



Copenhagen – 21th – 24th May, 2019

A discussion of stress corrosion cracking of pipelines based on today's understanding of the processes involved in cathodic protection

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Abstract

Stress corrosion cracking (SCC) of pipelines has the potential of severe damage. While corrosion due to AC and DC interference or insufficient levels of CP usually result in a leaks, SCC can cause rupture of the pipelines. This implies severe safety risks including casualties. Such events have indeed been observed in the past. The majority of the reported incidents occurred in North America, Australia and Russia. Interestingly there are very limited cases of SCC in Europe. In absence of reported cracks or damages limited attention has been payed to SCC in Europe. This changed with the observation of cracking of up to 50% of pipe wall thickness on a pipeline in Germany, as reported in UKOPA/GP/009. In the context of these damages it is relevant to readdress the concepts and the experience in association with SCC. There has been extensive investigations with respect to cracking in the last century. These investigations were primarily based on fracture mechanical concepts. The development of a complete and comprehensive understanding of the processes involved in cathodic protection (CP) in recent years allows today for a different view on these data. This paper presents a discussion of the different types of SCC in the light of today's understanding of the relevant mechanisms. It further highlights the possible contribution of hydrogen to SCC and draws some preliminary conclusions with respect to the implications on the operation of CP.

1. Introduction

In previous publications the relevant aspects of cathodic protection (CP) [1] as well as disbanded coatings [2] were discussed. In the present paper stress corrosion cracking (SCC) is discussed in the light of today's understanding of the involved mechanisms in CP. Although the focus is on near neutral stress corrosion cracking (NNSCC) the relevant aspects of high-pH SCC (HPSCC) are discussed as well. Due to the relevance of SCC for the integrity of the pipelines, the general understanding of the involved mechanism will be summarized in the following paper.

2. General principles of SCC

The relevance of concentration polarization, the resulting changes of the electrolyte composition and the subsequent passivation of the steel surface has been discussed previously [2]. There is widespread agreement on the relevance of these aspects in CP industry and the processes in the simple case of a steel surface with an individual coating defect are well understood. In this case the steel properties and the steel composition are of minor relevance. In contrast, SCC requires the additional consideration of the following influencing parameters:

- Mechanical stress and stress distribution resulting from pipe manufacturing, welding, pipe laying and pipe operation
- Fatigue resulting from cyclic pressure variations
- Presence of mill scale
- Coating systems and the grit blasting process resulting in surface compression
- Yield strength of the steel
- Metallurgical properties
- Coating properties and adhesion
- Hydrogen generation and hydrogen absorption into the steel matrix
- Soil characteristics

Considering the additional complexity of the problem of SCC it is remarkable that a solid understanding of the involved processes is available today. Key advances were possible in recent years with the establishment of generally accepted principles of the underlying mechanisms of CP. In particular the consideration of the electrochemical processes and the mass transport allows for explaining a number of relevant aspects that remained unclear in the past.

For SCC to occur three key conditions need to be fulfilled:

1. The presence of a susceptible material
2. The presence of critical mechanical stress
3. The presence of a critical environment

While steel is well known to be susceptible to SCC in a number of environments and increased mechanical stresses are unavoidable for high pressure gas pipelines, the only possibility to address SCC is the generation of an ideal environment that effectively assures corrosion protection and eliminates the risk of SCC. A detailed discussion of the environment that needs to be

avoided in order to prevent SCC is given by Parkins and Zhou [3]. There are two distinct forms of SCC occurring on pipelines:

- a. The NNSCC associated with trans granular cracking
- b. The HPSCC associated with inter granular cracking

The dependence of HPSCC (orange) and NNSCC (red) on pH and potential according to [3] is plotted in Figure 1. It is evident that the application of CP (green arrow) effectively prevents both types of SCC. It has been demonstrated by numerous authors that CP results in an increase of the pH and an associated decrease of the potential. This is shown for the data of Yan et al. [4] obtained in artificial soil solution purged with CO₂ which represents the very conditions relevant for NNSCC. These data obtained for various coating systems confirm the relevance of the processes taking place in the case of effective CP shown with the green arrow in Figure 1 as discussed in [2]. These data are well in line with the numerical model for describing the electrochemical processes of cathodic protection presented previously in [5].

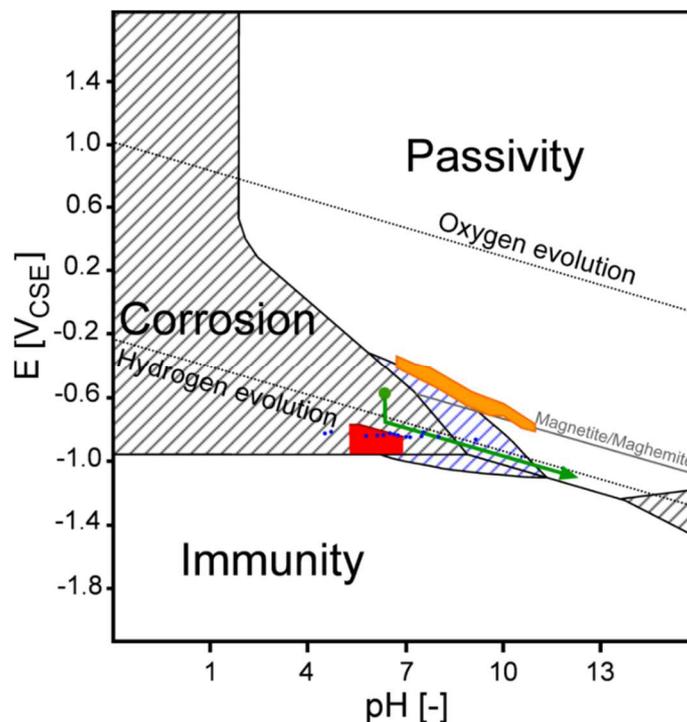


Figure 1: Pourbaix diagram [6] for iron with the increased corrosion domain (blue) in 1 M CO₂ according to [7]. The effect of cathodic protection on potential and pH of steel is shown with the green arrow. In red the area of NNSCC and in orange the area of HPSCC is shown [3]. The demonstrated limits of the SCC domains are marked with the darker coloured lines. Additionally, the corrosion potentials (blue dots) of steel in anaerobic electrolytes according to [8] are additionally shown.

Based on this analysis it is evident, that the use of a cathodic protection ensures that the IR-free potential (green arrow in Figure 1) of the steel surface stays well outside the SCC domains, for both NNSCC as well as HPSCC. This is true even in the case of fully disbanded coatings based on FBE and 3LPE in the case of an associated coating defect as demonstrated by [4] as discussed in [2]. While these data illustrate that in principle no problems with SCC have to be expected in case of effective CP, it is of key interest to understand the very conditions that may result in this specific type of corrosion. This will be discussed in the following.

Based on Figure 1 it is evident that the range of HPSCC is located at the transition from corrosion to passivity (orange area). In contrast, the NNSCC (red area) appears to be associated with processes taking place in the corrosion domain, which is confirmed by the corrosion potentials of steel in nitrogen purged solution marked by means of the blue dots. In Figure 2 the condition for steel in an electrolyte of pH 7 was calculated for ambient temperature based on the thermodynamic and kinetic considerations in order to further discuss the associated electrochemical mechanisms of Figure 1 in a simplified approach. A detailed description of the underlying principles of the model is given in [9]. The key aspects of the model were validated within an extensive research project {Büchler, 2018 #6783} funded by DVGW. The corresponding domains for NNSCC (within the corrosion domain) and HPSCC (at the transition from corrosion to passivity) according to [3] as plotted in Figure 1 are marked by means of red and orange circles in Figure 2. It becomes clear that the process for HPSCC (orange circle) is directly related to the transition from active corrosion to passivity. Correspondingly, the process of HPSCC is typically explained based on a repeated rupture and reformation of the passive film as a consequence of cyclic pressure loading of the pipeline under a disbonded coating in association with a coating defect as shown in Figure 3. This process results in repeated iron dissolution at the crack tip as a result of the cracking of the passive film. In the direct transition between corrosion and passivity these periods of corrosion may last longer resulting in a continued metal dissolution. Since the sides of the crack remain passive, the corrosion process is concentrated at the crack tip resulting in accelerated crack propagation. In the HPSCC the rupture of the passive film is favoured at the grain boundaries, which results in intergranular crack propagation. The rupture of the passive film is typically explained based on the creep of the steel under constant load or the repeated loading and unloading cycles.

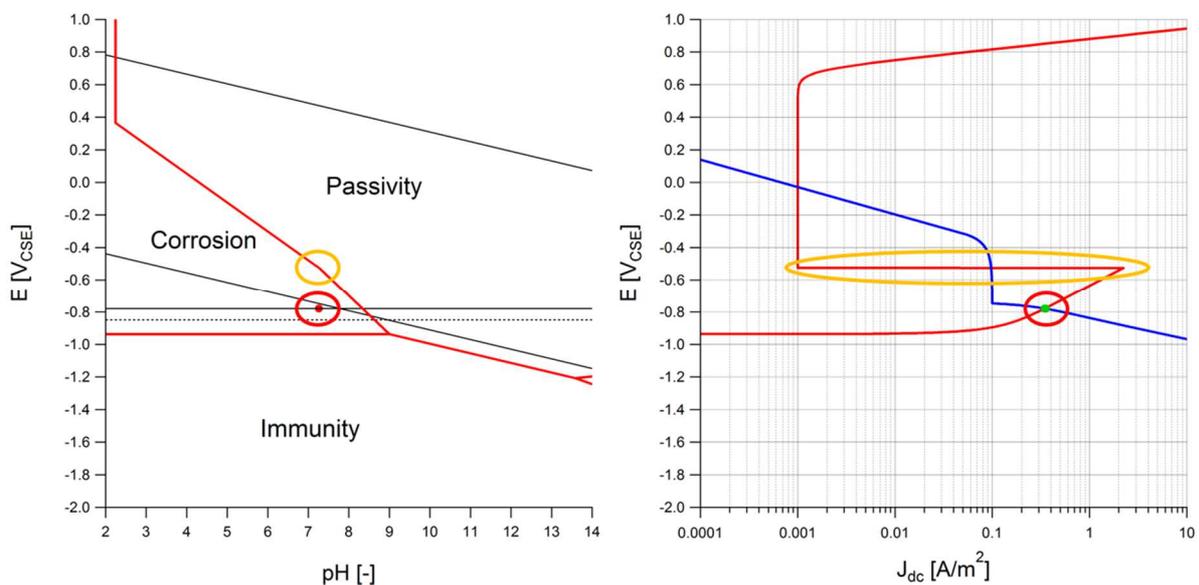


Figure 2: $E_{IR-free}$ calculated for steel in a near neutral electrolyte with normal aeration. Left: Pourbaix diagram with the red dot showing the conditions at the steel surface. The dashed horizontal line represents the protection criterion of $-0.85 V_{CSE}$ according to ISO 15589-1 and the solid horizontal line the corrosion potential of $-0.78 V_{CSE}$ that is expected under the given circumstances. Right: Polarization curves for anodic (red) and cathodic reactions (blue) on steel at the corresponding pH value. The red circle marks the domain of the NNSCC and the orange circle the domain of the HPSCC.

In contrast the NNSCC occurs within the corrosion domain in Figure 2 (red circle). Based on the polarization curves it is evident that the corrosion process is controlled by hydrogen evolution. A

corrosion rate of about 0.37 mm/year is to be expected based on the current density of 0.33 A/m². Since hydrogen evolution controls the corrosion process, the hydrogen usually observed in NNSCC in the steel can readily be explained. The atomic hydrogen entering the steel will contribute to decohesion within the iron atoms in front of the crack tip and generate voids in the metal (Figure 4). This will contribute to the crack growth by promoting plastic flow at the crack tip by decreasing the yield strength as suggested by Fessler [10]. This is in line with the increased creep in presence of hydrogen loading as reported by Parkins [11]. On a macroscopic level this results in an in a brittle fracture at stress levels well below the yield strength as a result of hydrogen loading of the steel.

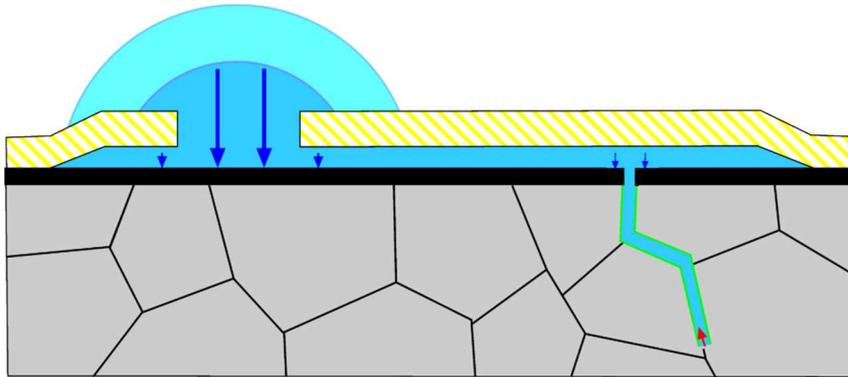


Figure 3: Schematic illustration of HPSCC occurring underneath disbonded coating on a mill scale (black) covered steel surface with intergranular crack propagation. The cathodic current entering at the coating defect causes concentration polarization and an increase of the pH underneath the disbonded coating.

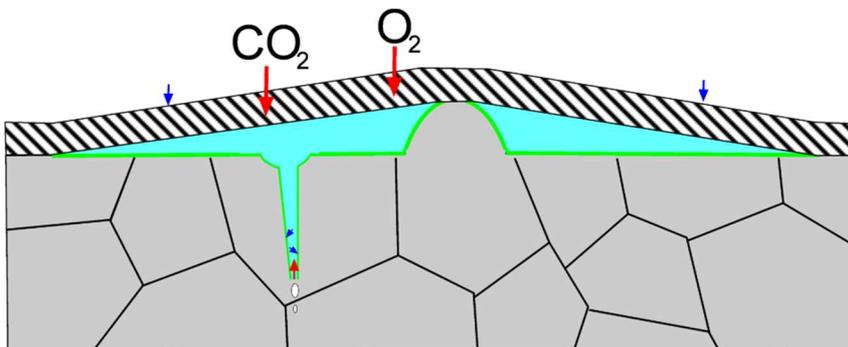


Figure 4: Schematic illustration of the mechanism of NNSCC with trans granular crack growth under disbonded coating in the case of a PE tape wrap of a field joint coating that results in tenting at the girth weld. No increase of pH due to an increased diffusion rate of carbon dioxide and a high electrical resistivity of the PE tape is observed. In the near neutral conditions passivity (green line) is established as a result of increased Fe²⁺ concentration. The hydrogen absorbed in the steel as a result of the corrosion process occurring at the crack tip causes decohesion of the iron atoms. This adsorbed hydrogen at the crack tip causes the formation of hydrogen filled voids (white), which increases the plasticity and creep of the steel.

This concept presented by Parkins [11] and Fessler [10] has, however, one key problem: It cannot explain the reason for the reported extended dormancy period of cracks. In particular, it is striking that the tests run in the corresponding potential/pH domains in Figure 1 results in significantly larger crack propagation rates than what is observed on pipelines. Failure to address these aspects is one of the main reasons for the lack of a more profound understanding of the associated effects. To further emphasize this aspect: Only a very small part of the cracks ob-

served on pipelines will ever reach depths that could become critical from an integrity point of view. The rest of them become dormant. Without understanding the influencing factors that turn growing cracks into dormant ones, it is impossible to adequately treat this problem with respect to the integrity of pipelines. In the following the most recent understanding is shortly summarized to provide a view on the present understanding for the two types of SCC.

3. Influencing factors

3.1. Introduction

In the context of SCC often the hydrogen embrittlement is discussed. The presence of hydrogen in the case of NNSCC is a result of the corrosion process under hydrogen evolution. Additionally, it is a common observation that both types of SCC are associated with the formation of carbonates. This emphasizes the need to further address these aspects. In a first approach the associated mechanisms with hydrogen embrittlement and the influence of carbonates will be discussed.

3.2. Hydrogen embrittlement

There is wide agreement that NNSCC is associated with hydrogen formation and an increase of the concentration of atomic hydrogen in the steel. As a result of this, hydrogen embrittlement represents a possible threat to the integrity of the pipeline and the associated mechanism needs to be discussed. Often it is assumed that this hydrogen can only be caused by CP. In this context it is important to compare this problem of hydrogen embrittlement with the requirements of EN ISO 15589-1:2017, since often the threshold of $-1.2 V_{CSE}$ is erroneously associated with the risk of hydrogen embrittlement. Unfortunately, EN ISO 15589-1:2017 describes both coating disbondment and hydrogen embrittlement as overprotection effects. This readily leads to confusion and a more differentiated discussion is required in order to address the relevant aspects.

EN ISO 15589-1:2017 clearly and exclusively links the threshold of $-1.2 V_{CSE}$ to cathodic disbondment. In particular, there is no threshold specified with respect to hydrogen embrittlement. Instead, ISO 15589-1:2017 requires the documentation of the applicable threshold for steels with designed yield strength above 550 N/mm^2 . It follows directly from **Figure 5** and it is further detailed in [12], that it is technically impossible to meet the cathodic protection criteria and simultaneously exclude relevant hydrogen evolution:

The threshold of $-1.2 V_{CSE}$ (red dot in **Figure 5**) will always be cathodic of the hydrogen evolution equilibrium line, even at significantly increased pH-values. Typically, IR-free potentials of $-1.2 V_{CSE}$ are associated with at least 1 A/m^2 cathodic current density associated with hydrogen evolution. At these current densities relevant hydrogen loading of the steel will occur. Furthermore, in anaerobic conditions any current entering the steel surface is bound to be associated with hydrogen evolution, since there is no other redox system that can carry the cathodic reaction. Taking the design current densities in EN ISO 15589-1 of 0.1 to 1 A/m^2 , these will inadvertently lead to relevant hydrogen loading of the steel in anaerobic conditions, since there is no oxygen available for cathodic reaction. As a consequence, there is no substance to associating $-1.2 V_{CSE}$ with any safety with respect to hydrogen evolution. In the contrary, its use in this context generates the illusion to the pipeline operator that the risk with respect to hydrogen embrittlement can be addressed.

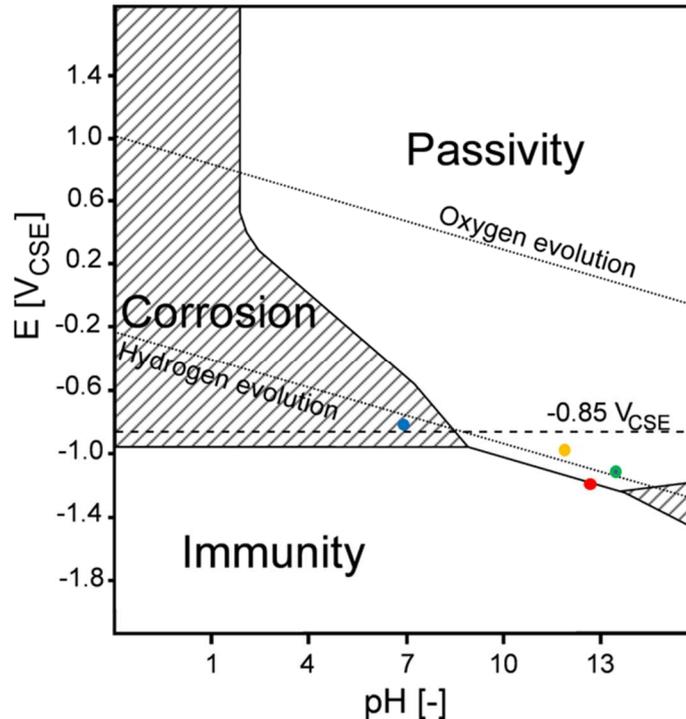


Figure 5: Relative position of threshold values with respect to overprotection. Description in the text.

This is clearly not the case and in particular not suggested in EN ISO 15589-1:2017. This is further emphasized by the threshold documented in EN ISO 12696:2016 "Cathodic protection of steel in concrete" with respect to hydrogen embrittlement: it quotes a value of $-0.97 V_{CSE}$ for the steel/concrete potential. This value was determined in saturated calcium hydroxide solutions of pH 12.5. It follows from the yellow dot in **Figure 5** that hydrogen evolution is not possible at this pH of 12.5 and potential value of $-0.97 V_{CSE}$, since it is positive of the equilibrium line for hydrogen evolution. Hence, hydrogen evolution is thermodynamically not possible and hydrogen embrittlement can, therefore, be excluded. This clearly explains the relevance and the effectiveness of this threshold. In contrast, it is evident that meeting $-0.95 V_{CSE}$ as most positive and concurrently $-0.97 V_{CSE}$ as most negative potential requirements is technically not possible. Consequently, hydrogen evolution and hence embrittlement on steels with increased yield strength must be expected, if effective CP has to be ensured. In this context the wording of EN 12954:2001 has to be considered:

"limiting critical potential should be determined by testing in each single case for pre- and post-tensioning steels with yield strength $> 700 N/mm^2$. In any case potentials lower than $-1.1 V_{CSE}$ should be considered dangerous."

Prestressing steels in concrete are embedded in a concrete of about pH 13.5. In such highly alkaline environment, the hydrogen evolution is excluded at IR-free potentials more positive than $-1.11 V_{CSE}$. This is in line with the requirement in EN 12954:2001 as shown with the green dot in **Figure 5**. The value is more positive than the hydrogen evolution line and hydrogen evolution is thermodynamically excluded. This again confirms that it is not possible to link the threshold of $-1.2 V_{CSE}$ to hydrogen embrittlement, which is 100 mV more negative and usually associated with lower pH values in the range of pH 12 as illustrated by means of the red dot in **Figure 5**.

This consideration has another important implication: If the pH at the steel surface cannot increase due to streaming soft water of pH 7 (as discussed in detail in [1]) the threshold with respect to hydrogen evolution will be at $-0.733 V_{CSE}$. As a consequence, IR-free potentials of $-0.8 V_{CSE}$ will already result in major hydrogen evolution (blue dot in **Figure 5**). If the increased pH at the steel surface cannot be guaranteed (e.g. in poor bedding conditions and streaming soft water) or in case of anaerobic conditions, the occurrence of relevant hydrogen evolution must be expected even at IR-free potentials more positive than $-0.85 V_{CSE}$ in case of cathodic protection. It is evident that it is impossible to ensure effective cathodic protection in absence of relevant hydrogen evolution in such conditions. The claim that CP is possible without relevant quantities of hydrogen evolution for buried structures is, therefore, wrong and misleading.

While it is readily possible to assign a potential threshold with respect to hydrogen evolution, there is significant debate with respect to the yield strength that makes a steel susceptible to hydrogen embrittlement. In our view it is technically impossible to determine such a threshold with respect to the yield strength, since in mild sour applications in presence of carbon dioxide and hydrogen sulphides it is well known that even pipeline steels with yield strength below $550 N/mm^2$ show hydrogen embrittlement and cracking. Correspondingly crack formation in association with hydrogen cannot be excluded for any pipeline steel irrespective of its yield strength. In this sense a more detailed consideration is required with respect to the associated mechanism. As described above the hydrogen entering the steel will result in decohesion within the iron atoms in front of the crack tip and generate voids in the metal (white zones at the crack tip in **Figure 4**). These voids will contribute to the crack growth by promoting plastic flow at the crack tip as a result of decreasing the yield strength as suggested by Fessler [10]. This is in line with the increased creep reported by Parkins [11] caused by hydrogen loading of the steel.

Increasing creep by promoting plastic flow will clearly be more pronounced at a high strength steel with high yield strength. These materials are usually under higher mechanical load, so that the plasticising effect of hydrogen will result in a more pronounced creep. In contrast a steel that has less mechanical load due to its poorer mechanical properties the plasticising effect will result in less creep. For this reason, a high strength steel is much more susceptible to failure as a result of hydrogen embrittlement. However, this effect is solely due to the enhanced creep as a result of higher mechanical load, rather than the susceptibility of the steel itself. Based on this consideration it is technically impossible to assign a threshold with respect to yield strength. The decohesion of the iron atoms will always occur and hence the crack formation and propagation of the crack will be impossible to be excluded. However, the lower mechanical load of steels with a lower yield strength will result in a less pronounced creep, and the crack propagation will, therefore, be slower.

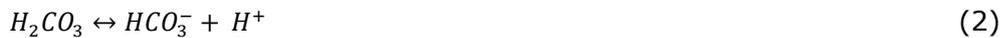
The accumulation of hydrogen in front of the crack tip has another relevant implication with respect to crack propagation: there is a need for continued supply of hydrogen to keep the process going, since each decohesion process will release some of the trapped hydrogen. Based on this consideration it may be expected that an increased supply rate of hydrogen should result in a faster crack propagation.

This aspect readily explains the pronounced effect of hydrogen cracking of mild steels in sour electrolytes that usually occurs in absence of cathodic protection. Since the corrosion process is driven by hydrogen reduction an increased adsorption into the metal matrix may be expected based on the process shown with the red circles in **Figure 2**. In the presence of carbonates and sulphides the formation of surface oxide films is hindered, and this will further drive the corrosion process and the associated hydrogen evolution, contributing to the fast hydrogen absorption, decohesion and crack propagation. It is relevant to understand that even for hydrogen embrit-

tlement of prestressing steel in concrete usually the local anode with the associated acidification within the alkaline mortar environment is considered to be the source of hydrogen and the reason for the failure of the component even within one year. These effects occur in absence of any CP simply as a result of hydrogen generation caused by a local corrosion process. These observations are fully in line with the above discussion: Hydrogen embrittlement is possible in absence of cathodic protection. The corrosion process in near neutral or mildly acidic environment is sufficient to cause hydrogen embrittlement.

3.3. The effect of carbon dioxide

The equilibriums carbon dioxide/carbonic acid/bicarbonate/carbonate are of central relevance for both types of SCC. The involved equilibria for carbon dioxide/carbonic acid according to reaction (1), for carbonic acid/bicarbonate according to reaction (2) and for bicarbonate/carbonate according to reaction (3) are shown below.



These dissociation/recombination equilibria are highly pH dependent. A representation of the relative proportions of the involved dissolved species is shown in Figure 6 according to Charles and Parkins [13]. It is evident that above pH 7 there is only a very low concentration of carbonic acid and above pH 9 no carbonic acid may be expected. In contrast at pH 10.4 (that is associated with an IR-free potential of $-0.95 V_{CSE}$) most of the bicarbonate has reacted to carbonate.

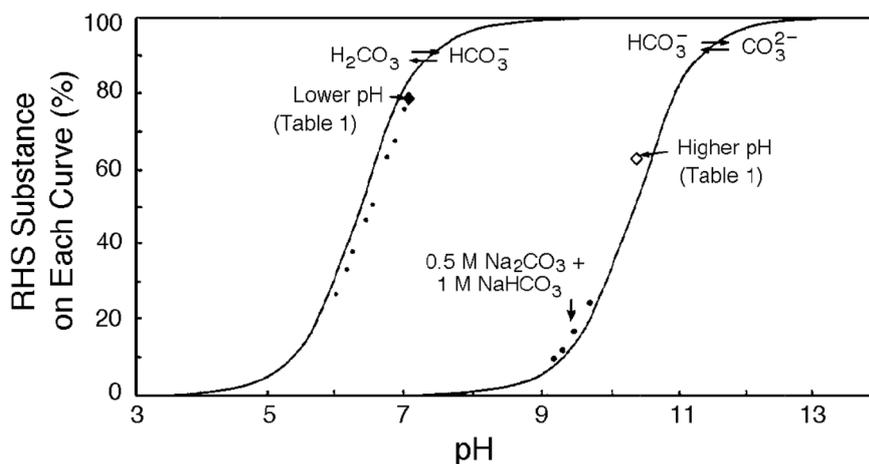


Figure 6: Relative proportions of carbonic acid and bicarbonate as well as bicarbonate and carbonate according to Parkins [13].

The reactions (1) to (3) have important implications for SCC on a cathodically protected steel surface. It is important to understand that all these reactions represent equilibria. As a consequence of this it is not possible to generate unlimited amounts of carbonic acid in water. As soon as the CO_2 from air in exchange with water has reached the equilibrium concentration it is no longer possible to form additional H_2CO_3 as long as the concentration of H_2CO_3 stays con-

stant. In presence of CP, however, a continued generation of alkalinity will occur. It follows from Figure 6 that this generation of alkalinity will cause a reaction of the H_2CO_3 to bicarbonate and ultimately carbonate. The continued withdrawal of H_2CO_3 will cause a continued formation of H_2CO_3 and thus the formation of more carbonates. This process very effectively results in the formation of saturated carbonate solutions as shown in [14]. To explain this with an analogy: A pipeline transporting cold gas will continue to withdraw humidity from the air through condensation. Similarly to the cooling effect of the cold gas, the generation of alkalinity will continue to withdraw CO_2 from the air until saturated carbonate solutions are formed. The Pourbaix diagram for a saturated carbonate solution is shown in Figure 1 by means of the blue lines.

It immediately follows from this discussion that cathodic protection and the accumulation of carbonates in front of the steel surface as a result of alkalinity formation is bound to increase the corrosion domain to higher pH values. These aspects play a major role in combination with SCC.

4. Conclusions

The above discussion highlights some of the relevant aspects associated with SCC. The presented discussion is limited to the key aspects of SCC. Nevertheless, it is possible to draw some conclusion with respect to a number of influencing factors in association with CP:

- Effective cathodic protection eliminates the risk of SCC
- The crack propagation follows the weakest part of the metal
- In the case of NNSCC the weakest part is the hydrogen filled void generated at the crack tip that results in trans granular crack propagation
- The preferred rupture of the passive film the grain boundaries promotes intergranular crack propagation in case of HPSCC
- Both types of SCC are associated with carbonates that play a central role in crack propagation

The discussion of the relevance of hydrogen voids in the case of NNSCC has revealed a number of aspects in association with hydrogen assisted cracking:

- The effect of hydrogen is macroscopically an embrittlement, but microscopically a plasticising
- Hydrogen assisted cracking has to be expected on all steels independent on the yield strength
- In absence of a well-defined pH-value at the steel surface, it is impossible to assign a critical limiting protection potential with respect to hydrogen embrittlement caused by CP
- Since the immunity domain of iron is cathodic of the hydrogen evolution equilibrium line, steel can always corrode under hydrogen evolution and deliver the atomic hydrogen required for the cracking mechanism
- No cathodic protection is required for hydrogen embrittlement to occur, since corrosion of steel can readily generate sufficient quantities of hydrogen
- The cracking rate is influenced by the absolute mechanical load and the supply rate of hydrogen

- Effective CP is inadvertently associated with an unavoidable risk of hydrogen embrittlement on buried structures

While the hydrogen evolution as well as hydrogen embrittlement can be expected in absence of CP, there are some aspects with respect to carbonate accumulation at the steel surface that are relevantly enhanced by CP:

- CP favours the accumulation of carbonates at the steel surface as a result of continued generation of alkalinity
- Increased carbonate concentration increases the pH required for passivation resulting in enhanced corrosion at the crack tip

The discussion of these basic effects reveals some basic mechanisms that need to be taken into account in the context of SCC. Their consequences on the process of crack initiation, crack growth and crack dormancy will be discussed in a following paper.

5. Literature

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