

A Review Of What Happens At The Metal/Electrolyte Interface When Cathodic Protection Is Applied. What Does This All Means In Terms Of The Protection Criterion?

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Abstract

Corrosion is an electrochemical phenomenon by nature which can be slowed down and virtually halted using various techniques. Cathodic Protection is such a technique that can be used to minimise corrosion. The technique involves applying a potential to ensure the current flows from the anode through the surrounding electrolyte (soil or water) to the metallic structure surface. In concept it is thought that if a sufficiently negative potential is applied, then corrosion of the metal structure should be mitigated.

This paper reviews studies that have identified what is the correct potential to apply to a steel surface to minimise corrosion. Furthermore, a review of what happens at the metal/electrolyte interface is assessed to ascertain a better understanding of what happens at the metal surface during the application of Cathodic Protection.

With a better understanding of the mechanism of Cathodic Protection the protection criterions will be assessed to determine whether the correct potential is being used to ensure that Cathodic Protection functions optimally to suppress the corrosion reaction.

Keywords: Cathodic Protection (CP), electrochemistry, potentiostatic method, scanning electron microscopy, surface films, weight loss measurements, x-ray diffraction analysis, surface films, calcareous deposits, Pourbaix Diagram, pH and protection criteria.

Introduction

Cathodic Protection (CP) is now widely accepted as one of the important corrosion mitigation techniques applied to buried or immersed steel structures. The technique involves applying a potential so that current flows from the anode through the surrounding electrolyte (moist soil or water) to the structure surface. In concept it is thought that if a sufficiently negative potential is applied, then corrosion of the metal structure should be mitigated.

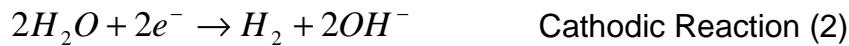
When CP is applied two reactions occur; reduction of oxygen and reduction of water. The first reaction occurring as potentials are made more negative is the reduction of oxygen dissolved in the electrolyte to form hydroxide ions (Cathodic Reaction 1).



Reduction of oxygen is limited by the amount of available oxygen, which is typically 8ppm dissolved in water at ambient temperature^[1]. At typical free-corrosion potentials of steel, this reaction is diffusion controlled. It can be shown theoretically that when reduction of oxygen is the dominant reaction, typically implying applied potentials less negative than -1.17 V (CSE), and assuming air-saturated solution, then the pH of the metal surface is never more alkaline than 10.57^[2]. This is because the diffusion of oxygen to the metal surface follows the same

path as the diffusion of hydroxyl ions away from the surface, so the surface pH is controlled by the oxygen concentration in the bulk solution, independently of the diffusion boundary layer thickness.

The second reaction that occurs is reduction of water (Cathodic Reaction 2). This reaction starts to occur as the applied potential is made more negative than -1.17 V (CSE). Since the reaction only involves water as a reactant, it is not subject to mass transport control though at high current densities it can be affected by blocking of the surface by hydrogen bubbles.



It has been found that as the applied potential is made more negative, the pH at the metal surface becomes progressively more alkaline. This can be explained by the reaction not being diffusion controlled and more hydroxide ions being retained on the metal surface when the surface films form, generating a greater diffusion barrier ^[3].

Figure 1 details diagrammatically the main reactions occurring at the metal surface when cathodic protection is applied to

The Mechanism of Cathodic Protection

Confusion exists as to the actual mechanism by which Cathodic Protection works. A common postulated mechanism discussed in more detail later is that CP is thought to result in protecting the metal by making the structure potential more negative to a level at which the corrosion rate is significantly reduced. In principle this is in agreement with the predictions given in the Pourbaix Diagram for steel where sufficiently negative potentials are in the region of immunity and corrosion is thermodynamically impossible. Alternatively if the applied negative potential is sufficient then in theory there should be adequate current present to prevent the metal surface from corroding so that any previous current discharge from any anodic sites should be stopped and the whole metal surface would become cathodic. Net current flow to a structure is one of the NACE Criteria for protection. This is where the problem lies; theoretically it should be possible to halt corrosion using Cathodic Protection. However, practically, it is not that simple. A potential of -0.85 V (CSE OFF) (NACE Criterion) is thought to be the potential at which protection is achieved. However, it has been found inadequate to prevent corrosion under all conditions ^[4]. The limitations of the -0.85 V OFF criterion are related to the characteristics of the soil (electrolyte) surrounding the metallic structure such as soil type and pH, resistivity, corrosivity and oxygen content. These are all implicated in the actual mechanism by which CP actually works to postulate the divide between corrosion and protection.

Passivity by Alkalisiation Theory

Firstly Evans ^[5] proposed in 1937 that Cathodic Protection was achieved due to passivity. Passivity was thought to occur by alkalisiation of the metal surface caused by cathodic polarisation. Evans theory was based on a series of experiments using iron cathode and zinc anode in different electrolytes consisting of sodium sulphate, calcium bicarbonate and Cambridge tap water.

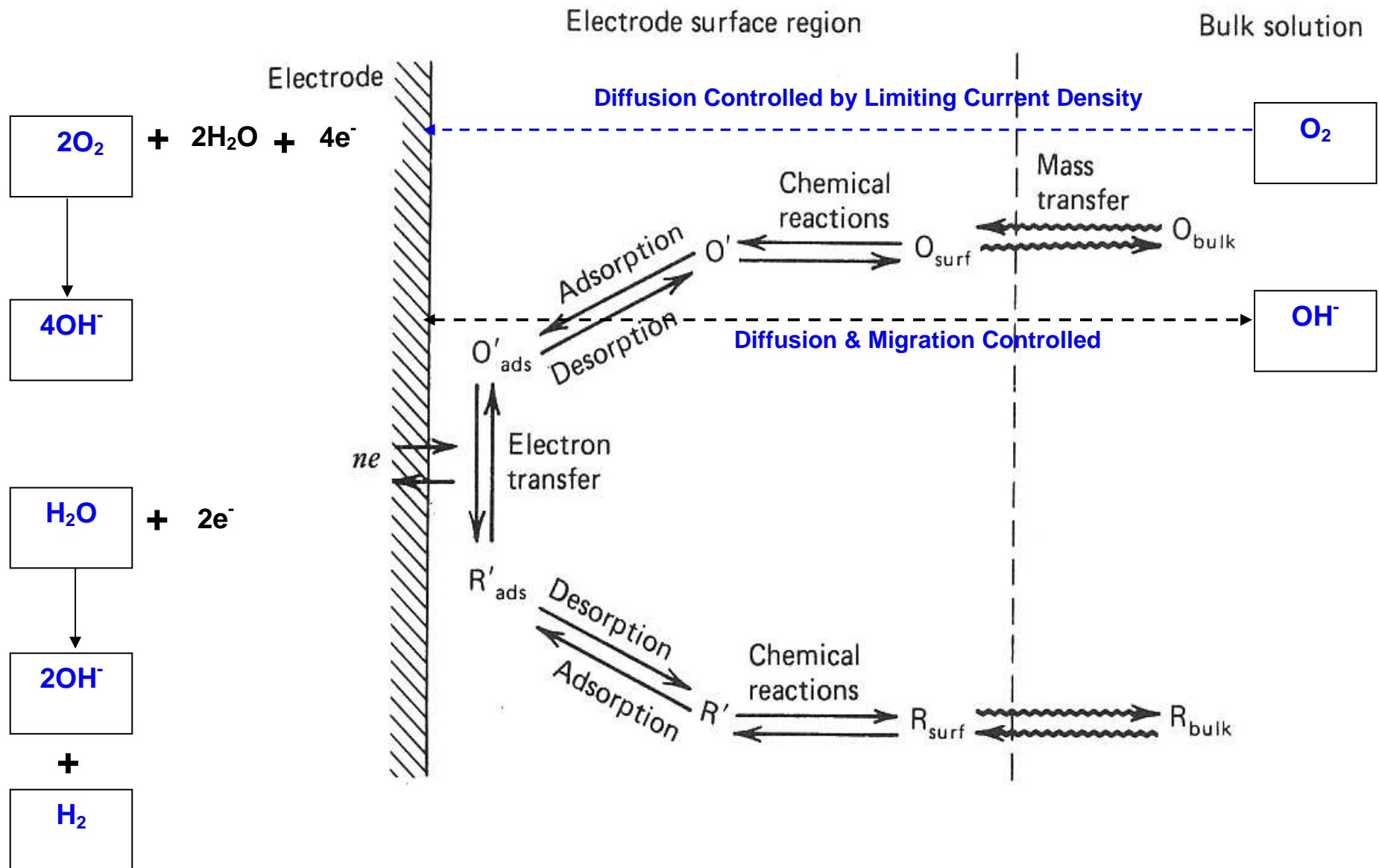


Figure 1: Schematic representation of the pathways of the general electrode reactions for Cathodic Protection ^[6]

It is thought that what Evans believed to be protection by passivation in his studies was actually due to the inhibitive properties of his electrolyte solutions. However, despite some mis-interpretation could Evans's concept have actually been correct? Could Cathodic Protection work because passivation blocks off the metallic surface from the corroding environment? Recent detailed studies of Leeds ^[2] agree with his concept.

Immunity Theory

Mears and Brown ^[7,8] and Hoar ^[9] separately in 1938 chose the immunity rather than the passivation mechanism. They suggested that complete corrosion mitigation could be achieved when the cathode is polarised to the open circuit potential of the anode. The basis of their proposed mechanism was that corrosion occurred due to the potential difference between local anodes and cathodes on the metal surface. If the cathodes were then polarised to the same potential as the local anodes then no current would flow and so corrosion would not occur. What they were actually finding was that copper could be protected from corrosion because it was being cathodically polarised and not because it was being held at the same potential as the zinc. They polarised to an anode instead of a cathode. The reason why they polarised to the potential of the local anode is not entirely clear. Normally to prevent corrosion the metal is polarised cathodically.

LaQue ^[10] alternatively suggested that complete protection could be obtained by polarising a structure to the reversible potential of the local cathode instead of the anode. The theory proposed by LaQue was investigated by Dexter *et al* ^[11] in 1985. Furthermore, Dexter, *et al* found that a reduction in the corroding areas was due to the existence of previously corroded areas prior to Cathodic Protection. They found that on a surface that had no appreciably corroded areas, when Cathodic Protection was applied there was no reduction in any of the anodic sites. Unfortunately the exposure time of their specimens was very short which probably limited their observations and hence interpretation.

Mixed-Potential Theory

The theories for the mechanism of Cathodic Protection previously introduced were based on the concept that separate local anode and cathodes are present on the same metal surface. LaQue's theory is based on the measured potential (E_{corr}) of the corroding metal being separated into their anodic and cathodic forms. This would be rather difficult to substantiate under current thinking, as it is believed that the measured potential consisted of the anodic and cathodic reactions, termed mixed potential.

It is also very difficult to apply LaQue's mechanism as not all anodic sites will stay anodic and likewise for cathodic sites.

The Mixed-Potential theory as described in Figure 2 introduced in 1957 is the theory most thought today to explain the mechanism of Cathodic Protection. Instead of polarising to local anodes as per Mears and Brown and Hoar theory; or polarising to local cathodes as per Laque's theory, the Mixed-Potential theory is thought to be accomplished by the polarising the metal from its corrosion potential (E_{corr}) to its redox / reversible potential ($E_{\text{o,a}}$). The amount of cathodic polarisation depends on the amount of applied current that is the difference between the anodic and cathodic currents at a particular potential. It can be seen that the anodic and cathodic species in a particular environment are combined. When cathodically polarising the metal surface at some set potential, the point of i_c on Figure 2 represents the amount of potential needed to be applied in order for there to be a potential change causing E_{corr} to be shifted cathodically to its reversible or equilibrium potential

($E_{Fe/Fe^{2+}}^o$) of its local anodes. It is assumed this is because at this potential, the anodic dissolution rate will equal the deposition rate, such that $i_a = i_{ac} = i_{oa}$. As in Figure 2 it can be seen to reduce the corrosion rate from i_{corr} to i_a' then iron must be polarised to i_c (potential change from E_{corr}) which should be in the order of 0.1 volts (CSE). This can be considered as the basis for the 100 mV shift which is one of the 6 NACE criteria^[12].

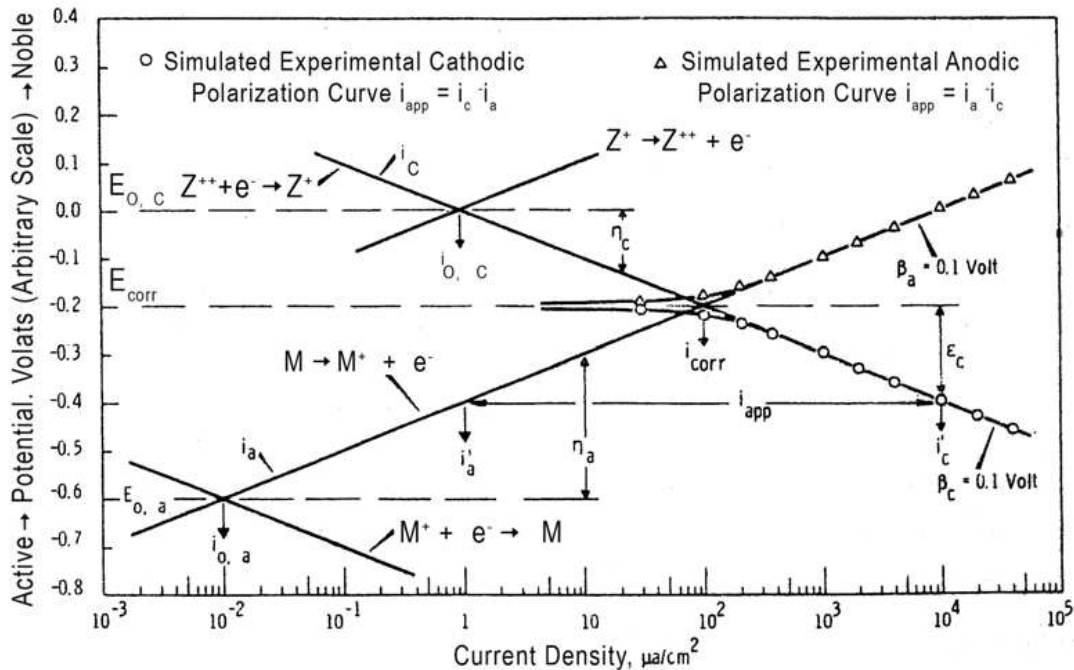


Figure 2: Explanation for the mechanism of Cathodic Protection as based on the Mixed-Potential Theory. Anodic and Cathodic Tafel plots for corrosion of a metal, M^[12]

Pourbaix Diagram

The potential – pH diagram (Pourbaix diagram) can be used to explain the possible anodic and cathodic behaviour of iron in electrolytes of different pH and categorizes the domains of corrosion, passivation and immunity (Figure 3)^[13]. Between lines 1 and 2 in Figure 3 and A and B in Figure 4 denotes the regions of stability of water. As the CP is increased and the potential applied to the metallic structure is made more negative, then the surface electrochemistry should move towards the region of immunity. This is identified as position B in Figure 3. At this position iron is thermodynamically stable and corrosion is impossible, except in the presence of strong complexants.

With the application of CP, the surface pH increases due to generation of alkalinity from the hydroxyl ions produced by the cathodic reactions. At the metal surface the effect is not only to move the potential towards a more negative value but also towards a higher pH as shown as position C on Figure 3. Depending on the relative changes in potential and pH the resultant conditions may be in a region of passivity or immunity. Evans^[5] proposed in 1937 that CP was achieved due to passivity. Evans thought passivity occurred by alkalisation of the metal surface caused by cathodic polarisation.

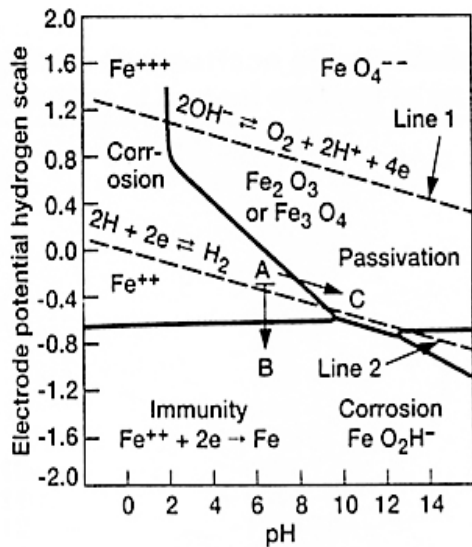


Figure 3: Potential – pH equilibrium diagram for iron in water at 25°C [13]

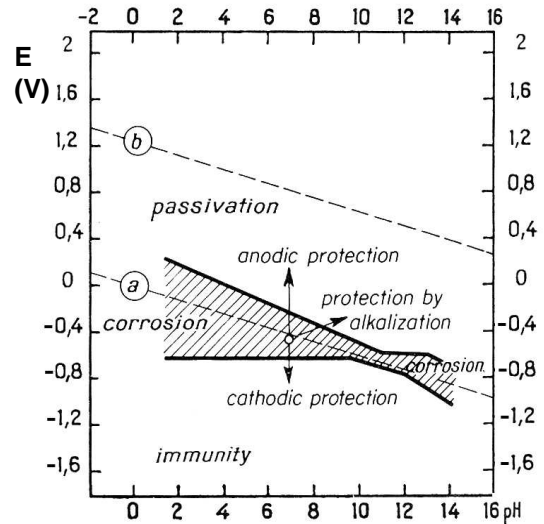


FIGURE 4: Schematic representation for protecting iron against corrosion in pure water [14]

Alkalisiation of the metal surface was suggested by Pourbaix as one of the 3 methods for protection of iron against corrosion (Figure 4) [14].

Experimental Approach

Twelve test specimens composed of C: 0.12%, Si: 0.18%, Mn: 0.85%, P: 0.026% and S: 0.031%. The test specimens were cylindrical in shape with a diameter of 6 mm and length of 40 mm. Specimens were prepared by abrading with 1200 grit silicon carbide, cleaned and degreased in acetone. Specimens were painted with electroplating lacquer to delineate test area under study and to minimise the water line effect. Specimens were pre-weighed and stored in a desiccator prior to use. Each test specimen was connected to a separate potentiostat. The potentials of the test specimens were controlled between -0.65 and -1.4 V (Ag/AgCl/3.5% NaCl). Further specimens were exposed to freely corroding conditions (approximately -0.671 V (Ag/AgCl/3.5% NaCl) in 3.5 % NaCl, -0.513 V (Ag/AgCl/3.5% NaCl) in artificial seawater or -0.318 V (SCE) in the alkaline solution). The specimens were exposed for 30 days. The current for each specimen was recorded automatically every 15 minutes. The potential of the freely corroding specimens were monitored every day. The pH of bulk electrolyte was measured periodically [2].

Film Analysis

To investigate nature of the films that formed after application of CP, all test specimens were carefully removed from their electrochemical cell, washed with deionised water and rinsed with ethanol to minimise flash rusting. Test specimens were air dried and stored in individual desiccators prior to examination of the surface films. The surface films were analysed using X-Ray Diffraction, operated at 60 kV / 40 mA using a cobalt tube with a Gonio scan axis. The crystalline structures were identified using a Powder Diffraction File Database. The deposit that formed on the metal surface was also analysed independently from the metal by grinding the deposit 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 analysis by X-Ray Diffraction the specimens were also analysed in the Scanning Electron Microscope (SEM). The morphology of the specimens was viewed and the composition of the entire specimen and sections of the film were analysed using energy dispersive analysis.

Weight Loss Measurements

To determine the effectiveness of CP at preventing corrosion the amount of metal loss was determined by weighing specimens before and after the test. At the end of the test period and after XRD and SEM analysis the specimens were cleaned according to ASTM G1 specification ^[15] prior to weighing.

Results

Potentiostatic Weight Loss Results

After thirty days the weight loss for each specimen for each environment was assessed. An industry standard for acceptable corrosion rate is 0.01mm/y was used as a comparison to test samples. None of the specimens studied had corrosion rates less than 0.01mm/year at potentials between -0.8 to -0.9 V regardless of the electrolyte composition. See Figure's 5,6,and7.

Specimens were found to have the lowest corrosion rate at an applied potential of -1.3 V (Ag/AgCl/3.5% NaCl) for specimens exposed to 3.5 % NaCl and the alkaline solution. The specimens exposed to artificial seawater suffered some cracking of calcareous deposits at the more negative potentials. It was determined that the lowest corrosion rate for specimens exposed to artificial seawater was at -0.9 V (Ag/AgCl/3.5% NaCl). The specimens exposed to the alkaline solution also had an acceptably low corrosion rate at -0.9 V (SCE).

The only specimens that achieved an acceptable corrosion rate of less than 0.01 mm/y were the -0.9 V and -1.3 V (SCE) specimens exposed to the alkaline pipe electrolyte, and specimens with applied potentials more negative than -1.1 V (Ag/AgCl/3.5% NaCl) in a 3.5% NaCl electrolyte.

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Current Density

Refer to Figure's 8,9 and 10. The 3.5% NaCl solution exposed specimens required the highest current density to maintain the potential at the start of the experiment compared to the specimens polarised in artificial seawater and the alkaline pipe electrolyte. The alkaline pipe electrolyte exposed specimens required the least amount of current to maintain the CP system at their applied potentials. At the end of the experiments the specimens polarised in artificial seawater and the alkaline pipe solution required the smallest current density compared to specimens polarised in 3.5 % NaCl. The reason for this could be due to the thicker calcareous films that form on specimens polarised in both artificial seawater and the alkaline pipe solutions.

All specimen samples had a 10 fold decrease in the current required for all specimens between the start current and the end current. Something, such as the surface film is causing this very significant reduction in current by blocking off the specimen surface leaving less steel exposed to receive current. Also important is the fact that the films must be relatively non conducting by insulating away the specimen surface. This reduction in current with time agrees with the practical application of CP where when CP is first applied to a buried pipe, currents are large and then decrease over a few days as the pipe is said to "polarise".

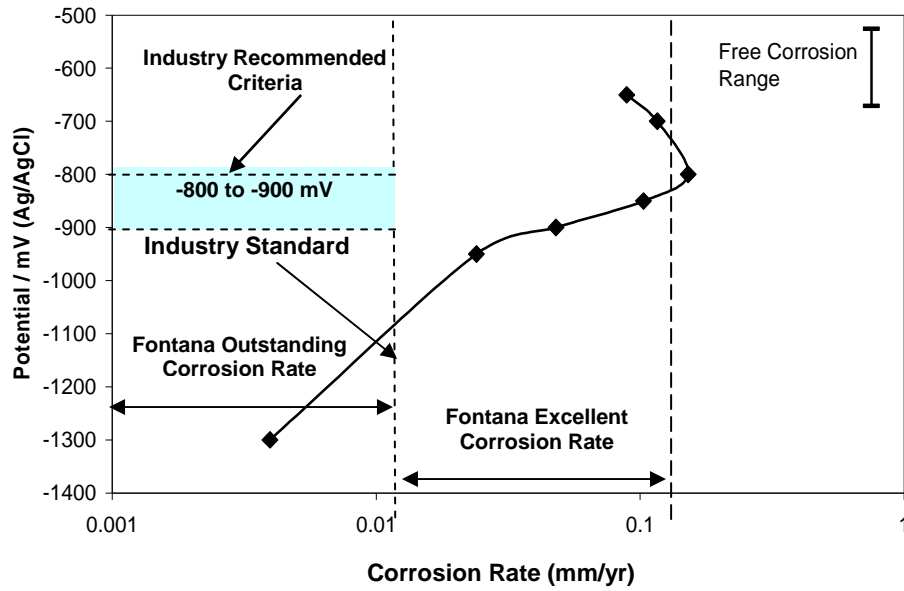


FIGURE 5: Average corrosion rate vs. potential in 3.5 % NaCl

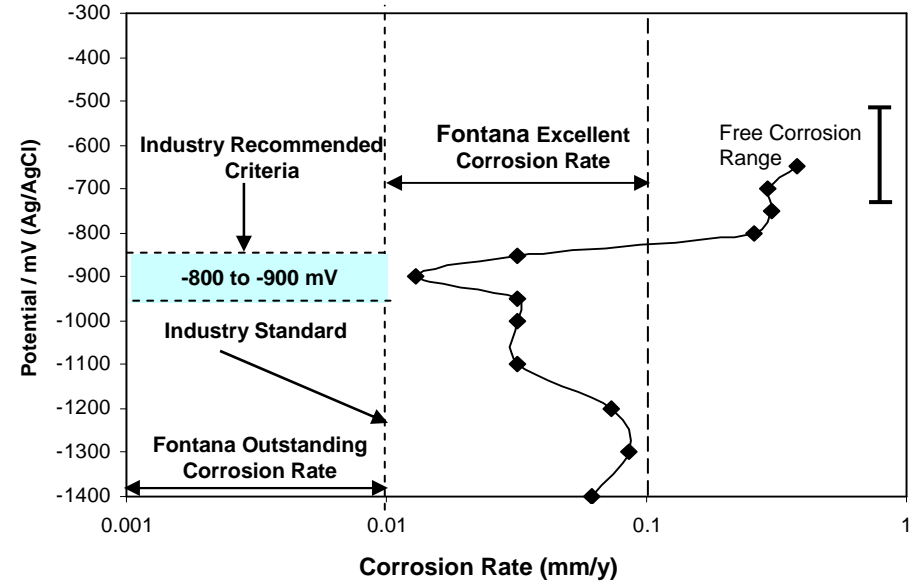


FIGURE 6: Average corrosion rate vs. potential in artificial seawater

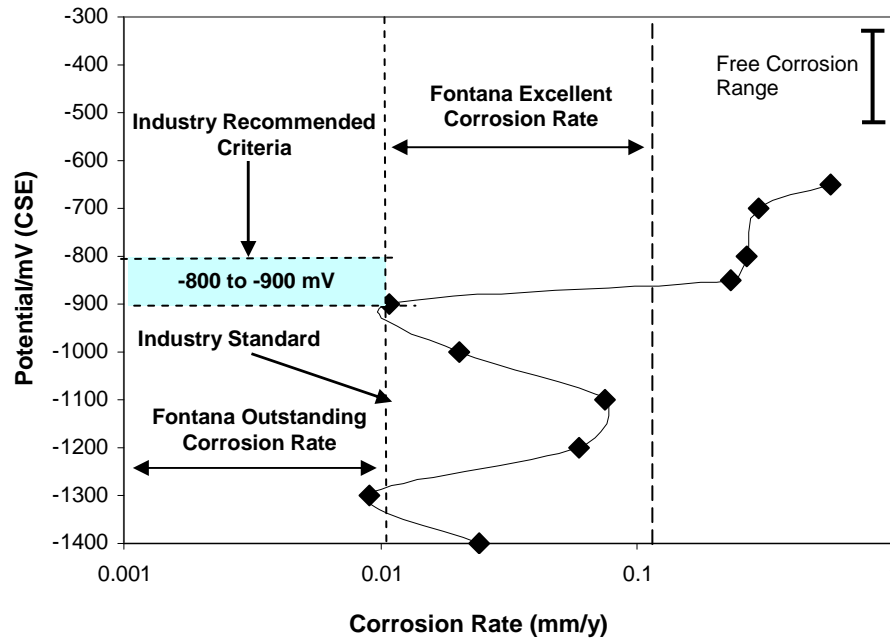


FIGURE 7: Average corrosion rate vs. potential in an alkaline pipe solution

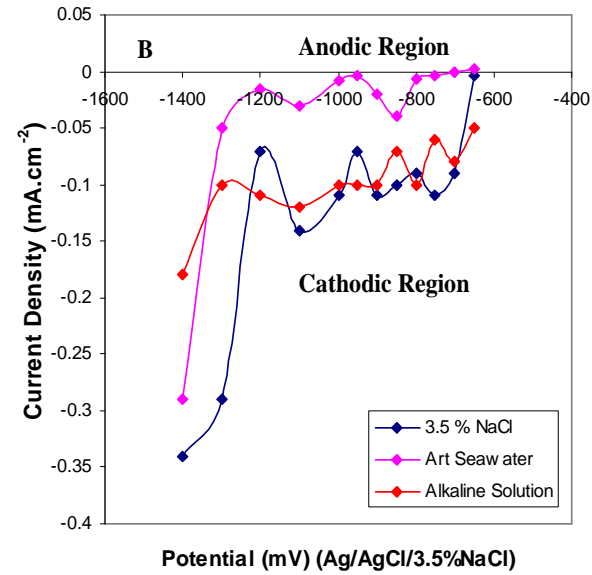
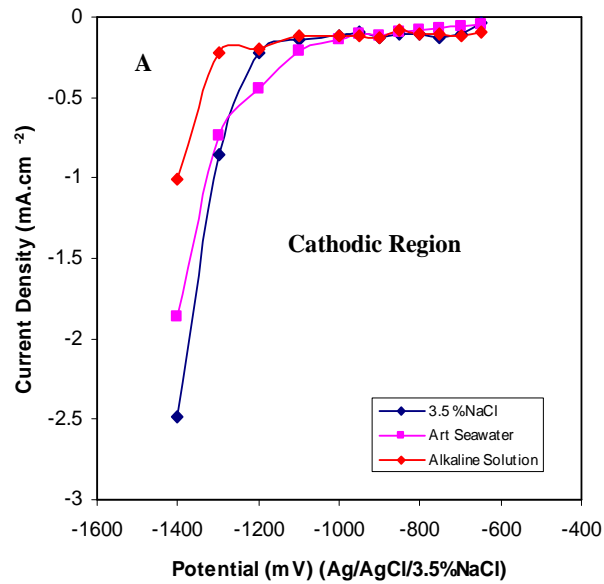


Figure 8: The current density required to maintain the potential at (A) Start of the experiment and (B) end of experiment

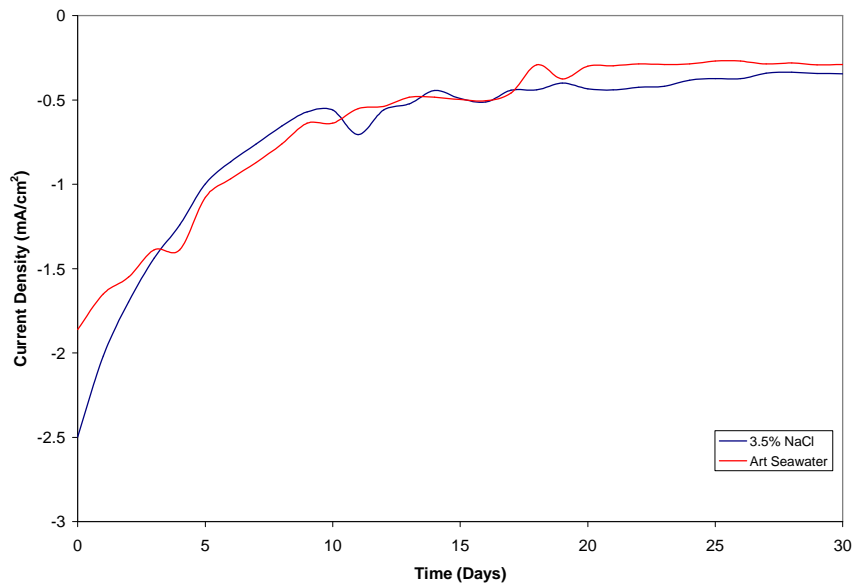


FIGURE 9: Average current density per day vs. time for the -1400 mV specimen in 3.5 % NaCl and artificial seawater

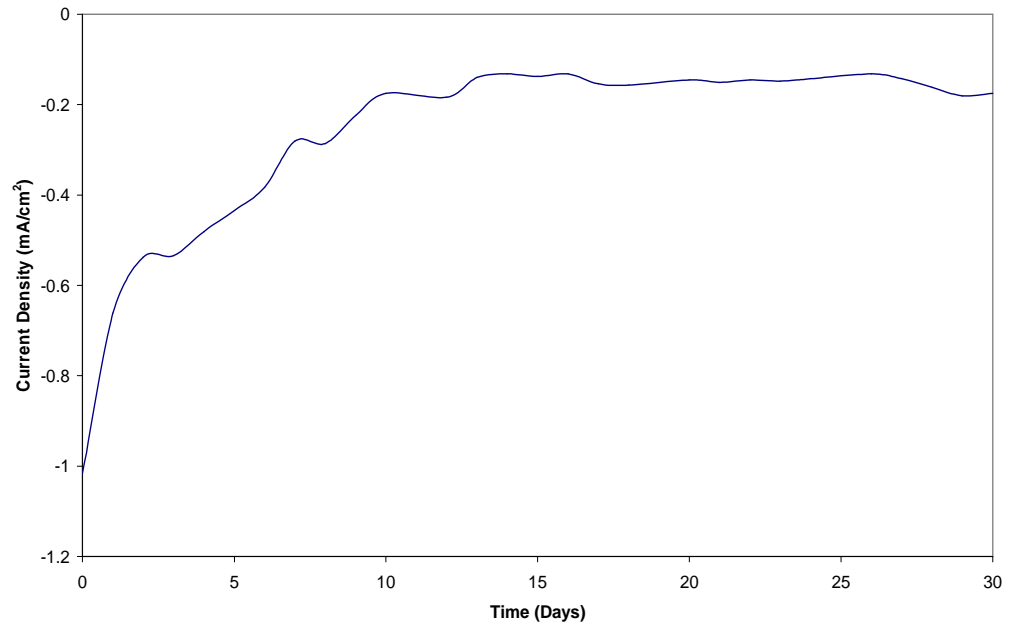


FIGURE 10: Average Current density per day vs. time for the -1400 mV specimen in an alkaline Pipe electrolyte

Morphological Changes

All samples were found to have morphological changes with time and depending on the applied potential. X-Ray Diffraction and energy dispersive analysis identified the freely corroding and -0.65 V for all exposed specimens to consist of iron corrosion products, goethite (α -FeOOH), lepidocrocite (γ -FeOOH), magnetite (Fe_3O_4) and akaganeite (β -FeOOH). As the applied potential was made more negative the constituents of the film / deposit changed from consisting of predominantly iron corrosion products to consisting of calcium carbonate containing products, calcite and aragonite for the alkaline and artificial seawater exposed specimens. The sodium chloride exposed specimen was found to consist of magnetite as the specimen was made more negative.

Figure's 5, 6 and 7 detail typical morphological changes to the metal surface as applied potential is made more negative.



FIGURE 5: -0.65 V Specimen

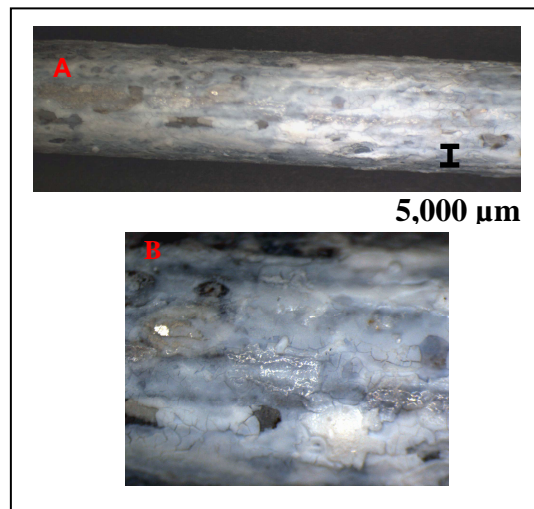


FIGURE 6: A & B: -1.2 V Specimen

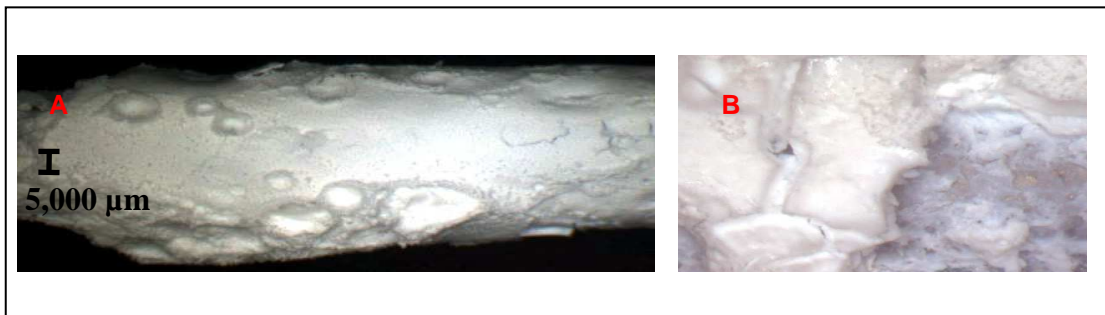


FIGURE 7: A & B: -1.3 V Specimen

From this study it can be concluded that films of iron corrosion products and calcareous deposits do form on the metal surface as a direct result of applying CP. The film composition was 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 formation of calcium carbonate ^[1,16,17]. Others ^[18,19] have found that the major components of calcareous deposits are magnesium hydroxide and calcium carbonate. The composition of the calcareous deposit can change depending on the current density and interfacial pH around a structure. The lower interfacial pH obtained at lower current densities favours calcium carbonate formation, while higher current densities, leading to an interfacial pH of greater than 9.48, are required before magnesium hydroxide will precipitate ^[19,20].

The protective nature of surface films and calcareous deposits is dependent on the constituents of the deposit. Generally under seawater conditions 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^[19,20]. This is thought to be because the current density required to produce the pH for deposition, is that where hydrogen gas is generated on the metal surface, which disrupts the deposit. Another factor influencing the protective nature of calcareous deposits is the film thickness, which can vary over different surface regions of a structure. It has been found that the more positive the potential or the higher the water velocity the thinner the calcareous deposit. The more negative the applied potential and lower the velocity, the thicker and more developed the deposit is^[19,20].

It has been shown that surface films can be formed on metals exposed to land-based conditions as a direct result of Cathodic Protection^[2,21,22]. However, there is little information available as to the constituents of surface films in such environments. The reason for this is that few studies are carried out on land-based system due to the complexity and variability of the electrolyte. Studies carried out by Leeds^[2,21,22] in pure 3.5% NaCl identified iron corrosion products as a major constituent of surface films. Magnetite was found to form on the metal surface as the potential was made more negative. It also formed a coherent film that was protective in nature.

Discussion

It is well-known that iron specimens exposed to moist soil or seawater will corrode to form iron corrosion products which during the course of this work were identified as goethite (α -FeOOH), lepidocrocite (γ -FeOOH), magnetite (Fe_3O_4) and akaganeite (β -FeOOH). Cathodically polarising the metal surface to a potential close to the freely corroding potential of -0.65 V (Ag/AgCl/3.5% NaCl) was shown to give a ten-fold reduction in the corrosion rate and hence demonstrated that even a small amount of CP had a significant effect. However, the application of CP did not completely halt corrosion at any of the potentials studied.

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

1. Increase in metal interface pH.
2. Decrease in anodic dissolution kinetics.
3. Increase on oxygen reduction kinetics (though this may be limited by mass transport).
4. Increase in hydrogen evolution kinetics (if the potential is sufficiently negative).

As a result of the above processes various changes happen to the metal surface. For all the polarised specimens exposed to a test environment, morphological changes to the metal surface occurred during the thirty day test period. No specimen was found to be the same shiny metal at the end of the experiment as it was at the start. All specimens were found to have a film on their surface and these started to form within the first three days of each experiment. The composition of the film formed was pH and potential dependent.

Films identified in the specimens exposed to an alkaline pipe solution mainly consisted of a black surface discolouration, too thin to be analysed by XRD, covered in calcite except when the applied potential was -1.3 V (SCE). Deposits formed at -1.3 V (SCE) were found to consist only of Lepidocrocite (γ -FeOOH). The amount of film forming on the specimens

exposed to the alkaline pipe solution was actually quite small even though exposed to a carbonate containing electrolyte. Even with small amounts of calcium and magnesium present in the electrolyte was sufficient to significantly restrict the formation of iron corrosion products to very thin films.

The current densities of all specimens studied were found to decrease with time, suggesting that an insulating coating was progressively blocking the steel surface.

In artificial seawater specimens, the films contained calcium as the carbonate in either aragonite or calcite forms on specimens polarised between -0.75 and -1 V (Ag/AgCl/3.5% NaCl). However, the concentration of aragonite decreased at more negative potentials than -1.1 V (Ag/AgCl/3.5% NaCl) when the concentration of magnesium as brucite in the film began to increase. This suggests that interfacial chemistry plays a crucial role in controlling the precipitation of a calcium carbonate and magnesium containing species. The pH of the electrolyte is also very critical because whilst calcium will precipitate at a pH greater than 8.1, the pH has to exceed 9.5 to precipitate magnesium. This is why a potential more negative than -1.1 V (Ag/AgCl/3.5 % NaCl) is required before any magnesium-containing species such as brucite are identified in the film. The presence of magnesium also caused the film to become more fragile and porous compared to a film without magnesium. The corrosion rate was also found to increase when more magnesium was present. Specimens with more aragonite present in the film were found to be more coherent and have lower corrosion rates. No significant iron containing films were identified in/under the calcareous deposit. Interestingly, experiments presented earlier, on specimens exposed to pure 3.5% NaCl, where no calcareous deposits were present, found the most coherent films formed on specimens that were polarised between -1.3 and -1.4 V (Ag/AgCl/3.5% NaCl). These specimens had the lowest corrosion rates and surface films where composed of magnetite [2, 21, 22].

Figure 8 gives an overall summary of the identified components of the films of all specimens studied at all applied potentials and exposed to all electrolytes. It can be concluded that the films with the best protection were those forming between applied potentials of -0.95 to -1.1 V and these were composed of aragonite and calcite exposed to seawater and alkaline solutions. When the films are composed of calcareous deposits, very little presence of iron corrosion products were present.

International standards and specifications set out the application and control of CP, but these generally give little consideration to the surface electrochemistry between the metallic structure and its electrolyte [23, 24, 25, 26]. The only standard that has a more definitive description of Cathodic Protection is ISO 8044 [27]. The ISO standard defines Cathodic Protection as “electrochemical protection achieved by decreasing the structure potential to a level whereby the corrosion rate of metal is significantly reduced”. At present the standards and specifications available as a guide for the best conditions to prevent corrosion using Cathodic Protection are very general. They recommend using an OFF potential of -0.85 V (CSE) in order to stop corrosion. However, this work suggests that -0.85 V (CSE) may not be sufficient to prevent corrosion. The results from this work suggest the use of a potential between -0.95 V and -1.1 V (CSE) is required in order to minimise corrosion. Others such as Barlo [28] have suggested that negligible corrosion could occur with a polarized potential of 0.85 V (CSE). Leeds [2,21,22], Scwerdtfeger and McDorman [29] and Toncre [30] all suggest that for a criterion based on a potential measurement then a polarised potential more negative than -1.0 V (CSE) should be used instead of -0.85 V (CSE) because significant corrosion has

still been found to occur between potentials of -0.9 and -0.95 V (CSE). Barlo also reports significant corrosion at potentials more negative than -0.85 V (CSE) ^[28].

Selecting which potential to use as the criterion for protection is not an easy decision. In some circumstances as seen in this work, applying -0.85 V (CSE) was not enough to stop corrosion. However, in other circumstances it is more than enough. Ewing ^[31] found that “in well drained and rather dry soil, the protective potential was -0.7 V (CSE)”. Barlo even reports values as positive as -0.6 V (CSE). In other soils -1.1 V (CSE) was required. This suggests that an understanding of the water/soil conditions that the structure is exposed to should be one of the most crucial parameters for the control of corrosion. These include pH, oxygen content and resistivity (corrosivity) of the electrolyte. Further research work is needed to cover a range of soil conditions, particularly acid soils, to determine the current density requirements that will produce sufficient alkali for film formation. All these conditions should be recognised and better defined by International Specifications and Standards as a guide for improved control of corrosion through the application of CP.

Conclusions

1. Surface films do form due to the application of Cathodic Protection, suggesting that the mechanism of Cathodic Protection could be due to passivation due to alkalisation.
2. The interfacial chemistry and electrochemistry of the metal / electrolyte interface and electrolyte properties should be taken into consideration when selecting parameters for minimising corrosion by Cathodic Protection under practical operating conditions.
3. The preferred Cathodic Protection OFF potential criterion to use as a way to minimise corrosion on a buried pipeline should be -1.0 V (CSE).

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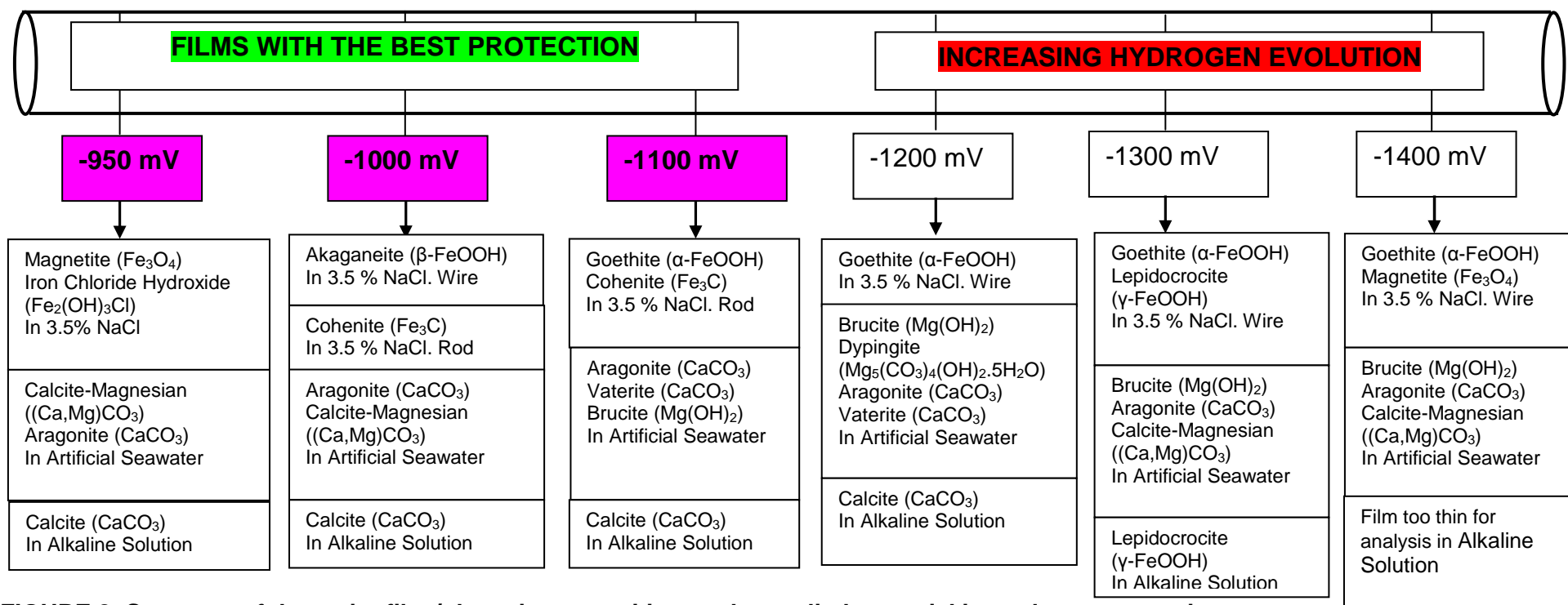
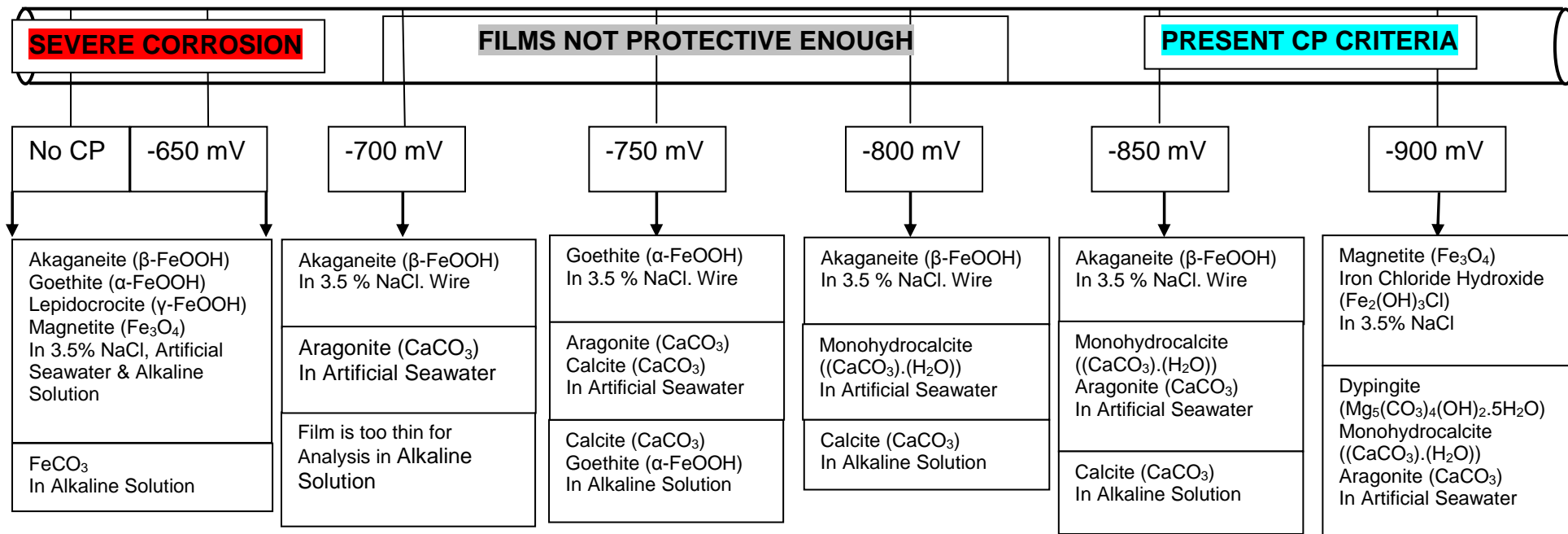


FIGURE 8: Summary of the major film / deposit composition as the applied potential is made more negative