

What Factors Influence The Criteria For Protection of Structures Subject To An Impressed Current Cathodic Protection System

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Abstract

Cathodically generated surface films have been identified on the surface of steel specimens subject to the application of cathodic protection (CP). The growth of these surface films depends upon parameters such as electrolyte composition, pH, mass transport and current density. The growth of surface films and the corrosion rate of specimens also vary considerably depending upon the applied potential. A review of these parameters is made in order to understand what is the best potential to use when applying CP. Furthermore what does this mean in terms of the Protection Criteria widely used by industry as a guide between corrosion and protection?

Introduction

Cathodic protection is a technique used worldwide to minimize corrosion of buried or immersed metallic structures. Cathodic protection involves applying a current that flows from the anode through the surrounding electrolyte (soil or water) to the metallic structure surface. The principle behind cathodic protection is that if a sufficiently negative enough potential is applied and the amount of current produced is great enough, then it will overpower the current discharging from previously anodic sites causing the entire surface to become cathodic and therefore protected. This, however, may not always be the case. There are examples of pipelines that have been reportedly adhering to the protection criteria of a polarized OFF potential of -0.85V (CSE), having been found to suffer metal loss and not being fully protected some years later ^[1,2].

When cathodic protection is applied to a metallic structures such as pipelines two reactions occur; reduction of oxygen and the reduction of water. The first reaction occurring is the reduction of oxygen which forms hydroxide ions (Cathodic Reaction 1).



Reduction of oxygen is controlled by the amount of available oxygen, which is typically 8ppm in water ^[3]. This reaction is controlled by a limiting current density, which is diffusion controlled. It has been found that when the reduction of oxygen is the dominant reaction and typically occurs at applied potentials less negative than -1.0 Volt (CSE), then the typical pH at the metal surface can never be more alkaline than 10.57 ^[4]. This is thought to be because there is such a small concentration of hydroxyl ions present at the metal surface and so the pH change is limited by the transfer of hydroxyl ions away from the metal surface.

The second reaction that occurs at the metal surface (pipeline) when cathodic protection is applied is the reduction of water. This reaction normally occurs as the applied potential is made more negative than -1.0 Volts (CSE). This reaction is not

controlled by the limiting current density but is controlled by diffusion and migration of ions to and from the metal surface.



As the applied potential is made more negative, the pH at the metal surface will become more alkaline. This can be explained by more hydroxide ions being retained on the metal surface when the surface films forming are thicker, generating a more alkaline surface pH.

Reduction of water also causes the formation of hydrogen which if the applied potential is very negative can cause detrimental degradation and break down of the coating. Thus, when applying cathodic protection a balance is required to ensure that the applied potential is not too negative to destroy the coating.

Figure 2 details the potential – pH diagram (Pourbaix diagram) often used to explain the anodic and cathodic behaviour of iron in electrolytes of different pH and categorizes the domains of corrosion, passivation and immunity. Position A relates to a pipeline that is at native, corroding state. As cathodic protection (CP) is energised and the potential applied to the metallic structure is made more negative then the surface electrochemistry will move to the region of immunity. This is identified in Figure 2, as position B on the Pourbaix Diagram. At this position iron is more thermodynamically stable and corrosion is unlikely to occur^[5,6,7].

Over time the pH on the metal surface will increase due to generation of alkalinity from the hydroxyl ions produced by the cathodic reactions. This will cause not only to move the potential towards a more negative potential but also towards a higher pH. This is identified on Figure 2 as position C on the Pourbaix Diagram. These conditions are suitable for bringing about passivity and as such films will form on the metal surface^[6,7]. In 1937 Evans^[8] proposed that Cathodic Protection was achieved due to passivity. Evans thought passivity occurred by alkalisiation of the metal surface caused by cathodic polarisation. Leeds^[9,10] proposed in 2006 and 2009 that films do form on the metal surface as a direct result of cathodic protection. In order for films / calcareous deposits to form on a metal surface it is dependent on the interfacial pH and applied potential. It has been well established that calcareous deposits only start to form on cathodically protected structures when the carbonate ion concentration in the near surface solution increases favouring the carbonate ion direction which will react with the calcium ions present in seawater to form calcium carbonate^[11,12]. The major components of calcareous deposits are magnesium hydroxide, calcium hydroxide and carbonate. The composition of the calcareous deposit can change depending on the current density and interfacial pH around a structure. At lower current densities that result in an initial increase in interfacial pH, calcium carbonate will form more readily. Alternatively magnesium hydroxide requires an interfacial pH of 9.48 before it will precipitate which is usually associated with higher current densities^[13,14,15].

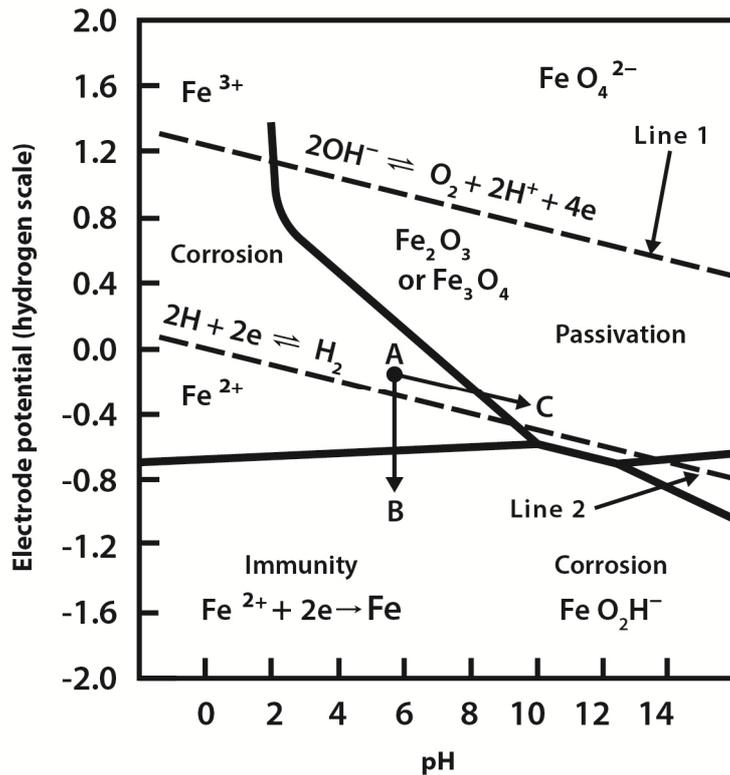


Figure 1: Potential-pH equilibrium diagram for iron in water at 25°C [6,7]

The protective nature of film/calcareous deposits is also dependent on the constituents of the deposit. Generally deposits rich in calcium carbonates are more protective than those rich in magnesium hydroxide. It is thought that magnesium hydroxide introduces a mechanical weakness into the deposits. This is thought to be because the current density required to produce the pH for deposition, is that when hydrogen is generated on the metal surface, which disrupts the deposit as it forms. Another problem of the protective nature of calcareous deposits is the film thickness which can vary over the different surface regions of a structure. It has been found that the more positive the potential or higher water velocity the thinner the calcareous deposit. The more negative the applied potential and slower the velocity, the thicker and more developed the deposit is in the central region of the metal specimen [14].

To understand better the mechanisms of cathodic protection and the influence of surface films an experimental study of mild steel specimens subjected to cathodic protection in differing electrolyte solutions was carried out. The electrolyte solutions chosen were sodium chloride, artificial seawater and an alkaline composition similar to the liquid found between the coating and a buried pipeline. The samples were then subjected to a range of potentials to determine which steel specimen had the least corrosion rate. From this study it was hoped to determine which the best applied potential to minimize corrosion was. Furthermore a review of criteria was made to determine which could be the best potential to apply to pipelines in industry.

Experimental Procedure

Material

Bright mild steel manufactured according to BS. 970 Pt3, 1991.
Composition of steel as given in Table 1:

Table 1: Composition of Experimental Specimen, Mild Steel

C	Si	Mn	P	S
0.12%	0.18%	0.85%	0.026%	0.031%

The experimental specimens were cylindrical in shape with diameter of 6mm and length of 40mm. Specimens prepared by abrading with 1200 grit silicon carbide, then cleaned and degreased in acetone. Specimens were painted with electroplating lacquer to delineate test area under study and to minimize the water line effect. Before use specimens were weighed and stored in a desiccator.

Test Electrolyte

- 3.5% w/v Analar grade sodium chloride (NaCl) in deionized water (pH 7.0).
- Artificial seawater corrosion test mixture to DEF 1053/B.S.3900/B.S.2011 (pH 7.5)
- Alkaline solution of composition similar to liquid found between the coating and a buried steel pipeline (termed alkaline pipe electrolyte). The composition of this solution was SO_4^{2-} : 300ppm; Ca^{2+} : 4ppm; Mg^{2+} : 0.05ppm; Na^+ : 9500ppm and K^+ : 64ppm (pH 10) (REF).

Test Cell

The aim of the work was to study the mechanisms of cathodic protection so an impressed current system was utilized to study this by creating individual test cells. In order to minimize influence of the products of the anodic reactions, particularly chlorine, the test cell was constructed to keep the anode and cathode areas separated. It was constructed such that it had concentric inner and outer cells. The plastic walled inner cell had holes in the bottom with a layer of agar gel made up in 3.5% NaCl to allow for ionic exchange and glass beads to weigh it down. The inner cell held the test specimen (WE), air bubbler and reference electrode (Ag/AgCl/3.5%NaCl) (0.243V on hydrogen scale) with the exception that when the alkaline pipe electrolyte was used a saturate calomel electrode (SCE) (0.241V on the hydrogen scale) was used as the reference electrode. The outer cell housed three graphite anodes in a triangulation configuration to allow for an even spread of the current.

Potentiostatic and Weight Loss Methods

Test specimens were investigated and each individual specimen was connected to a separate potentiostat. The potentials for the individual specimens were controlled in the range between -0.65 to -1.4V (Ag/AgCl/3.5%NaCl) or (SCE). A specimen was also exposed to freely corroding conditions (approximately -0.671V (Ag/AgCl/3.5%NaCl) or (SCE)). Specimens were exposed for 30 days in their test

electrolyte. The current for each specimen was recorded automatically every 15 minutes to determine any variation. The pH of the bulk electrolyte was measured periodically for each specimen.

A control specimen that had not been exposed to the test conditions was also cleaned and prepared in a similar fashion as a control for weight loss due to the cleaning procedure and as a control for the surface film analysis.

Surface Film Analysis Preparation

To determine if surface films formed due to application of cathodic protection and to determine what they are composed of all specimens were carefully removed from their test cell, washed with deionised water and rinsed with ethanol to prevent flash rusting. The specimens were air dried and stored in individual desiccators prior to examination of surface films. The surface films were analyzed using x-ray diffraction, operated at 60kv/40mA using a cobalt tube with a Gonio scan axis. The crystalline structures were identified using a Powder Diffraction File Database. Any deposits formed on the metal surface were analyzed independently from the metal by grinding the deposit down using a mortar and pestle and placing the deposit on to a single crystal backed substrate with silicon paste to keep it in place. After x-ray diffraction analysis the specimens were analyzed using a scanning electron microscope (SEM). The morphology of the specimens was viewed and the composition of the entire specimen and section of surface films were analysed using energy dispersive analysis.

Experimental Results

Corrosion Rates

Figures 2, 3 and 4 detail the variation of the corrosion rate with applied potential for the specimens exposed to 3.5% NaCl, artificial sea water and alkaline pipe electrolyte respectively. On each graph the industry recommendation for criteria (-0.8V to 0.9V depending on reference electrode used) and acceptable corrosion rates (0.01mm/y) have been plotted on graph to interpret what the experimental data means in terms of industry standards. A corrosion rate guide was also utilised from the Fontana and Greene “Corrosion Engineering” Book ^[16] as a guide for the corrosion rate as not many of the specimens achieved the most acceptable rate of 0.01mm/y:

0.02mm/y is an outstanding corrosion rate.

0.02 to 0.1mm/y is an excellent corrosion rate.

0.5-1mm.y is a fair corrosion rate.

Greater than 1mm/y are very poor corrosion rate.

In all of the experimental data gathered none had any corrosion rates less than 0.01 mm/y at potentials between -0.8 to -0.9V in any of the electrolytes. The experimental specimens with the lowest corrosion rates were found to be the specimens with applied potentials of -1.3V (Ag/AgCl/3.5% NaCl) for those specimens exposed to 3.5% NaCl with a corrosion rate of 0.004mm/y.

3.5% NaCl Exposed Specimens

For the specimens exposed to 3.5% NaCl there are no influences from calcareous deposits to consider as in those specimens exposed to artificial seawater and to the alkaline pipe electrolyte. This allows a study to be made of the generation of surface films purely due to the application of cathodic protection. Surface films were observed to form due to the application of cathodic protection.

Upon initial application of cathodic protection of 0.65V (Ag/AgCl/3.5% NaCl) or (SCE) to the specimens under study with the different electrolytes the corrosion rate were found to dramatically reduce and as you increased the amount of cathodic protection applied and made the potential more negative the corrosion rate was reduced even further. For the specimens exposed to 3.5% NaCl application of potentials between -0.7V and -1.3V (Ag/AgCl/3.5% NaCl) caused a further decrease in the corrosion rate. The lowest corrosion rate of approximately 0.0040mm/y were obtained for the -1.3V (Ag/AgCl/3.5% NaCl). A slight anomaly in the data is that the -0.75V (Ag/AgCl/3.5% NaCl) specimen had a lower corrosion rate compared to the -0.8 and -0.85V (Ag/AgCl/3.5% NaCl) specimens. This can be explained by the nature of the deposit. The -0.8 and -0.85V (Ag/AgCl/3.5% NaCl) specimen surface films had deposits breaking away due to agitation from the air bubbler which could expose fresh surface for additional corrosion to occur.

Only one specimen polarised at -1.3V(Ag/AgCl/3.5% NaCl) met the industry standard of a corrosion rate of 0.01mm/y or lower. The other specimens met a corrosion rate of between 0.01 and 0.1mm/y which lies in the excellent corrosion rate.

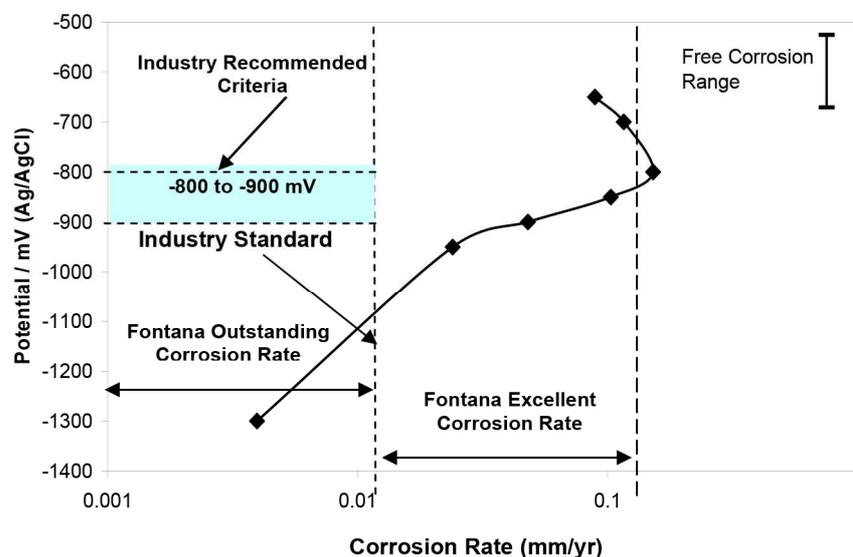


Figure 2: Average Corrosion Rate vs. Potential Exposed to 3.5% NaCl for 30 days

Artificial Seawater Exposed Specimens

When considering the corrosion rate between the freely corroding specimens in artificial seawater, the influence of calcareous deposits has to be taken into consideration. The freely corroding specimen had the greatest corrosion rate

compared to other specimens polarised in artificial seawater at different potentials but had a lower corrosion rate than that of similar specimens exposed to 3.5% NaCl.

Specimens that had been polarised to potentials more negative than -0.9V (Ag/AgCl/3.5%NaCl) had a 10 fold decrease in corrosion rate compared to the freely corroding specimen. The specimen with the lowest corrosion rate was that polarised to a potential of -0.95V (Ag/AgCl/3.5%NaCl) and had a corrosion rate of 0.013mm/y. There was a slight increase in the corrosion rate at specimens polarised to -1.2V (Ag/AgCl/3.5% NaCl) and then a decrease in the corrosion rate as specimens were polarised to -1.4V (Ag/AgCl/3.5% NaCl) but higher than the -0.95V (Ag/AgCl/3.5%NaCl).

No polarised specimens met the industry standard of a corrosion rate of 0.01mm/y or lower. Most of the other specimens met a corrosion rate of between 0.01 and 0.1mm/y which lies in the excellent corrosion rate. Four polarised specimens were in the range of 0.1 to 1mm/y indicating a fair corrosion rate.

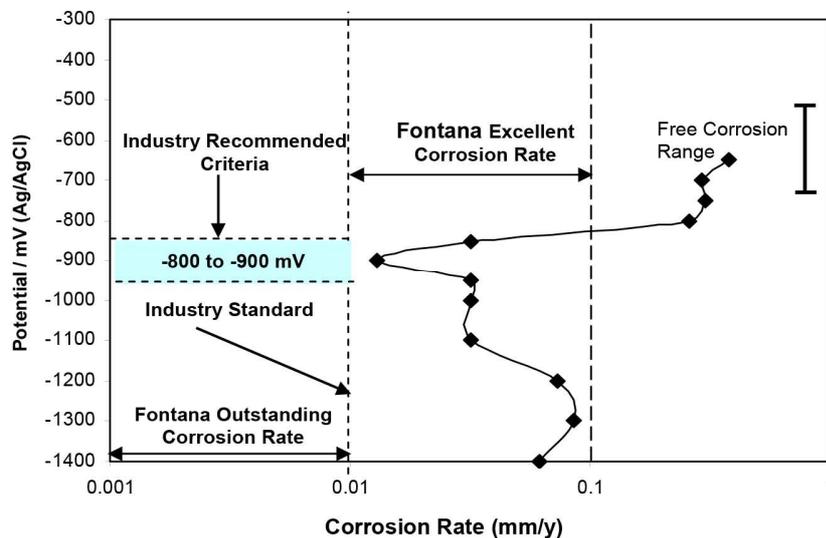


Figure 3: Average Corrosion Rate vs. Potential Exposed to Artificial Seawater for 30 days

Alkaline Pipe Electrolyte Exposed Specimens

The freely corroding specimen exposed to the alkaline pipe electrolyte had the greatest corrosion rate compared to the other polarised specimens. This freely corroding specimen also had an Ecorr potential that was more positive by 170mV compared to the other freely corroding specimens exposed to 3.5% NaCl and artificial seawater.

The lowest corrosion rate for the specimens exposed alkaline pipe electrolyte were found to be specimens with an applied potential of -0.90V (SCE) with a corrosion rate of 0.0109mm/y and at -1.3V (SCE) with a corrosion rate of 0.009mm/y.

Likewise to the specimens exposed to artificial seawater there was also an increase in corrosion rates of those specimens with polarised potentials between -0.9 and -1.3V (SCE) with a maximum corrosion rate at -1.1V (SCE). The cause of this could be due to the influence of the combination of a weakened surface film due to calcareous co-

deposits with iron corrosion products and vigorous agitation of the air bubbler. When a more coherent deposit is formed on the surface of the metal it blocks the surface to further corrosion. This may explain why there was a greater reduction in the corrosion rate with specimens exposed to artificial seawater but not in the alkaline pipe electrolyte exposed specimens where there are only low quantities of calcium and magnesium present in the deposit even though a small concentration of calcium and magnesium salts in the electrolyte.

Two polarised specimens met the industry standard of a corrosion rate of 0.01mm/y or lower and these were specimens polarised at -1.3 and -0.9V (SCE). Most of the other specimens met a corrosion rate of between 0.01 and 0.1mm/y which lies in the excellent corrosion rate. Four polarised specimens were in the range of 0.1 to 1mm/y indicating a fair corrosion rate.

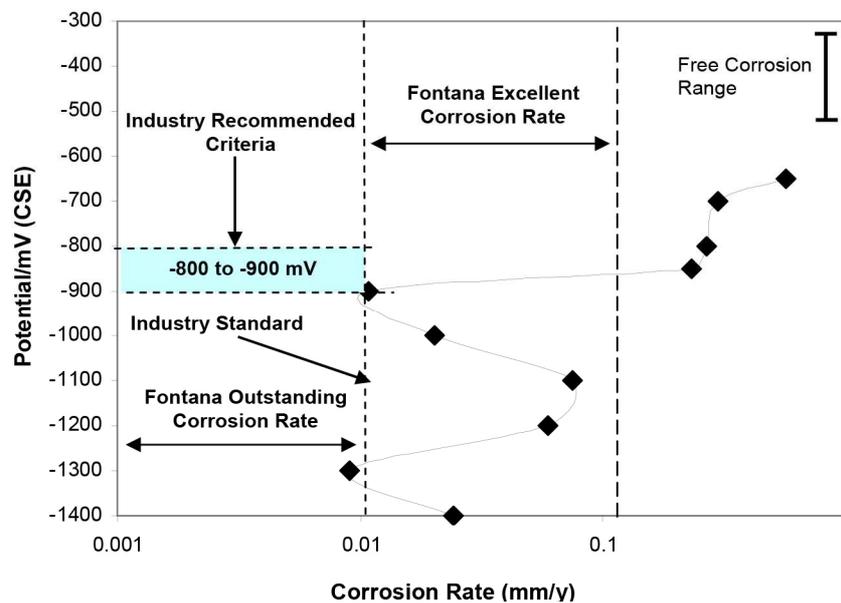


Figure 4: Average Corrosion Rate vs. Potential Exposed to Alkaline Pipe Electrolyte for 30 days

Current Density

Figure 5 detail the current density for the start (A) and end (B) of all specimens to maintain the polarised potentials between -0.65 and -1.4V. Initially a higher than what is thought normal current density was required to maintain all specimens at their polarised potentials. Typically a current density of 0 to 25 mA/m² is sufficient to apply cathodic protection to pipelines. The reason for the higher required current density could be due to the set up of the test cell. The current required for cathodic protection depends on the oxygen reduction rate at the cathode and during these experiments an air bubbler was placed near the test specimen giving rise to a high oxygen content and also depends on the resistivity of the environment. Normally as the resistivity of the electrolyte is below 50ohm.m then a design current of 30mA/m² would be required to operate a cathodic protection system as the resistivity of the electrolyte gets higher, then a greater than 1000ohm.m then the amount of current density required to operate the cathodic protection system gets lower such as to 5mA/m².

It can be seen that specimens polarised in 3.5% NaCl solution required the highest current density to maintain the potentials at the start of the experiment compared to the specimens polarised in artificial seawater or the alkaline pipe electrolyte. The alkaline pipe electrolyte polarised specimens requiring the least current at the start of the experiments. At the end of the experiments the specimens polarised in artificial seawater and the alkaline pipe electrolyte required the smallest current density to maintain the cathodic protection system compared to the 3.5% NaCl specimens. The reason for this could be due to the thicker surface films that formed on specimens polarised in both artificial seawater and the alkaline pipe electrolyte, There was a decrease in the current density for specimens polarised in the 3.5% NaCl solution but this was only when the potentials were made more negative such as at -1.3V (Ag/AgCl/3.5%NaCl).

Fluctuations in the B Figure could be due to the formation and detaching of the calcareous deposits that form together to form the surface films on the surface of the metal.

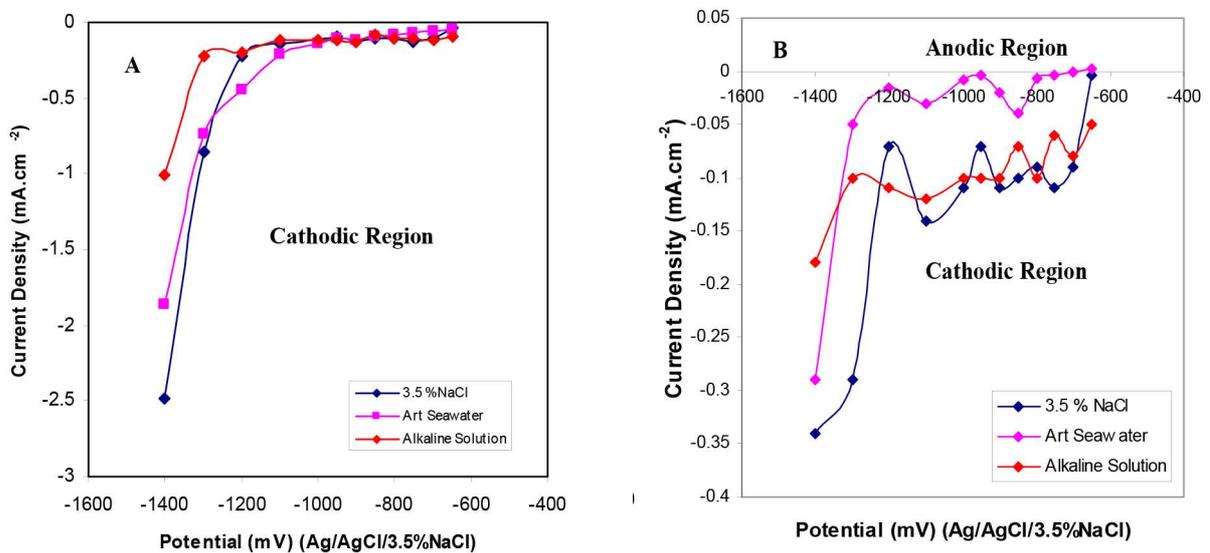


Figure 5: The Current Density Required to Maintain Potentials at (A) Start of the Experiment and (B) End of the Experiment

pH of the Electrolyte During Experiment

The pH of the bulk electrolyte was measured periodically during and at the end of the experiments for all test electrolytes. The pH of the bulk electrolyte in the outer cell containing the anode was measured six hours into the experiment and was found to be building up acidity in the test cells of specimens that were polarised at potentials more negative than -0.95V and a pH of 2 was found in the specimens polarised at potentials within the range of -1.2V to -1.4V. The bulk electrolyte of the cathode containing cell was also measured six hours into the experiment and was found to still have a pH of 7. The anode and the cathode cells should be kept separately to ensure that it does not influence results.

At the end of the experiments the specimens polarised in 3.5%NaCl had a higher pH compared to the artificial seawater or the alkaline pipe electrolyte. It was found that as

the polarised potential was made more negative then pH of the bulk electrolyte solution became more alkaline.

Morphology and Composition of Surface Film Formation

Surface films forming on specimens exposed to 3.5% NaCl were thinner than those exposed to artificial seawater specimens. The constituents forming on the metal surface were only iron oxides/hydroxides and no calcareous deposits. The corrosion products forming on the freely corroding and -0.6V polarised specimens were in the form of akaganeite (β -FeOOH), goethite (α -FeOOH), lepidocrocite (Y -FeOOH) and magnetite (Fe_3O_4). When the major film constituent was magnetite it was also present with ferrous hydroxide. Normally magnetite is very conductive but the effect of ferrous hydroxide was to make the magnetite films non-conductive blocking off the specimen surface which then reduced the current density required to maintain the cathodic protection potential at its required level.

The films formed on specimens exposed to artificial seawater were a lot thicker and in the form of corrosion products or calcareous deposits. Figures 6 to 14 detail the type of calcareous deposits that formed on the metal surface. There were extensive corrosion products formed on the freely corroding and the -0.65V polarised specimens. The corrosion products were in the form of three distinctive layers of goethite (α -FeOOH), lepidocrocite (Y -FeOOH) and magnetite (Fe_3O_4). Calcareous deposits only formed when the applied polarised potential was more negative than -0.7V (Ag/AgCl/3.5%NaCl). There was no calcareous deposit formed on the metal substrate control (Figure 6). The freely corroding and the -0.65V specimens (Figure 7 and 8) show a thick corrosion product with some underlying metal where the corrosion product has fallen off. Specimens polarised at -0.85V are detailed in Figure 9 and an enhanced magnification of the same specimen in Figure 10. These figures show spherical deposits forming on top of the metal surface. Often larger spherical deposits can be found lying onto of a deposit forming directly on the metal surface. Analysis of these deposits found them to be calcium carbonate containing products called calcite and aragonite. As the polarised potential was made more negative from 0.9V (Figure 11) a deposit was identified consisting magnesium containing components along with some calcite and aragonite. Interestingly the magnesium component could possibly be dypingite ($Mg_5(CO_3)(OH)_2 \cdot 5H_2O$), which has also been found as a constituent of dinosaur bone. This specimen was found to have the lowest corrosion rate and most uniform surface film of all the specimens exposed to artificial seawater. As the applied potential was made more negative than -0.9V the dominant constituent of the deposit was identified and magnesium hydroxide in the form of the brucite ($Mg(OH)_2$) (Figures 12-13) and as the potential was polarised to -1.4V the surface film consisted of mainly brucite with a scattering of calcite and aragonite (Figure 14).

Figures 15 to 23 detail SEM images of the surface films forming on specimens exposed to alkaline pipe electrolyte. Figure 15 details no surface films on the steel substrate specimen. The freely corroding specimen did not form a thick corrosion product like in the other specimens (Figure 16). It formed a thin layer of corrosion product with cracks in it. The corrosion products were identified as akaganeite (β -FeOOH), goethite (α -FeOOH), lepidocrocite (Y -FeOOH) and magnetite (Fe_3O_4). The 0.65V polarised specimen had black spots on it which is almost identical that is found on pipelines that have been excavated and only akaganeite (β -FeOOH) was identified (Figure 17 and 18). As the polarised potential was made more negative than -0.7V

then calcareous deposits were identified. The size and number of these spherical deposits increased as the potential was made more negative (Figure 19 to 21). Figures 22 and 23 show a more uniform surface film forming but a lot thinner than that of the specimens exposed to artificial seawater. Only calcite was identified as the component identified in the surface films as the polarised potential was made more negative

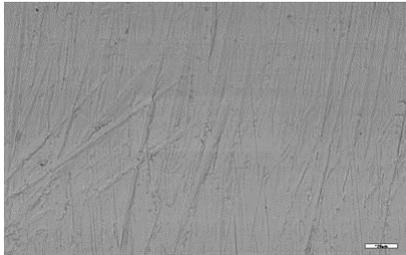


Figure 6: SEM Image of Steel Substrate, Secondary Electron (Size bar 20µm)

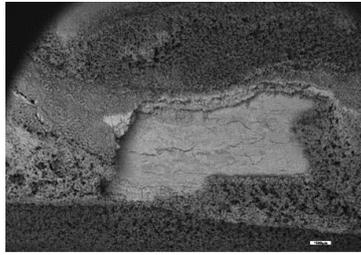


Figure 7: SEM Image of Freely Corroding Specimen, Secondary Electron (Size bar 500µm)

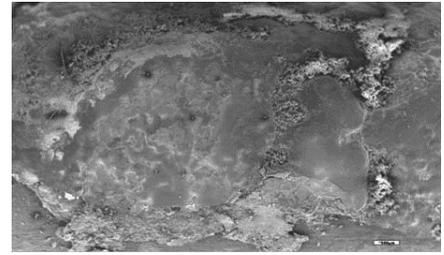


Figure 8: SEM Image of -0.65V Specimen, Secondary Electron (Size bar 500µm)



Figure 9: SEM Image of -0.85V Specimen, Secondary Electron (Size bar 500µm)

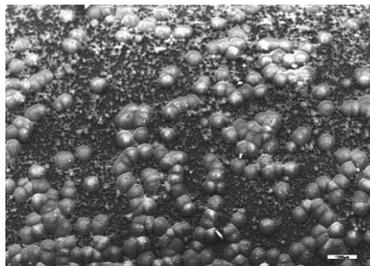


Figure 10: SEM Image of -0.85V Specimen, Secondary Electron (Size bar 2000µm)

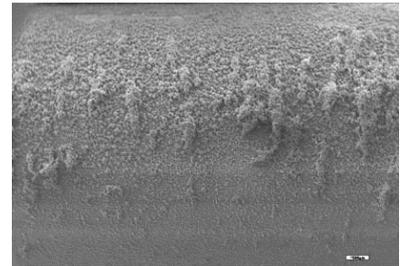


Figure 11: SEM Image of -0.9V Specimen, Secondary Electron (Size bar 500µm)

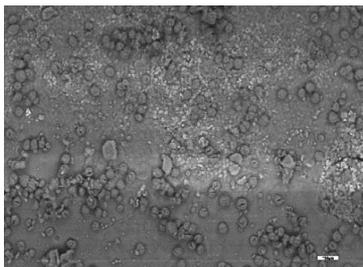


Figure 12: SEM Image of -1.2V Specimen, Secondary Electron (Size bar 500µm)

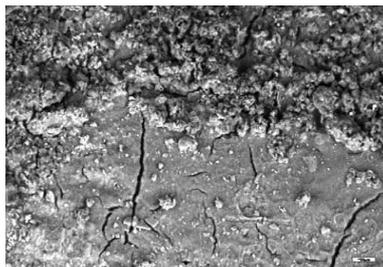


Figure 13: SEM Image of -1.3V Specimen, Secondary Electron (Size bar 500µm)

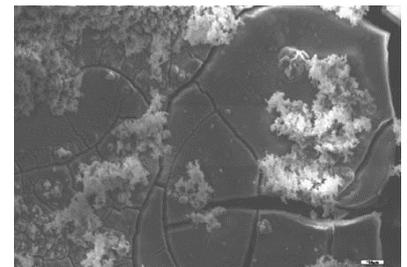


Figure 14: SEM Image of -1.4V Specimen, Secondary Electron (Size bar 500µm)

All Specimens exposed to artificial seawater.



Figure 15: SEM Image of Steel Substrate, Secondary Electron (Size bar 20 μ m)



Figure 16: SEM Image of Freely Corroding Specimen, Secondary Electron (Size bar 200 μ m)

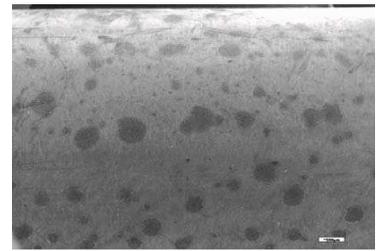


Figure 17: SEM Image of -0.65V Specimen, Secondary Electron (Size bar 50 μ m)

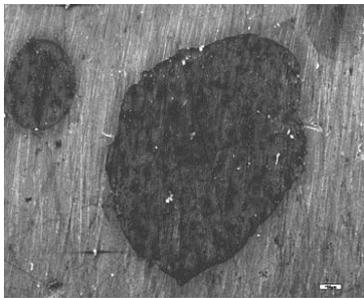


Figure 18: SEM Image of -0.65V Specimen, Secondary Electron (Size bar 500 μ m)

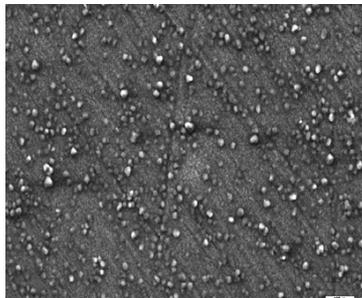


Figure 19: SEM Image of -0.85V Specimen, Secondary Electron (Size bar 20 μ m)

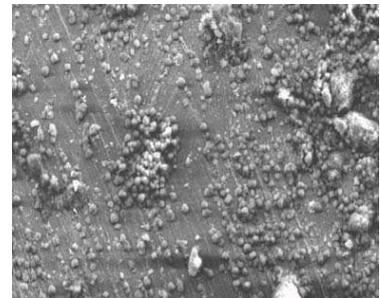


Figure 20: SEM Image of -1.0V Specimen, Secondary Electron (Size bar 20 μ m)

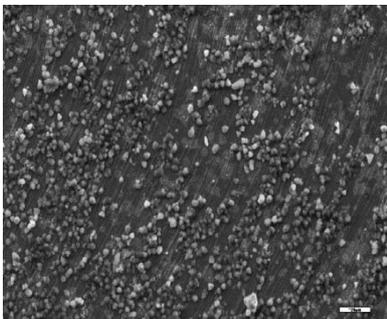


Figure 21: SEM Image of -1.1V Specimen, Secondary Electron (Size bar 20 μ m)

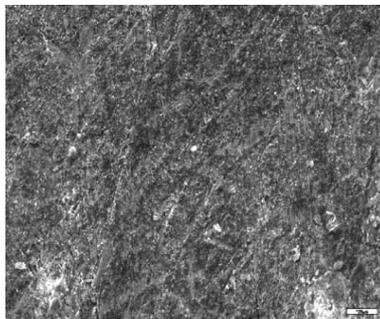


Figure 22: SEM Image of -1.3V Specimen, Secondary Electron (Size bar 20 μ m)

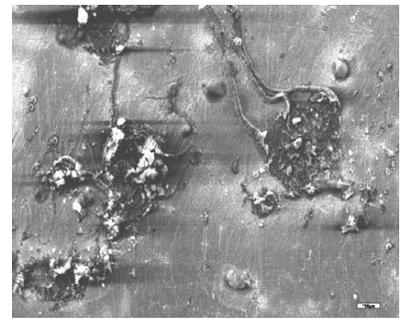


Figure 23: SEM Image of -1.4V Specimen, Secondary Electron (Size bar 500 μ m)

All Specimens exposed to alkaline pipe electrolyte.

Discussion

The study of this work was to try and understand better what happens at the metal/electrolyte surface when cathodic protection is applied. It was found that surface films/calcareous deposits did form on the metal surface as a direct result of applying cathodic protection to a piece of metal. The composition and thickness of the surface film depended on the type of electrolyte the specimen was exposed to and varied with the applied potential and was affected by pH. There was also a significant

reduction in the current density with time, particularly within the first few days of applying cathodic protection which are thought to be due to the formation of the surface film blocking off the metal surface in a similar fashion to a coated pipeline. These observations parallel what happen in practice when applying cathodic protection to a pipeline.

When cathodically polarising a metal surface the following processes occur at the metal/electrolyte surface interface:

- 1) There is an increase in the bulk solution pH and metal surface pH.
- 2) A decrease in anodic dissolution kinetics.
- 3) An increase in oxygen reduction kinetics, which will be limited by mass transport if relating it to the amount of oxygen available in areas like buried pipelines.
- 4) An increase in hydrogen evolution kinetics. There is a need to make sure that the polarised potential is not too negative.

All of these processes cause changes to the metal surface and can affect the way that cathodic protection works to prevent corrosion from occurring. The type of electrolyte/environment that the specimen/pipeline is exposed to does affect the way that cathodic protection functions. pH is a very important factor. When applying cathodic protection it causes hydroxide ions to be produced which cause the pH around the metal surface to become more alkaline. Kobayashi ^[17] studied the variation of pH with distance from a steel surface in 3% NaCl during cathodic polarisation and determined that the pH of the solution at the steel surface was 2 to 4 units greater than the bulk solution pH. Similar findings were found during this study.

To date in the pipeline industry there is no criterion that mentions the influence of pH but it seems a highly important consideration to take in to place when applying cathodic protection. Depending on the applied polarisation potential can cause a higher pH around the metal/Electrolyte interface. Also having the anode and cathode regions very close can also affect cathodic protection and can alter the pH.

The experimental studies carried out in this work looking at various parameters including pH, current density, surface films and polarised potential to understand the conditions required for cathodic protection to stop corrosion it can be concluded that corrosion can be slowed down. The work presented suggests the use of polarise potentials in the region of -0.95 to -1.1V (CSE) as this was the region of all the specimens studied that had the lowest corrosion rate. Though the lowest corrosion rate was recorded for the -1.4V polarised specimen in 3.5% NaCl but the potential for side effects such as SCC, hydrogen embrittlement and further coating damages, etc increase as the polarised potential is made more negative.

If looking at the pipeline industry it is very difficult to achieve a uniform distribution of cathodic protection over complex buried or immersed structures then the use of a single potential such as -0.85V (CSE) to represent the guide between corrosion and protection is limited. Soils have a wide variation in composition and corrosivity and a single structure such as a pipeline could travel through many different and potentially corrosive soils. Ideally each soil type requires its own criterion depending upon pH and soil resistivity and not one as present. As examples of variations Barlo ^[11] and Gumnow ^[18] who both found that -0.85V (CSE) did not necessarily provide the

required conditions to stop corrosion for their pipeline conditions. Gumnow recommended adopting a -1.0V (CSE) for circumstances where complete protection is desired. Barlo investigated what polarised potential to use to stop corrosion under differing soil conditions. Barlo found that under some conditions an applied polarised potential of -0.85V (CSE) did not provide protection but in other occasions an applied polarised potential either exceeding -0.85V such as -1.1V (CSE) was required for protection or a polarised potential with a much lower value, -0.55V (CSE), was all that was required to prevent corrosion. However, working to multiple criteria for one pipeline would be impractical. Attempts have been made to improve the effectiveness of cathodic protection in soils by matching soil resistivity to the polarised potential criterion ^[19,20]. More research is required when acidic soils such as peat soil are taken into consideration which have a low resistivity of less than 500ohm.cm but the application of cathodic protection, unless high currents are used will not generate enough alkali suggesting under these conditions the steel surface can not be passivated to form a surface film. More work is required to study the effective lower pH limits of cathodic protection.

Conclusion

Cathodic protection does not stop corrosion but slows it down to a very small corrosion rate and ideally to 0.001mm/y as specified by a number of standards ^[19, 20]. The work studied showed that the formation of a surface film was critical to effective cathodic protection and so any criterion to be used in industry should be selected according to what conditions produce a most coherent protective film. In seawater conditions the surface film is augmented by growth of calcareous deposits. Based on corrosion rates recognised by industry and from experimental observations, morphology studies and pH interpretation using a Pourbaix diagram the following criterion for protection has been suggested:

Land Based systems should be between -0.9 to -1.1V (CSE), over pH range of 7 to 13.
Sea Based systems should be between -0.95 to -1.1V (Ag/AgCl/3.5%NaCl), over a pH range of 7 to 11 to limit brucite formation.

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