Desalination and Water Treatment
www.deswater.com

21 (2010) 17–22
September

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doi: 10.5004/dwt.2010.1156

Corrosion failure 90/10 cupronickel tubes in a desalination plant

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Received 12 March 2009; accepted 25 February 2010

ABSTRACT

This paper presents finding of a failure investigation on a heat exchanger tubes in a desalination plant. Fabricated from Type 90-10 copper–nickel alloy, the tubes experienced sever corrosion after one year of operation. Leaks were observed due to pitting attack requiring repairs and eventual replacement of the cupronickel tubes. The cause of the failure was determined by conducting a physical inspection, and performing macro and micro examinations. The failure of the tubes was mainly attributed to the high iron content (up to 6%). The results of the failure investigation are discussed along with corrosion issues that were identified in the associated heat exchanger tubes.

Keywords: 90-10 cupronickel; Seawater; Pitting corrosion

1. Background

Copper-nickel alloys and in particular 90-10 Cu–Ni alloys have been extensively used as condenser and heat exchanger piping materials in marine engineering owing to its characteristic of good thermal and mechanical properties and outstanding resistance to corrosion with superior resistance to biofouling in seawater. The reliability service performance of these material depends largely on its metallurgical properties, design consideration and fabrication procedure. Other factors including seawater temperature, flow regimes, biological activity and the presence of sulfide species or oxidizing compounds are also playing major role in the alloy performance [1–5].

To obtain the high performance achievable from Cu–Ni, particular attention should be given to using alloy compositions which comply to international standards, maintaining flow velocities within accepted limits, avoiding areas of local turbulence and extended exposure to polluted water and ensuring good commissioning/start up practices.

Cupronickel alloys with compositions complying with international standard usually provides low uniform corrosion rates and excellent localized corrosion resistance in marine environment. 90-10 Cu–Ni alloys normally contains up to 2% Fe. The presence of such amounts have been recognized as beneficial effect. The solutionized iron was most beneficial in improving the corrosion resistance [5–9]. On contrast, the addition of iron, in excess of 2 wt% leads to severe segregation, which is detrimental to corrosion resistance of the material [9].

The most common cause of failure in cupronickel alloys is by impingement attack or corrosion-erosion. The 90-10 Cu–Ni alloys are velocity limited as impingement attack occurs when the hydrodynamic effect caused by seawater flow across the alloy surface exceeds the value at which protective films are removed and erosion-corrosion occurs. Thus, these

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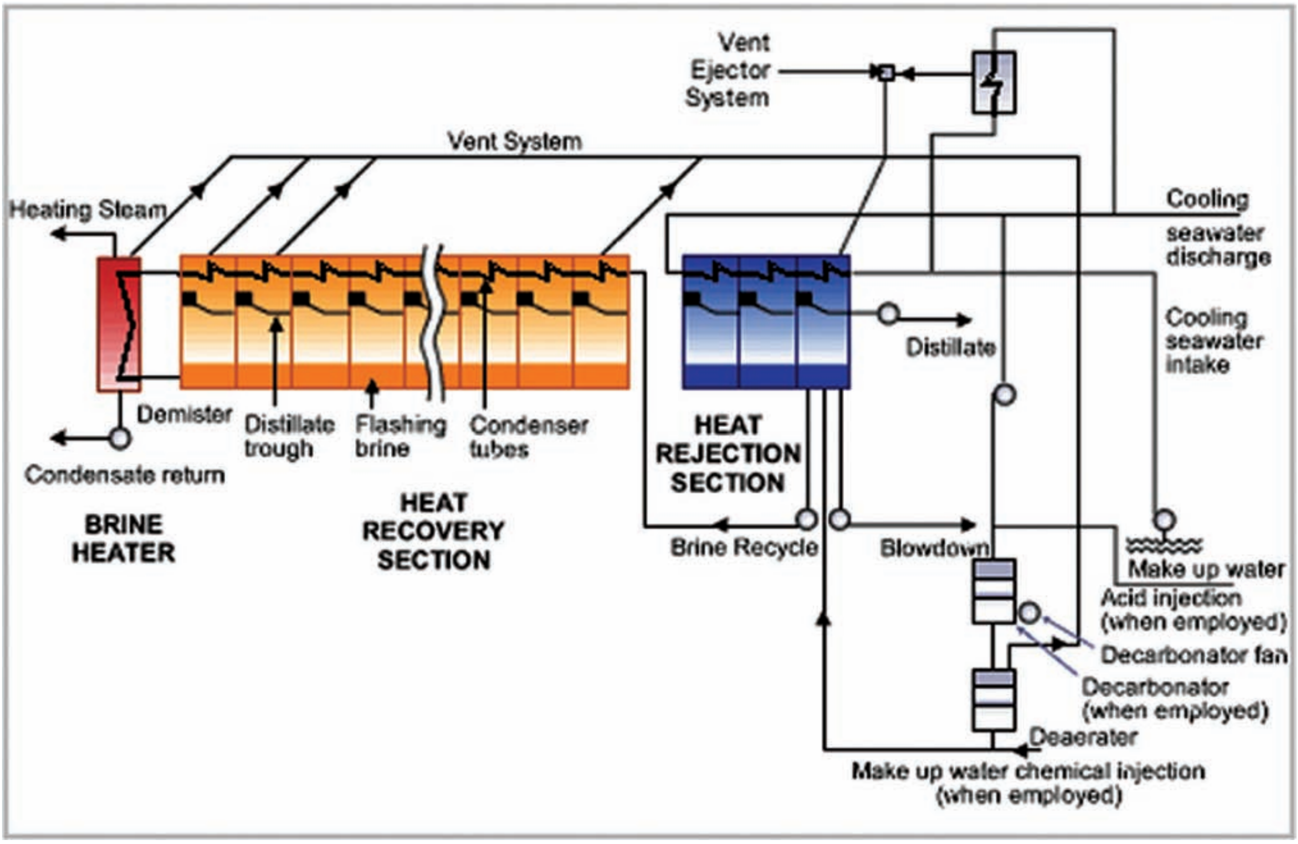


Fig. 1. Simplified flow diagram of a multi-stage flash (MSF) desalination plant.

alloys, if they are to exhibit high corrosion resistance must be used at design velocities below a limiting (breakaway) value [1,5]. Depending on the inner diameter, the maximum flow rates in Cu–Ni 90-10 systems should be conservatively limited to 3.5 m/s [10]. In sea water and water containing high levels of suspended matter, the minimum flow rate should be above 0.5–1 m/s (as it depends on pipe diameter as well) to prevent deposits forming [1].

In this paper a corrosion failure of 90-10 cupronickel heat exchanger (condenser type) tubing materials utilizing seawater of the multi-stage flash (MSF) desalination plant in petrochemical plant in Libya has been discussed. The heat exchanger (part of the heat recovery section, Figure 1) is made of one shell and two tube pass with 729 tube per pass. Each cupronickel tubes has outside diameter of 22 mm and a thickness of 1 mm. Pre-treated seawater (with antifouling and antiscale) flowing inside the tubes with an average velocity of 1.94 m/s and vapor resulting from heating seawater is on the shell side. The exchanger was first introduced to service in 1984 and was subjected to routine maintenance during the normal shut down period through which few tubes were plugged. It was decided to retube the plugged tubes of the heat exchanger in 2002 (after eighteen) years of service with similar material. Surprisingly, the replaced tubes showed severe pitting attack after one year in operation. The cause of failure is investigated and a corrosion mechanism was proposed.

2. Laboratory investigations

Samples from severely corroded heat exchanger Cu–Ni tubes of the desalination unit were received for investigation. Laboratory examination and tests were carried out in order to establish the main cause of failure. These include; visual examination, chemical analysis, ferrite-scope meter, microscopic examination (low magnification upto 40*X*), SEM-EDAX examination.

2.1. Visual examination

Scrutiny visual examination conducted on the received corroded tube samples revealed that the inner part of tubes suffered superficial erosion damage and sever pitting attack of different morphology and size. The pits shape varies from almost hemispherical from small

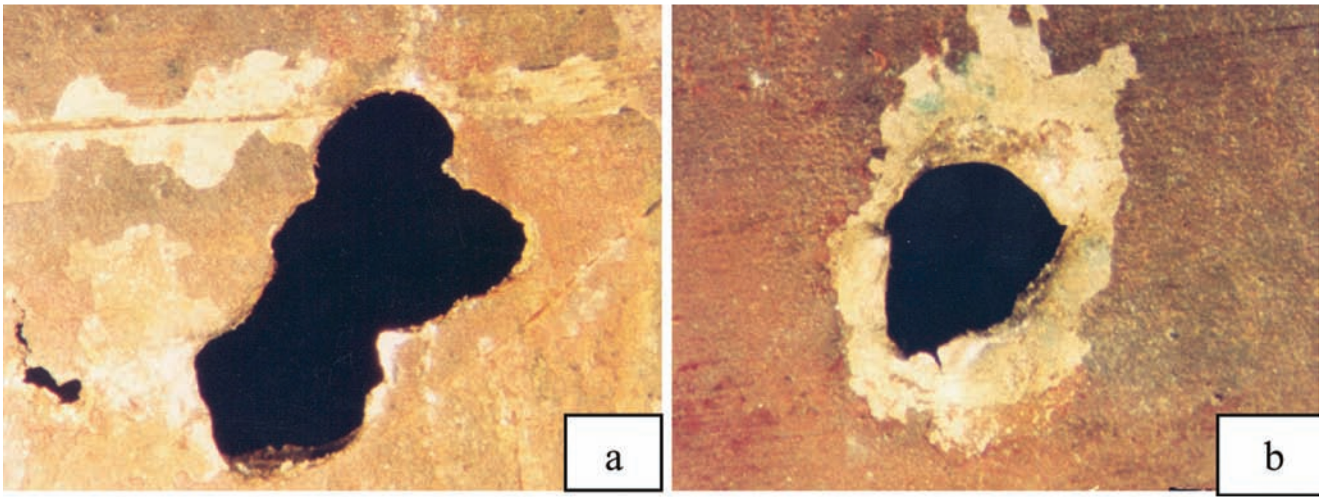


Fig. 2. Isolated pits of different morphology and sizes (on the inner surface of the failed tubes).

size pits to irregular with increased pit size (Figure 2a and b). The extent of the corrosion pits can be observed on the external tube surface. The samples developed discontinuous layers of thick, non-adherent, brown, greenish-brown corrosion product films interspersed with blackish deposits around some attacked area.

In the direction of seawater flow a kind of striation are found. Pitting attack was more pronounced closer to the flow marks (Figure 2a) indicating the role of fluid flow on the pitting process.

2.2. Low magnification microscopy

Results of the microscopic examination (low magnification up to 40X) on the inner part of the tubes are given in Figure 3. Flow groves as a result of high velocity within the tubes were observable around and remote from the corrosion pits. Thick non-adherent corrosion products and scaled deposits of different colors (green, black and brown or mixed) formed around the impingement area were visible. Isolated pits covered with corrosion product appears to form at the flow groves area. The extent of the corrosion damage can be seen from the deep pits that penetrating throughout the pipe wall thickness.

2.3. Chemical analysis

SEM-EDAX was utilized to analyze the chemical composition of the received metal tubes. The results are given in Figure 4. The results revealed that the tubes were made of Cu–Ni most properly 90/10 type. EDAX results showed relatively low Cu content which can be attributed to the fact that Cu usually identified as Cu_2O on the tube surface exposed to air prior to analysis [11].

The most interesting result was the detection of higher iron (Fe) content (up to 6 wt%). This was also confirmed by the ferrite-scope meter. High amount of iron (range of 3–6 wt%), was detected within the examined Cu–Ni tubes.

Figure 4 also showed higher carbon content. This may be attributed to the build-up of scale (carbonate-HCO_3) as a result of CO_2 gas present within the system (dissolved within the water droplet), particularly when the vacuum system working inefficiently [3,4].

2.3. Microscopic examination (SEM-EDAX)

Detailed examination on the failed Cu–Ni heat exchanger tubes was conducted using scanning electron microscopy (SEM). This was done to assist in establishing the corrosion mechanism, corrosion morphology and analysis of the corrosion/scale products.

As can be seen in Figure 5, parallel grooves around the perforated hole (pit throughout the wall thickness) as a results turbulence flow were evident.

The results presented in Figure 6 confirm the involvement of Cu, Ni, Fe, S and Cl in the corrosion deposits. This seems to indicate that the corrosion product deposits consist mainly of cuprous/cupric oxides and iron oxide. The presence of relatively higher sulfur content suggests the involvement of copper sulfide in the corrosion process.

3. Corrosion failure mechanism

In the light of the obtained results the suggested mechanism which led to tube corrosion and failure can be given as follows:

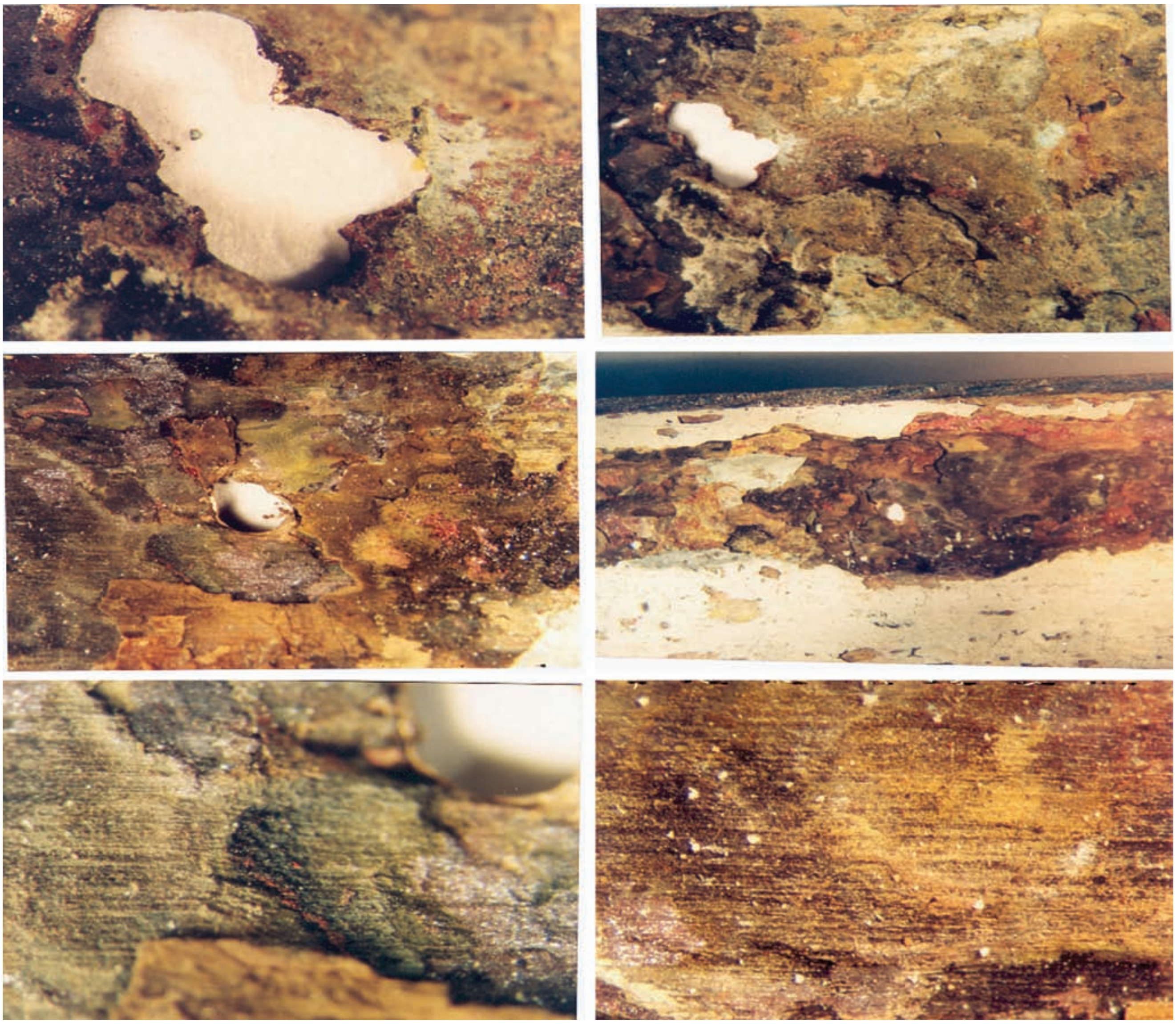


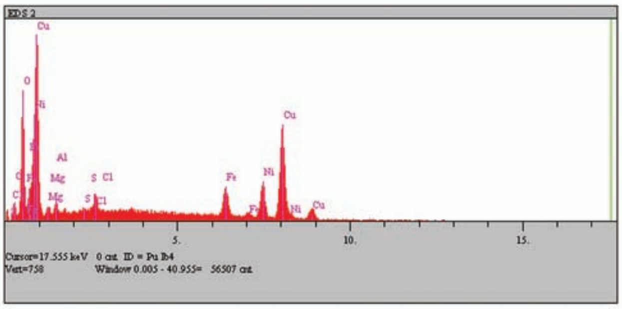
Fig. 3. Microscopic photograph of the inner part of the failed cupronickel condenser tubes (up to 40*X*).

It is well known that Cu–Ni alloys are widely used as piping materials for sea water heat exchangers, due to their attractive performance including anti-fouling properties and excellent resistance to uniform and localized corrosion. In spite of the good properties of the alloy, frequent failures were reported. This was mainly attributed to the composition and production of the Cu–Ni 90-10, occurrence of erosion corrosion and corrosion damage in polluted waters [4,12,13].

History of the failed heat exchanger indicated that the exchanger was working for 18 years with routine maintenance during the shutdown period before it was decided to retube the plugged tubes of the condenser. The new tubes suffered sever pitting attack after one year of service under similar operating conditions. The cause of failure is therefore become unlikely related to the operating condition and thus favor the role tubing material on the corrosion failure.

Typical chemical composition of 90-10 Cu–Ni alloys specifies that iron contents is the range of 1–2 wt%. The addition of iron to copper–nickel has been shown to be beneficial in increasing the strength of the alloy as well as in improving its erosion and corrosion resistance in seawater [5–9]. However, the addition of iron, in excess of 2 wt% to 90Cu–10Ni, is not practical since it leads to sever segregation which is detrimental to the corrosion resistance of the material [9].

In the current case, high iron (Fe) content (well above the design range) was detected both by ferrites-scope meter and SEM-EDAX analysis as shown



Elt.	Line	Intensity (c/s)	Conc	
C	Ka	8.62	7.841	wt.%
O	Ka	94.35	16.211	wt.%
Mg	Ka	6.10	0.642	wt.%
Al	Ka	9.42	0.806	wt.%
S	Ka	2.49	0.153	wt.%
Cl	Ka	16.43	1.037	wt.%
Fe	Ka	37.15	6.063	wt.%
Ni	Ka	45.01	11.704	wt.%
Cu	Ka	125.48	55.543	wt.%
			100.000	wt.%

kV 15.0

Fig. 4. EDX picture and composition of the failed condenser cupronickel tube.

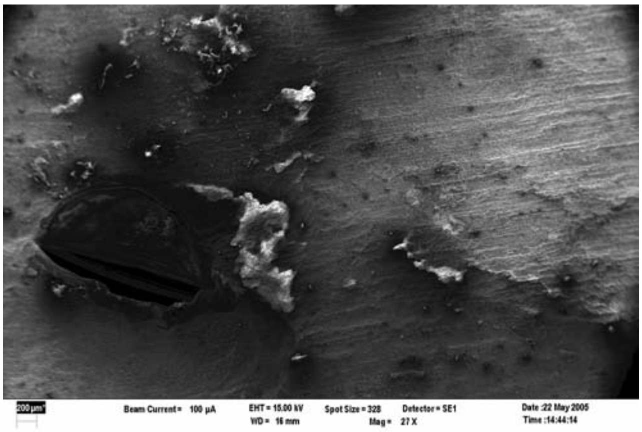
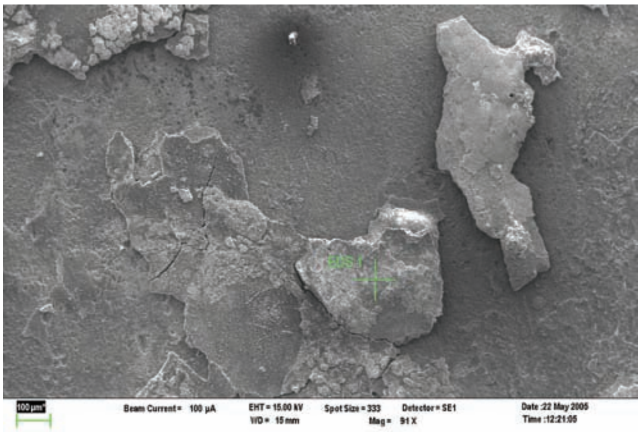


Fig. 5. High magnification image obtained by SEM for the inner part of the failed cupronickel condenser.



Elt.	Line	Intensity (c/s)	Conc	
C	Ka	3.13	3.133	wt.%
O	Ka	204.90	36.337	wt.%
Na	Ka	0.00	0.000	wt.%
Mg	Ka	15.97	1.908	wt.%
Al	Ka	6.55	0.648	wt.%
P	Ka	0.16	0.013	wt.%
S	Ka	1.41	0.103	wt.%
Cl	Ka	8.41	0.636	wt.%
Ca	Ka	1.30	0.114	wt.%
Mn	Ka	1.44	0.246	wt.%
Fe	Ka	11.88	2.302	wt.%
Ni	Ka	9.47	2.660	wt.%
Cu	Ka	95.00	51.900	wt.%
			100.000	wt.%

kV 15.0

Fig. 6. High magnification image obtained by SEM and EDX composition of the corrosion product formed on the inner part of the failed cupronickel condenser.

in the attached tables. The presence of excess iron in the 90Cu–10 Ni causes the formation of iron-rich phase in the grain-boundary network. This, in turn, promotes corrosion of the grain boundary material due to galvanic coupling, leading to localized attack [9].

In the current case the failure of the tubes is probably related to the higher iron content. Corrosion of heat-exchanger tubes seem to be first initiated at heavy iron containing precipitates and the corrosion process is aggravated by the seawater flow. Higher seawater velocity are expected to cause vortices leading to impingement attack which aggravates premature failure.

The formation of corrosion deposits leads to further localized attack. The build up of corrosion deposit may act as obstacles to the flow of seawater. This may create localized turbulence flow and speed up the corrosion process. It has been shown that water passing partial obstructions in a condenser tube can reach 8 m/s, even though the overall velocity in the normal 2 m/s range. This, however, leads to failures in condenser tubes [13].

The development of black friable deposits around the attacked areas along with the presence of small deep pits small and the detection of relatively higher sulfur content in the corrosion product as analyzed by EDX suggests the involvement microbial corrosion activity in the pitting corrosion process. However, the use of chlorination system and the results of the microbiological analysis on black deposits excluded this role. The presence of metal sulfide is probably related to the contamination of seawater with sulfide species. The presence of such species aggravates the pitting corrosion process and hinders alloy passivity. Seawater sample analysis was not provided to verify this point.

4. Conclusion

1. Chemical composition of Cu–Ni tubes was found not in accordance with the international standard. This due to high iron content detected by SEM-EDAX and confirmed by the ferrite-scope meter measurements. Maximum allowable iron content within Cu–Ni alloy is 2.0 wt%. However, high amount of iron (upto 7 wt%) was detected within the examined Cu–Ni tubes.

2. The premature corrosion failure of tubes can be attributed to high iron content. Severe and fast corrosion was initiated at potential sites (iron precipitates). Corrosion deposit was built-up at corrosion sites which in turn acted as obstacles to the flow of seawater. This created localized turbulence flow and speed up the corrosion process.

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