

Investigation of Corrosion Caused by Constituents of Refinery Wastewater Effluent Used as Circulating Cooling Water

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ABSTRACT: The corrosion rate of steel plate using single-factor, multifactor, and complex water systems was investigated via refinery wastewater effluents used as circulating cooling water. The results show that the primary corrosion factors of steel depend on the characteristics of the ions, the formation of the oxidized coating, the diffusion of dissolved oxygen, and other complex factors, although ions such as chloride, calcium, and carbonate play an important role. The corrosion rate of carbon steel exhibits two trends: The corrosion rate is high at low conductivity, increases to a maximum, and then decreases and becomes stable with increasing conductivity, as is the case with chloride, sulfate, nitrate and calcium ions. On the other hand, the corrosion rate is highest at low conductivity and then decreases and becomes stable with increasing conductivity, as is the case with carbonate, silicate, and sodium nitrate ions. Research results indicate that the anticorrosive ability is minimal at low conductivity; but is excellent at high conductivity. Pretreatment of low-conductivity water using air flotation and clarification to decrease the concentrations of chloride, calcium, and carbonate ions to a suitable level to satisfy the anticorrosion requirements is required. However, it is not necessary to significantly reduce the salt concentration or conductivity of the water by osmosis or ion exchange to obtain an anticorrosion effect when reusing wastewater effluents as circulating cooling water. *Water Environ. Res.*, **75**, 61 (2003).

KEYWORDS: carbon steel corrosion, ion characteristics, oxidized coating formation, dissolved oxygen diffusion, conductivity.

Introduction

With the development of the global economy and an increasing population, the need for high quality water has also grown. However, water shortage has become an unnegotiable and fatal crisis that has restrained economic development. In attempts to avoid the crisis, traditional methods for saving water, enhancing utility efficiency, or searching out new water resources have been used (Liu, 1997). Today, reusing wastewater as a new water resource has especially been recognized and embraced by governments and scholars in countries experiencing severe water shortages. Because fresh water is becoming an increasingly scarce and valuable resource in many parts of the world, programs to reclaim and reuse wastewater for circulating cooling systems have been undertaken (Bresnahan, 1997). While the investigation of water reuse began early in China, there has been little practical application of the technology. At petrochemical complexes, however, cooling water makes up approximately 65 to 80% of the total water use. Therefore, these complexes are prime locations where reuse of the wastewater effluents as circulating cooling water should be practical. Moreover, advanced-treated wastewater could be used for

other purposes (e.g., to irrigate the greenbelt and flowers) at these complexes as well (Guo, 2001; Ma, 2001; Zeng et al., 1999).

This paper introduces a conductivity method to study the relationship of carbon steel corrosion and water quality. Conductivity can characterize the concentrations of salt and ion to some extent and the method is simple and highly accurate. Moreover, conductivity can immediately indicate a change in water quality, and thus has further application. Considering the complexity of wastewater effluents, the corrosion of carbon steel is discussed using a single factor for independent ions, such as chloride (Cl^-), sulfate (SO_4^{2-}), carbonate (CO_3^{2-}), and silicate (SiO_3^{2-}) and a multifactor for the interaction of many ions, such as calcium (Ca^{2+}), magnesium (Mg^{2+}), chloride, ammonium (NH_4^+), and nitrate (NO_3^-). In addition, the influence of adding sodium nitrate to complex wastewater effluent systems to model wastewater quality is discussed.

Experimental Methods

A weightlessness experiment using a rotating hanging steel plate to determine the average corrosion rate influenced by water quality was carried out by Wu (1997). The experimental conditions are listed in Table 1.

The steel plate, which encompassed an area of 28 cm^2 and had a volume of 2.475 cm^3 (Jiangsu Gaoyou Apparatus and Equipment Factory, Gaoyou City, Jiangsu Province, China), was produced according to China's national standards for steel. Under controlled experimental conditions and at a set time, a 2000-mL beaker that contained the analyzing water and steel plate were placed in a rotating hanging corrosion apparatus (Model RCC-1, Jinling Petrochemical Research Institute, Nanjing City, Jiangsu Province, China, and Jiangsu Gaoyou Apparatus and Equipment Factory) that modeled the operating conditions for circulating cooling water. Within a range of $50 \pm 1 \text{ }^\circ\text{C}$, the temperature is held constant for 72 hours; the concentration cycle is initiated and when it has reached 1.5 times (i.e., 1800 mL of liquid in the 2000 mL beaker concentrates to 1200 mL), deionized water is added every 4 hours to maintain a constant concentration cycle. At the conclusion, based on the weight difference (Δw) of the steel plate between the beginning and end of the experiment, the average corrosion rate of steel at the experimental conditions can be calculated.

To evaluate the single- and multifactors influencing the corrosion rate, local city water amended with the necessary ions to model the wastewater was used. In the experiment involving the complex system, samples of wastewater effluents from the Liaohe Oilfield Petrochemical Corporation, Panjin City, Liaoning Province, China, were obtained on April 20, 2001; the water quality from this experiment is listed in Table 2.

Table 1—Conditions for weightlessness experiment.

Parameter	Value
Temperature (°C)	50 ± 1
Rotating speed (rpm)	75
Time (h)	72
V_{aw}/S_a (mL/cm ²) ^a	53.5–64.5
Condensed times	1.5

^a V_{aw} = Volume of analyzing water and S_a = Surface area of steel plate.

Results and Discussion

Single-Factor Experiment. Based on the quality of the refinery wastewater effluents, four common ions, including chloride, sulfate, carbonate, and silicate, were selected to study the primary factors that influence the corrosion rate of the carbon steel.

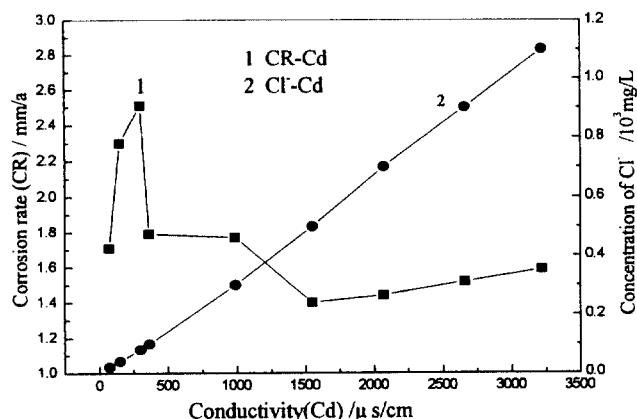
Influence of Chloride. Total dissolved solids and dissolved chlorides are considered to be general corrosion factors present in freshwater and wastewater, the latter at higher concentrations (Rebhun and Engel, 1988). Therefore, the influence of chloride was investigated first using sodium chloride to adjust the conductivity of the experimental deionized water. (There is a general opinion that the influence of the sodium ion on steel corrosion can be neglected, so the existence of this ion does not influence the corrosion of carbon steel.) The result of the experiment is depicted in Figure 1.

With an increase in conductivity, the corrosion rate of the steel plate immediately increases from an intermediate value of 1.70 mm/a to a maximum value of 2.50 mm/a, then decreases slowly to 1.40 mm/a (Figure 1) before reaching a stable value. This result supports the finding that dissolved chloride has a particularly strong influence on the corrosion of carbon steel (Puckorius, 1997). The trend shown in Figure 1 is also similar to the response of the electrical current density relative to the electrical potential on the positive electrode of the metal (Cheng, 1999). At high conductivity, the corrosion rate is lower than that of low conductivity for the reasons outlined in the following paragraphs.

When conductivity is low, the steel plate is at a stage of

Table 2—The quality of the wastewater effluents of Liaohe Oilfield Petrochemical Corp.

Parameter	Value
pH	7.80
Conductivity (μs/cm)	950
Ca ²⁺ (mg/L)	108.42
Mg ²⁺ (mg/L)	27.53
Total salinity (mg/L)	385.60
Total alkalinity (mg/L)	68.07
Total suspended solids (mg/L)	2
Chemical oxygen demand (mg/L)	72.86
Cl ⁻ (mg/L)	270.2
Total dissolved solids (mg/L)	980
Fungus concentrations (cell/mL)	1.4 × 10 ³
Oil content (mg/L)	16.24
Corrosion rate (mm/a)	1.2824
Calcium carbonate production (%)	99.47
Dissolved oxygen at 28 °C (mg/L)	3.23

**Figure 1—The influence of chloride on the corrosion rate.**

self-oxidation and dissolution. At that time, because the concentration of the ion as well as the oxygen dissolved in the solution by the ion is low, the dissolved oxygen may reach the steel plate surface immediately and react with the steel. However, the conductivity that results from the dissolved oxygen is low, which leads to a moderate corrosion rate. The chloride concentrations are too low to destroy the oxidized inactive coating on the surface of the steel plate and therefore minimize the corrosion (Cheng, 1999).

Increasing concentrations of chloride can activate the oxidizing reaction of steel (Cheng, 1999). Furthermore, when chloride concentrations are high they can destroy the inactive coating immediately. As a result, the corrosion rate increases with increasing conductivity.

When the conductivity and chloride concentrations continue to increase, the corrosion rate decreases to a constant value and a phenomenon known as *anode polarization* appears. According to the theory of electrochemistry and the dynamics of chemical reaction, the phenomenon is caused by the combined action of the following factors:

- With an increase in conductivity, ion concentrations also increase; this action blocks the diffusion of oxygen into the water and restrains the depolarization reaction on the cathode, which leads to a decrease in the corrosion rate.
- The generated ferrous ions may conjoin with the hydroxyl ion that is produced by the reduced reaction of oxygen and water and generate a precipitate of $\text{Fe}(\text{OH})_2$. The precipitate will adsorb on the surface of the steel plate (helped by the cooperation of static and stirring), block the subsequent oxidation reaction, and decrease the corrosion rate.
- The ferrous ions, however, have minimal reduction activity during the reaction, and the generated precipitate of $\text{Fe}(\text{OH})_2$ continues to react electrochemically with the dissolved oxygen and produce denser precipitates, such as ferric hydroxide $\text{Fe}(\text{OH})_3$ and magnetite (Fe_3O_4), which deposit on the surface of the steel plate. Because the concentration of the dissolved oxygen decreases during the corrosion reaction of oxygen and steel and the deposited precipitate coating shields the surface of the steel plate, the corrosion rate decreases. These are also the reasons why higher conductivity leads to a decrease in the corrosion rate.

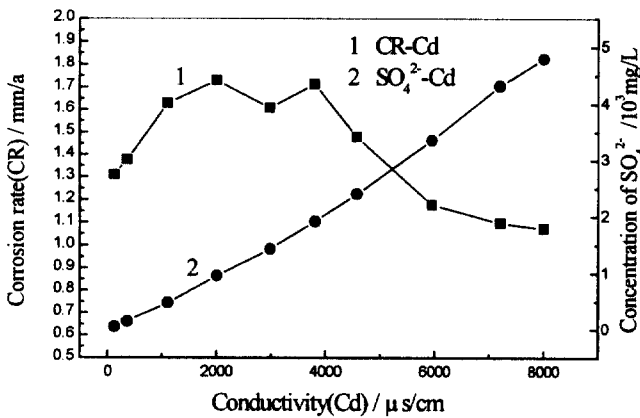


Figure 2—The influence of sulfate on the corrosion rate.

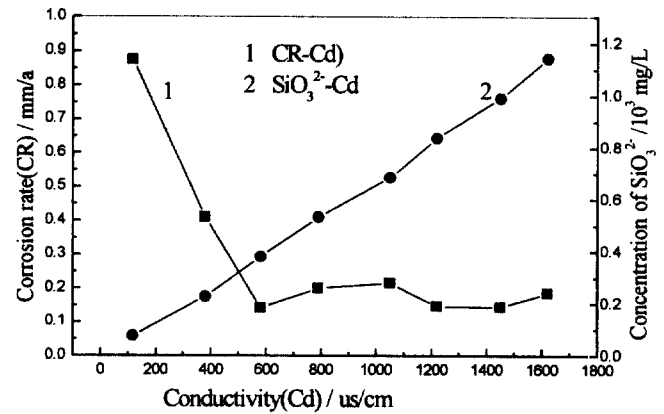


Figure 4—The influence of silicate on the corrosion rate.

Influence of Sulfate, Carbonate, and Silicate. The influence of sulfate, carbonate, and silicate on the corrosion rate was also studied and the results are depicted in Figures 2, 3, and 4. As shown, these ions have an effect similar to that of the chloride ion: the corrosion rate is low at low conductivity, high at intermediate conductivity, and low and constant at high conductivity. Because various ions have different characteristics, the relationship of the corrosion rate to conductivity (expressed as "CR-Cd") is also different. The highest corrosion rate of various ions and their CR-Cd relationships are listed in Table 3.

Silicate is most inclined to form an inactive coating because of its maximum conductivity (Cd_{max}), initial conductivity (Cd_{ini}), and dense coating. Conversely, sulfate has the most difficult time forming an inactive coating and when a coating is formed, it is extremely soft, loose, and unstable. As a result, sulfate has a higher conductivity than chloride but an inferior ability to corrode. While chloride can form a coating to protect the steel at a lower conductivity ($Cd \leq 1550 \mu s/cm$), the corrosion caused by chloride is the most serious because of its strong adsorption to the steel surface.

Multifactor Experiment. The influence of a single factor on corrosion caused by four anions has been discussed through an independent, single-factor experiment. Because the water solution is prepared and the components of the wastewater effluent and experimental conditions are relatively simple, the system is quite different than that for actual wastewater effluents. The multifactor

experiment can deal with a complex water system that contains many ions and the ions have a combined action on the corrosion. These experimental results can be used for practical applications.

According to water quality analysis of the wastewater effluents of the Liaohe Oilfield Petrochemical Corporation, a model experiment for water quality was conducted with calcium, magnesium, chloride, ammonium, and nitrate. First, the influence of changing the concentrations of calcium and nitrate on the steel corrosion rate while fixing the concentrations of magnesium, chloride, and ammonium was studied. (The influence of nitrate is less than that of calcium [Cheng, 1999].) The results are depicted in Figure 5. Second, the concentration of nitrate was varied while the concentrations of calcium, magnesium, chloride, and ammonium were fixed, and results are depicted in Figure 6.

When comparing the experimental results, it is easy to see that corrosion caused by the multifactors exhibited a similar trend to the corrosion caused by a single factor. The corrosion reaction again can be divided into three regions, although the region for the higher corrosion rate occurs at the higher conductivity range because of cooperative action of various ions. In addition, although the ions themselves play a role in increasing the conductivity, the conductivity producing the highest corrosion rate is still low considering the effect of total conductivity produced by various ions. This phenomenon indicates that these ions must have contributed to the corrosion reaction (e.g., the corrosion reaction under the fouling coating). Another interesting phenomenon is that the corrosion rate caused by the multifactors is a little lower than that of the single factor. The primary reason for this may be that the effect by calcium, magnesium, chloride, and ammonia in compensating

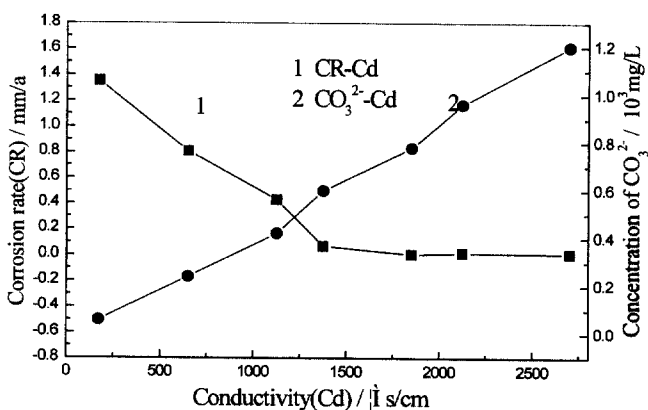


Figure 3—The influence of carbonate on the corrosion rate.

Table 3—The conductivity relative to the highest corrosion rate of various ions and the initial conductivity to form the coating.

	Cl^-	SO_4^{2-}	CO_3^{2-}	SiO_3^{2-}
CR_{max} (mm/a) ^a	2.5100	1.7300	1.3526	0.8757
Cd_{max} ($\mu s/cm$) ^b	298	2000	172.5	116
Cd_{ini} ($\mu s/cm$) ^c	1550	5500	650	600

^a CR_{max} = the maximum corrosion rate.

^b Cd_{max} = the conductivity at the maximum corrosion rate.

^c Cd_{ini} = the initial conductivity to form the coating.

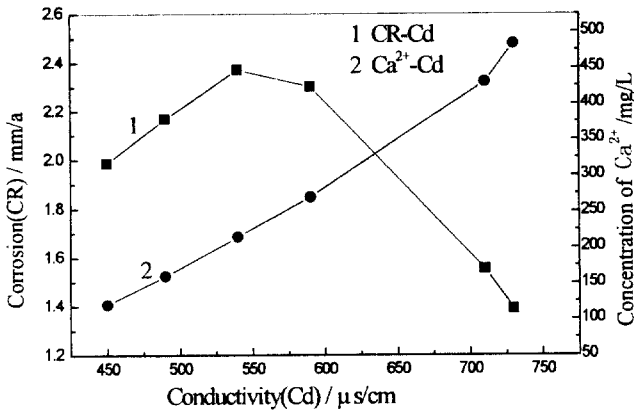


Figure 5—The influence of calcium on the corrosion rate with the existence of magnesium, chloride, and ammonium.

for the decrease of nitrate is less than the decreasing effect of nitrate, and this leads to a decrease in the corrosion rate. Because the existence of nitrate blocks the continuing-to-form corrosive fouling coating caused by calcium and magnesium and improves the intensity of the inactive coating, the cooperation of various ions mitigates the corrosion. In Figure 6, however, the corrosion rate is still high when the conductivity is less than 1200 $\mu\text{s}/\text{cm}$. In this stage, the concentration of nitrate is low, calcium and magnesium make the primary contribution to corrosion under the fouling coating, and chloride plays a role in point corrosion. Because calcium, magnesium, and chloride have strong corrosive abilities, it is necessary to remove these ions when deeply treating water of such low conductivity (Mujeriego and Asano, 1999).

Complex-Water Experiment. The corrosion experiment was carried out using wastewater effluents from Liaohe Oilfield Petrochemical Corporation as basic experimental water and amended by sodium nitrate, whose ion has little corrosive ability. The results of the experiment are depicted in Figure 7.

The CR-Cd line in Figure 7 shows that the corrosion trend belongs in the high conductivity range. In the high conductivity range, the diffusing rate of the dissolved oxygen is the key factor.

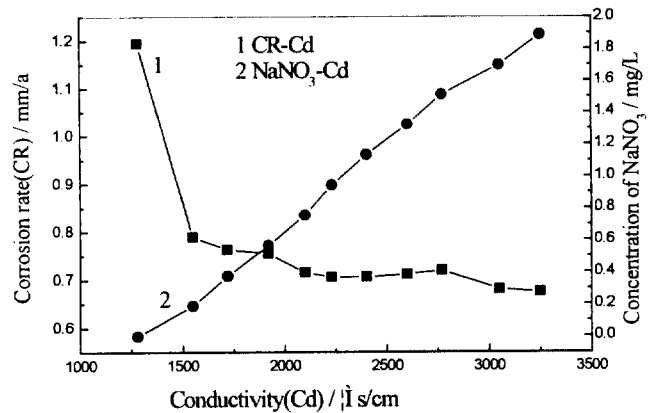


Figure 7—The influence of sodium nitrate on the corrosion rate of the wastewater effluents of Liaohe Oilfield Petrochemical Corp.

In this experiment, however, nitrate shows a strong ability in mitigation of corrosion. This phenomenon indicates that nitrate may cooperate with various ions in a complex water system and form a double protective electrical layer on the surface of the steel plate; this protective layer polarizes the anode. When a small amount of nitrate is added, the corrosion rate immediately decreases from 1.20 mm/a to 0.80 mm/a, then further attenuates by 0.12 mm/a as nitrate addition continues. Therefore, the final corrosion rate of carbon steel in a complex environment depends on the combined competitive effect of the cooperation of various ions, the diffusion rate of the dissolved oxygen, and the structure and generating rate of the inactivating coating. The ions have the most important contribution to corrosion because various ions have different characteristics in terms of adsorption, corrosive ability, and destructive effect on the inactivating coating, which leads to different corrosion rates.

Conclusions

The corrosion rate of carbon steel exhibits two trends: The corrosion rate is high at low conductivity, increases to a maximum, and then decreases and becomes stable with increasing conductivity, as in the case with chloride, sulfate, nitrate, and calcium. Alternatively, the corrosion rate of carbon steel is highest at low conductivity and then decreases and becomes stable with increasing conductivity, as in the case with carbonate, silicate, and sodium nitrate. In the initial stage of the first trend, reaction of the ions, is considered to be controlling. The carbon steel is actively dissolving and the corrosion rate increases with increasing conductivity at low conductivity values. Subsequently, the corrosion rate reaches a maximum value and enters a region characterized by oxidizing and inactivating coatings. In this stage, the coating is formed and blocks the reaction on anode. Therefore, the corrosion rate decreases with increasing conductivity and finally achieves a stable value. The second trend shows the highest corrosion rate at low conductivity for the same reason as the initial stage of the first trend. The rate decreases with increasing conductivity and finally achieves stable value because of the characteristics of ions.

When considering industrial applications, wastewater effluents can be used for circulating cooling water. However, in addition to anticorrosion treatment (especially the pretreatment of low-conductivity water using air flotation and clarification [Smith and

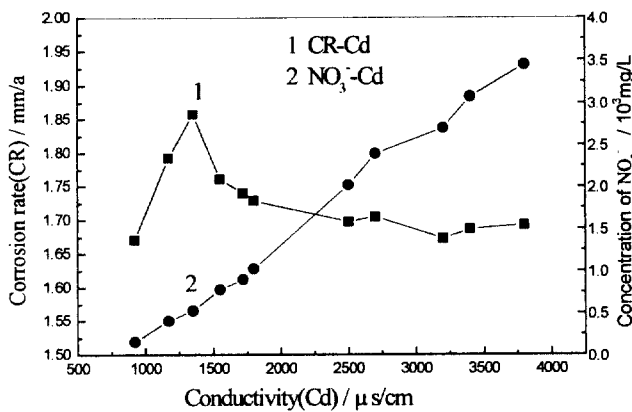


Figure 6—The influence of nitrate on the corrosion rate with the same concentrations of calcium, magnesium, chloride, and ammonium.

Walker, 1994] to decrease conductivity), the chloride, calcium, and carbonate must be reduced to suitable concentrations to ensure the anticorrosion levels.

Significantly reducing the salt concentrations or conductivity of the water by osmosis or ion exchange to obtain an anticorrosion effect when reusing wastewater effluents as circulating cooling water is not a perfect or economical pretreatment method because the corrosion rate does not increase linearly with increasing conductivity. However, in the high-salinity region, the corrosion rate of steel plate decreases to a stable stage. Although the cost of using inorganic salts to treat the wastewater may be high, the salts are not lost through evaporation and can be reused indefinitely. As a result, the average annual operating costs can be reduced to an acceptable level. However, the scaling tendency of salts should be considered as it is a safe and effective measure to add corrosion inhibitors and biocides for the pretreatment of wastewater. On the other hand, adding salts to increase the salt concentration must be studied along with the effect of the fouling inhibition.

Acknowledgments

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