Paper No.
03082

CORROSION 2003

RESISTOR CONTROLLED CATHODIC PROTECTION FOR STAINLESS STEELS IN CHLORINATED SEAWATER

A REVIEW AFTER 8 YEARS IN SERVICE

Guri E. Nustad
CorrOcean ASA
Claude Monet Alle 5
1338 Sandvika, Norway

Tone Solem, Roy Johnsen, Harald Osvoll and Per Olav Gartland
CorrOcean ASA
Teglgården
7485 Trondheim, Norway

Michael Brameld and George Clapp,
Woodside Australian Energy
Level 8, Central Park 152 – 158, St. George's Terrace
Perth, 6000 Western Australia

ABSTRACT

Highly alloyed stainless steel (SS) materials may be prone to local corrosion under certain conditions. To avoid corrosion in chlorinated seawater systems, a modified cathodic protection system called Resistor controlled Cathodic Protection (RCP) (1) has been developed. The method is based on having a resistor (or a diode) in series with the sacrificial anode to allow polarization of the SS steel to a potential level where corrosion does not occur, and where the current density requirement is small.

The RCP method has been commercially available since 1995 and today RCP anodes protect stainless steels exposed to chlorinated seawater on more than 50 offshore and onshore facilities. Each RCP anode is uniquely designed for a specific location using a computer program that calculates potential variations, current density distribution, anode resistor values and anode consumption rates. This paper presents the principles and practical experience of the RCP method with emphasis on the importance of sufficient chlorination and the effect of deposits sometimes seen building up at the anode surface. Through the experience gained, continuous chlorination giving 0.5 ppm residual chlorine is generally recommended, and laboratory investigations to examine how deposits may affect the anodes have lead to an improved RCP anode design.

Keywords: stainless steels, resistor controlled cathodic protection, chlorinated seawater, biofouling

(1) The Resistor controlled Cathodic Protection (RCP) method is based on patent claim no. 91.0093 from SINTEF (a Norwegian Research and Development body)

INTRODUCTION

Since the early 1980s highly alloyed stainless steels (SS) have been widely used for chlorinated seawater systems on offshore installations. Originally it was thought that SS qualities alloyed with 6% Mo or having 25% Cr would be corrosion resistant in seawater systems at temperatures up to at least 30 ºC. Experience, however, soon revealed that local corrosion, particularly crevice corrosion may occur at much lower temperatures. As a result, Norwegian oil companies reduced the safe upper temperature limit of SS alloys like UNS S31254, UNS S32550/S32759/S32760 to 15 ºC in areas with crevices. Lately, the safe limit has been increased to 20º C, but even so it is generally acknowledged that highly alloyed SS materials require additional corrosion protection in chlorinated seawater systems or, alternatively, be replaced with more corrosion resistant materials.

Conventional cathodic protection (CP) is less suitable for SS internals due to unacceptable anode consumption rates. In addition, UNS S2550/32750/32760 may be prone to hydrogen embrittlement initiated at the potential level created by conventional sacrificial anodes. Investigations to find alternative corrosion protection of SS internals resulted in a modified cathodic protection methods being developed in the early 1990s. The method is called Resistor controlled Cathodic Protection (RCP) and has been applied for corrosion protection of chlorinated stainless steels since mid-1995[1]. In this paper the principles of the RCP method, the establishment of a design tool and a review related to practical experience after 8 years in service are presented.

DEVELOPMENT OF RESISTOR CONTROLLED CATHODIC PROTECTION

All CP designs are based upon current density requirements. In the early 1990s current density requirements were not readily available for SS qualities and laboratory programs based on potentiostatic and galvanostatic tests were conducted to gain experience [2,3]. In these laboratory investigations SS qualities like UNS S31254, UNS S32550/S32750/S32760 and UNS S31600 were exposed in chlorinated seawater under varying chlorination levels, temperatures and flow conditions.

The experiments revealed that the potential of passive SS in chlorinated seawater rises to above 600 mV vs. SCE within a few hours[1]. The relation between critical potential and temperatures leading to local corrosion are shown in Figure 1. The bold curve is relevant for the SS qualities UNS S31254 and UNS S32550/S32750/S32760 and indicates that these alloys may be corrosion resistant up to 30º C. The dashed line representing UNS S31600 reveals that this grade may not be expected to be corrosion resistant at any temperature. More importantly, Figure 1 shows that SS may withstand higher temperatures before corrosion is initiated if the steel potential is lowered.

Typical current density requirements measured for highly alloyed SS in chlorinated seawater versus stainless steel potential are shown in Figure 2[1]. As can be seen, the current density requirements are relatively low at high potentials compared with the current density requirements at low potentials. Hence, using conventional sacrificial anodes of zinc or aluminum alloy that result in a polarization to relatively negative potentials will increase the current density requirements considerably and thereby lead to rapid anode consumption. This observation lead to the idea of finding a way to control the polarization to meet the potential level actually required to avoid local corrosion and simultaneously to limit the anodic current requirements. As a result, resistor controlled cathodic protection, i.e. use of a sacrificial anode having a built in resistor to limit the polarization was developed.

DESIGN OF A RESISTOR CONTROLLED CATHODIC PROTECTION SYSTEM

The principle of resistor controlled sacrificial anodes is schematically illustrated in Figure 3. The anodes protruding the piping are in electrical contact with the piping only through a built-in resistor i.e. the anodic current density output is limited. The piping potential near the anode is:

$$E_n = E_a + IR \quad (1)$$

E_n = Piping potential next to the anode
E_a = anode potential
IR = the potential drop over the built in resistor.

The piping potential at some distance away from the anode is

$$E_f = E_n + \Delta E_{seawater} \quad (2)$$

$\Delta E_{seawater}$ = the potential drop between the near and far position of the piping caused by the transport of current in seawater.

The low anode current demands result in relatively low seawater potential drops compared with conventional CP design. This allows resistor controlled anodes to protect quite large pipe lengths. The maximum spacing between the anodes is determined through calculations of the potential profile along the piping utilizing realistic boundary conditions. The objective is to ensure that the most positive pipe potential expected along the pipe is below (i.e. more negative) the defined pipe protection potential. If this objective is met, full corrosion protection is expected.

The protection potential is determined based upon:

- Base material composition
- If required, lowering of the protection potential to protect galvanic couplings must be considered
- Seawater temperature
- Presence of corrosion sites (if present, protection potential must be below the repassivation potential)

Based on the above each RCP anode is uniquely designed for a specific location. To handle all aspects, a computer program that calculates the potential variations, the current density distribution, anode resistor values and anode consumption rates has been developed. This computer program is linked to a database containing information on polarization behavior of SS materials under varying environmental conditions. The calculations are based upon the Finite Difference Method and complex boundary conditions are handled by linearisation and iteration. Complex pipe networks with branching pipes of varying diameter, presence of heat exchangers, valves, pumps etc. may be handled in one single model. Environmental parameters are allowed to vary within the geometric models and the results of the calculations are displayed numerically and graphically. Color plots showing the piping potential variations between anodes allow easy overview of expected protection degree. An example is shown in Figure 4. Optimal anode placing is obtained by repeating calculations with anodes at various locations.

If environmental parameters change, the model may be rerun with the new input parameters to determine any impact on the level of protection. If required, anode resistor modification or additional anodes may thereafter be advised.

PRACTICAL EXPERIENCE

The first installation with RCP anodes was completed in early 1995. The purpose was to protect a UNS S31254 seawater cooling system against local corrosion in welds and crevices. Originally temperatures up to 30 ºC were expected but as temperatures up to 60 ºC were measured in the heat exchangers between the cooler lines, corrosion soon became evident. At the time two options were evaluated:

- Replace piping with a corrosion resistant material
- Repair corroded areas and install RCP anodes to prevent future corrosion.

The latter option was selected and to date RCP anodes have been installed for corrosion protection of seawater and firewater piping systems on some 50 offshore installations. In addition, RCP anodes are also installed for corrosion protection of heat exchangers on onshore plants.

Figure 5 shows a RCP anode fixed to a blind flange. The anode material is zinc, cast as a cylinder on a central carbon steel rod. A PVC sleeve provides a barrier to avoid electrical contact between the anode and the piping since the electrical contact is to be through the built in resistor only. The anode therefore only corrodes from its upper face. In the early days the RCP anode had a perforated PVC front plate. At some installations a declining anode current output with time was experienced and visual examination revealed corrosion products building up at the anode top surface. Through a laboratory test program it was discovered that a combination of partial passivation and an ohmic potential drop through the layer of deposits caused a shift of anode potential in the positive direction[4]. If not removed this would with time lead to reduced anode current outputs. To avoid this in the future a new RCP anode has been designed with the perforated front plate removed, as can be seen in Figure 5. For existing anodes a front plate modification can be advised.

The anodes are equipped with a connector for potential drop measurement over the resistor. By applying Ohms law this reading gives a direct measure of the anode current output and when compared with the anode potential drop design value, the expected protection degree may be calculated.

In the early days, a monitoring program covering some 20% of the installed anodes was typically advised, as it was thought readings would stabilize at a level below design after some months in service. Experience has however revealed more varying anode current outputs than anticipated suggesting that operational parameters may alter considerably. To evaluate RCP anode performance, anode potential drop measurement series every 6th month covering all RCP anodes installed is the minimum monitoring frequency advised today. However, measurement series every 3 to 4 months are generally recommended to catch more fluctuations and thereby allow a better basis for remaining life calculations and any anode modifications if required. In addition, records of water temperature and chlorination level and a notification of the flow conditions are recommended to encompass all potential drop reading series. Any events that may have had an impact on the anode performance should also be stated. The mentioned parameters are of utmost importance to allow more accurate anode evaluations and particularly if any anode modifications should be required.

Proper seawater chlorination is of utmost importance to provide a cost effective installation. Chlorination is carried out to kill bacteria and other organisms that otherwise may cause a settlement of organic material that reduces the efficiency of heat exchangers. Lack of chlorination also increases the rate of corrosion as the biofilm formation enhances the cathodic reaction. In other words, insufficient chlorination increases the anodic current demand. This is seen as increased anode potential drop readings of the RCP anodes. An example is shown in Figure 6 where the potential drop readings of some RCP anodes were significantly increased in the December 2001 measurement series. Examinations revealed the chlorination system at the time was not operating. The chlorination system was operating normally again from to end February 2002 and the next measurement series, taken in April 2002 documented reduced anode current demands. The sudden increased current demand underlines the importance of regular monitoring to catch fluctuations and thereby be able to determine anode protection degree and anode remaining lives.

Since the built in resistors limit the RCP anodes outputs, poor chlorination will reduce the corrosion protection. Over the years the main problem related to RCP anodes not providing the required corrosion protection, typically identified as leakages, has been rerouted back to poor chlorination. Chlorination is typically provided by a system adding some 0.2 to 1 ppm chlorine continuously, or a hybrid biocide system continuously adding 5 ppb Cu and 50 ppb Cl. Through the experience with RCP anodes it has been revealed that the effect of chlorination may vary dramatically depending upon chlorination system and chlorination routines and today continuous chlorination at 0.5 ppm is generally recommended for piping and components to be protected by RCP anodes.

Case History 1:

The Goodwyn ‘A’ platform outside Perth, Australia is also operated by Woodside Australian Energy. Here, UNS S 32750 piping is used in the seawater and firewater systems. In 1998, after four years with corrosion causing leakages RCP anodes were installed to protect the piping against future corrosion in welds and crevices.

The RCP anode design criteria were temperatures up to 45 ºC and a residual chlorine concentration of 0.5 ppm and 0.2 ppm for the seawater and firewater system respectively. Due to previous corrosion problems the design pipeline protection potential was lowered to -100 mV vs. SCE to arrest any on-going corrosion activity. The design criteria are summarized in Table 1.

A total of 174 RCP anodes were installed, 63 anodes were placed in the seawater system and 111 in the firewater system. Frequent potential drop readings have provided a good basis for evaluation of RCP anode behavior and analysis of trends. Figure 7 and Figure 8 show typical potential drop readings versus time for anodes in the seawater and firewater system respectively. The potential drop readings have revealed values close to or below design, indicating less corrosive conditions than anticipated in the designed. This is as expected since the design accounts for the worst-case scenario. After an initial period of some months relative stable readings were expected for the seawater RCP anodes, but as can be seen in Figure 7, the potential drop measurements reveal fluctuations. Being similar, these suggest trends caused by temporary changes in the operational conditions. In Figure 8, the potential drop readings for 13 RCP anodes installed in the firewater system are summarized. The more pronounced fluctuations seen for the firewater anodes are attributed to varying flow conditions. Except during the regular firewater testing stagnant conditions apply resulting in depletion of oxygen and chlorine. Furthermore the firewater testing may compile all firewater lines, a section or just the ring main. Hence, anodes located in dead legs, i.e. lines where stagnant conditions normally apply are rarely affected by the regular firewater testing and here corrosivity generally is low. The 0mV readings indicate anodes positioned in a dry location or in a dry line.

Figure 11 gives an overview of the number of leakages registered per year and it reveals that after the installation of RCP anodes in 1999 no new leakages have been identified in the RCP protected areas.

<u>Goodwyn A Anode Replacements.</u> The 2001 status review of the RCP anodes revealed a trend of declining potential drop readings for a majority of the seawater anodes. If this decline could not be explained by a less corrosive environment, the possible risk of anode passivation was questioned. A method of analysis was developed to estimate the tendency of partial passivation for the anodes in the seawater system while these were still in operation. Based upon the decline in the anode potential drop with time the present anode potential was calculated. If the anode potential calculated was above (i.e. less negative) – 800 mV SCE actions to modify or replace anode was suggested. This resulted in 49 of the anodes being replaced in October 2001, while the remaining anodes were considered sufficiently operative without any remedial actions.

The visual inspection of the removed anodes identified 30 anodes with varying degree of deposits building up on the anode top surface. Most of these anodes were only slightly consumed, and after having the perforated front plates modified these have been stored for later used as replacement anodes. Figure 9 shows an example of the declining potential drop readings with time for one of these anodes. The anode was replaced and the visual examination of the retrieved anode revealed that its front surface was completely covered with deposits as can bee seen in figure 10.

Case History 2

Cossack Pioneer is a Floating Production, Storage and Offloading facility (FPSO) operated by Woodside Australian Energy. Local corrosion in welds of the UNS S32750 in the firewater system causing leakages was reported after 2 months in service.

As a first aid, a temporary installation including 15 RCP anodes was performed in 1998. At the time, a chlorination system was installed, but since its reliability was poor, it was decided to ensure maximum benefit from the anodes by maximizing the anodic current outputs. These 15 anodes were therefore shunted with a low value resistor in parallel with the original, high value resistor to allow increased anodic current outputs for an intermediate period. The objective was to have the low value resistors removed once all RCP anodes had been installed.

The installation of totally 91 RCP anodes was completed during the opportunity created by a major facility shutdown in 1999. The design was based on seawater temperatures up to 35 ºC and 50 ºC with a residual chlorine content of 0.5 and 0.2 ppm respectively. The piping protection potential was set to - 50 mV for seawater temperatures up to 35 ºC and -100 mV for seawater temperatures up to 50 ºC. These potential values are conservative in order to provide extra safety.

At the same time, it was decided that since the chlorination system had a history of poor reliability, it was to be replaced by an alternative anti-fouling system based on generation of copper ions. However, no new chlorination system was installed resulting in the RCP anodes, being designed for chlorinated seawater, revealed anode current outputs that largely exceeded the design values. The increased current outputs resulted in higher potential drop over the anodes and thereby the piping lengths receiving cathodic protection was reduced and after 7 months in service three leaks at welds were identified. To improve the corrosion protection degree installation of parallel resistors on most of the RCP anodes was decided. To begin with, the change was simplified by installing 1ohm resistors in parallel to secure protection. Approximately one year later, sufficient performance data were available to allow more optimal resistors to give both safe protection and reasonable lifetime. In some areas, reduced protection was identified and additional anodes were required to ensure full corrosion protection.

As an extra control measure, pipe potential readings were taken at hydrant locations using a portable Ag/AgCl reference electrode. These readings are considered to be of utmost importance in order to evaluate protection degree since the design parameters have not been met. During the last survey, January 2002 potential readings at 4 out of 47 locations indicated that corrosion might be expected. Since the modifications to the RCP system were completed in Autumn 2001 no new leakages due to internal corrosion of the SDSS piping has been reported. The anodes are now monitored at 6-month intervals. The anode consumption rates are estimated from the monitoring data and replacement anodes are purchased for installation as required.

At this stage the system is being monitored for performance before any decision is made to add anodes or to reinstate the chlorination system. This is based on previous experience that has shown that a small number of leaks can be economically more feasible than investing in a new chlorination system given that the Cossack Pioneer FPSO may only be in operation for an additional ten- year period.

CONCLUSIONS

After 8 years in service Resistor controlled Cathodic Protection have been installed on more than 50 offshore and onshore facilities. Through its track record the method has proved able to halt and prevent local corrosion of SS materials exposed to chlorinated seawater.

The computer program developed to handle RCP anode design allows changes in environmental parameters to foresee impact on corrosion protection degree related to changes in the operational parameters. If changes in operational parameters results in more corrosive conditions the computer program may define the required RCP anode modifications by the installation of parallel resistors or suggest installation of additional anodes.

Reported leakages caused by corrosion despite the presence of RCP anodes have typically been attributed to poor chlorination. Control of chlorination systems may be difficult and to avoid future problems in seawater and firewater systems continuous chlorination giving 0.5 ppm residual chlorine is generally recommended.

Build up of corrosion products on the anode top surface has been experienced in the past. Since this may cause reduced anode current outputs due to the potential drop through the deposits the RCP anode design has been improved. Combined with regular monitoring procedures allowing actions to be taken at an early stage if ever required such problems are now halted.

REFERENCES

1. R. Johnsen and P.O Gartland: "The RCP method – Practical experience and future applications" Stainless Steel World, July/August 1996.
2. SINTEF Report No. STF24 F96217, "Design data for resistor controlled cathodic protection of stainless steels in chlorinated seawater", 1996.
3. SINTEF Report No. STF24 F97362, "Resistor Controlled Cathodic Protection of AISI 316", 1997.
4. SINTEF Report No. STF24 F00288, "Testing of Various Designs of RCP Anodes", 2000.

TABLE 1

BASIS DESIGN CRITERIA FOR GOODWYN A RCP ANODES

Description	**Seawater System**	**Firewater System**
Minimum chlorination level	0.5 ppm	0.2 ppm
Minimum temperature	35 ºC	25 ºC
Maximum temperature	45 ºC	45 ºC
Pipeline protection potential	- 100 mV vs. SCE	- 100 mV vs. SCE
Dissimilar materials	Not included in design	Not included in design

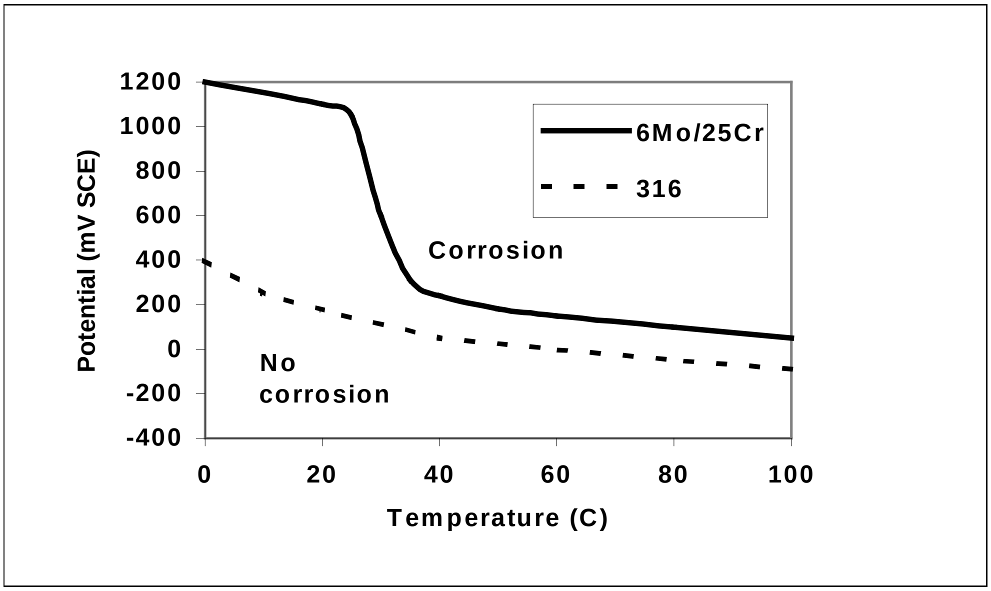

FIGURE 1 - Critical potential for initiation of local corrosion for stainless steel qualities UNS S31254 (6Mo), UNS S32550/S32750/S32760 (25Cr) and UNS S31600 (316) in chlorinated seawater versus temperature.

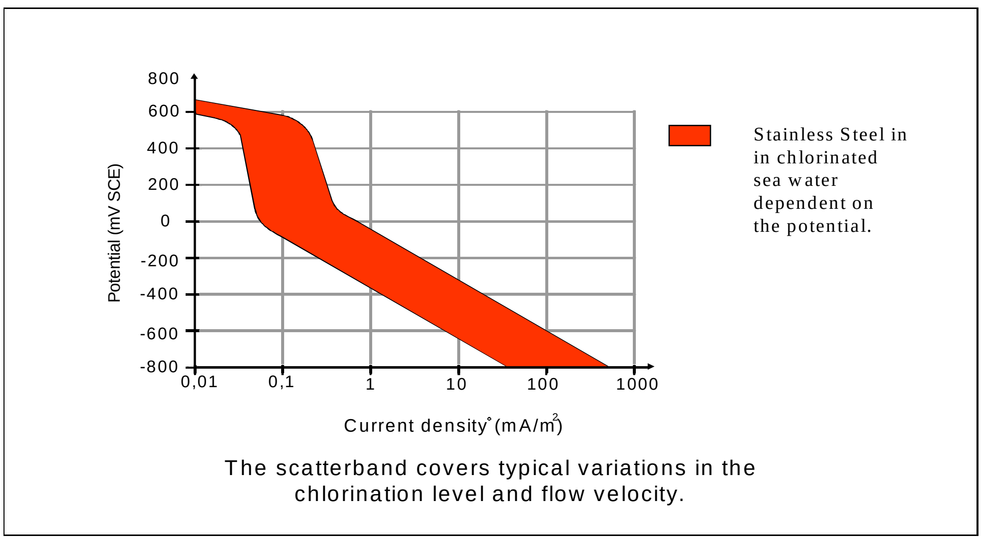

FIGURE 2 - Typical current density requirements versus potential for stainless steels in chlorinated seawater.

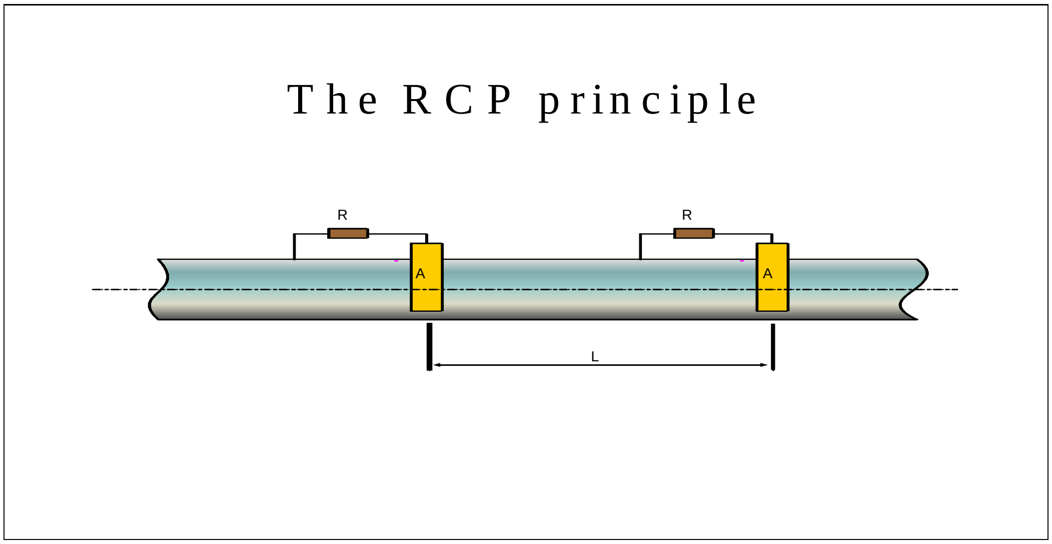

FIGURE 3 - Schematic drawing of resistor controlled anodes applied fro corrosion protection the internals of a piping system. R= Anode built-in resistor, A= anode, L = length between two anodes.

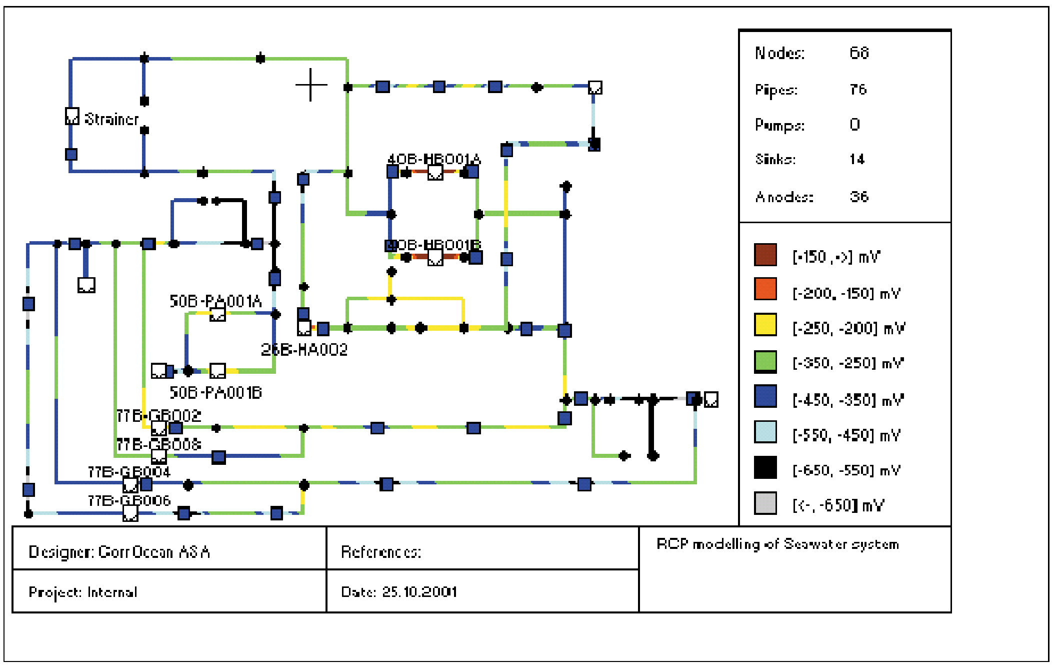

FIGURE 4 - An example of a color plot identifying the likely pipeline potentials for a RCP modeling of a seawater system. Input parameters are chlorination level, seawater temperature, piping dimensions, piping material quality and surface areas of all metallic components. The blue (filled) squares identify the RCP anodes. The computer program calculates the optimal anode resistor values. The model is not to scale.

FIGURE 5 - RCP anodes fixed to a blind flange. Only the anode front surface is exposed to the seawater. Connector for potential drop readings is behind the black cap.

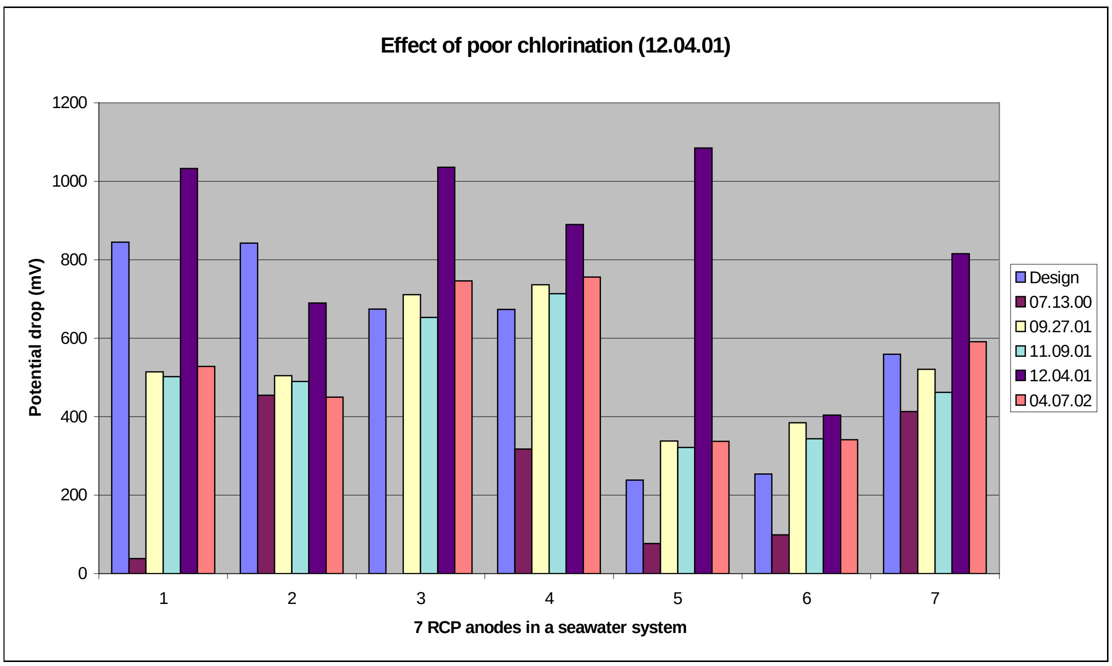

FIGURE 6 – Potential drop readings (measurements of the potential drop over the built in anode resistor) from 7 anodes designed for a chlorinated seawater system. The dates are given as mmddyy. The initial bar for each anode represents the designed potential drop, the other bars are actually measurements. The increased potential drop readings of 4 December 2001 (darkest bar) were caused by the chlorination system not running. By April 2002 the chlorination system was operating properly again.

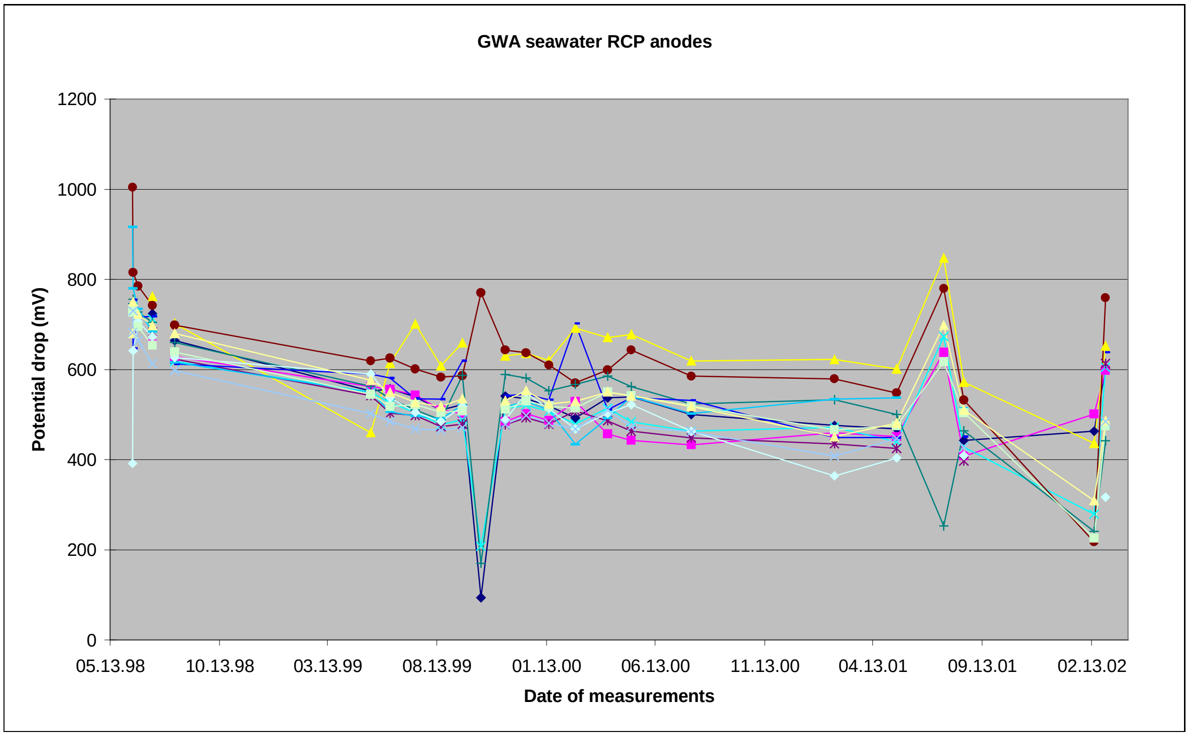

FIGURE 7 – Goodwyn A: Typical RCP anode potential drop readings from the seawater system. The dates are given as mmddyy. As can be seen the potential drop readings all follow a similar trend indicating that operational parameters vary.

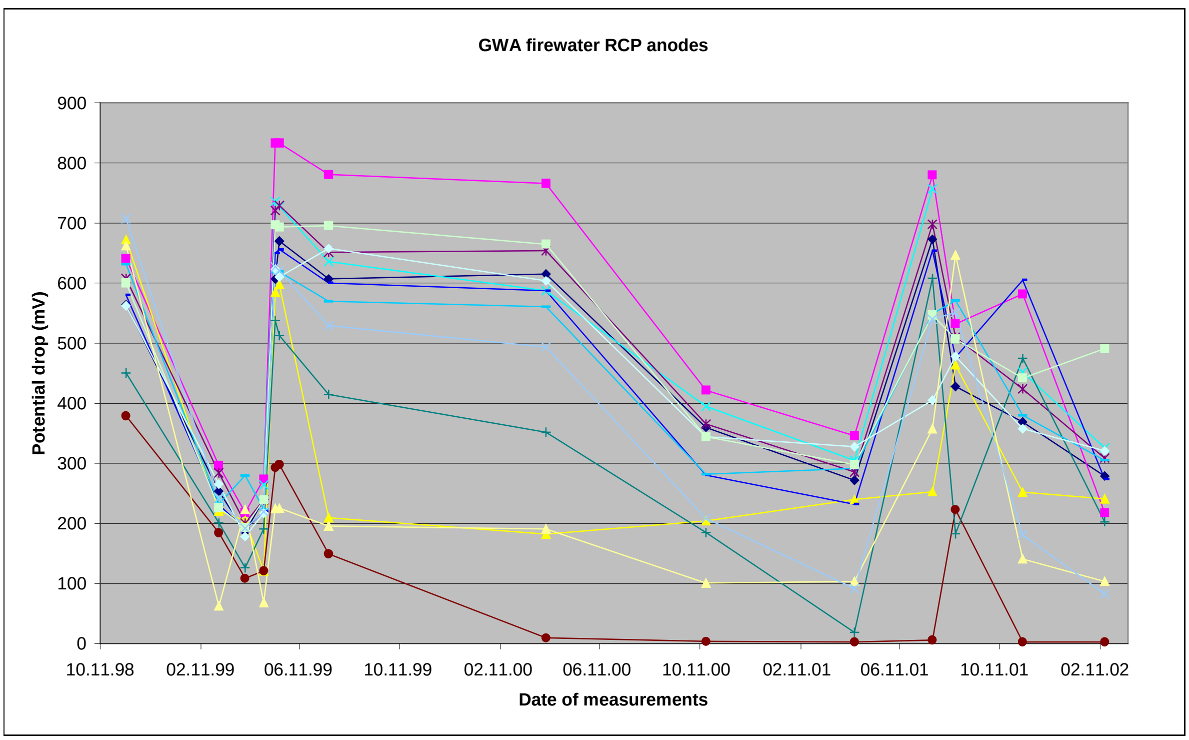

FIGURE 8 – Goodwyn A: 13 RCP anode potential drop readings from firewater system. The dates are given as mmddyy. These readings also follow similar trends but the values vary more due to varying flow conditions in the firewater system.

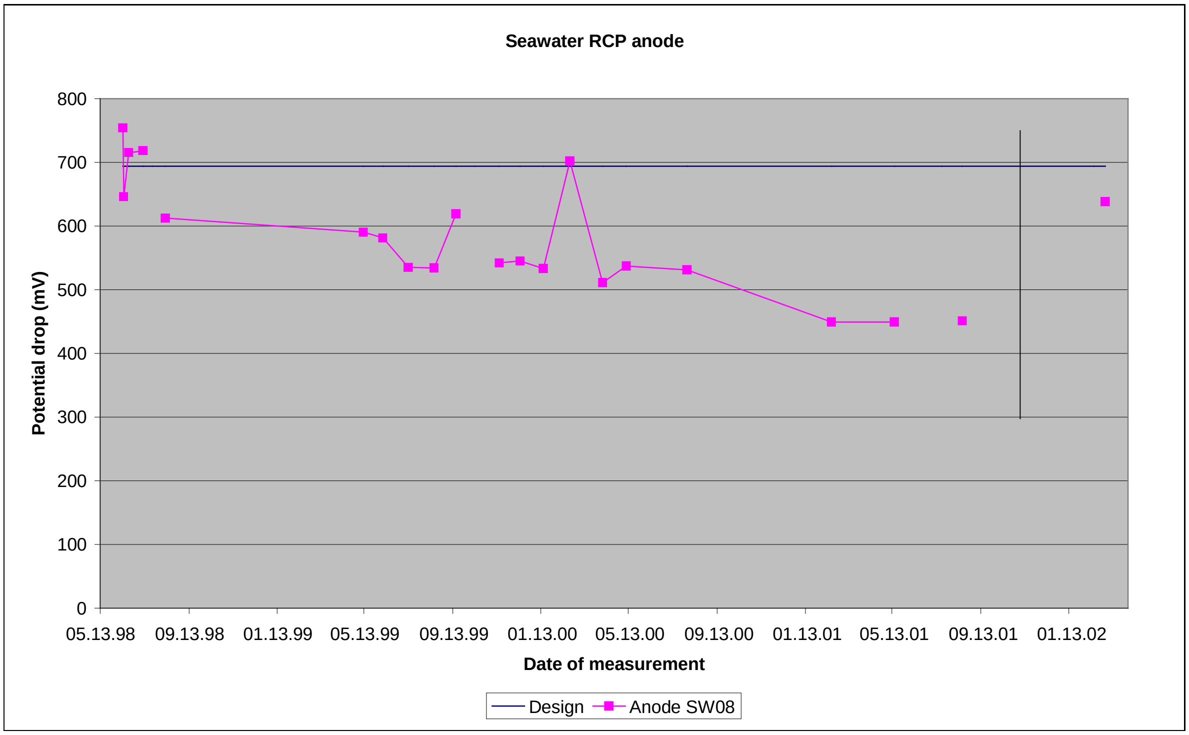

FIGURE 9 - Anode SW08 showed declining potential drop readings with time. The dates are given as mmddyy. The vertical line identified when anode was replaced.

FIGURE 10 - Anode SW08 after removal. Deposits building up on the anode top surface may explain the declining potential drop readings.

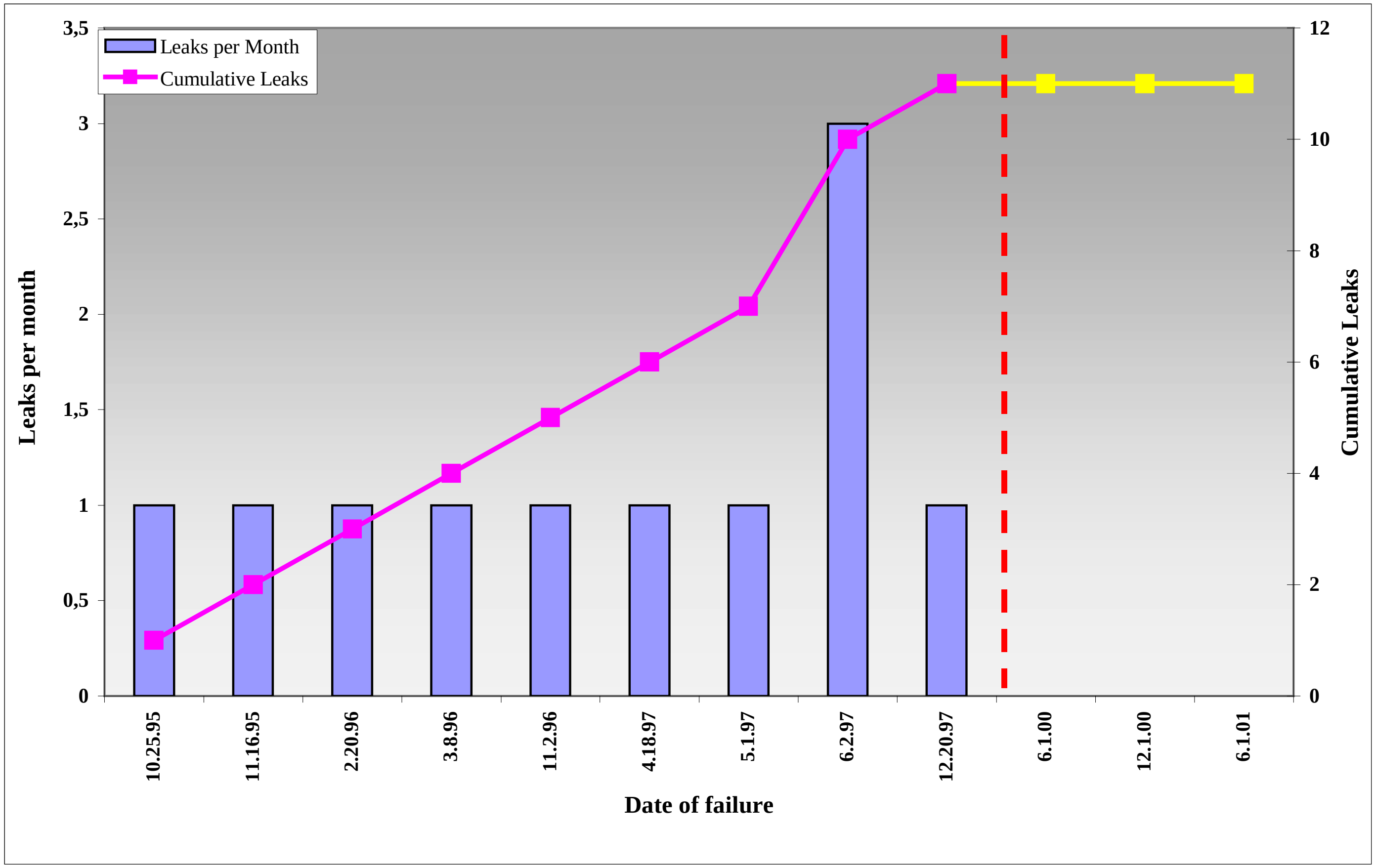

FIGURE 11 - Goodwyn A: Overview of number of leakages registered before and after installation of RCP anodes for corrosion protection of super duplex stainless steel piping in a seawater and a firewater system. Dates are given as mmddyy. Since commissioning in 1995 several leakages were discovered very year. In 1998 RCP anodes were installed and thereafter no additional leakages have been reported to date.

FIGURE 1 - Critical potential for initiation of local corrosion for stainless steel qualities UNS S31254 (6Mo), UNS S32550/S32750/S32760 (25Cr) and UNS S31600 (316) in chlorinated seawater versus temperature.

FIGURE 2 - Typical current density requirements versus potential for stainless steels in chlorinated seawater.

FIGURE 3 - Schematic drawing of resistor controlled anodes applied fro corrosion protection the internals of a piping system. R= Anode built-in resistor, A= anode, L = length between two anodes

FIGURE 4 - An example of a color plot identifying the likely pipeline potentials for a RCP modelling of a seawater system. Input parameters are chlorination level, seawater temperature, piping dimensions, piping material quality and surface areas of all metallic components. The blue (filled) squares identify the RCP anodes. The computer program calculates the optimal anode resistor values. The model is not to scale.

FIGURE 5 - RCP anodes fixed to a blind flange. Only the anode front surface is exposed to the seawater. Connector for potential drop readings is behind the black cap.

FIGURE 6 – Potential drop readings (measurements of the potential drop over the built in anode resistor) from 7 anodes designed for a chlorinated seawater system. The dates are given as mmddyy. The initial bar for each anode represents the designed potential drop, the other bars are actually measurements. The increased potential drop readings of 4 December 2001 (darkest bar) were caused by the chlorination system not running. By April 2002 the chlorination system was operating properly again.

FIGURE 7 – Goodwyn A: Typical RCP anode potential drop readings from the seawater system. The dates are given as mmddyy. As can be seen the potential drop readings all follow a similar trend indicating that operational parameters vary.

FIGURE 8 – Goodwyn A: 13 RCP anode potential drop readings from firewater system. The dates are given as mmddyy. These readings also follow similar trends but the values vary more due to varying flow conditions in the firewater system.

FIGURE 9 - Anode SW08 showed declining potential drop readings with time. The dates are given as mmddyy. The vertical line identified when anode was replaced.

FIGURE 10 - Anode SW08 after removal. Deposits building up on the anode top surface may explain the declining potential drop readings.

FIGURE 11 - Goodwyn A: Overview of number of leakages registered before and after installation of RCP anodes for corrosion protection of super duplex stainless steel piping in a seawater and a firewater system. Dates are given as mmddyy. Since commissioning in 1995 several leakages were discovered very year. In 1998 RCP anodes were installed and thereafter no additional leakages have been reported to date.