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The Research of Bohai Sea-Based Annulus Protection Fluid

Ren Yi[*]**, Lu Yuan, Zhang Mao, Cheng Yan, Sun Jixing, Wang Zhongguang**

CNOOC Energy Technology & Services LTD., Tianjin, China

Email address:
renyi5@cnooc.com.cn (Ren Yi)

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Abstract: The advantages and disadvantages of oil-based and freshwater-based annulus protection fluids were compared. According to the characteristics of freshwater shortage on offshore platforms, the quality of Bohai sea water was analyzed in detail. The sterilization effect of various fungicides was evaluated by extinction dilution method in the laboratory, and the quaternary ammonium salt YHZWJ-15 was determined as one of the basic components. After that, the method of industry evaluation standard was used to conclude that polyphosphate BH-701 has excellent scale prevention performance. For the most important corrosion inhibitor in the system, BHH-509, which is composed of gluconate, organic amine, zinc salt and organic phosphonic acid copolymer, is successfully compounded by static corrosion rate method. Finally, the polarization curve was used to analyze the action mechanism of the annulus protection fluid, and the basic ratio was seawater + 0.5% YHZWJ-15 + 0.01% BHF-701A + 0.01% thiourea + 0.5% BHH-509. It can reduce the corrosion rate to 0.0051 mm/a and the corrosion inhibition rate can reach more than 95%.

Keywords: Annulus Protection Fluid, Anti-salt Corrosion Inhibitor, Bactericide, Scale Inhibitor, Bohai Oilfield

1. Introduction

With the increasing water of produced fluid in Bohai Oilfield, the corrosion damage of tubing and casing in producing wells and water injection wells is becoming more and more serious, which leads to frequent workover and even scrap of oil and water wells, resulting in huge economic losses. Because of the complex water quality and high salinity of the water produced, corrosive gases such as CO_2 and H_2S are associated with crude oil, and corrosive bacteria SRB breed and propagate in large quantities in the annulus, resulting in frequent corrosion and scaling problems [1]. The annulus protection fluid can not only inhibit the corrosion of tubing and casing, but also reduce the pressure difference between tubing and annulus and the reservoir pressure borne by packer. According to its fluid properties, it can be divided into water-based annulus protection fluid and oil-based annulus protection fluid [2].

In 2006, according to the annulus characteristics of Changshen-1 well in Jilin Oilfield, an annulus protection fluid HSJ-JL-01 with independent intellectual property rights was developed indoors. On the one hand, the surfactant can effectively absorb the condensate water with high CO_2 content, prevent the condensate water from adsorbing on the metal surface, and keep the metal surface in contact with the oil-phase solvent. On the other hand, the corrosion inhibitor is alkaline and can effectively absorb CO_2 and prevent CO_2 corrosion. The chemical property of the corrosion inhibitor is stable, and the temperature resistance reaches 130°C [3]. Oil-based annulus protection fluid is non-corrosive and has better thermal stability than water-based annulus protection fluid, but its cost is relatively high.

Water-based annulus protection fluid is the most common fluid. According to its source, water-based annulus protection fluid can be divided into modified drilling annulus protection fluid, low solid annulus protection fluid and clean brine annulus protection fluid [4]. We have developed annulus protective fluid CP-01 for low salinity water, annulus protective fluid HKP-01 for oxygen corrosion, annulus protective solution HKP-02 for carbon dioxide corrosion and annulus protective solution HKP-01A for high temperature. However, the water-based annulus protection fluid is greatly affected by water quality and other factors. Especially for Bohai oilfield, the freshwater on the platform is relatively scarce. During workover operations, seawater are often used, and its salinity is generally 3000-30000 ppm. Therefore, how to overcome the factors of high salinity, dissolved oxygen, CO_2 and bacteria on the pipe string is the key to develop seawater-based annulus protection fluid.

2. Experimental Method

2.1. Chemicals

bactericide (YHZWJ-11, YHZWJ-12, YHZWJ-13, YHZWJ-14, YHZWJ-15, homemade products), scale inhibitors (BHF-04, BHF-11, BHF-16, BHF-07A, BHF-701A, homemade products), corrosion inhibitor (DYH-55, TZC-5205, TZC-2, DMH-9524, DWH-28A, BHH-509, 106M), thiourea (AR, Reagent plant of Tian Jin Kemiou), N80 steel sheet, Bohai seawater

2.2. Experimental Method

1) Measurement of corrosion rate: Using N80 carbon steel sheet, by atmospheric pressure static hanging piece corrosion rate measurement method, hanging piece was placed in the water sample, soaked at 60°C for a certain time, and the corrosion rate was calculated by the loss of hanging piece quality [5].

2) Scale-proof performance test: weigh each bottle and record it, then put it in oven after weighing, adjust it to the experimental temperature (60°C), constant temperature for 24 hours, wait for the temperature to cool down after constant weight, weigh again, and add distilled water to the weight before constant temperature, shake well and filter, then titrate [6].

3) Bactericidal test: Bacterial culture was carried out at 60°C by dilution method and the inhibition of microbial growth by protective solution was determined. SRB was more than 105/ml and the selection period was 7 days [7].

3. Experimental Results and Analysis

3.1. Research Ideas

To control the electrochemical corrosion caused by the dissolution of O_2, CO_2 and other gases in high salinity water is the most important research direction for choosing corrosion inhibitors. The annular protetive fluid is in the airtight space of the casing and tubing annulus. Because of the change of pressure and temperature, the liquid will have a certain tendency of scaling, and the long-term using will also lead to the growth of microorganisms. Therefore, in order to solve this problem, certain bactericides and scale inhibitors will be added. On the basis of summarizing and analyzing the above-mentioned water-based annulus protection fluids, we will optimize corrosion inhibitors, bactericides, scale inhibitors and other components to improve the stability of the system, and eventually form an annulus protection fluid against seawater corrosion [8].

3.2. Seawater Corrosion in Bohai

Seawater is an electrolyte solution containing a variety of salts, and the total salt content is about 3%, in which the chloride content accounts for 88%, and the PH value is about 8. It also dissolves a certain amount of oxygen. Except for magnesium and its alloys with very negative potential, most metal materials are oxygen depolarization corrosion in seawater. Its main characteristic is that the chloride ion content in seawater is very large, so the anodic polarization retardation of most metals in seawater is very small, and the corrosion rate is quite high. The conductivity of seawater is very large, so it not only corrodes the activity of microbatteries, but also the activity of macrocells. In addition, there are many kinds of microorganisms living in the ocean. Their life activities will change the state of the metal-sea interface and the properties of the medium, and have a significant impact on corrosion [9].

Table 1. *Analysis of Bohai water.*

Detection content	**mg/L**	**mmol/L**	**mmol/%**
K^++Na^+	8356.82	363.34	38.02
Mg^{2+}	1136.47	46.73	9.78
Ca^{2+}	421.24	10.51	2.20
Total	9914.53	477.82	50.00
Cl^-	15212.30	429.12	44.90
SO_4^{2-}	2207.25	22.98	4.81
HCO_3^-	141.57	2.32	0.24
CO_3^{2-}	12.60	0.21	0.04
TOTAL	17573.72	477.82	49.99
I-	0.13	Total mineralization (mg/l):	27488.25
Br-	42.72	Temporary hardness (HT):	6.50
B	4.67	Permanent hardness (HP):	314.04
Fe^{2+}	0.00	Total hardness (H):	320.54
Fe^{3+}	0.03	Total alkalinity (A):	2.74
Water type: Magnesium chloride		PH: 8.0	

Table 2. *The static corrosion result of Bohai water.*

N80 steel sheet	**Water type**	**Tem**	**Time**	**quality, g**			**Corrosion rate**	**Average rate**
		°C	**h**	**before**	**after**	**difference**	**mm/a**	**mm/a**
8801	seawater	60	42.5	8.9273	8.9214	0.0059	0.1176	0.141
8701		60	42.5	8.3473	8.3392	0.0081	0.1638	

From the above table, the total salinity of Bohai Sea water reaches 27488.25 mg/L, and the corrosion rate of N80 steel sheet is more than 0.14 mm/a, which is much higher than that of 0.076 mm/a of the control index of water quality corrosiveness. Anti-corrosion measures should be taken.

3.3. Experimental Analysis

3.3.1. Screening of Bactericide

SRB occur under hypoxic and water conditions, and TGB can reproduce as long as there is trace oxygen. FB exist in oxygen and iron. These three kinds of bacteria and other bacteria corrode metals in different forms. Although the above bacteria are very few in the filtered seawater, a large number of bacteria will breed and multiply in the sealed oil jacket annulus, so it is necessary to consider the corrosion effect of bacteria. In the selection of bactericides, the main target is the broad-spectrum bactericide, to ensure that the oil jacket annulus protective solution can inhibite the growth in which some bacteria may exist in. We choose quaternary ammonium salt, which is the most widely used bactericide in oilfields, and use extinction dilution method to evaluate the bactericidal effect at 60°C [10].

Table 3. *The evaluation data sheet of sterilization.*

number	Product code	Concentration of medicals (mg/L)	Bacterial quantity (individual/ml)
1	Blank water sample	--	>105
2	YHZWJ-11	50	5.0
3	YHZWJ-12	50	22.5
4	YHZWJ-13	50	46.0
5	YHZWJ-14	50	26.0
6	YHZWJ-15	50	0

The bactericide YHZWJ-15 had the best bactericidal effect under 50 ppm for 7 days. No SRB were found in the bottle, followed by YHZWJ-11. These bactericides mainly include quaternary ammonium cations, which adsorb negatively charged bacteria through electrostatic force, hydrogen bonding force and hydrophobic binding between surfactant molecules and protein molecules, and aggregate on the cell wall, resulting in bacterial growth inhibition and death; at the same time, their hydrophobic alkyl groups can also interact with bacterial hydrophilic groups and change. Membrane permeability, then lysis, destroy cell structure, cause cell dissolution and death.

3.3.2. Screening of Anti-scale Agents

Scale inhibitor is a chemical agent that can prevent or delay the formation of inorganic fouling deposits in water. After dissociation in water, anions and scaling cations produce stable water-soluble ring structure through reaction + complexation (chelation) [11].

Table 4. *The evaluation data sheet of scale inhibitors.*

agents	Concentration (mg/L)	calcium concentration after test (mg/L)	anti-scale rate%
blank	-	680.00	-
BHF-11	15	696.00	62.97
	25	696.60	69.26
BHF-04	15	700.00	78.71
	25	701.60	85.01
BHF-16	15	694.40	56.67
	25	704.80	97.60
BHF-07A	15	696.60	69.26
	25	700.80	81.86
BHF-701A	15	701.60	85.01
	25	704.80	97.60

The result shows that BHF-701A has the best anti fouling effect and BHF-16 is next. This type of agent is organic polyphosphonate, which has good chemical stability and is basically not damaged by acid and alkali, not easy to hydrolyze and degrade, withstand high temperature. It has a certain corrosion inhibition effect while scale prevention.

3.3.3. Screening of Corrosion Inhibitors

As the most important agent of annulus protection fluid, the choice of corrosion inhibitor is the core of the whole system. We have developed various imidazoline derivatives as corrosion inhibitors in offshore oilfield corrosion control. In marine environment, the concentration of electrolyte, oxygen content and microorganism in seawater will destroy and corrode the steel structure to varying degrees. For example, for salt content, ion concentration and resistivity, chloride ion is a very penetrating corrosion medium. When it touches the surface of steel, it quickly destroys the passivation layer on the surface of steel, which leads to the increase of conductivity of seawater and acceleration of corrosion. Secondly, the larger the dissolved oxygen content, the faster and more rust is formed, and the faster the anode is formed. At last, corrosion intensifies [12].

For saline water and dissolved oxygen corrosive water, the latest research and development achievements of corrosion inhibitors are multi-component systems, and their compounding routes are generally phosphorus-zinc-organic-molybdate. Among them, all-organic system is currently the most widely used one. Organic phosphate phosphate is used to compound zinc gluconate, organic amines, azoles and polycarboxylic acid. Under the condition that the existing corrosion inhibitors can not solve the corrosion problem of seawater on the pipe string, we have developed a new type of corrosion inhibitor through a lot of experiments in the laboratory, using seawater + 0.5% YHZWJ-15 + 0.01% BHF-701A + 0.01% thiourea as the base solution, and using indoor static corrosion rate measurement method to evaluate [13].

Table 5. *The anti-corrosion effect of different types of corrosion inhibitors.*

No.	**corrosion inhibitor**		**Tem**	**Time**	**quality, g**			**corrosion rate**
	type	**concentration%**	**°C**	**h**	**before**	**after**	**difference**	**mm/a**
7035	DYH-55	0.05	60	47	9.0186	9.0147	0.0039	0.0703
7212		0.1	60	47	9.5158	9.5123	0.0035	0.0620
7039		0.3	60	47	9.0533	9.0496	0.0037	0.0665
7216	TZC5205	0.05	60	47	9.4432	9.4396	0.0036	0.0640
7219		0.1	60	47	9.4953	9.4923	0.003	0.0536
7040		0.3	60	47	8.9154	8.9134	0.002	0.0361
7217	TZC-2	0.05	60	47	9.4920	9.4895	0.0025	0.0444
7038		0.1	60	47	8.8907	8.8882	0.0025	0.0449
7218		0.3	60	47	9.4783	9.4769	0.0014	0.0249
7213	BHH-509	0.1	60	47	9.4500	9.4469	0.0031	0.0551
7037		0.3	60	47	8.9935	8.9928	0.0007	0.0126
7211	106M	0.05	60	47	9.4524	9.4491	0.0033	0.0587
7214		0.1	60	47	9.3714	9.3663	0.0051	0.0908
7220	DMH9524	0.1	60	47	9.4940	9.4903	0.0037	0.0657
7215		0.3	60	47	9.4145	9.4105	0.004	0.0712
7034	DWH-28A	0.05	60	47	8.7432	8.7389	0.0043	0.0782
7033		0.1	60	47	8.9123	8.9065	0.0058	0.1053
7036		0.3	60	47	9.0474	9.0401	0.0073	0.1317

From the above experiments, it can be seen that the corrosion rates of DYH-55, TZC-5205 and TZC-2 gradually decrease with the increase of concentration. Although the corrosion rates are less than 0.076mm/a, there are more red rust deposits at the bottom of the bottle, and TZC-2 is insoluble in the preparation and suspended in the solution; The corrosion rates of DMH-9524 and DWH-28A increase with the increase of concentration. However, there are more rust deposits at the bottom of the bottle, and the solution is red for DMH-9524. The corrosion rate of DWH-28A is high, and you can see white deposits at the bottom. The corrosion rate of BHH-509 decreases with the increase of concentration, while that of 106M increases with the increase of concentration. The corrosion rate of both of them is proportional to the state of solution. It is ideal.

Table 6. *The comparison of two different corrosion inhibitors.*

No.	**corrosion inhibitor**		**Tem**	**time**	**mass, g**			**corrosion rate**	**average rate**
	type	**concentration%**	**°C**	**h**	**before**	**after**	**difference**	**mm/a**	**mm/a**
8027	BHH-509	0.3	60	148.5	8.5014	8.4974	0.0040	0.0229	0.0250
7031		0.3	60	148.5	8.9188	8.9141	0.0047	0.0271	
8028		0.5	60	148.5	8.5350	8.5341	0.0009	0.0051	0.0051
8029	106M	0.02	60	148.5	8.5730	8.5679	0.0051	0.0290	0.0290
8030		0.05	60	148.5	8.3519	8.3417	0.0102	0.0582	0.0579
7032		0.05	60	148.5	8.9786	8.9686	0.0100	0.0575	

From the above experiments, it can be seen that the corrosion rate and solution state of BHH-509 are very ideal at 0.5% concentration for 7 days, and the system is relatively stable. The corrosion rate of 106M decreases with the decrease of concentration, but there is a small amount of yellow precipitation at the bottom of the solution, and the solution is a little turbid, so BHH-509 is finally selected as a corrosion inhibitor for the system. It is mainly composed of gluconate, organic amines, zinc salts and organic phosphonic acid copolymers. The precipitation protective film formed by organic phosphoric acid and bivalent metal ions Fe^{2+}, Ca^{2+}, etc. plays a role in inhibiting dissolved oxygen corrosion and scaling ion precipitation. On the one hand, the formation of calcium carbonate scale in seawater is inhibited and dispersed by multi-copolymers. On the other hand, it can effectively control the precipitation of calcium phosphate that may be caused by the agent itself.

3.3.4. Mechanism of Corrosion Inhibitors

(1) Film forming properties of corrosion inhibitor

Iron reacts with copper ions in copper sulfate solution, and copper ions are reduced and adhered to the surface of the specimen to form a copper coating. The better the protective film formed on the surface of the specimen in the corrosion inhibitor solution, the less the copper coating on the surface of the specimen. According to the area of copper coating adhered to the surface of the test piece, the optimum film-forming concentration of various inhibitors can be obtained, and the film-forming performance of the inhibitors can be compared. The test method can quickly evaluate the film forming property of corrosion inhibitor and predict the performance of corrosion inhibitor [14].

Table 7. *The evaluation of film forming property with corrosion inhibitors.*

phenomenon	evaluation results
Total copper coating on test piece surface	The inhibitor has poor film-forming property at this mass concentration.
1/2 copper coating on the surface of test piece	The corrosion inhibitor has a general film forming property under this mass concentration.
1/3 copper coating on the surface of test piece	The corrosion inhibitor has good film forming property at this mass concentration.
The surface of the specimen is bright without copper coating.	The corrosion inhibitor has excellent film forming property under this mass concentration.

The film forming properties of the inhibitor BHH-509 were compared with those of other seawater inhibitors on the market. The experimental results are shown in Table 8. The corrosion inhibitor concentration is 1wt%. From table 8, we can see that BHH-509 has the best film formation effect, followed by S-2, and the last is I-870.

Table 8. *The evaluation of film forming property with three corrosion inhibitors.*

corrosion inhibitor	phenomenon	evaluation results of film formation
BHH-509	The surface of the specimen is bright without copper coating.	excellent
S-2	1/3 copper coating on the surface of test piece	preferable
I-870	1/2 copper coating on the surface of test piece	common

(2) Study on mechanism of BHH-509 by polarization curve method

The instrument used is Gamry 1000 and the test solution is 3% NaCl solution [15]. The three-electrode system is adopted, and the reference electrode is saturated calomel electrode, and the auxiliary electrode is platinum electrode, and the working electrode is A3 steel. In order to avoid corrosion of the electrode gap, white glue is used to coat the edge of the seam, and the actual area is 0.25 cm^2. Before determination, the working electrodes were polished with 240 mesh, 360 mesh, 600 mesh, 800 mesh, 1000 mesh and 1500 mesh sandpaper until bright. The working electrodes were cleaned with water, ethanol and acetone and dried by cold air. When the open-circuit potential stabilizes, the polarization curve scanning begins. The measurement range is -0.2V-0.2V vs OCP, and the potential scanning speed is 0.5mv/s.

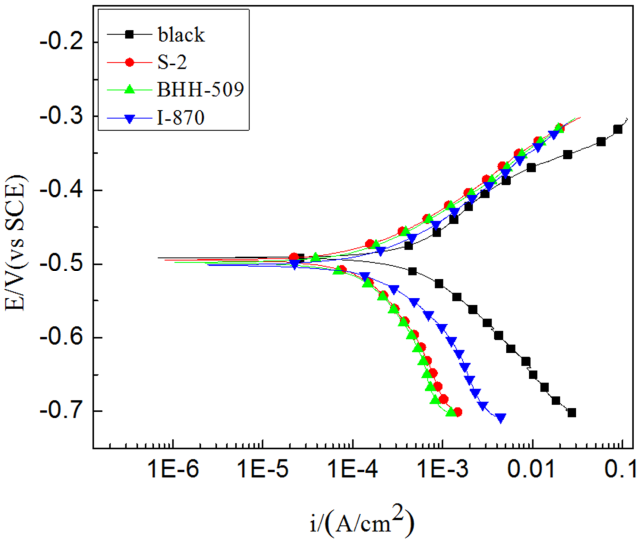

Figure 1. *The polarization curve of steel in 3%NaCl solution.*

It can be seen from Figure 1, compared with the blank polarization curve, after corrosion inhibitors were injected, the self-corrosion potential moves slightly to the negative direction, while the polarization curve moves obviously to the direction of small current, and the relative change of the anodic polarization curve is small. Therefore, the three inhibitors mainly inhibit the cathodic process, so it can be judged that in the simulated seawater solution, they are mainly used as the cathodic type inhibitors. It can be seen from Table 9, among these three corrosion inhibitors, when BHH-509 is added, the self-corrosion current density decreases most obviously, and the corrosion inhibition rate is higher, followed by S-2, which are obviously better than I-870.

Table 9. *The corrosion rate fitting from polarization curve.*

corrosion inhibitors	Ec/(mV)	Ic (mA·cm^{-2})	IE/%
blank	-492.06	0.5651	--
S-2	-495.45	0.1689	70.11
BHH-509	-497.69	0.1376	75.65
I-870	-501.88	0.2632	53.42

4. Conclusion

(1) Quaternary ammonium cationic fungicides were evaluated by extinction dilution method, and the concentration of YHZWJ-15 was 0.5%.

(2) Organic polyphosphonates have good anti-scaling effect, good chemical stability, basically not destroyed by acid and alkali, and are not easy to hydrolyze and degrade. They can withstand high temperature, and have a certain anti-scaling effect at the same time. The concentration of BHF-701A was 0.01%.

(3) A seawater corrosion inhibitor BHH-509 has been developed, which can resist mineralization up to 30,000 mg/L with a dosage of 0.5%. It consists mainly of gluconate, organic amines, zinc salts and copolymers of organic phosphonic acid. On the one hand, it can inhibit and disperse the formation of calcium carbonate scale in seawater, on the other hand, it can effectively control the calcium phosphate scale caused by the agent itself.

(4) A set of stable seawater-based annulus protection fluid has been successfully developed. The ratio of which is seawater + 0.5% YHZWJ-15 + 0.01% BHF-701A + 0.01% thiourea + 0.5% BHH-509, and it can reduce the corrosion rate to 0.0051 mm/a and the corrosion inhibition rate can reach more than 95%.

References

[1] LIU Qingyun, GAO Feng, LUO Yue, et al. The development of well annulus protection technology [J]. Henan Chemical Industry, 2010, 27 (10): 12-14.

[2] LI Xiaolan, LI Ling, ZHAO Yonggang, et al. The research and application of casing annulus protection fluid [J]. Drilling fluid and completion fluid, 2010, 27 (6): 61-64.

[3] WANG Zhongguang, SUN Jixing. The research report of water-based annulus protection fluid [R], CNOOC Energy Technology & Services-Oilfield Technology Services Co., 2012. 11.

[4] ZHENG Lihui, ZHANG Jinbo, YANG Hu. Study and application on new annular protecting fluid corrosion [J]. Oil Drilling &Production Technology, 2004, 26 (2): 13-16.

[5] SY/T 5273 -2000 Evaluation method for behavior of corrosion inhibitor for produced water of oilfield [S].

[6] SY/T 5673 -1993 Evaluation method for behavior of scale inhibitor of oilfield [S].

[7] SY/T 5890 -1993 Evaluation method for behavior of bactericide of oilfield [S].

[8] SONG Zhaohui, LI Zhoujun, XUE Yuzhi. Study and Application of Clay-free Salt Annular Protective Fluid [J]. Drilling Fluid & Completion Fluid, 2013, 30 (4): 49-51.

[9] LUO Yanan. The marine erosion-corrosion electrochemical detections of metallic materials [D]. Tian Jin: Tianjin University, 2006.

[10] WU Junwen, JIA Wenfeng, LEI Qun et al. Research and Performance Evaluation of Annulus Protection Fluid for Injection and Production Well of Gas Storage [J]. Oilfield Chemistry, 2017, 34 (2): 329-334.

[11] YU Lanlan, ZHENG Kai, LI Yan. Synthesis and Performance Evaluation of Silica Scale Inhibitou ACAA [J]. Oilfield Chemistry, 2017, 34 (4): 694-698.

[12] GUO Xuehui, WANG Dong, ZHAO Yi, et al. Study on seawater corrosion inhibitors [J]. Liaoning Chemical Industry, 2012, 41 (1): 15-17.

[13] LU Yuan, ZHAO Jingmao, ZHANG Mao, et al. Development of CO_2/H_2S Corrosion Inhibitors in the Mixed Water Injection System of Offshore Oilfield in the Bohai Sea [J]. Surface Technology, 2018, 47 (10): 59-65.

[14] MU Zhenjun, DU Min. The study of inhibitive mechanism of corrosion inhibitors for carbon steel in natural seawater [J]. Journal of Chinese society for corrosion and protection, 2005, 25 (4): 205-208.

[15] ZHAO Xiangyang, MENG Yingfeng, HOU Xutian et al. Corrosivity analysis of tubing-casing environment and optimization of packer fluids for Y oilfield [J]. Corrosion Science and Protection Technology, 2017, 29 (1): 91-96.