Heating Rate between the Third Critical Temperature and the Maximum Temperature (°C/s)	Temperature (°C)	Time (s)
Curve 1	1.88	230	346	34	546.88	478
Curve 2	1.56	230	509	1.63	238.75	517
Curve 3	0.25	230	575	0.31	232.88	590
Curve 4	—	—	—	—	—	—
Curve 5	—	—	—	—	—	—

4. Classification of Risk Levels

After establishing a risk assessment index system for the spontaneous combustion of PISs, it is necessary to classify the possibility and severity of spontaneous combustion [39]. In addition, the risk matrix method in the thermal safety analysis and evaluation method of the reaction process is used to establish the risk assessment matrix of the oxidation and spontaneous combustion so as to realize the semi-quantitative risk assessment of the oxidation and spontaneous combustion of PISs.

4.1. Risk Classification

4.1.1. Basic Principles

The risk level is usually divided into three to five levels, and each level is represented by good, medium, and poor language. According to the characteristics of the spontaneous combustion risk assessment index proposed in this paper, and in order to facilitate on-site safety assessment and detection, and referring to related literature [40–42], the possibility level and consequence severity of the spontaneous combustion of PISs are divided into five levels. The possibility of spontaneous combustion is lower, low, medium, high, and higher, and the consequences of spontaneous combustion are divided into mild, general, large, significant, and particularly significant.

4.1.2. Possibility Levels of Spontaneous Combustion

The parameters T_{max} and v_1 have been proposed to characterize the possibility of spontaneous combustion of PISs. Therefore, the product of the two is used to quantitatively represent the possibility L of the spontaneous combustion of PISs, such as Equation (1). The greater the product of the two, the greater the possibility of the spontaneous combustion of PISs. Table 3 is the classification of the possibility of the spontaneous combustion of PISs.

$$L = T_{max} \times v_1 \quad (1)$$

Table 3. Classification of the possibility L of the spontaneous combustion of PISs.

L	Spontaneous Combustion Possibility Level	Explanation
(0, 230)	A	Lower
[230, 500)	B	Low
[500, 1000)	C	Medium
[1000, 2000)	D	High
[2000, 3500)	E	Higher

4.1.3. Severity Grades of Oxidation to Spontaneous Combustion

In this paper, the product of two parameters characterizing the severity of spontaneous combustion is used to quantitatively represent the severity of the spontaneous combustion of PISs, as shown in Equation (2). The dimension of the product is °C, which means the temperature reached by the oxidation of PISs at the rate of PISs for τ time. It is the same as the severity evaluation index of the runaway reaction in the thermal safety analysis and evaluation method of the reaction process (the adiabatic temperature rise caused by the latent heat of the target reaction $\Delta T_{ad,rx}$) in terms of dimension and significance, so it is considered reasonable. Table 4 shows the classification of the consequence severity C of spontaneous combustion.

$$C = v_2 \times \tau \quad (2)$$

Table 4. Classification of consequence severity C of oxidation and spontaneous combustion of PISs.

C	Consequence Severity Level	Explanation
(0, 300)	1	Mild
[300, 800)	2	General
[800, 1200)	3	Large
[1200, 1600)	4	Significant
[1600, 2000)	5	Particularly significant

4.2. Risk Evaluation Matrix

The risk matrix method can intuitively and clearly characterize the risk of spontaneous combustion of PISs. The risk level of spontaneous combustion can be judged by the risk matrix, so as to take reasonable and effective measures to reduce the risk [43]. In this paper, when dividing the risk level of oxidation and spontaneous combustion of PISs, it not only combines the characteristics of oxidation and spontaneous combustion, but also refers to the risk level division principle.

As shown in Figure 6, the risk assessment matrix of the spontaneous combustion of PISs is shown. The horizontal axis of the matrix represents the possibility level of spontaneous combustion, and the vertical axis represents the severity level of the spontaneous combustion. For the three colors of green, yellow, and red in the risk matrix, green is the grade I risk area, indicating low risk; yellow is the grade II risk area, indicating medium risk; and red is the grade III risk area. The risk level and acceptability of each region are shown in Table 5.

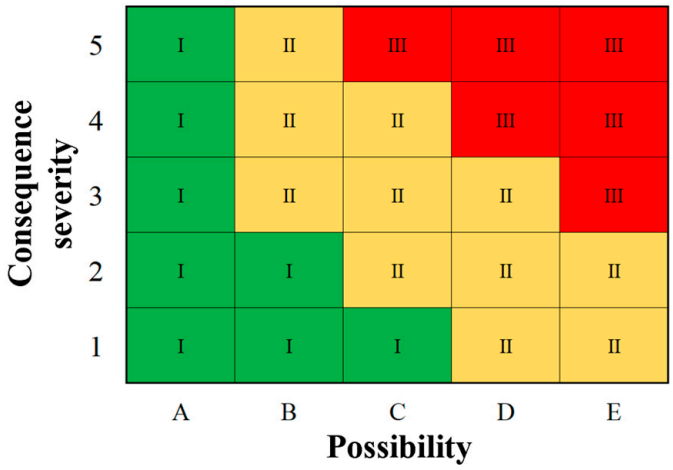


Figure 6. Risk assessment matrix.

Table 5. Classification of risk levels of spontaneous combustion of PISs.

Color	Risk Level		Risk Acceptability	Explanation
Green	I	Low risk	Acceptable	The risk level is within the acceptable range of the system without taking measures.
Yellow	II	Medium risk	Conditional acceptance	Reasonable and effective measures should be taken to reduce the risk level to grade I.
Red	III	High risk	Unacceptable	The risk level exceeds the acceptable range of the system. Effective measures should be taken immediately to inhibit the oxidation reaction and reduce the risk of spontaneous combustion.

The matrix is determined by the possibility and the severity of the consequences of the spontaneous combustion of PISs [44], but it does not strictly follow a certain rule. It can be seen from the diagram that there is no specific law for the distribution of each risk area. This is because the risk of spontaneous combustion of PISs is more focused on the possibility of its occurrence. For example, when the possibility of the spontaneous combustion of PISs is very small, regardless of the severity of the consequences of the spontaneous combustion, the risk level is always considered to be grade I.

4.3. Risk Assessment Procedures

The risk assessment process of the oxidative spontaneous combustion of PISs established in this chapter is summarized as follows:

1. The possibility evaluation indexes, T_{max} and v_1, are obtained using the experimental data, and its product is calculated to determine the possibility of the spontaneous combustion of PISs;
2. The consequence severity assessment indexes, τ and v_2, are obtained, and the product is calculated to determine the consequence severity C of the spontaneous combustion of PISs;
3. According to the possibility grade and the severity grade, the risk assessment matrix is used to determine the risk level of the spontaneous combustion of PISs.

In order to describe the risk assessment procedure of oxidation and spontaneous combustion of PISs more clearly, Figure 7 is drawn:

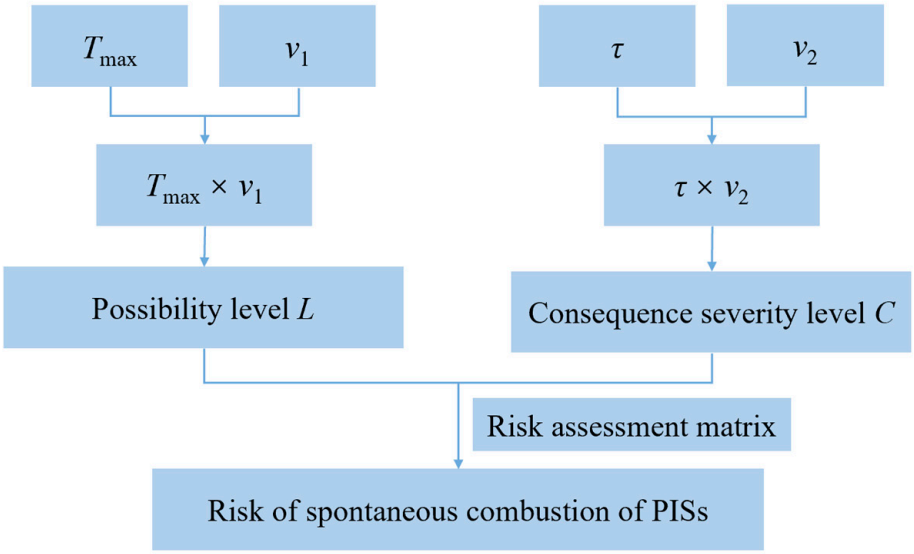


Figure 7. Risk assessment procedures of oxidative spontaneous combustion of PISs.

5. Application

The risk assessment method is applied to evaluate the risk of nine oxidation and spontaneous combustion cases, and the risk level of spontaneous combustion can be determined.

5.1. Possibility Calculation

In this section, nine typical oxidation processes in the oxidation experiment of PISs are selected. According to the obtained experimental data, the temperature–time curve of the whole oxidation process is drawn as shown in Figure 8. Each curve in the figure represents a PIS oxidation process.

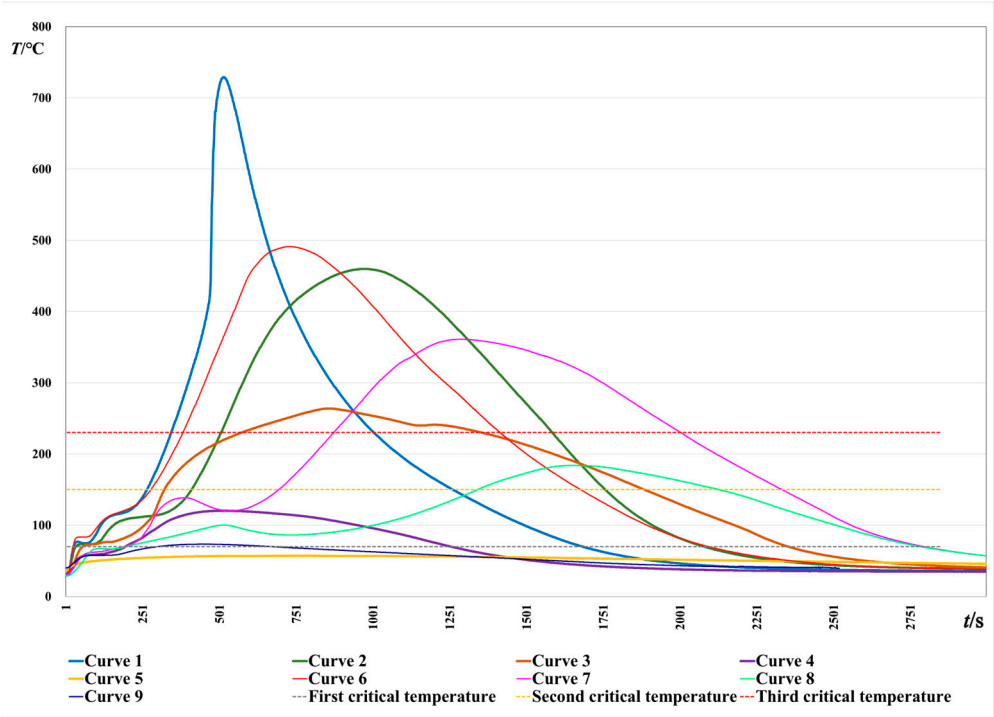


Figure 8. *T*–*t* curves of oxidation processes of nine different PISs.

In the process of the risk assessment of the spontaneous combustion of PISs, the T_{max} and v_1 of the nine curves and their products were first calculated, and the possibility levels of spontaneous combustion were determined according to the classification criteria, as shown in Table 6. It can be seen from the table that the possibility of oxidation and spontaneous combustion of PISs in curves 4, 5, 8, and 9 is grade A; curves 3 and 7 are grade B; curve 2 is grade D; and curves 1 and 6 are grade E. According to the classification standard of the possibility of spontaneous combustion of iron sulfide corrosion, it can be seen that the possibility of spontaneous combustion in curves 3, 4, 5, 7, 8, and 9 is small, while the possibility of spontaneous combustion in curves 1, 2, and 6 is large.

Table 6. T_{max} and v_1 values of nine curves.

Indexes	Curve 1	Curve 2	Curve 3	Curve 4	Curve 5	Curve 6	Curve 7	Curve 8	Curve 9
T_{max} (°C)	728.94	459.75	263.81	120.38	57.00	491.19	360.94	183.88	73.44
v_1 (°C/s)	4.50	3.56	2.00	1.44	0.81	4.81	1.19	1.13	0.69
$T_{max} \times v_1$	3280.2	1636.7	527.6	173.3	46.2	2363.8	428.6	206.9	50.5
Probability level	E	D	B	A	A	E	B	A	A

5.2. Severity Estimation

As shown in Table 7, according to the experimental data of PIS oxidation, the τ and v_2 of the nine curves and their products were calculated, and the possibility of spontaneous combustion was determined according to the grading criteria of the severity of consequences. From the table, it can be seen that curves 3, 4, 5, 8, and 9 of the PIS spontaneous combustion consequence severity are grade 1; curve 7 is grade 2; curve 1 is grade 4; and curves 2 and 6 are grade 5. According to the classification standard of consequence severity, curves 3, 4, 5, 7, 8, and 9 are less harmful to the surrounding environment and personnel, while curves 1, 2, and 6 have more serious consequences caused by spontaneous combustion.

Table 7. Consequence severity index values of nine curves.

Indexes	Curve 1	Curve 2	Curve 3	Curve 4	Curve 5	Curve 6	Curve 7	Curve 8	Curve 9
τ (s)	659	1078	781	0	0	1033	1133	0	0
v_2 (°C/s)	1.88	1.56	0.25	—	—	1.5	0.31	—	—
$\tau \times v_2$	1238.9	1681.7	195.3	0	0	1549.5	351.2	0	0
Severity	4	5	1	1	1	5	2	1	1

5.3. Risk Level Determination

The risk of spontaneous combustion can be determined according to the risk matrix according to the possibility and severity of spontaneous combustion of PISs, as shown in Table 8. Among them, curves 1, 2, and 6 are high risk, and the remaining curves are low risk. In order to show the risk level of different curves more clearly, the risk matrix diagram of different curves is drawn, as shown in Figure 9.

Table 8. Spontaneous combustion risk levels of different curves.

	Curve 1	Curve 2	Curve 3	Curve 4	Curve 5	Curve 6	Curve 7	Curve 8	Curve 9
L	E	D	B	A	A	E	B	A	A
C	4	5	1	1	1	5	2	1	1
Risk level	III	III	I	I	I	III	I	I	I

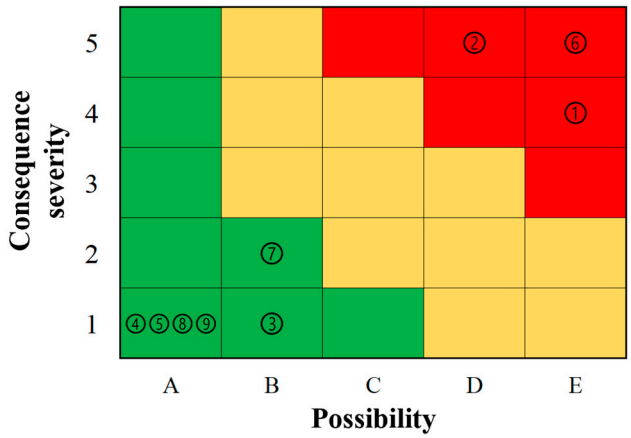


Figure 9. Risk matrix diagram of nine scenarios.

6. Conclusions and Future Works

Based on the preparation experiment and oxidation experiment of PISs, this paper proposes a risk assessment method for the oxidation and spontaneous combustion of PISs, which could reduce safety accidents and contribute to the sustainable development of high-quality equipment in the petrochemical industry. The main contents are as follows:

1. Through the analysis of experimental data, it was found that the oxidation temperature of PISs was different under different conditions, and the number of heating stages was also different. In addition, the oxidation and spontaneous combustion process of PISs experienced three heating stages, which is similar to the thermal runaway process caused by cooling failure in chemical processes;
2. Risk assessment indexes suitable for the oxidation and spontaneous combustion of PISs was proposed, including four risk assessment parameters: v_1, T_{max}, τ, and v_2. Among them, v_1 and T_{max} characterize the possibility of spontaneous combustion, and τ and v_2 characterize the severity of spontaneous combustion;
3. The product value of T_{max} and v_1 is used to represent the possibility of spontaneous combustion, and it is divided into five grades. The product of τ and v_2 is used to represent the severity of the consequences of oxidation to spontaneous combustion, and it is divided into five grades. A risk matrix is established to evaluate the semi-quantitative risk of PIS oxidation to spontaneous combustion. A complete risk assessment method for PIS oxidation to spontaneous combustion is established;
4. Risk assessment methods are used to assess the risk of nine oxidation processes of PISs. The results show that curves 1, 2, and 6 are high risks, while curves 3, 4, 5, 7, 8, and 9 are low risks.

The deficiencies of this paper and future works are as follows:

1. From the results of the risk analysis of cases, it is found that all the risk levels of the spontaneous combustion of PISs are level I and III, and there is no level II, which may be due to the small number of risk levels. In future studies, we plan to classify the risk level into five levels to assess the risk of spontaneous combustion of PISs in more detail;
2. In order to apply the risk assessment method practically, the prediction models of T_{max} and τ are established based on the experimental data using machine learning algorithms. In this way, it is possible to achieve early access to assessment index data for early warning and significantly reduce the risk of spontaneous combustion of PISs.

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