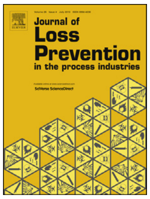
Journal of Loss Prevention in the Process Industries 38 (2015) 156–162

Contents lists available at ScienceDirect

Journal of Loss Prevention in the Process Industries

journal homepage: www.elsevier.com/locate/jlp



Experimental investigation on oxidation of sulfurized rust in oil tank

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ARTICLE INFO

Article history:
Received 2 June 2015
Received in revised form
21 August 2015
Accepted 16 September 2015
Available online 21 September 2015

Keywords:
Oil tank
Sulfurized rust
Oxidation process
Chemical reaction
Electrochemical reaction
Indicator for monitoring and early-warning

ABSTRACT

Oxidation of sulfurized rust in oil tank is complicated, and it is influenced by numerous factors such as water content, air humidity, operating temperature etc. The paper focuses on the oxidation process of sulfurized rust in the wild. Firstly, samples collected from a petrochemical company were put into the sulfurization & oxidation experimental apparatus to gain wet and dry sulfurized rusts. Their chemical compositions and phase were analyzed by Energy Dispersive X-ray Spectrometer (EDS) -scanning electron microscope (SEM) technique. The results showed that both wet and dry sulfurized rusts had S, Fe_2O_3, Fe_3S_4 and FeS_2, whereas FeS only existed in wet sulfurized rust. The two kinds of rusts gave a short length of side, diamond appearance and a large pore size in structure. Then oxidation of wet sulfurized rust was investigated, which included electrochemical reaction stage, electrochemical & chemical reaction coexisting stage and chemical reaction stage. The final oxidation product of wet sulfurized was determined to be Fe_2O_3. On the basis of this study, an indicator for monitoring and early-warning was proposed to prevent plants in vicinity of the accidental vessel or tank from fire and explosion.

1. Introduction

It is generally known that organic sulfur impurities of crude oil consist of non-active sulfides and active sulfides. The active sulfides including elemental sulfur, hydrogen sulfide and low-molecular weight thioalcohols often react with metals directly. In the field situation, only hydrogen sulfide can volatilize into the vapor space, then react with rust which is scatted throughout the inside-wall and inner cavity of respiratory/safety valve, and finally result in the formation of sulfurized rust. When the sulfurized rust is exposed to the air in the process of discharging crude oil or vessels maintenance, self-heating of sulfurized rust occurs with a faster heat production rate comparing to the heat diffusion rate (Hughes et al., 1974; Hughes et al., 1976; Walker et al., 1987; Walker et al., 1988). If the temperature of sulfurized rust is higher than the spontaneous combustion point, the sulfurized rust can be regarded as the ignition source which will lead to fire and explosion under the flammable gases intensive mixing with oxygen. In Sinopec Group or China National Petroleum Corporation (CNPC), several reported fire and explosion accidents occurred due to self-heating of sulfurized rust in oil tank (Zhao et al., 2011; Zhao et al., 2007). Therefore, it is important to know the oxidation self-heating process of sulfurized rust.

Based on all available literature, the oxidation of sulfurized rust has been studied in details (Li et al., 2011; Li et al., 2006; Li et al., 2005; Walker et al., 1997; Walker et al., 1996) along with some variables covering operating temperature, hydrogen sulfide concentration and ambient conditions of oil tank. It was declared that pyrophoric mackinawite (FeS), greigite (Fe_3S_4) and pyrite (FeS_2) produced sparks on exposure to the air (Walker et al., 1987; Walker et al., 1988; Walker et al., 1996; Li et al., 2011) as follows

$$4FeS + 7O_2 = 2Fe_2O_3 + 4SO_2, \quad \Delta H = -805\ \text{kJ/mol}$$

$$4Fe_3S_4 + 25O_2 = 6Fe_2O_3 + 16SO_2, \quad \Delta H = -2100\ \text{kJ/mol}$$

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2, \quad \Delta H = -827\ \text{kJ/mol}$$

Furthermore, the impact of water content on oxidation of sulfurized rust was investigated, and the obtained results showed the water in the sulfurized rust could enhance the pyrophoricity (Li et al., 2011). However, the mechanism of water acting on the oxidation self-heating has not been referred in any literature.

In this paper, a sulfurization & oxidation experimental

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http://dx.doi.org/10.1016/j.jlp.2015.09.009
0950-4230/

apparatus was constructed for simulating the formation and oxidation process of sulfurized rust. The chemical compositions & oxidation product of sulfurized rust were investigated by precision instrument. Then the oxidation process was analyzed on the basis of electrochemical mechanism and chemical thermodynamics. Finally, an indicator for monitoring and early-warning system was proposed.

2. Experimental

2.1. Sulfurized rust preparation

The sample was collected from inner cavity of respiratory valve equipped on the roof of a crude oil tank in Jinling Petrochemical Company, and its major ingredient was rust. The particle diameter of the sample was ground to less than 250 μm.

Before oxidation experiment, 40 g sample was divided into 4 equal shares, each share was sulfurized in the sulfurization & oxidation experimental apparatus at first. The sulfurization & oxidation experimental apparatus had four parts. Part 1 was the gas supply section, which included air bomb, nitrogen bomb, hydrogen sulfide bomb and gas buffering & flow rate control. Part 2 was the measurement of air flow rate and humidification section, which contained a cone bottle with water and flow meter. Part 3 was the sulfurization & oxidation section, which involved a quartz tube twined with an electric heating tape and thermocouple. Part 4 was the tail gas buffering & absorption section, which was comprised of an empty cone bottle and the other with sodium hydroxide solution. Fig. 1 shows the sulfurization & oxidation experimental apparatus.

Prior to the sulfurization, each 10 g sample was placed in quartz tube which was fitted with glass wool plugs and taps at both ends. Then the gas route was connected, and gas tightness of apparatus was checked. The air in apparatus was replaced by high purity nitrogen from N_2 bomb with valves V2, V4, V7 open and other valves closed. The quartz tube was wrapped with electric heating tape to keep the sample at 35 °C because of the operating temperature of crude oil tank ranging from 25 °C to 35 °C. Afterwards, the sulfurization gas (made up of H_2S and N_2, V_{H2S}:V_{N2} = 2:3) passed through the water at the rate of 500 ml/min with valves V2, V3, V4, V5, V6 open and other valves closed. This could make sure that the gas was saturated with water in a similar condition as found in the crude oil tank. As none of other gases was produced in this process, the residual hydrogen sulfide was absorbed by NaOH solution. After 6 h sulfurization, the sulfurized rust was cooled down to ambient temperature. The obtained sulfurized rust was named wet sulfurized rust (WSR). Among four wet sulfurized shares, two shares were dried at 80 °C for 60 min with valves V2, V4, V7 open and other valves closed, meanwhile N_2 passed through the quartz tube at the rate of 500 ml/min. After that, the dry sulfurized rust (DSR) was cooled to room temperature.

2.2. Oxidation of sulfurized rust

Two wet shares reacted with dry air (DA) and wet air (WA) at the rate of 500 ml/min respectively under ambient condition as well as the two dry shares. Before oxidation, the apparatus was filled with high purity nitrogen from N_2 bomb with valves V2, V4, V7 open and other valves closed. When the share reacted with DA, the valves V1, V4, V7 were open and other valves closed. On the contrary, the valves V1, V4, V5, and V6 were open and other valves closed.

In order to increase the accuracy of experiments, all the sulfurization and oxidation of sulfurized rust were repeated three times.

2.3. Investigation on components and microtopography

Both the wet and dry sulfurized rust shares were analyzed by the application of Energy Dispersive X-ray Spectrometer (EDS) -scanning electron microscope (SEM) technique in details. In this study, surfaces of the shares were scanned and the element compositions were determined with scanning electron microscope JEOL-JSM-5600 equipped with a dispersive X-ray spectrometer NORAN VANTAGE DSI.

The solid oxidation product of wet sulfurized rust reacting with wet air was analyzed by X-ray Diffract meter (D/MAX-RB) of Rigaku. XRD patterns were recorded with Cu K_α ($\lambda = 0.1542$ nm) radiation and the X-ray tube was operated at 40 kV and 20 mA with time constant of 0.5 s. Step scans were taken over a range of 2θ from 10° to 90° at a speed of 2 (°)/min.

2.4. Thermal decomposition of pre-oxygenized sulfurized rust

0.00 5 g WSR and DSR pre-oxygenized by wet air were examined respectively by TA Instrument SDT-Q600 equipped with Nicolet 6700 FT-IR Spectrometer of Thermo Scientific for thermal decomposition at heating rate of 20 °C/min from 30 to 900 °C in nitrogen atmosphere, and the N_2 was at flow rate of 100 ml/min.

3. Results and discussion

3.1. Sulfurized rust analysis

The energy dispersive X-ray spectrometry analysis electric heating tapes of wet and dry sulfurized rust shares are presented in

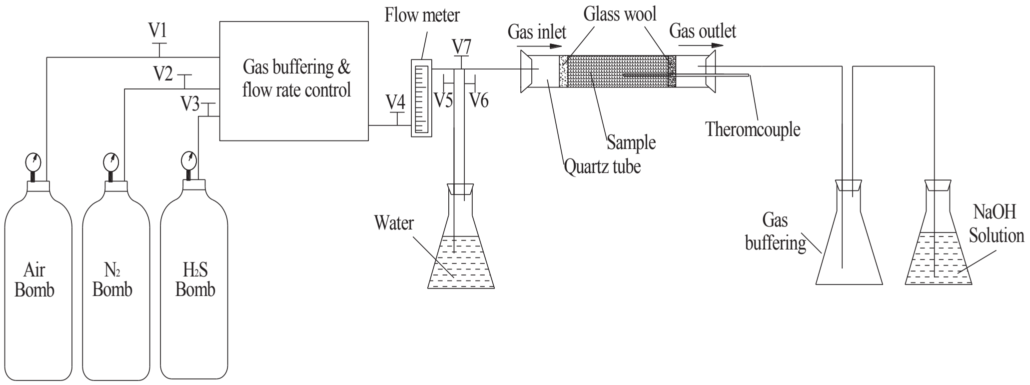

Fig. 1. Sulfurization & oxidation experimental apparatus.