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Application of Scavenger for Prevention and Remediation of Hydrogen Sulphide in Oil Exploitation

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Hydrogen sulphide, a notorious toxic gas, has been found in some areas of Qing Hai Oilfield of the P.R. China, especially in the heavy oil blocks. Not only does it endanger the lives of operators, but it also causes corrosion damage on pipelines and engines. Both N80 and 20 # type steel pipe have been tested with concentrations up to 200 ppm H_2S, It has been found that the corrosion products are made up of the Fe, Cl, S and Mn elements. A new type of scavenger named TEM-10-15 has been adopted to lessen the damage of the H_2S. Experiments carried out in laboratory show that this treatment agent can eliminate the effects of H_2S quickly and for a longer time. This method has also been used in on-site field trialsin the process of oil exploitation.

Keywords: Hydrogen sulphide, Corrosion, Corrosion inhibitor, Oil reservoir.

INTRODUCTION

Hydrogen sulphide (H_2S) has been found in some areas of Qing Hai Oilfield of the P.R. China, especially in the heavy oil blocks. With the drop of temperature and pressure of oil from underground to surface condition, the hydrogen sulphide can be observed flowing out of crude oil continuously, which causes stress corrosion fractures in the steel pipeline and rod pump and shortens the service life of production equipment, or even leads to accidents that may cause casualties[1-6].

While the H_2S without aqueous phase has no corrosive effects on metal materials, it is corrosive when dissolved in water[2,3]. In wet H_2S corrosive environment, carbon steel equipment prone to uniform corrosion and wet H_2S stress corrosion cracking. In the aqueous solution of H_2S, the embrittlement of steel is caused by molecular H_2S which is not dissociated[2,7]. This process is carried out in the following order[5,7].

$$H_2S + e \longrightarrow H_2S^-$$

$$H_2S^- \longrightarrow HS^- + H$$

$$H \longrightarrow H^+ + e$$

$$HS^- + H^+ \longrightarrow H_2S$$

The essence of wet H_2S stress cracking is hydrogen embrittlement. The major types can be classified as follows: Hydrogen blistering, hydrogen induced cracking, stress corrosion cracking and stress oriented hydrogen induced cracking[8]. The hydrogen adsorbed on the surface of steel provides necessary condition for steel hydrogen permeation and hydrogen embrittlement[7]. When the hydrogen atoms diffuse inward to the internal surface of steel, it will produce a brittle layer, which leads to sulphide stress corrosion cracking and hydrogen induced cracking[9].

Taken into account of the on-site circumstance, a series of indoor corrosion experiments are carried out on both of the N80 and 20 # steel, to evaluate corrosion status and study the principle of anticorrosion.

Corrosion of hydrogen sulphide

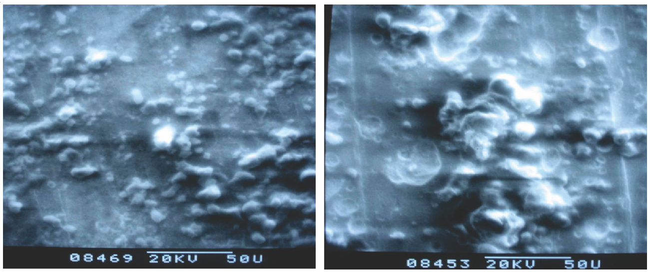
Procedure: Prepare aqueous solution of sodium chloride and the corrosion specimen (standard 50 mm × 10 mm × 3 mm specimen). Fix the corrosion coupon on the bracket of SAR-II high-temperature and high-pressure dynamic corrosion test instrument. Add sodium chloride water and shut the reactor and wipe out oxygen with nitrogen gas. Input H_2S gas as required and the instrument is then heated and pressured to the specified conditions. The coupon is taken out after 10 days. After the corrosion products are cleared, the coupons are weighted and recorded. The average (overall) corrosion rate is calculated with the following equation[10].

$$Va = 8.76\times10^{4} \times \frac{\Delta W}{(S\times t\times \rho)} \quad (1)$$

where: Va: Average corrosion rate (mm/a); ΔW: loss of coupon weight (g); ΔW_0: The weight loss of blank coupon (g); S: coupon corrosion area (cm^2); t: corrosion time (h); ρ: coupon density (g/cm^3).

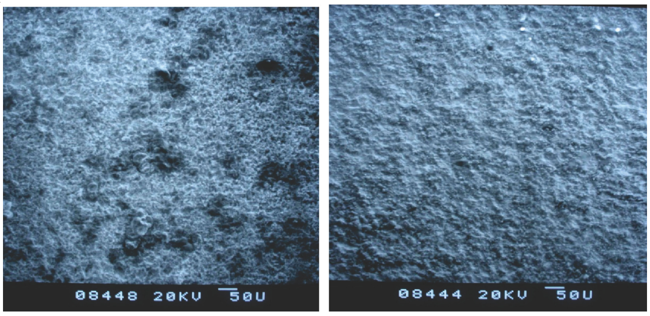
The corrosion morphology of coupon surface can be analyzed with S-450 type scanning electron microscope. The elements, composition and structure of the sample surface film on corrosive product were measured using X-ray energy dispersive spectroscopy (OV9100/65). The implemental standard followedis "analytical scanning electron microscope general rule", JY/T010-1996[11].

Corrosion made by the hydrogen sulphide: To test the corrosion of the N80 and 20 # steels in 200 ppm concentration of the hydrogen sulphide under various conditions. The reaction process lasts 10 days and the experiment is to be carried out at 45 ºC. The experiment results are shown in Table-1. The S-450 scanning electron microscope was used to evaluate the corrosion morphology of two kinds of steel coupons under a variety of test conditions. The representative morphologies are shown in Figs. 1-3.



20# steel (×500) N80 steel (×500)

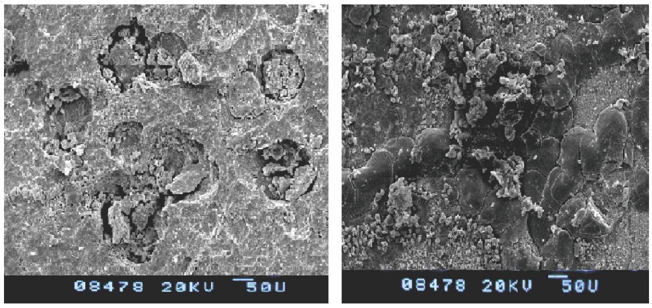
Fig. 1. Microstructure of the corrosion coupon under condition 1



20# steel (×500) N80 steel (×500)

Fig. 2. Microstructure of the corrosion coupon under condition 2

Various results can be seen from Table-1. The results under condition 1 are that the corrosion rate of 20 # steel coupon is 0.0311 mm/a, representing the moderate corrosion. The corrosion rate of N80 steel coupon is 0.0214 mm/a, showing mild corrosion and the corrosion degree is less serious than that of the 20 # steel coupon. It can be seen from Fig. 1 that 20# steel coupon show shallow pitting after removing the corrosion products and the N80 typecoupon shows similar results as that of 20#.



20# steel (×1000) N80 steel (×1000)

Fig. 3. Microstructure of the corrosion coupon under condition 3

The results under condition 2 are that the corrosion rate of 20 # steels is 0.0567 mm/a, which is moderate corrosion. The corrosion rate of N80 steels is 0.0345 mm/a, showing moderate corrosion. However, the corrosion is less serious than that of 20 # steels. It can be seen from Fig. 2 that the 20 # steel coupon show minor pitting after removing corrosion products and N80 coupon also shows similar pitting.

The results under condition 3 are that the corrosion rate of 20 # steel is 0.0615 mm/a, showing moderate corrosion. The corrosion rate of N80 steel is 0.0412 mm/a, showing moderate corrosion, but the corrosion is less serious than that of the 20 # steel. It can be concluded from Fig. 2 that 20 # steel corrosion specimens shows obvious pitting after the removal of corrosion products and the pits are deeper. The N80 # steel corrosion specimen also have pitting on the surface, but they are shallow ones.

By means of the energy dispersive analysis of the corrosion products on the corrosion coupon under three conditions, it can be concluded from Table-2 that the corrosion products are mainly made up of the complex compounds of Fe, Cl, S, Mn and other elements. The created corrosion process is realized by chloride ion to destroy the corrosion product films, as well as electrochemical corrosion effect of hydrogen sulphide[3,9].

Elimination of the hydrogen sulphide: There are three methods to control H_2S corrosion on site. The first one is using corrosion resistant material or double metal composite pipe. The second one is by means of inner wall coating or non metal lining. The last one is using corrosion inhibitor[6,8]. Corrosion inhibitors have been updated from the early natural materials and inorganic salts to the modern high efficient organic compound with free pollution in the near 100 years[12-15]. It is an economical and practical method used for oilfield and has the advantages of convenient operation, no need to replace equipment and so on.

Since hydrogen sulphide often appears in the oil and gas phase during oil field exploration and transport process, not only can hydrogen sulphide treatment agent absorb hydrogen sulphide in the gas phase, but can also adhere hydrogen sulphide to oil phase in a more stable form, preventing its overflow in the gaseous phase and doing little harm to pipes as well.

The experimental methods are as follows: Place a sealed 350 mL size container placed on an oscillator and the volume of fluid (oil or water) fixed at 200 mL. Switch on the oscillator

TABLE-1
CORROSION TEST OF SPECIMENS UNDER DIFFERENT CONDITIONS

Test under conditions	Material	Weight loss (g)	Surface area (cm^2)	Corrosion time (d)	Corrosion rate (mm/a)	Average corrosion rate (mm/a)
Condition 1 (pressure: 12 Mpa Salinity: 200000 mg/L)	20# Steel	0.0019	13.90	–	–	0.0311
		0.0091	13.85	10	0.0306	
		0.0093	13.85	10	0.0312	
		0.0094	13.86	10	0.0315	
	N80 Steel	0.0022	13.86	–	–	0.0214
		0.0065	13.84	10	0.0218	
		0.0067	13.86	10	0.0225	
		0.0059	13.83	10	0.0198	
Condition 2 (pressure: 20 MPa Salinity: 200000 mg/L)	20# Steel	0.0022	13.62	–	–	0.0567
		0.0165	13.91	10	0.0552	
		0.0169	13.77	10	0.0571	
		0.0173	13.88	10	0.0579	
	N80 Steel	0.0017	14.03	–	–	0.0345
		0.0106	13.98	10	0.0352	
		0.0103	13.97	10	0.0343	
		0.0102	13.92	10	0.0341	
Condition 3 (pressure: 60 MPa Salinity: 320000 mg/L)	20# Steel	0.0020	13.82	–	–	0.0615
		0.0179	13.91	10	0.0598	
		0.0187	13.89	10	0.0626	
		0.0185	13.86	10	0.0621	
	N80 Steel	0.0022	13.66	–	–	0.0412
		0.0126	13.74	10	0.0426	
		0.0119	13.75	10	0.0403	
		0.0121	13.83	10	0.0407	

TABLE-2
INGREDIENTS OF COUPON'S CORROSION PRODUCT

Element	Weight (%)					
	Condition 1		Condition 2		Condition 3	
	20# steel	N80 steel	20# steel	N80 steel	20# steel	N80 steel
C	0.19	0.37	0.27	0.35	0.24	0.37
Fe	55.34	62.79	47.35	56.28	45.37	49.82
Cl	21.13	20.01	29.63	23.80	36.50	28.03
S	21.97	14.43	21.68	17.23	16.71	19.52
Si	0.34	0.26	0.19	0.37	0.31	0.32
V	–	0.15	–	0.17	–	0.15
Ni	0.21	–	0.12	–	0.17	–
Mn	0.62	1.47	0.63	1.64	0.56	1.67
Cr	0.11	0.14	0.11	0.15	0.14	0.11

and input hydrogen sulphide into the container until it's concentration reaches 1000 mg/L. Add certain amount of treatment agent and keep the system closed immediately. Have the fluid mixed and test gas hydrogen sulphide concentration with detector.

Aging time of hydrogen sulphide scavenger: The oil sample is taken from the on-site oil well. Input hydrogen sulphide. In a similar container at normal temperature, until the content is increased to1000 mg/L. The dosage of scavenger TEM-10-15 is 1 mL. The experiment method is similar as that above. The required time totreat the hydrogen sulphide was studied.

It can be seen from the Fig. 4 that after the reaction of hydrogen sulphide treatment agent TEM-10-15, the concentration of hydrogen sulphide decreases rapidly, even reduces to near zero concentration at last. The hydrogen sulphide is removed faster in water samples but slower in crude oil, which is due to the fact that thesolubility of hydrogen sulphide in the crude oil is larger and hydrogen sulphide scavenger requires a longer time to react.

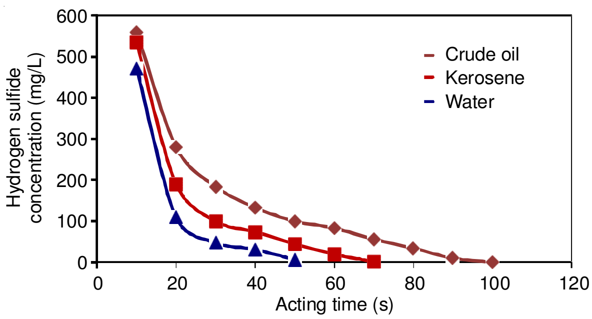


Fig. 4. Correlation between hydrogen sulfide concentration and acting time with different fluids

Influence of temperature on the scavenger: The volume of crude oil is set at 200 mL in a sealed containerand the hydrogen sulphide content is set at 1000 mg/L. The dosage and the time for the scavenger required to absorb the hydrogen sulphide at different temperatures is tested.

It can be concluded from the Fig. 5 that the effective time of scavenger accelerates with the increase of temperature. The

TABLE-3
ONSITE TREATMENT OF HYDROGEN SULFIDE

Wells tested	Concentration of H_2S (ppm)	TEM-10-15 consumption (kg)	Response time and the corresponding concentration of H_2S	Time in effect (h)
Q6-12	127	25	20 min/0 ppm	95
S3-2-3	250+	45	15 min/0 ppm	115
S3-2-2	200+	25	3 min/1 ppm	140

amount of scavenger increases abruptly after the temperature reaches above 80 ºC. It is due to the fact that the high temperature accelerates the reaction between the treatment agent and hydrogen sulphide and thus increases the consumption of the scavenger as well.

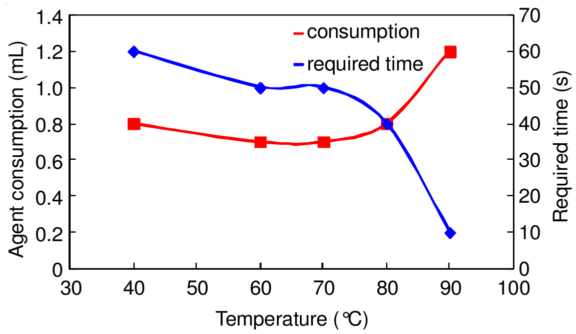


Fig. 5. Consumption of TEM-10-15 and the time required to adsorb hydrogen sulfide at different temperatures

The on-site effect of hydrogen sulphide treatment in the oil field: In the oil production plant of Qinghai oil field in P.R. China, scavenger TEM-10-15 is pumped into the casing head continuously, with the hydrogen sulphide content at the well head being monitored at the same time. The effect of on-site execution is shown in Table-3. It can be seen that the hydrogen sulphide treatment agent takes effect soon, absorbing hydrogen sulphide rapidly and preventing the generation of hydrogen sulphide in the long period.

Conclusion

With electron microscopy analysis, it can be concluded that most of the H_2S corrosion are point type corrosion and some are pitting type corrosion. The main mechanism of corrosion is the destruction of corrosion product film by the chloride ion, as well as the electrochemical corrosion of H_2S. The corrosion products are mainly Fe, Cl, S, Mn and other elements. During the indoor tests, it can been found that the hydrogen sulphide scavenger TEM-10-15 can take effect soon, absorb hydrogen sulphide rapidly and suppress the liberation of hydrogen sulphide for a long-term. Finally, On-site experiment also realized the hydrogen sulphide prevention successfully, proved the TEM-10-15 has reliable performance and can fully meet the on-site requirement.

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