AC Corrosion Tests of Carbon Steel, AlZnIn Anodes and 25Cr Duplex for Subsea Applications

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ABSTRACT

This paper presents results from AC corrosion tests on 25Cr duplex and cathodically protected carbon steel. The results show that the corrosion rate is independent of transfer current density (0-200 A/m^2) and power frequency (50-200 Hz) on cathodically protected carbon steel. On the anodes (AlZnIn), the corrosion rate increases as a function of transfer current density (0-80 A/m^2). However, the correlation is less prominent at higher frequencies (100-200 Hz). For the freely corroding super duplex, the correlation is similar to that on the anodes for the highest current density (1000 A/m^2). For the lowest current densities (100 A/m^2), the corrosion rate was independent of power frequency. Safe levels for AC induced transfer current densities are proposed at power frequencies of 50, 100 and 200 Hz.

KEY WORDS: Alternating Current Corrosion; Laboratory Tests; Carbon Steel; AlZnIn Anodes; 25Cr Duplex; Current Transfer Density.

INTRODUCTION

In recent years, alternating current (AC) corrosion has been a concern when installing electric power equipment subsea. In water tight systems, such as umbilicals, an AC voltage can be induced in metallic elements like 25Cr duplex (super duplex) tubes for hydraulic control and chemical injection, or in fibre optic protection elements. Ideally, the tubes are electrically insulated from the seawater and therefore, immune to AC corrosion. However, in the event of a coating defect in the umbilical, seawater may come in contact with metal, leading to AC corrosion, (OWPB, 2017; Gustavsen, 2019; Midttveit, 2017). In Direct Electrical Heating (DEH) systems for flow assurance, AC currents of several hundred amperes are transmitted in a controlled manner from carbon steel flowlines to surrounding seawater in a 30-100 m section at each side of the flowline in a Current Transfer Zone (CTZ). To mitigate AC corrosion for DEH, tens of sacrificial anodes are connected to the flowline, (Lervik, 2004), in order to maintain a low AC current density on the flowline and the anodes.

AC corrosion is caused by an alternating current crossing the metal/electrolyte interface. During the positive half-wave of the AC current, part of the current flow may be faradaic, i.e. contributing to the oxidation of solid metal to ions. In most situations, the current transfer across the metal-seawater interface is mainly capacitive, and the faradaic component amounts only to a minor part of the total current. The rate of AC corrosion depends on several parameters, including metal quality, cathodic protection level, power frequency, transfer current density (TCD), temperature and hydrostatic pressure.

For AC corrosion mitigation in DEH systems, TCD has been the governing parameter. Studies have identified threshold TCD levels below which AC corrosion rate is found acceptable. For cathodically protected carbon steel and aluminum (AlZnIn) anodes the TCD design levels are 100-240 A/m^2 and 20-40 A/m^2, respectively, (Nysveen, 2007). TCD design levels between 30 and 100 A/m^2 are also seen, (ISO 18086:2017). The standard covers cathodically protected steel only, but the quality is not defined. For 25Cr duplex materials without cathodic protection, no such design limits have been found. Therefore, TCD levels are chosen on project basis (hence the ranges in TCD levels) and are currently only applicable for power frequencies of 50/60 Hz.

This paper concerns the experimental set-up and results from AC corrosion tests on 25Cr duplex and cathodically protected carbon steel. An extensive test program is performed to study how the corrosion rate depends on power frequency and TCD, under conditions relevant for DEH (carbon steel-aluminum materials) and power umbilical elements (25Cr duplex material). TCD design levels based on the results are proposed and discussed. The tests have been carried out at 50, 100 and 200 Hz at various TCDs on carbon steel (100-400 A/m^2), aluminum (20-80 A/m^2) and 25Cr duplex (100-1000 A/m^2). Some initial results have been presented previously, (Solheim, 2017 and 2018).

EXPERIMENTAL PROCEDURES

Materials

The carbon steel specimens were machined from a 12" pipe joint manufactured in accordance with the flowline standard DNV OS F101 2007 HFW 450 PD. The AlZnIn anode specimens (named 'aluminum' in this paper) was machined from a bracelet anode. The anode was made according to ISO 15589-2 with typical anode composition of 94-96 % Al, 4-6 % Zn and 0.02 % In. The exact composition of the specimens has not been examined. The 25Cr duplex material fulfilled the standard UNS 32750 Norsok M-630 MDS D57. All specimens were ground and polished on the exposed side.

The specimens were coin shaped with a thickness of 2 mm. Two different sizes were machined, with exposed areas of 0.79 cm^2 and 3.84 cm^2. Often, the accepted TCD level for aluminum is 20% of that for carbon steel. The carbon steel-aluminum tests are therefore carried out at a surface ratio of 5:1.

The tests were conducted in plastic containers filled with ~20 L of artificial seawater produced according to ASTM D1141. The water was not stirred during the test period but was replenished with distilled water as water vaporized.

Test setup

The specimens were placed in special-designed holders, where only one side was exposed to seawater. An insulated electrical wire was terminated to the reverse side of the specimens. Each test consisted of four (25Cr duplex) or five (anode/carbon steel) pairs of specimens. The two specimens in each pair were connected to each other via the secondary side on a transformer. An AC current from a constant voltage source was applied between pairs of specimens, except for the references. For carbon steel/aluminum specimen pairs, carbon steel specimens were placed in one holder, aluminum in the other. For 25Cr duplex pairs, the same material was used in all holders. See Fig. 1.

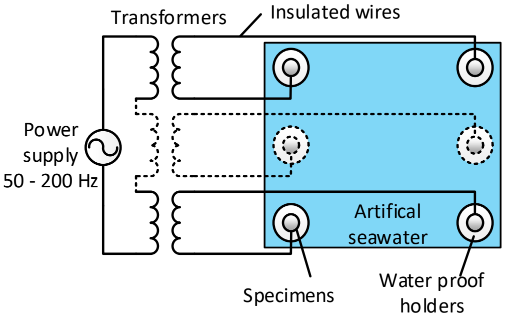

Fig. 1. Test set-up. Specimens are placed in water proof holders. They are exposed to seawater in one end and connected by insulated wires in the other.

Test program

The test program is given in Table 1 for carbon steels and anodes, and in Table 2 for 25Cr duplex steels. In addition, there was one set of reference specimens for each material with no applied AC current. The test period was 34 days. During the first 7 days no AC was applied (acclimatization period), then AC was applied for 27 days.

Table 1. AC current density and frequency test program on carbon steels and anodes. * denotes duplicated tests.

Frequency [Hz]	Carbon steel current density [A/m^2]	Anode current density [A/m^2]
50, 100, 200	100	20
50*, 100, 200	200	40
50, 100, 200	400	80

Table 2. AC current density and frequency test program on 25Cr duplex steels.

Frequency [Hz]	25Cr duplex current density [A/m^2]
50,	100
50, 100, 200	250
50, 100, 200	1000

The RMS-currents were recorded every 20 minutes for one specimen pair of each test. Ambient temperature, and for some of the tests also, the seawater temperature and RMS voltage drop across the specimens were recorded every 20 minutes.

Post-test treatment

All specimens were chemically cleaned, dried and weighed before and after the tests. After the tests, the carbon steel specimens were cleaned with a mixture of concentrated hydrochloric acid (HCl), antimony trioxide (Sb_2O_3) and stannous chloride ($SnCl_2$). This is according to ASTM G1. The aluminum specimens were cleaned by concentrated nitric acid (HNO_3) and chromium oxide (CrO_3). This is a variant of ASTM G1 that the authors have good experience with. Finally, the corrosion rates were calculated using the weight loss method.

RESULTS AND DISCUSSIONS

Cathodically protected carbon steel specimens

Deposits formed on all carbon steel specimens, including the references. A white and hard deposit was found on the exposed surface, see Fig. 2. This is believed to be calcareous deposits formed as a result of cathodic protection. The deposits were thicker at higher TCDs and lower frequencies. High AC impedance was measured across the objects with thickest deposits.

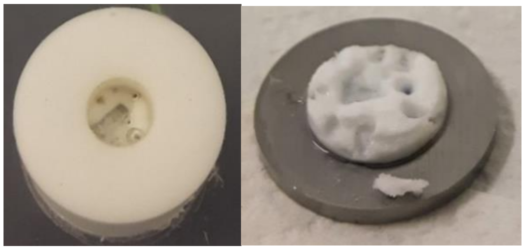

Fig. 2. Deposits on carbon steel specimen inside holder (left) and when removed from holder (right). TCD was 200 A/m^2 at 50 Hz.

Visual inspection of the specimens after cleaning did not uncover any corrosion or dissimilarity between the carbon steel specimens, only some discoloration. Microscopy revealed that the topography of the reference specimens was unaffected by the tests; during manufacturing the specimens were machine polished, producing a straight-lined pattern on the surfaces. This pattern was unchanged after the test period. However, on the surface of the specimens exposed to 400 A/m^2 (80 A/m^2 on aluminum), spots of a matte finish were found, proving that at least a minute part of the top layer is modified. This effect was found to be similar on the 50-, 100- and 200 Hz specimens and is indicated in Fig. 3.

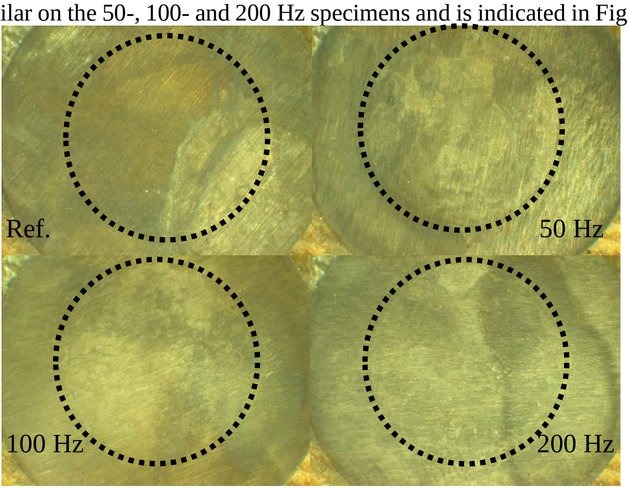

Fig. 3. Carbon steel specimens at 0-200 Hz after the tests. TCD was 400 A/m^2 on the 50, 100 and 200 Hz specimens. The exposed surfaces are indicated by circles.

The corrosion rate of the carbon steel specimens varied from 0.00 to 0.08 mm/year among the samples. The corrosion rate for each specimen (dashes) and the mean of each series (dots) are shown in Fig. 4. No clear correlation can be seen between corrosion rate and TCD or power frequency. The highest corrosion rate (0.08 mm/year) is seen for one of the specimens at 100 Hz with TCD of 400 A/m^2. The scatter between the duplicated tests (50 Hz / 200 A/m^2) is substantial; the reason for this is not known, as both tests were performed following the same procedures.

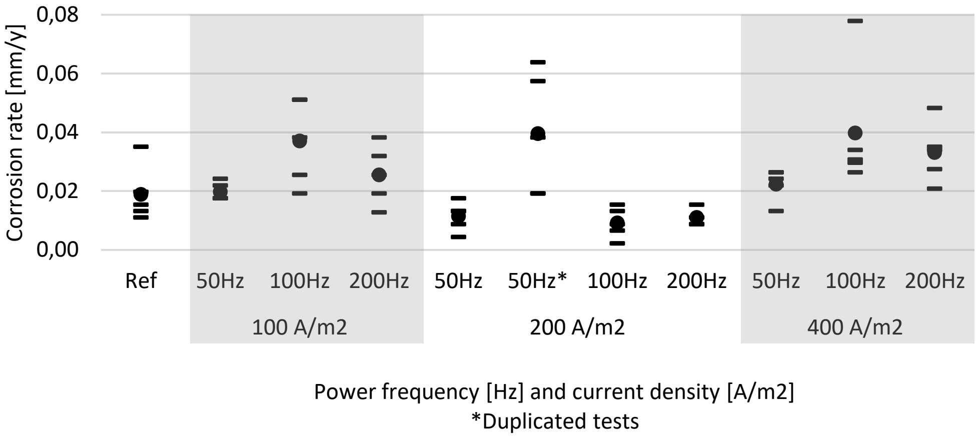

Fig. 4. AC corrosion rate of cathodically protected carbon steel specimens. The dashes are measured corrosion rates for each specimen, the dots represent the mean values of the series. The reference tests are without passing any current.

Due to very little material loss of the specimens (range from 0.1 to 4 mg), the sources of error may be considerable. The balance has a linear deviation of +/- 0.2 mg. This corresponds to a corrosion rate deviation of +/- 0.01 mm/year. Another error source, which cannot be quantified, is the effectiveness of the cleaning processes. The cleaning process was checked and found not to cause material loss on non-corroded specimens. However, it cannot be ascertained that all corrosion products were removed during cleaning.

Based on the scatter and deviation in the measured corrosion rate, the statistical dependence on frequency and TCD and measurement uncertainties, it cannot be concluded that the corrosion rate of the specimens exposed to AC currents (in the tested range) differs from the reference specimens.

Sacrificial aluminum specimens

Similar to the carbon steel specimens, deposits formed on all aluminum specimens, including the references. A soft white foam-like substance was created, as seen in Fig. 5. This is believed to be aluminum hydroxide. The deposits were more pronounced at higher TCDs and lower frequencies. This is expected since the formation rate of the deposit is proportional to corrosion rate of the specimens.

Fig. 5. Deposits on aluminum specimen at TCD of 80 A/m^2 at 50 Hz (left) and TCD of 40 A/m2 at 200 Hz (right).

On the cleaned aluminum surfaces, several smaller and larger regions of pitting corrosion were observed. This means that the corrosion rate in the pits was larger than the average calculated by the weight loss method. This is normally not a problem for anodes but may increase the probability for non-faradic material loss, i.e. material pieces that detach from the anodes. Fig. 6 shows images of aluminum specimens after the corrosion tests and cleaning process. The figure includes a reference specimen (no AC current applied), together with specimens subjected to 50, 100 and 200 Hz at 80 A/m^2. The white substance on the 50 Hz specimen could not be removed even by extended cleaning and is believed to be porous aluminum. Minor areas of white substance are observed on the 100 and 200 Hz specimens. A TCD of 80 A/m^2 greatly exceeds the present design level at 50 Hz, meaning that such corrosion rates are not relevant for DEH installations at 50 Hz.

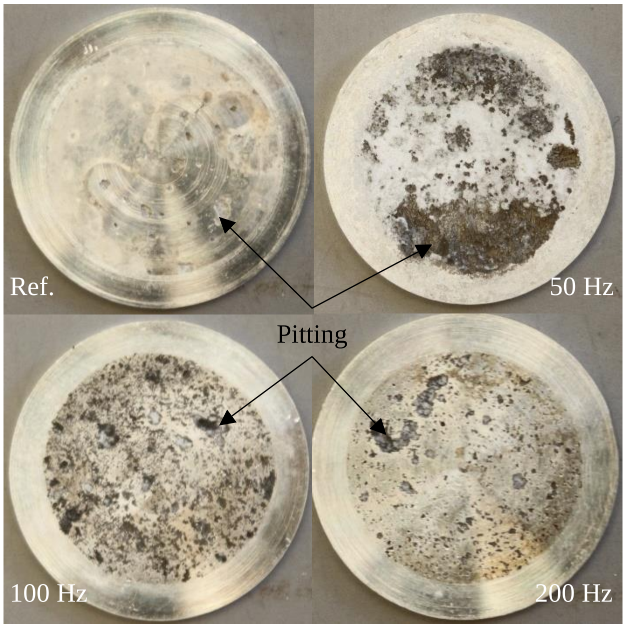

Fig. 6. Aluminum specimens at 0-200 Hz after the tests. TCD was 80 A/m^2 on 50, 100 and 200 Hz specimens.

The corrosion dependency of TCD and frequency is much more prominent for aluminum than carbon steel within the range tested. The AC corrosion rate of aluminum specimens varied between -0.2 and 4.1 mm/year, as shown in Fig. 7. This corresponds to a material loss from 8 to 315 mg, excluding the single negative corrosion value. Unsurprisingly and in accordance with other studies, (Hesjevik, 2006), the general corrosion rates of the aluminum samples are greater than for the carbon steel samples.

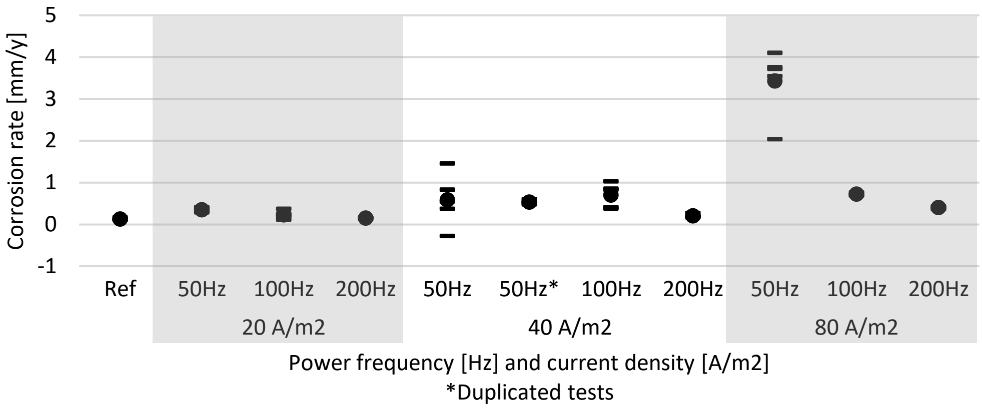

Fig. 7. AC corrosion rate of aluminum specimens. The dashes are measured corrosion rates for each specimen, the dots represent the mean values. The reference tests are without any current.

For an applied TCD of 80 A/m^2, the corrosion rate decreases uniformly with increasing power frequency. For the specimens exposed to 20 and 40 A/m^2, the trend is not as prominent due to the scatter in the results. There is a clear trend that the corrosion rate increases at increasing TCD at 50 Hz. A corrosion rate increase of a factor 10 is seen when increasing from a TCD level of 20 to 80 A/m^2. For 100 Hz and 200 Hz, the corrosion rate is less affected by TCD increase within the range tested.

The scatter is more significant at 50 Hz, than at 100 and 200 Hz. It seems that the corrosion morphology is more even at higher frequencies. For one sample at 50 Hz, a negative corrosion was measured. The negative corrosion rate of this specimen exceeds the expected weighing error and cleaning process error. Based on visual inspection after the tests, it seems plausiable that two of the samples were exchanged during the cleaning process, and this is the reason for the duplication of the test. The corrosion rate is much more even for the duplicated test.

25Cr duplex specimens

In contrast to carbon steel, the 25Cr duplex is considered a corrosion resistant alloy. The 25Cr duplex specimens were not cathodically protected in the tests. After the test period, corrosion products or discoloration was observed on all 25Cr duplex specimens, except on the references. The deposits were red-brown rust oxidized from the specimens. The amount of corrosion products seemed to correlate to the measured corrosion rate.

The difference in corrosion rate, visually and measured, is striking. Images from reference specimens and specimens at 50, 100 and 200 Hz with TCD of 1000 A/m^2 are shown in Fig. 8. These specimens are shown since it is easiest to see differences. For the reference specimens, no corrosion is observed. At 200 Hz, a few pits are located around the circumference of the exposed surface. At 100 Hz, the exposed surface has corroded evenly, in addition to some pits around the circumference. For the 50 Hz specimens, the exposed surface was evenly corroded.

The corrosion rate of the specimens varied from 0.0 to 6.3 mm/year, as seen in Fig. 9. The corrosion rate was highly dependent on power frequency for a TCD of 1000 A/m^2. The scatter is more prominent for the specimens with the highest corrosion rates.

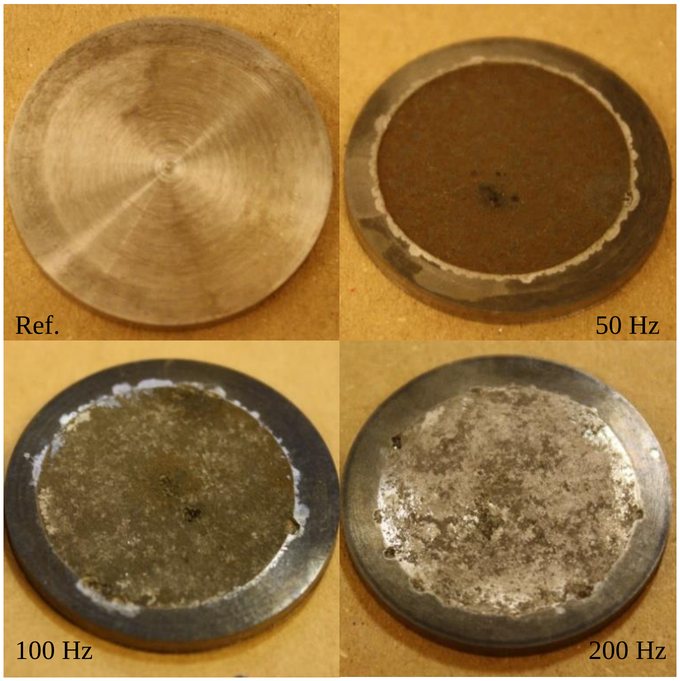

Fig. 8. Corrosion of 5 cm^2 specimens for TCD of 1000 A/m^2.

At 250 A/m^2, the dependency of power frequency is evident, but to a much smaller degree, as seen in Fig. 10. A selection of the data from Fig. 9 is presented at a different scale. At 50 and 100 Hz, it is seen that for some specimens, corrosion rate at a TCD of 250 A/m^2 exceeds the rate of the reference specimens.

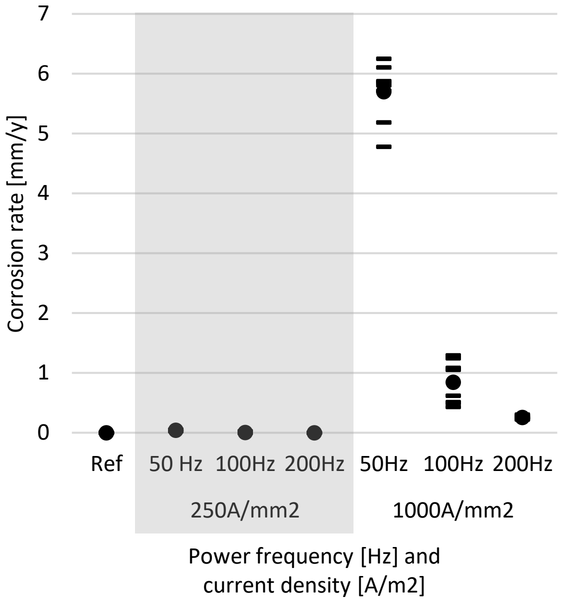

Fig. 9. AC corrosion rate of all 25Cr duplex specimens. The dashes are measured corrosion rates for each specimen, the dots represents the mean values.

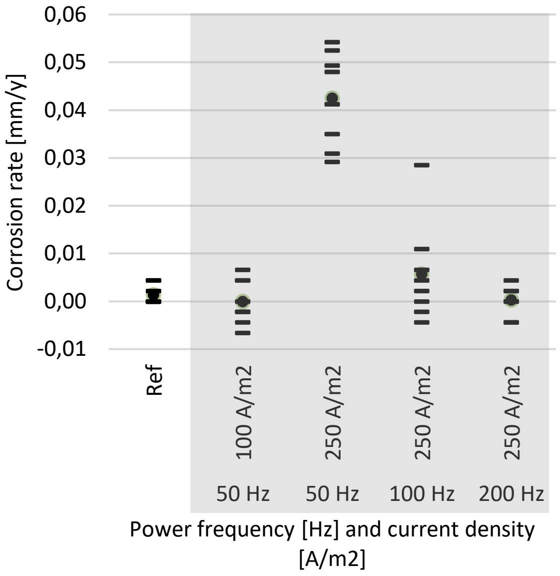

Fig. 10. AC corrosion rate for selected 25Cr duplex specimens from Fig. 9, in addition to 100 A/m^2 at 50 Hz. Dashes are measured corrosion rates for each specimen, the dots represents the mean values.

TCD DESIGN LEVELS

Based on the results from the corrosion tests, safe TCD levels are proposed. For the purpose of this work, the corrosion rate on steel materials is considered acceptable when it is similar to the reference tests. For sacrificial anodes, material consumption is always expected, and the acceptable consumption rate may vary on a case-by-case basis. Typically, anodes are expected to protect the steel for a certain number of years, corresponding to the time passed when the anodes are so much consumed that they are no longer able to keep the steel at the desired electrode potential. When proposing new TCD levels for the aluminum anode, the criterion chosen is to keep consumption rate below 1 mm/year at continuous operation.

Based on these criteria, proposed design levels are given in Table 3.
The levels are based on results from the results in this paper only.

For cathodically protected carbon steel, the results (Fig. 4) indicate that the corrosion rate at TCD of 200 A/m^2 is similar to or less than the reference tests. This is valid at 50, 100 and 200 Hz. In the laboratory tests a surface ratio of 1:5 between the steel-aluminum samples was used, i.e. for a TCD of 200 A/m^2 on steel, the TCD was 40 A/m^2 on the anodes. Therefore, the anode design TCD should be 40 A/m^2. As seen in Fig. 7, anode consumption is less than 1 mm/year at this level. The results also indicate that the anode TCD may be up to 80 A/m^2 at 100 and 200 Hz without significantly increasing consumption rate. However, it is not known whether the cathodic protection is maintained at this TCD level.

For 25Cr duplex, a TCD of 100 A/m^2 at 50 Hz and 250 A/m^2 at 200 Hz produce similar corrosion rates as the reference specimens. This is seen in Fig. 10. At 100 Hz, the lowest tested TCD of 250 A/m^2 indicate that the corrosion rate is higher than for the reference specimens. Therefore, the design TCD should be less than 250 A/m^2. It can be argued that the corrosion rate decreases as the power frequency increases, and that the TCD limit at 100 Hz can conservatively be set at 100 A/m^2, i.e. the same as for 50 Hz.

The design levels are up to 2.5 times higher than the common criteria used today. The consequences of a higher level may be:

- reduced number of anodes, which allows for simpler design and installation.
- increased service time due to less corrosion than anticipated by previous guidelines.
- more flexibility related to design of integrated umbilicals with both power cables and 25Cr duplex steel tubing.
- sharing right-of-way with DEH or other transmission lines imposes less stringent anti-corrosion requirements.

All of the above represent benefits that ultimately result in reduced costs. As such, they show the importance of identifying the correct constraints for mitigating the AC corrosion issue.

Table 3. Proposed design levels for maximum transfer current density

Materials	Maximum transfer current densities [A/m^2]			
	Today's commonly accepted levels	Proposed new design levels		
	50 Hz	50 Hz	100 Hz	200 Hz
Carbon steel (protected)	100-240	200	200	200
Sacrificial aluminum (anode)	20-40	40	40	40
25Cr duplex (freely corroding)	30-100	100	100	250

SUMMARY AND CONCLUSIONS

Small scale AC corrosion tests have been carried out on cathodically protected carbon steel and freely corroding 25Cr duplex specimens at various power frequencies (50-200 Hz) and transfer current densities (0-1000 A/m^2). The main findings are:

- The corrosion rate of the cathodically protected carbon steel cannot be seen to depend on the TCD level for TCD less than or equal to 200 A/m^2, for any power frequency in the tested range.
- The corrosion rate of the sacrificial aluminum (AlZnIn) anode increased at increasing TCDs and decreased at increasing power frequency. An exponential increase in the corrosion rate was seen for increasing TCDs at 50 Hz. Such corrosion rate increase was not observed at 100 and 200 Hz.
- For freely corroding 25Cr duplex materials, the corrosion rate was unaffected by TCD at 100 A/m^2 for all frequencies. At the highest TCDs (1000 A/m^2), high corrosion rates were observed for all frequencies.
- TCD levels for AC corrosion mitigation have been proposed. The new levels are up to 2.5 two times higher than today's commonly accepted values.

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