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Study on Stress Corrosion Characteristics of Different Grade H Sucker Rods

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In order to obtain the stress corrosion resistance of the different grade H ultra-high-strength sucker rods in high water-bearing fluids and their adaptability to typical well fluids, this paper takes orthogonal stress corrosion test method to research the stress corrosion cracking properties of 30Ni2CrMnMoVA and 30CrMoA under different corrosion conditions, including Cl^-, HCO_3^-, Ca^{2+} and Cl^--HCO_3^- based on the corresponding provisions of NACE TM 0177 and GB/T15970.1. In this paper, the stress corrosion susceptibility of 30Ni2CrMnMoVA and 30CrMoA materials in different corrosion conditions were investigated and the typical working conditions of different grade H sucker rods are clarified to provide the basis for selection and string design of grade H sucker rods.

1. Introduction

With the oilfield development in depth, the original pressure of the oil well and the liquid production capability, the producing fluid level and the pump setting depth has decreased continuously. In order to increase the production, water-flood development and great power pumping are often applied in oilfield. The load of sucker rod string has increased dramatically no matter by depth-pumping with small pump or great power pumping. In addition, formation water reinjection makes concentration of Na^+, Cl^-, HCO_3^-, Ca^{2+} , Mg^{2+}, etc increase greatly that exacerbated stress corrosion of sucker rod (Cao et al., 2008; Song et al., 2009; Liu et al., 2013). The fatigue life of sucker rod decreases sharply under the comprehensive action of large load and strong corrosive well fluid and stress corrosion is the main cause of the sucker rod string failure. Grade H sucker rod with ultra-high tensile strength that could reduce string load effectively gains popularity in oilfield. Grade H sucker rod is classified into three types: anti-corrosion type(HK), material rod(HL) and technical type(HY).
This paper took orthogonal stress corrosion test method on the basis of NACE TM 0177 and GB/T15970.1 to study the stress corrosion characteristics of two types sucker rods 30Ni2CrMnMoVA and 30CrMoA in different corrosion circumstances containing Cl^-, HCO_3^-, Ca^{2+} and Cl^--HCO_3^- and to acquire the stress corrosion susceptibility of two kind of rods in different corrosive solution with typical mediums. According to the comparative analysis of the reasons why different grade H sucker rods own great fatigue life discrepancy in high water cut condition, the suitability of different grade H rods for typical well fluid is presented in this paper. Therefore, this paper provides the theory basis for design of grade H sucker rod string.

2. Experimental design

2.1 Experimental methods

This paper take orthogonal experiment thought to conduct axial constant stress corrosion experiments among 30Ni2CrMnMoVA and 30CrMoA sucker rods on the basis of actual stress condition by the CORTEST stress ring test system. The ductility loss (elongation loss) and absorbed energy loss were used to measure the stress corrosion susceptibility of two types of grade H sucker rods in different corrosion mediums. The stress

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corrosion characters and the suitability of two rods in typical corrosive well fluid were acquired according to single factor experiments (Qu et al., 2015l; Zhu et al., 2008; Das, 2014; Liu et al., 2014; Shi et al., 2009; Zhang, 2011).

2.2 Materials and sample preparation

The chemical composition of the steel used for the making of the grade H sucker rods are listed in Table 1. Tests were performed on the samples depending on the criterion of NACE TM 0177.

Table 1: The chemical composition of two types of grade H sucker rods /%

Steel	C	Mn	P	S	Si	Cr	Mo	Ni	V
30Ni2CrMnMoVA	0.3~0.36	0.40~0.60	≤0.015	≤0.010	0.15~0.35	0.90~1.20	0.4~0.50	2.75~3.00	0.05~0.1
30CrMoA	0.26~0.34	0.4~0.7	≤0.025	≤0.025	0.17~0.37	0.80~1.10	0.15~0.25	≤0.30	

2.3 Corrosion solution and experimental procedure

After analyzing the water quality of 3962 Wells in Shengli oilfield, the well fluid mainly contains Cl^-, HCO_3^-, Ca^{2+}, Mg^{2+}, Na^+ and K^+ and the wells containing a lot of SO_4^{2-} and CO_3^{2-} accounted for less than 15%. Among them, the wells with concentration of Cl^- more than 20000 mg/L is only 2.46% and the Cl- in most wells distributed between 0 ~ 20000 mg/L. The wells with concentration of HCO_3^-800mg/L accounted for 6.5% and the HCO_3^- distributed between 0 ~ 800mg/L in most wells. The concentration of Ca^{2+} and Mg^{2+} is almost ranging from 0 to 800mg/L and few is more than 800mg/L in all wells. By literature, the corrosion mechanism of Ca^{2+} and Mg^{2+} to rod string is similar, they can react with CO_2 or high concentration of HCO_3^- in oil and gas wells to produce $CaCO_3$ and $MgCO_3$ that can scale in the rod surface. Na^+ and K^+ can't influence the corrosion of sucker rod. According to water quality analysis and the mechanism of various corrosion mediums, corrosive medium in stress corrosion test solution were identified as Cl^-, HCO_3^- and Ca^{2+}.Three kinds of corrosive medium Cl^- HCO_3^- and Ca^{2+} were selected in corrosion experiment based on the analysis results of water quality of Shengli oilfield and the research purpose of stress corrosion experiments. The experiments aim to research the stress corrosion resistance of two kinds of grade H sucker rod 30Ni2CrMnMoVA and 30CrMoA. Stress corrosion experiment has the trait of multiple factors and levels. So in order to reduce test number to acquire the stress corrosion sensitivity and their suitable conditions of the two materials, three factors and three levels orthogonal stress corrosion experiment ($L_9(3^3)$) was designed for the characteristic research of two materials. The experiment scheme is shown in Table 2.

Table 2: The orthogonal experiment scheme of two materials

Test number	ρ (Cl^-)/mg/L	ρ(HCO_3^-)/mg/L	ρ(Ca^{2+})/mg/L
1	1000	0	200
2	1000	250	400
3	1000	500	600
4	10000	0	400
5	10000	250	600
6	10000	500	200
7	20000	0	600
8	20000	250	200
9	20000	500	400
Notes: Do the orthogonal test on 30Ni2CrMnMoVA and 30CrMoA respectively; Test tensile stress $\sigma=70\%\sigma_b$			

Table 3: The single factor experiment scheme of two materials

Test number	ρ(Cl^-)/mg/L	ρ(HCO_3^-)/mg/L
1	1000	0
2	5000	0
3	10000	0
4	15000	0
5	20000	0
6	10000	200
7	10000	300
8	10000	400
9	10000	500
10	10000	600
Material: 30Ni2CrMnMoVA and 30CrMoA; Test tensile stress $\sigma=70\%\sigma_b$		

The orthogonal stress corrosion experiments are oriented toward qualitative analysis for the resistance ability of materials to typical corrosive mediums but can’t present the stress corrosion rule to single medium. Single factor experiments were designed to further gain the stress corrosion peculiarity of 30Ni2CrMnMoVA and 30CrMoA in the corrosive solution with different medium density of Cl- and HCO3-. Experiment scheme is shown in Table 3.
According to the NACE TM 0177 standard, the tensile stress of stress corrosion test applied by the stress ring is fixed at 70% σb that should be in the elastic range of rod material and stress corrosion time sustains 20 days. The samples used after stress corrosion test would be pulled off by WDML-10 tensile testing machine.

2.4 Evaluation indexes of stress corrosion susceptibility

Grade H sucker rods 30Ni2CrMnMoVA and 30CrMoA are plastic material and their deformation properties and plasticity would change after the stress corrosion for a certain time. This paper takes ductility loss (elongation loss) Iδ and absorbed energy loss IW that calculated by the area under the stress-strain curve to evaluate the stress corrosion susceptibility.

3. Result analysis

3.1 The result of orthogonal experiments

The rod samples of 30Ni2CrMnMoVA and 30CrMoA were all not pulled off in nine kinds of solution after 20 days. The result of orthogonal experiments is shown in table 4.

Table 4: The result of orthogonal experiments

Test number		$\rho(Cl^-)$/mg/L	$\rho(HCO_3^-)$/mg/L	$\rho(Ca^{2+})$ /mg/L	I_δ/% 30Ni2CrMnMoVA	I_δ/% 30CrMoA
1		1000	0	200	7.62	3.31
2		1000	250	400	15.51	4.12
3		1000	500	600	13.78	6.46
4		10000	0	400	20.14	7.16
5		10000	250	600	19.22	6.22
6		10000	500	200	14.81	4.31
7		20000	0	600	29.82	11.55
8		20000	250	200	21.37	7.98
9		20000	500	400	16.32	5.87
30Ni2CrMnMoVA	T1	12.303	19.193	14.6		
	T2	18.057	18.7	17.323		
	T3	22.503	14.97	20.94		
	R	10.2	4.223	6.34		
30CrMoA	T1	4.630	7.340	5.200		
	T2	5.897	6.107	5.717		
	T3	8.467	5.547	8.077		
	R	3.837	1.793	2.877		

Table 4 shows T3>T2>T1 in the $\rho(Cl^-)$ and $\rho(Ca^{2+})$ influence column of 30Ni2CrMnMoVA and 30CrMoA. Therefore, high concentration of Cl^- and Ca^{2+} accelerated stress corrosion within the test solution concentration scope, the susceptibility of both 30Ni2CrMnMoVA and 30CrMoA to Cl^- and Ca^{2+} is $\beta(Cl^-)>\beta(Ca^{2+})$. In the $\rho(HCO_3^-)$ influence column of two materials the levels result is T1>T2>T3 that reflected a certain concentration of HCO_3^- can suppress stress corrosion when HCO_3^-, Ca^{2+} and Cl^- coexist. The susceptibility of two materials is both significant in the corrosive solution with Cl^- reflected from the R range column for the three kinds of typical corrosive mediums. The results of orthogonal experiments can be concluded that 30Ni2CrMnMoVA is more sensitive to three typical mediums than 30CrMoA in stress corrosion experiments and 30CrMoA owns better resistance to the experimental mediums.

3.2 The result of single factor experiments

The rod samples of 30Ni2CrMnMoVA and 30CrMoA were all not pulled off in ten kinds of corrosive solution after 20 days.
(1) Analysis of experiment procedure
The photos shown On Figure 1-3 are the corrosion situation of 30Ni2CrMnMoVA and 30CrMoA respectively after 3 days, 10 days and 20 days.

Figure 1: Photos of stress corrosion after 3 days

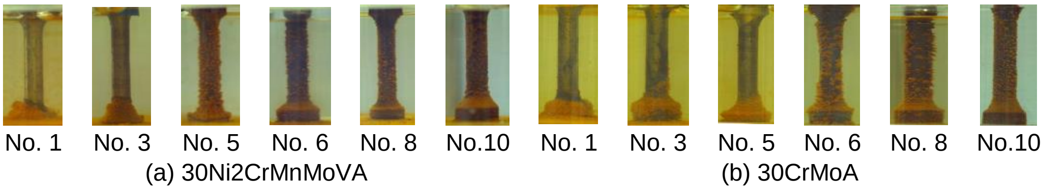

Figure 2: Photos of stress corrosion after 10 days

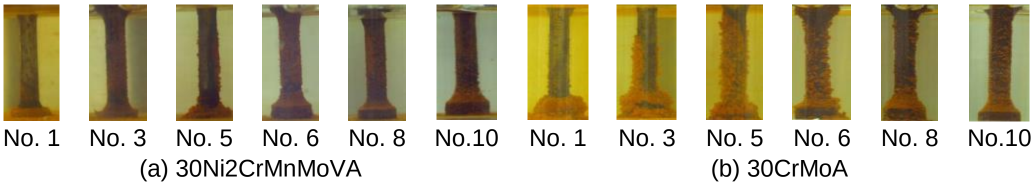

Figure 3: Photos of stress corrosion after 20 days

As shown on Figure1-3 (a)(b) from No.1 to No.5, the relationship between initial corrosion velocity of samples and the concentration of Cl^- is smaller in the environment with Cl^- and the corrosion velocity of two materials. Only a small amount of yellowish powder corrosive substance was produced and surface of rod samples were all smooth. But with the increase of corrosion time, Cl^- ions would penetrate the passive film on the surface of rod samples that results in serious local corrosion and high corrosive rate. The surface color of the samples continued to darken and lost the metallic luster, the surface after stress corrosion is shown in Figure 4. After the Cl^- penetrate through the sample surface, the higher the concentration of Cl^-, the greater the local corrosion rate. The Figure 1-3 (a) (b) from No.6 to No.10 show that the initial corrosion is faster and more obvious and the corrosion product is yellow-brown granular $FeCO_3$ in the alkaline environment containing HCO_3^- ion. With the time passage, the variation of corrosion degree is not obvious and the corrosion rate becomes slower than initiation. As shown on Figure 5, the corrosion rate of rod samples remains slow velocity and the surface presents uniform corrosion after 10 days. From the comparison of Figure 1-3 (a) (b), 30CrMoA owns more corrosion products than 30Ni2CrMnMoVA regardless of separate Cl^- ion or combination of Cl^- and HCO_3^- in the solution under the same conditions that reflects the resistance of 30CrMoA to static stress corrosion is poor.

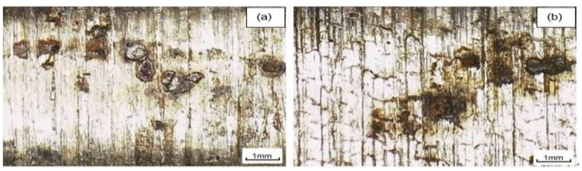

Figure 4: Localized corrosion surface of 30Ni2CrMnMoVA in the solution only with Cl^-

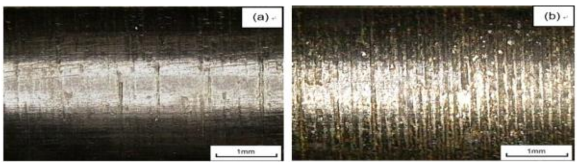

Figure 5: Surface of uniform corrosion

(2) Results and analysis of tensile test

The rod samples were dismantled and cleaned from stress rings after stress corrosion experiments. Then, they were pulled off and the stress-strain curves were acquired by the WDML-10 slow velocity tensile testing machine. Results are presented on Figure 6.

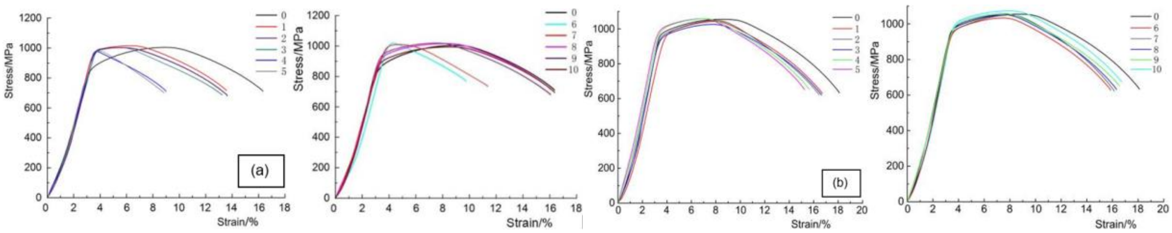

Figure 6: Strain curves of sucker rods after stress corrosion (a) 30Ni2CrMnMoVA; (b) 30CrMoA

$0^{\#}$ curve in Figure 6. is stress-strain curve of the specimen pulled off in air at room temperature. As seen in Figure 6(a) when 30Ni2CrMnMoVA experienced stress corrosion experiments, its elastic deformation zone extended and plastic deformation area shortened. The pull time and ductility decreased obviously after stress corrosion in the same pull velocity compared to $0^{\#}$ curve. Figure 6 (b) shows that in the solutions coexisting different concentration of HCO_3^- and constant concentration of Cl^- the plastic deformation area increased along with the increase of the concentration of HCO3$^-$. When the concentration of HCO_3^- is lower than 300mg/L, the plastic deformation area is small because of that the inhibition of HCO_3^- to Cl^- is weak. When the concentration of HCO_3^- is higher than 500mg/L, the plastic deformation area of $8^{\#}$, $9^{\#}$, $10^{\#}$ is similar to $0^{\#}$ curve that the inhibition of HCO_3^- to Cl^- is obvious. According to literature (Song et al., 2009), when 30Ni2CrMnMoVA samples are placed in the corrosive solutions, the Cl^- ion would intrude into the defect on the surface of the 30Ni2CrMnMoVA specimen. The combination of O_2 and Cl^- contributes to the rapid dissolution of Fe and the augment of acidic localized corrosion in the defect crack. As a consequence, chloride ions aggravate the stress corrosion. When Cl^- and HCO_3^- coexist, the hydrolysis of HCO_3^- enhances the pH value of the solution that neutralize the H^+ in the corrosion solution, so as to inhibit the surface corrosion of the samples. Figure 6(b) shows that the elastic deformation area of 30CrMoA samples were almost similar but the plastic deformation area changed obviously both in the solutions with separate Cl^- or combination of HCO_3^- and Cl^-. Along with the increase of $\rho(Cl^-)$, plastic deformation area of 30CrMoA narrowed and ductility loss increased.

The ductility loss of two kinds of rod samples in different corrosion conditions is shown in Figure 7(a), Figure 8(a) and the absorbed energy loss is shown in Figure 7(b), Figure 8(b).

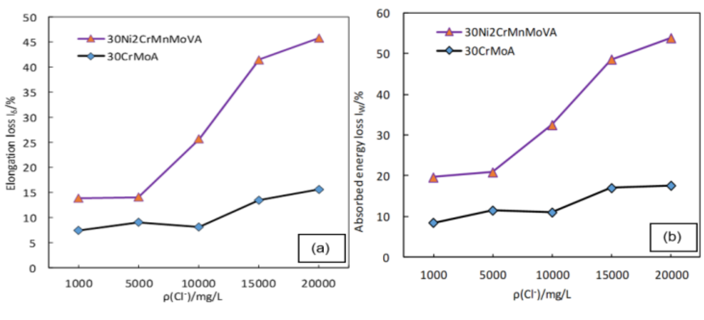

Figure 7: Stress corrosion susceptibility of the material at different ρ (Cl^-) (a)Elongation loss; (b)Absorbed energy loss

From Figure 7, the ductility loss characters of two kinds of rods is the same as the absorbed energy loss. Figure 7 showed that with the concentration increase of Cl^-, the ductility loss and absorbed energy loss of 30Ni2CrMnMoVA samples increased more rapidly than 30CrMoA after the stress corrosion experiments with different concentration of Cl^-. When the concentration of Cl^- was lower than 10000mg/L the ductility loss and absorbing energy were relatively small. When the concentration of Cl^- reaches 20000mg/L the ductility loss increased rapidly and then tended to be stable.

4. Conclusion

Through investigation and analysis of the water quality of Shengli oilfield well, the main corrosive media are Cl^-, HCO_3^-, Ca^{2+} and Mg^{2+} in well fluid. On the basis of this, the $L_9(3^3)$ orthogonal test and the single factor encryption test were designed based on the purpose of implementing stress corrosion research on two kinds of grade H sucker rods. According to the analysis of experimental results, the following conclusions could be obtained:

(1) According to the orthogonal experiment, the stress corrosive susceptibilities of 30Ni2CrMnMoVA and 30CrMoA were all highest in the environment with Cl^-, and the susceptibility to Cl^- and Ca^{2+} was $\beta(Cl^-)>\beta(Ca^{2+})$.

(2) In the presence of HCO_3^- and Cl^-, the hydrolysis of HCO_3^- can inhibit stress corrosion of 30Ni2CrMnMoVA sucker rods to Cl^- at 300mg/L. With Ca^{2+}, HCO_3^- can also inhibits the stress corrosion of the 30Ni2CrMnMoVA rod.

(3) With the increase of the concentration of Cl^-, the stress corrosion susceptibility of 30Ni2CrMnMoVA increased sharply. In the condition of high Cl^- concentration, the corrosion of 30Ni2CrMnMoVA sucker rod was pitting and local corrosion. However, the material surface appeared uniform corrosion in the alkaline environment containing HCO_3^-. The resistance of 30Ni2CrMnMoVA to stress corrosion is poor and 30CMoA has better property to resistant stress corrosion.

(4) 30Ni2CrMnMoVA sucker rod was not suitable for the conditions with high Cl^- concentration, but suitable for the environment with the co-exist of HCO_3^-, Cl^- and other corrosive media under strong alkaline conditions. 30CrMoA had more extensive scope of application. In the oil field during medium and high water cut the wells with high concentration of Cl^- accounted for a large proportion, therefore, it was significant to reconsider the extension of 30Ni2CrMnMoVA sucker rod.

(5) It can be seen from the experiment that the HL rod had better stress corrosion resistance than the HY sucker rod, and the HL sucker rod was preferred in the design of the high strength sucker rods.

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