

THE PROTECTION POTENTIAL – WHAT IS THE EVIDENCE?

Chris Googan

Anticorrosion Engineering Limited

Much Wenlock, England

ABSTRACT

The long-established target potential for the cathodic protection (CP) of steel has recently come into question. This has given rise to fundamental reassessments of the CP mechanism, or mechanisms. Workers have interpreted protection in terms of polarizing the structure into either the immune or the passive zone of a Pourbaix diagram. Present thinking leans towards passivity. This paper presents a re-examination of the models of cathodic protection. It advances, or rather it restates, the proposition that neither immunity nor passivity are relevant. It argues that protection is simply a consequence of a potential-driven lowering of the anodic dissolution rate. However, it also emerges that elucidating any mechanism convincingly requires dependable experimental data on the very low corrosion rates occurring on cathodically polarized specimens. A critical review of published data points to a lack of reliability in this area.

INTRODUCTION

In 2015 Büchler [1] made the point that reliable CP criteria could only be defined through an understanding of the mechanisms involved. Although that paper focuses primarily on onshore pipelines, as does a subsequent contribution by Gummow [2], the issues it raises also relate to the functioning of CP systems in other environments. This paper is a contribution to this debate. It critically re-examines experimental evidence obtained in various media, not just soils, underpinning the mechanisms of CP.

A SIMPLE PICTURE: CP IN SEAWATER

It is convenient to start by considering the CP of steel in seawater. But first, we should remind ourselves that this paper is concerned with the potential of a protected structure; or, more correctly, the potential difference between it and an agreed reference half-cell. The traditional reference for seawater use is the Ag|AgCl|seawater half-cell. As we are starting with seawater, **all potentials in this paper are on this reference scale**. Where necessary, the reference scale in the cited publication has been transposed.

At its simplest, CP involves applying direct current to a metal to polarize it in the cathodic direction. This suggests that CP could be interpreted as depressing the metal potential into a region of thermodynamic immunity in an E-pH (or Pourbaix) diagram (Figure 1).

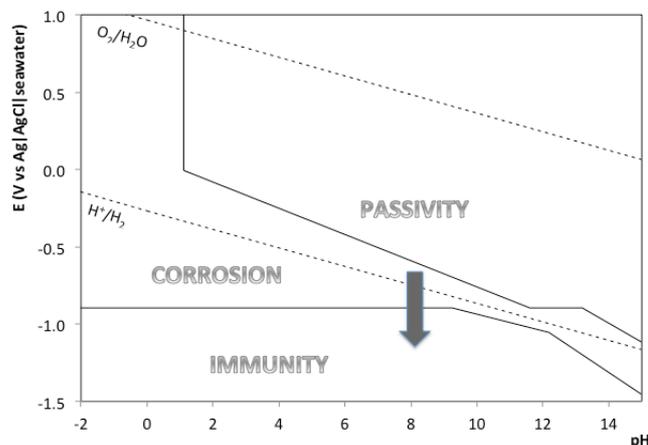


Figure 1 Simplistic E-pH Diagram for CP of Iron

The arrow in this figure suggests that the potential is shifted from the zone where corrosion is the thermodynamically favoured outcome to the zone of immunity, where iron is stable. At first sight this interpretation of CP aligns with Pourbaix's view that CP... *is based on the fact that the potential of iron is lowered, on reduction, into the domain of immunity in which the corrosion of iron is theoretically impossible* [3].

Unfortunately, the simple picture in Figure 1, which is based on the concept of thermodynamic immunity, is incorrect; at least for the iron-water system.

WHY DOESN'T THE SIMPLE PICTURE WORK?

The idea behind the immunity concept of CP is that the potential of the steel is depressed to a value more negative than the equilibrium potential for the iron electrode. That is the potential at which iron is in equilibrium with Fe²⁺ ions at a known concentration:



Here we come to the first of a number of problems in using Pourbaix diagrams to explain CP. There is no definition of what the Fe²⁺ concentration in the solution should be. Pourbaix diagrams are generally based on a metal ion concentration of 10⁻⁶ g.ions/L. This implies an assumption that, if iron is in equilibrium with its ions at this concentration, corrosion is not occurring. This concentration is arbitrary, and inappropriate for most environments.

For marine CP, the relevant concentration of Fe²⁺ is the natural concentration (or more precisely 'activity') to be found in seawater. This turns out not to be an easy figure to tie down. However, based on a seawater pH of 8, the concentration of Fe²⁺ is likely to be in the order of 10⁻¹⁰ g.ions/L. With this information, and the application of the Nernst equation, we would conclude that the protection potential would need to be more negative than **-1060 mV**. This is the potential at which the corrosion of iron, and by inference steel, in an aqueous solution containing ferrous ions at the found in natural seawater, becomes thermodynamically impossible.

However, this figure conflicts with all marine CP codes which set a target protection potential of -800 mV in aerated seawater [5 - 11]. Adopting -1060 mV as the protection criterion for steel in seawater would overturn almost a century of practical experience. Furthermore, it would mean that applying CP to steel by means of zinc or aluminium alloy sacrificial anodes simply could not work. But the evidence, dating back to the work of Sir Humphry Davy [12] is to the contrary. It follows that we have to discard the immunity model of CP.

This points to a fundamental problem with using thermodynamics to explain CP. Thermodynamics is the ultimate arbiter on whether any reaction, including a corrosion reaction, can or cannot proceed. However, where a reaction is possible, thermodynamics is silent on the subject of the reaction rate.

In corrosion engineering we almost always deal with metal-environment combinations that can give rise to corrosion. For example, iron displaces hydrogen from water at any pH value. So iron will always corrode in contact with moisture. Based on this reality, the key to understanding CP lies in appreciating that it never needs to be entirely effective. It just needs to be sufficiently effective.

To reconcile our inability to explain CP in terms of immunity with the observable fact that CP actually works we need to appreciate that any concept of CP acting as an electrochemical on/off switch is too simplistic. Switching corrosion 'off' is neither relevant nor is it practicable. Much of the literature on corrosion and CP, as well as most codes, set the desirable objective as achieving "full protection". This is not the same as "zero corrosion". This is illustrated by §5.3.1 of ISO 15589-1 which states...*"the metal-to-electrolyte potential at which the corrosion rate is less than 0,01 mm per year is the protection potential... This corrosion rate is sufficiently low so that corrosion will be within acceptable limits for the design life"* [13]. This is

a neat definition; but it has the profound practical problem that corrosion rates of less than 0.01 mm/year are exceedingly difficult to measure; so achieving this criterion is impracticable to demonstrate.

The requirement of this onshore pipeline ISO standard to target a corrosion rate of <0.01 mm/year is reasonable from an engineering perspective. It amounts to the loss of less than 1 mm of steel thickness per century. This is unlikely to be an issue for a pipeline; even one with a design life of many decades. However, 0.01 mm/year is not zero corrosion. This point is emphasised when one considers that even a rate of 1 mm per century means that about 3.7 trillion iron atoms are being lost from each square centimetre of the surface every second!

ACTIVATION CONTROL

The Theory

This theory of CP relies on the iron dissolution reaction being under activation control. In other words, the rate of the corrosion reaction is controlled by the rate at which Fe²⁺ ions are discharged into solution from the metal surface. This theory builds on the mixed potential electrode kinetic theory for corrosion first developed by U.R. Evans. This was applied to CP in the late 1930's by Mears and Brown [14] and, independently, by Hoar [15]. This theory has been developed and endorsed by other workers, for example: Jones [16], Ashworth [17,18] and Schwenk [19]. A very concise presentation of the theory is Annex B of EN 12473 [8].

Figure 2 provides an E-Log |i| (potential vs log current density) diagram for the idealized example of the CP of steel in seawater. The electrode kinetics of the anodic dissolution of iron to ferrous ions is shown as following Tafel (i.e. linear E-Log |i|) behaviour. The dominant cathodic process in seawater at ~pH 8 is the reduction of dissolved oxygen. This process is under diffusion control, so is shown as a vertical line with a value (i.e. i_{limo2}) around 100 mA/m². This is a reasonable ball park figure for i_{limo2} in slow moving seawater [20].

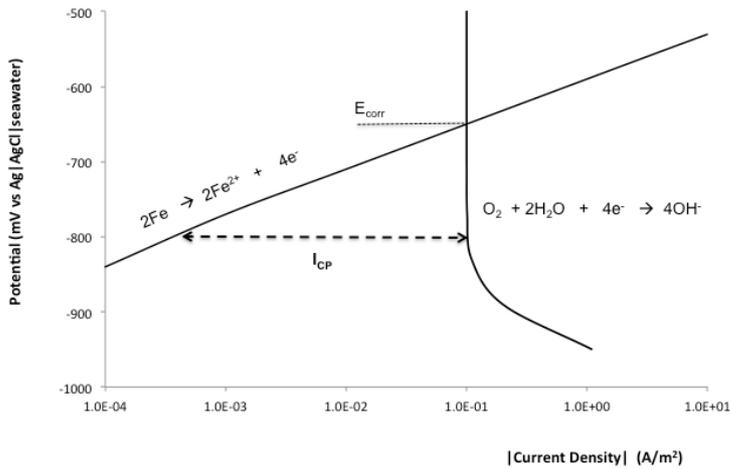


Figure 2 Electrode Kinetic Theory for CP (Activation Control)

Application of the mixed potential theory of corrosion tells us that the unique corrosion potential (E_{corr}) occurs where the anodic current supply equals the cathodic current demand. This is seen as the intersection of the anodic and cathodic kinetic curves. Typically, this potential settles down to around -650 mV in aerated seawater. The corrosion current density (i_{corr}), which is equal to i_{limo2}, equates by Faraday's Law to a metal loss rate quite close to

0.1 mm/year. This is within the range of rates observed in short term tests in seawater [21 - 24].

The application of CP polarizes in a negative direction. This forces the steel electrode down the anodic line, reducing the anodic current, and thence the rate of corrosion. It is seen that applying about 150 mV of cathodic polarization, which takes the potential to around -800 mV, causes the anodic current density to reduce by about two orders of magnitude. In other words, the corrosion rate is reduced to about 0.001 mm/year. This is unlikely to be of any practical engineering concern.

The early workers generally expressed the theory in terms of explaining the magnitude of the cathodic current needed to achieve full cathodic protection, which was taken to be at potentials more negative than the equilibrium potential for the anodic reaction (E_a). However, it may be noted that Figure 2 makes no attempt to represent E_a . In this context, E_a is a meaningless parameter. It is a function of the concentration of Fe^{2+} ions in the environment. Since that figure is unlikely to be known, we cannot relate CP to the equilibrium potential. Nor do we need to. Polarizing to E_a , or more negative, would guarantee a zero corrosion rate; but a zero corrosion rate is an excessive, and pointless, corrosion control target. As EN 12473 explains, by lowering the potential to a value... *above E_a , the metal may be partially protected with some economy in the current supplied.* In the event, if polarizing to -800 mV, *partially protected* is practically indistinguishable from fully protected.

The Predictions

For any theory to be accepted it has to generate predictions that can be tested by experiment. In the case of the electrode kinetic theory illustrated in Figure 2 there are two important predictions. The first derives from the proposition that the iron dissolution reaction:



is under activation control; so its rate is determined solely by the potential applied. It follows from this that the reaction should obey Tafel type behaviour: where the logarithm of the anode current density is directly proportional the applied potential shift. Furthermore, Faraday's Law tells us that there is a direct relationship between the anodic current density and the rate of iron dissolution. If the activation control theory of CP holds, therefore, the corrosion rate should reduce logarithmically as the potential is made more negative.

The second prediction, which is also implicit in the theory, is that the protection potential depends only on the characteristics of the anodic polarization curve. It is independent of the nature and rates of the cathodic processes giving rise to the corrosion.

Experimental Evidence in Favour

Prediction 1: Corrosion Rate versus Potential

The proposition that, when steel corrodes in seawater, the anodic dissolution of iron is under activation control is well documented. For example, it is illustrated in potentiodynamic polarization experiments [20]. However, this observation alone does not demonstrate that the mechanism of CP must also be based on activation control. Experimental evidence is needed.

In 1978 Moore and Knuckey [26] reported a series of experiments designed to determine the appropriate protection potential for steel ships' hulls. They examined the weight loss of steel specimens held at different fixed potentials for periods of between 6 and 25 days. They concluded that -790 mV was... *the least negative potential that will ensure complete cathodic protection.* However, they were not investigating the mechanism of protection; so they published their results with the corrosion rate plotted on a linear, not logarithmic, axis.

It is informative, therefore, to view their results when manually transposed to a logarithmic scale; as is shown in Figure 3. The individual points are the average of triplicate results. Dexter et al. [27] reported the results of similar experiments in 1985. The mean values of Dexter's duplicate results are also shown in Figure 3. Taken together, these result offers *prima facie* evidence that CP works by exerting activation control of the anodic dissolution of iron to ferrous ions. They also endorse the selection of -800 mV as the appropriate protection potential.

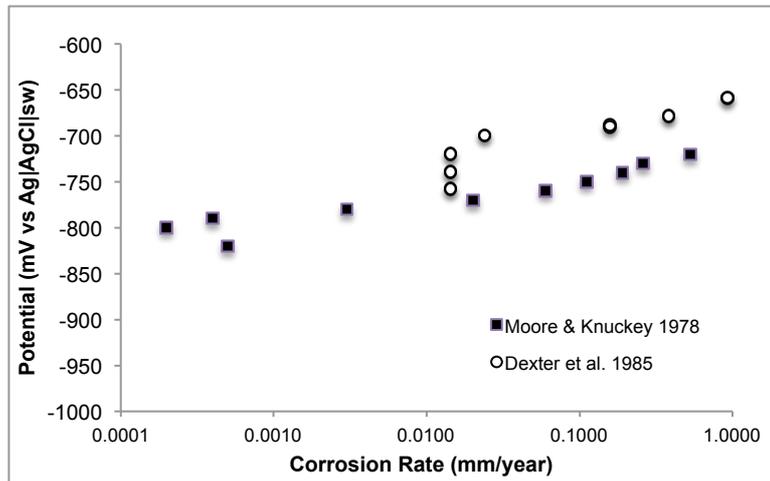


Figure 3 Log Corrosion Rate versus Potential (data replotted from [26] and [27])

Prediction 2: Protection Potential and the Environment

The second prediction arising from an activation control mechanism for CP is that it should be independent of the cathodic reactions involved in the corrosion process. Put another way, the protection potential for steel, which the codes tell us is -800 mV in aerated seawater, should also apply in any other aqueous environment.

Steel in nitric acid

This proposition has been shown to hold by potential versus weight loss experiments in dilute (0.1 M) nitric acid. No one suggests that CP is a viable corrosion control measure for steel in this medium. The magnitude of the current required would be prohibitive. Nevertheless, in laboratory tests, Dexter et al. held pre-weighed steel specimens at fixed potentials in this acid for 36 hours. Although they presented their results [27] as percentage weight loss versus potential, they provided the information necessary to convert their results into the corrosion rates (mm/year) as shown in Figure 4.

These results indicate that the protection potential criterion in 0.1 M nitric acid is essentially the same as it is in natural waters. This is a result that, even today, might seem counter-intuitive to many CP practitioners.

Microbiologically Influenced Corrosion

In 1973, BS CP 1021 [28] recommended a protection potential of -900 mV for anaerobic environments where microbiologically influenced corrosion (MIC) was deemed to be a credible threat. This recommendation has been replicated in numerous codes issued since.

In 2015 the present author reviewed the basis the -900 mV criterion [29]. The conclusion drawn was that its inclusion in the 1973 Code of Practice indicated the drafting committee's plausible, but incorrect, view that a more corrosive environment necessitated a more negative protection potential. A critical review of experimental evidence found no convincing argument in support of a more negative protection potential. Subsequently, in 2016, DNV has published

its observation that it is... *not aware of any documentation that a potential (IR free) in the range -0.80 to -0.90 V has ever led to any corrosion damage (including corrosion damage by bacteria) [30].*

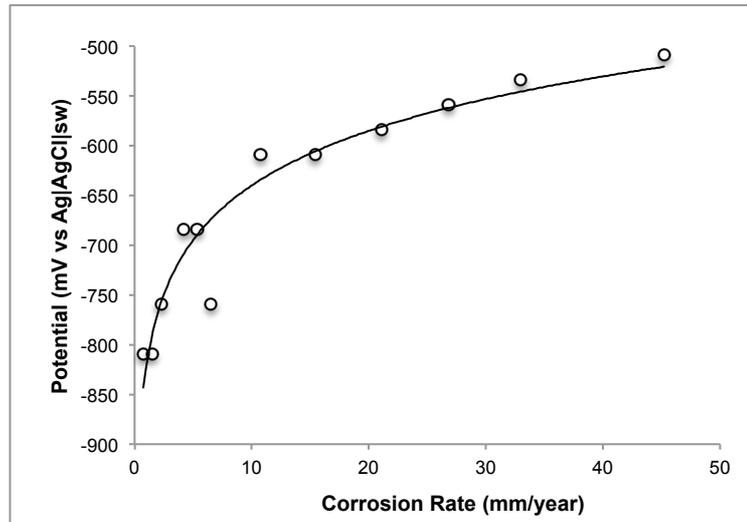


Figure 4 Corrosion Rate vs Potential: Steel in 0.1M HNO₃ [27]

Nevertheless, the issue of the protection potential for MIC remains open within the CP industry. In 2017 Kajiyama [31] presented experimental corrosion rate versus potential data for iron in aerated environments in the presence of iron oxidizing bacteria, and anaerobic environments containing sulfate reducing bacteria (SRB). With respect to the aerobic environment he concluded... *in this case, the protection potential of (-800 mV) (pH above 10.5) was sufficient to control the corrosion rate to steel less than 0.01 mm/y.* However, with respect to MIC by SRB, he posited that to... *ensure complete CP, polarized potentials more negative than (-1050 mV) at pH above 8.5 by excessive OH ions might be required.* It should be noted, however, that the latter view was not supported by experimental evidence. Furthermore, as the title of his paper makes clear, Kajiyama interprets the mechanism of CP in terms of the binary alternatives of immunity and passivity. The paper does not consider anodic activation control. We will return to this below.

In summary

Figure 3 and Figure 4 jointly support the view that CP works by its influence on the activation controlled iron dissolution reaction. Making the potential progressively more negative results in a monotonic reduction of the corrosion rate in line with electrode kinetic theory. These figures lend support to the code consensus that -800 mV is the appropriate protection criterion in seawater. More importantly, according to the theory, this potential applies irrespective of the nature of the corrosive environment. Furthermore, this view finds support, albeit not unequivocal, in the available experimental evidence on controlling MIC and the experience reported by DNV-GL.

Experimental Evidence Against

Corrosion Rate versus Potential

Offshore

Close scrutiny of Figure 3 and Figure 4 also shows that they fall short of categorically confirming the view that CP works by an activation control mechanism. This, in turn, brings into question the proposition that there is a single universal protection potential for steel.

The first problem emerges from a closer inspection of Figure 3. Given that both groups of workers conducted ostensibly the same experiments, the 50+ mV difference between the two data sets is both difficult to explain and is disconcerting in terms of using the data to evaluate theory.

The second problem arises from the slope of the reasonably convincing straight line in the semi-logarithmic plot of the 1978 data. This has a gradient of roughly 30 mV/decade. However, this value differs from the generally accepted range for the Tafel slope for the anodic iron dissolution reaction. For example, Baboian quotes a measured figure of 57 mV/decade for steel in seawater [32], which is close to the theoretical value for a two electron process of ~59 mV/decade. It is, therefore, not easy to reconcile completely the data in Figure 3 with the activation control model.

The third problem arises from close examination of Figure 4 which presents the data for dilute nitric acid. Here, although CP is seen to be generally effective, the apparent corrosion rate at -800 mV remains relatively high: ~ 0.8 mm/year. This apparently runs counter to the theory's prediction that the protection potential is independent of the corrosivity of the environment.

Furthermore, there is a body of other experimental data that appears to directly contradict the results presented in Figure 3. For example, in 1965 LaQue and May [33] presented the relationship between potential and corrosion rate for steel in seawater (flowing at ~2.4 m/s). Their paper characterised corrosion in terms of weight losses rather than rates of penetration. However, since they provided the area of the specimens and the duration of the test, their data can be presented as corrosion rate versus potential. The outcome is shown in Figure 5, with the Moore and Knuckey data from Figure 3 added as a trend line for comparison.

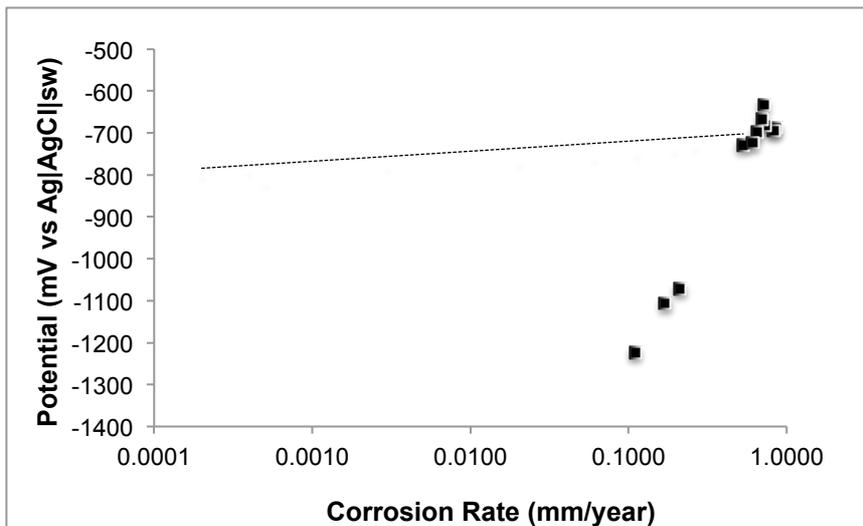


Figure 5 Corrosion Rate versus Potential (Data transposed from LaQue and May [33])

As can be seen, there is no correlation between the two data sets. More surprisingly, the LaQue and May data indicate that, even at potentials as negative as -1.25 V a corrosion rate of ~1 mm/year is obtained. They are not alone. Other workers have also claimed high corrosion rates under conditions of cathodic protection. For example, Cottis and Leeds reported a corrosion rate of 0.152 mm/year at -800 mV in 3.5% NaCl solution [39]; and that a potential of -1.3 V was required if CP was to reduce the corrosion rate to 0.001 mm/year. The same authors subsequently reported the results for seawater [40] which indicated a corrosion rate of about 0.25 mm/year for steel at a potential of -800 mV.

Other results for the relationship between corrosion rate and potential were published by Kobayashi [34] in 1972. Those results, which were obtained in stirred and unstirred 3.5%

NaCl adjusted to pH 6 and pH 3.5, are re-plotted in Figure 6. Again, it is hard to see any correspondence with the Moore and Knuckey data (dotted line), or with LaQue and May's data in Figure 5.

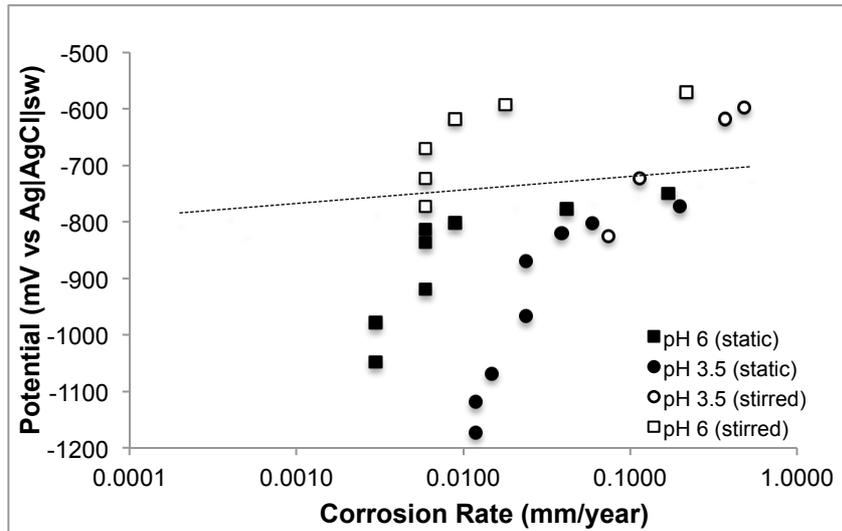


Figure 6 Corrosion Rate versus Potential (Data transposed from Kobayashi et al. [34])

All of the results reproduced above show a progressive reduction in corrosion rate with increasingly negative potentials. This provides qualitative support for the electrode kinetic interpretation of CP. Depressing the potential reduces the rate of the activation controlled anodic half-reaction:



However, viewed as a whole, these results fail to offer incontrovertible proof that the mechanism of CP in these environments involves activation control. The problem is that we do not always see a clear linear (Tafel type) relationship between potential and corrosion rate as seen in the work of More & Knuckey and Dexter et al. More important, the results produced by a number of these workers [33, 34, 39 & 40] are both mutually in conflict, and contrary to international standards [7 - 13] that state that -800 mV is the relevant protection potential for steel in seawater. These latter results are also at odds with the experience of the British Royal Navy which, for many years, set a protection potential of -0.75 V for its warships [41].

Soils

There have been various attempts to map potential versus corrosion rate data for steel specimens under CP in soils. It is fair to say that none of these experimental data sets provides strong support for an activation control mechanism. A case in point is the body of data presented by Büchler et al. [42], and reproduced in Figure 7. As can be seen, the data are so scattered in terms of both measured corrosion rate (up to 0.5 mm/year), and potential (+0.05 V to -2.45 V) that it is not possible to discern any obvious pattern. The results neither support an activation control nor a passivation explanation for CP. However, the data at potentials more negative than ~-1.1 support the view that immunity is achieved in this potential zone; but that is of limited relevance to the present case. This prompts a discussion of the experimental difficulties involved in obtaining dependable data.

The Experimental Difficulties

In view of the inconsistency in the results discussed above, it is useful now to consider some of the practical problems inherent in carrying out experiments of this type.

Early Studies

Ideally, the experiments discussed above should all involve holding steel specimens at a fixed potential for a period of time and then determining the corrosion rate. However, we should remind ourselves that this type of experiment was not an option for early workers in the field, such as Mears, Brown or Hoar. It only became practicable after Hickling assembled, and coined the name for, the first “potentiostat” in the early 1940s [35]. Subsequently, electrochemists and corrosionists constructed their own potentiostats; a process that became easier through the 1950’s as modular operational amplifiers became commercially available [36]. However, it was not until the late 1960’s that commercially available potentiostats started to be standard items of kit in corrosion laboratories.

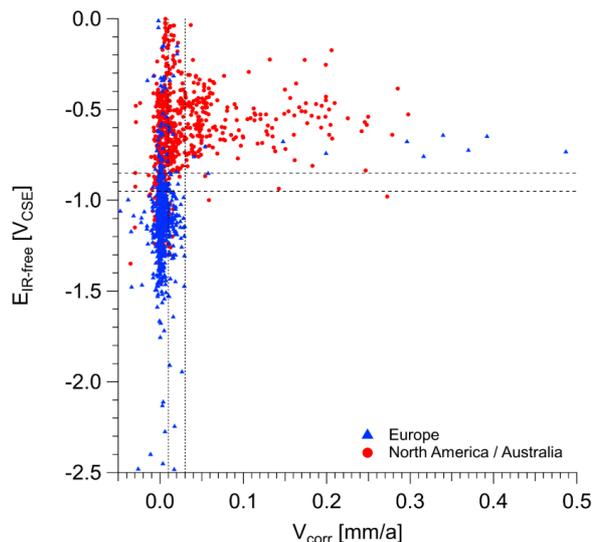


Figure 7 Site Data: Potential versus Corrosion Rate (Reproduced from [42])

This meant that the seminal experiments on CP were carried out galvanostatically. That is the workers used controlled currents rather than controlled potentials. Even then, the *control* exercised over the current was in no sense automatic. Experiments depended on the diligence of the experimenters, or their lab assistants, in adjusting variable resistors on a frequent basis; but, one presumes, less frequently overnight and at week-ends.

It is not surprising, therefore, that early CP studies focussed more on the current needed to control corrosion than on the potential. By way of example, a 1949 paper by Humble [37] on CP in seawater is based entirely on current density. In an eleven page CP paper, not a single potential measurement is reported.

It also means that we must be circumspect when reviewing the work of LaQue and May. Their 1965 paper [33] derives mostly from work carried out in the 1950’s when potentiostats were generally not available. In common with most experimenters of their era, they were more interested in the correlation between applied cathodic current and corrosion rate than that between potential and corrosion rate. Their experiments were carried out with the current adjusted manually by trimming resistors. Over the period of each test (typically 14 days), the potential would have drifted in a negative direction. However, they record only one value of potential for each experiment. One might surmise, therefore, that the specimens spent most of the exposure time polarized to potentials much less negative than the values shown in Figure 5.

However, this alone does not provide a convincing explanation for the discrepancy between LaQue and May’s data, and the results that might be expected from the today’s codes. The

corrosion rate reported for a specimen with an observed potential of ~ -1200 mV is a case in point. The cathodic current density is reported as 2300 mA/m². This is an order of magnitude higher than the figure recommended by present day codes for initial polarization in seawater. It seems unlikely, therefore, that the specimen could have spent any substantial part of the test period in a condition we would consider to be under-protected. Even so, the apparent experimental corrosion rate was exceptionally high (0.1 mm/year).

This problem is exacerbated when it comes to analysing populations of site data from onshore pipelines. There are various intractable problems with such testing. The first, and most obvious, is that onshore pipeline CP systems are generally not polarized potentiostatically. It follows that the single potential values assigned to each data point in Figure 7 are unlikely to be truly representative of the pipe-to-soil potential achieved during the duration of the exposure. Other problems derive from the dependability of the measurement itself.

This brings us to a consideration of experimental errors. All experiments are prone to experimental errors to a greater or lesser extent. In the case of the polarization experiments described above these errors can be classified as either “random” or “systematic”.

Random Experimental Errors

Random errors arise from such factors as the inherent limitations of electronic equipment, reference half-cell drift, and the inevitable imprecision involved in cleaning and weighing specimens. The problem is accentuated when the weight changes under investigation become very small. For the most part, however, these random errors can be minimized by diligent experimentation. Furthermore, their stochastic nature means that, in laboratory testing at least, their effect can be minimised by replicate testing.

The influence of the various random experimental errors is readily appreciated from a close inspection of in Figure 7. Here it may be seen that a significant proportion of the data points apparently exhibit “negative” corrosion rates. If we accept that negative corrosion is not possible then we must ascribe these results to the manifestation of inevitable random errors. This is in no way surprising. On the contrary, what is perhaps surprising is that so many other workers discussed have reported very low corrosion rates; but not “negative” corrosion rates.

Systematic Experimental Errors

Corrosion rate versus potential experiments also incur systematic errors which are not so easy to mitigate; and which give rise to a bias in the results.

In any gravimetric corrosion rate experiment it is customary to maximise the area-to-weight ratio of the specimen in order to maximise the accuracy of the result. However, in a laboratory electrochemical cell, increasing the surface area of the working electrode inevitably means a loss of control of the potential. The potential is controlled with respect to the reference electrode which is either bridge linked via a Luggin capillary to a single position very close to the surface, or else is sensing the potential in the solution a little way remote (in an electrolytic sense) from the specimen. In either case, the arrangement is apt to distort the potential versus corrosion rate result. Where a Luggin capillary probe is employed the potentiostat controls the potential in the proximity of the probe. In this case, depending on the geometry of the counter electrode, there would be less cathodic polarization at the specimen edges, or on the rear face of a flat coupon. Conversely, if the reference is somewhat more remote in the cell, it will be more prone to an IR error in the potential reading. This error will be more pronounced in tests at higher current densities.

Another source of bias becomes clear if we consider the tests carried out by Dexter et al. in nitric acid. The problems arise at the start and, more particularly, at the end of the test. At the end of the 36 hours of polarization, the applied polarization must be switched off and the specimen electrode extracted from the solution, cleaned, dried and then reweighed. This will

inevitably have exposed pre-cathodically polarized, oxide-free (and, therefore, very reactive) steel to the nitric acid; albeit for a relatively brief period. Thus, some metal loss will have occurred after the period of controlled polarization. The result of this will have been to exaggerate slightly the weight loss ascribed to the polarization period. This exaggeration of weight loss, which is not compensated for by the usual expedient of running blank experiments, is insignificant in those measurements at modest polarization levels where the corrosion rates are high. However, the relative contribution of this systematic error becomes more pronounced in the tests at more negative potentials where the corrosion rates are very low. Furthermore, although this source of error is easy to visualise in the case of an experiment carried out in nitric acid, it inevitably applies to experiments carried out in other media, including seawater or soil.

The overall effect of both these types of systematic error is that experimental corrosion rates at more negative potentials are erroneously high. This experimental bias, which applies to all experiments of this type, is inconsequential in any practical context. However, it does provide a problem when trying to interpret experimental data in terms of a mechanistic model. It seems likely that systematic errors of this type have distorted the above experimental potential versus corrosion rate results. In particular, they may have contributed to the small, but nevertheless higher than expected, corrosion rates observed at potentials more negative than -800 mV in many of the experiments.

There is no space in this paper to explore in any detail how such systematic experimental errors might be mitigated. Nevertheless, an obvious first step would be to use a planned interval experimental set-up, (see for example [38]) in which replicate specimens are polarized at the same potential for different periods of time. However, this approach has not been adopted in any of the reported experimental programmes.

Where does this leave us?

It seems likely that all of the experimental results discussed above have been prone, to a greater or lesser extent, to experimental errors. There is no evidence that any of the authors has truly addressed all the credible sources of error; although some have evidently been more diligent in their experimentation, or had better equipment, than others.

This author favours the activation control mechanism for CP, and is of the view that -800 mV is an appropriate value for the protection potential. On that basis, it would be tempting to reject the experimental data that conflict with the code consensus that -800 mV is adequate for protection. However, to do so would lack scientific rigour. All that we can reasonably conclude is that the theory of CP functioning through its effect on the activation control of the anodic reaction has support from the data; but does not have not unequivocal proof.

Implications for the Current?

The above discussion on the theory of CP by activation control makes almost no reference to the current. This omission is intentional. Thus far we have considered the theory of protection by activation control. This theory tells us that the value of the protection potential is independent of the cathodic current density required to polarize to that potential. Irrespective of the theory, however, from the practical standpoint of applying CP, the current is crucial. It is only by delivering sufficient current that we can polarize our structure to the target protection potential.

We have also so far ignored the chemical changes at the metal surface brought about by the action of the cathodic current: both the pH changes and the effect of those pH changes in forming protective deposits. Similarly, this does not mean that these changes are unimportant. For example, the calcareous scale generated cathodically in seawater is vital in the practical application of CP. As Evans [43] points out... *were it not for the formation of*

such a scale, cathodic protection as a means of protecting uncoated structural steelwork would be both unpractical and uneconomic because the current demand would be too large.

We now turn to the concept of passivity in relation to CP. It will emerge that, unlike activation control theory, the nature of the environment and the polarization current density are inextricably linked to this proposed protection mechanism.

PROTECTION BY PASSIVITY

What Do We Mean by Passivity?

The term passivity has a very specific meaning to a corrosion scientist. Evans used the word to denote... *a change of properties which continues after the treatment producing it is over... a three-dimensional film is needed to produce passivity* [51]. However, he acknowledged that other workers discussed passivity in terms of film formation at high anodic current density, in which case the metal... *becomes passive at the moment when film formation replaces the formation of a soluble salt*. The latter perspective is encapsulated by Burstein who defines passivity as... *a state of low corrosion rate brought about under a high anodic driving force, or potential, by the presence of an interfacial solid film, usually an oxide* [52]. This is essentially the same definition as given by Uhlig [53] and in figure 2 of ISO 8044 [54].

Thus, on the basis of the corrosion science definition, CP cannot work by a passivation mechanism. This is simply because *a high anodic driving force* cannot be achieved by the imposition of cathodic polarization. It follows that the proponents of the passivity model of CP have to interpret passivity in some other sense.

The Theory

Thermodynamics

For the moment, we will set aside the problem of the corrosion science interpretation of passivity. The theory that CP works by bringing about the passivation of the steel derives from the fact that cathodic polarization stimulates the cathodic reaction on the surface. This raises the interfacial pH through the production of hydroxyl ions.



Most CP workers who have adopted the passivation interpretation of CP have done so by reference to a Pourbaix Diagram. This is illustrated in Figure 8, the arrow in which shows the role of CP as being to shift the steel from the corrosion domain into a region of passivity. On this basis, the shift to higher pH on an E-pH diagram is considered to be more important in conferring protection than is the shift to more negative potential. The two shifts are, of course, inseparable.

Electrode Kinetics

Whereas the thermodynamic interpretation of passivity hinges on the relative stability of the chemical species involved, the kinetic interpretation is concerned with the rate at which Fe^{2+} ions enter the solution, and the rate at which they migrate away from the surface. If the anodic dissolution rate is sufficiently high that the interfacial concentration of Fe^{2+} ions exceeds their solubility limit then oxide precipitation on the surface ensues. If the oxide is sufficiently coherent to form a passive layer then the anodic dissolution rate slows down dramatically. When this change occurs, the anodic reaction is said to go through an active-passive transition.

Figure 9 shows a schematic polarization (E–log |I|) diagram for passivation. Proponents of the passivation theory for CP are obliged to assume that the steel surface exhibits a potential that is more positive than that of the active-passive transition.

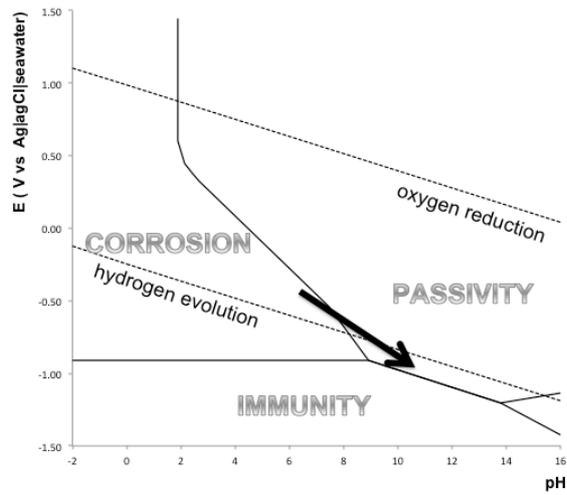


Figure 8 Schematic Pourbaix Diagram for Passivity under CP.

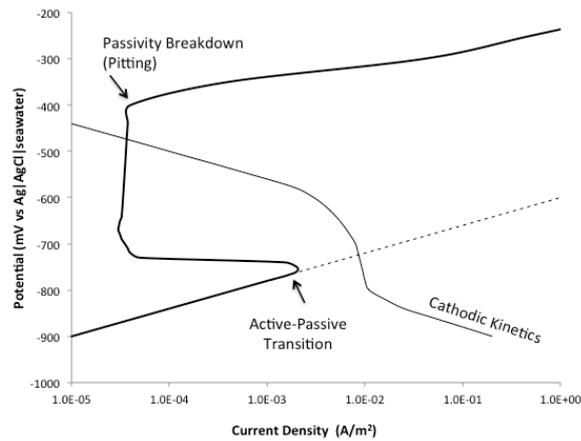


Figure 9 Schematic E-Log $|i|$ Diagram for Passivity

Passivity – The Evidence in Favour

Field Experience

In discussing passivation our attention is drawn to onshore pipelines. Peabody's original 1967 book on pipeline corrosion [44] makes no mention of passivation of the steel surfaces. However, the topic arises in the 2001 edition [45] under the final heading: *Environmental Polarization*. This states... *an increase in the rate of these reactions causes a pH increase to occur at the metal surface, creating a less acidic (more basic) environment. This pH increase is beneficial because the corrosion rate of steel decreases with increasing pH, even under freely corroding conditions. The decrease in corrosion rate is the result of the formation of a protective oxide film on the metal surface in the elevated pH environment, a process referred to as passivation.*

However, with the exception of steel reinforcement in concrete, Peabody's revised book does not provide any observations relevant to *passivation* in the context of buried steel pipes. However, two 1992 papers by J.M. Leeds [46 & 47] do provide such observations. In particular, he reports that the results of over 2500 pipeline excavations demonstrate that CP generates films on the steel surface. In particular, he considers the role of a *black film* (that

steadily spreads across the pipe surface as the coating progressively fails. Elsewhere in his papers he identifies this film as magnetite which he states... *imparts passivity to the steel, reducing the bare steel available for any corrosion or cathodic reactions.* He refers to this effect as *cathode passivity*. This *cathode passivity* seems to be equivalent to *environmental polarization* in the 2001 edition of Peabody. In passing, it is worth noting that, despite Leeds' emphasis on the importance of magnetite, there is no mention of magnetite corrosion product in either edition of Peabody.

Laboratory Experiments

Although there have been various papers that either invoke or assume a state of passivity when steel is under CP, there has been comparatively experimental work directed at elucidating the proposed passivation or its mechanism. The exception to this is the work of S.S. Leeds and Cottis [40] who carried out polarizations tests in 3.5% NaCl solution, synthetic seawater and a synthetic alkaline electrolyte. In respect of all of these test environments they concluded that... *The mechanism of CP in the conditions of this work is passive film formation due to alkaalisation.* We return to this below.

Passivity – Analysis of the Evidence

Thermodynamics

There are several very profound problems when attempting to reconcile any aspect of CP with thermodynamics as represented in a Pourbaix diagram. In addition to the fundamental problem that thermodynamics is silent on the topic of corrosion rates, the following limitations are also relevant to the application of thermodynamics to CP.

E-pH diagrams apply to pure metals only. We assume that the diagram for iron represents the behaviour of its alloy: steel. This assumption may seem reasonable but it is untested. For example all commercial steels contain manganese; albeit at levels of only around 1%. Thermodynamics tells us nothing about the behaviour of iron-manganese alloys; but the E-pH diagram for manganese [48] reveals more extensive domains for soluble species than does the corresponding diagram for iron [3].

Although E-pH diagrams can, in principle, be constructed for any aqueous species providing the thermochemical data are to hand, they are only fully established for the metal-water system. The water is considered to be pure, and the presence of solutes is ignored. This is problematic because CP is never applied in pure water. Importantly, the E-pH diagram tells us nothing about the role of ubiquitous species such as chloride and sulfate, or their contribution to solubilizing the corrosion product. A case in point is the E-pH diagram for the iron-water system at 25°C (Figure 6 in [3]). This indicates that, at the pH of natural seawater (~8.2), iron is passive. The experience of using steel in seawater is very much to the contrary.

The latter point extends to the selection of E-pH diagrams to represent CP. It may be noted that the E-pH diagram in Figure 8 differs from that in Figure 1. Both are based on figures found in [3]. Figure 1 makes the point that the corrosion of iron is thermodynamically credible at all pH values. Figure 8, on the other hand, which is used by various workers already cited [1, 2, 40 & 46], considers solid magnetite (Fe_3O_4) to be the thermodynamically favoured corrosion product in the pH range 8 to 13.5. It follows that substantiation of the passivity theory for CP depends to a considerable extent on the observation of magnetite formed under conditions of cathodic polarization.

Electrode Kinetics

If Burstein's definition is accepted, then we would have to discount Leeds' definition of *cathodic passivity* (p42 in [46]). The expression *environmental polarization* (p316 in [45]) might be more apt; but this is still not passivity. Nor, for that matter, is *chemical polarization* which is referred to by Gummow [2]. In all cases, these are descriptions of the reduction in the cathodic current density brought about by the presence of cathodically generated surface films. It is the general condition of which calcareous deposition in seawater is perhaps the best known example.

Even if we set Burstein's definition of passivity to one side, it would still be very difficult actually to confirm the existence of an active-passive transition of the type shown in Figure 9. For the passivation model to hold, the active-passive transition would have to occur at potentials more negative than those typically achieved in CP systems. In natural waters or soils, this would mean that it would have to occur at potentials more negative than the equilibrium potential for the hydrogen evolution reaction:



In principle, there is no problem in constructing theoretical **polarization diagrams** for an active-passive transition at such negative potentials (see for example [1]) although it requires an assumption that the equilibrium potential for the iron electrode is itself very negative. The problem arises when it comes to validating the theory by producing an experimental **polarization curve**. Any supposed active-passive transition would be masked by the excessive cathodic current due to the hydrogen evolution reaction.

Accordingly, efforts at demonstrating passivity have centred on equating the presence of oxide to passivity, and making observations of oxide film growth under the influence of cathodic polarization.

It is important to understand that the issue here is not just an abstract terminological debate in corrosion science. The difference between passivity and cathodically generated films has real meaning; and it has practical implications for CP. For example, the protection potential in seawater (-0.8 V) is independent of whether or when a calcareous deposit forms. The latter only affects the current needed to maintain that potential. However, if a passivity mechanism were involved then the formation and maintenance of the passive film would be critical. This, in turn, would impact on both the target potential for protection and the current needed.

Field Experience of Passivity

Seawater

This author is aware of no evidence pointing to the role of passivity in the CP of carbon steel in seawater. However, that is not the case for all metals in marine service. For example, the offshore hydrocarbon industry makes extensive use of 13 Cr martensitic and type 316 stainless steels for subsea flow lines. These alloys rely on thin passive oxide layers which confers sufficient corrosion protection for the internal exposure to crude reservoir fluids; but which insufficiently robust for the external marine exposure. In the absence of supplemental protection these flowlines would suffer external pitting or crevice corrosion.

Subsea flowlines are always protected by CP. Furthermore, the codes call for a target protection potential judged to be more negative than the pitting potential for the alloy in seawater. For example, EN 12473 [8] calls for a target protection potential of -500 mV for these grades of stainless steel. Thus, if the recommended target potential is achieved, the stainless steel is held in its passive zone.

However, it needs to be emphasised that in these instances, CP is not producing passivity. It is simply functioning to prevent the breakdown in passivity of an alloy that is naturally passive in that environment.

Concrete

There are engineering situations where carbon steel, like the stainless steels, can become passive. The most commonly encountered example is steel reinforcement in concrete. The chemical processes that take place when Portland cement cures result in a highly alkaline pore solution within the concrete. This environment induces passivity in the steel, as is evidenced by the positive natural potentials measured for steel in sound concrete.

If that situation were to persist there would never be a need for electrochemical protection of steel reinforcement. In practice, however, reinforced concrete structures might be subject to the inward diffusion of chloride (from de-icing salts), or carbonation from atmospheric CO₂. If or when the chloride or the carbonation front reaches the surface of the steel reinforcement then passivity is lost and corrosion ensues.

It has been appreciated since the 1960's that CP can control this corrosion, which in turn has spawned innumerable publications on the topic in general, and on the protection criteria in particular. That literature is too voluminous to attempt to review in any detail here. In brief, early workers advocated the protection potentials relevant to pipelines (i.e. -800 mV). However, it soon emerged that trying to achieve this potential, and more particularly trying to monitor it, was usually impractical. This led to the development of criteria, enshrined in standards (e.g. [49]) based on the measurement of potential decay after the applied CP current was switched off. At the time, such criteria owed more to their practicability of measurement than any deep theoretical understanding.

Since then there has been some development in the understanding. For example, Pedferri [50] has explained that externally applied polarization can counter the inward diffusion of chloride ions, thereby maintaining the passive condition. Alternatively, it can reduce the corrosion rate of steel depassivated concrete. The former process is termed cathodic prevention, because it maintains the passive state of the steel, the latter process is cathodic protection. However, as with stainless steels in seawater, it needs to be stressed that the application of cathodic polarization to the reinforcement does not create the passive state. It either preserves it or it re-establishes it.

Onshore Pipelines

Field experience supporting a passivity mechanism for CP include the observations in which J.M. Leeds [46 & 47] interprets the presence of magnetite in terms of *cathodic passivity*. Practical experience on real pipelines is unquestionably of paramount importance when evaluating CP systems. However, circumspection is needed when in evaluating such data. The first, and most obvious, point to make is that the data are inevitably opportunistic. They have not been generated as part of a controlled experiment. Thus, although Leeds refers to over 2500 excavations, the detailed polarization history will not be known for any of those locations. Indeed, the fact that the pipelines were excavated suggests that, in most of the locations, the above ground surveys indicated a CP issue.

A further problem with the evaluation of the role of magnetite is the classic issue of separating correlation from cause-and-effect. In other words, the visible presence of magnetite on a surface may, or may not, mean that it is implicated in the CP mechanism. Leeds [46] states that... *This film steadily spreads across the pipe surface as the coating progressively fails*. This could be interpreted in two ways. Leeds' interpretation appears to be that, as the coating fails, exposing bare steel to the environment, the CP system causes magnetite to be formed, and this magnetite is then implicated in the cathodic protection mechanism.

This may be correct. However, a contrary proposition is that the magnetite initially developed underneath area of poorly adherent pipeline coating. Then, even when the coating had degraded sufficiently to allow access of CP current onto the pipe surface, the potential achieved was insufficiently negative to reduce the magnetite layer.

The present author has only been involved in about 1% of the number of pipeline excavations that Leeds mentions in his report. However, in none of those was there any black colouration that could be ascribed to magnetite. This may reflect that this author's experience is slanted more towards factory applied pipeline coatings than the field applied systems reported on by Leeds. On the other hand, the present author was engaged for some years early in his career in the investigation of corrosion under protective coatings. As part of that work he became aware that magnetite was a common corrosion product under "poor" quality paint films.

Some further points need to be made in connection with the putative role of magnetite in CP. The first is that, even if it is implicated in (some) onshore situations it has not been reported on cathodically protected marine structures. The second is that care needs to be exercised when ascribing a passivity function to magnetite. Leeds refers to the corrosion mitigating benefits of magnetite formation in boiler tubes and in the Benfield process. Both of the latter processes are manifestations of anodic inhibition, which is incompatible with cathodic polarization. Generally speaking, since magnetite is the favoured corrosion product in low oxygen environments (e.g. under coatings, in boiler tubes and in Benfield liquors) it is associated with lower natural rates of corrosion than in (say) fully aerated natural waters. Nevertheless, the rates of corrosion are still high compared to the rates of attrition of truly passive metals.

There will always be uncertainty regarding the precise polarization history of an opportunistically sampled section of a pipeline. This uncertainty is exacerbated if the quality of the pipeline coating has been in doubt. The way to confirm or refute the claimed role of the magnetite is, therefore, either to study uncoated coupons buried with, and electrically connected to, the pipeline, or else to carry out laboratory studies.

Laboratory Studies

As noted above, S.S. Leeds and Cottis [40] have examined cathodic films formed on steel in various electrolytes. Their work does not support J.M Leeds' views on the importance of magnetite. In their experiments in synthetic seawater they only found magnetite on freely corroding specimens, or specimens polarized to near the free corrosion potential (-650 mV). This was also the case for the specimens polarized in the alkali pipe electrolyte. Thus, in neither of these two solutions did they observe the formation of magnetite at potentials that would occur under CP. However, the situation is complicated somewhat by their reporting of magnetite in experiments conducted in 3.5% NaCl at -750 mV, -900 mV and -950 mV; but not at intermediate potentials of -650 mV, -700 mV, -800 mV or -850 mV. The authors do not explain this pattern of results. All that the present author can do is reiterate the inherent experimental difficulties involved this type of work.

DISCUSSION

Immunity, Passivity and Activation Control

Much of this paper has been concerned with an analysis of the mechanism of CP. It is accepted, and readily demonstrated, that the CP of steel in natural environments such as soil or seawater, can be effective without conferring thermodynamic immunity. The same also holds for CP in synthetic environments as varied as nitric acid or concrete.

The failure of the immunity paradigm seems to have resulted in workers in onshore CP focussing predominantly on interpreting CP in terms of passivity. This is illustrated by the title of a recent paper [31]... *Achievement of Cathodic Protection of Buried Steel Pipelines by*

Either Passivity or Immunity... This is indicative of the binary thinking in the onshore CP industry. Electrode kinetics does not get a mention.

However, the failure to achieve immunity does not inevitably lead to a model based on passivity. Recent work has tended to overlook the fundamental tenets of electrode kinetics. These tell us that, irrespective of the nature of the environment and irrespective of the cathodic processes on the metal surface, making the potential more negative reduces the rate of the anodic reaction. This reduction in the anodic rate controls the corrosion. The cathodic electrochemistry taking place on the surface, and its attendant influence on surface pH and cathodic current demand do not change the electrode kinetic reality. Unless the steel is passive to begin with, as is the case in concrete, the rate of the anodic dissolution reaction must reduce, probably logarithmically, as the potential is made more negative.

It is accepted that the reported field and experimental data fall short of providing a complete endorsement of this author's view. By the same token, however, they also fall short of confirming a mechanism based on steel entering the passive state. There is no experimental polarization curve, as opposed to a theoretical polarization diagram, confirming an active-passive transition on a cathodically polarized specimen. Similarly, whilst oxides have been detected under some circumstances on cathodically polarized specimens, this author has seen no convincing evidence of a passive oxide film having formed on steel under such conditions.

In the latter respect, it is important to appreciate that there is an important and fundamental difference between cathodically generating conditions that would favour passivity if cathodic polarization were interrupted, and the attainment of passivity on a surface that is undergoing cathodic polarization. The nature of the environment is pivotal in determining how much current is needed to shift the potential. It also influences our ability actually to measure that potential; but it does not affect the reality that it is the anodic dissolution rate that has slowed down.

A Philosophical Conundrum

There remains an argument that both activation control and passivity could be operative, depending on the environment. Examples might be a pipeline transiting from offshore to onshore, or a desert pipeline passing through a sabkha region. All of the available evidence for saline zone CP points to activation control. Conversely, many workers engaged in CP evidently support a passivation mechanism for the onshore or non-sabkha zones of such pipelines, particularly if the steel is well compacted.

This raises an intriguing question: could both mechanisms operate on different parts of the same structure at the same time? If so then it raises a philosophical conundrum: what exactly happens at the point on the surface where the mechanism changes? The existence of this conundrum does not invalidate either the activation control or the passivation models. However, invoking the passivation model means that this conundrum would need to be explained.

Implications for the Protection Potential

It is useful to reflect briefly upon the origin of the present protection potential. The CP of land-based pipeline emerged in the 1920's with the application of forced current drainage to protect onshore welded petroleum pipelines in the USA. In 1928 Kuhn [55, 56] proposed -850 mV (measured against the Cu|CuSO₄ satd. half-cell) as the optimum potential for the protection of onshore steel pipelines. Schwerdfeger and Dorman [57] subsequently endorsed Kuhn's view. However, they pointed out that Kuhn's "optimum" potential had, in the interim, become adopted as the least negative potential for onshore pipeline CP.

It would appear that Kuhn's onshore value migrated into the sphere of offshore CP. A

potential of -850 mV vs Cu|CuSO₄(satd.) is essentially -800 mV vs Ag|AgCl|seawater. This may be simply a coincidence. This author has found no documentation supporting the view that the -800 mV protection potential for marine environments is simply adoption of Kuhn's onshore value. Nevertheless, this protection potential for steel has been in use in marine environments for at least half a century. It has been in CP codes since 1969 [58], and specifically advised for seawater since 1973 [28]. With this track record, it would need a heroic attitude on the part of any code drafting committee to gainsay the -800 mV figure for carbon steel in aerated seawater.

It is, therefore, reasonable to ask ourselves why, in the 21st century, are we re-assessing criteria that were established early in the 20th century, and which have been broadly satisfactory since? The answer to that is simple. We should always be prepared to challenge accepted wisdom; otherwise the earth would still be flat and sitting at the centre of the heavens.

Clearly, however, the impetus for the revaluation of CP protection criteria does not emanate from the marine sphere. It arises in connection with the concerns of workers involved with the CP of onshore pipelines. This is explained in a report of a 2015 CEOCOR panel discussion [59]. The panel's view was that, in the absence of a thorough mechanistic understanding of CP, protection criteria based on empirical data may not be applicable for other, as yet unforeseen, conditions.

The Law of Unintended Consequences

Pipelines are protected by a combination of protective coatings and CP. At the risk of offending some practitioners of the art, it can be claimed neither offshore nor onshore pipeline CP has changed a very great deal in the last few decades. The same, however, does not hold for pipeline coating systems. The introduction of high quality multilayer line pipe and field joint systems, applied to abrasively cleaned steel surfaces, has resulted in a step change in coating performance over this period. Generally speaking, this has improved the overall corrosion protection of pipelines, with the ancillary benefit of reducing the CP currents.

However, this has not always been good news. Ignoring its other faults, a mediocre quality pipeline coating can contribute to making a CP system easy to manage. The adventitious low impedance contact with the soil gives a couple of practical advantages. In the first place, it is often relatively easy to obtain a measurement of the pipe-to-soil potential using the so-called "instant-off" technique. Secondly, stray current interference effects are likely to be muted because the line is well earthed. As the coating quality improves, these advantages diminish. The higher impedance coatings complicate the obtaining of a true "IR-free" potential measurement on the line.

For the same reasons the discharge of induced stray AC current becomes more problematic as the coating improves. Although AC pick-up on pipelines has been recognised for many decades, instances of severe AC corrosion damage have only been reported since the mid-1980's. It is probably not just a coincidence that this upsurge in pipeline AC corrosion issues has lagged slightly behind the growing dominance of high quality fusion bonded epoxy and multilayer polyolefin pipeline coating systems.

Viewed simplistically, on a poorly coated pipeline the low impedance, high capacitance earth contact provides an earth escape path permitting the AC current to discharge at a low effective current density. This means that the anodic part of the cycle causes minimal electrolytic dissolution. On the other hand, improving the coating quality forces the AC discharge to take place at isolated small areas and at a locally high current density. This introduces the threat of intense electrolytic pitting on an otherwise adequately protected line.

In the opinion of this author, these issues are the consequences, albeit unintended, of improved protective coatings. However, they do not alter the basic electrochemistry taking

place at a cathodically protected steel surface. A corollary is that we should not be looking to change the fundamental protection criteria in order to adapt to present day issues. For example, just because it has become more difficult to convince ourselves of the accuracy of our pipe-to-soil potential measurement, does not mean that the potential we are seeking to achieve should be altered.

Similarly, it might be reasonable to mitigate AC corrosion by applying a greater degree of DC cathodic polarization. An alternative strategy might be to control the DC polarization level to generate optimise the chemical conditions at the steel-soil interface. However, irrespective of the strategy adopted, it would need to be understood that the modified DC potential has been assigned to combat an operational issue that cannot be resolved by diverting the AC safely to earth; not because there is a fundamental inadequacy in the protection criterion itself.

SUMMARY

There are three candidate mechanisms for the CP of steel. Depending on whether the role of the applied cathodic polarization is to:

- a) depress the potential of steel to a point at which the metal is the thermodynamically stable species (immunity), or
- b) reduce the anodic dissolution rate by reducing the overpotential driving the kinetics of the anodic dissolution half-reaction (activation control), or
- c) producing elevated pH conditions which cause the thermodynamically favoured corrosion product to be an insoluble oxide rather than soluble ferrous species (passivity).

There is no doubt that CP can work by producing **immunity**. However, immunity is not the explanation for the success of the long-established potential criterion (-800 mV) for protecting steel in seawater or in soils. On this basis, it is argued that thermodynamics has limited value when it comes to explaining CP. It essentially tells us that steel **can** corrode at any pH, but nothing about the **rate** of that corrosion.

There is good, but not unassailable, experimental evidence that **activation control** explains CP in aqueous media as varied as seawater and nitric acid. Moreover, the classical electrode kinetic theory that describes activation control should, in principle apply to other media including soils. However, the evidence needed to support the activation control model in soils is lacking.

There are examples where CP unquestionably functions through a **passivity** mechanism. In these examples, however, passivity naturally exists, for example stainless steels in seawater and carbon steel in concrete. The role of CP here is either to maintain passivity or to re-establish it after it has broken down.

In the case of soils, on the other hand, the pre-requisites for passivity, namely a passive film and an active-passive transition, have yet to be demonstrated. The evidence supporting the involvement of passivity in the functioning of land-based CP is circumstantial. In general, the experimental work confirms cathodically-driven changes in soil electrolyte chemistry, in particular the increase in the pH. Such conditions are known to favour passivity. It is then an intuitively reasonable assumption that CP functions in soil by causing passivity. This may be correct; but it remains unproven. Moreover, it raises questions that have not been addressed in the industry. These include the corrosion science objection that passivity is conditional on anodic polarization and, as such, is incompatible with CP.

A contrary proposition, consistent with the experimental evidence, is that CP in soils works by activation control, as it does in other environments; but that there are benefits in the pH changes brought about at the surface. Notably, the increased pH can instigate chemical

changes that lead to a reduction in the cathodic current demand. Furthermore, it might be posited that these electrolyte changes might be beneficial in the context of AC corrosion. For example, if cathodic polarization is overcome in the anodic part of the AC cycle, it may indeed be beneficial if the electrolyte at the metal surface favours passivity.

However, such a benefit would not mean that the CP was itself functioning by engendering passivity of the steel surface.

REFERENCES

1. M. Büchler *A New Perspective on Cathodic Protection Criteria Promotes Discussion* Materials Performance 54 (1) 44 2015.
2. R.A. Gummow, S. Segall & D. Fingas *An Alternative View of the Cathodic Protection Mechanism on Buried Pipelines* Materials Performance 56 (3) 32 (2017).
3. M. Pourbaix & N. de Zoubov §12.1 in [4].
4. M. Pourbaix *Atlas of Electrochemical Equilibria in Aqueous Solutions* M. Pourbaix Pergamon Press (Oxford) 1966.
5. DNV RP B401 *Cathodic Protection Design* 2010.
6. DNV RP F103 *Cathodic Protection of Submarine Pipelines by Galvanic Anodes* 2010.
7. EN 13173 *Cathodic protection for offshore floating structures* 2001.
8. EN 12473 *General principles of cathodic protection in sea water* 2014.
9. ISO 13174 *Cathodic protection of harbour installations* 2012.
10. NACE SP0169 *Control of External Corrosion on Underground or Submerged Metallic Piping Systems* 2013.
11. NACE SP 0176 *Corrosion Control of Submerged Areas of Permanently Installed Steel Offshore Structures Associated with Petroleum Production* 2007.
12. H. Davy, *On the corrosion of copper sheeting by sea water, and on methods of preventing this effect; and on their application to ships of war and other ships*. Phil. Trans. Royal Soc. 1824 p151-158.
13. ISO 15589-1 *Petroleum and natural gas industries – Cathodic protection of pipeline transportation systems Part 1 On land pipelines* 2015.
14. R.B. Mears & R.H. Brown *A Theory of Cathodic Protection* Trans. Electrochem. Soc. **74** 519 (1938).
15. T.P. Hoar (Three publications cited in the discussion to Ref. [14]) 1937 & 1938.
16. D.A. Jones. *Electrochemical Fundamentals of Cathodic Protection* Paper 317 Corrosion/87 NACE (Houston) 1987.
17. V. Ashworth. *The theory of cathodic protection and its relation to the electrochemical theory of corrosion* Chapter 1 in *Cathodic Protection – Theory and Practice* eds. V. Ashworth and C.J.L. Booker. Publ. Ellis Horwood (Chichester) 1986.
18. V. Ashworth. *Principles of Cathodic Protection*. Chapter 10.1 in *Corrosion 3rd edition*. Eds. L.L. Shreir, R.A. Jarman and G.T. Burstein. Butterworth-Heinemann (Oxford) 1994.
19. W. Schwenk. *Fundamentals and Concepts of Corrosion and Electrochemical Corrosion Protection* Chapter 2 in *Handbook of Cathodic Corrosion Protection 3rd edition*. eds W. von Bækmann, W. Schwenk & W. Prinz. (1989) English Translation: Gulf (Houston) 1997).

20. V. Ashworth. *Some basic design and operating parameters for cathodic protection* Chapter 1 in *Cathodic Protection – Theory and Practice Practice* eds. V. Ashworth and C. Googan. Publ. Ellis Horwood (Chichester) 1993.
21. W.K Boyd & F.W. Fink *Corrosion of Metals in Marine Environments* Metal and Ceramics Information Center Report No. MCIC-78-37 (1978).
22. B.S. Phull, S.J. Pikul and R.M. Kain, *Seawater Corrosivity Around the World: Results from Five Years of Testing in Corrosion Testing in Natural Waters* (ed. M. Kain and W.T. Young) ASTM STP 1300 (1997).
23. F. LaQue, p383 *Corrosion Handbook* (ed. H.H. Uhlig) Wiley, New York (1948).
24. R. Francis, p5 in *The corrosion performance of metals in the marine environment: a basic guide* (eds. C. Powell and R. Francis) EFC/NACE Publication No. 63. Maney Publishing (London) 2012.
25. E.D. Mor & A.M Beccaria *Influence de la pression hydrostatitque sur la corrosion du fer dans L'Eau de Mer*. Proc. Int. Symp. *Corrosion and Protection Offshore* Paris 1979.
26. B.T. Moore & P.J. Knuckey *Minimum Protective Potential of Mild Steel in Sea Water* *Corrosion Australasia* **3** (3) 4 1978.
27. S.C Dexter, L.N. Moettus and K.E. Lucas *On the Mechanism of Cathodic Protection* *Corrosion* **41** (10) 598 1985.
28. BS CP 1021 *Code of Practice for Cathodic Protection* (withdrawn) 1973.
29. C.G. Googan *Offshore Pipelines: Do We Need -900 mV?* Paper 100 EuroCorr 2015.
30. DNVGL-RP-0416 *Corrosion Protection for Wind Turbines* 2016.
31. F. Kajiyama *Achievement of Cathodic Protection of Buried Steel Pipelines by Either Passivity or Immunity*. Paper 8829 *Corrosion/2017*. NACE (Houston) 2017.
32. *NACE Corrosion Engineers Reference Book* 3rd edition p83 ed. R. Baboian NACE (Houston) 2001.
33. F.L. LaQue and T.P. May *Experiments Relating to the Mechanism of Cathodic Protection of Steel in Sea Water* p 789 Proc. 2nd Int. Cong. On Metallic Corrosion 1965. (Re-printed: *Materials Performance* **21** (5) 18 1982).
34. T. Kobayashi *The Effect of Environmental Factors on the Protective Potential of Steel* p692 Proc. 5th Int. Congress *Metallic Corrosion* 1974 (cited in [26], [40] and [59])
35. A. Hickling *Studies in Electrode Polarisation. Part IV – The Automatic Control of the Potential of a Working Electrode* *Trans. Faraday Soc.* **38** 27 (1942).
36. J.E. Harrar *The Potentiostat and the Voltage Clamp*. The Electrochemical Society **Interface** p42 Winter 2013.
37. R.A. Humble *The Cathodic Protection of Steel Piling in Sea Water* Proc. 5th Annual Corrosion Conf. NACE International (Houston) 1949.
38. *NACE Corrosion Engineers Reference Book* 3rd edition p103 ed. R. Baboian NACE (Houston) 2001.
39. R.A Cottis and S.S. Leeds *An investigation into the influence of surface films on the mechanism of cathodic protection* Paper 06084 *Corrosion/2006* Publ. NACE (Houston) 2006.

40. S.S Leeds & R.A. Cottis *The influence of cathodically generated surface films on the corrosion and the currently accepted criteria for cathodic protection* Paper 09548 Corrosion/2009 Publ. NACE (Houston) 2009.
41. *Marine Corrosion* T Howard Rogers p192 Newnes Limited (London) 1968.
42. M. Büchler, U. Angst and B. Ackland *Cathodic protection criteria: A discussion of their historic evolution*. Paper no. 76456 EuroCorr 2017 Prague.
43. T.E. Evans *Mechanism of cathodic protection in seawater* Chapter 7 in *Cathodic Protection – Theory and Practice* eds. V. Ashworth and C. Googan. Publ. Ellis Horwood (Chichester) 1993.
44. *Control of Pipeline Corrosion* A.W. Peabody NACE (Houston) 1967.
45. *Peabody's Control of Pipeline Corrosion* A.W. Peabody (ed. R.L. Bianchetti) NACE (Houston) 2001.
46. J.M. Leeds *Cathodic-generated film protects pipe surface – Part 1* p39 Pipeline Industry September 1992.
47. J.M. Leeds *Cathodic-generated film protects pipe – Part 2* p37 Pipeline Industry October 1992.
48. A. Moussard, J. Brenet, F. Jolas, M. Pourbaix & J. Van Muylder §11.1 in [4].
49. NACE RP0290-1990 *Impressed Current Cathodic Protection of Reinforcing Steel in Atmospherically Exposed Concrete Structures* (Re-issued as SP0290-2007).
50. P. Pedefferri *Cathodic Protection and Cathodic prevention of Aerial Concrete Structures*. p45 Proc. NACE Italia Conference. Grado 1995.
51. U.R. Evans *Factors deciding between Corrosion and Protective Film Formation* Proc. 1st International Congress on *Metallic Corrosion* (London) 1961.
52. G.T. Burstein *Passivity and Localised Corrosion* in *Corrosion*. 3rd Edition L.L. Shreir, R.A. Jarman & G.T. Burstein (eds.) Butterworth-Heinemann (Oxford) 1994.
53. H.H. Uhlig Chapter 5 in *Corrosion and Corrosion Control* 2nd edition. Wiley (New York) 1971.
54. ISO 8044 *Corrosion of metals and alloys – Basic Terms and Definitions* 2015.
55. R.J. Kuhn *Galvanic Current on Cast Iron Pipes Their Causes and Effects Methods of Measuring and Means of Prevention*. National Bureau of Standards 1st Soil Corrosion Conference December 1928.
56. R.J. Kuhn *Cathodic Protection of Underground Pipe Lines from Soil Corrosion*. p153-157 API Proceedings Vol. 14 section 4 November 1933. (Reprinted in *Cathodic Protection Criteria – a Literature Survey*. NACE International (Houston) 1989.
57. W.J. Schwerdtfeger and O.N. Dorman *Potential and Current Requirements for the Cathodic Protection of Steel in Soils*. J. Res. Nat. Bureau of Standards **47** (2) p104 (1951).
58. NACE RP0169 *Control of External Corrosion on Underground or Submerged Metallic Piping Systems* 1969 (superseded by NACE SP0169).
59. U. Angst, M. Büchler, B Martin, H.-G. Schöneich, G. Haynes, S. Leeds & F. Kajiya *Cathodic protection of soil buried pipelines – a critical discussion of protection criteria and threshold values*. *Materials and Corrosion* **67** (11) 1135 2016.