

Marine Corrosion of Steel with Aerobic and Anaerobic Biofilms under Changeable Nutrient Concentration Conditions

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Abstract: A diffusional model of marine corrosion wear for steel structures is developed and presented in this work, based on the assumption that long-term corrosion depends on both aerobic and anaerobic bacterial activity, which is connected with nutrient changes. This activity of bacteria biofilms is quantitatively evaluated and verified, based on observed data of hydraulic structures of Far East of Russia. It is shown that any short-term increases of nutrients and anthropological pollutant concentrations may significantly accelerate the corrosion rate. Results show that the influence of anaerobic biofilms on the corrosion rate acceleration of immersed steel structures is underestimated.

Keywords: A. Steel; B. Modelling Studies; C. Microbiological Corrosion

1. Introduction

Results of numerous researches suggest that the marine corrosion of steel is strongly associated to the vital activity of bacteria. As previously indicated^[1,2], the long-term corrosion process develops differently than the one of earlier stages. On the early stage, corrosion is controlled by an inflow of dissolved oxygen, while the activity of anaerobic bacteria under corrosion products layer controls the corrosion in later stages.

Usually, hydraulic structures with metal elements have lifetimes much longer than 2-3 years (depending on the absence or presence of protective coatings); consequently, the vital activity of anaerobic bacteria determines the long-term corrosion prediction. Initially, it is necessary to define the factors that have a predominant influence on the growth of bacteria. It has been shown^[1] that temperature and nutrient transfer are the most significant factors. Among groups of nutrients for different species of bacteria, one may include dissolved oxygen and inorganic nitrogen, represented by nitrates, nitrites and ammonium. Inorganic phosphorus and dissolved sulfates are other groups of bacteria nutrients. It is possible to assume that that nutrient group, which possesses the greatest deficit, controls the activity of bacteria.

The problem of water pollution by urban and industrial sewage is the reason of the growth of concentration of inorganic nitrogen and phosphorus in seawater. Hence, the corrosion rate for steel hydraulic structures grows accordingly and depends on zone location^[3]. For long-term forecast, it is necessary to create a model, which takes in account physical and biological factors of marine corrosion in the immersed zone.

Such a diffusional model is developed in the present work, assuming that long-term corrosion depends on both aerobic and anaerobic bacterial activity, which is connected with nutrient changes. Based on recorded data of steel sheet pile walls in ports of Far Eastern Russia, and quantifying the activity of aerobic as well anaerobic bacteria biofilms, it is shown that any short-term increases of nutrients and anthropological pollutants concentrations significantly accelerate the corrosion process.

2. Preliminary data elaboration for corrosion rate prediction

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-Before the actual presentation and validation of the model proposed herein, based on data available from steel sheet pilling walls of ports on the southern part of Far East of Russia, it is considered appropriate and necessary to use these data for the evaluation / prediction of corrosion rate via the model – with linear approximation – recently developed by Melchers^[1].

The data available come from "over the year" recordings of moorings for a lifetime of 0-50 years, and include, among other information, average annual and fixed maximum concentrations of Dissolved Inorganic Nitrogen (DIN) pollutants, given in **Tables 1** and **2** respectively.

XX 7 (A	Annual Av	Average							
Water Area	2009	2008	2007	2006	2005	2004	DIN mg/L		
Golden Horn Bay	0.23	0.278	0	0.154	0.153	0.118	0.1555		
Diomede Bay	0.0856	0.147	0	0	0.149	0	0.0636		
Nakhodka Bay	0.259	0.219	0	0	0.09	0	0.094667		
Table 1. Average annual concentrations of inorganic nitrogen									
TT <i>T t</i> A	Maximun	Average							
Water Area	2009	2008	2007	2006	2005	2004	DIN mg/L		
Golden Horn Bay	0.9	1.4	0	0.572	0.6	0.6	0.678667		
Diomede Bay	0.152	0	0	0	0.417	0	0.094833		
Nakhodka Bay	0.9	0	0	0	0.276	0	0.196		

Table 2. Maximum fixed concentrations of inorganic nitrogen

Fixed maximum concentration exceeds annual average values nearly 3 to 6 times. Defining the lifetime of each structure, for which data is available as t_e , the recordings also contain their corresponding observed average corrosion rate, designated as $c_p(t_e)$, average annual water temperature T_{av} and measured average annual concentration of inorganic nitrogen (DIN), represented by nitrates, nitrites and ammonium. Utilizing the linear model mentioned earlier, with parameters c_s and c_s for fixed temperature conditions (namely T_{av}) the predicted values of corrosion rate $C(t_e)$ is evaluated

for both unpolluted and polluted water conditions. For simplicity, the values of $c_p(t_e)$ are substituted by O, the ones of $C(t_e)$ without pollution by P and the corresponding ones including pollution by P₁. Thereafter, the ratios O/P, O/P₁ and P/P₁ are computed and their distribution is presented graphically throughout Figures 1-6. The available data mentioned above and the intermediate values acquired from the application of the linear model for both cases are contained in Tables 3 and 4.

Name	t _e (years)	T _{av} (⁰ C)	DIN (mg/L)	Water Area	c _p (t _e) (mm) (O)	c _s (mm)	rs (mm/y)	C(t _e) (mm) (P)
Vladprom №1,2 (1)	11	8.8	0.137	Diomede Bay	2.5	0.14	0.047	0.657
Passenger berth (2)	15	8.8	0.137	Diomede Bay	5.1	0.14	0.047	0.845
"Vladprom&K" (3)	23	8.8	0.137	Diomede Bay	1.9	0.14	0.047	1.221
Vladgidrostroy №43 (4)	15	8.9	0.302	Golden Horn Bay	2.7	0.14	0.047	0.845
№43 "Gaidamak" (5)	21	8.9	0.302	Golden Horn Bay	3.9	0.14	0.047	1.127

DBNIGMI №42 (6)	22	8.9	0.302	Golden Horn Bay	4.9	0.14	0.047	1.174
OMIS TOF №1 (7)	37	8.9	0.302	Golden Horn Bay	6.2	0.14	0.047	1.879
OMIS TOF №1 (8)	38	8.9	0.302	Golden Horn Bay	6.9	0.14	0.047	1.926
VSRZ №2 (9)	40	8.9	0.302	Golden Horn Bay	5.6	0.14	0.047	2.02
NRP №1 (10)	4	7.3	0.189	Nakhodka Bay	1.2	0.137	0.043	0.309
NRP №3 (11)	6	7.3	0.189	Nakhodka Bay	1.9	0.137	0.043	0.395
NRP №4 (12)	12	7.3	0.189	Nakhodka Bay	2.4	0.137	0.043	0.653
№2 NSRZ (13)	18	7.3	0.189	Nakhodka Bay	4.05	0.137	0.043	0.911
BAMR-№34 (14)	26	7.3	0.189	Nakhodka Bay	9.1	0.137	0.043	1.255
BAMR-№35 (15)	28	7.3	0.189	Nakhodka Bay	6.3	0.137	0.043	1.341
Nakhodka №47-48 (16)	33	7.3	0.189	Nakhodka Bay	4.5	0.137	0.043	1.556
NSRZ №6 (17)	38	7.3	0.189	Nakhodka Bay	4.6	0.137	0.043	1.771
BAMR-№39 (18)	38	7.3	0.189	Nakhodka Bay	6.4	0.137	0.043	1.771
№5 Transbunker-Nakhodka (19)	39	7.3	0.189	Nakhodka Bay	7.6	0.137	0.043	1.814
BAMR-№38 (20)	39	7.3	0.189	Nakhodka Bay	6	0.137	0.043	1.814
NSRZ (21)	47	7.3	0.189	Nakhodka Bay	3.2	0.137	0.043	2.158
№13 Transbunker-Nakhodka (22)	48	7.3	0.189	Nakhodka Bay	10.6	0.137	0.043	2.201

 Table 3. Predicted (unpolluted condition) and observed corrosion of immersed structures and local dissolved inorganic nitrogen (DIN)

N – WA (Table 3)	From Table 3			— D.C.			C(t _e)	Def	D (
	0	Р	DIN (mg/L)	O/P	cs (mm)	rs (mm/y)	(mm) (P1)	$(mm) \qquad P/P_1 (P_1) \qquad P/P_1$	Ratio O/P ₁
(1)-DB	2.5	0.657	0.137	3.8	0.31	0.048	0.84	1.28	2.98
(2)-DB	5.1	0.845	0.137	6.0	0.31	0.048	1.03	1.22	4.95
(3)-DB	1.9	1.221	0.137	1.5	0.31	0.048	1.41	1.16	1.34

(4)-GHB	2.7	0.845	0.302	3.2	0.52	0.053	1.32	1.56	2.05
(5)-GHB	3.9	1.127	0.302	3.5	0.52	0.053	1.63	1.45	2.39
(6)-GHB	4.9	1.174	0.302	4.2	0.52	0.053	1.69	1.44	2.91
(7)-GHB	6.2	1.879	0.302	3.3	0.52	0.053	2.48	1.32	2.50
(8)-GHB	6.9	1.926	0.302	3.6	0.52	0.053	2.53	1.32	2.72
(9)-GHB	5.6	2.02	0.302	2.8	0.52	0.053	2.64	1.31	2.12
(10)-NB	1.2	0.309	0.189	3.9	0.379	0.045	0.56	1.81	2.15
(11)-NB	1.9	0.395	0.189	4.8	0.379	0.045	0.65	1.64	2.93
(12)-NB	2.4	0.653	0.189	3.7	0.379	0.045	0.92	1.41	2.61
(13)-NB	4.05	0.911	0.189	4.4	0.379	0.045	1.19	1.31	3.41
(14)-NB	9.1	1.255	0.189	7.2	0.379	0.045	1.55	1.23	5.87
(15)-NB	6.3	1.341	0.189	4.7	0.379	0.045	1.64	1.22	3.84
(16)-NB	4.5	1.556	0.189	2.9	0.379	0.045	1.86	1.20	2.41
(17)- NB	4.6	1.771	0.189	2.6	0.379	0.045	2.09	1.18	2.20
(18)-NB	6.4	1.771	0.189	3.6	0.379	0.045	2.09	1.18	3.06
(19)-NB	7.6	1.814	0.189	4.2	0.379	0.045	2.13	1.18	3.56
(20)-NB	6	1.814	0.189	3.3	0.379	0.045	2.13	1.18	2.81
(21)-NB	3.2	2.158	0.189	1.5	0.379	0.045	2.49	1.16	1.28
(22)-NB	10.6	2.201	0.189	4.9	0.379	0.045	2.54	1.15	4.17

Table 4. Predicted (polluted condition) and observed corrosion of immersed structures and local dissolved inorganic nitrogen



Figure 2; Box Plot - Rate of O/P ratio.



Figure 3; Diagram of O/P1 ratio.



Figure 4; Box Plot - Rate of O/P1 ratio.





Comparing the preliminary results reported above, it is evident that for the unpolluted condition case the recorded corrosion rates significantly exceed the predicted ones, since the O/P ratio varies from 1.5 to 7. If pollution is accounted for in the linearized model, the corresponding ratio O/P_1 lies between the values of 1.3 to 6, revealing the same discrepancy. Moreover, predicted rates for polluted and unpolluted conditions (P/P₁) have a difference not greater than 1.2-1.8 times. These findings may, to a certain extent, be attributed to the omission of one or more significant factors in the simulation.

In this work, we suppose that substantial short time increases of pollutant concentrations might induce serious growth of bacterial activity, which dominates corrosion process on later times. The influence of bacterial biofilms, diffusion of nutrients from sea water, and consumption of these nutrients by any species of bacteria are accounted for in the proposed model described in what follows.

3. Proposed diffusion model of nutrients with aerobic and anaerobic biofilms

3.1 General description of the model

It is assumed that marine corrosion of later stages (more than 2-3 years) is primarily dominated by vital activity of bacteria. This activity, obviously, depends on the availability of nutrients, on their diffusion and on the intensity of their consumption by aerobic and anaerobic bacteria. The activity of anaerobic bacteria is the most interesting area for research, because, as assumed, the intensity of corrosion is fully defined by the aforementioned activity on the interface between steel substrate and the anaerobic bacteria biofilm.

The scheme of the proposed marine corrosion model is illustrated in **Figure 7**.



Figure 7; Schematic of the proposed diffusive corrosion model with biofilms.

More specifically, there are three layers between the steel substrate and sea water, namely: (1) aerobic bacteria layer in contact with seawater, (2) corrosion products layer, and (3) anaerobic bacteria layer between the steel substrate and corrosion products layer. It is also assumed that nutrient concentration in sea water is constant.

The first layer is characterized by three parameters; the diffusion coefficient D_1 , the concentration of nutrients C_1 in the layer and the intensity of nutrient consumption therein W_1 . As supposed, the limitative factor of aerobic biofilm growth is dissolved oxygen concentration. According to the model described in^[4], for accepted concentration of dissolved oxygen (7.8 mg/L), the thickness of the aerobic biofilm is equal to h_1 =35.1*10⁻⁶ m. All oxygen is consumed by the layer in given conditions. The existence of anaerobic layer directly under the aerobic one is possible, but this factor has been neglected for simplicity. This simplification is justified though, since any bacteria waste products are more easily transferred to water than through corrosion products to deeper layers via diffusion. Moreover, the surface biofilm is exposed to numerous influences, i.e. it may be damaged, peeled etc., and hence it cannot grow thick.

The second layer of thickness h2 consists of corrosion products. It is assumed that it is the barrier for nutrient transfer to the third (anaerobic bacteria) layer, and is related with the concentration coefficient C_2 and the diffusion coefficient D_2 . The latter is taken equal to $0.8*10^{-12}$ m²/s, a value experimentally obtained for the oxygen diffusion coefficient through corrosion product layer^[5].

The third fully consists of laver anaerobic bacteria, because all oxygen has been already consumed by the first layer of aerobic bacteria. The activity of anaerobic layer is characterized by its thickness h₃, which depends on the quantity of nutrient transfer and the rate of consumption by bacteria; this layer controls corrosion rate on later stages. It is necessary to determine the dependence of h₃ on incoming nutrients, because this will allow the evaluation of the volume of active bacteria and, consequently, the determination of the volumes of their waste products, which are the main cause of corrosion. For this layer, C_3 is the concentration of nutrients, and W₃ is the consumption rate of nutrients, while D₃ is the diffusion coefficient.

3.2 Model description and mathematical formulation

The model is described by the system of 2nd order ordinary differential equations of stationary diffusion with nutrient consumption given in Eq.(1a-c), considering the action of aerobic and anaerobic bacteria biofilms. The intensity of consumption is accounted for as a constant for simplification of the model.

$$D_{3} \frac{d^{2}C_{3}}{dx^{2}} - W_{3} = 0 \quad , \quad 0 \le x \le h_{3}$$

$$D_{2} \frac{d^{2}C_{2}}{dx^{2}} = 0 \quad , \quad h_{3} \le x \le h_{3} + h_{2}$$

$$D_{1} \frac{d^{2}C_{1}}{dx^{2}} - W_{1} = 0 \quad , \quad h_{3} + h_{2} \le x \le h_{3} + h_{2} + h_{1}$$
(1a b.c)

The above system is governed by a set of six boundary conditions presented in Eq. (2). These are the four joined conditions for the connection of layers at their interfaces, the absence of concentration changes at the interface between steel substrate and anaerobic layer, and the constant value of concentration C_0 at the external border.

$$C_{1} = C_{2} \text{ and } D_{1} \frac{dC_{1}}{dx} = D_{2} \frac{dC_{2}}{dx} \text{ at } x = h_{2} + h_{3}$$

$$C_{2} = C_{3} \text{ and } D_{2} \frac{dC_{2}}{dx} = D_{3} \frac{dC_{3}}{dx} \text{ at } x = h_{3}$$

$$C_{1}(x) = C_{0} \text{ at } h_{3} + h_{2} + h_{1}$$

$$D_{3} \frac{dC_{3}}{dx} = 0 \text{ at } x = 0$$
(2)

The solution of system (1) yields the following expression

$$C_{3}(x) = \frac{W_{3}x^{2}}{2D_{3}} + A_{1}x + A_{2} , C_{2}(x) = A_{3}x + A_{4} ,$$

$$C_{1}(x) = \frac{W_{1}x^{2}}{2D_{1}} + A_{5}x + A_{6}$$
(3)

where the values of constants $A_1 - A_6$ are found from the boundary conditions, given in (2), and are equal to $A_1 = 0$

$$\begin{split} A_{2} &= -\frac{1}{2} \frac{D_{3}W_{1}h_{1}^{2} - 2D_{3}C_{0}D_{1} + W_{3}h_{3}^{2}D_{1} + 2W_{3}h_{3}D_{1}h_{2} + 2h_{1}D_{1}W_{3}h_{3}}{D_{3}D_{1}} \\ A_{3} &= \frac{W_{3}h_{3}}{D_{3}} \\ A_{4} &= -\frac{1}{2} \frac{2W_{3}h_{3}^{2}D_{1} + D_{3}W_{1}h_{1}^{2} - 2D_{3}C_{0}D_{1} + 2W_{3}h_{3}D_{1}h_{2} + 2h_{1}D_{1}w_{3}h_{3}}{D_{3}D_{1}} \\ A_{5} &= -\frac{D_{3}W_{1}h_{3} + D_{3}W_{1}h_{2} - D_{1}W_{3}h_{3}}{D_{3}D_{1}} \\ A_{6} &= \frac{\left[D_{3}W_{1}h_{3}^{2} + 2D_{3}W_{1}h_{3}h_{2} + D_{3}W_{1}h_{2}^{2} - D_{3}W_{1}h_{1}^{2} + 2h_{3}D_{1}W_{1}h_{3}^{2} - 2h_{1}D_{1}W_{3}h_{3} \right]}{2D_{3}D_{1}} \end{split}$$

In the above expressions, one may calculate the thickness of the 1st layer through the following formula^[4]

$$h_{1} = \sqrt{\frac{2C_{0,axy}D_{1}}{W_{1}}}$$
(5)

where $C_{0,oxy}$ is the concentration of dissolved oxygen in seawater.

The next step is related to the evaluation of the thickness of the 3^{rd} layer, h_3 , which is the crucial parameter of the system, since it actually determines the corrosion rate. Evidently, its growth is influenced by bacteria consumption activity; when all nutrients vanish due to this activity, h_3 reaches its final value. This is valid for each group of nutrients, and the group corresponding to the minimum of h_3 becomes limiting for specific conditions. According to the above, for each group, h_3 is evaluated by setting:

$$C_3(x=0)=0$$
 (6)

Combining Eqs. (6), (3a) and (4a, b) we get

$$h_{3} = \frac{\left[\frac{-2W_{3}D_{1}h_{2} - 2h_{1}D_{1}W_{3} + \frac{1}{2}}{2\sqrt{W_{3}^{2}D_{1}^{2}h_{2}^{2} + 2W_{3}^{2}D_{1}^{2}h_{2}h_{1} + h_{1}^{2}D_{1}^{2}W_{3}^{2} - W_{3}D_{1}D_{3}W_{1}h_{1}^{2} + 2W_{3}D_{1}^{2}D_{3}C_{0}}{2W_{3}D_{1}}\right]}{2W_{3}D_{1}}$$
(7)

It can be readily perceived that h_3 does not depend on the diffusion coefficient of corrosion products layer, but it clearly depends on the thickness of this layer, on the concentration of nutrients in external water, and on the diffusion and consumption coefficients of both bacteria layers.

Based on this limiting value of h_3 , one may estimate the activity of bacteria and quantify it by evaluating the magnitude (in terms of mass) of their metabolic products, which are causing corrosion.

The mass of metabolic products P (kg) for a time interval of t (s), for any fixed volume of active bacteria $V(m^3)$ and rate of metabolic production Q (kg/m³s), is given by

$$P = QVt$$
 (8)

Hence, for a corroded steel structural element of surface area A, for fixed h_3 , it valid that

$$P = Qh_3St \tag{9}$$

For clarity, the flowchart associated with the consecutive steps of the model is depicted in **Figure 8**.



Figure 8; Flowchart of the model proposed in this study.

4. Numerical results, discussion and suggestions for future work

According to the above methodology, numerical results were obtained for the range of values of the anaerobic layer h_3 . In doing this, the inorganic nitrogen concentration C_0 is chosen to lie between 0.000001 and 0.002 kg/m³, while the corrosion product thickness h_2 ranges from 0.1 to 15 mm.

Moreover, the values of the rest of the parameters involved in the determination of h_3 are adopted from existing relevant literature. More specifically, coefficients of inorganic consumption for aerobic and anaerobic bacteria are assumed equal to $W_1=W_3=0.022$ kg/m³s^[6], while the diffusion coefficients were chosen equal to $D_1=D_3=0.176$ m²/s and $D_2=0.8*10^{-12}$ m²/s^[5,7]. Finally, for fixed dissolved oxygen concentration of 7.8 mg/L, the selected value of the aerobic layer thickness h_1 is35.1*10⁻⁶ m^[4].

It was found that h_3 varied from 0.0162 to 1.75 mm. Its distribution as a surface plot of the form $h_3 = f(C_0, h_2)$ is depicted in **Figure 9**, while contour plots of this surface for the selected variation of values of h_2 and C_0 are shown in **Figure 10**.





Figure 10; Contour plots of h_3 for the chosen variations of h_2 and C_0 .

The present modeling approach allows for the connection between physical, chemical and biological factors that control corrosion rate on later terms of exposure (more than 2-3 years). Based on observed data of corrosion losses for mooring facilities, pollution, physical properties of corrosion products and biofilms, the correlation between anaerobic layer growth and nutrient concentration changes is confirmed.

Evidently, nutrient concentration increase is the most important factor for anaerobic layer growth, while the corresponding one of corrosion product layer has an inhibitory effect on anaerobic layer growth, been although a factor weaker than the factor of nutrient concentration changes, as it can be perceived in **Figure 10**.

Additionally, it can be seen that the anaerobic layer thickness is significantly larger than the aerobic layer one, a finding confirming the important role of this specific layer in the whole corrosion process.

It should be noted that considering equal diffusion coefficients for different bacteria layers may be well

accepted in the foregoing approach, since molecular sizes of the nutrients engaged do not differ to a noticeable amount.

Beyond the above comments, the observed corrosion rates are larger than the predicted ones; hence, it can be concluded that short-term nutrient concentration changes accelerate the corrosion process. The duration of the valid influence of these factors is unknown at the present stage, but it surely exceeds a year time period.

Finally, the present modeling stage allows for the rough estimation of bacterial layer activity and waste product prediction. The model should be further enhanced and enriched, as soon as new recordings of bacteria activity biological data become available. Perhaps it would be necessary for the improvement of the model to postulate the accounting of the qualitative and quantitative evaluation of waste product, like for instance hydrogen sulfide, as well as the estimation of the effect of bacteria metabolism. On any event, the philosophy of the proposed model is not expected to transform significantly with the addition of the above.

5. Conclusions

The most important conclusions that can be drawn from this investigation are:

- The main factor which controls the 1 anaerobic bacteria growth is nutrient laver concentration is seawater Increases of concentration might increase anaerobic layer thickness. This thickness may reach 0.1-1.17 mm for observed conditions.
- 2. A growth of corrosion product thickness reduces anaerobic bacteria activity by reduction of nutrient transfer. Nevertheless, the influence of corrosion products is less significant than the influence of nutrient concentration growth. Consequently, random short-term and periodical concentration increases may seriously accelerate corrosion, in comparison with predicted corrosion rate based on average annual concentrations.
- A model of nutrient transfer through corrosion products, aerobic and anaerobic layers has been developed, concerning steel marine structures. Based on the intensity of nutrient consumption by bacteria, there is an opportunity of

a quantitative estimation of the growth limiting factor (a nutrient which provides minimal value of thickness h_3). Based on anaerobic layer thickness, it is possible to evaluate waste products rate and corrosion rate.

- 4. The model was verified with observed corrosion rates and pollutant concentration changes data (southern part of Far East of Russia).
- 5. Further work is due for enhancing and enriching the model.

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