Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2012.749006

51 (2013) 3133–3137
April

Taylor & Francis
Taylor & Francis Group

Molybdate-based corrosion inhibitor system for carbon steel in sea ice melt-water

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Received 2 June 2011; Accepted 1 May 2012

ABSTRACT

Because Bohai Sea is located at a higher latitude in China, there is huge amount of sea ice formed every winter that has brought about great attention to the value and utilization of the sea ice. To replace fresh water by the sea ice melt-water for industrial cooling and to reduce water shortage within the area of Bohai Sea, circulation system shall be of great positive significance. By orthogonal experiment screening, together with the molybdate-based multiple inhibitor system, the effects of corrosion inhibitor of molybdate compound in the sea ice melt-water on the corrosion of Q235 carbon steel were studied by using weight-loss method on static immersion suspension, rotation specimen method, and polarization curve method; and the inhibition of this formula in high cycles of concentration (2–5 times) of the sea ice melt-water was evaluated. The results show that in single usage of molybdate dosing lower than 30 mg/L, it can accelerate corrosion of carbon steel. Molybdate presents good synergistic effects in the sea ice melt-water together with sodium hexametaphosphate, sodium borate, zinc sulfate, and hydroxyethylidene diphosphonate. In the optimum inhibitor system, concentrations of each component are, respectively, 15, 20, 25, 44, and 20 ppm. For this inhibitor system in the concentration of 1–5 times of the sea ice melt-water, the corrosion rates to carbon steel, all satisfy the standard GB50050-2007 (corrosion rate $\leq$ 0.075 mm/a), the optimum inhibition efficiency of molybdate corrosion inhibitor compound is up to 99.35% which functions as an anodic inhibitor.

Keywords: Corrosion; Corrosion inhibitors; Sea ice; Molybdate

1. Introduction

As a nonconventional water source, sea ice melt-water has significant capacity and lower salinity than sea water. Many studies on the value and feasibility of the utilization of sea ice melt-water have been done in China. For example, Jing'ai has demonstrated the exploitation and utilization of ice in Bohai Sea used as fresh water resources [1, 2]. Peijun has summarized the utilization of sea ice resources, including development and integration of techniques for planting and irrigation using desalinated sea ice water [3].

Meanwhile, industrial water occupies a large proportion of urban water consumption. About 60–80% of industrial water is used in petrochemical industry [4]. If sea ice melt-water is used as industry cooling water, it is no doubt that tremendous amount of fresh

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water shall be saved and helps the shortage of water resources. Adding of inhibitors to the electrolyte is known as one of the main methods of inhibiting corrosion. This selected inhibitor system is based on molybdate, which is known as one of the enviromentally friendly corrosion inhibitor [5–7]. It is found that this system works efficiently with carbon steel [8–12].

The work is as follows:

(1) to judge the sea ice melt-water type, corrosion, or scaling type by analyzing the water quality;
(2) to determine the inhibitors and their perfect concentration of inhibition to carbon steel in sea ice melt-water;
(3) to check the inhibition efficiency (IE) of the selected inhibitor system in high cycle (1–5 times) of sea ice melt-water using immersion and rotation specimen measurements; and
(4) to analyze the function type of the inhibitors using potentiodynamic polarization measurements.

2. Experimental analysis

2.1. Water prepared and the analysis of the water quality

The high cycles of sea ice melt-water were prepared according to the water quality of natural sea ice melt-water. The quality of the prepared water is given in Table 1.

In Table 1, I_L (the Langelier Number) and I_R (the Ryznar number) are calculated. The two numbers indicate that all the sea ice melt-water is corrosive type, which is more likely to corrode the steel than to scale.

2.2. Weight-loss method

2.2.1. Immersion experiment

Carbon steel specimens (50 mm × 25 mm × 2 mm) were used for the immersion experiment. The specimens in triplicate were immersed in prepared sea ice melt-water in the absence or presence of inhibitors at different concentrations for 72 h at 50°C. The weight of specimens was determined before and after immersion. The corrosion IE was then calculated using the equation

$$IE = 100[1 - (W_2 - W_1)]\% \quad (1)$$

Where, W_1 is the corrosion rate in the absence of inhibitor and W_2 is the corrosion rate in the presence of inhibitor. The corrosion rate was calculated using the formula

Mils per year = 87,600 (W/DAT);
W = weight loss (g);
D = density of specimen (g/cm^3);
A = area of specimen (cm^2); and
T = immerse (h).

By virtue of the synergistic effect in different inhibitors, another four inhibitors were chosen to work together with molybdate. The best inhibitor system was selected in different choices of concentration of each component. Then, the selected system was used in high cycles of sea ice water to determine the effect.

2.2.2. Rotation specimen method

Rotation specimen experiments were carried out according to GB/T 18175-2000. The rotate speed was kept at 108 r/min. The effect of corrosion inhibitor system was determined after an experimental period of 72 h at a temperature of 50°C. The carbon steel specimens and calculation methods are as same as the above.

2.3. Potentiodynamic polarization measurements

Electrochemical experiments were performed on a TD3691 electrochemical analyzer (TD Co., Tianjin) with a carbon steel specimen as the working electrode, a platinum foil used as the counterelectrode, and saturated calomel electrode used as the reference electrode. The polarization curves were obtained from the corrosion potential (E_{corr}) up to ± 150 mV at a potential scan rate of 5.0 mV/s at room temperature.The specimens

Table 1
The quality of natural and dosing sea ice melt-water

Sea ice melt-water dosing	Conductivity (ms cm^{-1})	Cl$^-$ (mg L^{-1})	SO$_4^{2-}$ (mg L^{-1})	Total alkalinity (mg L^{-1})	TDS (g L^{-1})	pH	I_L	I_R
Natural	6.63	2,460	381.4	43.42	3.31	7.38	−0.9	11.20
Two times	12.80	4,790	788	75.9	6.72	7.78	−0.73	10.28
Three times	19.28	7,370	1,130	103	9.56	7.90	−0.62	9.99
Four times	26.20	9,800	1,540	124	13.20	7.78	−0.42	9.93
Five times	31.80	11,700	1,836	124	15.85	7.88	−0.37	9.83

were fitted into sample holder leaving an exposed area of 1 cm^2.

3. Results and discussion

3.1. Selection of molybdate-based inhibitors

3.1.1. Molybdate alone

As it is well known, molybdate is one of the green inhibitors. In this part of experiment, corrosion parameters, such as corrosion rate and inhibitor efficiency, were calculated for carbon steel in sea ice water in the absence and in the presence of sodium molybdate at different concentrations (e.g. 0, 30, 50, 100, 200, 500 and 1,000 mg/L) at 50℃ based on the weight-loss data collected. The results are summarized in Fig. 1.

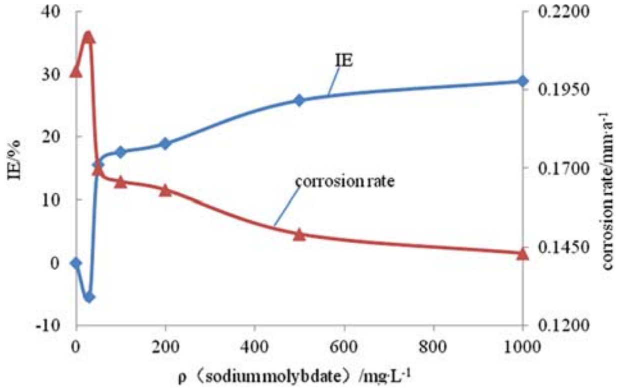


Fig. 1. Calculated corrosion rate and IE by immersion experiment in sea ice water in the presence or absence of sodium molybdate at 50℃.

The results show that molybdate accelerates corrosion below 30 mg/L, then with the increase of sodium molybdate concentration from 50 to 1000 mg/L, the corrosion rate of carbon steel decreases from 0.1700 to 0.1431 mm/year, and the corresponding IE increases from 15.56 to 28.91%. Obviously, although the concentration of sodium molybdate is up to 1000 mg/L, the IE of carbon steel in sea ice water is poor, and the corrosion rate is far over the rate (<0.075 mm/a) in GB50050-2007. Therefore, in order to enhance the IE, some other inhibitors should be added in to work together with the molybdate.

3.1.2. Orthogonal experiment of the inhibitor system

After single factor experiments, orthogonal designed experiments were carried out to obtain the optimum inhibitor system, including sodium molybdate, sodium hexametaphosphate (SHMP), sodium borate, zinc sulfate, and hydroxyethylidene diphosphonate (HEDP), named as A,B,C,D, and E, respectively (Table 2).

Table 1 shows that the optimum reaction case, $A_2B_2C_3D_4E_2$, was obtained by means of the five factors and four levels orthogonal experiment. The results of all cases are much better than the single molybdate experiments. Under the optimum conditions, the IE value in sea ice water can be up to 89.86%, and the corrosion rate can be 0.0204 mm/a, which is far below 0.075 mm/a specified in GB50050-2007.

Table 2
Orthogonal designed experiments of the molybdate-based inhibitor system

A (mg L^{-1})	B (mg L^{-1})	C (mg L^{-1})	D (mg L^{-1})	E (mg L^{-1})	IE (%)
11	20	15	11	15	80.13
11	25	20	22	20	75.83
11	30	25	33	25	74.25
11	35	30	44	30	67.36
13	20	20	33	30	79.65
13	25	15	44	25	82.14
13	30	30	11	20	66.25
13	35	25	22	15	72.18
15	20	25	44	20	89.86
15	25	30	33	15	74.10
15	30	15	22	30	72.65
15	35	20	11	25	70.14
17	20	30	22	25	62.18
17	25	25	11	30	77.29
17	30	20	44	20	78.37
17	35	15	33	15	72.56

This result is owing to the synergistic effect in the five different inhibitors; in addition, the concentration of molybdate is greatly reduced. In the optimum case, the concentration of molybdate is only 15 mg/L.

3.1.3. The inhibitor system in high cycles of concentration (2–5 cycles) of sea ice melt-water

For the purpose of saving water and energy, the cooling water system is always running in high cycles of concentration. Therefore, this inhibitor system was used in 2–5 cycles of concentration of sea ice melt-water. The results of corrosion rates and inhibition rates are summarized in Table 3.

The results show that the inhibitors in 2–5 cycles of concentration have 89.59–97.56% IE. The inhibitor system can be seen to exhibit good corrosion-inhibiting effects, which becomes more pronounced in high cycles of concentration of sea ice melt-water.

3.2. Rotation specimen experiment

The rotation specimen experiment was carried out with and without the presence of the inhibitors in 1–5 cycles of concentration of sea ice melt-water. The purpose is to further check the inhibition effect of the inhibitor system.

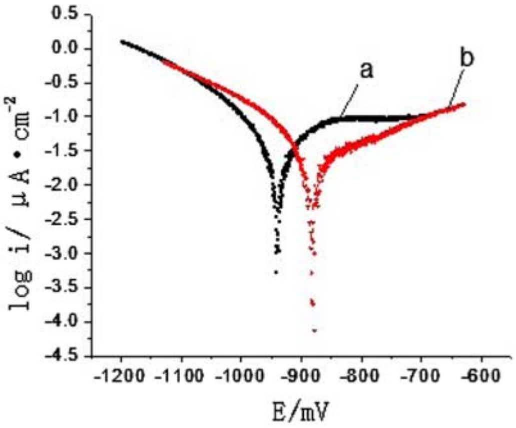
From Table 4, it can be seen that though the blank corrosion rates are significantly increased to 1.0834–1.3697 mm/year, the excellent performance of the inhibitors still remains; and the corrosion rates can also reach the standard specifications.

Table 3
Calculated corrosion rate and inhibitor efficiency by immersion experiment in 2–5 cycles of concentration of sea ice melt-water in the absence and in the presence of the inhibitor system at 50℃

Concentration cycle	Blank corrosion rate (mm year^{-1})	Corrosion rate (mm year^{-1})	IE (%)
2	0.2643	0.0276	89.56
3	0.2831	0.0085	96.98
4	0.1807	0.0188	89.59
5	0.1810	0.0044	97.56

Table 4
Calculated corrosion rate and IE by rotation specimen experiment in 1–5 cycles of concentration of sea ice melt-water in the absence and in the presence of the inhibitor system at 50℃

Concentration cycle	Blank corrosion rate (mm year^{-1})	Corrosion rate (mm year^{-1})	IE (%)
1	1.2556	0.0211	98.32
2	1.3697	0.0478	96.51
3	1.1290	0.0230	97.96
4	1.0936	0.0071	99.35
5	1.0834	0.0132	98.78



(a) 5 cycles of concentration of sea ice melt-water

(b) 5 cycles of concentration of sea ice melt-water containing the inhibitors

Fig. 2. Polarization curves of carbon steel immersed in five cycles of concentration of sea ice melt-water.

3.3. Potentiodynamic polarization

In order to classify this inhibitor system as an anodic-type, cathodic-type, or mixed-type inhibitor and to evaluate its effect on the kinetics of the anodic and cathodic reactions, the potentiodynamic polarization experiments in five cycle concentration of sea ice melt-water in the absence and in the presence of inhibitors were investigated.

Fig. 2 shows that in the presence of the inhibitors, the corrosion potential is shifted to anodic site. This indicates that the anodic reaction is controlled predominantly, thus this inhibitor system acts as anodic type.

4. Conclusions

The conclusions of the present study are as follows:

- In the sea ice melt-water, molybdate accelerates corrosion below 30 mg/L, and then, with the increase of the concentration from 50 mg/L, the IE is increasing. However, the corrosion rate of the inhibitor cannot yet reach the standard specifications even in the concentration of 1,000 mg/L.

- The selected five inhibitors show the synergistic effect in controlling the corrosion of carbon steel in sea ice melt-water. The formulation, consisting of 15 ppm of sodium molybdate, 20 ppm of SHMP, 25 ppm of sodium borate, 44 ppm of zinc sulfate, and 20 ppm of HEDP, has optimum IE.
- This inhibitor system performs good inhibition effect both in the immersion and the rotation specimen experiment in high cycles (2–5 cycles) of concentration of sea ice melt-water. In the presence of the inhibitors, the corrosion rates of carbon steel all satisfy the standard specifications (GB50050-2007); the optimum IE can reach up to 99.35%.
- Polarization study reveals that the formulation of inhibitors functions as anodic inhibitor.

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