

Offshore Pipelines: Do We Need -900 mV?

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SUMMARY

Various marine cathodic protection (CP) codes advise a target potential of -900 mV wrt Ag|AgCl|seawater for steel in anaerobic environments such as seabed sediments. This paper critically evaluates this criterion. The historical experimental and theoretical work underpinning its original inclusion in codes are examined; but found to be unconvincing or even flawed. Furthermore, the body of test work published since the codes were first developed, falls short of providing unequivocal endorsement.

Conversely, a consideration of basic electrode kinetics, combined with a realistic assessment of the objectives of CP, leads to the conclusion that relaxing the protection criterion from -900 mV to -800 mV would be justified. It would have no practical impact on the efficacy of corrosion control; but could significantly reduce offshore pipeline CP retrofit costs.

INTRODUCTION

Before We Begin

This paper deal with the 'potential' of the electrochemical half-cells formed when steel is immersed in seawater or seabed sediments. This brings us to our first problem: we cannot actually measure this potential. All we can do is measure the potential difference between this half-cell and some other half-cell; the potential of the latter also being both unknown and unknowable.

This problem was resolved during the early years of the development of electrochemistry by the arbitrary assignment of a potential of 0 V to the normal hydrogen electrode (NHE), revised in due course to the standard hydrogen electrode (SHE). Numerous secondary references have been developed, that exhibit stable and reproducible potential differences with respect to SHE, and that are more convenient for either laboratory or industrial applications.

This paper examines published work from the laboratory and the field. Those publications use reference half-cells appropriate to the medium (soil, seawater, laboratory electrolyte etc.). In this paper, where no reference half-cell is stated, potentials are quoted on the Ag|AgCl|seawater scale. This is in keeping with marine cathodic protection practice. Where necessary, the potential values have been transposed from the reference used by the original workers using the relationship indicated in Table 1.

Background

The requirement to polarize carbon steel to -900 mV in anaerobic environments has been established in CP industry codes for over 40 years. This criterion is now seldom challenged. The extra 100 mV of polarization, compared with the protection potential of -800 mV for open seawater, is argued to compensate for the enhanced threat of microbiologically influenced corrosion (MIC). This means that a design protection potential of -900 mV is invariably adopted for offshore pipelines; since they will either be intentionally buried in seabed sediments, or may become so over time.

Half-cell	(Typical) Target Steel Protection Potential (V)		Remarks
	Aerobic	Anaerobic	
SHE	-0.53	-0.63	Arbitrarily assigned primary reference
Hg Hg ₂ Cl ₂ KCl(satd.)	-0.78	-0.88	Used for laboratory electrochemical studies. Usually referred to (imprecisely) as the saturated calomel <i>electrode</i> (SCE)
Ag AgCl seawater	-0.80	-0.90	Used for offshore cathodic protection
Cu CuSO ₄ (satd.)	-0.85	-0.95	Used for onshore cathodic protection. Often referred to (imprecisely) as the copper sulfate <i>electrode</i> (CSE)

Table 1 Reference Half-Cells

The lack of challenge to the -900 mV criterion is understandable. In a code-driven industry, there is no career advantage to be gained from advocating a less conservative approach to protection. Furthermore, relaxing the target protection potential gives rise to the philosophical conundrum of having to prove a negative. Offshore pipelines, especially in seabed mud, spend most of their lives at near the anode potential (typically more negative than -900 mV). Experience confirms that they do not suffer external corrosion. There is scant experience of their behaviour in mud at -800 mV; so we have no practical basis for averring that -800 mV would confer adequate protection.

Accordingly, if we are to challenge the -900 mV criterion, we need to critically examine its theoretical and experimental basis.

A BIT OF HISTORY

In 1824 Sir Humphrey Davy presented the results of his investigations into preventing the corrosion of copper in seawater. He introduced his talk [1] by informing his audience that his findings ... “promise to illustrate some obscure parts of electro-chemical science”. He advanced the crucial proposition that, because ... “copper is a metal only weakly positive in the electrochemical scale...if it could be rendered slightly negative, the corroding action of seawater upon it would be null...”. This led him to the insightful view that ... “a very feeble chemical reaction would be destroyed by a very feeble electrical force”.

He reported a series of experiments, carried out with the assistance of Michael Faraday, that demonstrated the effectiveness of small lumps of zinc in protecting both copper and iron in seawater. That evening can reasonably be regarded as witnessing the birth of cathodic protection. Even so, at no point did Davy use the word potential, let alone attempt to measure it.

Indeed, he went on to design a trial sacrificial anode system, which effectively controlled the corrosion of copper sheathing on the hull of HMS Samarang, without considering the measurement of potential. Unfortunately, however, this trial proved to be an example of the Law of Unintended Consequences. As a result of the corrosion of the copper being controlled, the antifouling properties of the sheathing were lost. The fouling was a bigger problem than the corrosion; so cathodic protection was effectively shelved for the better part of a century.

It re-emerged in the 1920's with the application of forced current drainage to protect onshore welded petroleum pipelines in the USA. In 1933 Kuhn [2], having worked in the field for a decade, proposed -850 mV (measured against the Cu|CuSO₄ satd. half-cell) as the optimum

potential for the protection of onshore steel pipelines. As seen in Table 1, this is essentially the same potential as -800 mV measured against Ag|AgCl|seawater.

Eighteen years later, Schwerdfeger and Dorman [3] endorsed Kuhn's view. However, they pointed out that Kuhn's "optimum" potential had, in the interim, become adopted as the least negative potential. There has been no reason to challenge that value since that time; either onshore or in seawater¹.

CODES

NACE

The first internationally recognized standard on CP was the NACE Recommended Practice RP0169 [5] published in 1969. Although its title includes "immersed" pipelines, its focus is onshore. That document originally gave five criteria for achieving full cathodic protection:

- two based on achieving potentials of -800 mV
- two based on potential swings of -100 mV and -300 mV
- one based on the inflection in an E-Log I polarization curve.

Over the various revisions of the code the -300 mV swing and the E-log I criteria were dropped, and the requirement to achieve -800 mV clarified to emphasise that the potential had to be a true polarised potential.

The early version of RP 0169 did not include any requirement for anaerobic environments.

The 2007 version of the document, now issued as a Standard Practice (SP0169), stated that the -800 mV criterion might be inadequate... *"in some situations, such as the presence of sulphides, bacteria, elevated temperatures..."*. It was not until the 2013 edition that a requirement for a further 100 mV of polarization was advised *"...where MIC has been identified or is probable."*

British Standards Institution

The first internationally recognized code to specifically require the additional 100 mV polarization for steel in anaerobic environments, where sulfate reducing bacteria (SRB)² might be active, was BS Code of Practice CP1021 [6]. This was issued in 1973; albeit that the drafting committee started work on it prior to the issue of the 1969 NACE recommended practice.

Other Standards

Following the issue of CP1021, most other international marine CP standards offered the same guidelines for the minimum level of polarization that needs to be achieved to protect steel:

- -800 mV is required in open (aerated) seawater, and

¹ Up to the late 1960s, the British Royal Navy accepted a less conservative criterion of -750 mV [30].

² Recent microbiological studies have shown that many of the sulphate reducing organisms implicated in MIC are archaea rather than bacteria. Accordingly, we should refer to sulfate reducing prokaryotes (SRP), since the latter class includes both bacteria and archaea. However, since the abbreviation "SRB" is so established in the lexicon of corrosion engineers, it is used in this paper.

- -900 mV for anaerobic environments where there is a perceived threat of microbiologically influenced corrosion (MIC) due to the activity of SRB.

The origin of the value of -900 mV for anaerobic environments such as seabed mud, by contrast, is less clear. It would appear that following its introduction by the BSI committee into CP1021, it was adopted unchallenged by subsequent international standards.

A notable exception to this is the most recent version DNV RP B401 [26]. This advises a *design* potential -800 mV, even in anaerobic seabed mud.

It is, therefore, timely to review the background to the adoption of the -900 mV criterion.

ORIGINS OF THE -900 mV CRITERION

Work Prior to CP1021

As noted, the requirement to provide an additional 100 mV polarization for environments posing a threat of MIC seems to have entered the English language codes in the 1973 BS CP1021. With few exceptions, it has remained in those codes since. It is, therefore, useful to consider the evidence available to the drafting committee at that time.

Wormwell & Farrer (1952)

In 1952 Wormwell and Farrer [31] published extracts from a Chemical Research Laboratory report. In their experiments... *“mild steel specimens were held at definite potentials, the value of which was raised in steps of 25 mv. Between each trial the specimens were dried, polished with emery paper and degreased. The trials were carried out in uninoculated Baars’ medium and in the same medium inoculated with Desulphovibrio desulphurican”*. They reported the following results:

- *Sterile medium:*
 - *No corrosion below -0.80 V*
- *Inoculated medium*
 - *-1.15 to -0.9 V* *No corrosion.*
 - *-0.875 V* *Slight corrosion: green product.*
 - *-0.85 V* *Green product, slowly oxidizing*
 - *-0.825 V* *Black product*

They stated that the results ... *“suggest that a more negative potential is required in anaërobic conditions in which sulphate reducing bacteria are active.”*

On the face of it, the Wormwell and Farrer paper provides unequivocal support for adopting the -900 mV protection criterion in anaerobic environments. Unfortunately, however, the lack of supporting experimental detail makes it difficult to offer a clear endorsement of this work.

1. We are not told how the potentials were controlled or measured. These experiments were carried out before the introduction of automatic potentiostats in electrochemistry laboratories.
2. We are not told how the corrosion reported was actually measured.

With regard to the second point, Wormwell and Farrer do not report corrosion rates in terms of metal loss. We are only offered descriptions of the specimens. It seems that “black product” and “green product” are implicitly assumed to be *corrosion* product. However, no chemical analysis of these coloured products is presented. This is surprising since iron does not normally form green compounds; so the association of “green product” with “slight corrosion” is difficult to support.

Unless investigation of the original Chemical Research Laboratories report³ provides evidence to support the Wormwell and Farrer paper, it would be wise to maintain some scepticism about their interpretation of their observations.

For example, a plausible explanation could be advanced along the following lines:

- The deposits are magnesium and calcium bearing hydroxides and phosphates. These precipitates result from the interaction between the Baars' medium and the elevated pH at the surface of the cathodically polarized steel.
- The colouring may involve some contribution from the biological matter in the medium.
- The absence of scaling at the more negative potentials (-1150 to -900 mV) is possibly due to the descaling action of hydrogen that will be liberated on the steel surface at these more negative potentials.

It must be stressed that, just because we can offer an alternative set of explanations for the Wormwell and Farrer observations, does not mean that they were wrong or that we are correct. However, it does mean that their results are open to question.

It is interesting to note that, in their discussion section, Wormwell and Farrer cite the 1951 paper by Ewing [4]. They state that Ewing ... *"has shown that the minimum potential at which steel will be protected varies with the corrosive environment. This is reasonable on theoretical grounds and is confirmed by our own work."* This statement merits particularly careful analysis.

- The reference to Ewing's paper is slightly misleading. There are considerable problems with that paper; not least the method Ewing used for overcoming the effect of the IR error. Moreover, Ewing accepts that, in his experiments, the potentials ... *"were not maintained with the degree of accuracy required"*.
- Nevertheless, Ewing's work did indicate that adequate protection for steel in well aerated, low conductivity soils, can be achieved by polarizing to potentials less negative than -800 mV. This observation is reflected in §5.3.2.1 of ISO 15589-1 [22] for onshore pipelines.
- However, Ewing did not examine anaerobic environments containing SRB. Moreover, he did not conclude that there is a need for protection potential more negative than -800 mV.
- The statement that... *"This is reasonable"* might resonate with many CP practitioners. Superficially at least, it might seem intuitively obvious that a more negative protection potential is required for a more corrosive environment. However, this is not the case. It is not... *"reasonable on theoretical grounds"*; nor is it *confirmed* by their work. We return to this later.

One might reasonably make the case that Wormwell and Farrer were perfectly at liberty to publish their observations, and their interpretation, in an industry journal. Journals serve as a platform for floating ideas and for subsequent debate. However, when ideas are presented in text books, they tend to become more fixed.

A case in point is the U.R. Evans' classic textbook published in 1960 [34]. In chapter VIII (p285) Evan's explains that the potential that must normally be achieved to ensure protection

³ Attempts to obtain a copy have thus far been unsuccessful.

is -800 mV. However, he adds that, in the presence of SRB, the potential... “*must be kept at a still lower level; Wormwell and Farrer advise -0.90 volt.*”

That Evans put this clause in his textbook might seem unsurprising; particularly in view of the fact that Wormwell appears in the acknowledgements as the scrutiniser for chapter VIII. However, it becomes surprising when, later in the same book (p890-p891), Evans presented the electrochemical principles of cathodic protection⁴. Although he did not explicitly say as much, his theoretical presentation makes it clear that, although the current needed to achieve protection varies according to the environment, the actual potential at which protection is achieved does not.

Be that as it may, going forward from 1960, an authoritative textbook on corrosion endorsed the -900 mV criterion for protection in anaerobic environments.

It is not surprising, therefore, that the British Standards committee drafting CP1021 reproduced that requirement in the 1973 CP code of practice [6]; not least because Dr Wormwell was a member of that committee.

Horváth & Novák (1964)

In his chapter on MIC in the latest edition of the textbook “Shreir’s Corrosion”, Stott [29] states...

There is a long-standing precept, current in the industry, that structures need to be held at potentials more negative than ~ -0.9 V (vs Ag|AgCl) in order to protect against anaerobic corrosion by SRB. Horvath and Novak presented the most reasoned argument for this view, which has appeared numerous times in print, though the evidence is not very convincing.

Stott’s view that the Horváth & Novák paper [32] is *not very convincing* in its attempt to justify the -900 mV criterion merits further consideration. In this author’s view, the problem lies in the difficulty of trying to apply equilibrium thermodynamics to corrosion systems that, by definition, cannot be at equilibrium. We shall return to this issue of thermodynamics below.

Booth & Tiller (1968)

In 1968, while the CP1021 drafting committee was at work, Booth and Tiller published one of a series of papers examining the mechanism of the accelerated corrosion caused by SRB [33]. That paper concluded with the following (somewhat wordy) sentence.

“The practical criterion for the cathodic protection of ferrous materials that, in the presence of sulphate-reducing bacteria, the protective potential should be depressed by 0.10V below the protective potential in the absence of bacteria, appears to be a correct estimate in so far as it is possible to make a direct comparison between the system used in the present work and practical cases in the field.”

Given the authority of the publishing organization⁵, and the appearance of the work in a premier peer-reviewed journal, it is again unsurprising that the -900 mV criterion found its way into CP1021.

However, as with the case of the earlier Chemical Research Laboratory report by Wormwell and Farrer, it is now timely to re-appraise the Booth and Tiller paper with a more critical eye.

⁴ Evans used an electrode kinetic diagram to explain his theory. Such diagrams are now referred to as “Evans’ Diagrams”.

⁵ The UK National Physical Laboratory

In particular, it is necessary to consider how their experimental method relates to practical cathodic protection.

They studied the cathodic polarization characteristics of steel in a tris-buffer⁶, with and without SRB cells. Most of their work deals with the cathodic behaviour of steel. Their results demonstrate the role of SRB in stimulating the rate of the hydrogen evolution reaction at each of the cathodic potentials studied. They quantified ...*“the extra current required to keep an electrode cathodically polarized in the presence of the bacteria...”*. They interpreted this as meaning that a more negative potential is required for protection.

This is an incorrect interpretation. All their data actually show is that, in order to maintain a given protection potential, more current is required. The data do not show that a more negative potential is required for protection.

On the other hand, their paper does report some corrosion results. These are reproduced in the three left hand columns of Table 2 below.

Corrosion Data (as reported by Booth & Tiller)			Corrosion Data (customary units)		
Potential (NHE) V	Corrosion Rate (mg/dm ² /day)		Potential (Ag AgCl sw) mV	Corrosion Rate (mm/year)	
	Tris Buffer	Tris Buffer + SRB		Tris Buffer	Tris Buffer + SRB
-0.65	13.5	26.5	-920	0.062	0.121
-0.75	6.3	9.8	-1020	0.029	0.045
-0.85	3.1	3.9	-1120	0.014	0.018
-0.95	0	0	-1220	0.000	0.000

Table 2 Booth and Tiller Results (Table 2 of [33])

The first point to stand out from the Booth and Tiller data is that they do **not** support the proposition that a more negative protection potential is required in the presence of SRB. The only potential at which the corrosion rate is apparently zero (i.e. full cathodic protection is achieved) is -0.95 V (vs NHE). This is the same, irrespective of whether or not SRB are present. The observation that, at non-protected potentials, the corrosion rate is higher in the presence of SRB is interesting; but it is not relevant to the establishment of the protection potential.

There are also further problems with the data that only become apparent when we transpose the results to a more familiar reference electrode scale; and we use more familiar corrosion rate units. The right hand three columns of Table 2 re-present the Booth and Tiller data with:

- the reference electrode scale switched from NHE to Ag|AgCl|seawater, and
- corrosion rates converted from mg/dm²/day to mm/year.

Even if we ignore the effect of SRB, the results strain credulity. For example, at a potential of -920 mV (Ag|AgCl|seawater) we are told that the corrosion rate is 0.062 mm/year in a fully deaerated SRB-free solution buffered at pH 7. This corrosion rate of steel is within the range for carbon steel observed in fully aerated seawater [44]. It would be difficult to explain these results even in the absence of applied polarization. However, the specimen was polarized to -920 mV so it should have been fully cathodically protected!

⁶ Tris is tris(hydroxymethyl)aminohexane. It is a medium often used for biochemical studies.

Unfortunately, therefore, we have no choice but to conclude that either the authors' experimental set-up was seriously flawed, or they have made an important mistake in their methodology of recording or processing their results. At the very least, they should have commented on the discrepancy between their experimental results and the body of practical cathodic protection experience available at the time.

In Summary

It seems that the work underpinning the adoption of the -900 mV criterion for anaerobic environments in the 1973 British Standard was, at best, questionable.

Nevertheless, the criterion has been either suggested or advised in practically every internationally recognized offshore CP code published subsequently [7]-[25]; as well as CP reference books [42], [47- 49].

This remained the case until the 2010 versions of the DNV guidelines RP B401 [26] and RP F103 [27] relaxed the requirement.

REVIEW OF THE -900 mV CRITERION

Field Test Data

Onshore Pipelines

Most of the instances of claimed MIC activity on pipelines derive from onshore pipelines. Unfortunately, a review of this body of information is unlikely to enable us to take this issue forward. The reason for this is that nearly all of the instances of alleged MIC on onshore pipelines relate to corrosion under disbonded coatings on pipelines with an uncertain CP history.

Offshore Pipelines

As far as this author is aware, there are no published instances of reported external MIC on offshore pipelines under cathodic protection. Whilst this is comforting, it does not permit us to summarily change the protection potential advised by most standards.

The reason for this is that we do not have sufficient history from very aged pipelines. Practically all of the pipelines in the North Sea, and elsewhere, were so well-coated when laid that they have spent most of their lives polarized to near anode potential (about -1000 mV). In those instances where the pipeline CP has been compromised for some reason, retrofit cathodic protection systems have been installed aimed at achieving the code requirement of polarizing to -900 mV.

Thus, we simply have no experience of pipelines protected at -800 mV in seabed mud.

Laboratory Studies

Fischer 1981

In principle, it would be a simple matter to conceive the ideal set of experiments for our purposes. This would be to polarize steel in seabed mud (with and without active SRB), and to measure the rates of corrosion at different potentials.

Indeed, such work was carried out in the early 1980s; and reported by Fischer [37]. Steel samples were held at selected potentials in anaerobic North Sea mud containing SRB for 181 days. The current required to maintain a set potential was logged throughout. At the end of the test, the weight loss of the steel was recorded. Hence, the results are particularly relevant to this discussion. Amongst his conclusions Fischer states:

“The generally accepted protection criteria for anaerobic saline clay sediments of -950 mV (Cu/CuSO₄) seems adequate as the residual corrosion is only 5 mA/m² to 6 mA/m² (6 to 7 μm/year) for temperatures in the region of 5°C to 30°C”.

On the face of it this provides a straightforward endorsement of the code requirement to polarize to -900 mV in anaerobic mud.

However, the conclusions do not say to what extent a potential of -800 mV might, or might not, be adequate. It is, therefore, necessary to review the relevant data in Fischer's paper. These are presented in Table 3 below.

- Column 1: shows the potentials. As elsewhere in this paper, these have been transposed to Ag|AgCl|seawater scale.
- Columns 2, 3 and 4: are transcribed directly from Fischer's Table 3.
- Column 5: presents the corrosion rate from the electrochemical unit (mA/m²) used by Fischer to engineering units (mm/year).

The data in Table 3 lead to the following conclusions:

1. Fischer's conclusion that -900 mV ... *“seems adequate”* is reasonable.
2. However, the only experiment at -800 mV (i.e. at 30°C) also suggests that it would also be ... *“adequate”*. The reported corrosion rate (0.01 mm/year) would be considered as being cathodically protected per the current standards.
3. The current densities needed to maintain the prescribed levels of polarization are generally much higher (up to 117 mA/m²) than the values given in subsequently published codes for protecting steel in seabed mud⁷. The latter is typically 20 mA/m². (However, part of this may be explained by the fact that Fischer used sand-blasted steel specimens. The blast profile will have meant that the actual area of steel exceeded the nominal planar surface area).
4. The reduction in the residual corrosion rate gained is very modest given the levels of cathodic polarization imposed on the samples. This is contrary to the fundamental theory of cathodic protection (see for example [34, 39, 40, 41 and 42]).

Applied Potential (mV)	Temp. (°C)	Protection Current Density (mA/m ²)	Residual Corrosion Rate	
			(mA/m ²)	mm/year
Free corrosion	5	-	15	0.017
-745		18	11	0.013
-920		50	5	0.006
Free Corrosion	30	-	44	0.051
-720		52	22	0.026
-800		80	9	0.010
-895		117	6	0.007

Table 3 Fischer's Results (from Table 3 of [37])

⁷ It is interesting to note that DNV, who were sponsors of the joint research project, evidently chose to ignore these results when they published TNA 703 [7] the same year.

Thus, although the Fischer paper prompts further questions; it does not provide any substantial counter-argument to the proposition that the protection potential be set to -800 mV, even in seabed mud.

Barlo and Berry 1984

Another paper cited to justify the -900 mV criterion is that published by Barlo and Berry [38]. Although that study relates to soils, it should also be applicable to seabed mud.

The following conclusions are relevant to the present discussion.

1. In the absence of SRB, -800 mV ensures protection, although less negative potentials will suffice in soils with lower moisture content.
2. In anaerobic soils with SRB activity, their results... *"indicate that true polarized potentials more negative than (-0.90 V) are required to prevent corrosion"*.

The first of the above conclusions is interesting; but is not relevant to seabed mud.

The second, however, does again seem to support the general code requirement to design marine pipeline CP systems to a target protection potential of -900 mV. This conclusion cannot be ignored.

It is difficult to comment on the results because the paper does not present hard data. Instead, it provides thumbnail histograms. The only ones relevant to the issue of the relevant protection potential in the presence of SRB are Figure 8 and 11 of the paper. Unfortunately, this author has a great deal of difficulty interpreting the histograms.

For example, Figure 8a indicates that, in two of the three soil types studied, a potential of -900 mV is required to protect steel in the presence of SRB, whilst in the corresponding SRB-free experiments potentials around -650 mV suffice. However, in the third soil studied, it appears from the histogram that a potential more negative than -1050 mV is required in the presence of SRB. Moreover, in the same soil, but in the absence of SRB, it appears from the histogram that a potential of about -850 mV is required. The latter observation contradicts the first of their conclusions (see point 1 above); and conflicts with extant codes.

Unfortunately, there is insufficient detail in the paper to permit a deeper investigation of this observation.

However, various snippets of the text prompt concerns about the experimental techniques used. For example, corrosion at any given potential is assessed by weight loss measurements after a relatively short period of polarization (30 days). However, although the test specimens were cleaned in inhibited hydrochloric acid, there is no record the authors having used blanks to account for errors introduced by the cleaning process. If this was not done then the reported corrosion rates would be over-estimated; and this over-estimation would be proportionally high in cases where the actual corrosion rate was low.

Similarly, since the specimens were left in-situ for...*"approximately 12 to 18 hours"* before the cell was disassembled, there must be concern that the corrosion assessment was distorted.

Other Review Papers

Various authors have reviewed the criteria for protection; and some of these reviews have considered the protection potential required for anaerobic environments where SRB may be active. In general these reviews have simply summarized existing literature without applying too much of a critical faculty.

In other cases, e.g. [43], it is evident that the authors have implicitly assumed that cathodic protection will only control MIC if it controls the microbes. In practice this means polarizing much more aggressively in order to raise the pH at the steel surface to a level that inhibits

microbiological activity. This is unnecessary. The role of cathodic protection is to control corrosion electrochemically; not to act as a biocide.

In Summary

The fact that we can unearth solecisms in work published before a 1973 code of practice was drafted provides a good reason to question the code requirement. This is even though it, and its derivatives, have been in use for over 40 years.

However, our review of the published field and laboratory CP test data does not permit us to summarily over-rule the codes. The problem is that, although we can challenge the evidence offered in favour of the -900 mV criterion, this simply leaves the criterion unproven. It does not mean that the criterion is incorrect. Moreover, we do not have experimental data to support the converse proposition that -800 mV would suffice in seabed mud.

To pursue the matter further, we need to drill deeper into the electrochemical theory underpinning CP. This requires examining the process in terms of both thermodynamics and electrode kinetics.

THERMODYNAMICS

Immunity

The early theories of cathodic protection (see [34] for reviews) considered that it would provide protection if the potential was lowered to the equilibrium potential of the iron electrode. At that point, the reaction:



could not proceed, so corrosion would cease.

In principle this view provides a straightforward way of determining the appropriate value for the protection potential. The standard potential for iron in equilibrium with ferrous ions at a concentration of 1 g.ion/l is -0.71 V. However, if the iron were in equilibrium with a solution containing 1 g.ion/l of Fe^{2+} ions (i.e. 28 000 mg/l) it could hardly be claimed not to be corroding.

By convention, it is often taken that corrosion can be discounted when the interfacial iron concentration is 10^{-6} g.ion/l. This potential can be determined from the Nernst equation.

$$E = E^{\circ} + \frac{RT \log K}{nF}$$

where

- E = electrode potential under non-standard conditions
- E° = electrode potential under standard conditions
- R = the gas constant ($8.3413 \text{ J}^{\circ}\text{K}^{-1}\text{mol}^{-1}$)
- T = Temperature ($^{\circ}\text{K}$)
- n = number of electrons in the equilibrium reaction ($n=2$ for Fe/Fe^{2+})
- F = Faraday's constant ($96487 \text{ As g.mole}^{-1}$)
- K = equilibrium constant (Because Fe is a solid with an activity of unity, we can equate K to the activity of Fe^{2+} ions, Furthermore, at low activities, we can assume that the concentration equals the activity).

The result, however, turns out to be very nearly -900 mV. In other words, the well-established potential criterion of -800 mV for steel in aerated seawater is not supported by the application of classic thermodynamic principles.

The position becomes even more improbable if we assume that the corrosion only ceases if we lower the potential to a value at which the iron is in equilibrium with Fe^{2+} ions at their natural concentration in seawater. The latter parameter is hard to tie down. Iron is naturally present in seawater at levels of 0.002 to 0.02 mg/l. However, much of this is in the form of suspended particulates, or else the iron is in complex form in biogenic matter. Based on the solubility product of $\text{Fe}(\text{OH})_2$ and the pH of seawater (~8), the concentration of ferrous ions is likely to be of the order of 10^{-10} gions/l.

Using this concentration in the Nernst equation leads us to an estimate of a protection potential slightly more negative than -1.0 V.

This means that we cannot explain CP simply as the depression of the potential of the steel into the region of “immunity” indicated on the E-pH (Pourbaix) diagram for the iron-water system.

Passivity

A better case may be advanced for interpreting CP in terms of “passivity”. Ashworth [35] makes the point that, since the local pH at a cathodically protected surface in seawater exceeds 9, the local environment rapidly becomes saturated with ferrous hydroxide. He adds...*“thus it is plausible that the protection criterion (-800 mV) works so effectively because of the intervention of ferrous hydroxide deposition and not because of metal immunity. In short it is controlled by the thermodynamics and kinetics of precipitation, not by the thermodynamics of metal dissolution”*.

In other words, we may start with the view that corroding steel may be regarded as being in Zone ‘A’ as shown in Figure 1. Moving to Zone ‘B’ (immunity) seems to offer an unlikely explanation; because the potentials theoretically needed for protection are more negative than are found to suffice in practice. The alternative thermodynamic proposition is that the metal moves into Zone ‘C’ (passivity).

Leeds and Cottis [36], amongst others, have also considered the importance of surface films formed under cathodic polarization.

Generally speaking, depending on the composition of the test solution, and the cathodic potential, studies of this type show:

- films, including iron oxides, form on the metal surface, **and**
- a reduction in corrosion rate under applied cathodic polarization.

It is, therefore, tempting to interpret such experiments as indicating that the steel has, at least partially, passivated. However, it is also very important not to confuse correlation with causation. The fact that iron oxides are formed on steel does not necessarily mean that the steel is passive. After all: iron oxides are formed on freely corroding steel.

Our reading of the literature has not found any evidence that steel surfaces under CP exhibit the electrochemical characteristics of passivity.

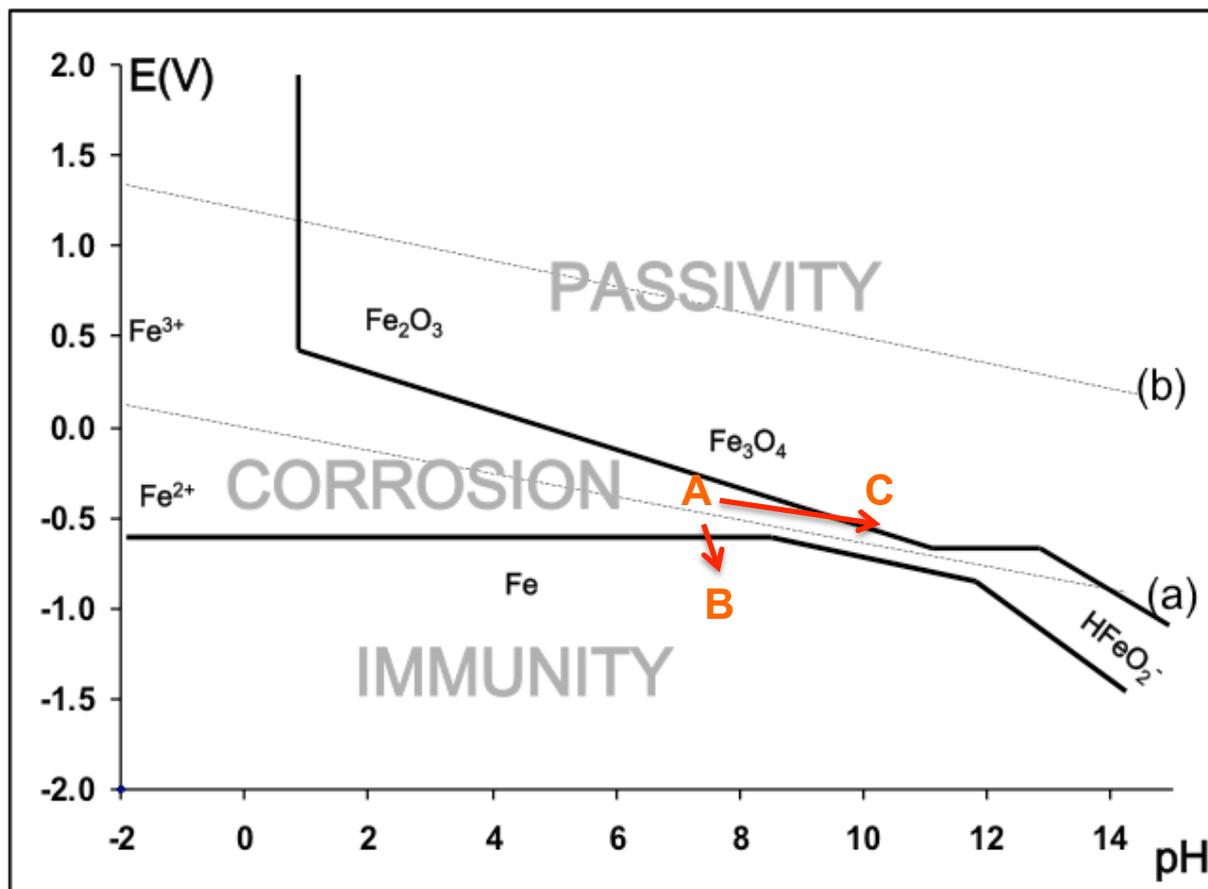


Figure 1 Interpretation of CP on a Pourbaix Diagram (Note Potential scale is V vs SHE)

To sum up: we cannot use straightforward thermodynamic considerations as a basis for setting the protection potential. Thermodynamics tells us what can and cannot occur. However, corrosion of steel can and does occur. The only interest of practical concern is how quickly, or how slowly, this occurs. Thermodynamics, which should perhaps be called “thermostatics”, remains silent on this.

It is largely due to the limitations of thermodynamics that, in this author’s view, the much-cited (but not so often read) work of Horváth & Novák, mentioned above, does not justify the adoption of the -900 mV protection criterion in the presence of SRB.

ELECTRODE KINETICS

What exactly do we mean by cathodic protection?

Proponents of CP often advance the technique as being the only means of reducing the corrosion rate of steel to zero. Many textbooks on corrosion and CP, as well as most codes, discuss the technique in terms of its ability to confer “full protection”; or, by implication, zero corrosion. However, the reality is more subtle. This is illustrated by §5.3.1 of ISO 15589-1 [22] 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*”.

The advice of ISO-15589-1 that a corrosion rate of <0.01 mm/year, is reasonable from an engineering perspective. It amounts to the loss of 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 very low corrosion rate of 1 mm per century means that ~3.7 trillion iron atoms are being lost from each square centimetre of the surface every second!

In discussing cathodic protection criteria, therefore, we need always to bear in mind that we are discussing reductions in the corrosion rate, not the complete cessation of corrosion. The latter concept has little practical significance.

The anodic behaviour of iron

The electrode kinetic interpretation of CP has, at its heart, the mixed potential theory of corrosion as developed by U.R Evans, and as applied by Evans himself [34], and others [39]-[42] to CP. If this interpretation is accepted, then it follows that the nett rate of anodic dissolution (i.e. corrosion) of the steel at any given value of potential depends solely on the kinetics of the anodic reaction:



It is not contested that the rate of this reaction follows Tafel like behaviour. In other words there is a logarithmic relationship between the rate of the reaction and shift in potential away from the equilibrium potential (termed the “overpotential”). This is illustrated in Figure 2. Furthermore, the slope of the Tafel plot for this reaction is known to be very insensitive to the nature of the electrolyte. Baboian [45] has published a figure of 0.060 V/decade for steel in 0.1N Na₂SO₄. There is no reason to expect this figure to be notably different if the environment were seawater, or seabed sediments.

The current on the abscissa of Figure 2 is related directly to the rate of metal loss by Faradays Laws of Electrochemical Equivalence. This means the Tafel plot, with Baboian’s value for its slope, is telling us that: for every 0.06 V negative (cathodic) shift in potential the corrosion rate of steel reduces by a factor of ten.

Implications for Cathodic Protection

This does not mean that we can translate a potential measurement directly into a corrosion rate. As discussed above, since we do not know the concentration of ferrous ions in the environment, we do not know the equilibrium potential. That means that we cannot translate overpotential into a measured potential on (say) the Ag|AgCl|seawater reference scale.

However, this is not a practical problem.

As a matter of experience steel corroding in aerated seawater adopts a steady state potential in the region of -0.65 V. There is also a considerable body of marine test data [44] that tells us that, in this condition, the steel is corroding at a rate of approximately 0.1 mm/year.

On the basis that the iron dissolution reaction follows anodic Tafel behaviour, and that Baboian’s figure of 0.06 V/decade is a reasonable value for the Tafel slope, we can offer ball-park estimates of the corrosion rate as a function of the level of cathodic polarization. These are set out in Table 4.

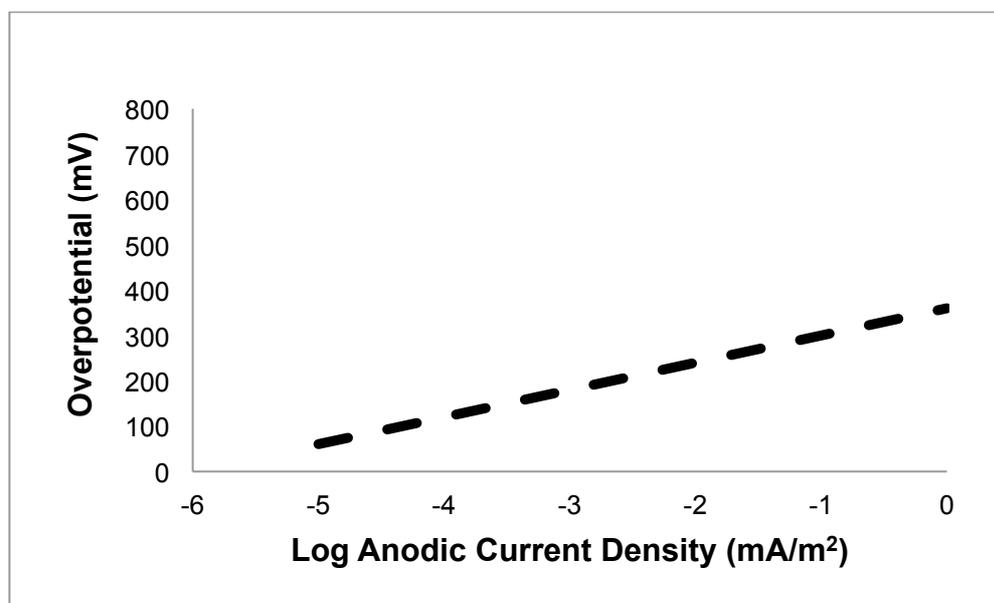


Figure 2 Schematic Tafel Behaviour for $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$

Potential Ag AgCl seawater (mV)	Reduction in Anodic Overpotential (mV)	'Ball-Park' Corrosion Rate		Remarks
		(A/m ²)	(mm/year)	
-650	zero	0.090	0.1	Free corrosion
-710	60	0.009	0.01	'Acceptable' corrosion rate
-800	150	0.000 3	<0.001	Code compliance (aerated seawater)
-900	250	0.000 006	<0.000 01	Code compliance (seabed sediments)

Table 4 Ball-Park Corrosion Rate of Steel as a Function of Potential

DOES IT MATTER?

It is reasonable to question whether it matters if a pipeline CP system is designed with a target protection potential of -800 mV or -900 mV. For most pipeline CP designs, the short answer to this question is: probably not.

In the case of well-coated new offshore pipelines, which are usually protected by bracelet sacrificial anodes, the only consequence of designing to -900 mV is that more anodes would be installed than if designing to -800 mV. This would have a barely noticeable effect on the total cost of the pipeline project.

However, the design protection potential does become significant when it comes to retrofitting CP to pipelines that are now required to operate well beyond their original design lives. Such retrofits are usually carried out by installing anode sleds on the seabed; and making sub-sea cable connections to the pipeline. Given the expense of offshore and sub-sea operations, there is clearly an incentive to minimize the number of retrofit sleds needed to protect a pipeline. In other words, the design intention is to maximize the distance between sleds.

There is usually little difficulty in providing ample anode mass on a sled; nor should it be too difficult to conjure up a design with an adequate instantaneous current output. It turns out that the limiting factor in the designs is the attenuation of potential along the line. There are a number of ways of estimating the attenuation of potential along a pipeline. In the case of offshore lines methodologies are given in [17] and [27]. However, for our purposes it is convenient to use a re-arrangement of the formula published by Uhlig [28].

$$\Delta E_{dp} = \Delta E_{min} \cosh \left\{ \sqrt{\frac{R_L}{R_C}} \frac{L}{2} \right\}$$

where:

- $L/2$ = protected length of line
- ΔE_{dp} = potential shift at drain point
- ΔE_{min} = potential shift at section end
- R_L = pipe wall resistance/unit length
- R_C = coating resistance . unit length

In this exercise, ΔE_{dp} is determined by the operating potential of the anodes on the sled. We may assume that, in the absence of CP, the steel pipeline would normally be corroding at about -0.65 V. The anodes will typically operate at -1.05 V; so ΔE_{dp} is about -0.4 V. The end of the protected section is reached at a distance ($L/2$) from the anode sled where the pipeline potential is at the least negative permitted target potential. If the target potential is -0.9 V then ΔE_{min} is -0.25 V. This means that the maximum permitted potential attenuation along the line would be $-0.25 \text{ V} - (-0.4 \text{ V}) = 0.15 \text{ V}$. However, if the target potential is relaxed to -0.8 V then the maximum permitted attenuation increases to 0.25 V.

The impact of this is seen in the Figure 3. This is an example of a retrofit CP design exercise for a pipeline buried in seabed sediments; with ΔE_{min} set at -0.25 V (blue line) and 0.15 V (red line). R_L is calculated from the known cross-sectional area of the pipe wall and the specific resistivity of steel. R_C assumes that the polarization resistance at any bare steel exposed by coating breakdown is $1 \Omega m^2$ [46]. As can be seen, relaxing the required protection potential in seabed mud from -0.9 V to -0.8 V effectively doubles the permitted spacing between the retrofit anode sleds.

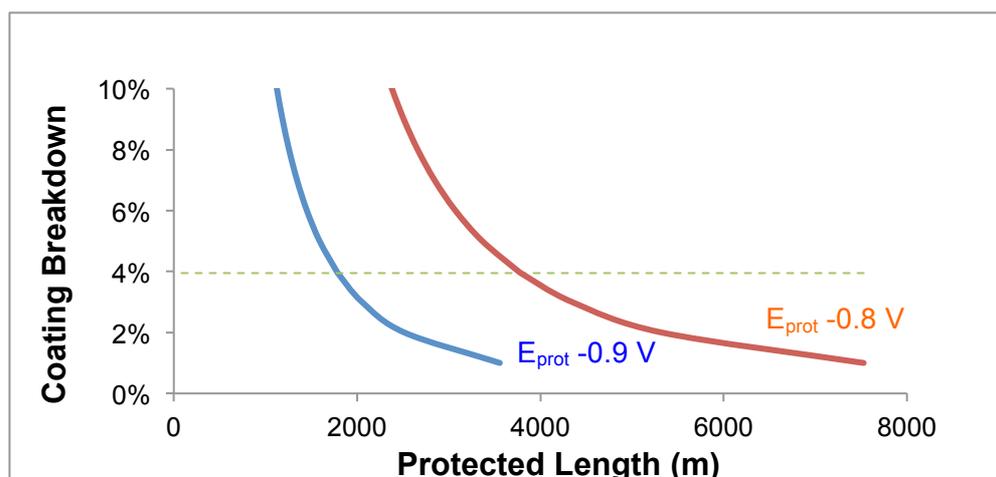


Figure 3 Protected lengths for 30" 16.7 mm WT line protected by Al-alloy anode sled.

CONCLUSIONS

The requirement in most cathodic protection design codes to set a protection potential 100 mV more negative in anaerobic environments than in aerobic environments seems to have emerged in 1973 with the publication of BS Code of Practice 1021. It seems that the requirement first arose because of a plausible, but incorrect, perception that a more negative potential was required for a more aggressive corrosion threat. It then seems that, once this requirement had entered one code, it was reproduced in others; and it remained largely unchallenged.

However, a critical examination of the literature underpinning the original adoption of this more negative protection potential has failed to find a convincing case. Alternatively, attempts to justify the -900 mV criterion for anaerobic environments on the basis of thermodynamic principles fails; as does the corresponding attempt to justify -800 mV for aerobic environments.

It is only when CP is viewed on the basis of electrode kinetics, whereby cathodic polarization reduces the anodic dissolution rate in accordance with a Tafel type relationship, does it emerge that -800 mV is appropriate. Furthermore, because the anodic Tafel slope for the iron dissolution reaction is essentially independent of the cathodic corrosion processes, this means that -800 mV is also appropriate for anaerobic conditions. This holds even if there is a threat of microbiologically influenced corrosion.

Thus, it is recommended that the -900 mV protection criterion for steel in anaerobic environments is relaxed to -800 mV. This will permit a considerable saving in the future costs of retrofit CP systems for buried offshore pipelines.

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