The corrosion influencing factors and its mechanism of N80 carbon steel in NaCl-NaHCO$_3$ solution

Gang Xie, Juan Xie, Haijun Yan, Qingzhen Du, Shuangyan Zhang,

Wei Zhang, Zhonghai Qin, Li Han, Wei Meng

Petroleum Production Engineering Research Institute of Huabei Oilfield Company

Renqiu Hebei, P R of China

Abstract—The N80 steel corrosion behavior of the produced water in Huabei oil field on behalf of NaCl/ NaHCO$_3$ solution were studied by the corrosion weight loss method，and the fitted chart board involved salinity and anion content was built based on the least squares principle. Results show that influenced by Cl$^-$ and HCO$_3^-$ control the corrosion curve involves three parts: passivating area，activated area and high corrosion area. The corrosion behavior shows that the area when Cl$^-$% content in 16.7~37.5% was HCO$_3^-$ passivating control；in 37.05 ~ 90.9% was HCO$_3^-$ and Cl$^-$ coordinated control；in 90.9 ~ 100% belong to Cl$^-$ perforation control. The fitted chart board considered water salinity and anion content could determine whether the corrosion occur or not，thus may provide theoretical foundation and guidance for the next support design of anticorrosion measures with carbon steel.

Keyword— Cl$^-$/ HCO$_3^-$ system; N80 carbon steel; corrosion behavior; chart board

1. INTRODUCTION

For the oil well formation water is an essential part in produced fluid, of which the corrosive medium consist high concentration of chloride ion，HCO3-，CO2，dissolved oxygen and other gases. The mild steel characteristics of polarization curve and surface oxides at various NaHCO3 solution were both studied，thus often lead to severe pitting behavior particularly in solutions contain high concentration of HCO$_3^-$, Cl$^-$ and Ca^{2+} （Jing-mao Zhao et al.[1]；Mao et al.[2]）. The typical water type of formation water and injected water in Huabei Oilfield are CaCl$_2$ by high salinity and NaHCO$_3$ as surface water[3]. With the waterflooding development due to the mix by injected water, formation water have been gradually diluted，and the properties of produced fluid would change to some degree，such as decrease of HCO$_3^-$ but rising Cl$^-$[4]. For example according to statistics，since development the mole ratio Cl$^-$/HCO$_3^-$ in produced fluid of some typical wells have dropped from the original 60~70 to 10~20 currently.

N80 steel pipe has been widely used in the oil and gas industry which accounted for over 50% of the total casing. Due to varieties of corrosive medium in produced fluid，the surface of N80 steel often suffered serious corrosion represented by casing damage and corrosion perforation，and such accidents that seriously affect the economic benefits of oil field. Therefore it is important to study local corrosion rules with influencing factors in NaCl/NaHCO$_3$ system，thus provide effective technical way and steps for further corrosion control and safety production in oil fields.

2. EXPERIMENTAL

2.1 Material and solution

The commercial carbon steel N80 was provided by Baoshan Iron & steel Co. Ltd, with compositions as listed in Table I. The test couples were machined to a size of 50mm×25mm×3mm. Prior to the experiments the surfaces of the specimens were ground with silicon carbide (SiC) papers progressively up to 600 grit rinsed with distilled water and then degreased in acetone. After drying in hot air the specimens were weighed (precision 0.1 mg) and then stored in a desicator for use.

All corrosion experiments were carried out in a high temperature and high pressure autoclave(OFITE company, USA). The corrosion medium was NaCl and NaHCO$_3$ solution as simulating the formation water in oil field. The test conditions are shown in Table II chosen by produced water analysis in huabei oilfield. Prior to the experiments，the solution was purged with purified N$_2$ to deoxidize for 2 h and then introduced into the autoclave.

TABLE I   CHEMICAL COMPOSITIONS OF N80 CARBON STEEL （WT%）

Steel elements	C	Si	Mn	P	S	Cr	Mo	Ni	Cu
Contents	0.24	0.22	1.1	0.103	0.004	0.036	0.021	0.028	0.019

TABLE II   TEST CONDITIONS

Test duration（h）	Temperature（℃）	Pressure（MPa）	Total salinity（g/L）	Cl^-/HCO_3^-（mole ratio）
72	70	Normal	10~100	10~50：1

2.2 Weight loss tests

According to industrial criterion "water corrosion test method"(China SY/T 00210-1999), the corrosion rate was measured by static corrosion weight-loss methods. Weight loss tests were conducted in a 10 L autoclave to investigate corrosion rate in simulated formation water. After the experiments, all specimens were taken out and immediately cleaned by distilled water and acetone. To remove the corrosion product scale, the specimens were bathed in 2% hydrochloric acid (HCl) inhibited with 10 g/L hexamethylenetetramine (urotropine) at room temperature, and then rinsed and dried. After that, the samples were weighed again to obtain the final weight. The weight loss of the specimen was determined and the corrosion rate was calculated by the following equation:

$$V_{corr} = \frac{8.76 \times 10^4 \Delta m}{S \rho t} \qquad (1)$$

Where V_{corr} is the corrosion rate, mm/y ; Δm is the weight loss, g ; S is the surface area of specimen, cm^2 ; ρ is the density of test steels, g/cm^3 ; t is the immersion time, h. The final value of the corrosion rate in this study was averaged from two individual measurements after 72 h corrosion tests.

3. RESULTS AND DISCUSSION

3.1 The influence of Cl^- on corrosion rate

Considered by its smaller radius (ion radius was only 1.81×10^{-10} m), Cl^- anion was easy to penetrate into the protective film which resulted in local corrosion, even in the anode zone high concentration of Cl^- lead to spread of the pitting corrosion, thus early research has shown that Cl^- anion is one of the most influencing factors in carbon steel corrosion[5].
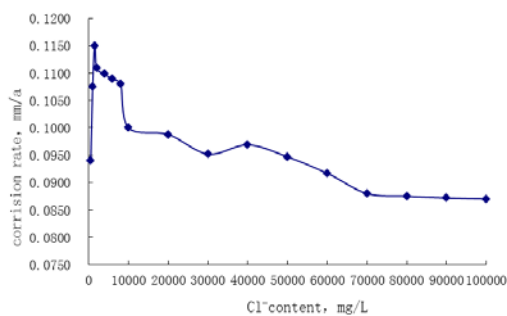

Fig.1 The influence of Cl^- on corrosion rate

Figure 1 showed corrosion rate curve of N80 steel in NaCl solution. It was found that steel surface was black, and after cleaning it become smooth even white without pitting. The corrosion rate was low when Cl^- content was 500 mg/L, but in concentration between 500 ~ 10000 mg/L corrosion rate increased significantly（average reached to 0.1100 mm/a）.Then continued to add NaCl corrosion rate decreased to a certain value. It is worth noting that while salt concentration exceeded to certain range, the solution activity of H^+ cation was increased which drove the metal state turned from passivation state to active state, that is to say the accelerated dissolution rate raised up the anodic corrosion reaction ; when the Cl^- concentration was above 10000 mg/L, due to the decreased solution conductivity and strong anion adsorption the corrosion rate was comparatively reduced as previous study showed excessive Cl^- anion may adsorb on the membrane surface and generate $[FeCl(OH)]^-$.

3.2 The influence of HCO_3^- on corrosion rate
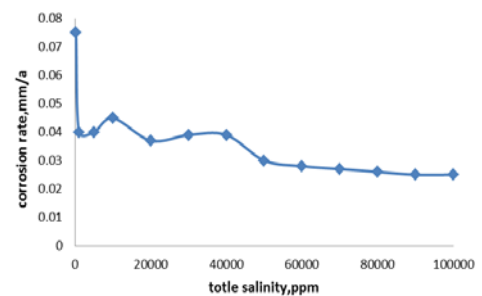

Fig.2   The influence of HCO3- on corrosion rate

As shown in figure 2 the critical concentration of HCO3- lied at 0.02 mol/L. Under that HCO3- anion had a strong corrosive to carbon steel as higher corrosion rate ; when above 0.02 mol/L , corrosion rate dropped by degrees as the passivation film on steel surface was formed. Agreed with the similar reports by Jing-mao Zhao[6], and Z. Xia[7], the H_2O reduction reacted in cathode at low concentration of HCO_3^-, however at high concentration particularly in CO_2 saturated salt solution a solid layer of $Fe(CO_3)_2$ membrane was formed on metal surface, thus had protective effect on carbon steel.

3.3 The influence of Cl^-/HCO_3^- on corrosion rate

(1)Experimental analysis

The properties of corrosion products and corrosion rate were shown in Tab.III and Fig.3. It was found that mole ratio Cl^-/HCO_3^- presented corrosion behavior as follows: (1) when the Cl^- content and salinity lied in 16.7 ~ 90.9% and 10000~100000 mg/L respectively, the corrosion rate was

only 0.033 mm/a, especially among 16.7 ~ 37.5% the generated passivating membrane on steel surface prevented the corrosion reaction because of the protective HCO_3^- anion. Continue to add Cl^- the corrosion rate increased slightly which indicated local activation of the steel was caused and

passivation film was destroyed step by step. (2) when the concentration of Cl^- ion was between 90.9 ~ 100% the corrosion rate grew up exponentially, and mainly corrosion products were $Fe(OH)_2$ at low salinity(10~20g/L).

TABLE III THE PROPERTIES OF CORROSION PRODUCTS

Total salinity(10g/L)	Cl^- content(%)	Carbon Steel description	The properties of corrosion products	Preliminary analysis	The liquid color
1~10	16.7~50	steel surface became black，and had a tight film	few white floccules	$Fe(OH)_2$	faint yellow/green
1~10	50~90.9		none	none	faint yellow
1~2	90.9~100		white floccules	$Fe(OH)_2$	
3~10	90.9~95.2	steel surface became black	few yellow floccules	$Fe(OH)_2/Fe(OH)_3$	colorless
3~10	95.2~99		some black and brown granular	Fe_3O_4、$Fe(OH)_3$、 Fe_2O_3	
3~10	99~100		few yellow floccules	$Fe(OH)_2/Fe(OH)_3$	

With the salinity increased while concentration of Cl^- anion was up to 95.2 ~ 99% the electrochemical corrosion reactions were aggravated with more black or brown granular ferromagnetic precipitation which preliminary analysis were Fe-oxides and $Fe(OH)_3$. As similar to the research by Z. Xia[7] and M. Abdelmoula[8], the pitting corrosion of carbon steel in NaCl solution using X-ray diffraction found that initially the corrosion products was $Fe(HCO_3)_2$ membrane with strong adhesion, by time lasting finally $Fe(HCO_3)_2$ turned into shrinked porous $FeCO_3$ product. The surface which covered by layer of corrosion products could stop the attack by HCO_3^- anion, and contacted with bare area with no corrosion products couple corrosion had happened by pitting. Mao[2] studied anode polarization curve of low carbon steel in solutions involved Cl^- and $NaHCO_3$, the results showed that the shape of the curve varied with the concentration of $NaHCO_3$. Take the solution as 0.005 mol/L $NaHCO_3$+0.00l mol/L NaCl for example, the passivating film was destroyed as small amount of Cl^- anion added in $NaHCO_3$ solution, and the curve display the active dissolution characteristics that passivation couldn't happen.

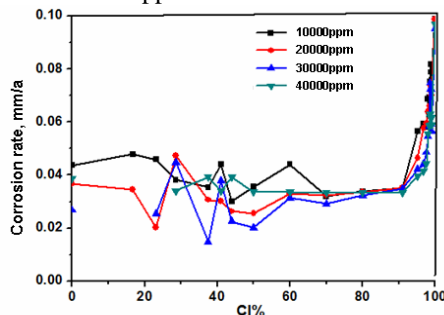

Fig.3 Experimental curve

(2)Data fitting and discussed

On the basis of the least squares principle, the experimental curve can be divided into three parts, namely：(1)the supersaturated zone, (2)the below-concave parabola, (3)exponential increasing part. The fitting curves of corrosion rate and chart board considered by Cl^- content as well as salinity were shown in figure 4.
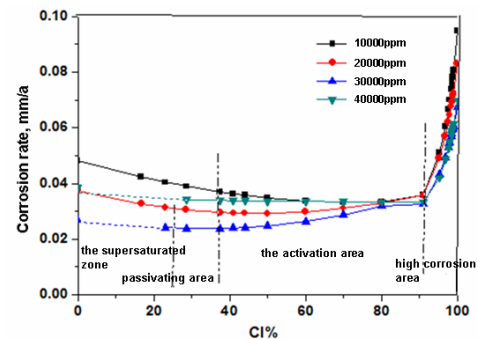

Fig.4 Data fitting curve

Likewise the chart board consist of three parts:(1)passivating area (including the supersaturated zone). When Cl^- content was below 37.5%, the corrosion of the carbon steel was controlled by polarization reaction between HCO_3^- and Fe, and the dense passivating film generated on the surface had prevented the latter corrosion reaction. While salinity was greater than 20000 mg/L and Cl^- content was lower than 23%, the solution was super-saturated state.(2)the activation area. When the Cl^- content was between 37.5% and 90.9%, the results of corrosion rate increased slightly followed by solution color turned faint yellow made it clear that passivating film was partly dissolved by Cl^- and thus the

stage could be called HCO$_3^-$ and Cl$^-$ coordinated control area.(3)high corrosion area. When Cl$^-$ content was higher than 90.9%, perforation corrosion caused by Cl$^-$ ion was the major factor that the passivating film had been serious destroyed, and corrosion rates rose up exponentially which was called Cl$^-$ perforation control area.

Jing-mao Zhao et al. found that after Cl$^-$ joining into NaHCO$_3$ solution passivating film was destroyed as corrosion potential turned negative shift, and local anodic dissolution happened at the active point even corrosion holes appeared on the electrode[5-6]. Due to its strong corrosion the Cl$^-$ anion could easily penetrate into passivating film that resulted in local damage, then the corrosion micro cell which formed between damaged area and passivating zone had created "large cathode small anode" for the accelerated pitting corrosion. Recent study indicated that the damaged Fe(CO$_3$)$_2$ membrane turned to be unstable poor FeCO$_3$ membrane which easily hydrolyzed Fe$_3$O$_4$、Fe$_2$O$_3$ and other iron oxides[9]. In addition the general white corrosion product Fe (OH)$_2$ demonstrated the cathode H$_2$O reduction on metal surface.

3.4 The influence of salinity on corrosion rate

As the salinity increased the corrosion rate of carbon steel declined a bit, but the impact on the corrosion was not consistent. When Cl$^-$% was in 16.7 ~ 90.9%, with the enlargement of salinity and the concentration of charged ions in solution, the increased solution conductivity accelerated the polarization process, however because of the weak FeCO$_3$ passivating film on steel surface by HCO$_3^-$, the higher salinity and stronger polarization reaction, the denser passivating film and lower corrosion rate. When Cl$^-$% was in 90.9 ~ 100%, the decreased solution conductivity and strong adsorption by Cl$^-$ restrained the cathode reaction, and thus reduced the steel corrosion rate, as shown in figure 5 .
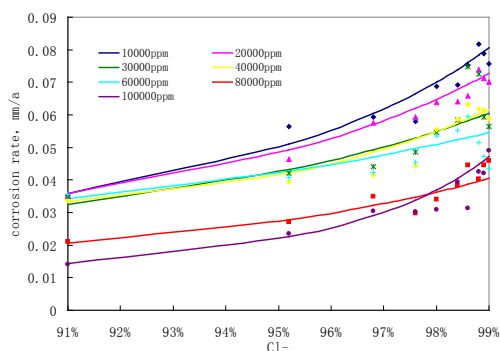

Fig.5　Enlarged drawing of high corrosion area

4. CONCLUSION

(1)The anions Cl$^-$ and HCO$_3^-$ had distinct influences on N80 steel corrosion. For Cl$^-$ the high corrosion area was at the concentration of 500~10000 mg/L , then corrosion rate decreased to a certain value by salt effect ; particularly above

0.02 mol/L HCO$_3^-$ anion play a protective role as the passivating film formed on steel surface.

(2)The corrosion behavior in NaCl/NaHCO$_3$ solution indicated that the Cl$^-$% in region of 16.7 ~ 37.5% was HCO$_3^-$ passivating control area ; in 37.5 ~ 90.9% was both HCO$_3^-$ and Cl$^-$ coordinated control ; in 90.9 ~ 100% was Cl$^-$ perforation corrosion control area.

(3)The fitted chart board contained salinity and anion content could determine whether the corrosion occur or not, thus may provide theoretical foundation and guidance for the next support design of anticorrosion measures with carbon steel.

REFERENCES

[1] Jingmao Zhao，Yu Zuo，Anodic polarization behavior of carbon steel in Na₂CO₃-NaHCO₃ solution ，Journal of Chemical Industry and Engineering[J] ，2005，56（8）:1526-1529；

[2] X. Mao，X. Liu，R. W. Revie，Pitting corrosion of pipeline steel in dilute bicarbonate solution with chloride ions，Corrosion，1994，50（9）:651-657.

[3] Qingzhen Du，Shengli Wang，Wei zhang et al. Application of HZ scale and corrosion inhibitor in Huabei Oilfield，Oil Drilling & Production Technology[J]，2006，28:39-41；

[4] Qingzhen Du，Gang Xie，Meihang Yang et al. The technology research about reason and mechanism of corrosion in Huabei Oilfield，Journal of Southwest Petroleum University（Science & Technology）[J]，2013，35（3）:142-147；

[5] Jingmao Zhao，Mingguang Gu，Yu Zuo，Influencing factors on corrosion of mild steel in carbon dioxide environment，Journal of Beijing University of Chemical Technology，2005，32（5）:71-74.

[6] Jingmao Zhao，Yu Zuo，Anodic polarization behaviors of carbon steel in bicarbonate solution，Electrochemistry，2005，11（1）:27-31.

[7] Xia Z，Chou K C et al.，Pitting corrosion of carbon steel in CO2-containing NaCl brine. Corrosion，1989，45（7）:636-642；

[8] M. Abdelmoula，Ph. Refait，S.H. Drissi et al. Corrosion electron mössbauer spectroscopy and x-ray diffraction studies of the formation of carbonate-containing green rust one by corrosion of metallic iron in NaHCO₃ and (NaHCO₃⁺ NaCl) solutions，1996，38(4):623-633.

[9] Qianlin Wu，Zhonghua Zhang，Xiaoming Dong et al. Corrosion behavior of low-alloy steel containing 1% chromium in CO₂ environments，2013，75:400-408.