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Spontaneous Combustion Mechanism and Influencing Factors of Sulfur Corrosion Products in Petroleum Refining Equipment

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Abstract: With the continuous development of China's economy, the demand for petroleum energy continues to rise. High sulfur crude oil leads to the formation of sulfur corrosion products in petroleum refining equipment and its spontaneous combustion hazard seriously threatens the safety production in the petrochemical field. To explore spontaneous combustion of the sulfur corrosion products in oil refining equipment, the formation of sulfur corrosion products and its preparing method were described in detail. And the spontaneous combustion characteristics and its influencing factors were interpreted and the current relevant prevention and control technology of sulfur corrosion products spontaneous combustion was classified. The results show that the spontaneous combustion of sulfur corrosion products can be divided into three stages. The spontaneous combustion characteristics of sulfur corrosion products are simulated under working conditions. The prevention and control technology can be divided into raw material desulfurization, equipment anti-corrosion, corrosion monitoring and industrial prevention and treatment. Influencing factors are divided into product properties and external environments. Based on the properties of sulfur corrosion products, the influencing factors include particle size, moisture content and vulcanization mode. In terms of the external environment, the influencing factors include air flow, oxygen concentration, ambient temperature, heating rate and oil products. It provides a theoretical basis for solving the spontaneous combustion of sulfur corrosion products in petroleum refining equipment.

Keywords: Spontaneous Combustion, Sulfur Corrosion Products, Prevention Technology, Influencing Factors

1. Introduction

China's proven oil reserves have been increasing in recent years and refining capacity has continued to increase, and crude oil demand has increased substantially. In 2021, China's crude oil demand will reach 1112.52 million tons, up 51.2% year on year, and the crude oil processing volume will exceed 700 million tons, up 4.3% year on year [1]. The sulfur content of imported crude oil is high. In the process of oil production, storage, transportation and use, the sulfur-containing substances in the oil corroded petrochemical equipment and formed sulfur corrosion products. Sulfur corrosion products have the characteristics of spontaneous combustion, which can easily cause fire, explosion and other major accidents in the inspection and maintenance of petroleum refining equipment due to contact with air, and seriously threaten the safe production process of petrochemical industry.

Sulfur corrosion products formed in the absence of oxygen in petroleum refining equipment are mainly pyrite compounds, which have strong spontaneous combustion reactivity at room temperature. The spontaneous combustion reaction process can be generally divided into induced oxidation period, medium speed oxidation period and accelerated oxidation period, during which heat will continue to be released. Under the condition of heat storage inside the equipment, the heat production rate of sulfur corrosion product spontaneous combustion is much greater than the heat dissipation rate, and the heat accumulation leads to spontaneous combustion often causes fire or even explosion accidents. Based on the comprehensive discussion of the formation mechanism, spontaneous combustion characteristics, spontaneous combustion prevention technology and influencing factors of sulfur corrosion products in petroleum refining and chemical equipment, this paper summarizes the current research status at home and abroad, and puts forward opinions on the current situation and problems, in order to provide some theoretical reference for the research of spontaneous combustion direction of sulfur corrosion products.

2. Study on Spontaneous Combustion Mechanism of Sulfur Corrosion Products

2.1. Formation of Sulfur Corrosion Products

Reactive sulfur (hydrogen sulfide, sulfur elements, low molecular thiols, etc.) reacts with metal or formed rust (Fe_2O_3, Fe_3O_4, etc.) inside the equipment containing sulfur to form corrosion, including chemical reaction corrosion, electrochemical corrosion, bacterial corrosion.

1) Chemical reaction corrosion [2, 3].

As temperatures rise during production, the active sulfur in the crude oil reacts with the metal, and the decomposition of the inactive sulfur is intensified when exposed to high temperatures. When the temperature exceeds 200°C, H_2S decomposition produces H_2 and S, When the temperature rises to340~400°C, sulfur elements with stronger corrosion than H_2S can react directly with metal to form sulfur iron compounds.

$$Fe+S \rightarrow FeS\downarrow \tag{1}$$

$$Fe+H_2S \rightarrow FeS\downarrow+H_2\uparrow \tag{2}$$

$$RCH_2CH_2SCH + Fe \rightarrow FeS\downarrow + RCH = CH_2 + H_2\uparrow \tag{3}$$

At the same time, in high temperature environment, sulfur can also react with rust components, part of the equipment into the equipment, and part of the equipment will adhere to the surface.

2) Electrochemical corrosion.

Electrochemical corrosion is the most destructive and difficult to avoid, resulting in device perforation and other phenomena seriously threaten the safe production and operation of petroleum refining equipment. It is mainly divided into two kinds: one is H_2O+H_2S corrosion system, the other is H_2S+HCI+H_2O corrosion system.

a) H_2O+H_2S corrosion system [4, 5].

This kind of electrochemical corrosion system mainly occurs in the environment of low temperature with water, mostly in the top of light oil storage tank, liquid separation tank, hydrotreating unit cooler, and the inside of LPG spherical tank. Due to the presence of water or water film on the metal surface, H_2S gas can be dissolved in water to dissociate to obtain sulfate ions and continues to ionize S^{2-}.

$$H_2S \rightarrow H^+ + HS^- \tag{4}$$

$$HS^- \rightarrow H^+ + S^{2-} \tag{5}$$

Equation of anode and cathode reaction for metal corrosion:

$$\text{Anodic reaction: } Fe+S^{2-} \rightarrow FeS\downarrow+2e \tag{6}$$

$$\text{Cathode reaction: } 2H^+ + 2e \rightarrow H_2\uparrow \tag{7}$$

b) H_2S+HCl+H_2O Corrosion system [6, 7].

After heating, NaCl, $MgCl_2$ and$CaCl_2$ in crude oil hydrolyzed and generated a small amount of highly corrosive HCl gas. Some HCl gas directly contacts with metal to form corrosion reaction, and others react with H_2S to form cyclic corrosion system. At the same time, the corrosion environment is formed at the location where gas-liquid two phases coexist. Owing to the mutual promotion of hydrogen sulfide and hydrogen chloride, the corrosion is intensified.

The reaction process formula is:

$$Fe+2HCl \rightarrow FeCl_2+H_2 \tag{8}$$

$$FeCl_2+H_2S \rightarrow FeS\downarrow+HCl \tag{9}$$

The FeS generated by the reaction of iron with hydrogen sulfide will be consumed and destroyed by HCl.

$$Fe+H_2S \rightarrow FeS\downarrow+H_2 \tag{10}$$

$$FeS+2HCl \rightarrow FeCl_2+H_2S \tag{11}$$

3) Bacterial corrosion.

Bacterial corrosion mainly occurs at the bottom of the oil tank. It is the low oxygen content in the oil, tank bottom in low oxygen environment that provide a better environment for anaerobic sulfate-reducing bacteria to grow and reproduce [7]. Sulfate-reducing bacteria reduced SO_4^{2-} to S^{2-}. After the more stable sulfate is converted to the more active sulfide, electrochemical corrosion throughout the environment and corrosion inside tank bottom is promoted quickly. The main reaction equations are as follows:

Anodic reaction: Sulfate reducing bacteria consume hydrogen atoms in the bottom water of the tank through metabolic reactions, which leads to the shedding of the internal anticorrosive coating and promotes electrochemical corrosion.

$$Fe \rightarrow Fe^{2+}+2e \tag{12}$$

$$Fe^{2+}+S^{2-} \rightarrow FeS\downarrow \tag{13}$$

Cathode reaction: Sulfate-reducing bacteria use organic matter as carbon source and combine hydrogen produced in their own biofilm to reduce sulfate to sulfide.

$$SO_4^{2-}+8H^{+}+8e\rightarrow S^{2-}+4H_2O \qquad (14)$$

2.2. Mechanism of Spontaneous Combustion of Sulfur Corrosion Product

2.2.1. Preparation of Sulfur Corrosion Products

Scholars used commercially available analytical pure FeS to study the spontaneous combustion mechanism of sulfur corrosion products. There are some differences between commercially available analytical pure FeS and sulfur corrosion products formed in working conditions. And its spontaneous combustion reactivity is far lower than the actual sulfur corrosion products. As shown in Figure 1, it is the TG-DSC curves of spontaneous combustion of commercially available analytical pure FeS. The spontaneous combustion process of FeS is divided into three stages: oxidation stage, medium-speed oxidation stage and accelerated oxidation stage. The reaction process with oxygen is divided into physical adsorption, chemical adsorption and chemical reaction [8].

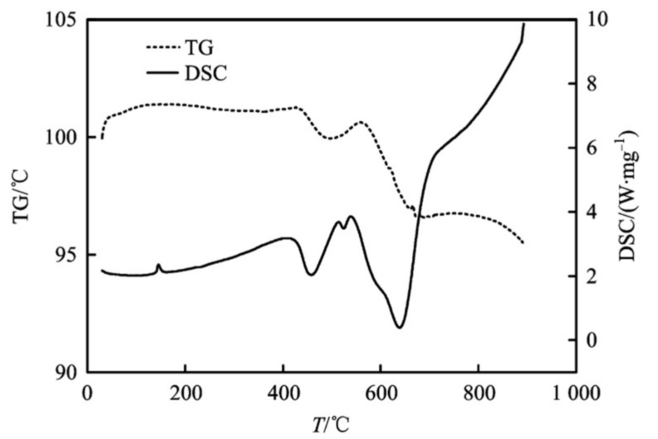

Figure 1. *TG-DSC curve of spontaneous combustion of analytical pure FeS.*

With the further study on the spontaneous combustion of sulfur corrosion products, scholars proposed to prepare pyrite compounds by simulating the low-temperature sulfur corrosion process in crude oil storage tanks and took this sample to explore the spontaneous combustion mechanism of sulfur corrosion products. The sulfurization of Fe_2O_3, Fe_3O_4 and $Fe(OH)_3$ in storage tank was simulated directly [9-10]. Zhang [11] obtained wet and dry sulfur corrosion products based on self-developed sulfur oxidation test system. Gao [12] prepared ferrous sulfide by liquid phase synthesis method, which has stronger spontaneous combustion reactivity at room temperature than the commercial analytical of pure FeS. Figure 2 shows the change of heat flow under different heating rates of active FeS. In the actual production process, the corrosion process of hydrogen sulfide is accompanied by other gases such as oxygen, which is different from the sulfuration preparation method under anaerobic conditions. Shang [13] sulfurized Fe_2O_3, Fe_3O_4 and $Fe(OH)_3$ under aerobic conditions to obtain sulfur corrosion products, which is closer to the actual working conditions. She confirmed by experiments that elemental sulfur produced in the process of aerobic vulcanization can react with the sulfide products to produce highly active polysulfides, thereby enhancing the spontaneous combustion reactivity of corrosion products. By comparing the spontaneous combustion reactivity of sulfur corrosion products obtained by different preparation methods, it is found that the low temperature electrochemical corrosion products have lower spontaneous combustion tendency than H_2S corrosion [14-17]. The order of oxidation rate of sulfide products is Fe_3O_4 > Fe_2O_3 > mixture > $Fe(OH)_3$. As shown in Figure 3, Hong carried out TG-TDG analysis of sulfur corrosion products sampled on site and the inner wall of diesel tanks. It was found that the spontaneous combustion tendency of corrosion products on the inner wall of gasoline tanks was weaker than that of diesel tanks. And the spontaneous combustion tendency of corrosion products on the bottom of diesel tanks was significantly higher than that on the inner wall of tanks [18, 19].

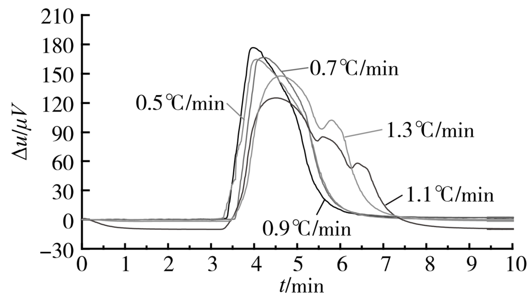

Figure 2. *Heat flow changes of FeS at different heating rates in air.*

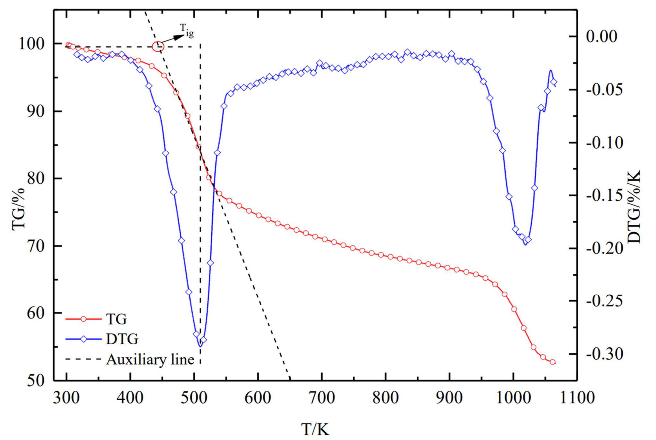

Figure 3. *TG-DTG curves of sulfur corrosion products on the inner wall of diesel tank heated at 20K/min.*

2.2.2. Spontaneous Combustion of Sulfur Corrosion Products

The main components of sulfur corrosion products include FeS, FeS_2 and so on. Most of these compounds are concentrated on the inner wall or bottom of petrochemical refining equipment. Heat releases from oxidation reaction after sulfur corrosion products contacting with air. Due to the relatively poor heat dissipation capacity in the equipment, heat accumulation leads to the continuous increase of temperature to ignite oil, leading to fire and explosion accidents.

As for the structure of sulfur corrosion products, the outer layer is loose and porous. As shown in Figure 4, it is the SEM images of sulfur corrosion products in the tank. Due to the special crystal structure and crystal defects of ferrous sulfide, oxygen molecules are easily adsorbed on the surface of ferrous sulfide and penetrate into the inner layer to oxidize with it and emit a lot of heat. From the elemental composition of sulfur corrosion products, Fe as a transition metal has unpaired d electrons. It has strong chemical adsorption capacity. After contacting with air, oxygen molecules are adsorbed by the active center on the surface of sulfur corrosion products. At the same time, oxygen molecules are activated by the heat released from the adsorption. The activated oxygen molecules rapidly react with the activated sulfur corrosion products to release a large amount of heat. During the spontaneous combustion of sulfur corrosion products, the content of SO_4^{2-} ions increases with the reaction [20].

As for the external environment of sulfur corrosion products, good oxygen supply and heat storage conditions are the main influencing factors of spontaneous combustion [21]. The probability of spontaneous combustion of sulfur corrosion products in low oxygen content or inert atmosphere is small, but the oxidation reaction heats rapidly when exposed to large amounts of air. When the oxygen supply is sufficient, the effective diffusion coefficient of oxygen in ferrous sulfide increases, which is easier to diffuse to increase oxygen consumption and faster oxidation reaction. Due to the poor thermal conductivity of sulfur corrosion products, the heat released during oxidation cannot be dissipated in time, resulting in the rapid increase of temperature and finally spontaneous combustion.

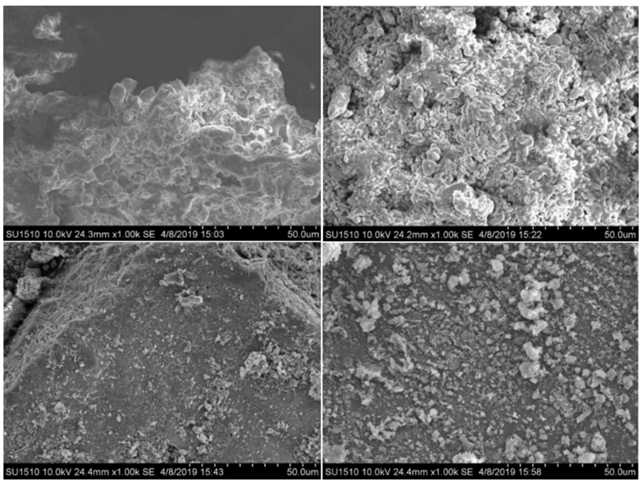

Figure 4. *Sulfur corrosion products of oil storage tanks under 1000 times scanning electron microscope.*

Spontaneous combustion process of sulfur corrosion products [22, 23]:

$$FeS_2(s)+O_2(g) = FeS(s)+SO_2(g)+223.02 \text{ kJ/mol} \quad (15)$$

$$FeS(s)+3/2O_2(g) = FeO(s)+SO_2(g)+49.14 \text{ kJ/mol} \quad (16)$$

$$Fe_2S_3(s)+3/2O_2(g) = Fe_2O_3(s)+3S(s)+223.02 \text{ kJ/mol} \quad (17)$$

The main equations for ferrous sulfide combustion in the presence of water in the environment are as follows:

$$FeS(s)+H_2O+2O_2(g) = FeSO_4\cdot H_2O \quad (18)$$

$$FeS(s)+7H_2O+2O_2(g) = FeSO_4\cdot 7H_2O \quad (19)$$

3. Prevention and Control Technology of Spontaneous Combustion of Sulfur Corrosion Products

In recent years, fire and explosion accidents of petrochemical equipment caused by spontaneous combustion of sulfur corrosion products have occurred frequently, which seriously threatens the safety production process of petrochemical industry. On January 2, 2018, a deflagration accident caused by spontaneous combustion of ferrous sulfide occurred in a desulfurization tower of Ruixiang Company in Ruzhou City, Henan Province during maintenance, resulting in 1 death, 1 disappearance and 4 injuries. On July 11, 2020, Ningxia Baofeng Energy Group Coal Coking Co., Ltd. formed explosive gas due to gas leakage and air mixing, leading to residual ferrous sulfide spontaneous combustion in the pipeline. This accident resulted in 1 death and 2 injuries. In order to prevent the production accidents caused by spontaneous combustion of sulfur corrosion products, scholars have proposed a series of prevention and control technologies [24-27].

3.1. Raw Material Desulfurization Technology

Through raw material desulfurization technology, it can control sulfur content of crude oil and the formation of sulfur corrosion products. The desulfurization efficiency of ordinary desulfurization methods is different and the cost is high. More efficient and environmentally friendly desulfurization technology needs to be developed and put into production. Wet flue gas desulfurization technology can remove sulfide and particulate matter. The desulfurization cost is relatively low, which can be adapted to a variety of catalytic cracking unit [28, 29].

3.2. Anticorrosion Technology of Refining Equipment

The anticorrosion technology of tank mainly includes electrochemical protection, setting metal and non-metal coating and metal conversion film protection [30]. At present, the use of a more common transformation film technology is through the immersion method, spraying method, brushing method of phosphating and passivation of steel plate. It is particularly important for the anticorrosion measures of sulfur-containing oil floating roof storage tanks. By setting metal and non-metal coatings, coating with good anticorrosion properties can effectively achieve anticorrosion effect [31].

3.3. Sulfur Corrosion Monitoring Technology

Strengthening the monitoring of sulfur corrosion in petroleum refining and chemical equipment is the most effective and direct way to prevent fire and explosion. Sulfur corrosion monitoring technology [32] can monitor the corrosion rate of petrochemical equipment in real time, including corrosion coupon method, resistance probe method, electrochemical method, MICROCOR inductance impedance method, CEIONTM weight loss method, etc. The corrosion monitoring technology can accurately find the corrosion site of equipment and then inform people to timely treat and maintain the equipment, which can effectively reduce the degree of sulfur corrosion. As shown in Figure 5, the on-line wall thickness monitoring system uses ultrasonic reflection to detect the wall thickness through ultrasonic detection technology. Real-time monitoring on prevention and reduction of sulfur corrosion on the device can also effectively reduce the formation of sulfur corrosion products [33, 34].

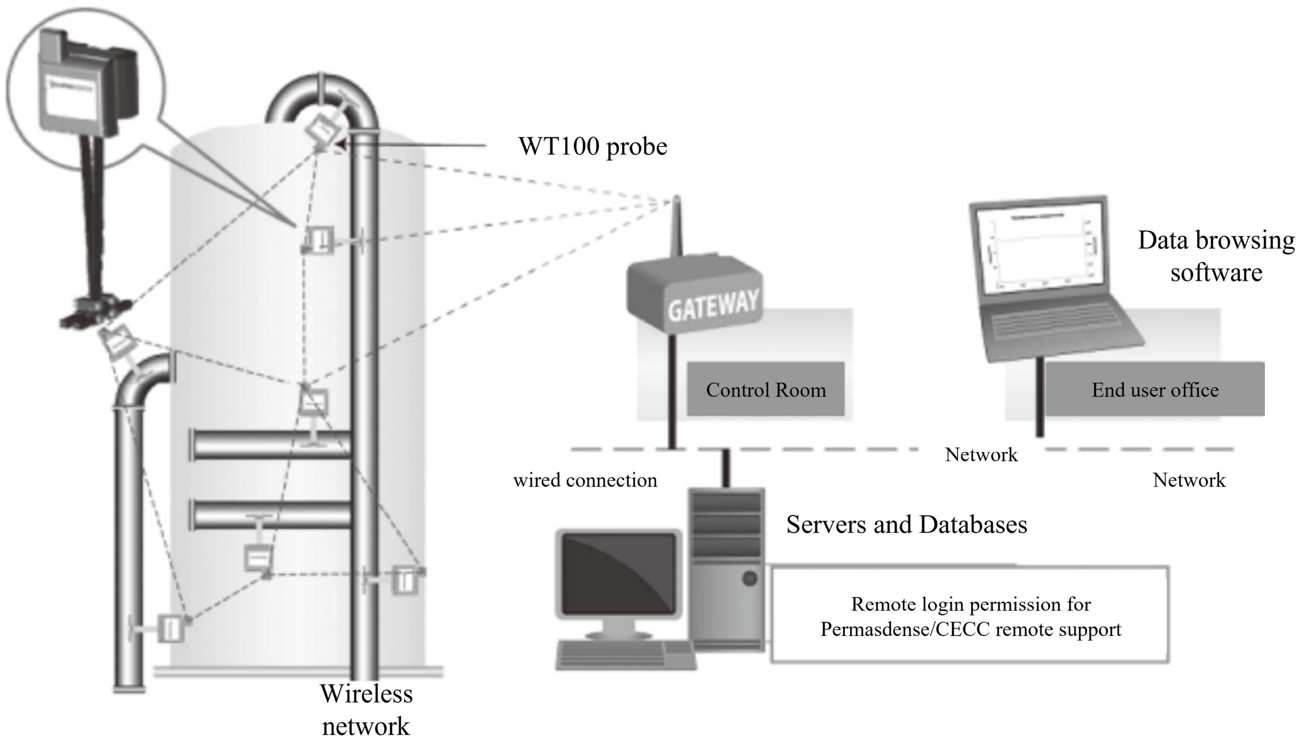

Figure 5. Work diagram of permasdense online wall thickness monitoring system.

3.4. Industrial Preventive Treatment of Sulfur Corrosion Products

Treatment of sulfur corrosion products from the perspective of industrial prevention mainly includes isolation method, cleaning method and passivation method [35].

a) Isolation method

Through the method of nitrogen sealing and water sealing, the sulfur corrosion tank is sealed to prevent sulfur corrosion products from contacting with air to effectively prevent its spontaneous combustion process [36]. Feng proposed that the nitrogen sealing technology could effectively prevent air from entering the storage tank to prevent the occurrence of FeS oxidation reaction [37]. Xiao believed that the nitrogen sealing technology can form a gas mixture that is not easy to explode in the tank, which effectively reduce the risk caused by spontaneous combustion of sulfur corrosion products and respiratory loss inside the equipment to improve economic benefits and avoid oil-gas pollution [38].

b) Cleaning method

The equipment with sulfur corrosion products is cleaned by using special chemical cleaning agents. Composite cleaning method combining cleaning and passivation is widely used in China [39]. Geng proposed a chemical cleaning agent suitable for corrosion products of sulfur-containing oil storage tanks. A new foam cleaning agent was prepared by adding thickening agent xanthan gum and hydroxyethyl cellulose as surfactant and foaming agent to sulfuric acid solution, which can effectively clean sulfur corrosion products and reduce the content of waste liquid after cleaning [40]. Korovnikova believes that hydrogen peroxide solution can effectively clean the self-ignition of corrosion products in petroleum equipment [41]. Figure 6 shows the application effect of ferrous sulfide cleaning agent on the cleaning treatment of atmospheric and vacuum distillation unit. In the later stage of cleaning, the content of passivator no longer reduces and the PH value keeps unchanging. And the sulfur ions at the end point are not detected. The ferrous sulfide and sulfur-containing harmful gases are basically processed.

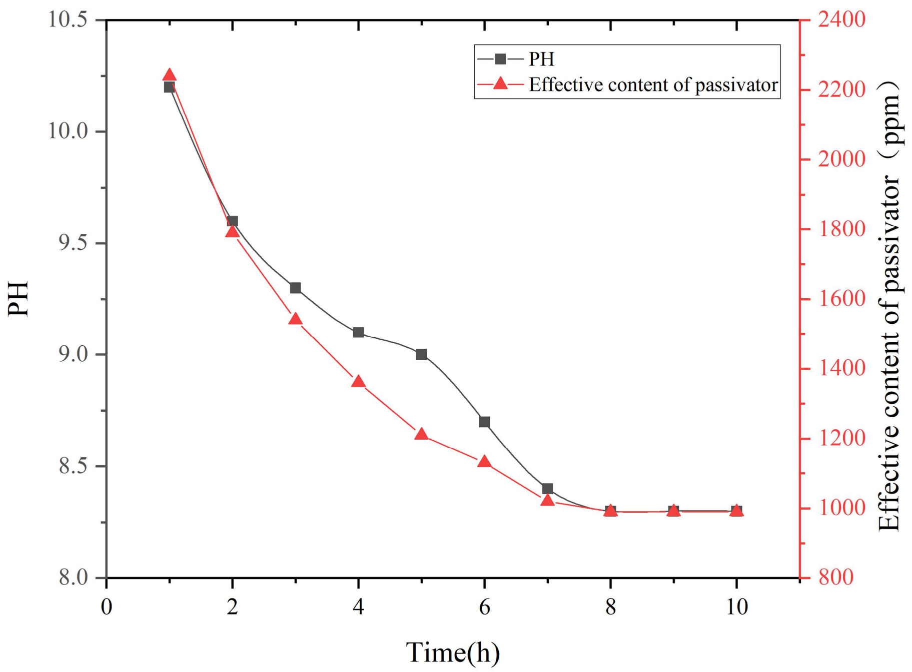

Figure 6. *Application of SGR-1350 FeS cleaning agent in parking maintenance of atmospheric and vacuum decompression unit.*

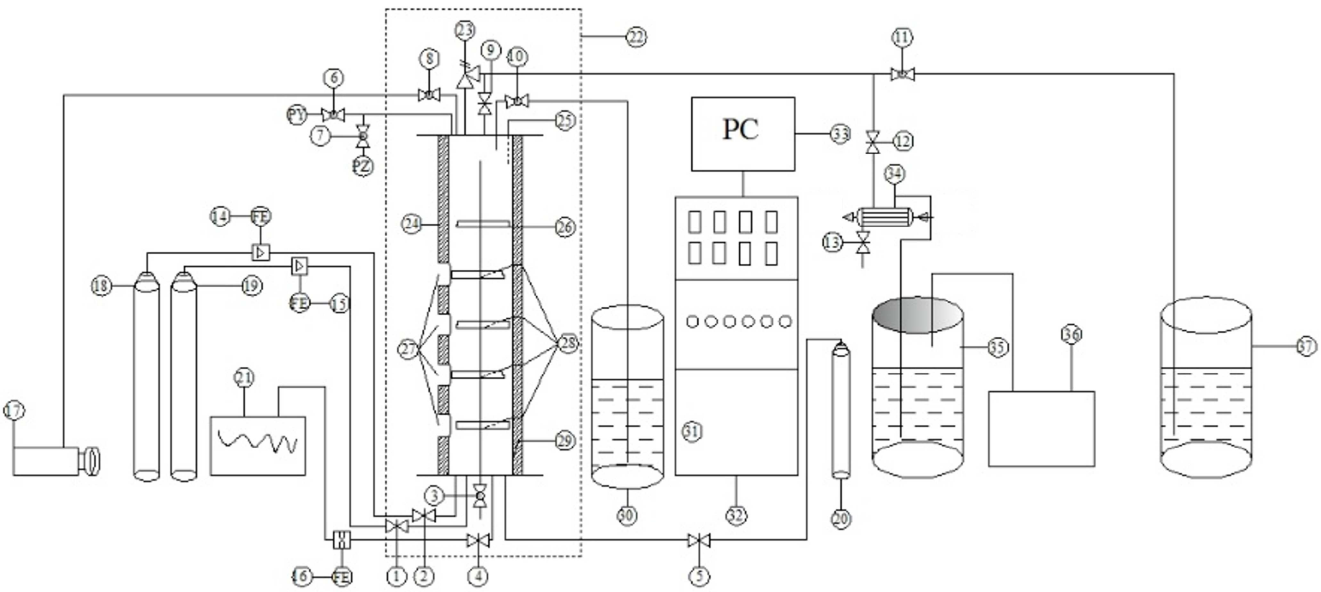

Figure 7. *Gas phase passivation device.*

c) Passivation method

Sulfur corrosion products have strong spontaneous combustion reactivity at room temperature. The passivation method converts the sulfur corrosion products attached to the equipment into stable compounds by passivator, which effectively inhibits the spontaneous combustion reactivity [42, 43]. Wang effectively passivated the spontaneous combustion reactivity of sulfur corrosion products by injecting oxidizing gas into the packed tower through gas phase passivation method [44]. The spontaneous combustion reactivity of sulfur corrosion products in the packed column was effectively passivated by the gas phase passivation method. As shown in Figure 7, Song designed a gas-phase passivation device and used a controllable proportion of oxygen and water vapor to passivate pyrite compounds to reduce their spontaneous combustion reactivity [21, 45]. Montgomery used oxygen-containing gas to safely passivate iron sulfide with spontaneous combustion reactivity [46]. Dou effectively passivated iron sulfide by mixing oxygen-containing gas and applied this passivation process to the prevention and control of spontaneous combustion of sulfur corrosion products in the distillation column, achieving good inhibition effect and low cost [47]. Dai studied the passivation process of active ferrous sulfide under low oxygen concentration. It was found that the oxygen volume fraction was less than 1.25% and the passivation process was less exothermic and safer [48]. After the active sample was passivated by gas phase, a dense passivation film was formed on the surface and the main component was Fe_2O_3. The main equation for the formation of the passivation film was as following [49]:

$$4FeS+3O_2 \rightarrow 2Fe_2O_3+4S \quad (20)$$

The activation energy of FeS was greatly increased and the spontaneous combustion reactivity was inhibited. Zhao found it is the low flow rate of air passivation changed the oxidation reaction path and increased the proportion of iron sulfide in the incomplete oxidation reaction. It reduced oxidation reaction rate, resulting in a decrease in the reaction exothermic rate [43].

4. Influencing Factors of Sulfur Corrosion Products Spontaneous Combustion

In order to further reveal the spontaneous combustion mechanism of sulfur corrosion products, the influencing factors of spontaneous combustion are classified and summarized. Based on the properties of sulfur corrosion products, the influencing factors include particle size, moisture content and vulcanization mode. In terms of the external environment, the influencing factors include air flow, oxygen concentration, ambient temperature, heating rate and oil products [50, 51].

4.1. Properties of Sulfur Corrosion Products

a) Particle size

Asakiz found that single granular FeS (particle size is 51-89μm) spontaneous combustion time is in 0.1s, which is more reactive than dense plate-like and spherical FeS [52]. Li found that the specific surface area became smaller with the increase of FeS particle size, which reduced the contact area between ferrous sulfide and oxygen molecules to reduce the reaction probability [53]. Zhao also proved this view through experiments [8, 23, 54]. But when the particle size continues to increase, the specific surface area decreases to increase the spontaneous combustion time of FeS [55]. In the mixture of FeS_2 and FeS, the specific surface area, average pore diameter and fractal dimension increase with the increase of FeS content. The internal structure is looser and it is easier to adsorb oxygen, which is easy to lead to spontaneous combustion of FeS [13, 56].

b) Moisture content

Moisture content has a significant impact on the spontaneous combustion of sulfur corrosion products. The presence of a small amount of water will rapidly increase the spontaneous combustion tendency of ferrous sulfide [57]. Figure 8 shows oxidation weight gain rate curves of sulfur corrosion products with different moisture content. In the range of 0% – 9% moisture content, the oxidation rate increases with the increase of moisture content. When the moisture content was in the range of 5% – 60%, the effect of water on spontaneous combustion tendency of ferrous sulfide slowed down. When the moisture content reached 60%, the spontaneous combustion of ferrous sulfide was basically inhibited [58]. Water evaporation absorbs the heat generated by oxidation reaction, destroys the heat storage process of pyrite particles and inhibits the self-heating process of pyrite particles. The thermal conductivity will be greatly improved when the internal pores are filled with water, which is beneficial to the heat loss of ferrous sulfide system [59].

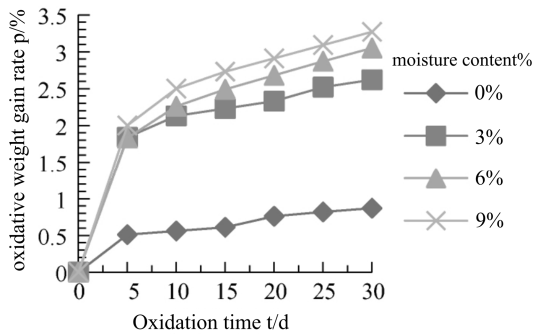

Figure 8. *Oxidation weight gain rate curve of sulfur corrosion products with different moisture content.*

c) Vulcanization mode

Dou et al. conducted on-site sampling of petrochemical equipment, sulfur corrosion products were treated by dry vulcanization and wet vulcanization. It was found that ferrous sulfide only existed in the wet vulcanization products and the final spontaneous combustion product was iron oxide. The disappearance of FeS in dry vulcanization rust was due to the change of sulfide from FeS to Fe_3S_4 and FeS_2 with the increase of temperature [60, 61]. It was found that the spontaneous combustion tendency of $Fe(OH)_3$ sulfide products was much higher than that of Fe_2O_3 and Fe_3O_4. The heating rate of spontaneous combustion, the content of active pyrite compounds and the growth rate of temperature increases with the increase of vulcanization time. Under the condition of relative humidity of 10%–15%, the sulfide product has higher reactivity and could accelerate the spontaneous combustion process. However, with the increase of relative humidity, the spontaneous combustion and oxidation rate of sulfide products slowed down and the spontaneous combustion reactivity decreased significantly [62].

4.2. External Environment of Sulfur Corrosion Products

a) Heating rate

With the increase of heating rate, the characteristic temperature and weight loss rate increase in oxidation decomposition stage of sulfur corrosion products. The oxidation induction period increases and the degree of spontaneous combustion slows down [9, 50]. Zhao et al. believed that with the increase of heating rate, the initial oxidation temperature of FeS increased and the oxidation temperature range widened [8, 23]. Liu et al. studied the spontaneous combustion tendency of sulfur corrosion products at different heating rates and found that it increased with the increase of heating rate [63]. Zhao calculated the activation energy of spontaneous combustion of FeS at different heating rates. It was found that the activation energy was similar when the heating rate was 2K/min and 5K/min and the activation energy decreased in turn when the heating rate was 5-15K/min. The spontaneous combustion characteristics of ferrous sulfide were enhanced [64].

b) Air flow

The increase of air flow increases the oxygen concentration in the system, increasing the probability of sulfur corrosion products contacting with oxygen molecules to promote the spontaneous combustion of sulfur corrosion products. Yan studied the spontaneous combustion process of ferrous sulfide under the air flow of 100ml/min, 200ml/min and 300ml/min. It was found that with the increase of air flow, the heating rate of ferrous sulfide spontaneous combustion increased. As shown in Figure 9, with the increase of air flow rate, the maximum temperature value and the maximum heating rate during spontaneous combustion process show a trend of increasing first and then decreasing [65].

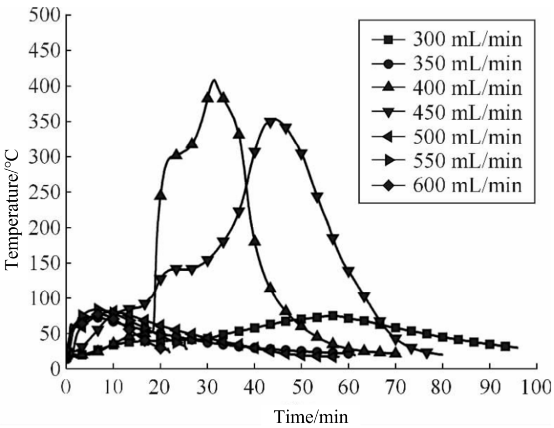

Figure 9. *Oxidation temperature-time curves of FeS under different air flow rates.*

c) Oxygen concentration

Wan found that the higher oxygen concentration and spontaneous combustion tendency made ferrous sulfide spontaneous combustion more intense [66]. Lv et al. explored the oxidation kinetics of FeS in a specially designed thermo gravimetric reactor (TGR) and found that the rate constant of ferrous sulfide oxidation increased with the increase of oxygen partial pressure [67]. Zhang studied the oxidation heating process of Fe_2O_3 sulfide products under different oxygen concentrations. It was found that with the decrease of oxygen concentration, the maximum temperature of spontaneous combustion decreased and the spontaneous combustion tendency under low oxygen concentration decreased [68].

d) Ambient temperature

The ambient temperature has an obvious influence on the spontaneous combustion of sulfur corrosion products. The higher the ambient temperature, the greater the possibility of spontaneous combustion. When the ambient temperature was 80°C, the spontaneous combustion of pyrite released more heat and significantly increased the heating rate [69]. The heat dissipation rate decreases with the increase of ambient temperature, which is not conducive to the heat dissipation of sulfur corrosion products during spontaneous combustion process [59, 70]. Hu used ANSYS finite element method to analyze the temperature field of sulfur-containing oil storage tanks. It was found that with the increase of ambient temperature, the smaller the ambient temperature difference in the abnormal area of the outer surface temperature of the tank, the greater the difficulty in detecting the source of spontaneous combustion in the tank [71, 72]. Affected by seasons, the external environmental temperature of petroleum refining equipment changes frequently to affect the spontaneous combustion tendency of sulfur corrosion products.

e) Oil products

There are mixture of sulfur corrosion products and oil products in petrochemical refining equipment. And the presence of oil products reduces the spontaneous combustion tendency of sulfur corrosion products [73]. Zhao et al. found that with the increase of oil content, the temperature-rising rate of iron sulfide slowed down. With the increase of oil content, iron sulfide did not enter the stage of deep oxidation and the temperature began to decline [59]. Zhao et al. dropped naphtha into FeS and found that it was difficult for oxygen molecules to adsorb on its surface, which greatly reduced the spontaneous combustion and oxidation rate of FeS when the oil wrapped FeS [58]. Yin et al. explored the oxidation weight gain process of sulfur corrosion products in the presence of oil pollution. Without oil pollution, the weight gain rate of sulfur corrosion products initially maintained a rapid increase rate. In the presence of oil pollution, the oxidation weight gain rate changed slowly and the sulfur corrosion products did not increase weight after 5 days [74]. Oil pollution wrapped the sample surface and penetrated into the sample gap to prevent it from contacting with air.

At present, the research on the influencing factors of spontaneous combustion of sulfur corrosion products is mostly carried out from the above aspects. Due to the interaction of the influencing factors of spontaneous combustion, it cannot be studied from a single aspect. Scholars have studied the interaction of multiple influencing factors on spontaneous combustion of sulfur corrosion products by explaining the structural model and established a multi-level ladder ISM to classify the influencing factors [75]. The research results provide a certain reference for the prevention and control of spontaneous combustion hazards of sulfur corrosion products in petroleum refining equipment.

5. Conclusions

With the increasing demand for crude oil in China ' s petrochemical industry in recent years, high sulfur content crude oil leads to sulfur corrosion in petrochemical equipment. The hazards of fire and explosion accidents caused by spontaneous combustion of sulfur corrosion products cannot be ignored. Scholars have conducted relatively sufficient research on the spontaneous combustion mechanism and influencing factors of sulfur corrosion products. This paper further classifies the prevention and control technologies of spontaneous combustion of sulfur corrosion products and discusses influencing factors of spontaneous combustion of sulfur corrosion products. This paper is of great significance to further study the spontaneous combustion of sulfur corrosion products. The following conclusions and further research prospects are obtained.

(1) The formation process of sulfur corrosion products is divided into chemical reaction corrosion, electrochemical corrosion and bacterial corrosion, which are mainly composed of pyrite compounds and other impurities. Most of the early studies took commercially available pure FeS as sample to explore spontaneous combustion of sulfur corrosion products. In recent years, the preparation of sulfur corrosion products by simulating the sulfur corrosion process was studied and sulfur corrosion products obtained from working place were also taken as experimental samples. The spontaneous combustion characteristics of sulfur corrosion products under different sulfur iron ratio and mass ratio need to be further studied.

(2) The spontaneous combustion process of sulfur corrosion products is mainly divided into oxidation period, medium-speed oxidation period and accelerated oxidation period. The internal structure of sulfur corrosion products is loose and porous. And the unpaired d electrons of internal Fe have strong adsorption capacity, which is conducive to combination with oxygen in spontaneous combustion process. Sufficient oxygen supply and heat accumulation conditions are the external environment for spontaneous combustion of sulfur corrosion products. The reaction path of sulfur corrosion products spontaneous combustion process can be simulated from the perspective of quantum chemistry and its spontaneous combustion mechanism can be revealed, which will provide a basis for the development of spontaneous combustion prevention and control technology.

(3) For crude oil, reducing the sulfur content of oil by desulfurization technology, anti-corrosion treatment of storage tanks and monitoring the sulfur corrosion of storage tanks can fully and effectively reduce the formation of corrosion products. For refining equipment with sulfur corrosion products, the sulfur corrosion products are effectively removed by isolation, cleaning and passivation method and the spontaneous combustion reactivity is inhibited to effectively prevent the spontaneous combustion accidents of sulfur corrosion products during inspection and maintenance. Due to the clean, convenient and comprehensive characteristics of gas phase passivation technology, it is necessary to study the passivation method suitable for field working conditions in the future and find the most suitable passivation parameters.

(4) From the properties of sulfur corrosion products, the influencing factors include particle size, moisture content and vulcanization mode. The external environmental factors include ambient temperature, heating rate, air flow, oxygen concentration and oil products. The research mainly focuses on the influence of single factor and a small amount of model analysis is used to analyze the interaction of multiple factors on the spontaneous combustion of sulfur corrosion products. It is significant to study the spontaneous combustion characteristics of sulfur corrosion products under multi-factor interaction, which will provide a basis for the research and development of prevention and treatment methods suitable for working conditions.

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References

[1] Wang, Jiayi., T, Lei., F, Xiaoqing. (2022). Seven new trends in the oil industry and five reform proposals. Energy of China, 44 (03), 39-43.

[2] Walker, R., Steele, A. D., Morgan, D. T. (1996). Pyrophoric nature of iron sulfides. Industrial & engineering chemistry research, 35 (5), 1747-1752.

[3] Zhang, Z. H. (2009). Study on influence factors for the formation of iron sulfides and its pyrophorisity. Northeastern University.

[4] Backensto, E. B., Drew, R. D., Vlachos, J. N. (1956) Hydrogen sulfide corrosion in sovaformers. Petroleum Refiner, 35 (8), 165.

[5] An, C. X., & Ning, Z. (1999). Sulfur corrosion and prevention in petroleum processing. petroleum Refinery Engineering. (08), 61-67.

[6] Jianli, L. I. (2000). Hydrogen sulfide corrosion in petro chemical industry. Corrosion Science and Protection Technology, 12 (6), 346-349.

[7] Gao, X. D., Zhu, Y. Z. (2001). Effects of processing high sulfur crude oil on storage tanks. Corrosion and Protection of Petrochemical Industry. (06), 39-41.

[8] Sheng-Ping, Z., & Jun-Cheng, J. (2010). Thermal analysis hydrodynamics study on fes. Journal of China University of Petroleum (Edition of Natural Science). (05), 164-167+173.

[9] Cai X. (2015). Pyrite compound low temperature oxidation process and dynamics research. Zhengzhou university.

[10] Li, Z. J., Jiang, W., & Chen, T. (2018). Kinetic analysis on oxidation and spontaneous combustion of iron sulfides. Journal of Safety Science and Technology. (01), 24-29.

[11] Zhang, Y., Juncheng, J., Longsen, H., Fengyi, M., Zhan, D., & Mingguang, Z., et al. (2017). Oxidation experiment of sulfurized rusts in crude oil tank. Journal of Nanjing Tech University (Natural ence Edition).

[12] Gao, J. C., Man, X., Shen, J., Meng, Q., & Zhou, S. (2017). Synthesis of pyrophoric active ferrous sulfide with oxidation behavior under hypoxic conditions. Vacuum, 143, 386-394.

[13] Shang, L. Y. (2018). Study on formation and pyrophorisity of iron sulfides and its process of spontaneous combustion. Northeastern University.

[14] Shao, W. Y., Tang, Z. F., Zhang, Z. H., Zhao, S. L., & Shang, L.. (2015). Research on the oxidation reactions of ferrous sulfide. Journal of Safety and Environment. (05), 119-122.

[15] Gao, J. C., Man, X. M., Zhu, J. H., & Meng, Q. Q. (2016). Spontaneous combustion of active ferrous sulfide and its apparent kinetics. China Safety Science Journal. (10), 30-35.

[16] Gao, J. C., Zhou, S. Y., Zhu, J. H., Yang, J. L., Sun, W., & Zhao, Y., et al. The preparation of active ferrous sulfide and the study on it's self-ignition characteristics. Journal of Beijing Institute of Petro-Chemical Technology. (01), 1-5.

[17] Dou, Z., Jiang J. C., Zhao, S. P.,& Mao, G. B.. (2014). The generation and spontaneous combustion of low temperature sulfur corrosion products in storage tanks. Corrosion science and protection technology (04), 365-372.

[18] Hong, R.. (2020). Oil tank corrosion products thermal dynamic characteristics, and the evaluation of the self-ignition orientation. China university of measurement.

[19] Hui, L., Zhao, S., Xie, Z., Zhu, K., Xu, X., & Ding, X., et al. (2018). Investigation of the pyrophoric tendency of the powder of corrosion products in an oil tank. Powder Technology. 339, 296-305.

[20] Zhang, L. J.. (2017). Study on the iron sulfide oxidation process under low temperatures. Zhengzhou University.

[21] Song, H. R.. (2014). Pyrite compound gas phase passivation mechanism. Qingdao university of science and technology.

[22] Yang, Y. X., Jiang, J. C., & Zhao, S. P.. (2010). Study on the oxidation tendency of ferrous sulfide based on thermo-gravimetric analysis. journal of safety and environment. (01), 178-180.

[23] Zhao, S. P., Jiang, J. C., & Yang, Y. X.. (2010). Thermal kinetic analysis on oxidation of FeS based on thermal gravimetric experiments. Acta Petrolei Sinica (Petroleum Processing Section), 26 (6), 972.

[24] Xd, A., Xd, B., Zl, C., Xd, D., Hs, D., & Jw, D., et al. (2021). Corrosion analysis and anti-corrosion measures of oil casing of sulfur content gas wells: a case study of daniudi gas field in the ordos basin - science direct. Energy Reports, 7, 1280-1292.

[25] Yang, R. R., Wang, Z. R., Jiang J. C., & Lu, Y. W.. (2020). Cause analysis and prevention measures of fire and explosion caused by sulfur corrosion - science direct. Engineering Failure Analysis 108, 104342.

[26] Bian, H., Jiang, J., Zhu, Z., et al. (2022). Design and implementation of an early-stage monitoring system for iron sulfides oxidation. Process Safety and Environmental Protection, 165: 181-190.

[27] Chu, C. W., Zhu, Z. C., Bian, H. T., & Jiang, J. C.. (2021). Design of self-heating test platform for sulfide corrosion and oxidation based on fuzzy pid temperature control system. Measurement and Control -London- Institute of Measurement and Control-(5), 002029402110203.

[28] Zhu, X. G.. (2018). Present situation and development of fcc fgd technology. Chemical Engineering Design Communications.

[29] Shui, C., & Company, S. J.. (2019). Application status and existing problems of fcc flue gas de-so$_x$/de-no$_x$ technology. (05), 49-55.

[30] Tong, J. L.. (2019). Analysis of corrosion status of sour crude oil on storage tanks and discussion on anti-corrosion measures. Total Corrosion Control (02), 76-78.

[31] Lu, Y., Wang, Z., Dou, Z., Zhen, Y., & Jiang, F.. (2018). Study of corrosion of oil tank parts and gas-phase space in different tanks. Process Safety Progress, 37 (3), 419-426.

[32] Zhang, D. P., Sun, M. M., Cao, X. K., & Dong, Z. H.. (2020). Progress in corrosion inhibitor evaluation and corrosion monitoring technology in oil and gas industry. Surface technology (11), 1-12.

[33] Guo, S. Q., Ai, J. Q., & Wang, D. P.. (2020). Analysis of on-line corrosion monitoring technology for oil refining units. Current Chemical Research (20), 28-29.

[34] Guo, L.. (2021). Application of corrosion monitoring technology in refining plant. Total Corrosion Control (08), 168-173.

[35] Zhan, J. D., Gao J. C., Liu, S. S., Zhang, Y., Cao, X. D., Yang, Z. Y. F., & Ma F. F.. (2021). Research progress on spontaneous combustion mechanism and accident prevention of active ferrous sulfide. Industrial Safety and Environmental Protection (09), 11-16.

[36] Reformatskaya, I. I., Begishev, I. R., Ascheulova, I. I., & Podobaev, A. N.. (2020). Nitrogen protection as anticorrosion and fireproofing measure in the use of sour crude oil storage tanks. Chemical and Petroleum Engineering, 56 (7-8), 563-568.

[37] Feng, X.. (2006). Spontaneous burning in sulfur contained oil tank and protection measures. Process Equipment & Piping. (04), 61-64.

[38] Chi, X.. (2004). Important significance of application of nitrogen sealed technology to light oil tank. Petrochemical Safety Technology.

[39] Qi, Z. J.. (2017). Cause analysis and disposal of spontaneous combustion of ferrous sulfide during cleaning of oil storage tanks. Safety, Health and Environment, 017 (004), 5-7.

[40] Xun, G., & Xin, J.. (2013). A novel foam cleaning agent for removal of sulfur-iron compounds in petrochemical storage equipments. Petrochemical Technology. (09), 1035-1038.

[41] Oliinik, V., Korovnikova, N., & Dubyna, O.. (2021). Research of pyrophoric compounds in order to reduce their hazard. Materials Science Forum, 1038, 454-459.

[42] Shen, J., Yuan, T. Y., Zhang, Y. P., Long, Z. C., Xi, H. E., & Gao, J. C.. (2019). Study on spontaneous combustion characteristics and activity inhibition of ferrous sulfide. Applied Chemical Industry. (05), 1110-1113.

[43] Zhao, X., Liu, M., Feiyue, X. I., & Zhang, L.. (2019). Research on the air passivation mechanism of iron sulfide. Industrial Safety and Environmental Protection. (01), 30-33.

[44] China Petroleum and Chemical Co., LTD. & China Petroleum and Chemical Co., LTD. Qingdao Safety Engineering Research Institute (2014-02-05). CN101988179B.

[45] Xi, F. Y.. (2017). The cleaning technology of pyrite compounds research. zhengzhou university.

[46] Montgomery, B.. (2015). Method for Treating Oil Refinery Equipment to Oxidize Pyrophoric Iron Sulfide. US20150217343A1.

[47] Dou, Z., Shen, S., Jiang, J., Wang, Z., & Chen, Q.. (2020). Oxidizing-gas-based passivation of pyrophoric iron sulfides. Chemical Engineering Communications (4), 1-10.

[48] Dai, H. Y., Dai, S. b., Gao, J. C., Shen, J., Bai, S. X. & Liu, X. l.. (2021). Effect of oxygen concentration on passivation behavior of spontaneous combustion ferrous sulfide. Journal of Safety and Environment (05), 2045-2050.

[49] Zhan, J. D.. (2021). Experimental gas-phase passivation offerrous sulfide and molecular simulation study. Beijing Institute of Petrochemical Technology.

[50] Kong, D., Liu, P., Ping, P., & Chen, G.. (2016). Evaluation of the pyrophoric risk of sulfide mineral in storage. Journal of Loss Prevention in the Process Industries, S0950423016302170.

[51] Liu, H., Hong, R., Xiang, C., Lv, C., & Li, H.. Visualization and analysis of mapping knowledge domains for spontaneous combustion studies - science direct. Fuel, 262.

[52] Asaki, Z., & Kondo, Y.. (1989). Oxidation kinetics of iron sulfide in the form of dense plate, pellet and single particle. Journal of thermal analysis. 35 (6).

[53] Ping, L. I., Jian Dong, L. I., Zhai, Y. C., Zhang, Z. H., & Zhang, F. H.. (2004). Spontaneous combustion behavior of ferrous sulfide in oil tank containing suplhur. Corrosion Science and Protection Technology. (06), 401-403.

[54] Zhao, S. P., Wu, Y. H., & Jiang, J. C.. (2010). Rheology-mutation study on spontaneous combustion of sour oil storage tanks. Fire Protection Technology and Product Information, 000 (009), 36-39.

[55] Wei, X. U., Zhang, S., & Wang, Z.. (2015). Study on auto-ignition temperature of ferrous sulfide. Industrial Safety and Environmental Protection. (06), 36-38.

[56] Zhu, W. F. (2018). Study on correlation between quantitative structures of sulfur corrosion products and spontaneous combustion of oil storage tanks. Fuzhou university.

[57] Wan, X.. (2009). Effect of water on rust sulfide pyrophoricity from inner-face of tank. Yunnan Chemical Technology. (03), 5-7.

[58] Ping, L. I., Wei, Y. E., Zhang, Z. H., Zhao, S. L., & Zhai, Y. C.. (2004). Investigation of natural oxidation tendency for ferrous sulfide. Journal of Combustion Science and Technology. (02), 168-170.

[59] Zhao, X. E., & Jiang, J. C.. (2007). Mechanism and effect factors for spontaneous combustion of iron sulfide in natural environment. Journal of Combustion Science and Technology. (05), 443-447.

[60] Dou, Z., Jiang, J., Wang, Z., Zhao, S., Yang, H., & Mao, G.. (2014). Kinetic analysis for spontaneous combustion of sulfurized rust in oil tanks. Journal of Loss Prevention in the Process Industries, 32, 387-392.

[61] Dou, Z., Jiang, J. C., Zhao, S. P., et al. (2015). Experimental investigation on oxidation of sulfurized rust in oil tank. Journal of Loss Prevention in the Process Industries, 2015, 38: 156-162.

[62] Wan, X., & Zhao, S. L.. (2009). Influence of relative humidity on pyrophoricity of iron sulfides. Journal of Qingdao University of Science and Technology (Natural Science Edition). (04), 304-306.

[63] Liu, H., Hong, R., Lang, Z., Yao, J., & Liu, X.. (2021). Evaluation of the spontaneous combustion tendency of corrosion products in oil tanks based on topsis methodologies. Journal of Loss Prevention in the Process Industries, 71 (3), 104475.

[64] Zhao, X. F.. (2013). Experimental Investigation on the Spontaneous Combustion Kinetics of Ferrous Sulfide. Wuhan University of Technology.

[65] Cai, Z. L., Jiang, J. C., Zhao, S. P., Zhan, D., & Mao, G. B.. (2016). The impact of air flow rate on the oxidation self-heating of sulfur corrosion products in oil tank. Fire Science and Technology. (02), 145-148.

[66] Wan, X., Zhao, S. L., Ping, L. I., & Zhang, Z. H.. (2005). Influence of oxygen concentration on pyrophoricity of iron sulphide. Corrosion & Protection. (12), 512-514+526.

[67] Lv, W., Yu, D., Wu, J., Yu, X., Du, Y., & Yao, H., et al. (2016). A kinetic study on oxidation of ferrous sulfide (fes) in mixtures of CO_2 and H_2O. Proceedings of the Combustion Institute, 36 (2), 2173-2180.

[68] Zhang, F. H., Zhang, Z. H., Li, P., Zhao, Y., & Zhao, S. L. (2005). Investigation of natural oxidation tendency for oil tanks containing sulfur. Journal of Petrochemical Universities. (02), 5-7+87.

[69] Yan, B. L., Liu, G. C., & Wang, L. D. (2009). Formation and spontaneous combustion tendency of sulfide products from oil refinery equipment corrosion in low-temperature location. Petro-Chemical Equipment. (02), 4-8.

[70] Li, Z., Cai, R., & Xu, Y. (2021). Numerical Analysis of the Spontaneous Combustion Accidents of Oil Storage Tanks Containing Sulfur. Processes, 9 (4), 626.

[71] YunFei, H. U., Liu, H., Wang, Z. X., & Xie, Z. W. (2014). Identification of spontaneous combustion disaster source for tank of oil containing sulfur based on inversion method of point heat source. China Safety Science Journal. (08), 49-55.

[72] Yunfei, H. U., Liu, H., Yueming, F. U., Xie, Z., & Wang, Z. (2014). Numerical simulation of temperature field of spontaneous combustion disaster sources for oil tanks containing sulfur. Journal of China University of Metrology. (04), 366-371.

[73] Depeng Kong, Peng, R., Sun, X., Zhang, J., Ping, P., & Jin, D. (2019). Study of the influence of crude oil on the spontaneous combustion risk of sulfurized rust in crude oil tanks. Fuel. 2019. 255 (C).

[74] Yin, M., & Zijun, L. I.. (2019) Experimental study on factors influencing spontaneous combustion of oil containing sulfur storage tanks. 29 (03): 45-50.

[75] Yang, F., Zhu, W., & Liu, X.. (2016). Analysis of factors influencing spontaneous combustion of oil tanks containing sulfur based on ism and interval-numbe. China Safety Science Journal. (09), 62-66.