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Cathodic protection of ships in brackish water

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Abstract The operation of ice-going vessels depends on the condition of the hull surface. Corrosion increases the roughness of ship hull, which increases drag and fuel consumption. The hull surface smoothness is maintained by using coatings and cathodic protection. The cold brackish water is different from ocean water as it has lower salt content, lower conductivity, and higher concentration of dissolved oxygen. These factors mean that the design of the cathodic protection system for ship hulls requires different design values, such as protection current density and protected length, than those given in cathodic protection standards. In this paper, we have estimated the protection current density with polarization curves and the protected length by using Wagner number and dimension and conductivity scaling. In brackish water the protection current density was two times that in ocean water. The protected length in brackish water varied between 10 and 15% of that in ocean water. In poorly conducting brackish water, the current capacity of a cathodic protection system is used mostly for overcoming the solution resistance, not for delivering protection current.

Keywords Cathodic protection · Seawater · Steel · Protection current

Introduction

The Baltic Sea is a relatively shallow inland sea surrounded by the countries of North-eastern Europe and Scandinavia. The Baltic Sea is connected to the North Sea through narrow and shallow sounds between Denmark and Sweden. The outlet consists of a series of basins separated

by shallow sills, which obstruct efficient water exchange. The environmental conditions of the Baltic Sea are defined by the fresh water input from rivers and precipitation and by the limited and occasional inflow of more saline water from the North Sea. The salinity varies from the almost oceanic conditions to the almost fresh water conditions in the Northern Gulf of Bothnia. The most important factors that affect corrosion in cold brackish water are low concentration of dissolved solids, low conductivity, and high concentration of dissolved oxygen. According to Katz [1], the conductivity of brackish water with $T=5^{\circ}\text{C}$ and salinity 5.45% NaCl is 5.2 mS/cm, whereas the conductivity of warm ocean water with $T=25^{\circ}\text{C}$ and salinity 36.1% NaCl is 54.5 mS/cm. The solubility of oxygen in brackish water with $T=5^{\circ}\text{C}$ and salinity 5.45% NaCl is 8.6 ml/l, whereas the solubility in warm ocean water with $T=25^{\circ}\text{C}$ and salinity 36.1% NaCl is 5.1 ml/l [2]. The conductivity of cold, brackish water can be as low as 10% of that in ocean seawater and the solubility of oxygen can be 60–70% higher than in warm ocean water. All these factors affect corrosion resistance of materials and design of cathodic protection systems.

The greater part of Finland's foreign trade relies on shipping and Finland is one of the few countries in the world where all harbors are ice-bound during normal winters. The operation of ice-going vessels depends heavily on the condition of the hull surface. Corrosion increases the roughness of ship hull, which increases drag and fuel consumption. The cathodic protection is widely used to protect underwater areas of ship hulls. The idea of cathodic protection is to supply external current by using sacrificial or inert anodes to decrease the rate of anodic corrosion reactions. With impressed current cathodic protection, the potential of the protected structure is changed by using a DC power source to provide a cathodic reaction on the whole protected surface. The protected structure is connected to the negative terminal of the power source. Inert anodes are connected to the positive terminal. The current is controlled by comparing the measured protected structure potential to a reference electrode. If the protected structure potential is below a certain value, i.e.,

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the protection potential, the structure is considered to be cathodically protected. The potential distribution along the protected surface is determined by the configuration of the system, surface coating, and environment conductivity.

In seawater, steel is protected when it has a potential of -800 mV, or more negative when measured with a Ag/AgCl/seawater reference electrode [3]. Cathodic protection is achieved by supplying anodic current by using sacrificial or inert anodes. The current density needed for protection depends on the rate of cathodic reaction, flow rate, and condition of the coating. According to the mixed potential theory, supplying external current that is equal or larger than that consumed by the cathodic reaction gives complete cathodic protection. This protection current density is approximately equal to corrosion current density. Initial polarization of uncoated steel requires $110\text{--}220$ mA/m², maintaining protection requires $60\text{--}100$ mA/m² [3], and good coating can decrease these values by 95–99%. Cathodic protection standards give different protection current densities for different geographical areas. In areas with moderate temperature and high salinity, such as Mediterranean Sea and Gulf of Mexico, the protection current density is 50–60% of that in cold ocean water.

The protected length around single anode depends on protection current density, output current of the anode, coating quality (resistivity), and seawater conductivity. Poor current distribution due to low conductivity can be improved by an electrically resistant coating, dielectric shields around the anodes, installation of more anodes (protected areas will overlap), and higher current output from an anode (increases the initial polarization around the anode). A simple method to estimate the protected length is to use the Wagner number, which is the surface polarization resistance divided by electrolyte resistivity. The Wagner number is the characteristic distance over which current will flow [4] and it is often related to the secondary current distribution over a surface [5, 6]. The Wagner number can be calculated using Eq. 1,

$$Wa = \left(\frac{\partial \eta}{\partial i} \right) \cdot \left(\frac{\kappa}{L} \right) \quad (1)$$

where $\partial \eta / \partial i$ is the polarization resistance, κ is the solution conductivity, and L is a characteristic length. A large Wagner number indicates that potential does not change much along the surface. High polarization resistance means low current density so the active metal does not draw much current. A resistive coating will also increase this apparent polarization resistance value. High solution conductivity means that potential difference is not used in solution resistance and the current from an anode can have a longer effect over the surface. Good potential distribution is expected with low corrosion rates, a resistive coating, and

high seawater conductivity. According to Hack [4], the Wagner number can give qualitative predictions on current distribution effects in cathodic protection.

The effect of seawater conductivity, flow rate, etc. on configuration and current demand of a cathodic protection system were studied using dimension and conductivity scale (DACS) modeling [7–10]. In this technique, scale models are floated or immersed in tanks containing seawater, which was diluted such that its electrical conductivity was reduced by the same factor as that employed for the model. The models are fitted with anodes, propellers, rudders, etc. Cathodic protection parameters are measured with miniature reference electrodes or by potential mapping.

Materials and methods

The effect of conductivity and flow rate on protection current density was studied by measuring cathodic polarization curves with rotating unalloyed steel disk electrode. The electrode was made from thermomechanically rolled weldable fine-grain structural steel according to standard SFS-EN 10113-3. The nominal composition of the steel is shown in Table 1. The diameter of the electrode was 0.5 cm. Cathodic polarization curves were measured at 0–900 rpm using scan rate at 100 mV/min. The experiments were done in synthetic ocean seawater after DIN 50905, Teil 4 [11] that was diluted with distilled water to get brackish water with the desired salinity. The composition of the synthetic ocean water is given in Table 2. The test temperature was room temperature.

The salinity was measured using Merbabu Sinar salt meter NS-3P. The salinity of ocean water was 3.6% NaCl, Gulf of Finland brackish water was 0.6% NaCl, and Gulf of Bothnia was 0.25% NaCl. The seawater conductivity was measured with Knick Konduktometer 702. The conductivity of the ocean water was 53.1 mS/cm, Gulf of Finland brackish water was 11.9 mS/cm, and Gulf of Bothnia was

Table 2 The composition of the synthetic ocean water according to DIN 50905 [11]

Chemical	Amount (g)
NaCl	28
MgSO ₄ 7 H ₂ O	7
MgCl ₂ 6 H ₂ O	5
CaCl ₂ 6 H ₂ O	2.4
NaHCO ₃	0.20
H ₂ O	985 ml

The dilution of Gulf of Finland brackish water was 17% of the ocean water salt content and dilution of Gulf of Bothnia brackish water was 7%

Table 1 The nominal composition of steel used in the rotating disk and DACS experiments according to SFS-EN 10113-3

% C max.	% Si max.	% Mn max.	% P max.	% S max.	% Nb max.	% V max.	% Al total min.	% Ti max.	% Mo	% Ni	% N
0.16	0.60	1.70	0.030	0.025	0.05	0.12	0.02	0.05	0.20	0.45	0.025

5.15 mS/cm. The polarization curves were measured in a three-electrode cell using Princeton EG&G model 273 potentiostat and M352 SOFTCORR II software and Tacussel M04A rotating disk electrode. During measurements, a constant airflow was maintained through the rotating electrode to protect it from corrosion. This airflow also maintained a constant oxygen supply. The purpose of polarization curves was to determine limiting current density of oxygen reduction. Limiting current densities at different rotating speeds gave an estimate on the changes of cathodic oxygen reduction rate with salinity and the effect of flow rate. This allowed the evaluation of changes in protection current demand for stationary and moving vessel.

The effect of conductivity was studied using DACS. This physical scale modeling method is based on the change of seawater conductivity. Scaling was done by diluting synthetic seawaters. The scaling was 1:25 for Gulf of Bothnia water and 1:30 for Gulf of Finland and ocean water. Model tests were done in 200 l plastic tank to estimate current distribution in seawater and brackish water using a 600×30 mm uncoated steel plate whose composition is shown in Table 1. The method used was a potentiostatic test using Wenking ST 72 analog potentiostat capable up to 3 A current. The test was arranged to use a single Pt/Ti anode and two Radiometer Analytical REF201 Ag/AgCl reference electrodes. The anode was isolated from steel using nonconductive adhesive tape. One reference electrode was used for potentiostatic control and the other for potential mapping. The dielectric anode shield was simulated by using nonconductive adhesive tape. Preparation of calcareous deposits for the DACS tests was done by cathodically polarizing the steel plate at 300 mA/m² for 1 week in synthetic ocean seawater. The schematic arrangement of the DACS tests is shown in Fig. 1.

Results and discussion

The corrosion current densities in synthetic ocean and brackish waters were measured with a rotating disk elec-

trode using polarization resistance method. The anodic and cathodic Tafel slope value used in the calculation was 100 mV, based on the polarization curves. The corrosion current densities are shown in Fig. 2. The corrosion current densities increase with increasing rotating speed at the same rate in all test waters. At rotating rates higher than 200–300 rpm ($\sqrt{\omega} = 5.6(rad/s)^{1/2}$), the corrosion current densities reach a constant level of approximately 3,300 mA/m².

The effect of flow velocity was estimated by measuring cathodic polarization curves with rotating disc electrode.

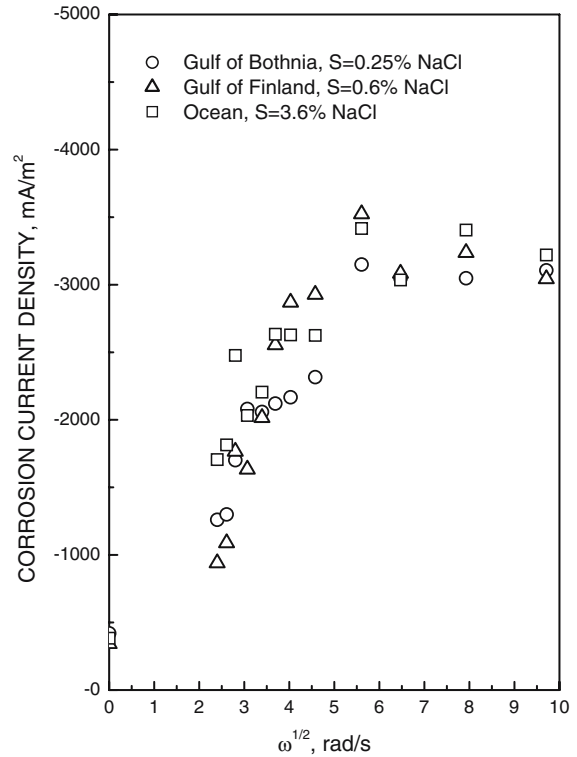


Fig. 2 Corrosion current densities of steel determined by polarization resistance method

Fig. 1 Test arrangement for dimension and conductivity scaling tests

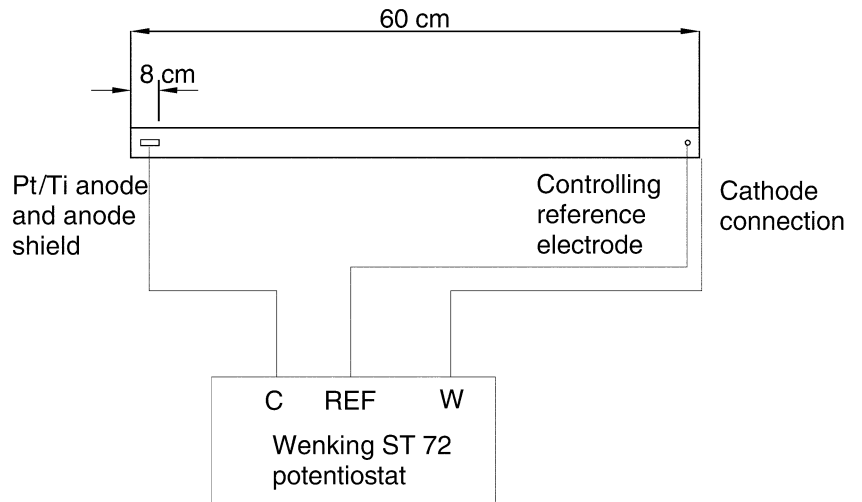


Figure 3 shows polarization curves for steel in synthetic ocean water and Fig. 4 shows polarization curves in synthetic Gulf of Finland brackish water. The limiting current density at the protection potential -800 mV is 50–100% higher than the initial protection current densities (110 – 220 mA/m²) given in [3]. This can be explained by the fact that the laboratory experiments measure instantaneous current densities. The design values of initial protection current densities are related to field conditions where reaction rates are assumed to decrease with time. The design current densities as given in [3] are values that were found to be suitable in practice. When the rotating speed is increased to 130 rpm, the limiting current density becomes ten times higher than that for a stationary electrode. Khambhaita et al. [12] showed that protection current requirement for steel free of deposits increases by ten times or more as flow rate changes from static seawater to 3 m/s.

The solubility of oxygen increases with decreasing salinity and temperature, so the cathodic reaction is more rapid in cold brackish water than in warm ocean water. Based on the mixed potential theory, the limiting current density gives an estimate of the required protection current density. When using a rotating disk electrode, the limiting current density is related to the square root of flow velocity according to the Levich equation (Eq. 2):

$$j_{lim} = 0.62 \cdot z \cdot F \cdot D^{2/3} \cdot \nu^{-1/6} \cdot \omega^{1/2} \cdot c \quad (2)$$

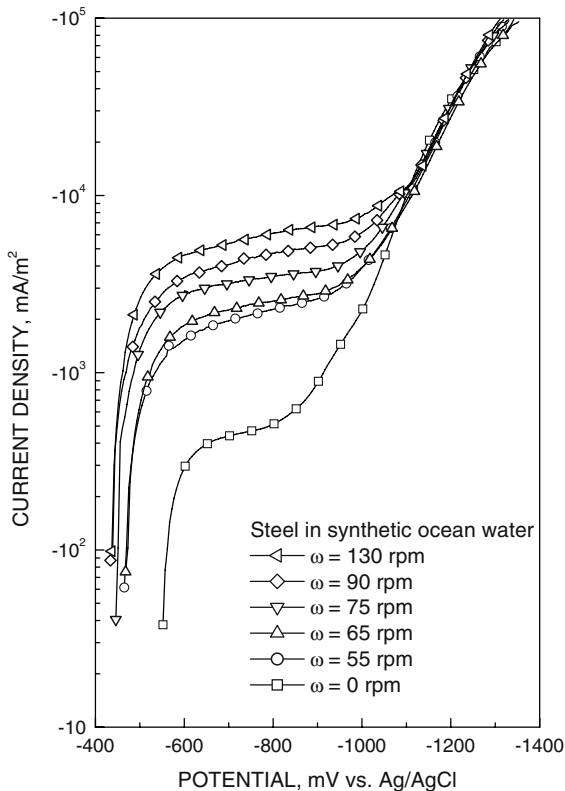


Fig. 3 Cathodic polarization curves for steel in synthetic ocean seawater at rotating speeds of 0–130 rpm

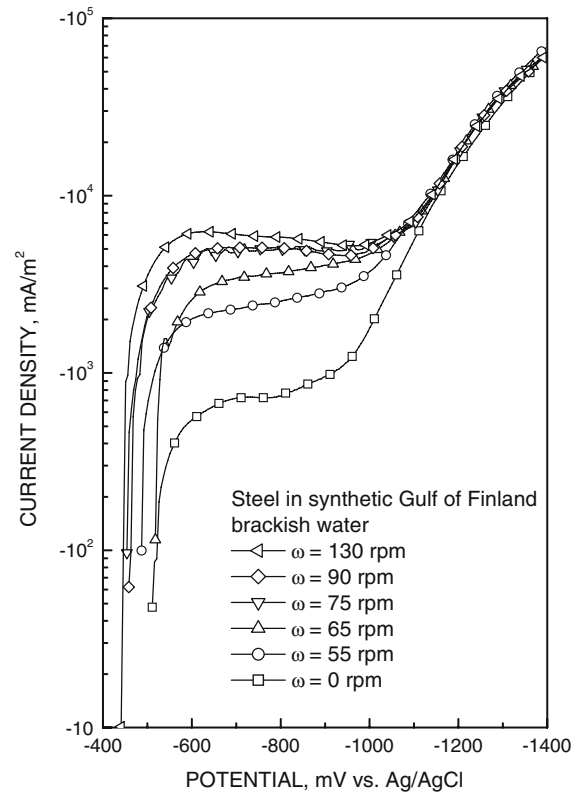


Fig. 4 Cathodic polarization curves for steel in synthetic Gulf of Finland brackish water at rotating speeds of 0–130 rpm

where j_{lim} is the limiting current density (A/cm²), z is the number of electrons involved in the reaction, F is Faraday’s constant (96,485 C/mol), D is the diffusion coefficient (cm²/s), ν is the kinematic viscosity (cm²/s), ω is the angular frequency [1/s ($=2\pi f$)], and c is the concentration (mol/cm³). If other factors remain the same, the limiting current density would depend on rotating speed and oxygen concentration.

Figure 5 shows the measured limiting current densities as a function of square root of angular velocity and theoretical values calculated using the Levich equation (Eq. 2). The oxygen concentrations were calculated using data in [2] that gives oxygen concentration in ocean water as 2.13×10^{-7} mol/cm³ and in brackish water 2.63×10^{-7} mol/cm³. The value of diffusion coefficient of oxygen was 1.74×10^{-5} cm²/s and kinematic viscosity of water was 10^{-2} cm²/s [13]. The measured limiting current densities were higher than the values predicted by Eq. 2. The deviation from linearity of Eq. 2 indicates that the cathodic reaction rate is not determined only by oxygen diffusion but can be dependent on the surface state of the electrode.

The main problem of cathodic protection in low conductivity water is how to assure uniform current distribution along the structure. Areas close to the anode take more current and the structure potential is lowest close to the anodes and increases when moving away from them. The protected area around a single anode depends on protection current density, output current of the anode,

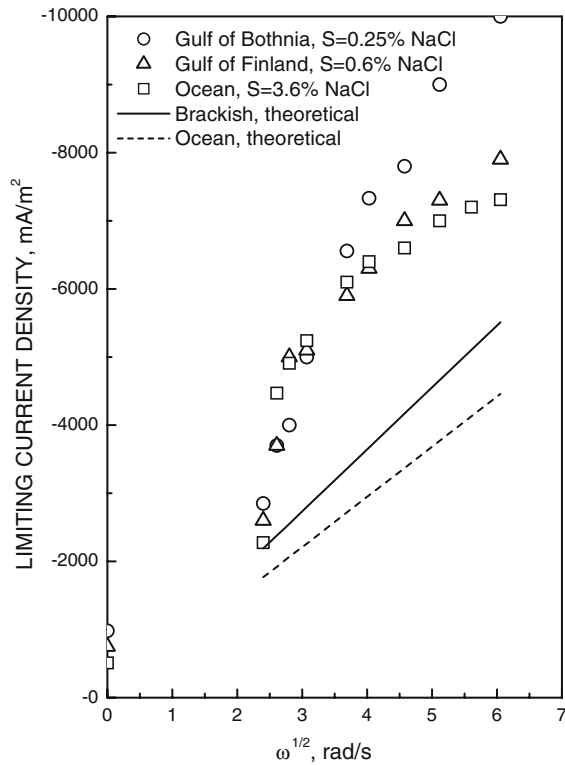


Fig. 5 The cathodic limiting current density as a function of angular velocity for the different waters

coating quality (resistivity), and seawater conductivity. Poor current distribution due to low conductivity can be improved by an electrically resistant coating, dielectric shields around the anodes, installation of more anodes (protected areas will overlap), and higher current output from an anode (increases the initial polarization around the anode).

The effect of salinity on protected length was estimated by using the Wagner number that was calculated using measured steel polarization resistance ($\Omega \text{ cm}^2$) and seawater conductivity (mS/cm) values, Eq. 1. As the salinity increased, the polarization resistance decreased but the conductivity relatively increased more. This resulted in an increased Wagner number with increasing salinity (Fig. 6). The Wagner number decreased with increasing rotating speed because the polarization resistance decreased. The Wagner number in ocean seawater was seven to ten times larger than in brackish water. This indicates that the protected length from an anode is, in brackish water, only 10–15% from that in ocean water.

The effect of seawater conductivity on cathodic protection distribution and protection current demand was measured by using the DACS method. The reference electrode controlling the cathodic protection system was set to distance corresponding to 11–12 m on actual structure. Figure 7 shows the effect of seawater conductivity on the protection length and initial current demand for steel free of deposits measured by the DACS method. In stagnant ocean seawater with salinity corresponding to 3.6wt% NaCl, the potential distribution is smooth and

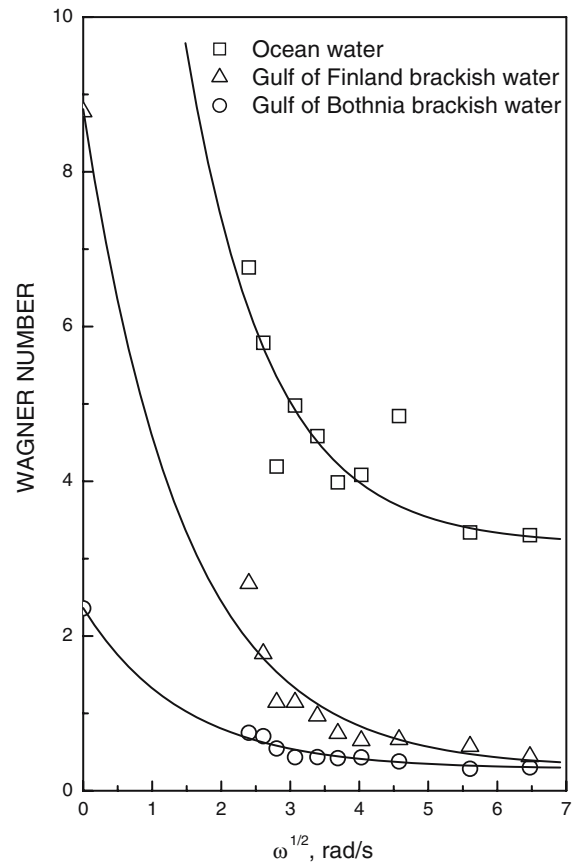
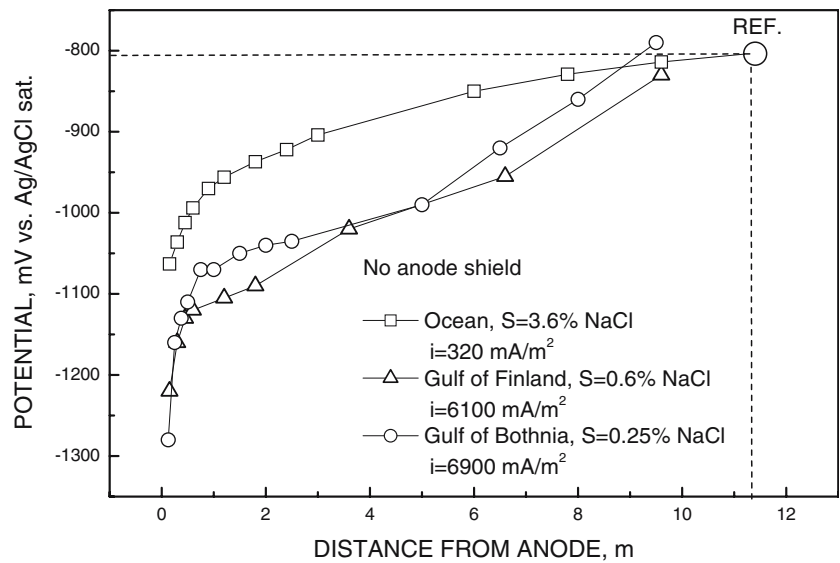


Fig. 6 Wagner numbers calculated by using measured polarization resistance and conductivity values in brackish water and ocean water

current demand for the test sheet was 5.7 mA, corresponding to 320 mA/m². This current density level corresponds with the measured limiting current densities shown in Fig. 3. In stagnant brackish water, complete protection was not achieved and the current demand was 110–125 mA, also nearly 20 times higher than in ocean water. The calculated current density for DACS tests in brackish water is 6,100–6,900 mA/m². These results indicate that in well conducting seawater, the limiting current density at the protection potential is a good design value for cathodic protection. In less conducting brackish water, clearly higher current capacity is needed to overcome the solution resistance.

Figure 8 shows the beneficial effect of calcareous deposits. Calcareous deposits were formed by constant cathodic polarization over a week. The deposit forms an additional coating layer that reduces the corroding surface area. The currents in Fig. 8 indicate the current needed for maintaining cathodic protection. In ocean water, the effect of calcareous deposit was not large. The calculated current density was now 280 mA/m², which is only 12% smaller than for steel free of deposits. Most likely, the deposit was not fully formed as in standards, for example in [3], the maintenance current density is given as 50% of the initial current density. For brackish water, the calculated current density decreased to 1,000 mA/m² in Gulf of Finland water and to 2,300 mA/m² in Gulf of Bothnia water. In brackish

Fig. 7 The effect of seawater conductivity on cathodic protection distribution and current demand measured by DACS



waters, the calcareous deposits had a significant effect lowering the current demand by 84% in Gulf of Finland water and 67% in Gulf of Bothnia water. Even with the presence of calcareous deposits, in brackish water the current demand was still much higher than calculated by using the limiting current density.

Figure 9 shows the effect of dielectric shield around the anode. A dielectric anode shield is a highly resistive compound, for example, thick epoxy coating that prevents areas near the anode to capture too much protective current. The measurements in Fig. 9 were done for steel sheet with a calcareous deposit. In the presence of a calcareous deposit, the current demand in brackish water is already significantly lower than for steel without deposits. The use of an anode shield can decrease the current demand further. Depending on the size of the anode shield and conductivity of the water, the current demand can be lowered in ocean water and in brackish water by 70–80%.

Table 3 shows a compilation of the current density values acquired in this study. The starting point of cathodic protection system design is the required current density. Standards, such as in [3], give different values for initial polarization of surface free of deposits for maintaining protection of deposit-covered surface and for repolarization in case the deposit is removed. The measured corrosion current densities in stagnant solution were higher than the standard values for initial polarization current densities. In ocean water, the corrosion current density was two times higher and the limiting current densities at the protection potential of -800 mV vs Ag/AgCl were two to three times higher than the initial protection current density given in the standard. In brackish water the corrosion current density was approximately the same as in ocean water, but the limiting current density could be two to three times higher. The effect of flow rate increased corrosion current density current and limiting current density the same way. This suggests that the effect was caused by enhanced

Fig. 8 The effect of calcareous deposits on cathodic protection distribution and current demand measured by DACS

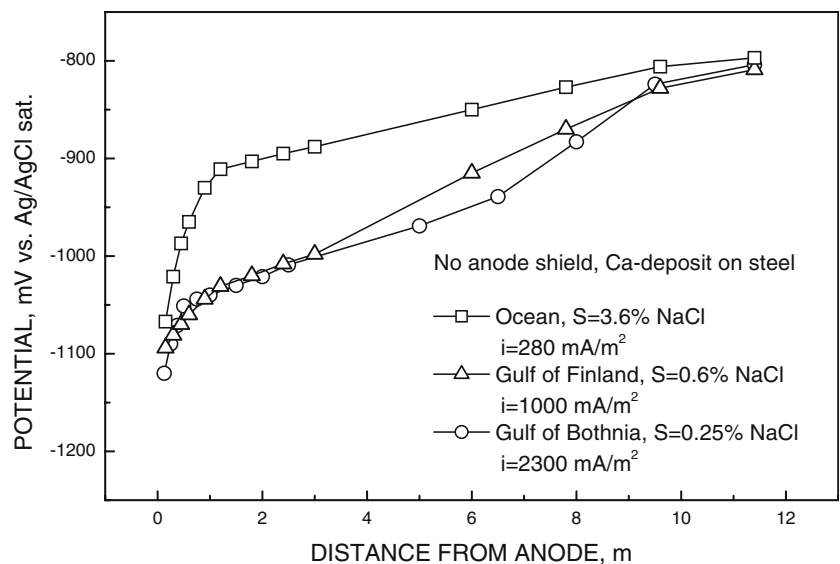
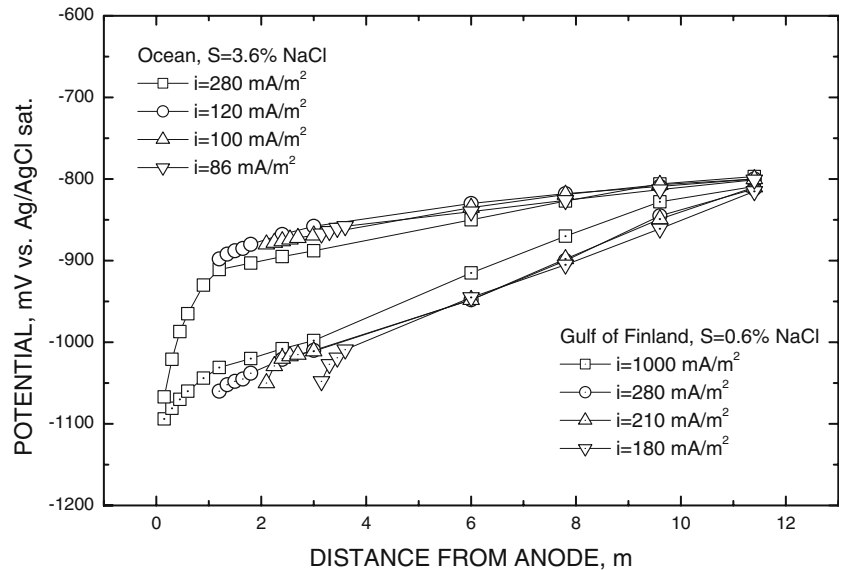


Fig. 9 The effect of dielectric shield around the anode on cathodic protection distribution and current demand measured by DACS



cathodic reaction. The current densities calculated in the dimension and conductivity scaling experiments point out that without calcareous deposits and anode shields, cathodic protection will not work in low conductivity water.

The use of dielectric shield around the anode is absolutely necessary. Osvoll et al. [14] calculated that to maintain protection and avoid overprotection of floating production storage and offloading unit hull, anode shields as large as 8 m are theoretically needed [14]. In low-conductivity brackish water, anode potentials are high, which means that areas near the anode have extremely low potential. Measurements by divers on Finnish icebreakers using portable potential logging devices indicate that the potential of hull near anode can be as low as -4 V vs Ag/AgCl in brackish water. In brackish water the hull potential can be lower than the limit of

overprotection ($-1,100$ mV Ag/AgCl) up to 4 m from the anode. The overprotection will cause disbondment of protective coatings and damages to anode shields.

Conclusions

The polarization curves measured in synthetic ocean seawater and brackish water showed that the limiting current density at the protection potential -800 mV vs Ag/AgCl/seawater is two to three times higher in brackish water than in ocean water. This relative change agrees with the solubility of oxygen at different salinities and initial protection current densities given for steel free of deposits in tropical and cold ocean water [3].

Based on the cathodic polarization curves, flow increases current demand at least by a factor of ten. Even

Table 3 Comparison of measured and calculated current densities in different experiments in mA/m²

Name	Purpose	Measured by	Gulf of Bothnia	Gulf of Finland	Ocean water
Initial current density for North Sea	Design value for surface free of deposits	Given in [3]			180–220
Maintenance current density for North Sea	Design value for surface covered with deposits	Given in [3]			90–100
Corrosion current density at $\omega=0$ rpm	Corrosion rate on surface free of deposits	RDE	420	340	380
Corrosion current density at $\omega=130$ rpm	Corrosion rate on surface free of deposits	RDE	2,100	2,500	2,600
Limiting current density at $\omega=0$ rpm	Cathodic reaction rate on surface free of deposits	RDE	980	750	510
Limiting current density at $\omega=130$ rpm	Cathodic reaction rate on surface free of deposits	RDE	6,600	5,900	6,100
Initial total current density, stagnant water	Needed for cathodic protection of surface free of deposits and to overcome solution resistance	DACS	6,900	6,100	320
Maintenance total current density, stagnant water	Needed for cathodic protection of deposit covered surface and to overcome solution resistance	DACS	2,300	1,000	280

a rather low flow rate of 3 m/s can cause a tenfold increase in current demand [12]. The relative increase in current demand was smaller in brackish water than in ocean water.

Based on dimensional and conductivity scaling, for the same protected length the initial current demand for uncoated steel is about 20 times higher in brackish water than in ocean water. The maintenance current demand for steel covered with calcareous deposit is four to ten times higher in brackish water.

Depending on the size of the dielectric anode shield and water conductivity, the shields can lower current demand by 70–80%. They have stronger effect in brackish water than in ocean water.

Based on the results, the design of cathodic protection system for ships in brackish water should use different design values than given in standards to ensure that the protection system has enough current capacity. The initial and maintenance current densities are estimated to 50–100% higher than the standard values. The lower conductivity of brackish water requires 4–20 times higher current densities to maintain the same protected area around one anode as in ocean water. Such an increase in current capacity is usually not possible, so to ensure good protective current distribution, the number of anodes should be higher than in systems designed for ocean water conductivity. The use of dielectric shields in brackish water is very effective to reduce the output current capacity of the system.

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