

MICROBIOLOGICALLY INDUCED CORROSION AND IT'S MITIGATION IN COOLING CYCLES

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ABSTRACT: The paper presents the data obtained by monitoring the cooling cycles of different industrial plants: ammonia plants, urea plants, power plants, fluid catalytic cracking units, desulphurization units. The typical bacterial populations for each system type and their action against the equipment are presented. The use of oxidizing and nonoxidizing biocides in cooling water treatment is emphasized.

KEYWORDS: biocides, cooling towers, microbiological control, microbiological induced corrosion, process industries, water chemistry, water treatment

INTRODUCTION

Microbiologically induced corrosion (MIC) refers to corrosion that is influenced by the presence and activities of microorganisms and/or their metabolites. Although MIC is not a form of corrosion, biomass induces and exacerbates other forms of corrosion [1] by secreting cells or enzymes that act like depolarizants, by producing corrosive substances (i.e. CO₂, H₂S, NH₃, mineral and/or organic acids), or by creating a corrosive

environment through establishing the oxygen concentration [2]. There are several potential mechanisms involved in MIC: cathodic depolarization, formation of occluded area on metal surfaces, fixing the anodic sites, under deposit acid attack [3]. In the past decade, frequent cases of MIC of austenitic SS in water have been reported [4, 5].

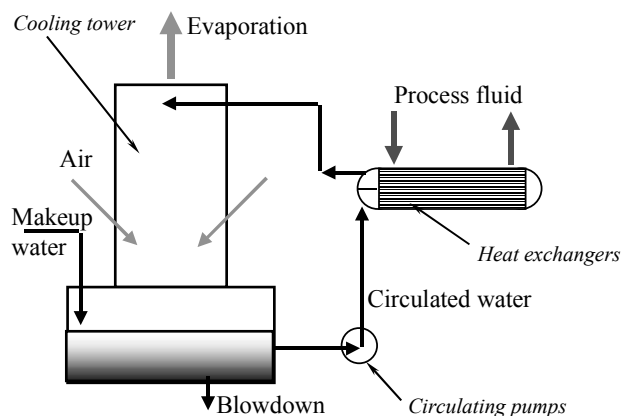


Fig. 1. Evaporative cooling system using a cooling tower

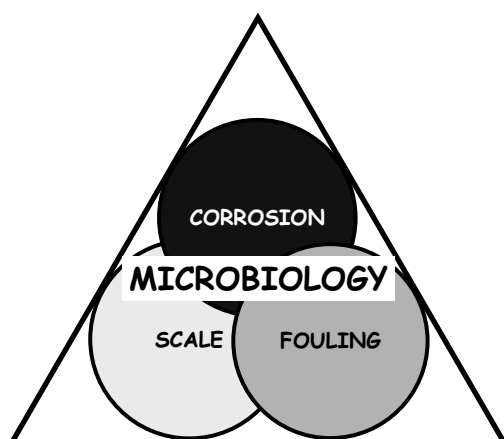


Fig. 2. Interconnection between microbiology, corrosion, fouling and scale

monitored through field and laboratory chemical analyses and with on-line devices. Water pH and conductivity were continuously measured with an on-line LAKEWOOD™ pH/conductivity-meter and a portable MYRON™ pH/conductivity meter. Chemical tests were performed on a HACH DR-2000™ spectrophotometer and a HACH DR-700™ photocolormeter [6]. Total bacterial counts were performed using a BIOSCAN™ counting device and BART™ qualitative tests for biological activity. Continuous on-line corrosion rate and pitting tendency index measurements by linear polarization resistance technique [7] were performed using a CORRATER® remote data collector unit with carbon steel (G10100) probe electrodes flushed by circulating water. Corrosion of mild steel, stainless steel and brass has been evaluated using corrosion coupons placed in a coupon rack connected to the circulated water line [8]. Scaling

Open circulated cooling systems (fig. 1) contain organic and mineral nutrients that provide an excellent environment for bacteria, algae and fungus development. An inappropriate control of these microorganisms leads to biological fouling and corrosion. Even the best corrosion control program can fail if biological growth isn't kept under control. Corrosion, scaling and fouling are interdependent (fig. 2), each of them leading to efficiency decreasing of cooling systems. For an efficient cooling water treatment program, focus on the interdependence between corrosion, scaling and fouling is necessary.

The paper analyses the behavior of several industrial cooling systems, in various operating conditions, with regard to the microbiological activity and its influence on corrosion, fouling and heat transfer effectiveness.

EXPERIMENTAL

During operation of cooling systems, the quality of make up water and circulated water has been

tendency was measured using an on-line electrical heated heat exchanger simulator connected to a computerized DATS™ data acquisition system [9]. Technical characteristics of the analyzed cooling systems are summarized in table 1.

Table 1. Main characteristics of cooling systems

FEATURES	SYSTEM No. 1	SYSTEM No. 2	SYSTEM No. 3
Cooling tower type	mechanical draft	mechanical draft	natural draft
System volume, m ³	5,000	10,000	10,000
Circulated flow, m ³ /h	4,600 – 6,000	13,000 - 17,000	4,800 - 5,000
Cold water temperature, °C	20 – 32	20 - 33	20 – 35
Warm water temperature, °C	25 – 42	25 - 44	25 – 40
Tower temperature drop (ΔT), °C	8 – 15	8 - 15	5 – 7
Number of heat exchangers	22	19	37
Total heat transfer area, m ²	4,000	6,500	7,800
Cooling water flow	tube side / shell side	tube side / shell side	tube side
Maximum water temperature in heat exchangers, °C	45 – 55	45 – 55	55 – 65
Heat exchangers metallurgy	mild steel tubes in mild steel shell stainless steel tubes* in mild steel shell stainless steel tubes** in stainless steel shell brass*** or copper tubes in mild steel shell		

* - S30400; S31600; S31603 austenitic stainless steel;

** - S30400; S30403 austenitic stainless steel;

*** - C44300 admiralty brass

Average values of the chemical composition of make up water and circulated water from the three systems are shown in tables 2 and 3 respectively, together with the most frequent contaminant either from process leakage, either from airborne compounds.

Table 2. Make up water analysis

Component	SYSTEMS No. 1 & 2*			SYSTEM No. 3		
	min.	max.	typical	min.	max.	typical
pH	6.3	8.1	7.7	6.8	8.9	7.9
Conductivity, μS/cm	220	520	340	250	1425	730
“m” alkalinity, ppm CaCO ₃	80	155	125	67	315	155
Total hardness, ppm CaCO ₃	120	210	165	105	435	220
Calcium hardness, ppm CaCO ₃	90	160	120	70	340	170
Total iron, ppm	0.01	0.27	0.08	0.01	0.90	0.09
Chlorides, ppm Cl ⁻	11	36	18	13	684	138
Sulfates, ppm SO ₄ ²⁻	27	268**	42	6	165	61
Silica, ppm SiO ₂	3	12	6	0.5	49	8
Organics, ppm	20	130	38	9	39	18
Suspended solids, ppm	3	78	12	4	122	21

* - System 1 and System 2 use the same make up water source

** - Make up water treated with alum

Table 3. Circulated water analysis

Component	System No. 1		System No. 2	System No. 3
	Controlled pH	Free pH	Free pH	Controlled pH
pH	7.2 – 7.8	7.6 – 8.4	7.0 - 9.0	6.8 - 8.1
Conductivity, $\mu\text{S}/\text{cm}$	362 - 2300	1080 - 2230	1600 - 3300	990 - 3820
“m” alkalinity, ppm CaCO_3	30 - 350	105 – 330	35 - 400	30 - 170
Total hardness, ppm CaCO_3	170 - 685	305 - 775	200 - 650	230 - 1190
Ca hardness, ppm CaCO_3	120 – 550	170 - 700	160 - 500	180 - 875
Total iron, ppm	0.05 – 2.62	0.03 – 0.39	0.03 - 0.76	0.12 - 4.95
Copper, ppb	0 - 39	NA	NA	0 - 7
Chlorides, ppm Cl^-	20 - 320	68 – 260	34 - 224	91 - 671
Sulfates, ppm SO_4^{2-}	70 – 850	60 – 295	75 - 310	75 - 1200
Silica, ppm SiO_2	4.5 – 23	3.8 – 28	NA	7.7 - 65.4
Phosphates, ppm o- PO_4^{3-}	0 – 13.6	2.5 – 8.8	2 - 9.0	0 - 11.3
Molybdates, ppm Mo	0 – 6.9	-	-	0 - 8.7
Suspended solids, ppm	8 – 89	17 – 46	10 - 95	26 - 383
Organic substances, ppm	47 – 465	NA	NA	27 - 134
Ammonium ions, ppm NH_4^+	0 - 77	0.25 – 40	0 - 30.5	-
Nitrites, ppm NO_2^-	0 – 463	0 – 80	0 - 120	-
Nitrates, ppm NO_3^-	0 - 1200	50 – 500	10 - 1000	-

NA - not available

Table 4. Main features of the “Controlled pH” and “Free pH” treatments

Features	Controlled pH	Free pH
pH limits & control	6.8 - 8.0 - addition of 98% sulfuric acid	8.0 - 9.4 - no acid addition
Corrosion control (steel)	- Mineral and organic phosphates: 6 - 9 ppm (as orto-phosphate) - Alkaline molybdates: 3 - 7 ppm (as MoO_4^{2-})	- Mineral phosphates: 3 - 8 ppm (as orto-phosphate) - Zinc: 0.5 - 3.0 ppm
Corrosion control (yellow metals)	- Tolyltriazole: 0.5 - 1.5 ppm	- Tolyltriazole: 0.5 - 1.5 ppm
Scale control	- Phosphonates	- Phosphonates: 3 - 8 ppm (as orto-phosphate) - Polydicarboxylic acids
Dispersing agent	- Nonionic surfactants	- Nonionic surfactants
Microbiological control	- NaClO : 0.2 - 0.4 ppm (as free chlorine) - daily shocks - Glutaric aldehyde: 25 - 50 ppm - monthly shocks	- $\text{NaClO} + \text{KBr}$: 0.2 - 0.4 ppm (as free chlorine) - daily shocks - Bromochlorodimethylhydantoin: 20 - 40 ppm - monthly shocks

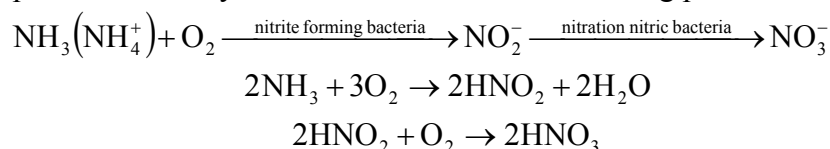
The recirculated water from the cooling circuits is chemically treated in order to avoid scaling and corrosion. The “Controlled pH” treatment denominates a corrosion inhibitor intensive program, meanwhile the “Free pH” treatment denominates a scale inhibitor intensive program (table 4).

RESULTS AND DISCUSSIONS

The type of bacteria found in the cooling circuits depends mostly on the type of nutrients that are present in the recirculated cooling water. The contaminants existing in water may offer to the bacterial populations the necessary nutrients.

Nitrifying bacteria

In the ammonia and urea plants, a common contaminant of the cooling water is ammonia. This contaminant may enter in the cooling circuit either from process fluids - by leakage, either from atmosphere - by absorption (N.B. - ammonia was found also in the cooling circuit of a power plant placed nearby the urea plant). Even small quantities of ammonia (15 ppm) are sufficient for inducing the growth of bacterial mass. The nitrification process is strictly aerobic and follows the following pattern:



In the nitrite production *Nitrosomonas*, *Nitrocystis*, *Nitrospira* and *Nitrosoglea* are involved, meanwhile the nitrite oxidation to nitrate is performed by *Nitrobacter*, *Nitrocystis*, *Bactoderma* and *Microderma* [10]. The optimal conditions for nitrification are: 15 - 400 ppm NH_3 , pH = 7.5 - 8.0, T = 298 - 313 K. The carbon source for the up mentioned bacteria is represented by the carbon dioxide and carbonates dissolved in the cooling water. Figure 3 shows the evolution of nitrites and nitrates concentration in the cooling water and figure 4 shows the corrosion rate and pitting tendency for carbon steel - as monitorized by CORRATER[®]. It can be observed that the increase of nitrate concentration, that denotes an increase of the nitrifying bacteria population lead to corrosion rate and pitting increase.

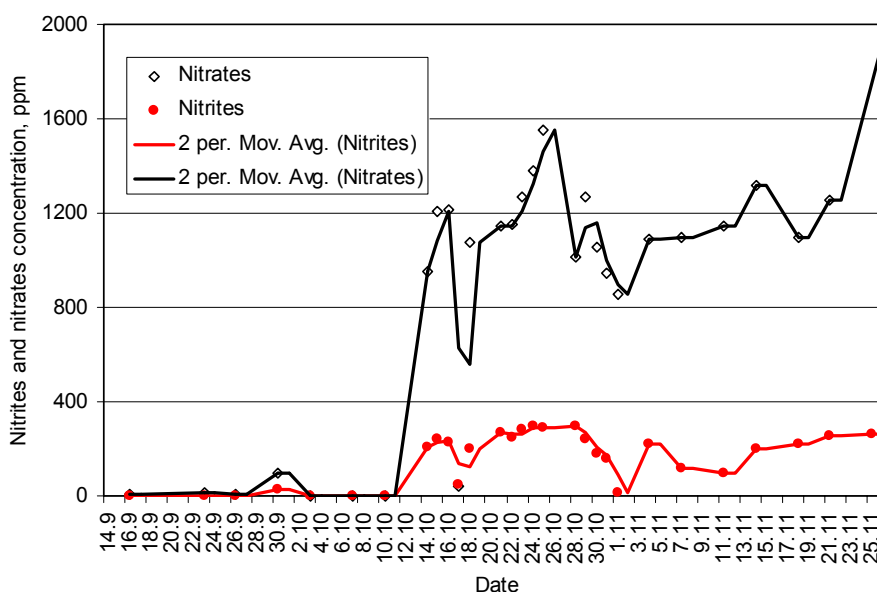


Fig. 3. Nitrites and nitrates in System no. 1 - Controlled pH

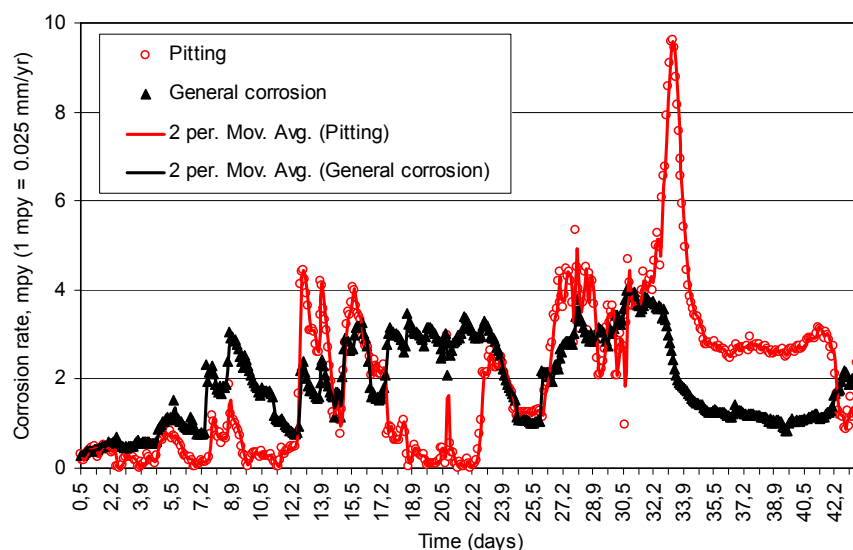


Fig. 4. Corrosion rate and pitting tendency (carbon steel) in System no. 1 – Controlled pH

Sulfate reducing bacteria



Fig. 5. Corrosion due to the SRB on carbon steel

Sulfate reducing bacteria (SRB) are specialized bacteria that in anaerobic environments transform the sulfates into H_2S : *Desulfovibrio*, *Desulfobacter* etc [2, 10, 11].

In the analyzed cooling systems SRB have been reported only in that systems that have been using “Controlled pH” treatment

programs. Due to the use of H_2SO_4 as pH regulator, the recirculated water has an increased content in sulfate ions (850 - 1200 ppm SO_4^{2-}) than in those systems that use no pH regulation (295 - 310 ppm SO_4^{2-}). SRB colonies have been reported in the mud from the cooling tower basin, but also on several corrosion coupons placed in System no. 1. Figure 5 presents the pits generated by SRB colonies on the surface of carbon steel coupons. This hemispherical shape of the pits is particular for SRB [12].

Other bacterial populations

Important developments of **slime forming bacteria** have been reported in system no. 3. In this system the main contaminants from the process side are hydrocarbons (table 3), the cooling system being part of a fluid catalytic cracking (FCC) unit. Bacterial activity produced slimy films in the heat exchangers, thus reducing the heat transfer efficiency (figure 6). A larger amount of dispersing agents and frequent back washing of the heat

exchangers was necessary in order to eliminate the slime and to improve the thermal transfer. Somewhat less quantities of **iron reducing bacteria** have been evidenced mainly in system no. 3 - but also have been reported in systems 1 and 2, regardless of the cooling water type of treatment (table 5). The iron reducing bacteria are mainly responsible for the tuberculation encountered in carbon steel pipes and heat exchangers (figure 7).

Microbiological control

As it has been shown in table 4, each treatment program uses a combination of oxidizing and nonoxidizing biocides in order to keep under control the bacterial growth in the cooling circuits. The total counts expressed as CFU/mL (table 5) indicate a globally satisfactory biological control in all three studied systems.

CONCLUSIONS

Despite this satisfactory control, microbiological induced corrosion (MIC) has not been totally avoided. The main cause of MIC initiation is the local bacterial rapid growth favored by the contaminants from the process, contaminants that played the role of nutrients for several bacterial families: ammonia for nitrifying bacteria, hydrocarbons for slime forming bacteria. On the other hand, even treatment chemicals fed to cooling water (i.e. sulfuric acid) created a proper environment for sulfate reducing bacteria.

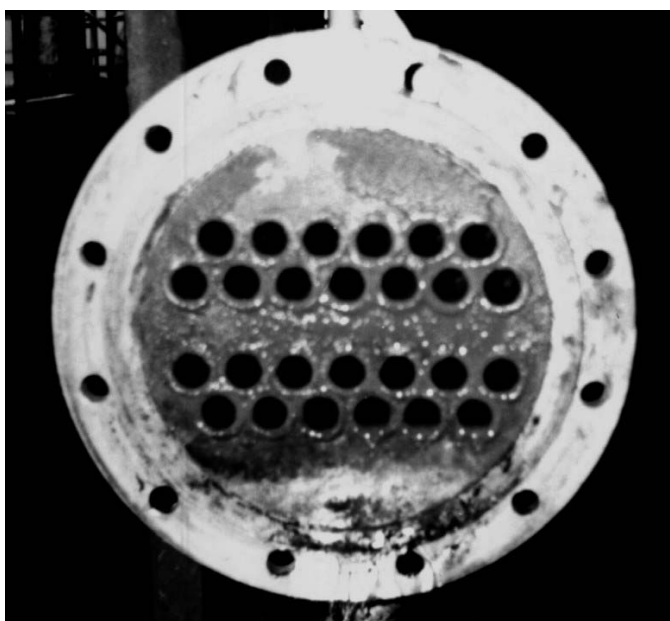


Fig. 6. Slimy film on the stainless steel tubesheet of a heat exchanger



Fig. 7. Tubercles in a recirculated water pipe (System no. 3)

several bacterial families: ammonia for nitrifying bacteria, hydrocarbons for slime forming bacteria. On the other hand, even treatment chemicals fed to cooling water (i.e. sulfuric acid) created a proper environment for sulfate reducing bacteria.

Table 5. Qualitative and quantitative estimation of bacterial populations from cooling systems

Bacteria	System No. 1		System No. 2	System No. 3
	Controlled pH	Free pH	Free pH	Controlled pH
Nitrifying Bacteria	□□□	□□□	□□□	NR
Sulfate Reducing Bacteria	□	NR	NR	□
Slime Forming Bacteria	□	□	□	□□□
Iron Reducing Bacteria	□	□	□	□□
Total counts, min., CFU/mL	10 ⁰	10 ⁰	10 ³	10 ¹
Total counts, max., CFU/mL	10 ⁷	10 ⁵	10 ⁶	10 ⁵
Total counts, typical., CFU/mL	10 ³	10 ³	10 ⁴	10 ⁴

□□□ - frequent in considerable amounts;

□□ - frequent in moderate amounts;

□ - accidental in moderate amounts;

NR - not reported

CFU - Colonies Forming Units

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Received: 08.31.2003

