Asian Journal of Chemistry; Vol. 26, No. 17 (2014), 5824-5828

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.18215

Study of Chemical Cleaning Technology in Compressed Natural Gas Water-Cooling System†

CHANG-SHAN HUANG[1,*], HUI-WU XU[1], JIN-YING WU[1], YU-SHAN CHENG[1], MIN CHEN[1], MIAN XUE[1] and CAN HUANG[2]

[1]Energy Research Institute of Henan Academy of Sciences Co. Ltd., Zhengzhou 450008, Henan Province, P.R. China
[2]Department of Chemistry and Chemical Engineering, Shangqiu Normal University, Shangqiu 476000, Henan Province, P.R. China

*Corresponding author: Tel: +86 371 65726456; +86 13937140170; E-mail: 13937140170@163.com

AJC-15802

This paper is focused on the study of the chemical cleaning technology of the water-cooled piston compressor cooling system in compressed natural gas filling stations and the solution of practical problems such as equipment jams, high temperature, *etc*. The rotary coupon corrosion and weight loss methods corrosion inhibition properties of the cleaning agent and the electrochemical workstation and scanning electron microscopy (SEM) are used to investigate the electrochemical properties of the cleaner and the corrosion of the metal, respectively. Under proper cleaning conditions in the cleaning solution with the compound of 1-hydroxyethylidene-1,1-diphosphonic acid and urotropine, the descaling rate can reach 97.2 % and the corrosion rate of stainless steel and carbon steel are 0.0043 and 0.0784 g/m^2 h, respectively. The potentiodynamic polarization curves show that the urotropine can reduce corrosion current and thus inhibit the corrosion of the metal. The SEM results reveal that the surface of the metal is complete and smooth after cleaning.

Keywords: Gas compressor, Cooling system, Dirt, Chemical cleaning, Descaling rate, Corrosion rate.

INTRODUCTION

Circulating water cooling systems with water-cooled piston compressors in compressed natural gas (CNG) filling stations include collecting tanks with low temperature connected in turn through pipelines, booster pumps, heat exchangers of gas compressors and cooling towers, which are connected to the collecting tank with low temperature by pipelines[1]. For medium and large compressors with large displacement, high pressure and high heat load needed to transfer. They commonly use water as a cooling medium, due to its high specific heat capacity, low cost and easy to obtain[2]. Because of the wide use of the local tap water as cycle medium in cooling compressor, in order to achieve better cooling effect, the cooling towers or collecting tanks with low temperature are generally open in the atmosphere, which is liable to be polluted by the impurities in the environment, such as suspended solids, bacteria, oxygen, sulfur dioxide, nitrogen oxides, acid rain, *etc.*[3]. In addition, due to the constant evaporation in large amounts of cooling water during the operation, the ion concentrations of Ca^{2+}, Mg^{2+}, Fe^{2+}, Cl^-, NO_3^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}, SiO_4^{2-}, PO_4^{3-} in the circulating water are gradually increased. When reached to a certain extent, they may cause corrosion and scaling of the equipment and pipeline, propagation of bacteria and algae[4]. Especially, once cylinder jackets of compressors or cooler tube walls and circle pipes are blocked by the slime of bacteria and algae and dirt debris, it may seriously affect normal and safe operation of the compressors, cross-sectional area of the circulating water channel is reduced, resistance of water cycle is increased, heat transfer coefficient is reduced and heat exchange efficiency is poor, all of which result in reduction of the heat transfer efficiency and increase of power consumption in the compressors[5-7]. According to theoretical calculations, exhaust temperature of the compressors increases by 3 ºC, the power consumption will increase 1 %[8].

Therefore, the dirt in the cooling water system of the gas compressor can cause not only huge waste of energy and water in the gas station, but also severely perforated pipes and equipments, gas leaks, which gives rise to greater loss of the production and operation in the gas stations. As a result, from the viewpoint of safety production, energy saving and so on, the dirt in the cooling system needs to be cleaned. According to the testing result, the gas transportation temperature of the CNG compressor gas is reduced by 10 ºC after cleaning[9].

This article focuses on the perspective from the chemical cleaning, studies the cleaning process and its effect on metal corrosion and dirt, which provides the reference for managers in CNG filling stations.

†Presented at 2014 Global Conference on Polymer and Composite Materials (PCM2014) held on 27-29 May 2014, Ningbo, P.R. China

Mechanism of chemical cleaning and metal corrosion inhibition

Basic components of cleaning agents: When selecting the basic components of the cleaning agents, it mainly considers two factors: the effects of corrosion inhibitors and cleaning agents. Because the main metal material of the cooling circulation system in the gas compressor is stainless steel and carbon steel, it should be avoided using an inorganic acid, especially hydrochloric acid[10]. Combined with the literature data and experimental results, the basic components and their mass fractions in water which is used as the solvent of the chosen cleaning solution are as follows: 1-hydroxyethylidene-1,1-diphosphonic acid 5.0 %, urotropine 0.25 %, ethoxylated alkyl sodium sulfate 0.05 %.

The amounts of all components mentioned in this paper refer to the mass fractions of corresponding substance in water which is used as the solvent of the cleaning solution.

The 1-hydroxyethylidene-1,1-diphosphonic acid is chosen as the main agent for acid cleaning (the main cleaning agent mentioned in the whole paper is 1-hydroxyethylidene-1,1-diphosphonic acid). Compared with inorganic acid, it not only has extremely lower toxicity and is easier to dissolve in water, but also is less corrosive to the metal, so it is very convenient and safe. Furthermore, it also has a good chelating scavenging effect with inorganic salt such as $CaCO_3$ and $MgSiO_3$ and thus it is a kind of chelating cleaner. Meanwhile, the metal can be easily passivated after pickling by the chelating cleaner and is not easy to produce floating rust[11].

Urotropine is the common name of hexamethylene tetramine. It plays a main role in inhibiting corrosion during the cleaning process and avoiding increase of the metal surface roughness and it can inhibit the metal surface to produce hydrogen embrittlement phenomenon which will influence on the mechanical properties of the steel[12].

Ethoxylated alkyl sodium sulfate, named as AES in the market, it has excellent properties of penetration, emulsification, dispersion, wetting, solubilization and washing and its rich foam can increase the speed and uniformity of the descaling, which plays an important role in improving clean rate of the dirt especially of bacterial sludge[13].

Mechanism of chemical cleaning: The analysis test shows the main components of the dirt in the circulating water of the gas compressor are calcium carbonate ($CaCO_3$), magnesium carbonate ($MgCO_3$), iron oxides (rust), the slime of bacteria and algae, *etc*. After adding acidic chemical cleaning agents, it mainly occurs the following chemical reactions:

$$CaCO_3 + 2H^+ = Ca^{2+} + CO_2\uparrow + H_2O$$
$$MgCO_3 + 2H^+ = Mg^{2+} + CO_2\uparrow + H_2O$$
$$FeO + 2H^+ = Fe^{2+} + H_2O$$
$$Fe_2O_3 + 6H^+ = 2Fe^{3+} + 3H_2O$$

Because 1-hydroxyethylidene-1,1-diphosphonic acid is a kind of pentabasic acids, it not only has five H^+ can dissociate, which exhibits strong acidity, but can also react with metal iron (Fe^{3+} and Fe^{2+}), Ca^{2+} and Mg^{2+} ions generated during the cleaning process to form a stable six-ring chelate, which promotes the dissolution rate of iron oxides and incrustation in the dirt[14,15]. With the gradual dissolution of incrustation, the dirt such as slime of bacteria and algae will gradually fall off into the cleaning effluent and finally it will be exhausted with sewage through blowdown.

Mechanism of metal corrosion inhibition: Urotropine shows a good corrosion inhibition on a variety of metal materials such as steel[16,17]. Because of its easily obtained and low cost, it is commonly used as the corrosion inhibitor or the main components during the research of the corrosion inhibitors' complex technology in the industry of chemical cleaning. Some researchers believed that the inhibiting process belonged to the adsorption mechanism of the filming agent, which means the formation of a protective film on the metal surface by adsorption and thus inhibit the occurrence of metal corrosion[18,19]. The literature[20] reported that in the acidic cleaning environment, when the mass fraction of urotropine in the cleaning solution exceeds a certain amount, or the cleaning temperature increases to a certain extent, its effect of corrosion inhibition declines instead. The reason is that the molecular structure of the urotropine has a large six-membered ring in a chair form, shown in Fig. 1. With the increase of the mass fraction or the cleaning temperature, the space steric effect is generated during the adsorption process of the metal surface, which inhibits its coverage on the metal surface and thus reduces the effect of corrosion inhibition. While the coverage area of a single molecule with a six-membered ring in a chair form is large, it can achieve a high corrosion inhibition when its content is low. Therefore, the determination of the mass fraction of urotropine must be combined with the cleaning process conditions.

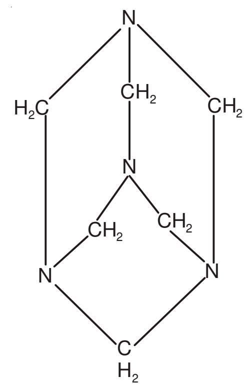

Fig. 1. Structural formula of urotropine

EXPERIMENTAL

Main equipments in the experiment: BT224S electronic analytical balance, 768-3 type far-infrared drying oven, RCC-I rotary coupon corrosion rate tester, CS2350 type electrochemical workstation, KYKY2800B scanning electron microscope (SEM), 501BS super constant temperature water bath, glass dryer.

Main drugs: Anhydrous ethanol (analytical pure), acetone (analytical pure), 1-hydroxyethylidene-1,1-diphosphonic acid (industrial pure), urotropine (industrial pure), ethoxylated alkyl sodium sulfate (industrial pure).

Test of corrosion inhibition

Test method: Referring to the method offered by GB/T 18175-2000 "The determination of corrosion inhibition for water treatment agent-The rotary coupon method", the corrosion rate of metals and the efficiency of the corrosion inhibitor can be calculated according to the eqns. 1 and 2, respectively:

$$\nu = \frac{m_1 - m_2}{At} \times 100\ \% \quad (1)$$

$$\eta = \frac{\nu_0 - \nu}{\nu_0} \times 100\ \% \quad (2)$$

where: ν: the corrosion rate of metal specimens in the cleaning solution with the existence of corrosion inhibitor, with the unit of gram per square meter per hour (g m^{-2} h^{-1}). m_1: the mass of the metal specimens before cleaning and corrosion, with the unit of gram (g). m_2: the mass of the metal specimens after cleaning and corrosion, with the unit of gram (g). A: the total surface area of the metal specimens, with the unit of square meter (m^2). t: the time of the specimens immersing in the cleaning solution, with the unit of hour (h). ν_0: the corrosion rate of metal specimens in the cleaning solution without the existence of corrosion inhibitor, with the unit of gram per square meter per hour (g m^{-2} h^{-1}). η: the efficiency of corrosion inhibitors (%).

In addition, the experimental testing equipments used in the rotary coupon method are shown in Fig. 2.

Fig. 2. Experiment testing equipments used in the rotary coupon method. (RCC-I rotary coupon corrosion rate tester)

Influence of different dosage of the main cleaning agent on the metal corrosion rate: During the cleaning process, descaling and metal corrosion are chemical reactions. Based on the chemical reaction mechanism[21], the mass fraction of the main cleaning agent-1-hydroxyethylidene-1,1-diphosphonic acid is higher, the metal corrosion rate should be faster. According to the previous method, when the temperature is 30 ºC, the mass fraction of urotropine is 0.25 % and the test time is 10 h, the experimental results of the metal corrosion rate are shown in Table-1.

As the results shown in Table-1, with the mass fraction of 1-hydroxyethylidene-1,1-diphosphonic acid gradually increased, the corrosion rate of stainless steel is increased with a quite gentle amplitude, which illustrates that the influence is insignificant. However, its influence on the corrosion rate of carbon steel is relatively large; especially when the mass fraction of 1-hydroxyethylidene-1,1-diphosphonic acid is more than 5.0 %, the growth of the corrosion rate is quite obvious.

TABLE-1
INFLUENCE OF DIFFERENT MASS FRACTIONS OF 1-HYDROXYETHYLIDENE-1,1-DIPHOSPHONIC ACID ON THE METAL CORROSION RATES

Mass fraction of 1-hydroxyethylidene-1, 1-diphosphonic acid (%)	Corrosion rate of stainless steel (g m^{-2} h^{-1})	Corrosion rate of carbon steel (g m^{-2} h^{-1})
1	0.0028	0.0339
3	0.0035	0.0555
5	0.0043	0.0784
7	0.0047	0.1325
9	0.0052	0.1571

When the mass fraction reaches to 9.0 %, the growth is almost doubled. Therefore, the mass fraction of the main cleaning agent-1-hydroxyethylidene-1,1-diphosphonic acid is optimum at 5.0 % during the actual cleaning process.

Influence of different dosage of the corrosion inhibitor on the metal corrosion inhibiting efficiency: In the cleaning solution of 1-hydroxyethylidene-1, 1-diphosphonic acid with its mass fraction of 5.0 %, the corrosion inhibitor-urotropine with different mass fractions are added respectively. According to the previous method, the corrosion rates of stainless steel and carbon steel specimens are determined, thus the corrosion inhibiting efficiency of urotropine for the stainless steel and carbon steel can be calculated and the experimental results are shown in Fig. 3.

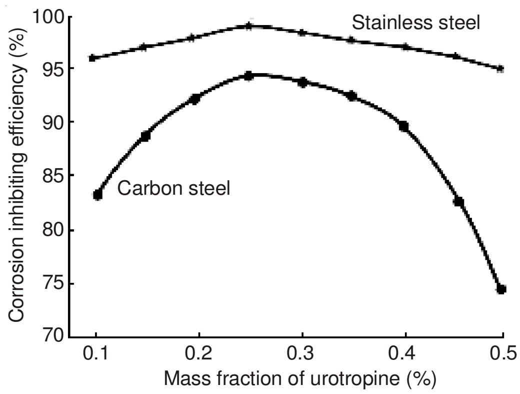

Fig. 3. Influence of different dosage of the urotropine on the corrosion inhibiting efficiency

Fig. 3 shows that as the mass fraction of corrosion inhibitor-urotropine in the cleaning solution increases to 0.25 %, the corrosion inhibiting efficiencies for the stainless steel and carbon steel reach maximum values of 97.5 and 94.6 %, respectively. When the mass fraction is greater than 0.25 %, the corrosion inhibiting efficiency is worse instead. Therefore, the mass fraction of the corrosion inhibitor-urotropine is optimum at 0.25 % during the actual cleaning process.

Influence of different dosage of the cleaning agent on the rate of descaling: The weight-loss method is adopted in the experiment and specific steps are as follows: Marble ($CaCO_3$) with uniform particles as the fouling sample is screened by a sieve with a diameter of 8 mm. An array of samples with 0.5 g are weighed using BT224S type electronic analytical balance and they are put into 100-mL tubes filled by 1-hydroxyethylidene-1,1-diphosphonic acid with the mass fraction of 5.0 %, respectively. They are standed in the 501BS type constant temperature water bath with the temperature of 30 ºC for 10 h and then they are filtrated by a buchner funnel in vacuum. The residual fouling sample is dried to a constant weight in a 768-3 type far-infrared drying oven under 50 ºC and then it is placed in a glass dryer for cooling to room temperature, finally, it is weighed again on a BT224S electronic analytical balance. The descaling rate of the cleaning agent is calculated according to eqn. 3 and the experimental results are listed in Table-2:

TABLE-2
INFLUENCE OF DIFFERENT MASS FRACTIONS OF 1-HYDROXYETHYLIDENE-1, 1-DIPHOSPHONIC ACID ON THE EFFECTS OF DISSOLVING FOULING SAMPLE

Mass fraction of 1-hydroxyethylidene-1,1-diphosphonic acid (%)	Weight loss of the fouling sample (g)	Descaling rate (%)
1.0	0.394	78.8
3.0	0.459	91.8
5.0	0.486	97.2
7.0	0.467	93.4
9.0	0.452	90.4
11.0	0.438	87.6

$$\rho = \frac{\Delta m}{m} \times 100\ \% \qquad (3)$$

where: ρ: The descaling rate, %; Δm: The mass of the fouling sample dissolved in the cleaning solution, namely the weight loss of the fouling sample with the unit of gram (g); m: The mass of the fouling sample before dissolved in the cleaning solution with the unit of gram (g).

As can be seen from Table-2, the weight loss of the fouling sample, $CaCO_3$, is increased with increasing the mass fraction of 1-hydroxyethylidene-1,1-diphosphonic acid and it reaches a maximum with the mass fraction of around 5 %. However, the effect of dissolving fouling sample is declined when the mass fraction is further increased. The appeared maximum should be related to the sharp increase of the chelating ability when the concentration of 1-hydroxyethylidene-1,1-diphosphonic acid is relatively high[10] and regarding to the reason of the declined dissolving effect, some researchers[15] thought that when the mass fraction of 1-hydroxyethylidene-1,1-diphosphonic acid is increased to a certain extent, a large amount of calcium ions (Ca^{2+}) is generated due to the continuous dissolution of the incrustation in the cleaning solution and 1-hydroxyethylidene-1,1-diphosphonic acid and calcium ions are combined to from a kind of white flocculent complex which is "organic calcium phosphonate". The content of calcium ion and phosphonate are higher, more prone to generate floccule and precipitation, resulting in the effective content of 1-hydroxyethylidene-1,1-diphosphonic acid in the decreased, affecting the pharmacodynamic play and leading to the descaling effect hard to reach the desired level. Therefore, the mass fraction of 1-hydroxyethylidene-1,1-diphosphonic acid is selected at 5 % during the actual cleaning process. In addition, the purpose of adding ethoxylated alkyl sodium sulfate into the cleaning agent formulation is using it to generate rich foam and penetration, which can inhibit the deposition of the "organic phosphonate" precipitate on the surface of incrustation and thus achieve the goal of improving descaling rate.

Influence of temperature on the corrosion inhibiting efficiency: In the cleaning solution of 1-hydroxyethylidene-1,1-diphosphonic acid with its mass fraction of 5 %, the corrosion inhibitor-urotropine with mass fraction of 0.25 % is added. The corrosion rates of carbon steel specimens at different temperatures are determined according to the eqn. 1 and the corrosion inhibiting efficiency of urotropine for metal carbon steel is calculated by eqn. 2. The test results are shown in Fig. 4.

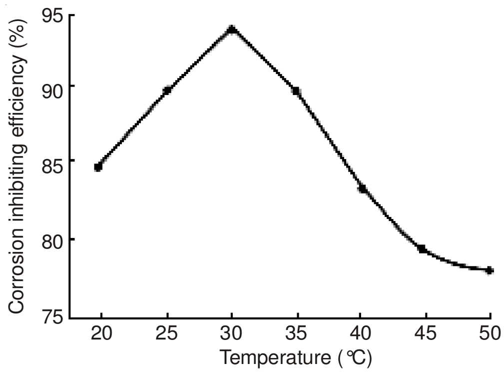

Fig. 4. Influence of temperature on the corrosion inhibiting efficiency

As can see from Fig. 4, the corrosion inhibiting efficiency of urotropine for metal carbon steel first increases with the rise of temperature and begins to decline after reaching the extreme of 94.6 %. Therefore, the corrosion inhibitior can achieve good effects when cleaning in the temperature range of 25-35 ºC.

RESULTS AND DISCUSSION

Electrochemical test of metal corrosion[22]

Polarization curves: Through the above-mentioned experiments, the influence on the corrosion rate of stainless steel is very small, therefore, the electrochemical corrosion is tested only on the metal carbon steel. During the experiments, the mass fractions of 1-hydroxyethylidene-1,1-diphosphonic acid and urotropine are 5.0 and 0.25 %, respectively. The CS2350 type electrochemical work station is applied, with the polarization range of ± 300 mV, scan rate of 0.2 mV s^{-1} and the test temperature of 30 ºC and the tap water is used as solvent for the preparation of the cleaning solution. Conventional three-electrode system is used, where a large platinum electrode and a saturated calomel electrode (SCE) are used as an auxiliary electrode and a reference electrode, respectively and the carbon steel specimens corresponds to a working electrode. Before each experiment, the working electrode is polished sequentially by metallographic sandpapers 1-6 to bright, washed by deionized water, ethanol and acetone successively and then dried in cold air. The surface of the working electrode is checked carefully and it should be smooth, bright, clean and without pits. The electrode which meets the requirements is soaked in the cleaning solution with and without urotropine for 0.5 h and then tested. The test results are shown in Fig. 5.

As can be seen from Fig. 5, compared under similar conditions with the carbon steel specimens in the cleaning solution without urotropine, the corrosion potential of the carbon

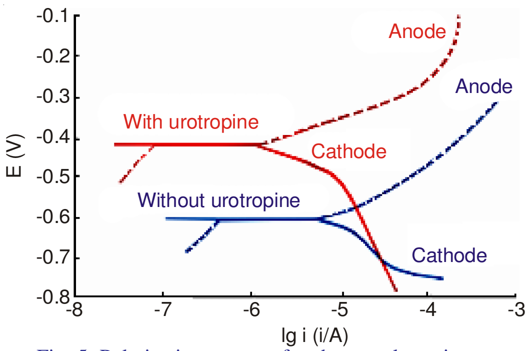

Fig. 5. Polarization curves of carbon steel specimens

steel specimens in the cleaning solution with urotropine shifts positively and more significantly, indicating that urotropine is a kind of corrosion inhibitor which can suppress the polarization of anode and it can prevent the corrosion of the metal in the cleaning process.

Scanning electron microscope (SEM) analysis: When rotary coupon corrosion test ends, the metal carbon steel coupon is removed from the solution. After the specimens are cleaned, they are glued to sample platform which are affixed with double-sided adhesive respectively. In order to ensure that everywhere of the specimen surface can conduct uniformly and avoid charge accumulation caused by point discharge which will affect the image quality, specimens need to be coated by gold before the test. After spraying, the specimens are placed in a KYKY2800B SEM and observed under an acceleration voltage of 15 kV and magnification of 5000. Its result shows that in the cleaning agent containing 5.0 % 1-hydroxyethylidene-1,1-diphosphonic acid with the existence of urotropine, the corrosive trace of carbon steel specimen is not distinct, displaying complete substrate surface. However, the surface of carbon steel specimen in the cleaning agent without corrosion inhibitor appears some pit-like corrosion and it is slightly rough, which are shown in Figs. 6 and 7.

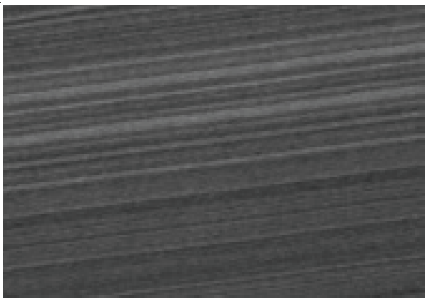
Fig. 6. SEM of specimens with urotropine

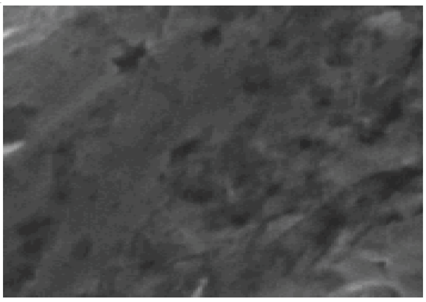
Fig. 7. SEM of specimen without urotropine

Conclusion

The experimental results of the rotary coupon method and weight-loss method show that in the cleaning solution with the compound of 5 % 1-hydroxyethylidene-1,1-diphosphonic acid as the main cleaning agent, 0.25 % urotropine as the corrosion inhibitor and 0.05 % ethoxylated alkyl sodium sulfate (AES) as the adjuvant, when the cleaning temperature is 25-35 ºC, the cooling system of water-cooled gas compressor is cleaned continuously for 10 h, the descaling rate can reach 97.2 %, the corrosion rates of metal stainless steel and carbon steel are 0.0043 and 0.0784 g/m^2 h, respectively and the inhibition efficiencies reach 97.5 and 94.6 %, respectively. The potentiodynamic polarization curves show that the urotropine used in the cleaning agent is a kind of corrosion inhibitor which mainly suppresses the polarization of anode by generating adsorption film on the metal surface. Furthermore, the SEM results reveal that the urotropine in the cleaning compound has a fine inhibition on the corrosion of the metal and the surface of the metal is complete and smooth after cleaning.

REFERENCES

1. X.-L. Liu, *Urban Gas*, **314**, 5 (2001).
2. Z. Zheng, S.-L. Wang and B. Yang, *Gas Heat*, **30**, 15 (2010).
3. P.-H. Yang, J.-Y. Luo, D.-X. Yuan and Q.F. He, *J. Hydraul. Eng.*, **40**, 67 (2009).
4. C.-S. Huang, J.-Y. Wu, R.-J. Liu, H.M. Li and H.X. Li, *Heat. Ventilat. Aircondition.*, **39**, 145 (2009).
5. C.O. Gill and J. Bryant, *Int. J. Food Microbiol.*, **3**, 239 (2003).
6. Z. Xing-Hua and W. Dong-Hong, *Henan Technol.*, **12**, 158 (2010).
7. F. Xing-Quan and D. Hong, *Compressor Technol.*, **6**, 33 (2002).
8. Z.W. Zou, J.P. Liu, Y.M. Zhou, Z.Y. Wang and C.L. Yang, *Compressor Technol.*, **4**, 18 (2004).
9. S.M. Wang, H.B. Liu, F.Z. Xu, J.F. Rong and H.P. Yan, *Gas Heat*, **33**, 76 (2013).
10. C. Wang, F. Jiang and H.C. Lin, *Corrosion Protect.*, **22**, 115 (2001).
11. H. Jin-Ying, X. Li-Ming and W. Hui-Fang, *Petrochem. Corros. Protect.*, **29**, 61 (2002).
12. D. Liu, X.-Z. Lin and X.-M. Zhu, *Contemp. Chem. Ind.*, **40**, 111(2011).
13. J. Xue-Shun, Surfactant Practical New Technology, Chinese Light Industry Press, Beijing, p. 141 (1993).
14. S. Ghareba and S. Omanovic, *Corros. Sci.*, **52**, 2104 (2010).
15. L. Zhang, B.-R. Zhang and F.-T. Li, *Ind. Water & Wastewater*, **40**, 63 (2009).
16. W. Doherty, C.M. Fellows, S. Gorjian, E. Senogles and W.H. Cheung, *J. Appl. Polym. Sci.*, **91**, 2035 (2004).
17. X. Yong-Cheng, *Si Chuan Ye Jin*, **2**, 49 (1994).
18. Z. Rong-Chang and H. En-Hou, Corrosion and Protection of Materials, Chemical Industry Press, Beijing, p. 296 (2006).
19. J.-L. Lei, L.-J. Li, S.-H. Yu, M.-L. Chen, S.-T. Zhang and F.-S. Pan, *Chem. Res. Appl.*, **20**, 461 (2008).
20. P.C. Okafor, M.E. Ikpi, I.E. Uwah, E.E. Ebenso, U.J. Ekpe and S.A. Umoren, *Corros. Sci.*, **50**, 2310 (2008).
21. X. Yue, Chemical Reaction Kinetics, Chemical Industry Press, Beijing, p. 5 (2005).
22. C.-N. Cao, *Corros. Sci. Protec. Technol.*, **2**,1 (1990).