Study on Oxidation and Self-ignition of Ferrous Sulfide Based on the Thermo-gravimetry Experiments

Sisi Liu, Jing Shen, Haoyuan Dai, and Jiancun Gao

Abstract—**Self-ignition of ferrous sulfide compounds is one of the important causes of fire and explosion accidents in oil and gas production facilities and storage tanks. Systematic research on the self-ignition characteristics of ferrous sulfide is of great significance to chemical safety. In this paper, ferrous sulfide samples with high activity were prepared by liquid precipitation method. The pyrophoric properties of the prepared ferrous sulfide sample in a different atmosphere were studied by a synchronous thermal analyzer. The results show that the self-ignition reaction of ferrous sulfide contains two parts: self-heating and combustion; Accelerating the gas flow and increasing the oxygen concentration in the atmosphere inhibits the combustion reaction. And accelerating the rate of temperature rise make the autothermal reaction more difficult to undergo.**

Index Terms—**Thermal analysis, ferrous sulfide, self-heating, self-ignition, security of chemical industry.**

I. INTRODUCTION

In the oil and gas storage equipment, ferrous sulfide is produced due to corrosion. The ferrous sulfide is a highly active substance, which can spontaneously ignite under normal temperature and pressure, so it is easy to cause fire accidents during equipment maintenance [1]. In recent years, there have been many petrochemical safety accidents caused by spontaneous combustion of active ferrous sulfide compounds [2]. The long-term use of the equipment has produced ferrous sulfide, which is prone to spontaneous combustion in the air [3]. Systematic research on the self-ignition characteristics of ferrous sulfide is of great significance to chemical safety. [4]-[6].

The spontaneous combustion of ferrous sulfide was discovered as early as the nineteenth century. And researchers have also studied different aspects of ferrous sulfide [7]-[10]. Y. X. Yang and B. P. Wang studied the thermal oxidation process and thermodynamics of ferrous sulfide by thermogravimetric analysis. Studies have shown that the characteristic temperature rise and the activation energy value increase of the ferrous sulfide thermal oxidation process. At this time, the oxidative autoignition characteristics of ferrous sulfide were enhanced [11]. X. F. Zhao *et al.* performed a thermogravimetric and heat flow

analysis on a commercially available ferrous sulfide reagent using a synchronous thermal analyzer. The oxidation heating process was divided into three stages, a physical adsorption stage, a chemical adsorption stage and a chemical reaction stage [12]. In the above study, the commercially available ferrous sulfide was used for thermal analysis, and the commercially available ferrous sulfide content was about 80 %. It did not have the characteristics of self-ignition in the air, and different from the properties of ferrous sulfide in actual industrial production. J. C. Gao, S. Y. Zhou *et al.* used four different preparation methods to prepare ferrous sulfide, and the activity of four samples were compared, among which the ferrous sulfide prepared by liquid-liquid precipitation method had the best activity [13]. In this paper, high activity ferrous sulfide was prepared by liquid precipitation method, and the sample was subjected to thermogravimetric analysis. It can more accurately reflect the igniting characteristics and influencing factors of ferrous sulfide oxidation, so as to take targeted safety technical measures in production practice, and provide a certain theoretical basis for the prevention and control of ferrous sulfide spontaneous combustion.

II. EXPERIMENTS

Experimental instruments: There are two balances in the synchronous thermal analyzer, and the mass of the sample can be obtained by comparing the two balances. It can also measure the thermogravimetric and heat flow curves of the sample at the same time, and obtain the characteristic temperature points such as the initial reaction temperature and peak temperature through the internal integration function. This analysis mainly uses the characteristic temperature point as the starting point, and finds the regular line to explore.

Structural principle: The sample S and the reference R are respectively placed in two crucibles, and each has a thermocouple under the crucible, and the two thermocouples are reversely connected to each other. Simultaneously temperature-raising the sample and the reference material. When heating to a certain temperature and the sample is exothermic or endothermic, the sample temperature T_S will be higher or lower than the reference material temperature T_R to generate a temperature difference. ΔT will be sent to the differential thermal amplifier by the above two reversed thermocouples, the reversed thermocouples form is differential thermoelectric potential, and then amplified and input into the recorder to obtain the differential thermal curve; On the other hand, the signal corresponds to the reference material temperature T_R taken from the reference side of the

The authors are with the Beijing Institute of Petrochemical Technology, Beijing 102617 China (e-mail: liusisi644@bipt.edu.cn, 0020160023@bipt.edu.cn, daihaoyuan@bipt.edu.cn, gaojiancun@bipt.edu.cn).

differential thermocouple is compensated by the cold junction and sent to the recorder for the temperature curve. The synchronous thermal analyzer is shown in Fig. 1.

Fig. 1. Synchronous thermal analyzer.

A. Experimental Steps

a. Determine the influencing factors and set the corresponding program on the synchronous thermal analyzer. The temperature range set in this experiment is 25 °C to 400 °C. The first set of experiments: heating rate of 10 °C/min, air flow, set the air flow rate of 40 mL/min, 60 mL/min, 80 mL/min and 100 mL/min respectively; the second set of experiments: heating rate of 10 °C/min, air flow of 100 mL/min, respectively, gas with oxygen concentration of 10 %, 15% and 21 %; the third group of experiments: air flow, air flow rate of 100 mL/ min, respectively set the heating rate of 5 °C/min, 10 °C/min, 15 °C/min and 20 °C/min.

b. Connect the nitrogen bottle and the air bottle (adjusted to 0.1Mpa) to the synchronous thermal analyzer, and put the clean crucible into the synchronous thermal analyzer for leveling by the synchronous thermal analyzer.

c. The crucible is put in the glove box, add about 10mg of the sample, then put the crucible on the synchronous thermal analyzer, and start running the program for experiment.

III. RESULTS AND DISCUSSION

Effect of air flow on oxidation reaction of ferrous sulfide: The oxidation reaction of activated ferrous sulfide with air flow rates of 40, 60, 80 and 100 mL/min was detected by a synchronous thermal analyzer, and the thermo-gravimetry and heat flow diagram of ferrous sulfide at different air flow rates were obtained. Fig. 2 shows the thermogravimetric graph and Fig. 3 shows the heat flow graph.

According to Fig. 2, the initial reaction temperature of ferrous sulfide self-heating can be obtained. The heat flow curve of Fig. 3 can be integrated to obtain the reaction heat of ferrous sulfide combustion. Table I shows the initial reaction temperature and the reaction heat of ferrous sulfide combustion under different air flows.
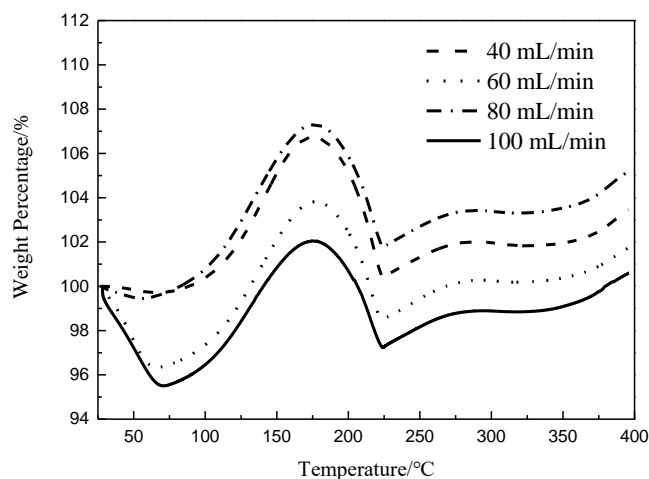

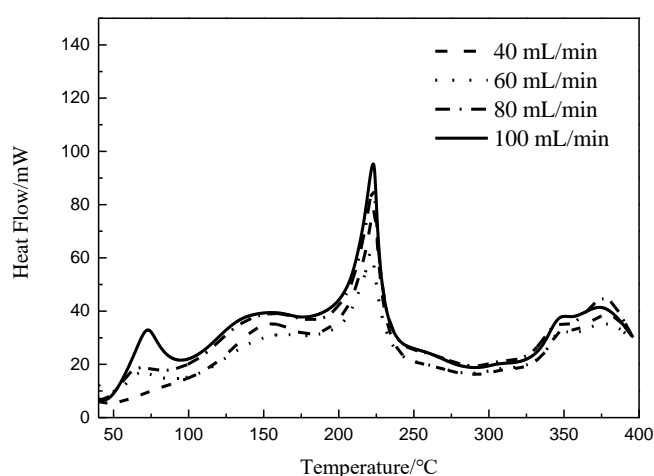Fig. 2. Thermogravimetric curve of oxidation reaction of ferrous sulfide under different air flow rates.

Fig. 3. Heat flow curve of ferrous sulfide oxidation reaction under different air flow rates.

TABLE I: INITIAL TEMPERATURE AND HEAT OF REACTION OF FERROUS SULFIDE UNDER DIFFERENT AIR FLOWS

gas flow / mL·min^{-1}	40	60	80	100
initial temperature of reaction system/°C	71.25	66.34	57.26	68.98
reaction heat/ J·g^{-1}	685.4	625.0	608.9	573.5

It can be seen from Fig. 2 that the oxidation process of the entire ferrous sulfide is divided into two parts. The first part is the self-heating reaction of ferrous sulfide. As the temperature increases, the mass of sample increases due to the adsorption of oxygen on sample. The second part is vulcanization. The ferrous combustion reaction causes a decrease in the mass of the solid sample due to the formation of sulfur dioxide by the reaction. In Fig. 3, the self-heating reaction of ferrous sulfide is physical adsorption with little change of reaction heat; the ferrous sulfide combustion emits a large amount heat, and there is a large peak in the heat flow curve. With the increase of gas flow rate, the initial temperature of self-heating reaction of ferrous sulfide showed a downward trend, indicating that the gas flow rate promoted the self-heating reaction of ferrous sulfide. When

the air flow rate is low, relatively less oxygen is supplied during the oxidation reaction of the ferrous sulfide, and the initial reaction temperature is relatively high. The reaction at a low flow rate is more difficult to occur than that at a high flow rate. As the gas flow rate increases, the heat of the ferrous sulfide combustion reaction gradually reduced. Moreover, purging by a large amount of gas for the ferrous sulfide sample reduces the heat of reaction of the ferrous sulfide.
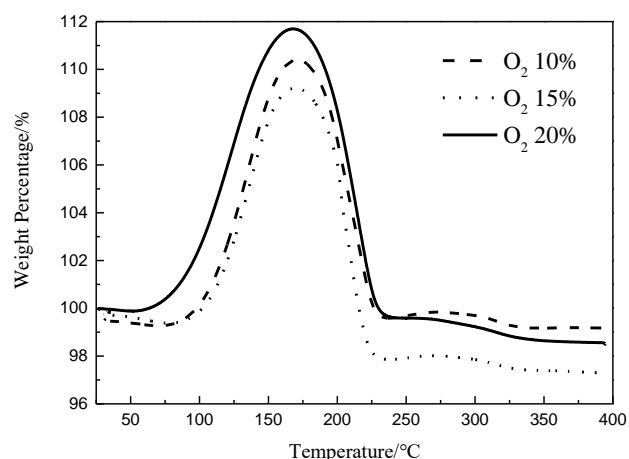

Fig. 4. Thermogravimetric curve of ferrous sulfide oxidation reaction under different oxygen concentration conditions.
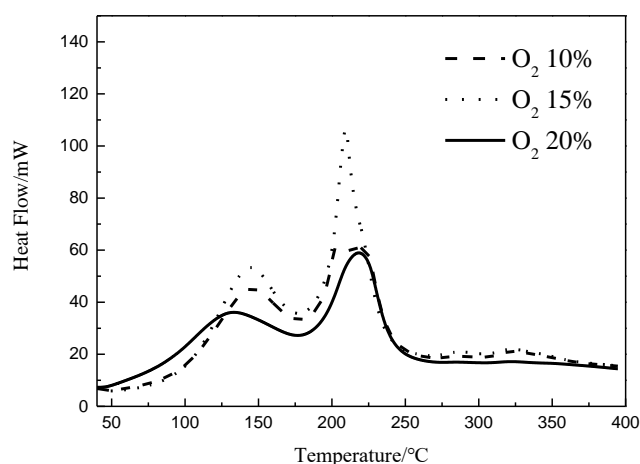

Fig. 5. Heat flow curve of ferrous sulfide oxidation reaction under different oxygen concentration conditions.

According to Fig. 4, the initial reaction temperature of ferrous sulfide self-heating can be obtained, and the heat flow curve of Fig. 5 can be integrated to obtain the reaction heat of ferrous sulfide combustion. Table II shows the reaction temperature of ferrous sulfide self-heating reaction and the reaction of ferrous sulfide combustion.

TABLE II: INITIAL TEMPERATURE AND HEAT OF REACTION OF FERROUS SULFIDE UNDER DIFFERENT OXYGEN CONCENTRATION CONDITIONS

oxygen concentration /%	10	15	20
initial temperature of reaction system/°C	81.46	79.57	61.04
reaction heat/ J·g^{-1}	11174.0	1120.2	421.6

With the increase of oxygen concentration, the initial temperature of self-heating reaction of ferrous sulfide

showed a downward trend, indicating that the oxygen concentration in the atmosphere promoted the self-heating reaction of ferrous sulfide. For the reaction at low oxygen concentration, little oxygen can be adsorbed on the ferrous sulfide. The initial reaction temperature is relatively high. The reaction at low oxygen concentration is more difficult to happen than that at the high oxygen concentration. As the oxygen concentration decreases, the exothermic heat of the ferrous sulfide combustion gradually increases. The amount of oxygen is slowly supplied to the ferrous sulfide. The ferrous sulfide is sufficiently contacted with oxygen. Therefore, the reaction releases a large amount of heat.

Effect of heating rate on oxidation reaction of ferrous sulfide: The heating rate was 5, 10, 15, and 20 °C/min respectively. The thermogram and heat flow diagram of the ferrous sulfide oxidation reaction were obtained under different heating rate. Fig. 6 below shows the thermogravimetric graph and Fig. 7 shows the heat flow graph.
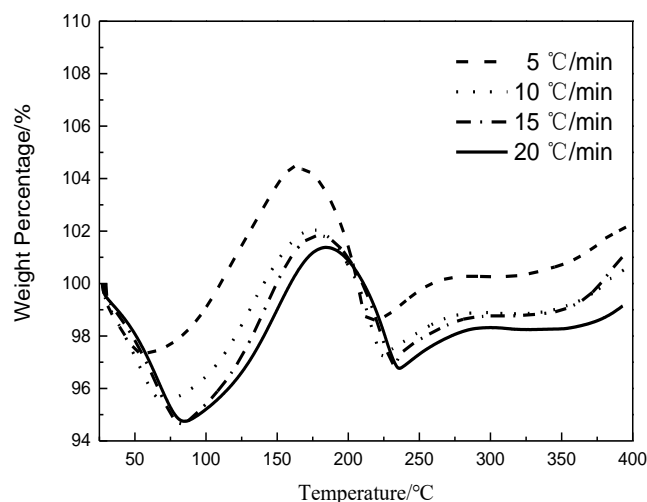

Fig. 6. Thermogravimetric graph of oxidation reaction of ferrous sulfide under different heating rates.
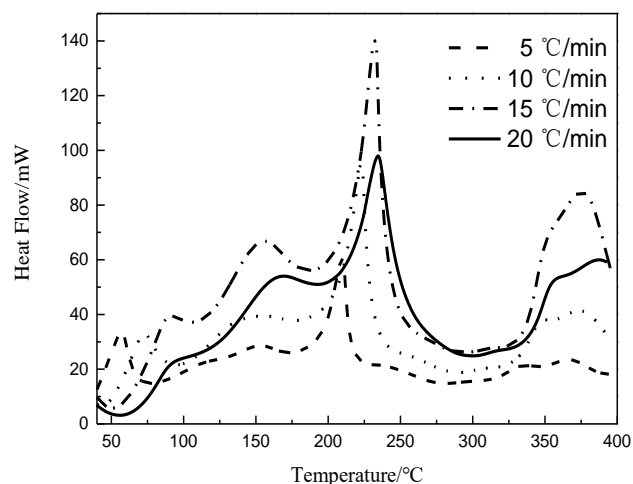

Fig. 7. Heat flow curve of ferrous sulfide oxidation reaction under different heating rate conditions.

According to Fig. 6, the initial reaction temperature of ferrous sulfide self-heating can be obtained (Table III). The heat flow curve of Fig. 7 can be integrated to obtain the reaction heat of ferrous sulfide combustion (Table III).

TABLE III: INITIAL TEMPERATURE AND HEAT OF REACTION OF FERROUS SULFIDE UNDER DIFFERENT HEATING RATES

heating rate /°C·min^{-1}	5	10	15	20
initial temperature of reaction system/°C	53.48	70.12	82.59	85.62
reaction heat/ J·g^{-1}	540.5	620.8	654.7	569.1

With the acceleration of the heating rate in the atmosphere, the initial temperature of the self-heating reaction of ferrous sulfide increases, indicating that the heating rate in the atmosphere promotes the self-heating reaction of ferrous sulfide. In the case of a higher heating rate in the atmosphere, the initial temperature of the self-heating reaction of the ferrous sulfide is higher, and the self-heating reaction of the ferrous sulfide is suppressed. With the increase of the temperature rise rate, the heat of ferrous sulfide combustion increases first and then decreases. In this experiment, the temperature rise rate is 15 °C/ min.

CONCLUSIONS

The thermogravimetry and heat flux of the ferrous sulfide sample oxidation process were detected by a synchronous thermal analyzer. The gas flow, oxygen concentration, and heating rate were analyzed respectively. Main conclusion can be obtained:

a. The whole ferrous sulfide oxidation process is divided into two parts. The first part is the self-heating reaction of ferrous sulfide. The temperature is generally between 60 °C and 170 °C. The ferrous sulfide sample adsorbs oxygen. The second part makes the ferrous sulfide combustion reaction. The temperature is generally between 170 °C and 240 °C, that is the oxidation of ferrous sulfide combustion process.

b. With the increase of gas flow rate, the initial temperature of ferrous sulfide self-heating reaction gradually decreases, the heat of combustion reaction gradually decreases, and the gas flow rate promotes the self-heating reaction of ferrous sulfide. For the combustion reaction, a large amount of gas is purged, which reduces the combustion reaction heat.

c. As the oxygen concentration increases in the range of 10 %-20 %, the initial temperature of the ferrous sulfide self-heating reaction gradually decreases, and the heat release from the ferrous sulfide combustion gradually decreases. The oxygen concentration in the atmosphere promotes the self-heating reaction of the ferrous sulfide. However, slow supply of oxygen to the ferrous sulfide contributes to the contact of the ferrous sulfide and oxygen and releasing of a large amount of reaction heat.

d. With the increase of the heating rate of the atmosphere, the initial temperature of the self-heating reaction of ferrous sulfide gradually increases, and the heat of combustion of ferrous sulfide increases first and then decreases. The heating rate in the atmosphere promotes the self-heating reaction of ferrous sulfide.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

Jiancun Gao conducted the research; Sisi Liu carried out the experiment, Jing Shen analyzed the data; Haoyuan Dai wrote the paper; all authors had approved the final version.

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Si-Si Liu is a master's student at the Beijing Institute of Petrochemical Technology. She was born on November 6, 1993, in Beijing, China. Her research area is chemical safety.