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Research Article

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H_2S leakage grading alarm and protective measures in the high-sulfur crude oil process

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ABSTRACT

As one of the major risks in high-sulfur crude oil processing, the H_2S *exposure could be reduced by early warning of* H_2S *leakage. Based on the source and distribution of* H_2S*, the four-level warning mechanisms of* H_2S *leakage is developed by using HSE risk identification system, which makes the* H_2S *concentration values as the grading index. The appropriate emergency measures are formed. To provide guidance for* H_2S *poisoning protection during high-sulfur crude oil processing, the safeguards to prevent* H_2S *poisoning are presented according to the cause of* H_2S *poisoning and "Human-Machine-Material-Regulation-Environment".*

Keywords: High-sulfur Crude Oil, H_2S, Grading Warning, Protection

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INTRODUCTION

With the rapid development of petroleum industry, conventional energy is drying up due to the mass consumption of word petroleum resource. According to related investigation, more than 50% of the total oil production is high-sulfur crude oil[1]. Therefore, the development trend of world oil is heavy, poor quality and high-sulfur content, etc.

In recent years, most of domestic oil refineries have changed to refine the poor quality crude oil because of the low-cost and expanding import of high-sulfur crude oil[2]. Originally, the refining devices of the domestic refineries were designed for the process of low-sulfur crude oil, so that the process of high-sulfur crude oil will bring a series of problems, such as equipment corrosion, hydrogen sulfide poisoning and the spontaneous combustion of ferrous sulfide, especially the risk and damage from hydrogen sulfide poisoning can not be increased. Hydrogen sulfide leakage can be resulted from various reasons, which is mainly contributing to the threat of life safety.

THE SOURCE, DISTRIBUTION AND HARM OF H_2S

The Source of H_2S

The common oil refining devices are mainly including Atmospheric and Vacuum Distillation, Catalytic Cracking, Catalytic Reforming, Hydrofining, Hydrocracking, Delayed Coking, Hydrogen Production, Stripping and Sulfur Recovery, etc. Under corresponding higher temperature, pressure and the action of catalyst, cracking will bring a series of proton acid reaction, hydrogen transfer process, isomerization reaction, alkylation reaction and cracking reaction, etc. which makes the combined sulfur in the oil separated out.
Hydrogen sulfide can be generated by the following reaction in the oil process:

1.Thiol Reaction:

$$RSH + H_2 \rightarrow RH + H_2S$$

2.Thioether Reaction:

$$RSR' + H_2 \rightarrow RSH + R'H$$

$$\downarrow H_2$$

$$H_2S + RH$$

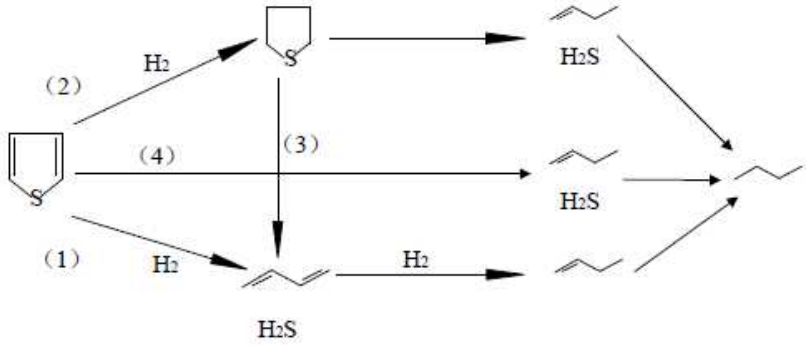
3. Disulphide Reaction:

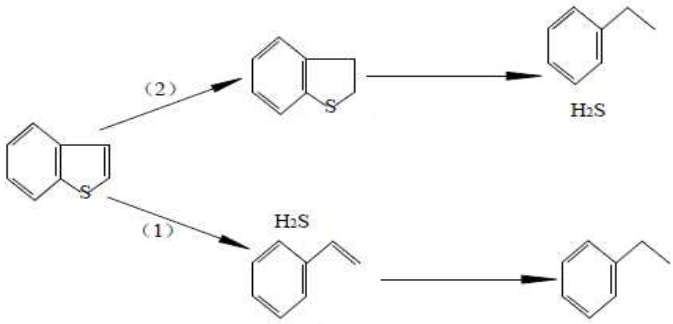
$$RSSR' + H_2 \rightarrow RSH + R'SH$$

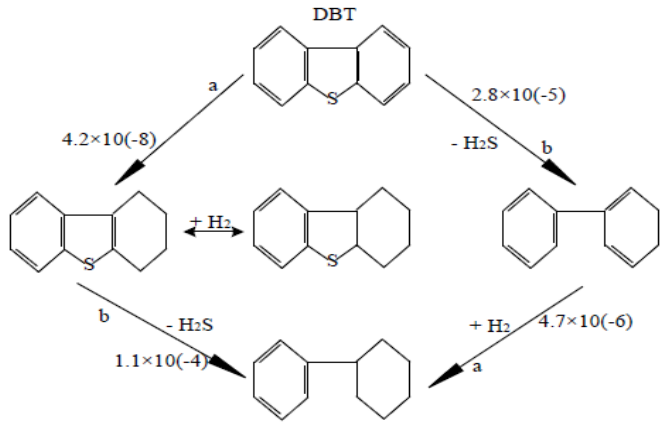
$$\downarrow H_2 \qquad \downarrow H_2$$

$$H_2S + RH \qquad H_2S + R'H$$

4.Thiophene sulfur Reaction:







These show that it will produce a large number of hydrogen sulfide in the process of Catalytic Cracking，Catalytic Reforming and Hydrofining Cracking[3], etc.

According to the varieties of refinery processing crude oil and various sulfide existing forms, the source of hydrogen sulfide in oil process mainly includes the following three types [4]:

（1）The hydrogen sulfide contained in crude oil.

（2）Sulfides in oil after thermal decomposition form the hydrogen sulfide.

（3）For removing the sulfur in oil or improve the quality of products, sulfur element will be transformed to hydrogen sulfide through hydrogenation process.

The Distribution of H_2S

Hydrogen sulfide exists in most refinery devices. In the process of refining crude oil, hydrogen sulfide, which produced by sulfides after thermal decomposition and hydrogenation process, accumulated mainly in the overhead gas, light component oil and dissolved in sulfur-containing wastewater on top of tower. The distribution characteristics of hydrogen sulfide in typical refining devices are summarized in Table 1[5].

Table 1 Key location of hydrogen sulfide in common refinery devices

Typical devices	Key location of hydrogen sulfide
Atmospheric-Vacuum Distillation Unit	Overhead gas compressor of atmospheric tower; Overhead gas compressor of decompression tower; Overhead reflux and production tank of atmospheric tower; Water separator of decompression tower; Overhead reflux and production tank of stabilization tower; Overhead air cooler heat exchanger; Sulfur-containing sewage pump; Sulfur medium sampling port; Dehydration port, etc.
Delayed Coking Unit	Rich gas compressor; Coking furnace; Coke drum; Coking fractional distillation column; Blowdown tower; Gas-Liquid separation tank at the top of fractionating tower; Blending and coking dry gas separation tank; Coking rich gas balance tank; Absorption tower; Desorption tower; Stabilization tower; Overhead air cooler heat exchanger; Sulfur medium sampling port; Dehydration port, etc.
Catalytic Cracking Unit	Rich Gas Compressor; Sulfur-containing sewage tank; Sewage pump; Oil-Gas separator; Gas compressor condensate; Condensate pump; Overhead reflux tank of stabilization tower; Reflux pump; Absorption tower; Desorption tower; Stabilization tower; Overhead air cooler heat exchanger; Sulfur medium sampling port; Dehydration port, etc.
Hydrofining Unit	Recycle hydrogen compressor; Hydrofining reactor; Production fractionator; H_2S Stripping tower; Recycle hydrogen desulfurization tower; Recycle hydrogen separation tank; Overhead reflux pump of reflux tank; Sulfur medium sampling port; Dehydration port, etc.
Continuous Catalytic Reforming Unit	Pre-hydrogenating reactor; Pre-hydrogenating production separation tank; Pre-hydrogenating stripping tower; Reflux tank at the top of stripping tower; Reflux tank of stripping tower; Reflux pump of stripping tower; Overhead air cooler heat exchanger; Sulfur medium sampling port; Dehydration port, etc.
Sour Water Stripping Unit	Sour water tank; Sour water degassing tank ; Sour gas separation tank; Sulfur medium sampling port; Dehydration port, etc.
Desulfurization and solvent regeneration unit	Dry gas separation tank; Dry gas desulfurizing tower; Flooded tank; Solvent regenerator; Flooded pump; Regeneration tower water-cooled air cooler; Sulfur medium sampling port; Dehydration port, etc.
Sulfur Recovery Unit	Combustion furnace of sulfur manufacturing; Waste heat boiler; Sour gas accumulator tank; Sulphur condenser; Heat exchanger; First and second claus reactor; Tail gas treatment combustion furnace; Liquefied sulfur pool; Liquefied sulfur tank; Sulfur medium sampling port; Dehydration port, etc.
Gas Holder and the Torch System	The compressor input or output seperation tank; Gasometer and relevant manual sampling port; Water-Cutting off-take point; Sulfur medium sampling port; Dehydration port, etc.

The Harm of H_2S

Hydrogen sulfide, which is a kind of nerve agents, can easily cause poisoning and also has strong stimulation to mucous membrane. High concentrations of hydrogen sulfide can restrain respiratory center directly and then causes death by suffocation. Table 2 shows it's harm to people in different concentrations of hydrogen sulfide.

Table 2 The harm to people in different concentrations of hydrogen sulfide

Concentration /（mg·/m^3）	The harm to people
15	Obvious bad smell, long-term exposure is allowed
30	In the open air, safe exposure work for 8h
70~150	After 2~5min, olfactory fatigue, no longer smell the odor. Respiratory and eye irritation symptoms will occur in 1~2h
150~300	Inhibition of the sense of smell, coughs, eye inflammation in 2~5mins. Eye pain and breathing disorder in 8h and it will lead to the deaths of hemorrhage in 8~48h
450~600	Collapse, loss of consciousness, and make artificial respiration immediately in 2mins, eye severe inflammation and cardiac arrhythmias in 15~30mins, , headache, arms and legs tremble and even death in 30~60mins
900~1000	Loss of consciousness and leads to the death in 2mins
1200	In seconds, respiratory arrest suddenly, and then sudden cardiac arrest, people will be rescued with implementation of artificial CPR in time
1500	In seconds, electric shock death
Over 3000	Immediately kill people and can not to be rescued

From 1984 to 1994, about 80 cases of hydrogen sulfide poisoning death accident had occurred in the United States, 20 cases happened in oil industry. 86.3 percent of H_2S poisoning accidents happened in Limited Space. Many

workers, which were not aware of being in dangerous working area and were also trying to rescue companions, died of poisoning[6].

Hydrogen sulfide mainly enters the body through the respiratory tract, in which a small percentage of hydrogen sulfide by respiratory tract is expelled from the body and will not be accumulated. The most part of hydrogen sulfide in the body will be oxidized under the action of metabolism into non-toxic sulfide, sulfate or thiosulfate, and then excreted into urine by the kidneys. According to "Classification for Hazards of Occupational Exposure to Toxicant" （GB5044-85）, hydrogen sulfide occupational hazards classification as follows: high hazard (Ⅱ). On the other hand, the body reactions to hydrogen sulfide are different. The main influence factors are individual differences, concentration and contact time, etc. With the combination of concentration and contact time, hydrogen sulfide poisoning symptoms can be divided into three types: mild poisoning, moderate poisoning, severe poisoning[7].

GRADING WARNING SYSTEM OF H_2S

Grading warning system is widely applied in all kinds of emergency plans and is an important basis and reference of direct emergency rescue. Grading warning is usually based on the likelihood and consequences of the incident as a premise for classification, after the incident it directs workers to enter a state of grading warning and timely to be prepared for possible emergency action in advance.

Accurate monitoring of the hydrogen sulfide in refining system is the basis of the H_2S poisoning prevention job. In this paper, grading warning system is mainly carried out in accordance with the density of H_2S. As a result, grading warning is closely connected with the concentration of hydrogen sulfide.

HSE Risk Identification System

Rapid and effective risk identification is the key to the HSE management system. So, how to accurately identify risks is the premise to prevent hydrogen sulfide poisoning. First of all, setting testing alarming device and necessary protective equipment in the place where H_2S is easy to leak and the concentration is high; Secondly, establishing special, complete emergency contingency plans, establishing risk identification group and accident treatment group; At last, work sites should be divided into safe area, emergency assembly area, evacuation area and alert area, and set up the escape route. When the concentration of hydrogen sulfide is more than 15mg/m^3, all passageways should order the rules of warning signs, set appropriate warning signs (Each letter and blank are black print over yellow) to remind workers of potential hazardous situations around. When the concentration of hydrogen sulfide is more than 30mg/m^3, all workers should be taken away from the sites[8].

Grading Warning System of H_2S

The grading warning system makes the H_2S concentration values as the grading index. According to "Recommended Practice for Safe Drilling Operations involving Hydrogen Sulfide" (SY/T5087—2005) and "Specification of Hydrogen Sulfide Monitoring and Protecting for Operation Personnel in Oil and Gas Field involving Hydrogen Sulfide" (SY/T6277—2005), the concentration threshold of H_2S monitor should be set up and instruments can automatically give a warming when the concentration of hydrogen sulfide reaches 15mg/m3.
According to the concentration of hydrogen sulfide measured by monitoring devices, grading warning is divided into blue, yellow, orange and red alert, which respectively indicates workers in different circumstance should take corresponding measures. Table 3 shows the situation of grading warning.

Table 3 Grading warning system of H_2S

H_2S concentration /（mg·/m^3）	Warning Situation	Warning Level	Countermeasures
C＜15	Allowable concentration in the air	blue	Fixed-point real-time monitoring
15≤C＜30	Little H_2S leakage	yellow	Risk monitoring and warning
30≤C＜150	More serious H_2S leakage	orange	Use breathing apparatus, real-time monitor the wind and the H_2S content
C≥150	H_2S Serious leakage	red	Wearing gas masks, evacuate the site

H_2S blue indication: No H_2S in the air or the concentration of H_2S is below 15mg/m^3, there is still a potential risk of H_2S leakage, fixed-point real-time monitoring is required.

H_2S yellow indication: There is a small amount of H_2S leakage but have not reached 30 mg/m^3 safety critical concentration, the respirator is not necessary and also do not need immediately evacuate the site, but it must be monitor and give warning against potential danger and be ready to enter the orange alert.

H_2S orange indication: Serious H_2S leakage accident happened, the H_2S concentration exceeds the safe critical concentration. The respirator is necessary in leakage areas. Continuous monitoring of wind direction and concentration of H_2S in the ambient air are required, also it needs to be further processing if there are any changes.

H_2S red indication: Sever H_2S leakage accident happened, the H_2S concentration has greatly exceeded the safe critical concentration. The operation personnel have been threatened and they should immediately evacuate the site with gas masks.

According to warning system, the corresponding grading treatment measures should be established, Table 4 shows the detail treatment measures.

Table 4 Grading warning treatment measures

H_2S concentration /（$mg·m^3$）	Grading Treatment Measures
C＜15	Check, monitor and protect devices, real-time monitoring of the concentration of H_2S and be prepared for emergency.
15≤C＜30	Wind direction, wind speed should be monitored and be charged by designated employee, wear positive pressure breathing apparatus in the danger zone to check leakage and dispose emergency.
30≤C＜150	Wear positive pressure respirator, report to the superior, monitor H_2S concentration change at the downwind distance of 100m,initiate emergency response plans, control the leakage source, count and evacuees, cut off potential ignition source and inform the aid agencies.
C≥150	Evacuate leakage danger zone with wear positive pressure respirator, Set the alert zone on the spot, workers wear protective clothing before entering into the leakage field to control leakage source and report to the superior or request support。

When H_2S leakage occurs, starting grading warning model can deal with it efficiently and orderly and make full use of available emergency resources and protective equipment to minimize or control the harm.

SAFEGUARDS OF H_2S POISONING

Based on the reason analysis of H_2S poisoning and combined with refinery field conditions, the safeguards to prevent H_2S poisoning are presented according to five factors of "Human - Machine - Material - Regulation - Environment"[2].

(1) Strengthen ideological education, raise safety awareness

In the process of high-sulfur crude oil, H_2S leakage has become the focus of safety management and risk prevention and control. According to relevant statistics, 50% of H_2S poisoning accidents were caused by poor safety management and poor safety awareness [9]. Therefore, the basic safeguard to prevent H_2S poisoning accident is to strengthen the popularization of H_2S hazards and the safety awareness of staffs or leaders.

(2) Ensure the integrity of the equipment and realize the intrinsic safety of the equipment

The unplanned interface between pipeline materials with the surrounding environment is the essential reason of H_2S leakage. As a result, to ensure the maximum intrinsically safe and the integrity of the equipment in the all life-cycle can reduce H_2S poisoning accidents from the source. Especially the integrity detection of acidic gas pipeline and the overhead pipeline is the key of the H_2S corrosion leakage monitoring.

(3) Master the H_2S dynamic distribution, the key control

To establish refinery H_2S dynamic map according to the technological process and H_2S generation area, and set up intensive monitoring and management in H_2S possible leakage area such as hydrotreating unit and diesel hydrogenation unit, in which setting H_2S alarm device and providing related personnel protective equipment. H_2S poisoning accidents can be reduced by knowing well about hazardous substances and improving safety awareness during the normal running of equipment.

(4) Set relevant safety management regulations and standard operations of H_2S

The refinery should formulate corresponding safety operation procedures for H_2S process operation and eliminate violations of rules to reduce H_2S leakage or H_2S poisoning accidents caused by anthropogenic factors.

(5) Consider the surrounding environment, reducing secondary accidents caused by H_2S leakage

Because of the crowded around large refineries and natural environmental factors such as topography and wind direction, H_2S leakage is easy to spread out of the factory. Therefore, preliminary design and process equipment arrangement should fully consider the effect of environment factors to reduce secondary accidents caused by H_2S leakage[10]. Meanwhile, when making contingency plans of H_2S, the natural environment and the surrounding personnel concentration areas should be taken into account to avoid accidents because of improper emergency.

CONCLUSION

At present, there is still no very perfect grading warning system for H_2S leakage. Based on the source and distribution of H_2S, grading warning system is established according to the possibility and maximum concentration of hydrogen sulfide leakage. The disposal measures of different risk levels are formed on the basis of grading warning system. This paper mainly discusses the prevention of H_2S poisoning accidents according to the factors of "Human-Machine-Material-Regulation-Environment", and proposes that the safety of people's lives and properties could be guaranteed by reducing H_2S leakage probability, strengthening the personnel and equipment safety management and completing the H_2S poisoning emergency measures.

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