Cathodic protection modelling of a propeller shaft

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1   **Abstract**

2   Current and potential distributions on a stainless steel propeller shaft protected by galvanic anodes

3   were investigated by means of Finite Element Method (FEM) modelling. The effect of seawater

4   flow and shaft rotation was evaluated. The results of simulations are compared with experimental

5   measurements performed on steady shaft in natural seawater. Modest polarization can be noticed in

6   all operating conditions, not sufficient for preventing biofilm action on localized corrosion

7   initiation. Only in stagnant conditions, without any water renewal, the consumption of oxygen leads

8   to an appreciable potential decreasing to match the limits of normal protection indicated in the

9   European standards.

10

13

14   **1. Introduction**

15   Cathodic protection is the main technique for preventing corrosion on external surfaces of carbon

16   steel parts in the submerged zones of ships, harbour installations and offshore structures that operate

17   in direct contact with seawater. Such protection is frequently used also for internal parts of marine

18   equipment in which seawater flows - such as tanks, filters, pumps, valves - even if made of

19   corrosion resistant alloy. The combination of cathodic protection and corrosion resistant alloys may

20   be a convenient solution. The cathodic protection of stainless steel can avoid localized corrosion

21   induced by chlorides and makes possible the utilization of alloys with lower contents of chromium

22   and molybdenum compared to the levels needed for the corrosion resistance in seawater, thus

23   allowing the use of less expensive steels.

24   This work deals with feasibility study of a galvanic cathodic protection system of a ship propeller

25   shaft-stern tube assembly made of stainless steels, by galvanic carbon steel anodes. Experimental

studies using both impressed current method and sacrificial galvanic anodes of the cathodic

protection of the propeller system considered in this work are described in previous papers [1-3].

This work reports on a study of current and potential distributions through a simulation by Finite

Element Model (FEM) under more general conditions of exposure, covering longitudinal flow of

water between shaft and stern tube and shaft rotation.

2. The apparatus

The apparatus studied in this work is a propeller system of a ship (Fig. 1) equipped by a stern tube

made of AISI 304 stainless steel and a shaft of AISI 630 stainless steel, better known as 17-4 PH.

The chemical composition of the steels is reported in Table 1.

Stainless steels are traditionally used for these applications, where also other stainless steels are

used, such as AISI 303 and AISI 316, or more recent alloys including duplex stainless steels

(22Cr5Ni) and super duplex (25Cr7Ni), as valid alternative to non-ferrous alloys (i.e. copper-nickel

alloy Monel K-500).

In seawater, stainless steels are susceptible to pitting and crevice corrosion. The insurgence of such

localized corrosion forms can lead to premature failures of propeller shaft, because pits act as

preferential sites for fatigue initiation. The resistance to localized attack depends on alloy

composition. Chromium and molybdenum contents and nitrogen content - for the most recent

austenitic and duplex stainless steels - enhance it.

The Pitting Resistance Equivalent Number ($PREN$) is usually adopted in order estimate the relative

pitting corrosion resistance of stainless steels in chloride-containing environments. Higher $PREN$

values indicate greater corrosion resistance. The $PREN$ is defined as

$$PREN = wt.\%\mathrm{Cr} + 3.3 wt.\%\mathrm{Mo} + 16 wt.\%\mathrm{N} \qquad (1)$$

where $wt.\%$(Cr, Mo and N) are the weight percentages of the elements present in the alloys.

3

1 In seawater, which has a typical amount of chlorides of about 19000 ppm, and under the most

2 critical exposure for localized attack initiation, that is in stagnant conditions, a $PREN$ over 40 is

3 necessary to achieve complete corrosion resistance. The risk reduces in flowing water and it

4 becomes nil in turbulent flow constantly over a threshold, commonly assumed at about 1.5 m/s in

5 pipes, for AISI 316 stainless steel, having $PREN$ 25-27.

6 The pitting initiates in oxidizing chloride containing solutions, such as aerated seawater, under

7 exposure conditions giving free corrosion potentials higher than the pitting potential (E_{pit}).

8

2.1. Cathodic protection of stainless steel propeller system

10 Generally speaking, cathodic protection is able to prevent the localized corrosion. The main effect

11 consists in the lowering of the potential. Two situations can arise: the cathodic protection is applied

12 since early stage of exposure, before any corrosion initiation, or later, once localized attack initiates.

13 The attack cannot initiate in any case if cathodic protection is applied since early stage and

14 polarization is sufficient to maintain the potential stably under the pitting potential. Thus, the

15 protection potential matches with the pitting potential and it depends on the $PREN$ of the alloy and

16 environmental characteristics, primarily chloride concentration, temperature and pH.

17 The cathodic protection applied after localized corrosion initiation requires polarizations enough to

18 reach the re-passivation potential (E_{rep}), which is typically 200-300 mV lower than the pitting

19 potential. Such pronounced polarization is needed because the modifications induced by the

20 mechanism of the occluded cell produces strong acidification and considerable increase in the

21 chloride concentration inside the pit. Such modifications contrast the re-formation of passive film

22 on the active areas of the localized attack. As a consequence, the protection potential for stopping

23 corrosion attack becomes equal to the re-passivation potential. Fig. 2 shows the two different

24 conditions for cathodic protection.

25 The European standard EN ISO 15589-2 [4] gives the protection conditions for stainless steels with

26 respect to the composition of the alloy and its $PREN$. It suggests a protection potential of -0.3 V vs

4

SCE for austenitic stainless steels with *PREN* greater than 40. For steels with lower *PREN* values, the potential decreases to -0.5 V vs SCE. This limit is also considered for martensitic and duplex stainless steels. A different limit, equal to -0.6 V vs SCE, is reported in the EN 12473 [5].

As far as the over-protection conditions are considered, the austenitic stainless steels are fully compatible with the cathodic protection and thus they have the normal limit of -1.1 V vs SCE assumed for steels not susceptible to hydrogen embrittlement. However, other type of stainless steel with different microstructures may be susceptible to hydrogen embrittlement, depending on their mechanical strength and the level of applied loading. In the matter of hydrogen embrittlement risk, the susceptibility of 17-4 PH stainless steels after ageing at low temperature - in order to achieve high strength - is known since the '70s [6]. Thus, in accordance with the mentioned standards for avoiding the risk of ruptures on susceptible alloys, the potential should never decrease below -0.8 V vs SCE.

An intrinsically safe solution for avoiding any risk on susceptible alloys is the use of galvanic carbon steel anodes (Fig. 1). Actually, the galvanic coupling with these anodes limits the polarization to the free corrosion potential of the carbon steel, hence at polarization level much nobler than the critical limit for the overprotection.

3. Theoretical background

3.1. The numerical model

The current and potential distributions were studied by means of commercial finite element software.

The interspace between shaft and stern tube was discretized by using a three-dimensional model, by $2 \cdot 10^5$ tetragonal elements with dimension in the range of 0.5-50 mm, refined near the anode areas. Two carbon steel anodes are placed on a same generatrix of the stern tube (Fig. 1). The anodes are two steel bars of 35 mm diameter that protrude from the tube wall up to half of the interspace.

1 *3.2. Field equations and boundary conditions*

2 Assuming negligible the concentration gradients, the distribution of the potential (ϕ) and current

3 density (i) in the water is governed by Laplace's equation (Eq. 2) and Ohm's law (Eq. 3). It can be

4 calculated, knowing the electrical conductivity of the water (k) [7,8]

5 $$\nabla^2 \phi = 0 \qquad (2)$$

6 $$\boldsymbol{i} = -k\,\mathbf{grad}\,\phi \qquad (3)$$

7 The solution is obtained by solving the two equations within the electrolyte domain (i.e. the water)

8 by imposing the boundary conditions that describe on the surface the relation between flowing

9 current density and potential. On insulating surfaces, which do not exchange current, the boundary

10 condition is to set a null current density in the normal direction to the surface (i_n) that is equivalent

11 to set at zero the gradient of potential over this direction:

12 $$i_n = 0 \qquad \text{equivalent to} \qquad \frac{\mathrm{d}\phi}{\mathrm{d}n} = 0 \qquad (4)$$

13 On the surface of the structure to be protected (cathode) and anode, the current density exchanged

14 through the surface is a function of the potential of the metal in the electrolyte, E_c and E_a

15 respectively. The boundary conditions match with the polarization curves of the materials.

16 The potential distribution in the domain describes the ohmic drop in the water between two generic

17 points ($\Delta\phi_{ij}=\phi_i-\phi_j$). The potential ($E$) assessed by a reference electrode placed in the electrolyte in a

18 generic position, at some distance from the cathode, is given by the algebraic sum of the potential of

19 the cathode (by definition, measured with respect to the reference electrode placed in the electrolyte

20 immediately adjacent to the cathode itself) and the ohmic drop in the electrolyte ($\Delta\phi_{ic}$) between the

21 generic point and the cathode

22 $$E_i = \Delta\phi_{ic} - E_c \qquad (5)$$

23 Therefore, by a change of variables, Eqs. 2 and 3 govern also the distribution of the potential E.

24 Considering that the ohmic drop ($\Delta\phi_{ic}$) vanishes at the cathode, as it has been defined, the boundary

25 conditions on the protected structure become

$$E = -E_c \qquad (6)$$

In the case of impressed current cathodic protection system, the boundary conditions on the anode is related to the anode potential through the following relationship derived by considering the feeding voltage (V) of DC power supplier and the ohmic drops (IR) in the cables,

$$E = -E_a + V - IR \qquad (7)$$

With galvanic anodes directly connected to the cathode without any external electrical power supply ($V=0$), the ohmic drops in the connectors is negligible. The Eq. 7 becomes

$$E = -E_a \qquad (8)$$

3.3. The expression of polarization curves

The polarization curves of the materials define the boundary conditions. Several papers reported the mathematical equations defining non linear boundary conditions based on polarization curves of steel, especially applied to boundary elements method [9-15] and finite element methods [16]. The mathematical equations of the polarization curves adopted for cathodic protection modelling in seawater are reported by several authors [17,18]. In previous works [19,20], the behaviour of a HSLA steel grade X65 was studied in synthetic seawater and then used for modelling current and potential distributions on offshore structures [21,22], underground tanks [23] and for evaluating internal electrical interference on insulating joints of pipelines for water transport [24].

The polarization curve is the sum of the anodic and cathodic processes which can occur on the metal surface. Its description is based on the Butler and Volmer equation for electrochemical processes that are not limited by transport phenomena. For the oxygen reduction at the typical potential of carbon steel corrosion, the limiting current density can be estimated from mass transport coefficient, which can be estimated by dimensionless relationship derived by fluid dynamics. Selman and Tobias [25] describe empirical correlations for mass transfer in a large variety of geometries.

The processes involved in corrosion and cathodic protection of steel are the anodic process of metal oxidation (corresponding to the current density i_a), the cathodic process of reduction of dissolved oxygen in the water (i_{c,O_2}) and the cathodic process of hydrogen evolution from water reduction ($i_{c,H}$). The total current density (i) flowing through the metallic surfaces is the sum of these three contribution, according to the following equation (negative sign for cathodic currents)

$$i = i_a - i_{c,O_2} - i_{c,H} \tag{9}$$

On the submerged part of marine structures, the formation of calcareous scale gradually reduces the current required for the protection. A thick compact scale is a barrier to the oxygen access to the metal surface and decreases the exposed surface. This phenomena plays an important role during structure polarization and is fundamental for effectiveness of cathodic polarization [26,27]. As a consequence, cathodic protection modelling has to take into account time-dependent boundary conditions. Since the 80s, empiric models were proposed for describing time variation of polarization curves [17,18,20]. Recently, further models were proposed to explain precipitation and growth mechanisms [28,29].

Nevertheless, only the initial stages of polarization - in absence of relevant growing of calcareous deposit on the protected surface - are considered in this paper. The reason of such an approach is based on the specific nature of the cathodic protection of stainless steels. Because the absence of calcareous scale gives very uneven current distribution, the initial polarization period is critical especially in complex geometries. Cathodic protection could not prevent the risk of localized corrosion initiation on the areas where the current cannot penetrate. The early initiation of the attack then makes difficult to reach a complete corrosion protection, because higher polarization is required to re-passivate corroded areas, in zones where the penetration of currents is indeed limited due to the geometry.

Furthermore, cathodic protection of stainless steels is applied at cathodic current densities lower than the usual values adopted for carbon steel structures. Consequently, limited alkalinisation on the protected surface occurs, with a slower kinetic of scale growth. The deposit forms over long time,

1 on surfaces where a fouling layer is already developing, which reduces calcareous scale adhesion

2 and make it easily removable by turbulent flow. Johnsen and Bardal [30] reported the absence of

3 scale formation during potentiostatic tests carried out in natural seawater, on different types of

4 stainless steel, for water flow rates in the range 0.5-1.2 m/s, even for high protection current

5 density. Long periods of scale formation are not helpful to prevent the localized corrosion initiation

6 on complex geometries.

7

8 *3.3.1. Anodic process of dissolution*

9 Because the active behaviour in seawater, the anodic characteristic of the carbon steel $(i_{a,Fe})$ as a

10 function of potential E can be expressed by Tafel law

11
$$i_{a,Fe} = i_{0,Fe}\exp\left(\frac{E - E_{eq,Fe}}{B_{Fe}}\right) \tag{10}$$

12 where $i_{0,Fe}$, $E_{eq,Fe}$ and B_{Fe} are respectively the exchange current density, the equilibrium potential

13 and the Tafel constant on a natural logarithm scale corresponding to carbon steel.

14 Stainless steel has more complex behaviour, due its passive nature. At the pH of seawater, the

15 anodic process rapidly achieves passive state due to the formation of protective chromium oxide,

16 without a relevant activity peak. From the equilibrium potential, very close to that of carbon steel,

17 the current density reach the passivity current density $(i_{a,p})$. The anodic curves of stainless steel

18 $(i_{a,inox})$ can be expressed by modifying Eq. 10 with an asymptotic approach to the passivity current

19 density, through the relationship

20
$$\frac{1}{i_{a,inox}} = \frac{1}{i_{a,Fe}} + \frac{1}{i_{a,p}} \tag{11}$$

21

22 *3.3.2. Oxygen cathodic process*

23 Both charge transfer and mass transfer limit the current density for oxygen reduction. The total

24 current density (i_{c,O_2}) is given by

25

1
$$\frac{1}{i_{c,O_2}} = \frac{1}{i_{ctc,O_2}} + \frac{1}{i_{lim,O_2}}$$
(12)

2 where i_{ctc,O_2} and i_{lim,O_2} are charge transfer current density and mass transfer limiting current

3 density, respectively.

4 Charge transfer current density as a function of potential E is given by the following law

5
$$i_{ctc,O_2} = i_{0,O_2} \exp\left(\frac{E - E_{eq,O_2}}{B_{O_2}}\right)$$
(13)

6 where i_{0,O_2}, E_{eq,O_2} and B_{O_2} are respectively the exchange current density, the equilibrium potential

7 and the Tafel constant on a natural logarithm scale corresponding to oxygen.

8 The charge transfer term defines the free corrosion potential of passive stainless steels. In natural

9 seawater, the biofilm settlement depolarizes the oxygen reduction reaction. This effect - described

10 by Mollica and Trevis since the late 80s [31] - produces a shift of the free corrosion potential of

11 passive alloys toward noble potentials (ennoblement) during early periods of exposure. Faimali et al

12 [32] reported corrosion potential increase of 350-400 mV for super austenitic steels with high

13 resistance to localized corrosion. On stainless steels with lower chromium and molybdenum content

14 (lower PREN), such an increase leads to the initiation of localized corrosion after free corrosion

15 potential reaches the pitting potential. After the initiation, the anodic curve of stainless steel is no

16 longer described by Eq. 11. The mechanisms by which the biofilm causes "cathodic depolarisation"

17 were discussed in the works of Beech and Sunner [33], Little et al [34] and Landoulsi et al [35].

18 To consider this effect on the polarization curve, it is conveniently to modify Eq. 13 in terms of free

19 corrosion potential ($E_{cor,inox}$) and corrosion current density ($i_{cor,inox}$). In passive conditions, the

20 corrosion current density is equal to the passive current density ($i_{cor,inox} = i_{a,p}$)

21
$$i_{ctc,O_2} = i_{a,p} \exp\left(\frac{E - E_{cor,inox}}{B_{O_2}}\right)$$
(14)

22 In the absence of deposits covering the surface - which can reduce the access of oxygen - the fluid

23 dynamic conditions at the shaft/stern tube surfaces define the limiting current density. The mass

1 transport of oxygen towards the steel surfaces is determined by the shaft rotation and water flow in

2 the annulus.

3 For modelling the propeller system considered in this work, two different situations are assumed,

4 one related with anchored or moored ship in harbour, the other with rotating propeller shaft during

5 ship navigation.

6 In the first case, water has a longitudinal flow in the annulus or is stagnant. These conditions were

7 those considered during experimental studies for assessing current and potential distributions

8 directly on the propeller system [2].

9 For mass transfer in turbulent flow in an annulus, Lin et al [36] proposed a relationship in terms of

10 dimensionless numbers of Sherwood (Sh), Reynolds (Re) and Schmidt (Sc), valid for Re between

11 2100 and 30000

12 $$Sh = 0.023 Re^{0.8} Sc^{\frac{1}{3}}$$ (15)

13 Table 2 summarizes the definitions for parameters and dimensionless numbers used in the

14 relationships. The oxygen mass transfer coefficient (k) is calculated from the Sherwood number.

15 Then the limiting current density ($i_{\lim,O_2}$) can be estimated from the concentration of oxygen (C_{O_2})

16 in the water

17 $$i_{\lim,O_2} = 4 F k C_{O_2}$$ (16)

18 where F is the Faraday's constant.

19 During ship navigation, in the hypothesis of the relative speed between metallic walls and water is

20 determined only by the shaft rotation and water movement in the longitudinal direction is

21 negligible, the oxygen limiting current density can assessed by equations for the turbulent Couette

22 flow between a rotating inner cylinder and an outer coaxial and stationary cylinder proposed by

23 Eisemberg [37] Gabe and Robinson [38,39], Kishinevskii et al [40]. In particular, the equation of

24 Eisemberg is assumed for 1000 <Re <100000, 835 <Sc <11490, 0.093 < d_i/d_o <0.83

25 $$Sh = 0.0791 Re^{0.7} Sc^{0.356}$$ (17)

1. Fig. 3 shows the variation of the limiting current density of oxygen estimated for the two situations,

2. in aerated water at 15 °C, as a function of the shaft rotation speed and of the flow rate of

3. longitudinal flux (without shaft rotation), expressed as relative velocity between water and metallic

4. surface.

5.

6. *3.3.3. Hydrogen cathodic process*

7. The hydrogen evolution process from water reduction can be described by the expression of the

8. corresponding cathodic current density ($i_{c,H}$)

9.
$$i_{c,H} = i_{0,H} \exp\left(\frac{E - E_{eq,H}}{B_H}\right) \tag{18}$$

10. where $i_{0,H}$, $E_{eq,H}$ *and* B_H are respectively the exchange current density, the equilibrium potential

11. and the Tafel constant on a natural logarithm scale corresponding to hydrogen.

12. The pH influences the electrochemical kinetic to limited extent at pH less than 10. At room

13. temperature, the slope on decimal logarithm scale is close to 120 mV/decade and tends to increase

14. at high overvoltages [41,42].

15.

16. *3.3.4. The overall curves*

17. The overall polarization curves (i) for carbon steel and stainless steel are expressed by Eqs. 19 and

18. 20 (negative sign for cathodic currents): Eq. 19 is obtained combining Eqs. 10, 16 and 18 whereas

19. Eq. 20 is obtained combining the inverse of Eqs. 11 and 12 with Eq. 18. The active behaviour of

20. iron dissolution is expressed by the Eq. 10, which is transformed in Eq. 21 so as to use i_{Fe} pre-

21. exponential parameter published in previous works [9,12] and reported in Table 3.

22.
$$i = i_{a,Fe} - i_{lim,O_2} - i_{c,H} \tag{19}$$

23.
$$i = \frac{1}{\frac{1}{i_{a,Fe}} + \frac{1}{i_{a,p}}} - \frac{1}{\frac{1}{i_{ctc,O_2}} + \frac{1}{i_{lim,O_2}}} - i_{c,H} \tag{20}$$

24.
$$i_{a,Fe} = i_{Fe} \exp\left(\frac{E}{B_{Fe}}\right) \tag{21}$$

From the mentioned works, in addition to i_{Fe}, $i_{a,p}$ and $i_{0,H}$, also the Tafel "b" constants on decimal logarithm scale (Table 3) were used in Eqs. 19, 20 and 21 ($B_S = b_S/2.3026$ where S is the oxidizing or the reducing species).

Figs. 4 and 5 show the plots relative to Eqs. 19 and 20, respectively.

For comparison, Fig. 6 shows the anodic and cathodic potentiodynamic curves of 17-4PH stainless steel in natural seawater reported by Bellezze et al [1,3]. The curves were obtained in stagnant conditions, within one hour from the immersion of the specimen in the water. The anodic curves show the initiation of pitting corrosion, with a clear hysteresis in the return curve. The pitting potential is about 0.06 V vs. SCE, with the re-passivation potential at about -0.03 V vs SCE.

4. Results and discussion

4.1. Validation of the model

In order to validate the model, the distributions derived by simulation were compared with experimental measurements performed on stationary shaft, in aerated natural seawater, under stagnant conditions or with 40 L/min of longitudinal flow. The experimental setup is described by Bellezze et al [2]. During the experimentation, the potential was measured by means of reference electrodes placed at regular intervals on the stern tube in correspondence of the opposite generatrix with respect to that where the anodes are placed (Fig. 1). The currents were measured by shunt resistances between the anodes and the protected structure.

During modelling, it was assumed a temperature of 15 °C, a typical composition of seawater with an electrical resistivity of 0.2 Ωm and a saturation concentration of dissolved oxygen (8 ppm). For the definition of the boundary conditions on the stainless steel, the free corrosion potential ($E_{cor,inox}$) was assumed equal to 0.078 V vs. SCE (Table 3), on the basis of experimental measurements at early exposures. The same polarization curve is assumed for shaft and stern tube, despite the propeller system is made of two different type of stainless steel.

13

1   Fig. 7 shows the potential distribution in the annulus, at 40 L/min of longitudinal flow. The

2   polarization is limited to the areas next to the anodes, thus denoting a poor penetration of protection

3   current both along the longitudinal direction and the circumference. The maximum polarization

4   near the anodes is about 0.4 V with respect to free corrosion potential, but it reduces to a few tens of

5   millivolts on the generatrix of the stern tube far from the anodes. The potential distribution is in

6   good agreement with the experimental data (Fig. 8).

7

8   *4.2. Simulation of distribution in stagnant water and stationary propeller shaft*

9   Fig. 9 and Fig. 10 compare the model results with experimental measurements performed at

10   different times with stagnant water, in closed annulus without any oxygen exchange. Because the

11   Eqs. 15 and 17 do not apply under these circumstances, for the initial limiting current density to be

12   introduced in Eqs. 19 and 20 it was assumed the value required for producing the same initial

13   galvanic current measured during experimental polarizing tests on the propeller system. Then, the

14   evolution of the polarization curves was estimated by considering the oxygen consumption and the

15   variation that it determines on the limiting current density (Eq. 16). The oxygen consumption by the

16   cathodic process leads to a decrease of the galvanic current exchanged between the anodes and the

17   structure and a considerable increase of the polarization, which brings the potential at about -0.6 V

18   vs SCE even in the zones far away from the anodes, after 70 hours (Fig. 11). For simplicity, it was

19   considered that the whole flowing current contributes to oxygen consumption, ignoring the

20   hydrogen cathodic process, because it only becomes important at very low potentials.

21   From the Eq. 16 and Faraday's law, the following relationship can be derived for describing time

22   evolution of limiting current

$$\frac{\mathrm{d}i_{\mathrm{lim,O_2}}}{\mathrm{d}t} = -\frac{k}{V}I(t) \tag{22}$$

24   where *V* is the volume of water end *I(t)* is the cathodic current flowing between anodes and

25   structure.

26   Considering constant the mass transport coefficient k, it can be related with the initial values of

1   oxygen concentration and limiting current density through Eq. 16. From these assumptions, the

2   following relationship can be written

$$3 \qquad i_{\text{lim},O_2}(t) = i_{\text{lim},O_2}(0) - \frac{k}{V}\int_0^t I(\tau)d\tau \qquad (23)$$

4   Despite the approximations assumed for the mass transfer coefficient, the results allow a reliable

5   interpretation of the experimental data, which confirms the main effect due to the depletion of

6   oxygen concentration. Only once it becomes relevant, the polarization reaches the protection

7   potential of stainless steels (Figs. 10 and 11). This fact is evident after tens of hours, which is a

8   relatively long time compared to the normal periods of ship in harbour, but much lower than the

9   periods of mooring of occasionally used yachts.

10

11   *4.3. Shaft rotation effect*

12   Fig. 12 and Fig. 13 show the results of simulations with rotating shaft. They show the distributions

13   along the generatrix of the shaft opposite to the anodes. The distributions are compared to the

14   stationary shaft, with 40 L/min longitudinal flow. Rotational speeds of 5 Hz and 1 Hz have been

15   considered. The boundary conditions have been defined according to Eqs. 15, 17 and 20, by

16   considering the same transport conditions both on shaft and on stern tube, for simplicity.

17   Stationary conditions have been assumed without any polarization transients. Actually, the

18   polarization conditions in the zones close to the anodes are variable as a function of the rotation. In

19   the zones of the shaft facing to the anodes, each point of the circumference passes from high

20   polarization, when it is near the anode, to a low one, when it is in the opposite zone. In first

21   approximation, the cycle is that described in Fig. 14. Each point is subjected to a pulsed cathodic

22   protection with a frequency equal to the rotation of the shaft. The waveform of the current depends

23   on the circumferential distribution. Only if the rotational frequency is low, the behaviour tend to the

24   stationary distribution described by the model (Figs. 12 and 13). The polarization changes as

25   frequency increases, producing minor fluctuations.

1 Even with these limitations, however, the model is representative of the maximum possible

2 polarization in the most polarized zones and of the minimum polarized zones in remote positions,

3 where fluctuation becomes negligible.

4 The results of simulations indicate that the polarization reached by the cathodic protection system

5 considered in this work is poor with aerated water and longitudinal flow or rotating shaft. The

6 potential are far from protection potential indicated in the technical standards. Furthermore, as the

7 rotation speed increases, the increase of the current demand reduces the throwing power. Thereby,

8 the current density that reaches the back side of shaft -far away from the anodes- decreases as

9 shown in Fig. 13.

10

11 ### 4.4. Conditions of protection

12 Except in stagnant water without renewal, all the other situations analysed do not show sufficient

13 polarization for achieving the protection potentials indicated by the technical standards on cathodic

14 protection. As far as these limits are taken into account, the propeller system cannot be considered

15 protected. Thus, only large zones are in conditions of moderate polarization during early exposure,

16 when calcareous scale deposit is not yet formed.

17 However, even if it is low, a polarization of tens of millivolts is able to lower the potential below

18 the value of pitting potential measured by the potentiodynamic tests (Fig. 6). Thus, although

19 limited, the polarization would seem to be able to prevent the initiation of localized corrosion, but

20 this interpretation is not reliable. The low polarizations estimated by simulations should be

21 interpreted as inadequate to prevent the risk of localized corrosion, according to the following

22 considerations.

23 First of all, there is an intrinsic difficulty for assessing the pitting potential from short-time

24 potentiodynamic tests. Secondly, it is important to consider that the localized attack mainly initiates

25 in crevice or under fouling deposits. Under these conditions, the critical potential is lower than the

26 pitting potential obtained on bare steel surface.

Furthermore, biofilm growth can also play a crucial role. At usual temperatures found in seawater - well below 40 °C - the biofilm modifies the cathodic process of oxygen. The bacteria activity raises the exchange current density, thus reducing the activation overvoltage and producing the previously described ennoblement [31]. The bacteria can also act under cathodic protection. Johnsen and Bardal [30] explain the considerable increase of current demand at low cathodic polarizations induced by biofilm phenomena. Such effect was observed in natural seawater on different types of stainless steel. At very low cathodic current densities – typical of cathodic protection at moderate polarizations - the potential is mainly determined by the activation overvoltage of the oxygen reduction process, similarly to free corrosion conditions. Thus - on low polarized zones of the structure - an increase of the exchange current density due to the presence of bacteria can also cause an increase of the potential under cathodic protection. At protection potentials recommended by the technical standards, this effect becomes negligible because the process of oxygen reduction is mainly governed by the mass transport phenomena rather than charge transfer on the metal surface. Such recommended polarization levels are suitable to prevent localized attack promoted by potential ennoblement induced by bacteria activity.

5. Conclusions

The potential and current distributions in a propeller shaft-stern tube system under cathodic protection by means of two carbon steel galvanic anodes was analysed by means of a finite element model. The model describes the initial polarizing period, when the calcareous deposit is not yet formed.

The results of the simulations are in good agreement with experimental data obtained on a full scale propeller system, with stationary shaft in contact with stagnant or flowing natural seawater.

The analysis of the system confirms a modest polarization in all operating conditions with aerated water and stationary or rotating shaft. Only in stagnant conditions, without any water renewal, the rapid consumption of oxygen stimulated by cathodic protection leads to an appreciable potential

1 decrease below the limits of normal protection indicated in the European standards, after tens of

2 hours.

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Figure Captions

Fig. 1 Geometry of the propeller shaft-stern tube system (all dimension are in millimetres). Agi (i=1,…,7) are the silver/silver chloride reference electrodes; SCE is the saturated calomel reference electrode. The interspace between propeller shaft and stern tube is an annulus with thickness equal to 24 mm.

Fig. 2 Cathodic protection zones for a metal with an active/passive behaviour for the prevention and stop of localized corrosion determined by chlorides attack.

Fig. 3 Oxygen limiting current density at 15 °C, in aerated water (8 ppm of oxygen), as a function of water /metallic wall relative speed (X identify the reference values for the three cases considered in the modelling).

Fig. 4 Polarization curve of carbon steel (Eq. 19), used as boundary condition for the calculation of potential and current distributions in the FEM model.

Fig. 5 Polarization curve of stainless steel (Eq. 20), used as boundary condition for the calculation of potential and current distributions in the FEM model.

Fig. 6 Potentiodynamic anodic polarization (dotted line; from [3]) e cathodic polarization (solid line) curves of 17-4 PH stainless steel in natural sea water, at room temperature, obtained with scan rate of 10 mV/min in two different tests.

Fig. 7 Potential distribution obtained by means of FEM model with stationary shaft in aerated water, with longitudinal flow at 40 L/min.

Fig. 8 Comparison of the FEM model results with potential values measured [2] on the stern tube with the reference electrodes placed on the opposite generatrix with respect to that relative to the anodes (Fig. 1). Seawater longitudinal flow was 40 L/min.

Fig. 9 Decrease of cathodic current in the propeller system containing stagnant water [2] compared with the results of FEM model with variation of boundary conditions due to the oxygen consumption.

Fig. 10 Polarization potential [2] at the location of SCE reference electrode placed in the stern tube (see Fig. 1) with stationary shaft and stagnant water. Comparison with results of FEM model with variation of boundary conditions due to the oxygen consumption.

Fig. 11 Experimental potential distributions as a function of time, measured [2] by the reference electrodes placed along stern tube (see Fig. 1) with stagnant water and stationary shaft. Comparison with results of FEM model with variation of boundary conditions due to the oxygen consumption.

Fig. 12 Potential distribution on the back generatrix of the shaft, with respect to the anodes position (Fig. 1), with rotating shaft or stationary shaft with 40 L/min of longitudinal water flow.

Fig. 13 Current density distribution on the back generatrix of the shaft, with respect to the anodes position (Fig. 1), with rotating shaft or stationary shaft with 40 L/min of longitudinal water flow.

Fig. 14 Cyclic variation of the polarization potential on the shaft points facing the anodes.

Table 1. Chemical composition of 304 and 17-4PH stainless steels (wt.%).

Table 2 Symbols and definition of parameters used for the calculation of the oxygen limiting current density.

1

2　**Table 3** Values of the parameters used for the description of the polarization curves.

3

1   **Table 1.** Chemical composition[*] of 304 and 17-4PH stainless steels (*wt.%*).

Alloy	C	Si	Mn	P	S	Cr	Mo	Ni	Cu	Nb	Co
304	0.04	0.53	1.27	0.01	-	18.13	0.33	9.24	0.20	0.01	0.12
17-4PH	0.03	0.34	0.77	0.01	0.02	15.55	0.04	5.15	3.10	0.34	0.03

2   [*]The rest is Fe.

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1

2 **Table 2** Symbols and definition of parameters used for the calculation of the oxygen limiting

3 current density.

v	water velocity (longitudinal flux in the annulus)		
ω	rotation speed of the propeller shaft		
d	characteristic dimension	$\begin{cases} d_o\text{-}d_i & \text{for longitudinal flux in the annulus} \\ d_i & \text{for the shaft rotation} \end{cases}$	
d_o	outer cylinder diameter (inner stern tube diameter)		
d_i	inner cylinder diameter (propeller shaft diameter)		
$Sh = \dfrac{kd}{D}$	Sherwood number		
k	oxygen mass transfer coefficient		
D	oxygen diffusion coefficient		
Re	Reynolds number	$\begin{cases} Re = \dfrac{vd}{v} & \text{for longitudinal flux in the annulus} \\ Re = \dfrac{\omega d_i^2}{v} & \text{for the shaft rotation} \end{cases}$	
$v = \dfrac{\mu}{\rho}$	water kinematic viscosity		
μ	water viscosity		
ρ	water density		
$Sc = \dfrac{v}{D}$	Schmidt number		

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5

1   **Table 3** Values of the parameters used for the description of the polarization curves.

$i_{a,p}$	10^{-3}	A/m^2
$E_{eq,H}$	-0.713	V vs SCE
$i_{0,H}$	$2 \cdot 10^{-3}$	A/m^2
b_H	-0.114	V/dec
$E_{cor,inox}$	0.078	SCE
b_{O_2}	-0.057	V/dec
i_{Fe}	$4.4 \cdot 10^5$	A/m^2
b_{Fe}	0.058	V/dec

2

3