Corrosion Risk Assessment and Failure Analysis in Industrial Water Systems

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ABSTRACT

Industrial water system components are at increasing risk of damage due to corrosion and metal loss as they get close to the end of their design life or if the system exhibits any of the following: accelerated corrosion, perforation, deposit build up (plugging), discoloration, and excessive attack due to corrosive bacteria.

The purpose of this paper is to provide failure analysis case histories on corrosivity, pitting tendency and the risk associated with corrosion activity in industrial water systems. Failure analysis methods, failure mechanisms, primary cause and sources of corrosion attack with recommendations are described at the end of each case history. Corrosion mitigation recommendations and risk ranking is based on many years of experiences and water system studies in industrial water systems.

Keywords: corrosion risk, inspection, failure analysis, industrial water systems, corrosion mitigation, corrosivity, pitting corrosion.

INTRODUCTION

Corrosion is defined as degradation of materials due to reaction with environment. The corrosion of metals can be broken down into several simple processes that must occur in series, the anodic reaction, cathodic reaction, electron migration through the metal and ions leaving the metal surface and going into solution all occur simultaneously. At its root, corrosion protection of pipes, as with all corrosion protection, is aimed at suppressing one of these elements. Corrosion is accelerated by low pH, corrosive bacteria, dissolved oxygen, high flow rate, galvanic action, high water temperature, high corrosive ion concentrations (chlorides and sulfates…), stagnation, high carbon dioxide, high oxygen and high suspended solids.

In general, the steps and/or strategies for developing corrosion control program are: 1-5

1. Develop and understand water related corrosion concepts and mechanisms
2. Determine the severity of the corrosion
3. List possible causes of corrosion
4. Develop a list of possible corrosion control alternatives
5. Develop a corrosion control strategy or treatment
6. Implement the treatment or program
7. Monitor the effectiveness of the program
8. Modify and optimize the program based on corrosion monitoring

The most common techniques for corrosion control are: 6-13

1. Adequate system design and proper materials selection
2. Modification of water chemistry, removal of corrosive ions and adjusting hardness
3. Use of corrosion inhibitors
4. Application of protective coatings, linings and paints
5. Design and implement cathodic protection for tanks and vessels
6. Corrosion monitoring
7. Preventive maintenance

In this paper, we presented two case studies regarding corrosion problems in the industrial water systems. Through those case studies, we can get to know how important to apply advanced corrosion technologies to failure analysis in order to fully understand the corrosion mechanism in the industrial water systems as well as to know what steps we should take in order to effectively mitigate the corrosion.

CASE STUDY 1: METALLURGICAL CORROSION FAILURE ANALYSIS FOR APPLICATION IN THE ELECTRIC POWER GENERATION STATION

The travelling screens were reported damaged at various locations down the East River in Queens, New York City after exposure to the salt water intake systems of electric power generation station. The travelling screen system was installed in the building about 46 years ago and has not experienced any problems until as recently as one year ago. The biocide chemical sodium hypochlorite has been added to the water circulating system since 2011. Our investigations indicated that the existing bleach-based (sodium hypochlorite) biocide feeding system didn’t function properly in the salt water intake systems. Instead, the biocide chemical sodium hypochlorite in the system has extensively attacked type UNS S31600 stainless steel traveling screens and caused the severe corrosion damage. This is an example to show how incorrect approaches to the corrosion problems in the industrial water systems can cause further corrosion damages.

Background

The biocide chemical sodium hypochlorite has been added to the water circulating system as biocide four times per day. The new rotation screen systems were made of UNS S31803 duplex stainless steels and installed recently. All other screen systems were made of type UNS S31600 stainless steels. In this case, laboratory analysis and onsite investigations have been conducted in order to fully understand the corrosion mechanism. The analysis results, conclusions and recommendations are described in detail on the following pages.

Laboratory Root Cause Analysis

In order to determine the corrosion mechanism of traveling screen damage, visual examination, metallographic examination, scanning electron microscopic examinations with energy dispersive X-ray spectroscopy (SEM-EDS) and chemical analysis have been employed for the required analysis.

Four corroded metal frame samples #1–4 from damaged traveling screen #52 and 2 liters of contaminated water sample have been received for laboratory corrosion failure analysis & testing. As-received photograph, SEM-EDS analysis and water chemistry analysis results are presented in the following Figure 1 and Table 1, respectively. Visual examination indicated the directionality of corrosion pits, the pit morphology and pits being present on one side only (see Figure 1(a)). Detection of chlorine (Cl)
element by SEM-EDS indicated the presence of corrosive chloride (Cl\(^-\)) ions inside the pits. Possible sources of corrosive chloride (Cl\(^-\)) ions are biocide hypochlorite and/or sodium chloride salts. Water chemistry analysis results indicated that the water was corrosive due to high concentrations of chloride ions and high total dissolved solids (TDS) and high conductivity.

Figure 1: Photographs of traveling screen sample #1 (a) and SEM-EDS spectra of pitted hole area (b) and water residues (c).

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Result</th>
<th>Unit</th>
<th>Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride</td>
<td>14,000</td>
<td>mg/L</td>
<td>9056A, Anions, IC</td>
</tr>
<tr>
<td>Sulfate</td>
<td>1,900</td>
<td>mg/L</td>
<td>9056A, Anions, IC</td>
</tr>
<tr>
<td>Nitrate as N</td>
<td>1.0</td>
<td>mg/L</td>
<td>9056A, Anions, IC</td>
</tr>
<tr>
<td>Calcium</td>
<td>310</td>
<td>mg/L</td>
<td>6010C, Metals ICP</td>
</tr>
<tr>
<td>Copper</td>
<td>Not Detected</td>
<td></td>
<td>6010C, Metals ICP</td>
</tr>
<tr>
<td>Iron</td>
<td>76</td>
<td>mg/L</td>
<td>6010C, Metals ICP</td>
</tr>
<tr>
<td>Magnesium</td>
<td>960</td>
<td>mg/L</td>
<td>6010C, Metals ICP</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.44</td>
<td>mg/L</td>
<td>6010C, Metals ICP</td>
</tr>
<tr>
<td>Potassium</td>
<td>300</td>
<td>mg/L</td>
<td>6010C, Metals ICP</td>
</tr>
<tr>
<td>SiO(_2), Silica</td>
<td>2.5</td>
<td>mg/L</td>
<td>6010C, Metals ICP</td>
</tr>
<tr>
<td>Sodium</td>
<td>7,200</td>
<td>mg/L</td>
<td>6010C, Metals ICP</td>
</tr>
<tr>
<td>Total hardness</td>
<td>4,700</td>
<td>-</td>
<td>SM2340B- total hardness</td>
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<tr>
<td>Total alkalinity</td>
<td>110</td>
<td>-</td>
<td>General chemistry</td>
</tr>
<tr>
<td>Bicarbonate alkalinity</td>
<td>110</td>
<td>-</td>
<td>General chemistry</td>
</tr>
<tr>
<td>Total Dissolved Solids (TDS)</td>
<td>27,000</td>
<td>mg/L</td>
<td>General chemistry</td>
</tr>
<tr>
<td>pH</td>
<td>6.65</td>
<td>SU</td>
<td>General Chemistry</td>
</tr>
<tr>
<td>Specific Conductance</td>
<td>40,000</td>
<td>µS/cm</td>
<td>General Chemistry</td>
</tr>
</tbody>
</table>
It can be seen that severe corrosion pits/pitted holes are elongated or lined up along one direction in the traveling screen sample. SEM-EDS analysis of pitted hole area in the traveling screen sample and water residue sample, showing corrosive compounds containing chloride(Cl\(^{-}\)).

**Field Evaluation**

In order to further determine the root causes of the traveling screen failures, on-site corrosion assessments have been performed at the facilities which include four drain systems, biocide feeding system and a control room in a pump house and traveling and rotation screens. The on-site corrosion assessment includes visual examination, observations, photographic documentation, stray current and potential measurements and water sampling.

It was found that the existing bleach-based (sodium hypochlorite) biocide feeding system didn’t function properly in the salt water intake systems. As can be seen in Figure 2, bio-film was observed in all the water circulating systems including UNS S31600 stainless steel drains and screen systems and newly installed duplex stainless steel rotation screen systems.

![Figure 2: Photographs of brown colored biofilm on the newly installed duplex stainless steel rotation screen #32. The formation of bio-film in the new rotation screen #32 indicates that the existing biocide system didn’t effectively kill microbes.](image)

It is most likely that the use of sodium hypochlorite in water circulating system is a primary cause of traveling screen damage. This has been confirmed by the laboratory evaluation and the experimental details can be found in the next session. In general, the hypochlorite ion (OCl\(^{-}\)) is very aggressive and dangerously pitting corrosion hazardous to stainless steels. Pitting or crevice corrosion can occur on most stainless steel grades in a 5% solution at ambient temperatures. There is an additional risk for stress corrosion cracking (SCC) at higher temperatures. Stainless steels should not be used with hypochlorite solutions greater than 5%.

Potential measurements indicated that water circulating system and traveling screens were not protected against corrosion. They include four stainless steel drain systems, four stainless steel traveling screens and four UNS S31803 duplex stainless steel rotation screens. Consequently, they are at high risk of corrosion due to presence of sodium hypochlorite in the water system. No significant current was detected in any of water circulating systems, drain pump system and traveling screen systems, indicating no stray current corrosion.

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Laboratory Evaluation to Understand Corrosion Mechanism

The similar corrosion pitting damage as observed on the traveling screens has been recreated at the laboratory by immersing type UNS S31600 stainless steel coupons in the provided concentrated sodium hypochlorite (15 wt.%, pH=7) at room temperature for 36 hours. In a comparison, no or negligible corrosion was observed in the stainless steel test coupons after 36 hours exposure to 3.5% (wt.) sodium chloride salt solution. SEM micrographs of exposed coupons indicated that there were similarities in pit morphology between exposed UNS S31600 test coupons at our laboratory and damaged travelling screen #52 in the field, as shown in Figures 3.

Figure 3: SEM micrographs of severe corrosion pits in UNS S31600 stainless steel test coupons after 36 hour immersion exposure to the concentrated sodium hypochlorite. There is similarity in pit morphology between UNS S31600 stainless steel test coupon and corrosion damaged traveling screen #52.
Conclusions from Case Study 1

Based on on-site and laboratory evaluation, it is most likely that severe corrosion damages of type UNS S31600 stainless steel traveling screens have been primarily caused by exposure to the corrosive compounds of sodium hypochlorite from the existing biocide system.

Our investigations indicated that bleach-based (sodium hypochlorite) biocide system didn’t function properly in the salt water intake systems, and as a result, the stainless steel traveling screen surfaces showed bacterial biofilms and noble potential relative to saturated calomel electrode (SCE). It is also noted that traveling screen system has worked very well for nearly 40 years until application of biocide chemical hypochlorite in 2011. Therefore, microbially induced corrosion (MIC) would be considered causing minor damage to stainless steel traveling screens.

Recommendations from Case Study 1

1). Corrosion Testing and Monitoring

Considerations should be given to laboratory corrosion testing and on-site corrosion monitoring in order to determine the best methods for corrosion mitigation and this includes long-term (e.g. 8 weeks) corrosion testing of UNS S31600 stainless steel, duplex or super duplex stainless steel in the sodium hypochlorite solutions, installation of corrosion sensors and deposit sampling and analysis to identify the change in microbial activities as well as PMI testing. On-site corrosion monitoring will be conducted with or without bleach-based (sodium hypochlorite) biocide system. In addition, a CP system should be reviewed and re-designed, considering alternate immersion of the system.

2). Corrosion Mitigations

Based on above the test data and results, we recommended the following.

- Use a suitable, effective, non-corrosive and cost-effective alternative disinfectant system in place of existing bleach-based biocide system in order to effectively kill microbes and minimize corrosion damage to traveling screen system. Possible biocide candidates are peroxide, bromine chemistry, ozone and non-oxidizing biocide, etc. Any new biocide chemical candidates should be tested before their application.
- Select high corrosion resistant materials including super duplex stainless steels (e.g. UNS S32750 & UNS S32760). New alloy candidates should be tested in the sodium hypochlorite solution before application.
- Select and apply suitable coatings for protecting the structures above the water.
- Install more effective CP systems.

CASE STUDY 2: CORROSION TESTING AND ANALYSIS, METALLURGICAL CORROSION FAILURE ANALYSIS AND SELECTION OF CORROSION INHIBITORS FOR OIL-FIELD APPLICATION

Severe corrosion damage and a significant wall thickness loss was reported at the high pressure side of the piping, elbows and valves at the double-well facilities in a short time period of 57 day service due to pitting and uniform corrosion. No corrosion protective measures including corrosion inhibitors have been applied to any of those UNS G41300 low steel components, except for water treatment. It has been speculated that the water treatment was a suspected cause of component corrosion damage at the double-well facilities. This has been proved wrong based on our investigations. Finally, we tested and identified the best candidate corrosion inhibitor which can provided the greatest protection of UNS G41300 alloy piping against corrosion in contact with high chloride environment. This is an example of
the misunderstanding of the corrosion mechanism and lack of proper corrosion protection in the oil-field application.

**Background**

This is a double-well facility located at Barnhart, TX. Various equipment components at high pressure side including UNS G41300 low steel pipes, elbow pipes and valves had experienced corrosion damage in a short time period of 57 days' service. There was a water treatment system which was suspected to cause severe pitting corrosion damage. No corrosion inhibitors were applied to any of components at the double-well facilities. In order to determine the root causes, sources and protection measures of component failures, laboratory analysis and testing and onsite inspection have been conducted.

**Field Evaluation**

In order to understand the corrosion mechanism and corrosion sources, onsite corrosion inspection of various equipment components at Barnhart, TX, has been performed. During a site inspection visit, we had conducted non-destructive ultrasonic thickness (UT) measurements and visual examination of corroded piping and elbow sections at the backyard of facilities at the oil-well sites, water treatment system, work tanks, blends and piping systems. Fluids in acid tanks and blends and additional water samples from the different stages of process were collected for further lab analysis. Iron piping sample sections have been removed for the required analysis at the laboratory, and they include pipe, elbow and valve sections and tank hose connections.

The on-site UT inspection and visual examination indicated the severe pitting corrosion observed in the piping and elbows and high wall thickness loss of elbow sections during the short service time, as shown in Figures 4-5. The pitting corrosion played a major role in the corrosion damage of 4” alloy steel tubes after 57 days of service, with minor wall thickness loss (≤2%) found in the corroded tube section. For the elbow sections, both pitting and flow-induced corrosion occurred after 57 days of service and approximately 50% wall thickness loss was found in the worst elbow section. For the valve components, severe damage was found on the ID surfaces, resulting in 78% wall thickness reduction.

![Figure 4](image)

Figure 4. Photographs of new pipe section (a) and used pipe sections (b). Randomly distributed corrosion pits are visible on the inside diameter surface of the used pipe section.
Laboratory Root Cause Analysis

In order to determine the root causes of component corrosion failure, we have conducted laboratory corrosion testing of UNS G41300 low steel in treated and untreated water samples, corrosion failure analysis of various equipment components and corrosion testing/analysis of acid/fluid samples obtained from oil field. Laboratory corrosion failure analysis and testing techniques include visual examination, pipe wall thickness measurements, chemical analysis of piping materials, SEM-EDS analysis, Fourier transform infrared spectroscopic (FTIR) coating analysis, metallographic examination, microhardness measurements, pH measurements and chemical analysis, instantaneous corrosion rate monitoring and corrosion pit evaluation.

Two major corrosion mechanism of chloride pitting corrosion and erosion-corrosion was found dominant on the inside diameter surfaces of piping system and valve parts. All the acid/fracture fluids analyzed are very corrosive to carbon steel. Acid fluids from acid tank have low pH and high content of chloride and they are very corrosive to carbon steel if steel piping system is not protected. Fracture fluid/blender has neutral pH, but the presence of high concentration of chloride may lead to pitting corrosion damage on the inside diameter surface if protection measures are not made.

Severe pitting corrosion was observed in the piping and elbows and high concentration of chlorine was detected at the bottom of pits, as shown in Figure 6. It is most likely that accelerated corrosion has been taking place in the piping and elbows as a result of high concentrations of chloride ions in water. The presence of elevated levels of the chloride ions in both treated and untreated water is the primary cause of accelerated corrosion. Water treatment technologies provided by the client didn’t accelerate pitting and flow-induced corrosion based on measured corrosion rate and corrosion pit depth. Further testing of inhibitors will determine optimum concentration that provides the highest protection and if the corrosion inhibitor injected is adequate for this water system.
Figure 6: SEM images of cross section cutting through corrosion pits on the piping ID surface, showing the presence of high concentration of chloride ions up to 4.7% at the bottom of corrosion pit. This suggests that chloride ions are major sources of pitting corrosion observed in the piping section.

Conclusions from Case Study 2

The treated water samples didn’t exhibit any signs of accelerated corrosion and any additional corrosiveness to carbon steel, when compared to untreated water sample. Damage to steel pipes was from flow-induced corrosion and chloride-induced pitting corrosion. Pitting corrosion was a result of high concentrations of chloride ions present in water, where no corrosion inhibitor was used. The water treatment process provided by the client did not contribute or accelerate the corrosion observed in this system.
Laboratory Corrosion Testing to Test Validity and Reliability of Corrosion Inhibitors

Since chloride pitting corrosion is a major concern for corrosion damage of UNS G41300 alloy steel pipes with flowing blender, corrosion inhibitors can provide the best protection of UNS G41300 alloy steel pipes against corrosion. In general, an addition of corrosion inhibitors to downstream of UNS G41300 alloy pipes is cost effective way to greatly reduce corrosion pit damage. Based on our research, we selected the following five (5) different candidate corrosion inhibitors that meet a desired corrosion inhibition target for the operating parameters of for UNS G41300 alloy steel pipes.

After further review of product data sheet, MSDS data sheet and test reports, it has been determined that the two corrosion inhibitors VpCl-637* (hereafter called “Corrosion Inhibitor A”) and Corr7466* (Hereafter called “Corrosion Inhibitor B”) are suitable for high chloride environment and both of them are water soluble. Corrosion Inhibitor A is a product of Cortec Corporation. Corrosion Inhibitor A is a combination of vapor phase, neutralizing, and film-forming corrosion inhibitors to combat the broadest range of corrosive attack from moisture and condensation, oxygen, carbon dioxide, hydrogen sulfide, and other corrosive contaminants in natural gas and petroleum. Corrosion Inhibitor B is a product of Clariant Company. It prevents pitting corrosion, provide high temperature protection, high shear protection, high CO\textsubscript{2} and H\textsubscript{2}S protection and top of the line protection. Corrosion inhibitor B is also developed as multifunctional products, increasing efficiency and reducing costs, and in compliance with the most stringent environmental regulations.

Laboratory corrosion inhibitor testing and analysis has been conducted, including immersion testing by weight loss measurements and electrochemical testing of Corrosion potential monitoring and electrochemical impedance spectroscopic (EIS) Measurements.

Immersion testing per ASTM G31 has been performed in the following. 3.6% (wt.) chloride aqueous solution served as a base solution (control solution). UNS G41300 steel coupons were immersed in base solutions with and without addition of corrosion inhibitors, and run in duplicate, to determine weight loss due to corrosion. The coupons, which measured approximately 1 x 2 inches, were cleaned with acetone, weighed and then immersed. After 143 hours of immersion exposure testing, the test coupons were removed from the water samples, cleaned with acetone and a soft bristle brush and re-weighed. Based on the weight loss measurements, the average corrosion rate can be calculated by Faraday’s law. The equation is indicated below.

\[
\text{Corrosion Rate (mpy)} = \frac{(K \times W)}{(A \times T \times D)}
\]

Where:
- \(K\) = a constant (=3.45\times10^{6})
- \(T\) = time of exposure in hours to the nearest 0.01 h,
- \(A\) = area in cm\(^2\) to the nearest 0.01 cm\(^2\),
- \(W\) = mass loss in g, to nearest 1 mg (corrected for any loss during cleaning) and
- \(D\) = density in g/cm\(^2\).

Corrosion potential monitoring and EIS measurements have been conducted in the following. A flat cell was mounted on 3 x 3 inches cut sections of UNS G41300 carbon steels for the purpose of performing standard electrochemical testing. The exposed surface area was approximately 2.1 square inches. For each coupon, the cell was filled with 3.6% chloride aqueous solution with or without additions of Corrosion Inhibitor A and/or B. Data Acquisition/Switch Unit was used for making the electrochemical measurements. Each electrochemical cell was filled with a 40 ml test solution and was electrically connected to a standard calomel reference electrode, a counter electrode of graphite rod and a working electrode to Data Acquisition/Switch Unit. The open circuit potential (OCP) of the coupon was measured

* Trade Name

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versus a saturated calomel electrode (SCE) and recorded continuously for approximately 105 hours. EIS measurements were taken before and after 94 hours of immersion in 3.6% chloride aqueous solution with or without additions of Corrosion Inhibitor A (500ppm) and/or Corrosion Inhibitor B(200ppm). A Gamry® PCI4/750 potentiostat was used to record impedance spectra.

Results

The average corrosion rate of UNS G41300 carbon steels in water samples is presented in Table 2. As can be seen, the lowest corrosion rate and the shallowest corrosion pits were found in test coupons exposed to 3.6% chloride aqueous solution with an addition of 500 ppm of Corrosion Inhibitor A, when compared to test coupons exposed to 3.6% chloride aqueous solution only and/or 3.6% chloride aqueous solution with Corrosion Inhibitor B.

TABLE 2
Immersion Test

<table>
<thead>
<tr>
<th>Water Sample ID</th>
<th>Sample Description</th>
<th>Corrosion Rate C_R (0.025 mm per year (= 0.001 inches per year))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Deionized water without corrosion inhibitor</td>
<td>3.49</td>
</tr>
<tr>
<td>B</td>
<td>Deionized water without corrosion inhibitor</td>
<td>3.61</td>
</tr>
<tr>
<td>E</td>
<td>Deionized water with 20 ppm of corrosion inhibitor B</td>
<td>4.44</td>
</tr>
<tr>
<td>F</td>
<td>Deionized water with 20 ppm of corrosion inhibitor B</td>
<td>3.89</td>
</tr>
<tr>
<td>G</td>
<td>Deionized water with 50 ppm of corrosion inhibitor B</td>
<td>3.54</td>
</tr>
<tr>
<td>H</td>
<td>Deionized water with 50 ppm of corrosion inhibitor B</td>
<td>3.26</td>
</tr>
<tr>
<td>I</td>
<td>Deionized water with 20 ppm of corrosion inhibitor A</td>
<td>3.19</td>
</tr>
<tr>
<td>J</td>
<td>Deionized water with 20 ppm of corrosion inhibitor A</td>
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</tr>
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<td>K</td>
<td>Deionized water with 500 ppm of corrosion inhibitor A</td>
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</tr>
<tr>
<td>L</td>
<td>Deionized water with 500 ppm of corrosion inhibitor A</td>
<td>2.15</td>
</tr>
</tbody>
</table>

Corrosion potential measurements and monitoring indicates that the test corrosion inhibitors are mixed types. Electrochemical impedance spectroscopic (EIS) measurements indicate that corrosion inhibitor A (500ppm) performed the best in high chloride water, and Corrosion Inhibitor B (200 ppm) performed the second, when compared to 3.6% chloride aqueous solution only.

Based on our review of material data and corrosion performance data, laboratory corrosion testing and evaluation of candidate corrosion inhibitors for UNS G41300 alloy piping in contact with high chloride environment, the corrosion inhibitor A performed the best in salt water and it provided the greatest reduction in chloride-induced pitting corrosion.

* Trade Name

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CONCLUSIONS

Two case studies regarding corrosion problems in the industrial water systems have been presented. As can be seen from those case studies, it is important to correctly understand the corrosion mechanism and to take appropriate steps to mitigate the corrosion. Incorrect approaches to the corrosion problems in the industrial water systems (e.g. use of corrosively chemical biocide sodium hypochlorite in the water circulating systems) and/or lack of corrosion protection (e.g. steel pipes in the corrosive water) may result in severe corrosion damages. In addition, it is also important to develop new corrosion-monitoring and corrosion-prevention technologies as the responses to the increasing risks of corrosion damage in the industrial water systems.

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