ISSN: 2414-1895 DOI: 10.6919/ICJE.201909_5(10).0030

Measures of selective catalytic cracking for sulfur removal and corrosion prevention

Qiurong Zhang [1, a], Jianguo Wu [2, b]

[1]Shanghai Maritime University, Shanghai 201306, China;

[2] Shanghai Maritime University, Shanghai 201306, China.

[a] zhqiurong@163.com, [b]1262116549@qq.com

Abstract

The international maritime organization (IMO) has decided to reduce the sulfur content of Marine fuel to 0.5% m/m worldwide starting from January 1, 2020, making great contribution to global environmental protection and shipping industry. In this paper, the corrosion problems in the process of hydrotreating low-sulfur ship fuel oil in the process of selective catalytic cracking for sulfur removal in pre-fuel technology are discussed[1]cars .

Keywords

Sulfide; Selective catalytic cracking; Corrosion resistant.

1. Introduction

With the development of the modern shipping industry, the shipping industry has become the largest mode of transport to undertake the largest foreign trade volume of bulk goods. Shipping is responsible for about 80% of the world's foreign trade goods, the pollution caused by ship exhaust has become a hot topic of concern.[2]The economic benefits brought by shipping industry to our country are incalculable. At the same time, one of the problems that cannot be ignored is the environmental problem. The pollutants it brings not only threaten human health, but also cause some damage to the natural environment. In addition, sulfide will also cause some damage to equipment and instruments, and lead to acid rain, etc., which will cause more damage to the environment and drive us to the era of low sulfur.

2. Ship Sulfur Emission Control Scheme

Up to now, there are several technologies to deal with the emission index of ships, including pre - and post-treatment technology. The treatment of sulfur oxides in ship exhaust gas is mainly classified as shown in figure 1 below.

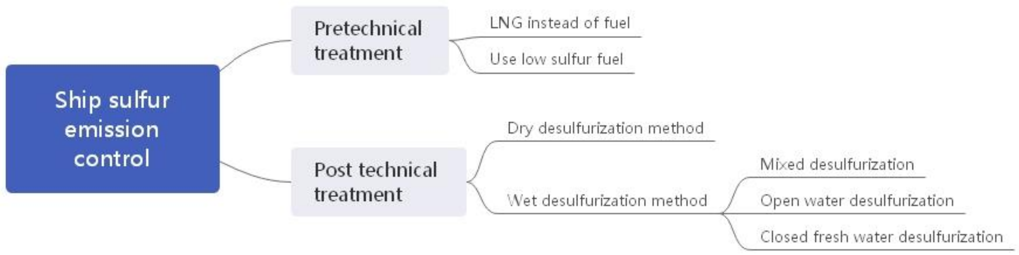

Fig. 1 classification of major desulfurization schemes

ISSN: 2414-1895 DOI: 10.6919/ICJE.201909_5(10).0030

No matter what kind of sulfur treatment, there are sulfide corrosion problems, especially the low sulfur treatment in the pre-technology, often produce a variety of sulfide products in the hydrogenation stage, causing serious damage to equipment and metals.

3. Use low sulfur fuel

There will be many technical and safety problems in the actual use of LNG replacement technology.[1]In terms of installation, one is the installation on the use device, and the other is whether it meets the requirements on the technical level. Second, it's operating procedures also face huge challenges, including vacating the LNG location, ship stability, and later endurance. If LNG is used, maintenance and personnel training are also essential, so it will take a long time for LNG to be implemented.

So far, ships still use mostly low-grade fuel, known as heavy fuel oil (HFO).Due to the low price of heavy oil and high energy, it saves a lot of costs, but it also brings environmental pollution problems.[5]So the pre-technical treatment of the fuel is very important, which can reduce the sulfur content, thus reducing the emission of pollution. Unlike other technologies, using low-sulfur fuels does not require other equipment modifications or additional equipment, reducing equipment costs. So far, China's heavy oil desulfurization technology has been quite mature, but there are still some problems in the follow-up problems have not been solved, the most serious is the sulfur compounds generated in the process of sulfur removal equipment damage and old loss, resulting in serious reduction of the service life of the equipment. In this paper, the hydride sulfurization process is studied and the corresponding measures are put forward.

4. Selective catalytic cracking desulfurization process

Heavy oil extraction mainly goes through two processes, one is hydrogenation process, the other is decarburization process.[3]Because the decarburization process is through internal heating, there is no external hydrogen element, so the heating process tends to produce coking phenomenon. Later, with the breakthrough of processing technology, super floating bed was invented and put into use. The idea is to use a micro catalyzer that prevents coking while keeping the hydrogen element saturated. If this technology is applied to the pre-treatment of ship fuel, the sulfur content of the refined fuel can be guaranteed to be less than 0.5%m/m.

The second process is the hydrogenation route. In order to improve the efficiency and utilization ratio of traditional hydrogenation, I take the selective catalytic cracking process as the hydrogenation guidance, and its process is shown in figure 2.

This process in the heavy oil refining can effectively improve the efficiency of hydrocarbon utilization, and can effectively reduce the carbon dioxide emission intensity, heavy oil treatment prospects have a great impact. And what's interesting is that delta H is produced at high temperatures$_2$S will combine with steel to produce Fe$_2$The S is attached to the metal surface to form a mechanical isolation layer.[6]We know from chemical properties that dry sulfides have little or no corrosive effect on metals, but are quite different when they contain water. However, after this high temperature process, when the temperature drops to the dew point, there will be water condensation point, which will precipitate out water and condense on the wall of the pipe. After fusion with sulfur, metal will be corroded. The general process is shown in figure 3.

4.1 H_2S corrosion mechanism.

Both petroleum and LNG natural gas fuel containing sulfur in corrosive environments are produced by O_2, S_8, CO_2, H_2S. The corrosion environment is also closely related to temperature, PH value and pressure. In this corrosion mechanism, there are many corrosion relations. One of the H$_2$The corrosion mechanism of S is the most serious, so we mainly study H here$_2$S - related corrosion mechanism.

The corrosion of pipe and equipment in sulfide is mainly H_2S corrosion, followed by low - grade mercaptan corrosion mechanism. In the various complex reactions, because of H_2S plus water has a

ISSN: 2414-1895 DOI: 10.6919/ICJE.201909_5(10).0030

solubility of 1.026×10¯ cubed mol/ (L·kPa). In this environment, ions able to coexist in solution are HS^-, S ^ 2 ¯, H +, and H_2S.

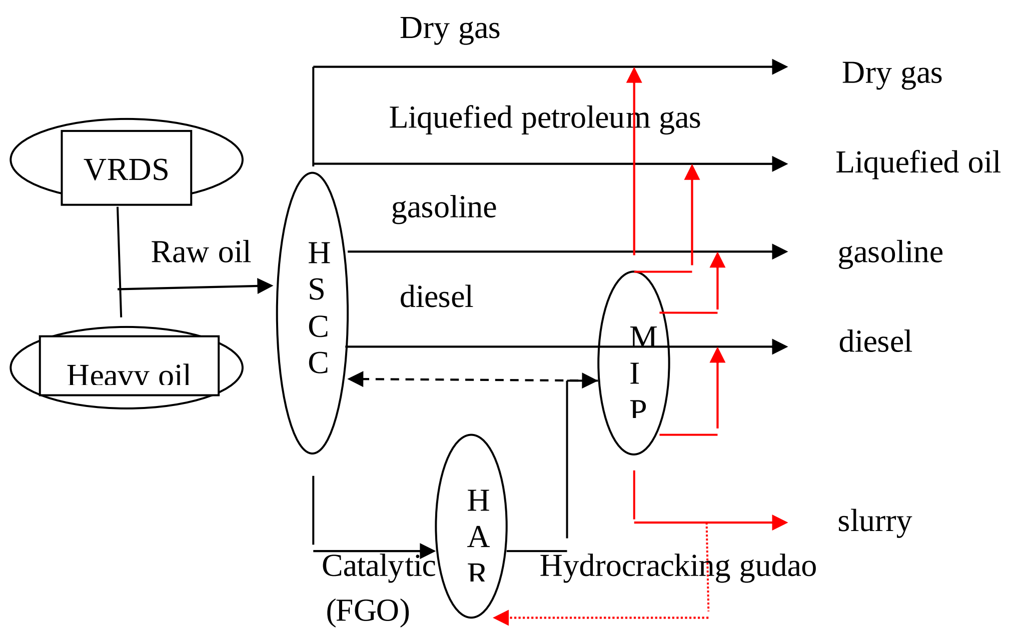

Fig. 2 Flow chart of selective catalytic cracking process

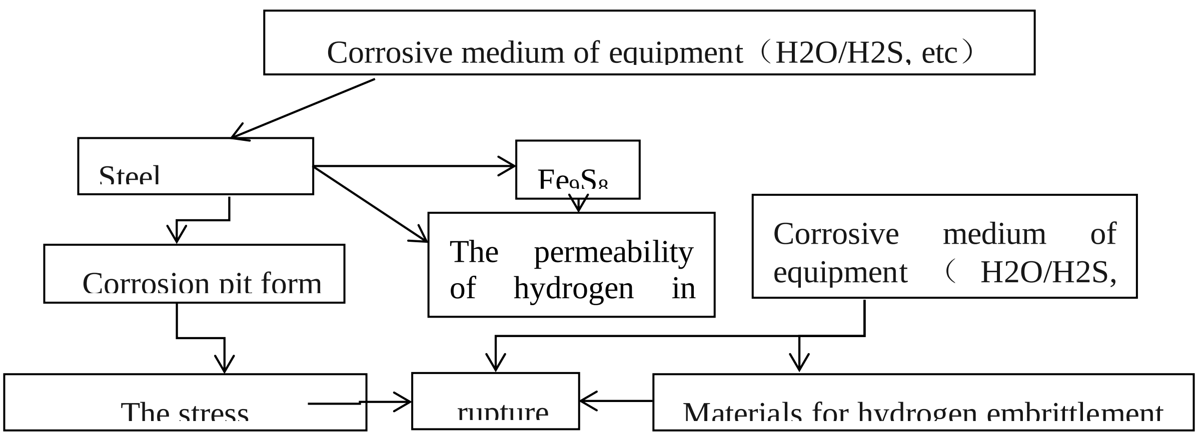

FIG. 3 steel in H_2Diagram of corrosion process in S aqueous solution

The ionic reaction of H_2S in aqueous solution is:

$$H_2S \rightleftharpoons H^+ + HS^- \qquad HS^- \rightleftharpoons H^+ + S^-$$

The reaction of H_2S in aqueous solution with steel is an electrochemical reaction of corrosion and the reaction equation is:

The cathode reaction $3H^+ + 3e^- \longrightarrow 3H_{\text{吸附}}$

$\longrightarrow H_{\text{吸附}} + H_2\uparrow$

Anodic reaction $Fe \rightarrow Fe^{2+} + 2e^-$

The precipitation reaction $Fe^{2+} + S^{2-} \rightarrow FeS\downarrow$

Based on the above studies on the reaction mechanism of cathode and anode, it can be seen that there is still a great dispute in the scientific community about the final product. Due to the influence of

ISSN: 2414-1895 DOI: 10.6919/ICJE.201909_5(10).0030

environment and the free state of other ions in solution, the final corrosion mechanism of anode and cathode is more complex, which increases the difficulty of research. But it's definitely H_2Corrosion mechanism of S, whose dissociated ionic products are adsorbed on steel surface to form $Fe(HS)^-$.While the negative ion will move the metal's electrical displacement to negative value, accelerating the rate of releasing oxygen from the cathode, while hydrogen atom is easy to gain electrons, which greatly weakens the strength of the metal bond, thus promoting the rapid dissolution of the anode and the corrosion of steel.

4.2 Influence of H_2S corrosion factor

In the H_2S aqueous solutions, corrosion products of steel under different environments are mainly listed in table 1.

Table 1 corrosion rates of steel in different environments

Corrosion products	The name	structure	features
$Fe_{1-x}s$.	Pyrrbotite	Hexagonal or monoclinic crystal system	P- type semiconductor, insoluble
Fe_9s_8	Kansite	Cubic crystal system	Unstable and soluble
Fe3O4	Greigite	/	unstable
$Fe_{1+x}S$	Mackanawitc	Tetragonal crystal system	Unstable and soluble
FeS2	Pyrite	Cubic crystal system	P- type semiconductor, most difficult to dissolve, most stable
FeS	Troilite	/	It is unstable and more soluble
FeS2	Mareasite	Orthogonal crystal system	/

(1) Temperature versus FeS_2The influence of. For H saturated$_2$S solution, at room temperature and humidity, the steel surface is formed without protection of $Fe_9s_{.8}$; When the temperature is 50℃, the final product of the solution is unprotected FeS_2And $Fe_{1+x}S$;When the temperature rises to 100℃, the product in the solution is still unprotected $Fe_{1+x}S$;However, when the temperature rises again, at 100-200℃, the iron sulfide film produced by the solution has a very good protective property. According to this property, if the reaction is at low temperature, we can make full use of this property to prevent the corrosion of steel.

(2) H_2S Effect of solution concentration of on corrosion velocity. In the H_2The influence of its concentration on metal corrosion in the environment with S aqueous solution is shown in figure 4.

As can be seen from the figure, the corrosion rate of mild steel gradually increases with the increase of H_2S concentration in distilled water at low concentration. After 1500 mug /mL, the higher the H2S concentration, the lower the corrosion rate. But reality is often not as desirable as we would like, because it is also affected by other impurities (such as CO_2, CN^-, CL^-, O_2, etc.).To prove this hypothesis, the following is the corrosion rate of a mild steel tested under different conditions, as shown in figure 5.

ISSN: 2414-1895 DOI: 10.6919/ICJE.201909_5(10).0030

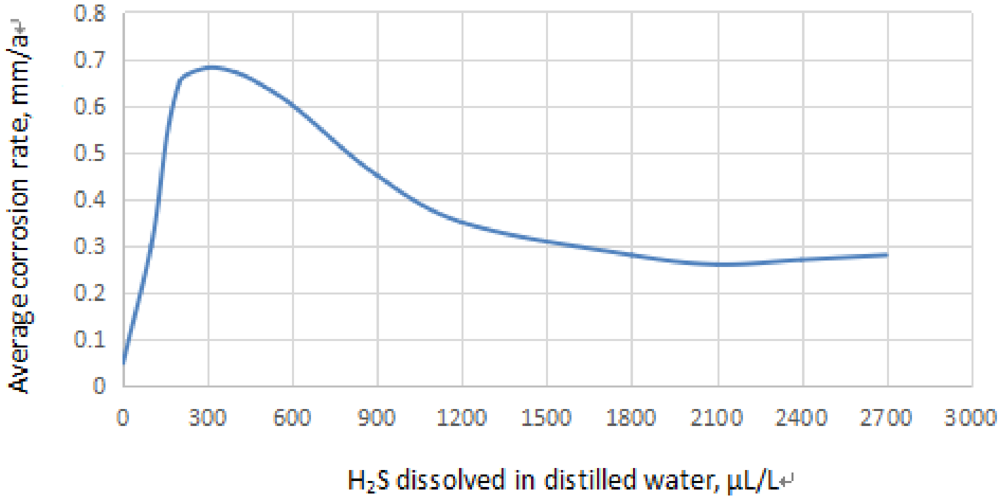

FIG. 4 Corrosion process diagram of steel in H_2S aqueous solution

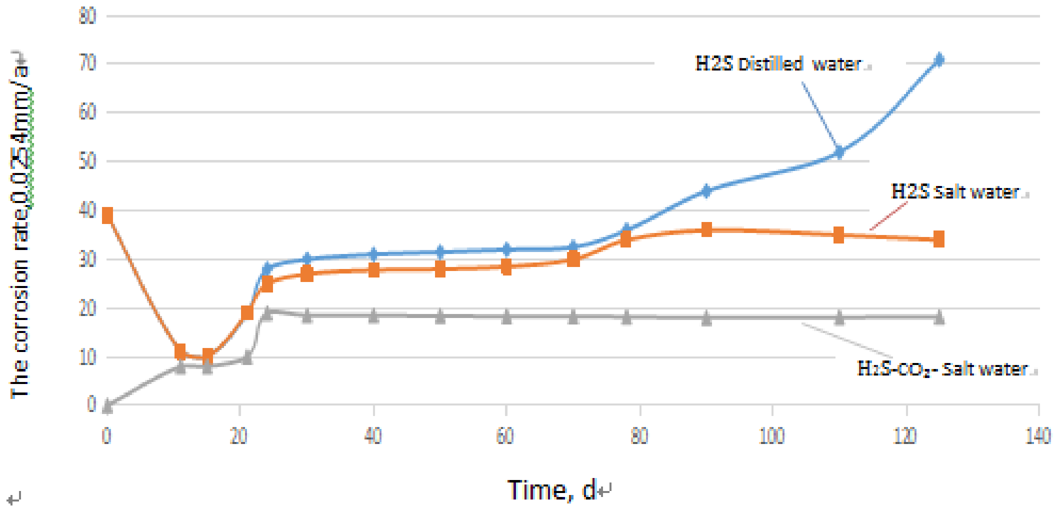

Fig.5 corrosion rate of steel under different environments

After 80 days, we start making $Fe_9s_{.8}$ and Fe_{1+x}. At this time, the corrosion rate of steel increases significantly and reaches the highest level.

Effect of PH value on corrosion rate and iron sulfide film of steel.[6]We all know that the PH value refers to the PH of the environment, and steel and iron sulfide can change with a certain PH value. To this end, three different kinds of steel were selected as experimental objects to conduct the test and the following table 2 data were obtained.

Table 2 corrosion rates of steel in different environments

steel PH	2.5	3.0	3.5	4.0	4.5	5.0	5.5
Martensitic stainless steel	/	0.8	0.08	0.03	0.009	0.006	/
Carbon steel and low alloy steel		0.75	0.55	0.42	0.40	0.36	/
Austenitic and duplex stainless steel	0.012	0.0042	0	/	/	/	/

ISSN: 2414-1895 DOI: 10.6919/ICJE.201909_5(10).0030

In saturated H2S aqueous solution, when PH is around 3.3, the steel surface is mainly composed of FeS2 and FeS, and the corrosion rate decreases significantly. When the PH is greater than 5.5, the corrosion rate is particularly high, resulting in the liquid appearing directly black and cloudy. According to statistics, when the PH of the tubing is lower than 6, the service life of the tubing is less than 20 years. In addition, PH will damage the structure and composition of steel. For example, in saturated H2S solution at low PH, FeS2 with protective film is mainly used, while at high PH, FeS2 with protective film is mainly used[6].

Influence of time and temperature on corrosion velocity. At the beginning, the steel reacts faster, but over time, a layer of steel rust forms on the surface, reducing the corrosion. At low temperature, the corrosion rate of steel will accelerate with the increase of temperature. However, it does not go up all the time, but there is a critical value. When the temperature is reached, the corrosion rate will decrease as the temperature rises again. The reaction rate is shown in Fig. 6.

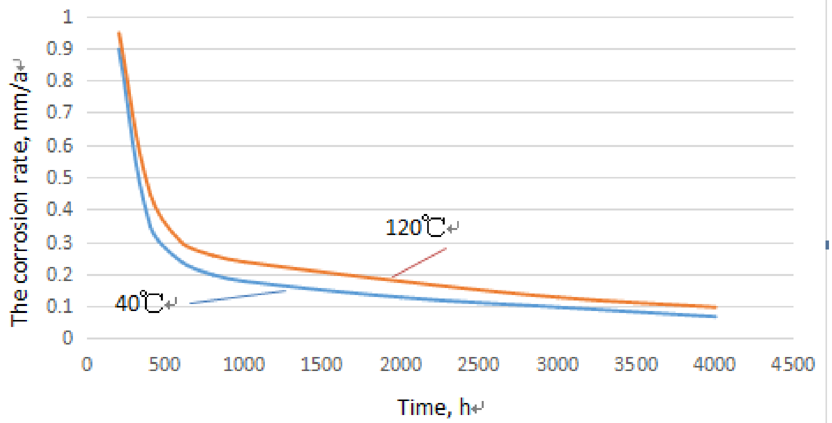

Fig.6 corrosion rate of steel under different environments

In conclusion, we can know that steel will have different reactions in different environments, which are affected by many factors. Therefore, according to the above research and analysis, corresponding measures can be given.

5. Technical measure can be taken to prevent H2S steel corrosion

1) electrochemical cathodic protection law

Electrochemical method mainly refers to the method of sacrificing the anode to protect the cathode, so that the party to be protected is used as the cathode, such as underground pipeline or chemical equipment. A metal block can be used as the anode to be connected with it, and the current can be used to protect it. This method can strengthen the protection of pipes, change the corrosion medium of steel under artificial changes, play a role in protecting steel, and extend the service life of pipeline equipment.[7]

Choose materials that resist corrosion

With the progress of science and technology, more and more alloy materials have good properties, such as corrosion resistance, high temperature resistance and hardness, etc. Selection with strong corrosion is a safe and efficient method, and compared to the addition of other procedures to prevent corrosion, to improve the performance of their own materials to come more easily. Corrosion - resistant steel alloys are mostly made by adding elements such as nickel, nitrogen, manganese and chromium to improve the properties of the alloys.

At present, the commonly used materials in the market are synthetic composite glass steel, alloy steel, steel-plastic composite pipe, HDR duplex stainless steel and PE pipe.

Steel cladding protection act

As the name implies, the coating protection law is to add a protective layer on the surface of the material that needs to be protected, so that its reaction medium is isolated from each other, thus

ISSN: 2414-1895 DOI: 10.6919/ICJE.201909_5(10).0030

playing a protective role. There are mainly two kinds of coating protection laws in industry, one is the metal layer protection law, the other is the non-metal layer protection law. The metal layer protection act is to cover the surface of the material with a metal material, so as to play the role of isolation and protection. The non-metallic layer protection law USES electrochemical and chemical properties to protect the pipe, so as to improve the corrosion resistance of the material.

4) environmental temperature protection law

According to the above test results, at the same concentration of H_2In S solution, the corrosion rate of steel increases with the increase of temperature at low temperature. When the temperature rises from 55℃ to 84℃, the corrosion rate increases by 20 percentage points. However, as the temperature continues to rise, the corrosion rate decreases. And has the minimum corrosion rate, exists in 110~120℃.As can be seen from the figure, the corrosion rate at 120℃ is about twice as low as that at 40℃.

5) apply corrosion inhibitors and additives

Corrosion inhibitors are used to slow down the corrosion of steel. There are two commonly used corrosion inhibitors, one is organic corrosion inhibitor, one is inorganic corrosion inhibitor.

Compared with inorganic corrosion inhibitors, organic corrosion inhibitors are more helpful to slow down H_2S Corrosion of steel pipe. The application principle of organic corrosion inhibitors is chemical adsorption (phosphorus, sulfur, nitrogen, fluorine and other non-covalent electron pairs) and physical adsorption (mainly electrostatic attraction), which plays a protective role when applied to the metal surface. This kind of corrosion inhibitor are: amide (A - 162 chuan tian 2-1, , chuan tian 2-2, chuan tian 2-3, 7019, PA - 75), fatty acid amine salt (PA - 50 and PA40, etc.), quaternary ammonium salt (4502 and 7251, etc.), pyridine (heavy crude pyridine and pyridine, 1901, etc.), rice azole Lin (1017), amine (double hydrogenous amine, cantor and every J18, methyl propyl alum amine, etc.), polyamide, etc.

If it's remission with H_2S and CO_2 Double-corroded steel tube, imidazoline and thiazole derivative corrosions are better than other corrosions. However, it needs to be understood that the steel pipe of the desulfurization equipment is often not a single material, so there may be corresponding countermeasures; And the singleness of corrosion inhibitor is also worth considering, so compound corrosion inhibitor should be used in combination to better meet the required requirements.

The additives are mainly alkaline additives to change the PH value and thus change the solution environment. H + + is the concentration of water in an alkaline environment$_2$S is difficult to form, thus protecting the steel pipe.

References

[1] Tian Ming. Analysis on the impact of the Marine fuel sulfur emission control policy of the international maritime organization. International petroleum economics.2017.25(5); 77-82.

[2] Yang qiming. Li qin. Li youlv. Corrosion and protection of petrochemical equipment. Beijing petroleum industry press.2010.4

[3] Li chensheng. Influence of hydrogen sulfide on steel corrosion in gas field and its prevention. Fault block oil and gas field.2008.15(4); 126-128.

[4] Liu wei. Research status and progress on corrosion mechanism and protection of hydrogen sulfide in oil field. Oil drilling technology.2008.36(1); 83-86.

[5] Deng zichang. Zhang qinliang. Marine fuel oil, lubricating oil and water treatment: professional use for Marine engine management. People's communications press.1983

[6] Wei baoming. Theory and protection of metal corrosion. Beijing chemical industry press.2001

[7] Peng rong. Application of power failure method in the evaluation of pipeline cathodic protection effect. Corrosion and protection.2005 (05); 210.216