

Study on Cathodic Protection Parameters of X100 Steel in Three Types of Simulated Soil Solutions

Xinhua Wang*, Cui Wang, Xinghua Tang, Zhenzhen Guo

College of Mechanical Engineering and Applied Electronics Technology, Beijing University of Technology, Beijing, 100124, China

*E-mail: wangxh103@163.com

Received: 18 June 2014 / *Accepted:* 24 September 2014 / *Published:* 28 October 2014

Cathodic protection is usually used to control the corrosion in service pipeline. The optimum cathodic protection potential (OCP) becomes a vital part in order to get the best protective effect in the whole research of cathodic protection. Up to now, depending on experience, the OCP is often defined between 200mV to 300mV more electronegative than the free corrosion potential under usual circumstances (neutral aqueous solution or soil). However, the phenomena of over-protection and under-protection usually occur in service pipeline with the complexity of soil environment. The cathodic protection parameters of X100 pipeline steel in Dagang, Daqing and Lasa simulated soil solutions have been investigated by using the polarization test and electrochemical impedance spectroscopy (EIS). The value of R_t (the charge transfer resistance) by analyzing EIS curves showed that the polarization resistance of the specimen had a maximum value with negative shift of the polarization potential. If the value was negative to $1000 \Omega \cdot \text{cm}^2$, the hydrogen evolution reaction would occur. The potential of hydrogen evolution in the three simulated soil solutions from low to high was Dagang, Daqing and Lasa. This research could offer theoretical guideline and technique support for the cathodic protection of pipeline steel.

Keywords: cathodic protection; OCP; X100; simulated soil solution

1. INTRODUCTION

With the continuously raising demand in energy consumption, extensive attentions have been paid to the more economic and safer transport ways about the supply oil and natural oil [1-2]. With the development of high-strength steel pipelines, the energy industry can receive a significant saving in the total cost of long-distance oil/ gas transmission in view of the much thickness wall and high operating pressure of high-strength steel pipeline [3-8]. The protection of steel pipeline buried in ground seems very significance in the transmission industry, what is more, the insulating coating and cathodic

current methods are usually used to keep the pipelines working normally in the aggressive environment[9]. The external coating can protect the metallic structure against external corrosion effectively; however, the effect of physical protection from external coating will degrade gradually with time. The cathodic protection (CP) system can effectively compensate the loss in physical protection of metal external coating, and CP technology has been widely applied to protect the buried steel pipeline [10-14]. Actually, over-protection or under-protection often appears during the operation of cathodic protection. "Over-protection" can result in the excessive cathodic hydrogen evolution, and it will also improve the susceptibility of hydrogen induced cracking significantly [15-16]. "Under-protection" cannot drop the loss in the protection of metal external coating effectively.

In order to improve the efficiency of cathodic protection and prevent over-protection, some researchers have proposed the OCPP to take the place of the protection potential [17]. The OCPP is just the potential that both the product degree of cathodic protection and efficiency of cathodic protection current have maximum values. Under the condition of OCPP, the degree of cathodic protection and the efficiency of cathodic protection current in the protection system will coordinate with each other in the best way, and the whole system protective efficiency will be the highest. The OCPP is often defined between 200mV to 300mV more electronegative than the free corrosion potential in the field [18] or by the inflection point of polarization curves in laboratory tests. Both results of the two methods are ambiguous. Tsuru, [19-20] a Japanese researcher, has used the electrochemical impedance spectroscopy (EIS) and constant current method to determine the OCPP of carbon steel in water and clean river sand, and the two methods have been used to prove the relationship between the OCPP and the extremum of Faraday impedance.

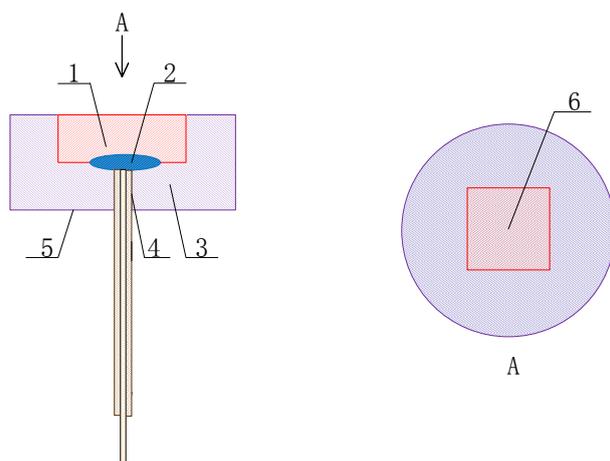
The surface of pipeline used to transport oil or gas mainly buried in soil, which contact with various types of soils directly, so the soil corrosion evidently becomes one important underlying factor to threaten the safe of pipeline. If the buried pipeline is corroded, the leading consequence will be serious, which not only causes great loss of natural resources, but also causes the environmental pollution. Therefore, the problem is needed to solve urgently. Many studies have conducted into the relevant parts of buried pipelines, such as that Zhang Guohu has studied the cathodic protection parameters of X80 pipeline steel by using electrochemical technology [21]. However, there are few studies focusing on the cathodic protection parameters of X100 pipeline steel, one excellently new type of pipeline steel, in different soils. Considering the complexities in soils environment in different districts of China, Dagang soil, Daqing soil, and Lasa soil are selected as typical soils in this work. The study on cathodic protection parameters of X100 pipeline steel in the three soil simulation solutions have greatly useful value and practical significance.

This work is mainly about the cathodic protection parameters of X100 pipeline steel in Dagang, Daqing and Lasa simulated soil solutions. The results of polarization curves and EIS are used to investigate the cathodic polarization behaviors of X100 in the three kinds of soil solutions. The cathodic protection parameters are also obtained. All the results obtained above would offer some theory and technique supports for the cathodic protection system.

2. EXPERIMENTAL SECTION

2.1 Materials

The sample used in this work was X100 pipeline steel. As shown in Fig. 1, the specimens were mounted in epoxy resin after de-rusting and removing oxide scale, and a exposed area about 100 mm² were leaved, which were polished mechanically with finer SiC papers (400, 600, 800, 1000, 1200 grit) successively. All the specimens were degreased with acetone and distilled water and placed in a dryer to reserve after drying in a cold wind.



1-specimen; 2-welding spot; 3-epoxy resin; 4-copper interconnect; 5-plastic; 6-working face

Figure 1. Schematic diagram of the electrochemical test samples

Table 1. Ion contents in the three simulated soil solutions (g/ L)

	NO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	HCO ₃ ³⁻	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺
Dagang	0.188	15.854	2.040	0.181	0.378	0.643	0.225	9.982
Daqing	0.053	0.054	0.098	1.254	0.067	0.006	0.011	0.624
Lasa	0.031	0.052	0.036	0.040	0.034	0.007	0.004	0.019

Table 2. Chemical compositions of the three simulated soil solutions (g/ L)

	pH	CaCl ₂	NaCl	Na ₂ SO ₄	MgSO ₄ .7H ₂ O	KNO ₃	NaHCO ₃
Dagang	8.80	1.049	25.020	0.000	5.227	0.306	0.249
Daqing	9.80	0.084	0.000	0.109	0.061	0.086	1.726
Lasa	7.06	0.081	0.000	0.0118	0.071	0.050	0.055

The experiments were performed in simulated soil solution of Dagang, Daqing and Lasa, which were all important oil-producing areas in China. Soil-simulating solutions were replaced the field soil

to avoid uncertainty caused by impurities and other factors influence. By using analytically pure chemical reagents and deionized water for the preparation of soil solutions, according to the physicochemical properties of the soils in analysis results [22]. Ionic concentration, chemical composition and some other related parameters in Dagang, Daqing, Lasa soils were listed in table 1 and 2. All experiments were carried out at a constant temperature of 25°C.

2.2 Methods

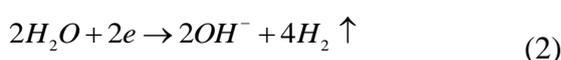
The electrochemical tests were carried out using the three electrode cell assembly. The specimen of X100 pipeline steel, the platinum electrode and the saturated calomel electrode (SCE) were served as the working electrode (WE), the auxiliary electrode and the reference electrode (RE), respectively. The area of the auxiliary electrode was much larger than that of the working electrode, which can make sure that the working electrode exerted a uniform potential field. An electrochemical cell contained about 250 mL test solutions. All potentials were reported against SCE. In order to obtain stable conditions, 10 minutes was set for all the experiments before starting tests.

Polarization curves and the AC impedance spectroscopy (EIS) were recorded by using a PARSTAT 2273 Integrated Test System which was controlled by computer with a power-suit software. The cathodic polarization curves for specimens in the test solutions were recorded at a scan rate of 0.5 mV/ s. The potentiostatic tests with protection voltages from -1200 to -500 mV SCE were carried out in soil-simulating conditions in order to search the OCPP. The testing frequency ranged from 100 KHz to 0.01 Hz and the AC sine excitation signal was 10 mV. The experimental data were evaluated and analyzed by the commercial software “Zsimpwin”.

3. RESULTS AND DISCUSSION

3.1 The polarization tests

The potentiodynamic polarization curves of X100 pipeline steels in Dagang, Daqing, Lasa simulated soil solutions are shown in Fig. 2, Fig. 3 and Fig. 4, respectively. It can be noticed that the shapes of these polarization curves are similar. Further, there are two obvious inflection points in all curves. A is just the point that the cathodic reaction is controlled by oxygen diffusion instead of activation. The reaction is an oxygen reduction reaction, which can be shown by equation (1), prior to point a. Cathodic protection can maintain the cathodic reduction of metal in a stable state by applying a current or potential, to avoid oxidation of the surface or hydrogen corrosion. Cathodic reaction after point b is controlled by the hydrogen depolarization [23-24], which can be shown as equation (2):



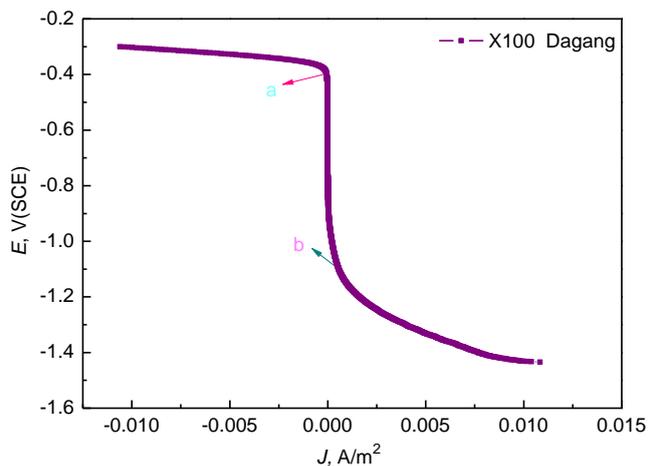


Figure 2. Polarization curve of X100 steel in Dagang simulated soil solution

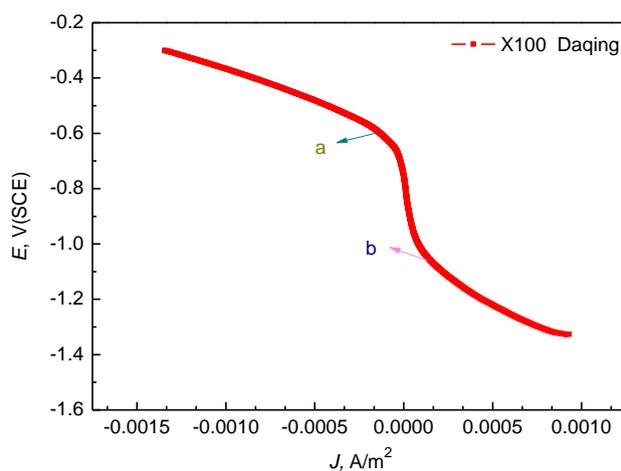


Figure 3. Polarization curve of X100 steel in Daqing simulated soil solution

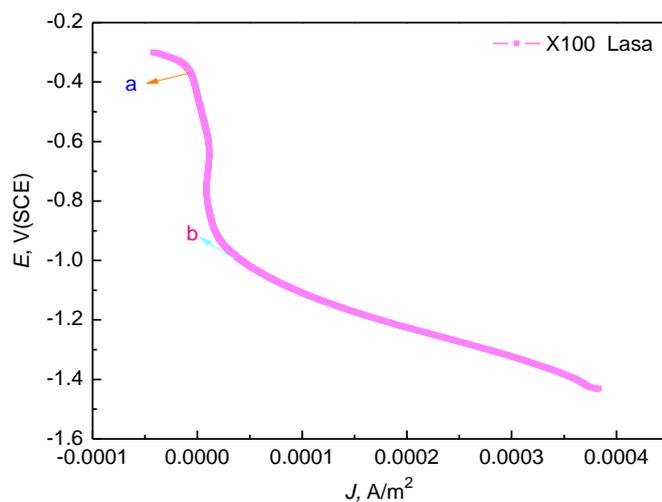


Figure 4. Polarization curve of X100 steel in Lasa simulated soil solution

From the three polarization curves above, it is found that the cathodic current densities tend to increase with the raise of DC electrode potential toward to the negative direction. The current density is relatively stable in the area from point a to point b. If the electrode potential is lower than the potential of point b, the cathode current will increase rapidly, and this phenomenon is attributed to that the hydrogen ion can produce in the reduction reaction and then the hydrogen releases from the surface of sample. Based on the results above, it can be obtained that the OCP of X100 in Dagang soil solution ranges from -380 mV to -1130 mV. The OCP of X100 steel specimen in Daqing simulated soil solution ranges from -600 mV to -1130 mV, while the OCP of X100 pipeline steel specimen in Lasa simulated soil solution ranges from -400 mV to -1100 mV. Polarization tests can give the protection potential range of protection potential, and the accurate value of best potential needs to combine the impedance spectra of cathodic protection parameter to analysis further.

3.2 The EIS tests

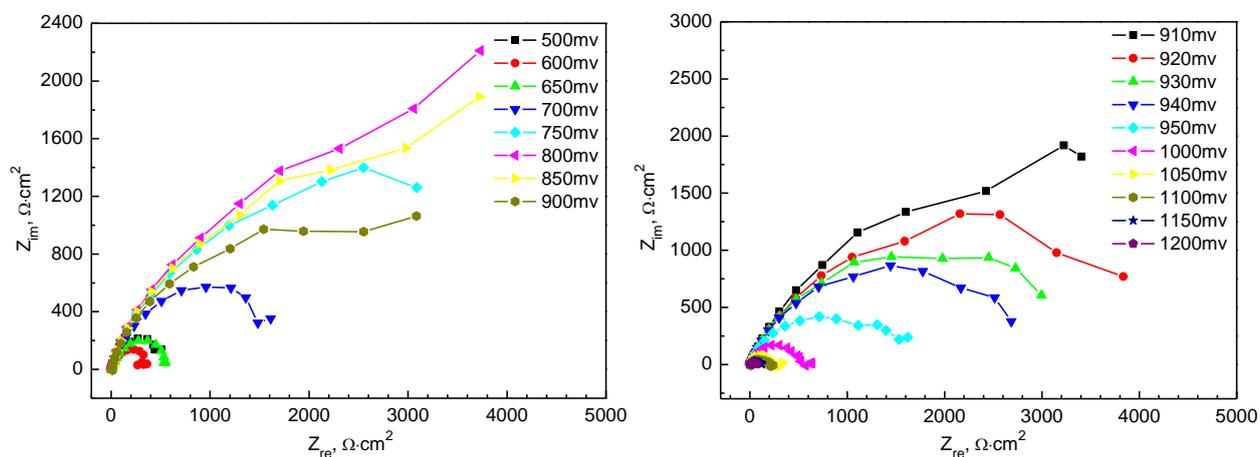


Figure 5. Effect of Nyquist plot of X100 steel at different cathodic polarization voltages for Dagang simulated soil solution

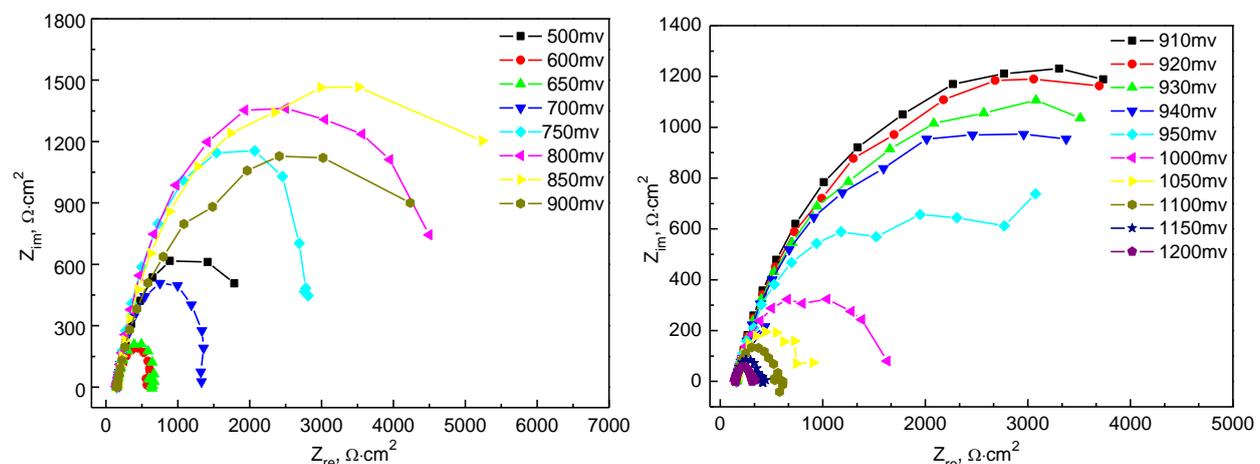


Figure 6. Effect of Nyquist plot of X100 steel at different cathodic polarization voltages for Daqing simulated soil solution

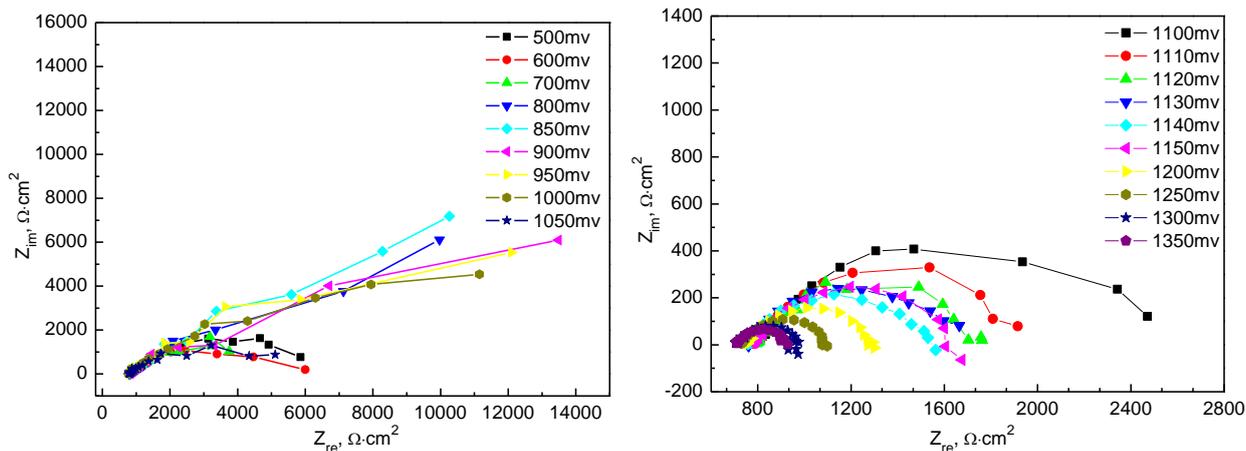


Figure 7. Effect of Nyquist plot of X100 steel at different cathodic polarization voltages for Lasa simulated soil solution

To study the cathodic polarization behaviors of X100 steel in Dagang, Daqing, Lasa simulated soil solutions, EIS measurements have been performed at various cathodic polarization potentials (-1200 mV SCE to -500 mV SCE), as shown in Fig. 5, Fig. 6 and Fig. 7, respectively. The Nyquist plots can be divided into two parts, the high frequency parts, which reflect the information of corrosion products, are similar, while the low frequency parts are quite different, and this implies that there are different electrode reactions. The phenomena show that the corrosion products change lightly at the cathodic polarization potential, while the charge transfer resistance (R_t) shows a regular pattern when the cathodic polarization potential changes [25].

The results of EIS in Dagang, Daqing and Lasa soil solutions with different potential are analyzed by Zsimpwin 3.10 Software, the corresponding equivalent circuits are also proposed in Fig. 8 according to the theoretical analysis [26]. Where, L means inductance and R_s means medium resistance. R_1 stands for the resistance between corrosion products and solution, while R_t stands for the charge transfer resistance. Constant phase element Q is commonly used to replace the capacitance, because it hardly has pure capacitance in real electrochemical processes. Q_1 is the combined capacitance of product and solution and Q_2 is the double layer capacitance. The charge transfer resistance, R_t , is coincident with the Faraday impedance, R_F . The OCPP can be obtained by studying the Faraday impedance characteristics of the steel with impressed current cathodic protection in soil solution.

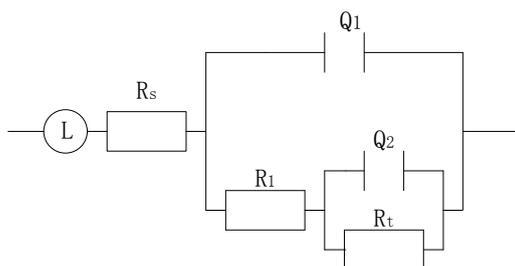


Figure 8. Equivalent circuit of the EIS

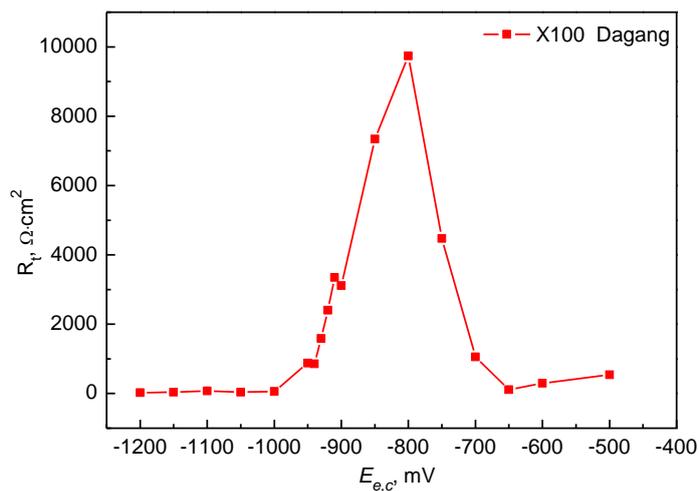


Figure 9. R_t - $E_{e,c}$ curve in Dagang simulated soil solution

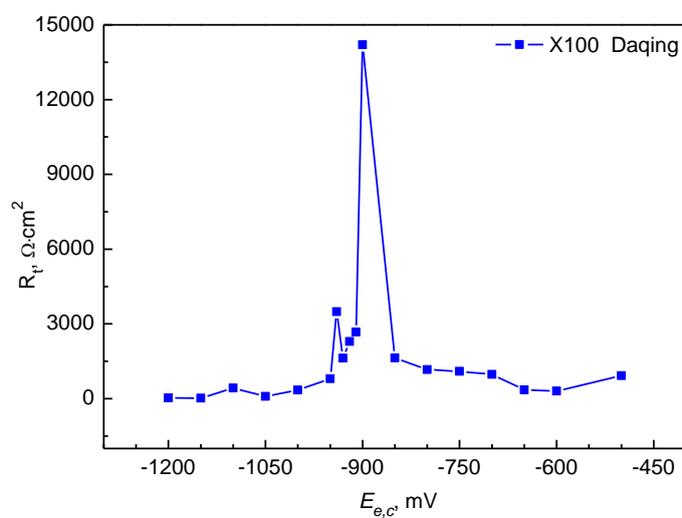


Figure 10. R_t - $E_{e,c}$ curve in Daqing soil solution

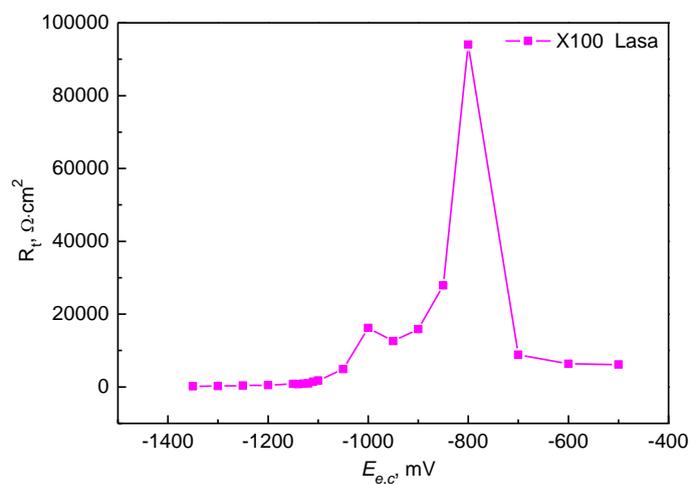


Figure 11. R_t - $E_{e,c}$ curve in Lasa soil solution

The OCPP is approximate equal to the electric potential at the maximum of the Faraday impedance [27], R_F . Based on the results of EIS, the R_t - $E_{e,c}$ curves in Dagang, Daqing and Lasa soil solutions can be shown in Fig. 9, Fig. 10 and Fig. 11, respectively.

At the open circuit potential, there are two reactions, anodic reaction and cathodic reaction. The impedance is the balance result between the anodic and cathodic reactions. According to the electrochemical theory [27], the analytic formula of this case can be shown as following:

$$1/R_t = 1/R_{t,a} + 1/R_{t,c} \tag{3}$$

Where, R_t , $R_{t,a}$ and $R_{t,c}$ stand for the charge transfer resistance of the electrode reaction, the anodic reaction and the cathodic reaction, respectively.

While adding cathodic polarization to the electrodes, the value of $R_{t,a}$ increases with the negative of potential, however, the value of $R_{t,c}$ declines at a slow pace, which is due to the activation of oxygen electrochemical process control. The electrochemical reaction can be represented by the equivalent circuit and shown in Fig. 12. When the electrode potential reaches one specific point of protection potential, the reaction of hydrogen cathodic reduction will occur, besides oxygen cathodic reduction reaction. In this case, the reaction can be represented by the equivalent circuit, shown in Fig. 13. Impedance spectroscopy analytical formula is listed as follows:

$$1/R_{t,c} = 1/R_{t,o} + 1/R_{t,H} \tag{4}$$

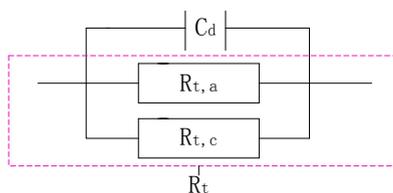


Figure 12. Equivalent circuit at OCP

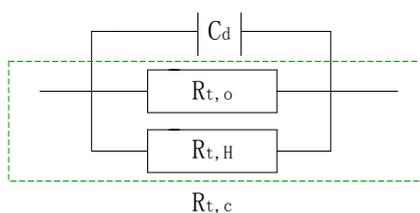


Figure 13. Equivalent circuit in polarization potential

The protection degree is defined by following:

$$p = \frac{\text{corrosion rate at open circuit potential(OCP)} - \text{corrosion rate at CP}}{\text{corrosion rate at OCP}} \tag{5}$$

The utilization of protection current:

$$q = \frac{\text{corrosion rate at open circuit potential(OCP)} - \text{corrosion rate at CP}}{\text{protection current}} \tag{6}$$

Where, corrosion current stands for corrosion rate. As shown in equation (5) and (6), p increases with the negative shift, while q decreases with the negative shift. This is due to that the hydrogen evolution reaction can consume cathodic protection current. The result of $p \times q$ can reflect overall efficiency of the entire cathodic protection system, and it is defined as the actual protection efficiency by $r = p \times q$. The two parameters have opposite trends, which can lead to a maximum value. The potential corresponding to the maximum is just the OCPP. Based on literature [28], the potential corresponding to the maximum of r and R_t are nearly consistent, so the OCPP is the potential that corresponding to the maximum of R_t .

The $R_t-E_{e,c}$ curve (Fig. 9) shows that R_t of X100 steel in Dagang soil solution rapidly increases and then reduces with the decrease of the cathodic polarization potential. Before reaching to the maximum point (-785 mV), the relationship between R_t and the potential can be explained by equation (3), while the range below -785 mV, the relationship between R_t and potential can be analyzed by equation (4). If the ratio of hydrogen evolution reaction in the total cathode reaction is very small, it can be thought that $R_{t,H} \rightarrow \infty$. $R_{t,c}$ is approximately equal to the transfer resistance of cathodic oxygen reduction reaction ($R_{t,o}$). $R_{t,c}$ gradually decreases as the cathode potential negative shift. When the hydrogen evolution reaction occurs obviously in the reaction system, $R_{t,H}$ becomes smaller, and works along with $R_{t,o}$ to affect $R_{t,c}$. Due to the influence of $R_{t,H}$, $R_{t,c}$ decreases rapidly, which leads an inflection point in the $R_t-E_{e,c}$ curve. This point is the potential of hydrogen evolution corresponding to the cathodic polarization potential. Therefore, the potential of hydrogen evolution of X65 pipeline steel in soil simulated solution is -940mV and the OCPP is -785mV.

The $R_t-E_{e,c}$ curves (Figs. 10-11) have similar trends. R_t in soil solution rapidly increases and then reduces with the decrease of the cathodic polarization potential. The results can be obtained that the potential of hydrogen evolution and the OCPP in Daqing simulated soil solution are -950 mV and -890 mV, respectively. Similarly, it can be obtained that the hydrogen evolution potential and OCPP in Lasa simulated soil solution are -1115 mV and -1000 mV using the same method. The OCPP and hydrogen evolution potential in three simulated soil solutions are listed in Table 3.

Table 3. The OCPP and hydrogen evolution potential in three soil simulated solutions

Soil types	Dagang	Daqing	Lasa
OCPP	-785mV	-890mV	-1000mV
Hydrogen-cherged potential	-940mV	-950mV	-1115mV

As shown in Table 3, the hydrogen and OCPP in Dagang, Daqing and Lasa simulated soil solutions orderly increase. Ion content is an important parameter considered in the experiment system. As shown in Table 2, the ion concentrations in Dagang simulated soil solution are higher than that in Daqing and Lasa simulated soil solutions, and the higher ion concentrations can cause the higher conductivity and corrosivity. The OCPP and the hydrogen evolution potential in Dagang simulated soil solution are both the maximum. The results are consistent with the ion concentrations.

Combining the potential of hydrogen evolution (as shown in Table 3) and experimental phenomena, the R_t can be analyzed by calculation. It is concluded that when R_t is less than $1000\Omega\cdot\text{cm}^2$, the hydrogen evolution begins to occur (fewer bubbles precipitate); when R_t is less than $600\Omega\cdot\text{cm}^2$, the hydrogen evolution is very obvious (more bubbles); when R_t is less than $150\Omega\cdot\text{cm}^2$, the hydrogen evolution occurs violently. Therefore, the cathode potential (R_t is less than $1000\Omega\cdot\text{cm}^2$) is just the hydrogen evolution potential.

As shown in the $R_t-E_{e,c}$ curves, it can be divided into four areas: the first one is the area from the OCP to the OCPP with the largest slope, the second area is from the OCPP to the potential of hydrogen evolution with a larger slope, the third one is the origin potential of hydrogen to the potential of obvious evolution with a smaller slope, and the last one is after the obvious hydrogen reaction with a slope almost to zero. The value of slope can supply some useful information. If the slope is relatively gentle, it indicates that the degree of hydrogen evolution is not very sensitive to the cathodic protection potential. A more negative point for the OCPP may be selected in order to improve the degree of protection or to extend the length of pipeline protection. If the slope value changes big, the degree of hydrogen evolution will be very sensitive to the potential in the interval, the minimum of the OCPP should be chosen.

4. CONCLUSION

(1) The shapes of polarization curves in Dagang, Daqing and Lasa soil solutions are similar with two obvious inflection points, and the potential corresponding to the second point is the potential of hydrogen evolution.

(2) The potential of hydrogen reaction and the OCPP in Dagang, Daqing and Lasa soil solutions increase orderly.

(3) Hydrogen evolution begins to occur when R_t is less than $1000\Omega\cdot\text{cm}^2$, the hydrogen evolution becomes obvious when R_t is less than $1000\Omega\cdot\text{cm}^2$ and the hydrogen evolution occurs violently when R_t is less than $150\Omega\cdot\text{cm}^2$. So, the hydrogen evolution potential is just the cathode potential.

(4) The $R_t-E_{e,c}$ curves can be divided into four areas, and they are the areas from the OCP to the OCPP with the largest slope, from the OCPP to the potential of hydrogen evolution with a larger slope, from the origin potential of hydrogen to the potential of obvious evolution with a smaller slope, and after the obvious hydrogen reaction with a slope almost to zero, respectively.

ACKNOWLEDGEMENTS

This research is supported by National High Technology Research and Development Program of China (No. 2012AA040105).

References

1. M. Hudson, PhD thesis, Cranfield University, UK (2004).
2. F. Mohammadi, F. F. Eliyan, Akram Alfantazi, *Corros. Sci.*, 63 (2012) 323.

3. K. T. Corbett, R. R. Bowen, C. W. Petersen, *International Journal of Offshore and Polar Engineering*, 14 (2004) 75.
4. F. J. Sanchez, B. Mishra, D. L. Olson, *Scripta Mater.*, 53 (2005) 1443.
5. C. R. F. Azevedo, *Engineering Failure Analysis*, 14 (2007) 978.
6. A. B. Forero, J. A. C. Ponciano, I. S. Bott, *Mater. Corros.*, 63 (2012) 9999.
7. G. M. Omweg, G. S. Frankel, W. A. Bruce, G. Koch, *CORROSION*, 2 (2002) 48.
8. M. Ueda, T. Omura, S. Nakamura, T. Abe, K. Nakamura, P. I. Nice, J. W. Martin, *CORROSION*, 5 (2005) 89.
9. R. Montoya, F. R. Garcia-Galvan, A. Jimenez-Morales, J. Galvan, *Corros. Sci.*, 82 (2014) 432.
10. Y. S. Wu, B. Cao, *Cathodic protection and anode protection principle, technology and engineering application*, Petrochemical Press, Beijing (2007).
11. Y. Wan, L. Ding, X. M. Wang, Y. B. Li, H. Sun, Q. Wang, *Int. J. Electrochem. Sci.*, 8 (2013) 12531.
12. Z. M. Gao, Y. Y. Liu, F. Lin, L. H. Dang, L. J. Wen, *Int. J. Electrochem. Sci.*, 8 (2013) 10446.
13. J. X. Zhang, J. L. Lu, L. C. Yan, Y. Feng, L. S. Zhang, Y. Zhang, *Anti-Corrosion Methods and Materials*, 57 (2010) 249.
14. Q. M. Ding, Z. L. Li, H. N. Hao, *Anti-Corrosion Methods and Materials*, 60 (2013) 283.
15. J. C. Barker, Health and Safety Executive, London (1998).
16. W. L. Zhen, *Environment sensitive fracture of steel*, Metallurgical Industry Press, Beijing (1988).
17. X. Guo, H. Zhang, Y. Tang, *Corrosion Science and Protection Technology*, 1 (1989) 6.
18. M. Oonishi, *Boosei Kanri*, 20 (1976) 24.
19. X. G. Li, C. W. Du, C. F. Dong, Z. Y. Liu, *Corrosion behavior of X70 steel and experimental research*, Science Press, Beijing (2006).
20. G. H. Zhang, M. Gong, Q. Tang, T. Zhang, X. M. Zeng, *Corrosion & Protection*, 11 (2011) 868.
21. Y. Liu, Y. Li, Q. Li, *Acta Metall.*, 9 (2013) 1089.
22. T. Tsuru, *Boshoku Gijutsu*, 34 (1985) 36.
23. T. Tsuru, *Bosei Kanri*, 30 (1986) 1.
24. G. H. Zhang, M. Gong, Q. Tang, T. Zhang, X. M. Zeng, *Corrosion & Protection*, 32 (2011) 868.
25. M. C. Li, H. C. Lin, C. N. Cao, *Journal of Chinese Society for Corrosion and Protection*, 20 (2000) 111.
26. Z. L. Li, Q. M. Ding, Y. F. Zhang, J. J. Li, S. L. Li, *Corrosion & Protection*, 31 (2010) 436.
27. C. N. Cao, J. Q. Zhang, *An introduction to electrochemical impedance spectroscopy*, Science Press, Beijing (2002).
28. P. R. Sere, J. D. Culcasi, C. I. Elsner, A. R. Di Sarli, *Surf. Coat. Technol.*, 122 (1999) 143.