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Study on the Effect of Different Deposition States of Elemental Sulfur on the Corrosion of L290 Steel

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Abstract: ***Through wet gas pipeline corrosion simulation experiments, with SEM testing and EDS analysis, to study the effect of different deposition states of elemental sulfur on the corrosion of L290 steel. The results show that the metal below the deposited sulfur area is subject to serious local corrosion, and the increase in the deposited sulfur content will accelerate the corrosion rate; surrounded by a pool of liquid will further promote the corrosion rate, the metal immersed in the pool of liquid is uniform corrosion characteristics; sporadic sulfur particles attached to the metal surface will cause serious pitting corrosion. The corrosion product film is loose, easy to crack, corrosion mechanism for the catalytic reaction, the main components of the product is FeS, FeS_2.***

Key words: elemental sulfur; deposition state; corrosion rate

1. Introduction

In some high sulfur gas reservoirs, there are usually hydrogen sulfide, hydrogen polysulfide, thiol, thioether and other sulfur-containing substances, which generate elemental sulfur through chemical reactions under certain conditions, and the elemental sulfur generated is first dissolved in the gas during the process of natural gas production[1].The elemental sulfur is gradually deposited in the pipeline by gravity, water molecule adsorption and friction of the pipe wall as the gas is transported[2-7]. However, the complex conditions in the pipeline lead to different deposition states of elemental sulfur, such as sporadic adhesion and large area coverage, etc. Different deposition states of elemental sulfur will cause different types of corrosion, which seriously affects the safety of pipeline production. Therefore, we conduct simulation experiments of elemental sulfur corrosion in wet gas pipelines to study the corrosion law of pipelines under different deposition states of elemental sulfur, so as to provide a basis for the corrosion protection of gathering pipelines[8].

2. Experimental Methods

The experimental corrosion system is S-H_2S-H_2O, hanging sheet for L290 steel type III, successively using petroleum ether and anhydrous ethanol cleaning, cold air blowing dry weighing and ready for use. The visualization of wet gas pipeline simulation device as shown in Fig.1, adjust the hanging sheet attitude so that the elemental sulfur deposited on the hanging sheet appears in different states, simulating the corrosion of the pipeline when the elemental sulfur deposited in different states; H_2S in the wet gas from Na_2S hydrolysis generated, the tail gas treatment using a concentration of 1g/L NaOH solution, other experimental conditions as shown in Table 1.

Table 1: Experimental conditions for wet gas pipe simulation

Sulfur particle size	Elemental sulfur mass	Temperature	Air source pressure	Moisture content
d<63μm	10g	25℃	0.8MPa	3%

Figure 1: Visualization of wet gas pipeline simulation device

The experiment is put into 6 pieces at a time in different positions, using moisture to bring sulfur monomers from the beginning of the pipe into the pipe, the simulation experiment time is 72 h. After the end of the corrosion experiment to remove the hanging pieces to dry, using scanning electron microscopy and energy spectrum analysis to observe the corrosion morphology, analysis of corrosion products[9-10]. Finally remove the specimen corrosion

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products, using deionized water rinse and dry, weigh the mass of the specimen after corrosion and calculate the corrosion rate, the calculation formula reference standard T/CSTM 00127-2019 metal materials autoclave corrosion test guidelines are shown below.

$$v=\frac{365000\times\Delta W}{\rho\times t\times S}$$

Experimental steps for wet gas pipeline corrosion simulation:

1) Sieve 10 g of sulfur monomer with particle size d<63 μm;
2) Take 6 prepared L290 pegs and place one peg in the straight pipe every 50 cm from the starting point;
3) Place 2 g of sulfur monomers at the starting point and replenish 2 g of sulfur monomers at 5 h intervals;
4) blowing sulfur monomers into the pipe with wet air for a simulated experiment time of 72h;
5) Remove the hanging sheet after the end of the experiment and use cold air to dry it quickly before conducting the SEM test and energy spectrum analysis;
6) after the completion of the test, rinse the pendant with hot water to remove corrosion products, followed by cleaning with deionized water, and then using anhydrous ethanol to clean and quickly blow dry;
7) Use microscope to observe the local corrosion morphology;
8) Weighing the cleaned pegs, calculate the mass loss and uniform corrosion rate.

3. Experimental results and analysis

3.1 Deposition state of elemental sulfur

After the experiment was started, the elemental sulfur was distributed in the pipe in two states, as shown in Fig.2, part of the elemental sulfur was suspended in the pipe following the wet gas, and the other part was deposited on the inner wall of the pipe and the hanging sheet.

Figure 2: Suspension and deposition state of elemental sulfur

After 72h of experiment, the wet gas source was turned off, and the distribution of elemental sulfur in the pipe was observed from the starting point as shown in Fig. 3(a), and a large amount of elemental sulfur had been deposited on the inner wall of the pipe and on the surface of the No. 1 pendant; the wet gas pipe simulation device was disassembled after the fourth pendant, and a small amount of deposited sulfur was observed on both the No. 4 pendant and the inner wall of the pipe, as shown in Fig. 3(b), and there was a small amount of liquid accumulation at the location of the No. 4 pendant; there was only a thin layer of deposited sulfur on the pipe wall after the No. 4 pendant, and there were very few water droplets condensed on the inner wall, as shown in Fig. 3(c).

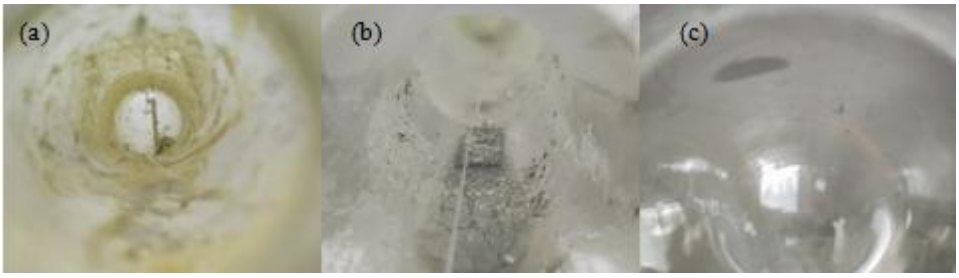

Figure 3: Internal view of elemental sulfur distribution after 72h

2.2 The effect of different deposition state on corrosion rate

Hanging piece of weight loss test and corrosion rate calculation data as shown in Table 2. Corrosion rate of the largest for the No. 4 pendant, the maximum corrosion rate of 0.621mm/a, the degree of corrosion for very serious corrosion; followed by the No. 1 pendant, corrosion rate of 0.521mm/a, the degree of corrosion for very serious corrosion; No. 6 pendant is the farthest from the starting point, the corrosion rate is the smallest, 0.108mm/a, the degree of corrosion for light corrosion.

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Table 2: Elemental sulfur corrosion experimental data

Serial Number	surface area/（cm^2）	Quality before corrosion/（g）	Quality after corrosion/（g）	Average corrosion rate/（mm/a）
1	12.486	8.040	7.998	0.521
2	12.591	8.124	8.094	0.369
3	12.486	7.810	7.769	0.509
4	12.470	8.013	7.963	0.621
5	12.520	8.058	8.042	0.198
6	12.943	7.950	7.941	0.108

Elemental sulfur deposited under different states of corrosion rate of the specimen as shown in Fig. 4. 3, 4 pendant around the ponding, its corrosion rate is the largest; 1, 2 pendant is closer to the starting point, the elemental sulfur deposited in large amounts leading to a higher corrosion rate; and 5, 6 pendant is the farthest from the starting point, the deposited sulfur content is the least, the corrosion rate is the smallest. It can be seen that the increase in deposited sulfur content will accelerate the corrosion rate, if at the same time there is a buildup of liquid around the generation will further promote the corrosion rate accelerated.

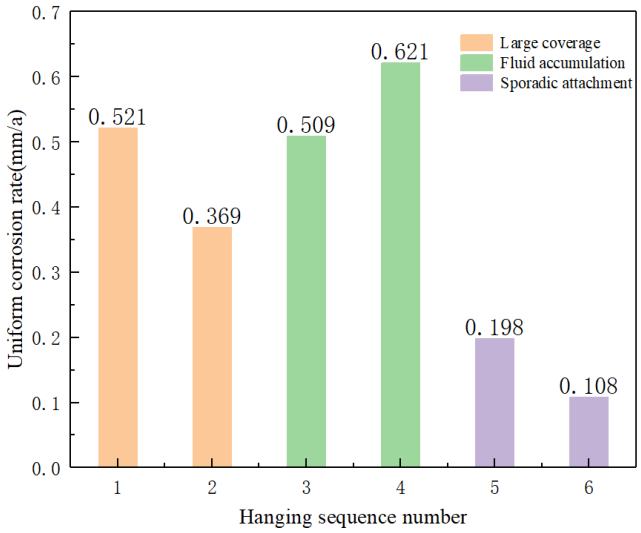

Figure 4: Specimen corrosion rate

2.3 Analysis of corrosion morphology

At the end of the experiment to take out all the pegs as shown in Fig. 5, it is observed that from No. 1 to No. 6 pegs deposited sulfur content gradually reduced, No. 1, No. 2 pegs surface covered by deposited sulfur larger area, and moisture and elemental sulfur involved in the reaction, so its corrosion rate is faster. 3, No. 4 pegs surface not only has a large number of elemental sulfur deposited, but also around the accumulation of liquid, resulting in a faster corrosion rate. In No. 5, No. 6 hanging piece only a very small amount of sulfur attached, and a certain metallic luster, hanging piece surface has a slight oxygen corrosion traces and a small number of etching pits.

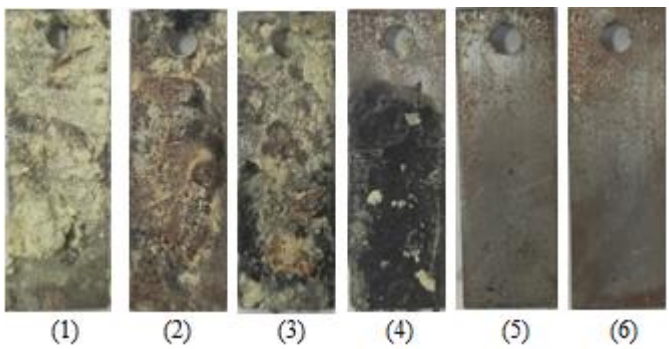

Figure 5: Different positions of hanging corrosion products chart

The use of ultrasonic cleaning instrument to clean the products of all pegs to get the morphology of corrosion as shown in Fig. 6, No. 1 and No. 2 pegs deposited sulfur below the obvious corrosion traces, which is due to the deposition of sulfur below the corrosion rate is fast, the surrounding area corrosion rate is slow. 3 and No. 4 pegs deposited sulfur below the corrosion traces more uniform, which is due to the deposition of sulfur coverage at the same time part of the metal immersed in the accumulation of liquid, resulting in the immersion site of the uniform corrosion. Uniform corrosion. 5 and 6 hanging sheet surface with dense corrosion pits, which is due to the small volume of elemental sulfur deposited in the metal surface under the action of moisture, accelerating the surrounding corrosion rate to form small pits.

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Figure 6: Macroscopic morphology after corrosion of hanging pieces at different locations

After the end of the weight loss experiment on all corrosion pegs SEM test, different deposition state pegs 200μm SEM test figure shown in Fig. 7, which 1, 2 pegs similar characteristics, the deposition area generated more corrosion products, tiny volume of elemental sulfur will be attached to the generated product film, the formation of product film cracking less. Among them, the 3, 4 pendant features are similar, the surface generated thicker corrosion products, cauliflower-like growth, the product has signs of cracking. 5, 6 pendant surface only scattered granular corrosion products attached to it, but also a small amount of sulfur particles attached to the surface.

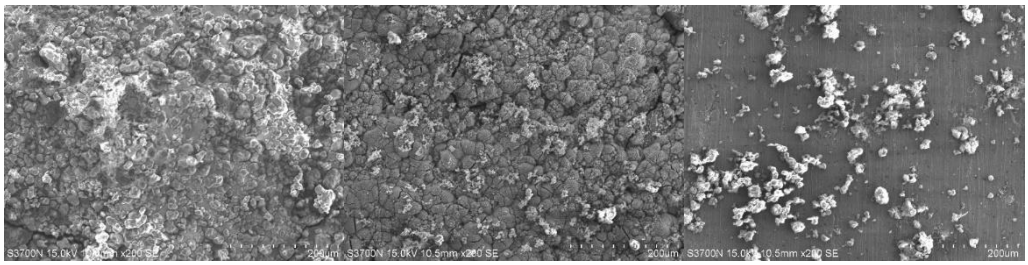
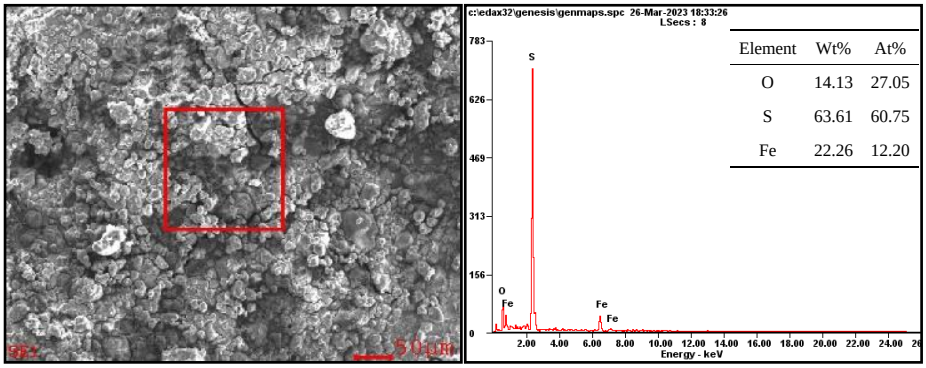


Figure 7: Corrosion morphology under different deposition conditions

Elemental sulfur corrosion SEM test and EDS analysis as shown in Fig. 8, No. 1, 2 pendant is covered by deposited sulfur over a large area, the corrosion morphology is similar, the surface products are mainly loose granular material, in addition to the surface of the product film and deposited singlet sulfur. 3, 4 pendant around the presence of both elemental sulfur and cumulus, observed that the deposited area and the undeposited area have different corrosion conditions, the deposited area surface products cracked, while There are granular products attached to the surface, and cauliflower-like products growing on the cracked product film. 5, 6 pendant surface only a very small amount of granular corrosion products and deposited sulfur particles.



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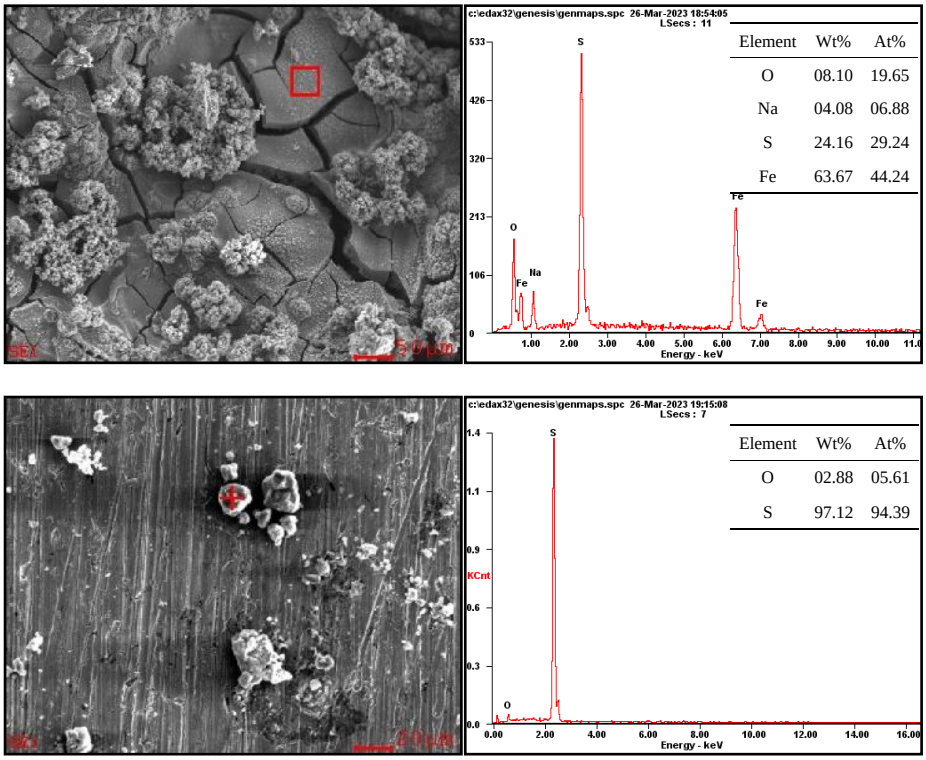

Figure 8: Specimen SEM test and EDS analysis

From the energy spectrum that the system under the production of corrosion products to Fe, S, O elements are dominant, so the analysis of particulate matter and the main components of the product film is FeS, FeS_2.

2.4 Corrosion mechanism

Based on the morphology and composition analysis of corrosion surface products, it is concluded that the mechanism of elemental sulfur corrosion in the S-H_2S-H_2O system is a catalytic reaction, wet H_2S ionizes HS^-, HS^- continues to ionize S^{2-} and H^+, S^{2-} reacts with Fe to form FeS, FeS catalyzes the reaction between S and water to form S^{2-}, Fe^{2+} reacts with S^{2-} to form more and more FeS. As the reaction proceeds, the system As the reaction proceeds, the S^{2-}content in the system increases and continues to react with the generated FeS to form FeS_2, and the main reactions occur as shown below.

$$H_2S \longrightarrow HS^- + H^+ \quad (1)$$

$$HS^- \longrightarrow S^{2-} + H^+ \quad (2)$$

$$Fe \longrightarrow Fe^{2+} + 2e^- \quad (3)$$

$$Fe^{2+} + S^{2-} \longrightarrow FeS \quad (4)$$

$$(x+y+1)S + yH_2O \xrightarrow{FeS} (y+1)HS^- + S_xO_y^{2-} + (y-1)H^+ \quad (5)$$

$$HS^- \longrightarrow S^{2-} + H^+ \quad (6)$$

$$Fe^{2+} + S^{2-} \longrightarrow FeS \quad (7)$$

$$FeS + S^{2-} + 2H^+ \longrightarrow FeS_2 + H_2 \quad (8)$$

4. Conclusion

Wet gas pipeline corrosion simulation experiments in the deposition of sulfur area below the metal is subject to serious local corrosion, and the increase in the content of deposited sulfur will accelerate the corrosion rate; if the surrounding liquid will further promote the corrosion rate accelerated, the metal immersed in the liquid is uniform corrosion characteristics; if only scattered sulfur particles attached to the metal surface, it will cause serious pitting corrosion.

Wet gas pipeline S-H_2S-H_2O system in the metal corrosion products film loose, easy to crack, corrosion mechanism for the catalytic reaction, the main components of the product is FeS, FeS_2.

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