CO₂ Corrosion Behaviors of Tubing and Casing Steels in Simulation Produced Water for Deep Natural Gas Wells

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Abstract. The influence of temperature and CO_2 partial pressure on tubing and casing steels widely used in Daqing Oilfield including J55, N80 and P110 steels in simulation water for deep natural gas wells with CO_2 corrosion was studied, using autoclave, Scanning Electron Microscope (SEM), Energy Spectrum Analysis (ESA), X-Ray Diffraction (XRD). The results show that the average corrosion rate of the test steel increases rapidly at first as temperature rises until 60°C, then decreases rapidly as temperature continues to rise; the average corrosion rate increases rapidly as CO_2 partial pressure rises until a peak is reached, then tends to be flat as temperature continues to rise; CO_2 corrosion products are mainly CO_3 and $CaMg(CO_3)_2$.

Introduction

 CO_2 corrosion and protection are one of the hottest issues all over the world^[1,2]. Up to now, many studies have been done to obtain some achievements, including mechanism of the corrosion, analysis of influence factors on the $corrosion^{[3-7]}$. However, the corrosion is influenced by many factors, such as medium conditions, working conditions and so on, so that there are many problems different from one another^[8,9]. Therefore, researchers have studied a lot and many achievements obtained about these problems. As to Daqing, one of the biggest oil and gas fields in the world, there is a large content of CO_2 in natural gas wells in Xushen Gasfield. Since the gasfield was fully developed, the corrosion of downhole tubing and casing have become more and more serious. Through simulation of real working environment in lab experiment, the influence of temperature and CO_2 partial pressure on tubing and casing steels widely used in Daqing Oilfield including J55, N80 and P110 steels in simulation water for deep natural gas wells with CO_2 corrosion was studied and analyzed, using autoclave, Scanning Electron Microscope (SEM), Energy Spectrum Analysis (ESA), X-Ray Diffraction (XRD), the results of which are of certain significance to CO_2 protection on natural gas wells in Xushen Gasfield.

Experiment

Experimental steels used were J55, N80 and P110, respectively. The size of all test specimens were 50mm×10mm×3mm. The contents of microelements of the steels are shown in Table 1. Experimental medium was simulation water, in terms of the produced water from a gas well in Xushen Gasfield, the pH of which was 6.5. The main contents of the simulation water are shown in Table 2.

Table 1 Percentage contents of microelements of the steels

(%)										
Steel	C	Si	Mn	P	S	Cr	Mo	Ni	Al	Cu
J55	0.190	0.226	1.544	0.017	0.015	0.049	0.007	0.026	0.052	-
N80	0.240	0.292	1.090	0.015	0.013	0.220	0.018	0.028	0.033	0.001
P110	0.265	0.310	1.320	0.017	0.008	0.958	0.350	0.042	0.062	0.097

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Table 2 7	l'he main	contents	of the	cimii	lation	water
-1 at $n \cup Z = 1$		COHILDING		2111111	14111111	wall

Ion	HCO ₃ -	Cl ⁻	SO_4^{2-}	Ca ²⁺	$\mathrm{Mg}^{2^{+}}$	Na ⁺
Concentration (mg/L)	1735.5	520.7	10.4	120.2	178.3	721.6

The simulation water solution was made up of analytical NaHCO₃, NaSO₄, NaCl, CaCl₂, MgCl₂ and pure water. HCl solution, the mass fraction concentration of which was 0.1%, was used to adjust pH value of the simulation water solution.

Firstly, N₂ gas had been used to inject into the solution for at least 1 hour. Then, static simulation corrosion experiment was done in autoclave, shown in Fig.1. Next, micro-feature of the test specimens after the experiment in autoclave and micro-feature of those blocks after washed and cleaned were observed, using SEM, shown in Fig.2. Then, corrosion products on the surface of the test specimens after the simulation experiment were analyzed and elemental composition of the corrosion products was given, using ESA. Finally, phase composition of the corrosion products was analyzed and chemical compound of the products was given, using XRD, shown in Fig.3.



Fig. 1 Autoclave



Fig. 2 Scanning Electron Microscope



Fig. 3 X-Ray Diffraction

The experimental period is 72 hours. Parameter combinations of simulation temperature and CO₂ partial pressure are as follows: when CO₂ partial pressure is 5MPa, temperature is 20°C, 40°C, 60°C, 80°C, 100°C; when temperature is 80°C, CO₂ partial pressure is 2MPa, 8MPa, 10MPa, 12MPa.

Results and Discussion

Under the condition of different temperatures, average corrosion rates of J55, N80, P110 test specimens in simulation produced water for deep natural gas wells were compared, shown in Fig. 4.

Under the condition of different CO₂ partial pressure, average corrosion rates of J55, N80, P110 test specimens in simulation produced water for deep natural gas wells were compared, shown in Fig. 5.

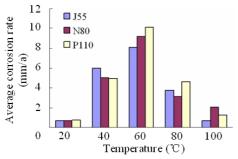


Fig. 4 Comparison of average corrosion rates of the steels under different temperatures

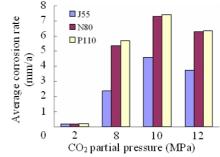


Fig. 5 Comparison of average corrosion rates of the steels under different CO₂ partial pressure

From Fig.4, it can be seen that the influence of temperature on the J55, N80, P110 test specimens is great; the average corrosion rate of the steel starts at 20°C, then increases rapidly at first as temperature rises until 60°C, at which there is a peak, then decreases rapidly as temperature continues to rise.

From Fig.5, it can be seen that the influence of CO₂ partial pressure on the J55, N80, P110 test specimens is great; the average corrosion rate of the steel increases rapidly at first as CO₂ partial pressure rises until 10MPa, at which there is a peak, then tends to be flat as CO₂ partial pressure continues to rise. This phenomenon may be related to solubility of CO₂ in water and protection of corrosion products on the steel. As CO₂ partial pressure increases, concentration of CO₂ in water increases, so that hydrogen depolarization reaction is enhanced, which leads to fast corrosion. But, as CO₂ partial pressure continues to increase, corrosion scale on the surface of the test specimen may protect the steel to some extent, which might counteract what CO₂ partial pressure did to the corrosion of the specimen.

Take J55 steel as an example. When temperature is 80°C and CO₂ partial pressure is 10MPa, its micro-features of pitting corrosion and uniform corrosion in simulation produced water for natural gas wells were obtained, using SEM, shown in Fig. 6.

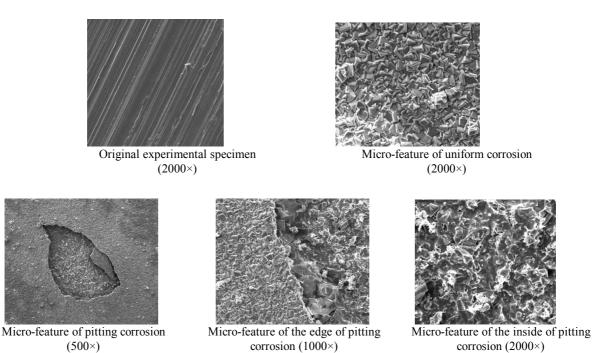


Fig. 6 Micro-feature of uniform and pitting corrosion of J55 steel

From Fig.6, it can be seen that uniform corrosion scale is flat and compact; pitting corrosion scale is loose; pitting corrosion can be aggravated from outside to inside gradually and corrosion perforation is formed eventually; pitting corrosion can be gradually aggravated in side direction, which makes uniform corrosion scale come off, so that new corrosion happens again.

Take P110 steel as an example. When temperature is 80°C and CO₂ partial pressure is 8MPa, results of observation and analysis on corrosion in simulation produced water for natural gas wells were obtained, using ESA, shown in Fig.7, and using XRD, shown in Fig.8, respectively.

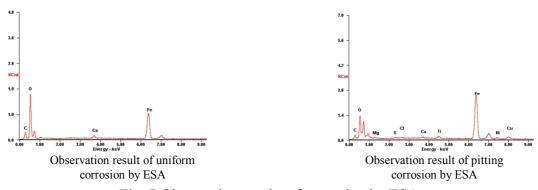


Fig. 7 Observation results of corrosion by ESA

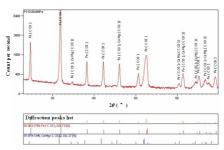


Fig. 8 Analysis results of corrosion by XRD

From Fig.7 and Fig.8, it can be seen corrosion products mainly contain FeCO₃ and CaMg(CO₃)₂. Through semi-quantitative analysis, the corrosion products mentioned above account for 73% and 27%, respectively. In addition, due to some amount of Ca²⁺ and Mg²⁺ in the simulation produced water, which may cause chemical reaction with CO₂ and water, CaMg(CO₃)₂ may be generated and adhere to the surface of the test specimen, which leads to formation of cathode. Then, the difference between the anode, metal specimen, and the cathode may become larger and larger, so that corrosion may be aggravated.

Conclusions

- (1) The influence of temperature on J55, N80 and P110 steels in simulation produced water for natural gas wells is great. The average corrosion rates of the steels increase rapidly at first as temperature rises until 60°C, then decreases rapidly as temperature continues to rise.
- (2) The influence of CO₂ partial pressure on the J55, N80 and P110 steels in simulation produced water for natural gas wells is great. The average corrosion rates of the steels increases rapidly at first as CO₂ partial pressure rises until 10MPa, at which there is a peak, then tends to be flat as CO₂ partial pressure continues to rise.
 - (3) CO₂ corrosion products mainly contain FeCO₃ and CaMg(CO₃)₂.

References

- [1] J. K. Heuer, J. F. Stubbins, An XPS characterization of FeCO₃ films from CO₂ corrosion. J. Corros Sci, 41(7) (1999): 1231-1243.
- [2] J. Li, Study on the corrosion behavior and mechanism of tubular steel in carbon dioxide environment, Beijing USTB Doctor Dissertation, pp.2-10. (2000). (In Chinese)
- [3] J. M. Zhao, M. G. Gu, Y. Zuo, Influencing factors on corrosion of mild steel in carbon dioxide environment, J. Beijing Univ. Chem. Tech., 32(5) (2005):71 -74. (In Chinese)
- [4] C. F. Li, B. Wang, Y. Zhang, Research progress of CO₂ corrosion in oil/gas field exploitation, J. Southwest Petroleum Institute, 26(2) (2004): 42-45. (In Chinese)
- [5] G. F. Lin, Q. Z. Bai, X. W. Zhao, M. S. Zheng, M. X. Lu, Effect of temperature on scales of carbon dioxide corrosion products, Acta. Petrolei. Sin., 25(3) (2004):101 -105. (In Chinese)
- [6] L. P. Wan, Y. F. Meng, F. S. Liang, Carbon dioxide corrosion and its influence factors in oil/gas field exploitation, J. Total Corrosion and Control, 17(2) (2003):14 -17. (In Chinese)
- [7] Q. A. Li, Q. Zhang, J. B. Wen, Z. Q. Bai, Prediction and prevention of CO₂ corrosion of oil tubular goods, J. Corros. Sci. Prot. Tech, 16(6) (2004): 381-384. (In Chinese)
- [8] S. L. Wu, Z. D. Cui, F. He, Characterization of the surface film formed from carbon dioxide corrosion on N80 steel, J. Material Letters, 58(6) (2004): 1076-1081.
- [9] W. H. Ma, X. H. Pei, F. Gao, Corrosion behaviors of N80 Steel in simulated water from deep gas well containing CO₂, J. Chinese Society for Corrosion and Protection, 27(1) (2007): 8-12. (In Chinese)