

An Alternative View of the Cathodic Protection Mechanism on Buried Pipelines

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Abstract

The conventional understanding of the cathodic protection mechanism is illustrated in the definition of cathodic protection arising from the research of Mears and Brown in 1938. That is, cathodic protection is complete when the corrosion cell cathodes are polarized electronegatively to the open circuit potential of the most electronegative anode site on the structure. Typically, the reduction reactions, that transfer cathodic protection current across the structure/electrolyte interfaces produce hydroxyl ions, raise the pH at the interface. For steel, an increase in pH reduces the corrosion rate, depending on the degree of aeration of the environment. Where the interfacial environment is either naturally unaerated or deaerated, because of the cathodic protection reduction reactions, a pH > 9.5 is enough to reduce the corrosion rate to less than 25 $\mu\text{m}/\text{y}$ (~ 1mpy). When the interfacial environment is aerated, a pH>10.5 is sufficient to reduce the corrosion rate to less than 25 μm (~ 1mpy). Although measuring the interfacial pH is not as easy as measuring the polarized potential, the interfacial pH is thermodynamically related to the polarized potential, if the polarized potential resides at the hydrogen line of the Pourbaix diagram, such as when the structure/electrolyte interface is unaerated. Therefore, the polarized potential is an indirect indication of the interfacial pH, which in turn is an indication of the corrosion rate. It can therefore be considered that the increase in pH is the predominant protection mechanism and the polarized potential, except in aerated conditions, is simply an indication of the interfacial pH.

Key Words: Cathodic protection mechanism, reduction reactions, pH, corrosion rate, aerated environment, unaerated environment, polarized potential, chemical polarization

Background

The conventional understanding of the cathodic protection mechanism is founded in the results of experiments carried out by Mears and Brown in 1938¹. They stated that “for cathodic protection to be entirely effective, the local cathodes on the corroding specimen must be polarized to the potential of the unpolarized local anodes”. At that point, as illustrated in Figure 1, the corrosion current density is reduced to the exchange current density (i_o) at which point the corrosion current density is zero.

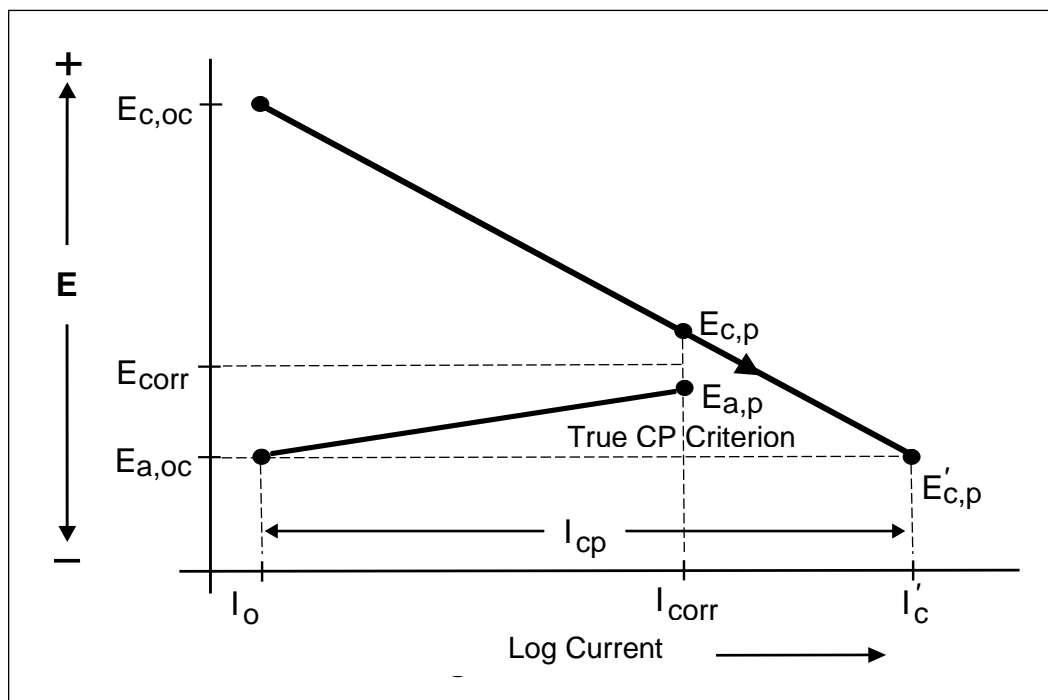


Figure1: Polarization diagram illustrating the Mears & Brown cathodic protection mechanism

This theory was supported by Dexter et al² who conducted polarization tests on steel in sea water and concluded “that cathodic protection was achieved by polarizing to, or at least toward, the potential of the local action anodes in agreement with the Mears and Brown and Hoar theories”.

Therefore, for complete protection, the true criterion for any corrosion cell is the open circuit potential of the corrosion cell anode ($E_{a,oc}$). Extending this electrical analogy to a structure having many corrosion cells, means that for complete cathodic protection all cathode sites need to be polarized electronegatively to the most electronegative anode site on the structure. However, this presented a serious problem because of the impracticality of determining the potential of the most electronegative open circuit anode on the structure.

R.J. Kuhn³, addressed this problem based on empirical data obtained on the cathodic protection of cast iron water mains in New Orleans. He proposed a potential of -850mVcse “to which a pipe must be lowered in order to stop corrosion”. Although there was no verification on the effectiveness of this criterion at the time, it was assumed that this potential criterion was more electronegative than any open circuit anode potential on a steel structure.

The effectiveness of cathodic protection was further investigated by Schwerdtfeger and McDorman at the National Bureau of Standards⁴ in the early 1950s. The potential of steel electrodes, placed in soil samples of varying pH, were measured and plotted against pH as illustrated in Figure 2.

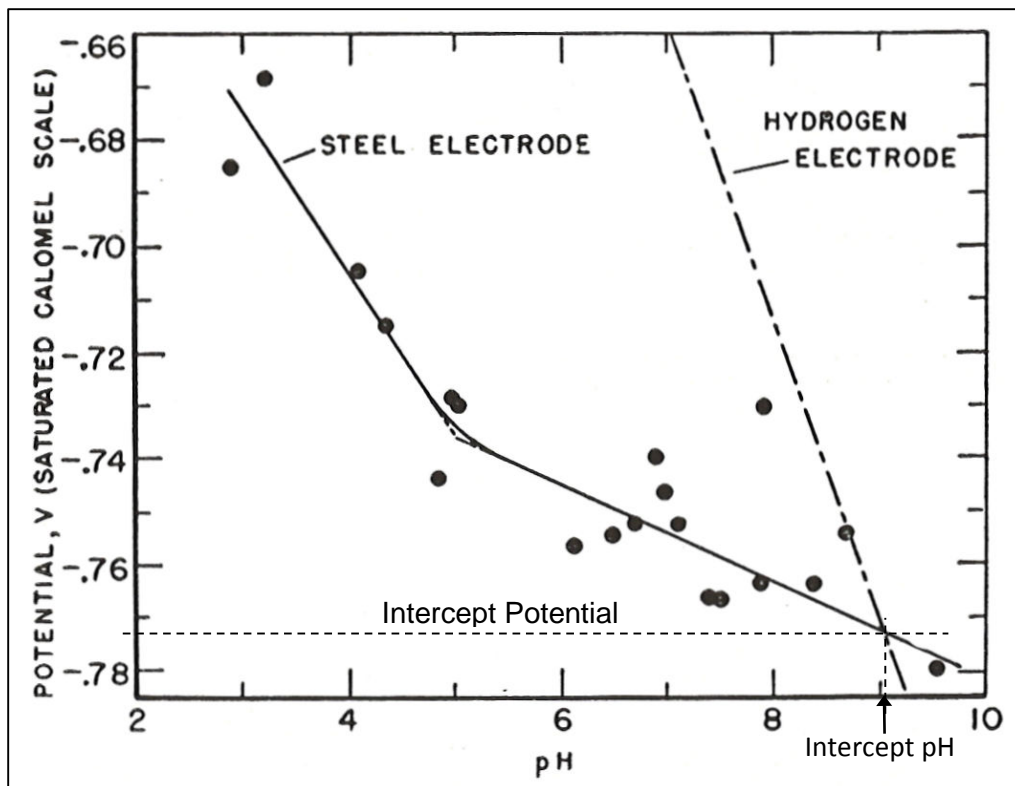


Figure 2: Steel and hydrogen electrode potentials versus soil pH

The soil samples, which were collected from different geographical locations across the US, were intentionally deaerated so that the only possible cathodic reaction on the steel electrode would be the reduction of hydrogen ions (i.e. $H^+ + e^- = H^0$). The potential of a hydrogen electrode is thermodynamically related to pH and this relationship is plotted on Figure 2 along with the steel electrode corrosion potential.

For a steel electrode in a deaerated environment, the corrosion cell cathode potential would be the hydrogen electrode potential and the steel potential is assumed to be the anode potential of the corrosion cell. The potential difference between the steel coupon and the hydrogen electrode is considered the corrosion cell driving potential, which gradually diminishes as the soil pH increased and reached zero at a potential of about -0.77V_{sce}, at which point the corrosion current would be expected to be zero. This point equates to a potential of -845mV_{sce} and occurred at approximately pH9. Besides providing theoretical validity to the -850mV_{sce} criterion, the results also suggest that increasing the pH would result in corrosion reduction.

The Role of pH in Controlling Steel Corrosion

The effect of pH on the reduction of the steel corrosion rate was demonstrated in 1983 by Barlo et al⁵ for aerated, oxygenated, and deaerated conditions as shown in Figure 3.

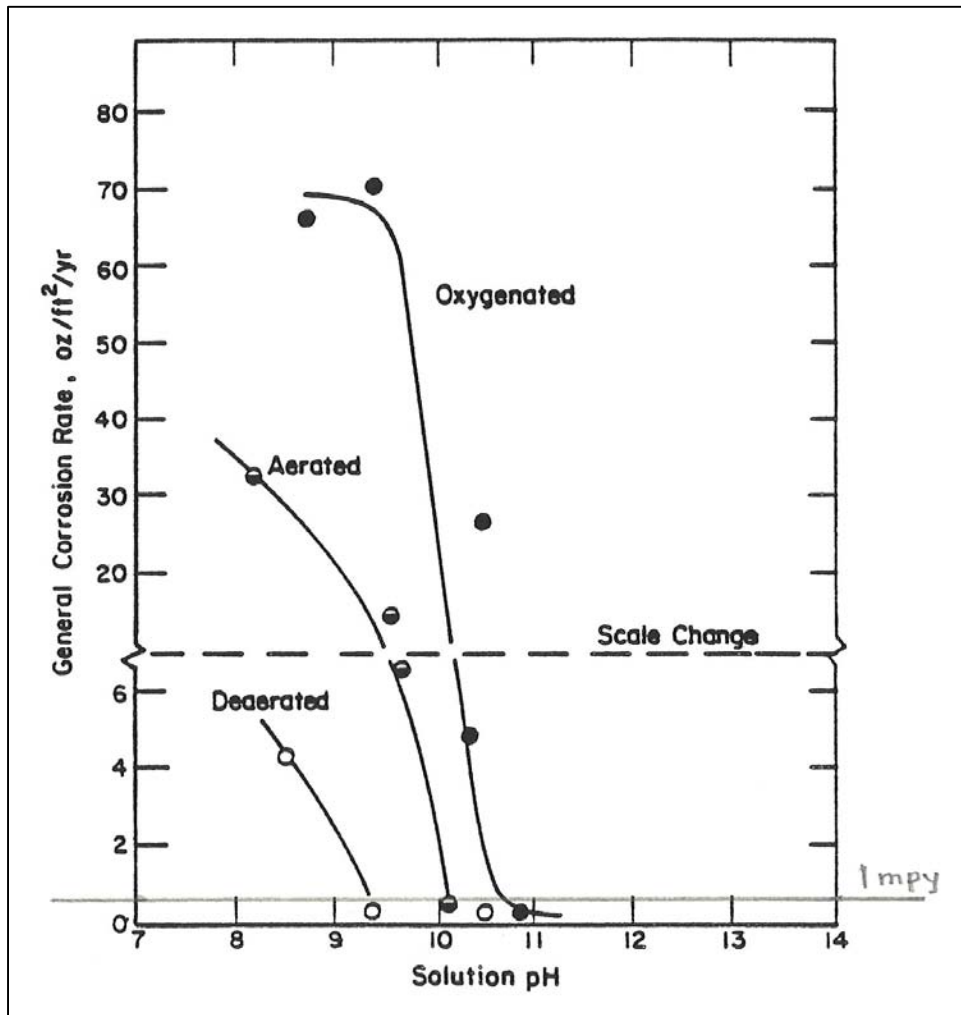


Figure 3: General corrosion rate of bare steel in a simulated groundwater at the free corrosion potential as influenced by pH and oxygen level

It is apparent that, as the pH is increased from pH 8, steel corrosion rates diminish to less than 1mpy at pH 9.3 in deaerated conditions, at pH 10 for aerated conditions, and at pH 10.7 for oxygenated conditions.

Furthermore, increasing the environmental pH has been shown to be effective in reducing other forms of corrosion.

In 1986 Parkins and Fessler⁶ found that the potential range associated with stress corrosion cracking was narrowed as the pH increased due to the application of cathodic protection, as shown in Figure 4

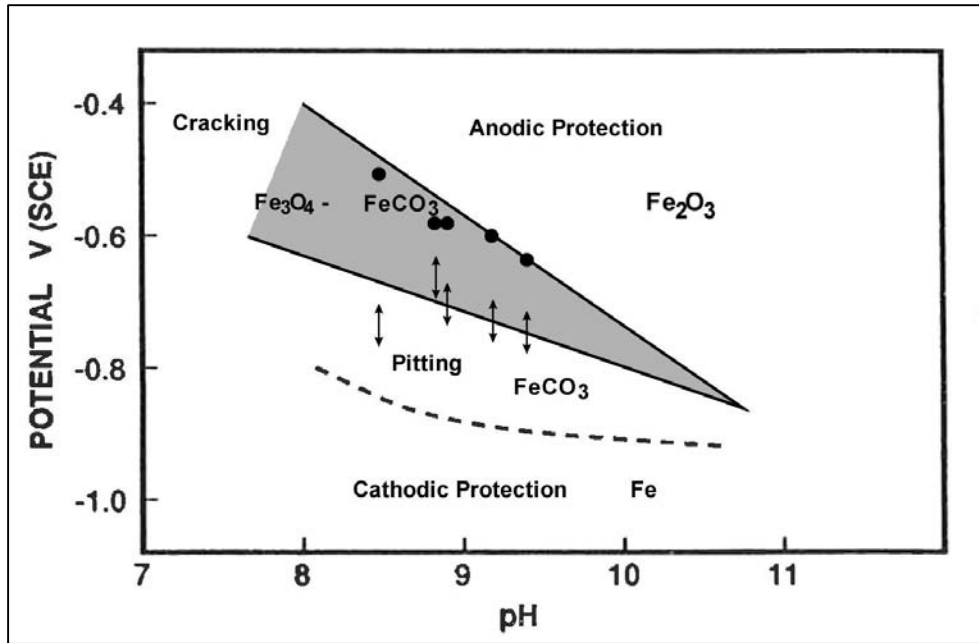


Figure 4: Stress corrosion cracking potential range vs cathodic protection potentials and pH in carbonate-bicarbonate solutions

Prakesh et al⁷ found that the corrosion weight loss caused by sulfate reducing bacteria was decreased as the environmental pH was increased, as illustrated in Figure 5

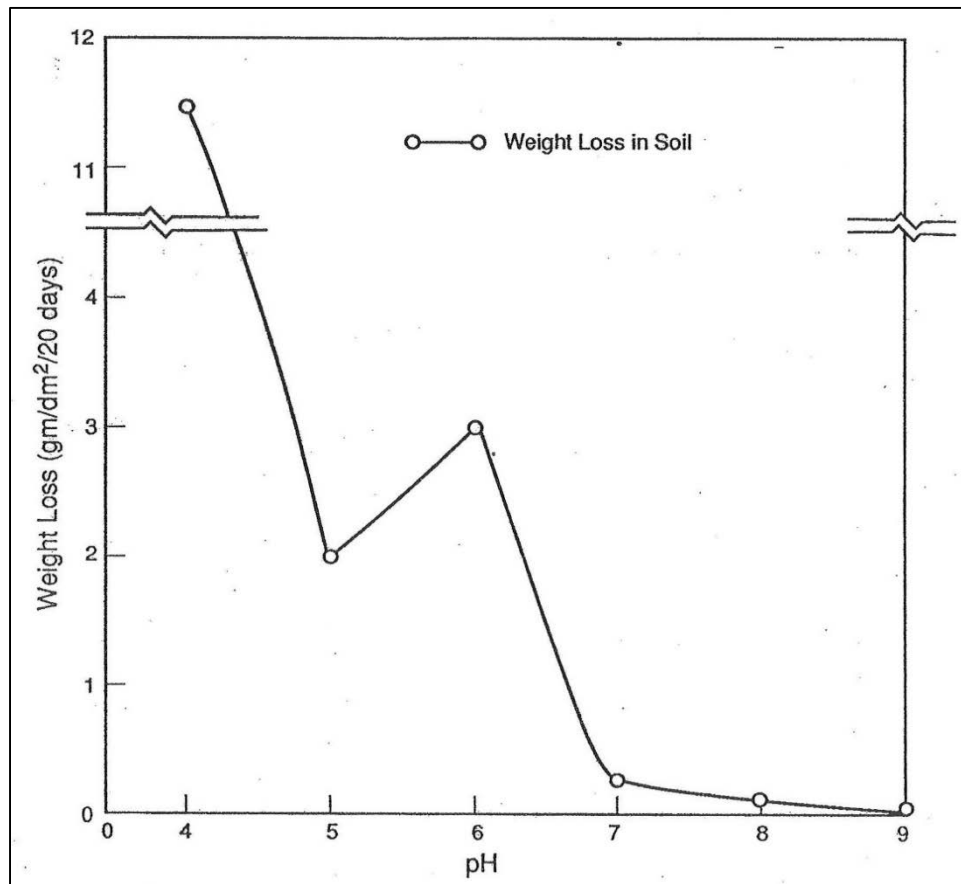
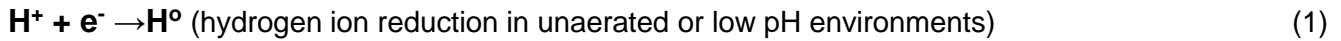


Figure 5: Effect of pH on bacterial corrosion of mild steel

Cathodic Protection and pH

When cathodic protection current is applied to a structure, the current is transferred across the structure/electrolyte boundary by one or more of the following reduction reactions depending on the environment and the magnitude of the current density. The common reduction reactions are;



All the foregoing reduction reactions result in an increase in the concentration of OH⁻ ions at the structure/electrolyte interface and a proportionate increase in pH. Buchler⁸, in 2013 illustrated this increase in pH on a Pourbaix diagram as shown in Figure 6

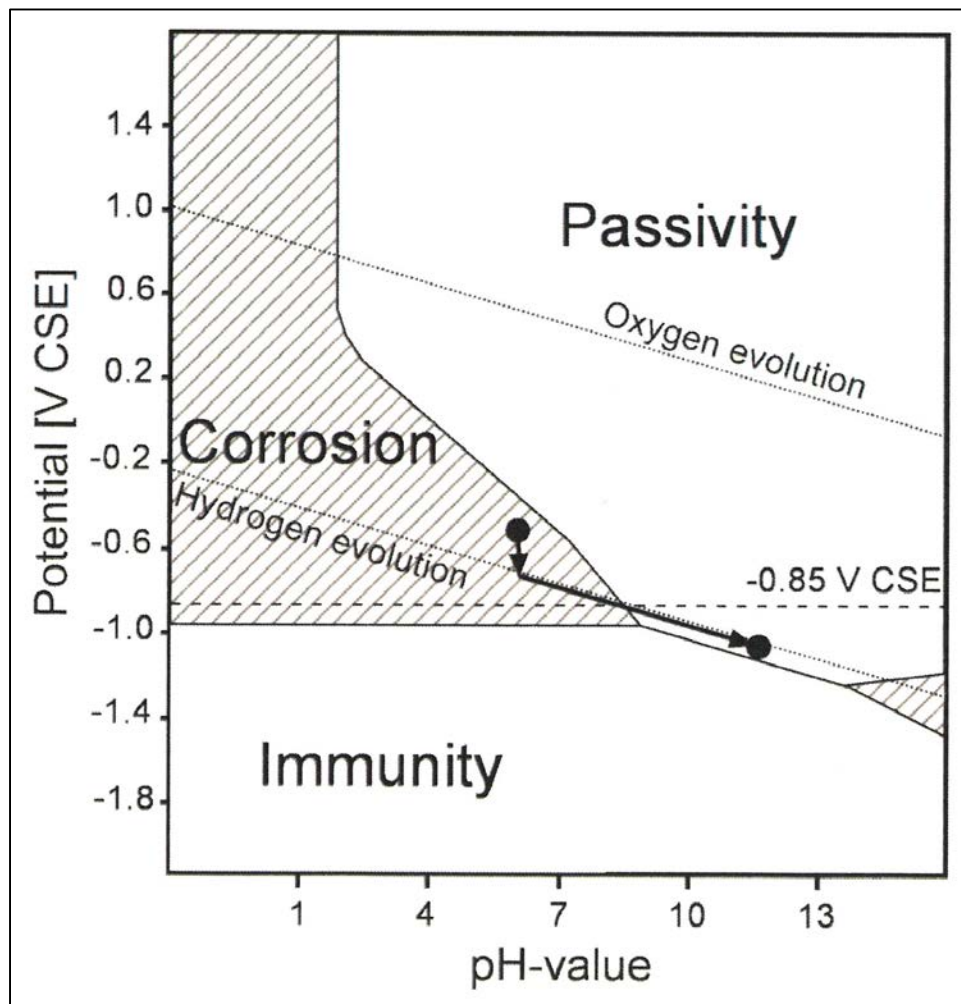


Figure 6: Cathodically polarized potentials on steel are limited by the hydrogen line on a Pourbaix diagram and increased CP current increases the steel/electrolyte interfacial pH

When cathodic protection current polarizes steel in the negative direction, the steel polarized potential cannot be normally forced more negative than 80 mV passed the hydrogen line⁹, where the electrolysis of water occurs and hydrogen gas is produced. Increasing the cathodic protection current density results in an increase in pH, where an increase in a single pH unit typically requires an order of magnitude increase in cathodic protection current density. When the structure polarized potential resides (E_p) on the hydrogen evolution line, the potential and the interfacial pH are linearly related by the following equation.

$$E_p = -316\text{mVcse} + (-59\text{mV} \times \text{pH}) \quad (4)$$

The calculated potential for pH9 and pH10 is -847mVcse and -906mVcse respectively. It follows then that the structure polarized potential is an indirect indication of the interfacial pH, when the structure polarized potential is at the hydrogen line.

In aqueous aerated solutions the polarized potential of a structure may not be a linear relationship with pH because the structure/electrolyte potential does not meet the hydrogen line until the cathodic protection current density exceeds the oxygen limiting current density (i_L). This situation was illustrated by cathodic polarization scans carried out by Thompson and Barlo¹⁰ in simulated groundwater solutions, as shown in Figure 7.

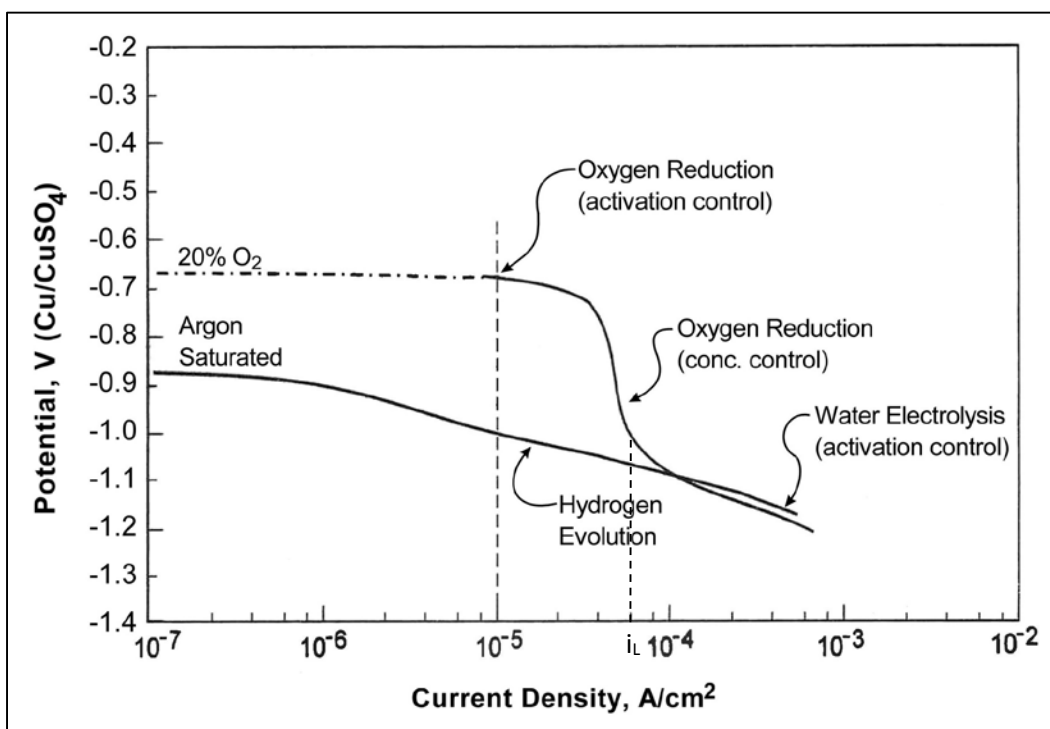


Figure 7: Cathodic polarization scans on steel in a deaerated and a 20% aerated aqueous solution at pH7

Argon saturation of the aqueous solution removed dissolved oxygen to obtain a deaerated condition, where the structure/electrolyte potential is linearly related to the logarithm of applied current density. This is the hydrogen line, where water electrolysis and hydrogen evolution occurs. It should be noted that to change the structure/electrolyte potential by 100mV of cathodic polarization requires approximately a 10 times increase in the cathodic protection current density. Comparing this data with Figure 6 indicates that there is a direct proportional relationship between pH and the logarithm of current density. Similar to the potential/pH relationship on the hydrogen line.

For the 20% aerated condition, where 100% aeration would be about 8 ppm of dissolved oxygen, the structure polarized potential does not indicate the interfacial pH until the limiting current density for oxygen reduction is reached at a current density of about 10^{-4} A/cm². The limiting current density increases as the dissolved oxygen concentration in the electrolyte increases.

Nevertheless, in an aerated solution the charge transfer reaction is the reduction of dissolved oxygen and the production of OH⁻ ions, even though the polarized potential is not linearly related to the pH. Even in an aqueous solution purged with air, the dissolved oxygen concentration at the structure/electrolyte interface is reduced to negligible concentrations, as the structure is polarized to more negative values. This was demonstrated by Lewandowski et al¹¹ in 1988, when conducting cathodic polarization tests on stainless steel in a solution purged with air, as shown in Figure 8. At potentials more negative than $-0.800V_{SCE}$ the interfacial dissolved oxygen concentration was negligible.

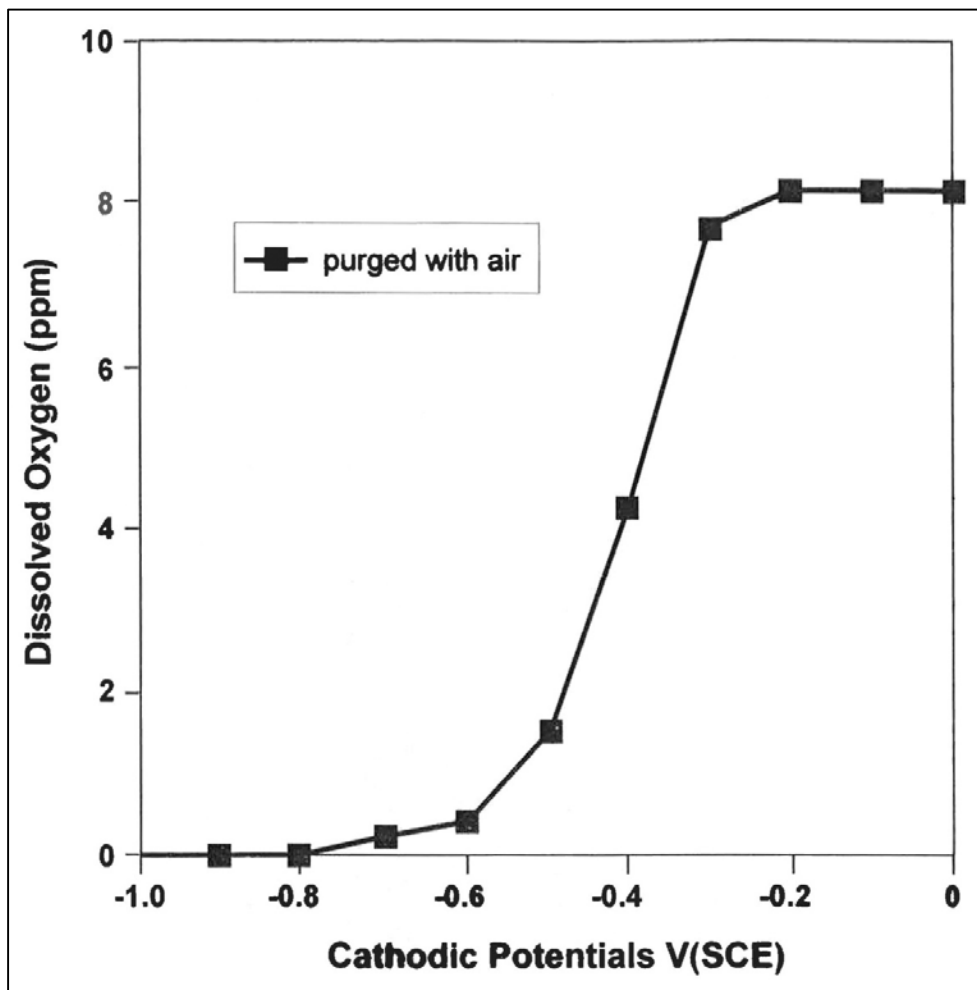


Figure 8: Dissolved oxygen as a function of applied cathodic protection in 3.5% artificial sea water purged with air on stainless steel

The Interfacial pH Gradient

The highest pH occurs at the interface but diminishes rapidly moving away from the interface as shown in Figure 9. Measurements of pH with distance from the interface were taken by Kobayashi¹² for various bulk solution pHs in aqueous solutions at a relatively high current density of $38 \mu\text{A}/\text{cm}^2$.

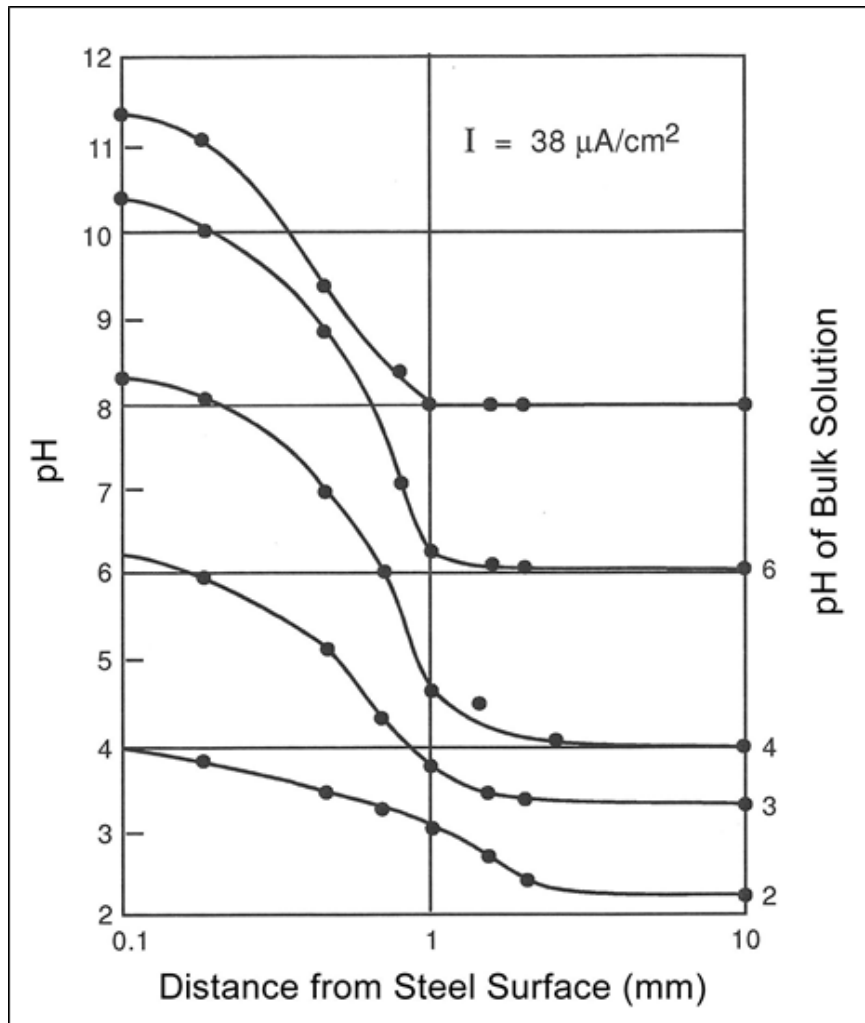


Figure 9: Variation in pH with distance from the steel interface when cathodically polarized at a current density of $38\mu\text{A}/\text{cm}^2$ in a 3% NaCl solution at different bulk solution pH

The solution pH generally drops to the bulk solution pH within a millimeter of the interface. It also illustrates the difficulty in achieving protection on structures in a low pH solution, since even at a bulk solution pH of 4, the pH at the interface is only a little more than 8. To raise the interfacial pH by one would require increasing the cathodic protection current density by a factor of 10.

Steel Corrosion Potential vs pH

It has been shown that the application of cathodic protection polarizes steel in the electronegative direction, while at the same time raising the pH at the interface. However, electronegative corrosion potentials can also be obtained in deaerated aqueous solutions simply by placing the steel in a high pH solution. This is predicted on the Pourbaix diagram for iron. But in aerated solutions the steel corrosion potential is somewhat independent of pH as shown in Figure 10.

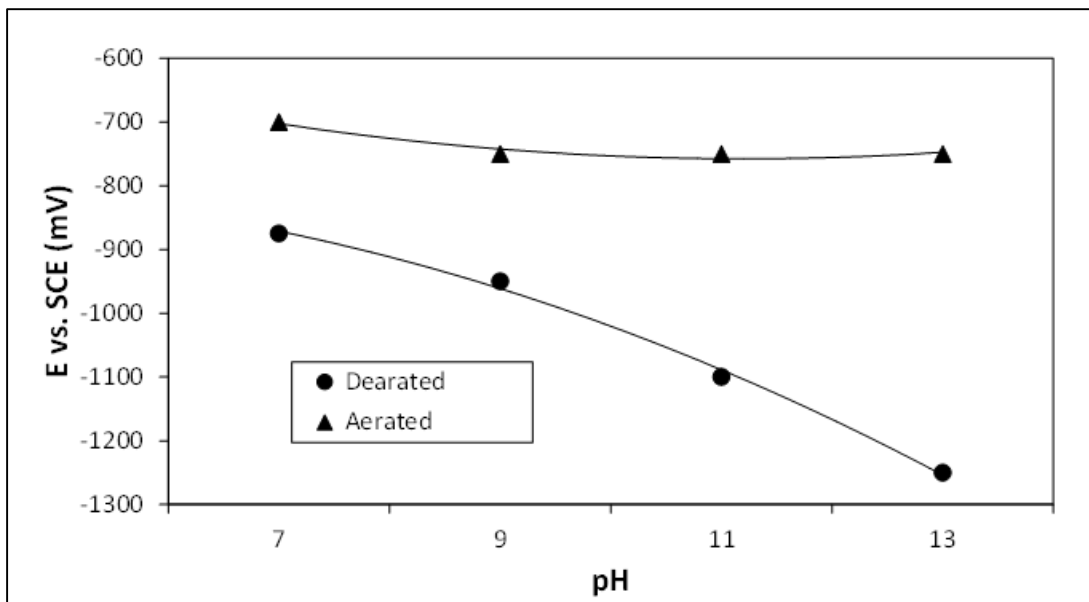


Figure 10: Steel corrosion potentials versus pH in 100mM Na₂SO₄ aerated and deaerated solutions

This corrosion potential data was produced as a result of cathodic polarization tests on steel samples in a 100mM Na₂SO₄ solution at varying pH values conducted by Perdomo and Payer¹³ in 1995. It shows that the corrosion potentials in the deaerated solutions were dependent on the pH while in the aerated solutions they were independent of the pH.

The cathodic protection mechanism could be interpreted as the increase in pH at the structure electrolyte interface coupled with the consumption of dissolved oxygen in the oxygen reduction reaction, which creates a deaerated environment. Furthermore, in high resistivity, well drained soils, both the NACE and ISO cathodic protection standards¹⁴¹⁵ permit less negative potential criteria than the -850mVcse criterion, such as -750mVcse and -650mVcse. But the pH in very aerated soils can be very high at the interface despite these lower potentials, in which case the cathodic polarization mechanism can be considered due to the high pH developed at the interface. Therefore, the cathodic protection mechanism can be considered as “chemical polarization”.

Summary

- Increasing the pH at the steel/electrolyte interface decreases the corrosion rate in the absence of cathodic protection.
- The reduction reactions that transfer cathodic protection current from the electrolyte to the structure, increases the pH and decreases the dissolved oxygen concentration in the electrolyte at the structure/electrolyte interface.
- In unaerated environments the steel polarized potential is directly dependent on the interfacial pH produced by cathodic protection.
- In aerated environments the steel polarized potential is generally independent of the interfacial pH which can be high, even though the polarized potential is significantly less negative than the -850mVcse criterion.
- In both unaerated and aerated conditions the cathodic protection mechanism is arguably the development of a high pH caused by the operation of the cathodic protection system which can be called “chemical polarization”.

REFERENCES

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- ¹ R.B.Mears and R.H.Brown, A Theory of Cathodic Protection, Transactions of the Electrochemical Society, 1938, 74 p527
 - ² S.C Dexter, L.N.Moettus, and K.E Lucas, On the Mechanism of Cathodic Protection, NACE Corrosion, Vol 41, #10,Oct,1985, p606
 - ³ R.J. Kuhn, Cathodic Protection Underground Pipe Lines from Soil Corrosion, API Proceedings, Nov 1933.,Vol14,Section 4, p157
 - ⁴ W.J.Schwerdtfeger and O.N.McDorman, Potential and Current Requirements for the Cathodic Protection of Steel in Soils, Corrosion, Nov.1952, p392
 - ⁵ T.J. Barlo et al, An assessment of the criteria for Cathodic Protection of Buried Pipelines, AGA, Corrosion Supervisory Committee, June,1983,p2-5
 - ⁶ R.N.Parkins and R.R.Fessler, Line Pipe Stress Corrosion Cracking –Mechanism & Remedies, NACE Corrosion'86, Paper #320
 - ⁷ Neeti Prakash et al, Corrosion of Mild Steel by Soil Containing Sulphate Reducing Bacteria, Journal of Microbiological Biotechnology, Vol.3, p 82
 - ⁸ M.Buchler, The Physical-chemical Significance of the IR-free Potential, p 2
 - ⁹ S. Gladstone, An Introduction to Electrochemistry, D. Van Nostrand Company, 1942, P443
 - ¹⁰ N.G.Thompson and T.J. Barlo, Fundamental Processes of Cathodically Protecting Steel Pipelines, Gas Research Conference Proceedings, 1983
 - ¹¹ Z.Lewandowski et al., Dissolved Oxygen and pH Microelectrode Measurements at Water Immersed Metal Surfaces, NACE Corrosion/88, Paper #93,p12
 - ¹² T.Kobayashi, Effect of Environmental Factors on the Protective Potential of Steel Proceedings of the 5th International Metallic Congress, Tokyo, 1972, p628
 - ¹³ J.J.Perdomo and J.H.Payer, Chemical and Electrochemical Conditions on Steel at Disbonded Coatings, Pipeline Research Committee, AGA, Catalog # L51736, June 1995,pp109-119
 - ¹⁴ ISO15589-1 2013 – Petroleum and Natural Gas Industries – Cathodic Protection of Pipeline Transportation Systems – Part I On-land Pipeline, Section 5
 - ¹⁵ SP0169-2013, Control of External Corrosion on Underground and Submerged Metallic Piping Systems, NACE International, 2013, Section 6