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Thermodynamical Considerations on the Local Chemistry Formed at the Steel-Soil Interface of Cathodically Protected Pipelines

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Abstract

This paper takes a thermodynamical approach to chemical- and electrochemical processes that are likely to occur at cathodically protected steel surfaces buried in sediment. The alkalisation of the near environment caused by cathodic protection (CP) is discussed in view of the well-known Pourbaix-diagram, emphasising that besides the corrosion domain in the diagram at acidic or neutral pH, a strong alkalisation may set up conditions favouring corrosion in a small, high alkaline region in the diagram. Further, from simple solubility theory, it has been reviewed how local alkalisation may cause precipitation of salts at the cathodically protected surface (cathodic scaling). Besides metal hydroxides, these salts are primarily carbonates but also sulphates of earth alkaline cations (Mg^{2+} and Ca^{2+}). Such precipitations may introduce ohmic resistance that adds to the resistance of the soil solution, hence increasing the total pipe to soil ohmic resistance. CP may then produce a local environment, which is strongly alkaline and leading to corrosion when AC is superimposed onto the CP. Alternatively, the alkalisation may create protective layers. Which condition is actually created depends on the chemistry of the soil, in particular the presence of earth alkaline cations, but also pH buffering agents like carbonate. This buffer system is reviewed as well.

Introduction

This paper deals with theoretical considerations on the environment formed nearby cathodically protected steel surfaces buried in soil and the consequences this may have on factors that are considered important in relation to AC induced corrosion.

In general, when assessing the risk of corrosion of a metal exposed in a certain environment, the Pourbaix-diagram relating to the metal-environment system is normally consulted as a first approach. This diagram shows, as a function of the electrochemical potential and the pH, domains for thermodynamical stability of possible corrosion products, and on this basis predicts whether the metal corrodes, passivates or shows immunity to corrosion. In section 1, this diagram (in the case of iron/steel) is reviewed and briefly discussed.

Cathodic protection (CP) of buried pipelines involves a displacement in the cathodic direction of the electrochemical potential of the pipeline. A side effect of this measure is enhancement of the cathode reactions occurring at the pipe surface. Whether these reactions include reduction of hydrogen ions or reduction of oxygen (if aerobic conditions are present) the net result is a pH increase nearby the pipe surface since acid (H^+) is consumed by any of these reactions:

$$2H^+ + 2e^- \rightarrow H_2 \tag{1}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{2}$$

Depending on the chemistry of the soil solution, the raise in pH may cause precipitation of solid products (cathodic scaling) at the pipe surface. Based on the chemical laws of solubility products, the possibility of precipitation of a number of common solid substances on a cathodically protected pipe surface is discussed in section 2.

The production of alkalinity (OH^--ions) typically results in a rise in solution pH, however, presence of chemical buffer systems in the environment may depress this pH increase to a certain extent depending on the buffer capacity of the system. In soil solutions, the carbonate-bicarbonate system, which is discussed in brief terms in section 3, is an important buffer system.

The ohmic resistance of the soil in which the pipe is exposed may be a key parameter controlling the level of the IR-drop occurring when polarising the pipe by a cathodic protection system. It may also be a key parameter controlling the level of AC current flowing out of a coating defect when the pipe is subjected to AC voltage superimposed onto the CP. In section 4, chemical factors determining the ohmic resistance of the soil are discussed in view of molar ion conductivity theory. The possible effect of precipitation of solids on the ohmic resistance is included in the discussion.

1. The Pourbaix-Diagram

The Pourbaix-diagram[1] provides a measure of the condition of e.g. steel as a function of the electrochemical potential of the steel and the pH existing in the solution adjacent to the steel. The diagram is prepared on a thermodynamical basis, but verified on an experimental and empirical basis as well. Hence, it is considered to be a powerful tool when making a first judgement of the corrosion situation.

The Pourbaix diagram is constructed by considering the thermodynamics of a range of chemical- and electrochemical reactions/equilibria such as:

$$Fe = Fe^{2+} + 2e^- \tag{3}$$

$$Fe + 2H_2O = HFeO_2^- + 3H^+ + 2e^- \tag{4}$$

$$2Fe + 3H_2O = Fe_2O_3 + 6H^+ + 6e^- \tag{5}$$

$$3Fe + 4H_2O = Fe_3O_4 + 8H^+ + 8e^- \tag{6}$$

$$Fe^{2+} = Fe^{3+} + 2e^- \tag{7}$$

$$2Fe^{2+} + 3H_2O = Fe_2O_3 + 6H^+ + 2e^- \tag{8}$$

$$3Fe^{2+} + 4H_2O = Fe_3O_4 + 8H^+ + 2e^- \tag{9}$$

$$2Fe_3O_4 + H_2O = 3Fe_2O_3 + 2H^+ + 2e^- \tag{10}$$

In addition to the above electrochemical equilibria (3-10), the thermodynamics of the hydrogen equilibrium as presented by either of the equilibria:

$$2H^+ + 2e^- = H_2 \tag{11}$$

$$2H_2O + 2e^- = H_2 + 2OH^- \tag{12}$$

and the thermodynamics of the oxygen equilibrium as presented by either of the equilibria:

$$O_2 + 2H_2O + 4e^- = 4OH^- \tag{13}$$

$$O_2 + 4H^+ + 4e^- = 2H_2O \tag{14}$$
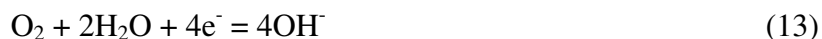
are taken into account. Reactions (11-14) represent the common cathode reactions in a corrosion element.

The Pourbaix concept involves applying the Nernst equation on all possible electrochemical equilibria of the types described above. For the general equilibrium reaction:

$$aA + bB \rightarrow cC + dD + ne^- \qquad (15)$$

the Nernst equation becomes:

$$E_0 = E^0 + 2.3 \cdot \frac{R \cdot T}{n \cdot F} \log \frac{[A]^a \cdot [B]^b}{[C]^c \cdot [D]^d} \qquad (16)$$

where E_0 denotes the equilibrium potential, E^0 denotes the standard equilibrium potential, R is the gas constant, T is temperature in Kelvin, n is number of electrons involved in the process, F is Faradays number, and [A] is the activity (~ concentration) of the species A.

Implementing measures for activities (gases: partial pressure of the gas, solids = 1, dissolved species arbitrary e.g. 10^{-6} mol/L), the Nernst equation applied on all relevant equilibria yields equilibrium lines (E_0 as a function of pH) ready to fit into the pH-potential diagram. Comparing the relative position of these lines makes it possible to establish which species are stable in each pH-potential region. Based on this, the domains (corrosion, passivity, immunity) in the Pourbaix-diagram can be established, figure 1.
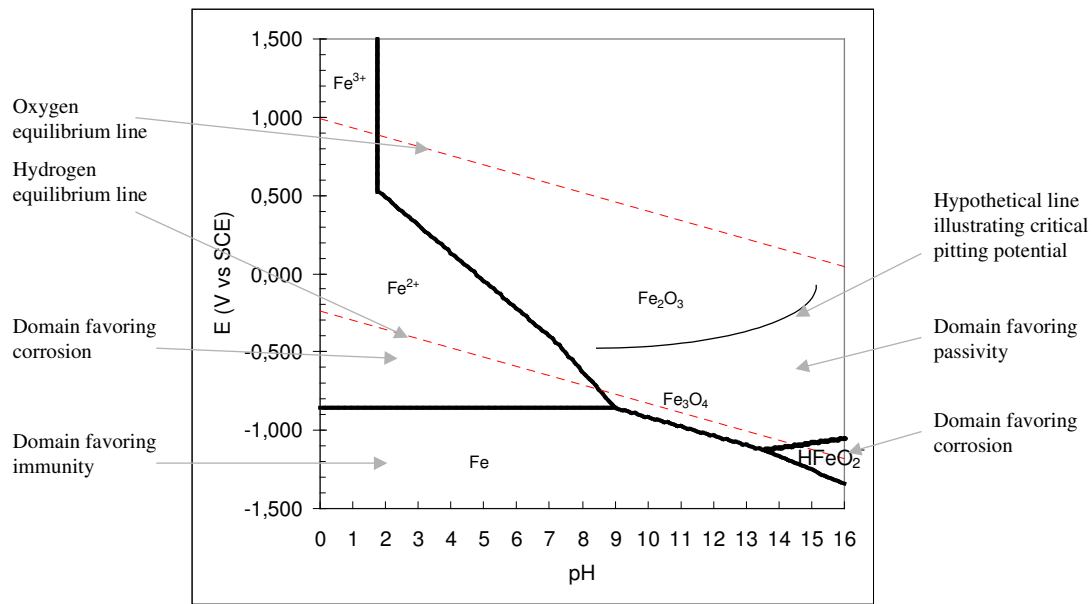

Figure 1. Pourbaix diagram of steel in aqueous environment showing the corrosion condition (actively corroding, passive or immune) as a function of the electrochemical potential and pH.

Active corrosion is expected in case Fe^{2+}/Fe^{3+} or $HFeO_2^-$ is stable (defining the two corrosion domains in the diagram), immunity is expected in case Fe is stable, whereas passivity is expected in case ferrous oxides (Fe_2O_3, Fe_3O_4) or ferrous hydroxides ($Fe(OH)_2$, $Fe(OH)_3$) are stable. Oxygen reduction can be utilised as the cathode process at potentials lower than defined by the oxygen equilibrium line, and reduction

of H^+ can be utilised as the cathode process at potentials lower than defined by the hydrogen equilibrium line.

The above electrochemical equilibria are just examples. Several others are outlined originally by Pourbaix[1] including those taking into account the passivating effects of ferrous hydroxides like $Fe(OH)_3$ in addition to the ferrous oxides. However, the basic domains of the diagram outlined in figure 1 can be regarded as a general guideline.

The conditions defining whether or not steel corrodes in the simple DC-situation may inspire also when dealing with the AC-situation. It may even be suggested that the AC introduces no mechanisms of corrosion that are not known already, hence simply creates a condition that would cause corrosion in a pure DC condition as well. This condition however, may be realised only during a short period of time during the AC-cycle, e.g. at some interval of the anodic half wave of the AC.

In addition to the above, pitting corrosion may propagate particularly if chloride is present in the environment. The pitting phenomenon requires a passive surface to be locally disrupted by e.g. the chloride thus creating a localised self-catalytic corrosion reaction usually with a high penetration rate. Further, for a certain concentration of chloride (activating ion causing pit initiation), the potential of the steel has to be raised above a certain critical value (the critical pitting potential, CPP) before pitting initiates. The CPP shifts towards more cathodic values when raising the concentration of the activating ion. A higher pH usually stabilises the passivating layer of the steel, thus demanding a higher concentration of the activating ion to be present before pitting sets on. In figure 1, this has been illustrated by the hypothetical line (corresponding a certain critical concentration of activating ions like chloride) giving the critical pitting potential in the passive region of the Pourbaix-diagram.

2. Precipitation of Solids at the Pipe Surface

When added into a solution, a salt (M_mX_n) may dissociate and dissolve in the solution:

$$M_mX_n \;=\; mM^{n+} + nX^{m-} \tag{17}$$

The solubility product of the salt is expressed as (assuming that the activity of the dissolved species can be regarded as equal to the concentration):

$$K_{sp} = [M^{n+}]^m \cdot [X^{m-}]^n \tag{18}$$

Accordingly, if the ions of the salt (M^{n+}, X^{m-}) are present in concentrations, which exceed the solubility product (18), a solid precipitation (M_mX_n) forms. Since precipitated solids do not contribute to the conductivity of a solution, the precipitation of solids inevitably leads to an increase in the ohmic resistance in the soil.

The solubility products or equilibrium constants for selected equilibria are assembled in table 1.

Equilibrium	Solubility product, K_{sp}
Hydroxides	
$Na^+ + OH^- = NaOH$	$3.05 \cdot 10^{17}$
$K^+ + OH^- = KOH$	$4.03 \cdot 10^{10}$
$Fe^{2+} + 2OH^- = Fe(OH)_2$	$4.87 \cdot 10^{-17}$
$Mg^{2+} + 2OH^- = Mg(OH)_2$	$5.61 \cdot 10^{-12}$
$Ca^{2+} + 2OH^- = Ca(OH)_2$	$4.68 \cdot 10^{-6}$
Carbonates	
$2Na^+ + CO_3^{2-} = Na_2CO_3$	$5.02 \cdot 10^{0}$
$Na^+ + HCO_3^- = NaHCO_3$	$4.00 \cdot 10^{-1}$
$2K^+ + CO_3^{2-} = K_2CO_3$	$1.21 \cdot 10^{5}$
$K^+ + HCO_3^- = KHCO_3$	$9.59 \cdot 10^{0}$
$Ca^{2+} + CO_3^{2-} = CaCO_3$	$4.96 \cdot 10^{-9}$
$Mg^{2+} + CO_3^{2-} = MgCO_3$	$6.82 \cdot 10^{-6}$
$Fe^{2+} + CO_3^{2-} = FeCO_3$	$3.07 \cdot 10^{-11}$
Sulphates	
$2Na^+ + SO_4^{2-} = Na_2SO_4$	$2.30 \cdot 10^{-1}$
$2K^+ + SO_4^{2-} = K_2SO_4$	$3.97 \cdot 10^{-6}$
$Ca^{2+} + SO_4^{2-} = CaSO_4$	$7.10 \cdot 10^{-5}$
$Mg^{2+} + SO_4^{2-} = MgSO_4$	$2.13 \cdot 10^{5}$
$Fe^{2+} + SO_4^{2-} = FeSO_4$	$3.49 \cdot 10^{0}$

Table 1. Solubility products for selected solids that potentially precipitate in soil solutions.[3] Calculated from Gibbs functions / chemical potential theory.

As mentioned, the solubility data can be used to derive critical concentrations of ions above which a solid precipitation forms (equations (17) and (18)).

2.1 Precipitation of hydroxides

Figure 2 shows the critical concentration of various cat-ions as a function of pH. As observed from the right figure, a precipitation of NaOH or KOH demands extremely (unrealistic) high concentrations of the cat-ions (Na^+, K^+) before solid precipitates form, whereas the divalent cat-ions (Ca^{2+}, Mg^{2+}, and Fe^{2+}) easily form precipitates in the form of hydroxides. The ferrous hydroxide is a special case, since the corrosion of iron in alkaline environments may involve a passivation due to this species, however, according to the Pourbaix-diagram, the soluble $HFeO_2^-$ may form in strong base.

The figure to the left outlines the relative tendency of Mg^{2+} and Ca^{2+} to form precipitation of hydroxides. As observed, the affinity of Mg^{2+} to form precipitate is 6 orders of magnitude higher than the affinity of Ca^{2+}.
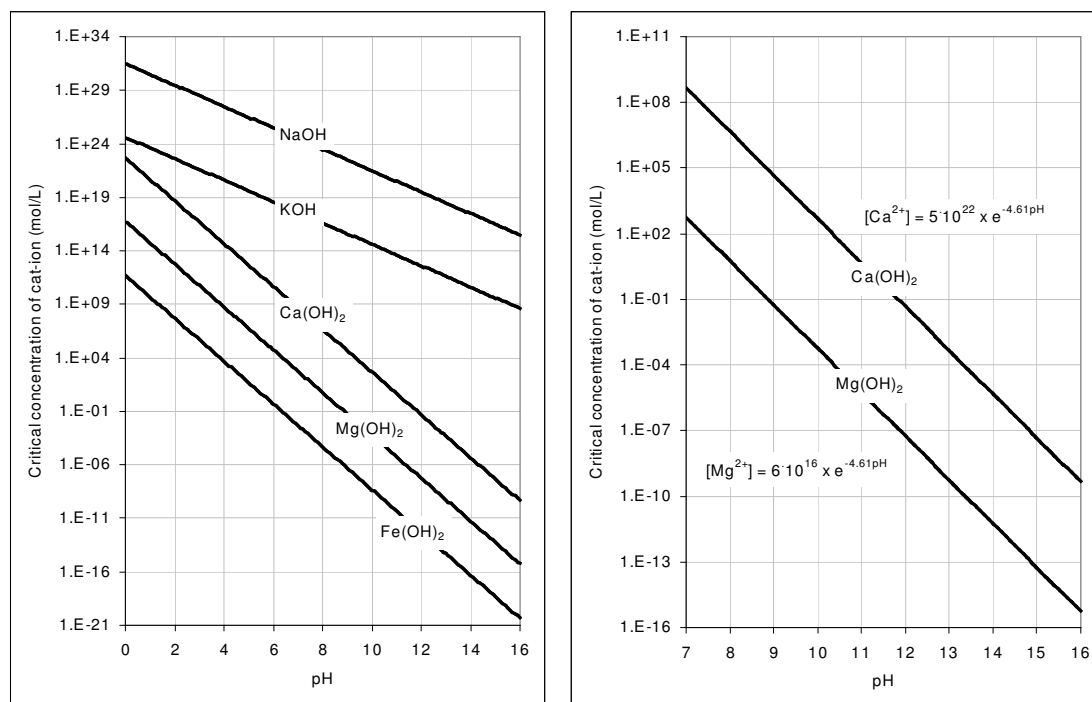
1.6

Figure 2. Critical concentration of cat-ion for precipitation of hydroxides as a function of pH (concentration of OH⁻).

2.2 Precipitations of carbonates

Figure 3 shows the critical concentration for precipitation of carbonates of various cat-ions as a function of carbonate concentration. Again the figure to the right shows that precipitations based on monovalent cat-ions demands very high (unrealistically high) concentration of the cat-ion before a carbonate precipitate form, whereas the divalent ions (outlined in the figure to the left) more easily form precipitates. However, the affinity of Fe^{2+} to form solid carbonate is two decades higher than that of Ca^{2+} and 5 decades higher than that of Mg^{2+}.
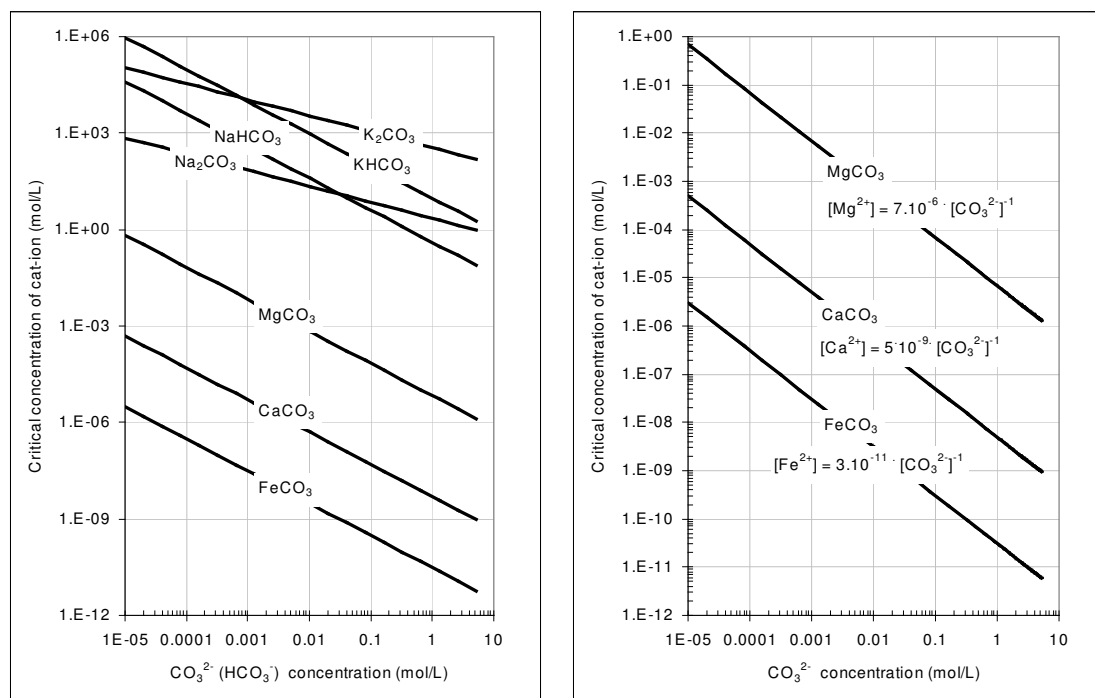
Figure 3. Critical concentration of cat-ion for precipitation of carbonates.

2.3 Precipitations of sulphates

The affinity of the cat-ions to form solids from sulphate is illustrated in figure 4. Potassium-sulphate (K_2SO_4) and calcium-sulphate ($CaSO_4$) forms reasonable easy, while sulphates of Mg, Fe and Na demand quite high concentrations.
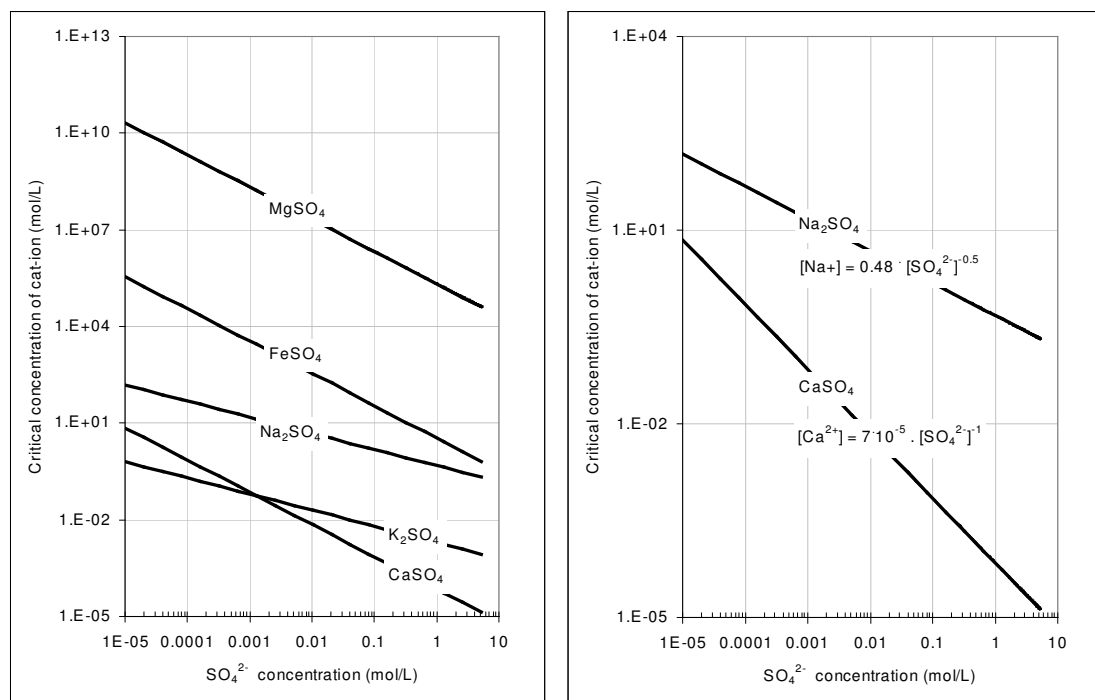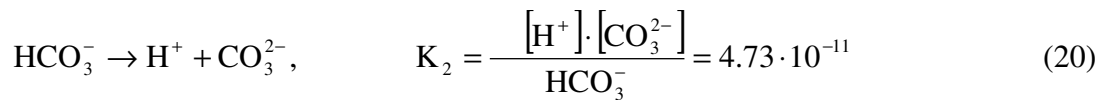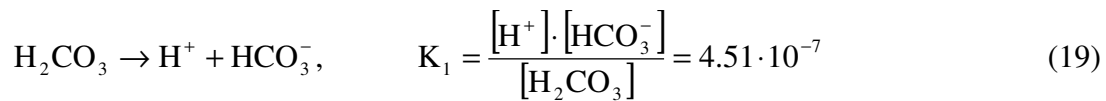

Figure 4. Critical concentration of cat-ion for precipitation of sulphates.

3. Considerations on Buffer Capacity

A buffer solution is defined as a solution that resists changes in pH as a result of either dilution or small additions of acid or base.[4] The buffer capacity of such solution is defined as the number of equivalents of strong acid or base to cause 1 litre of the solution to undergo a 1-unit change in pH. The most effective buffer solutions contain large and approximately equal amounts of a conjugate acid-base pair.

In soil solutions, the carbonate/bicarbonate system is a very important buffer system that stabilises pH due to the reactions:

$$H_2CO_3 \rightarrow H^+ + HCO_3^-, \qquad K_1 = \frac{[H^+] \cdot [HCO_3^-]}{[H_2CO_3]} = 4.51 \cdot 10^{-7} \qquad (19)$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-}, \qquad K_2 = \frac{[H^+] \cdot [CO_3^{2-}]}{HCO_3^-} = 4.73 \cdot 10^{-11} \qquad (20)$$

The maximum buffer capacity is at the pH where the conjugate acid and base pair is in equal concentration, hence, the pH at which the buffer is at maximum can be calculated according to:

$$pH = -\log[H^+] = -\log K \qquad (21)$$

meaning that the carbonate system has two pH-values (6.36 and 10.33) where the buffer effect is at maximum. The distribution as a function of pH of the three carbonate species can be calculated using (19) and (20), see figure 5.
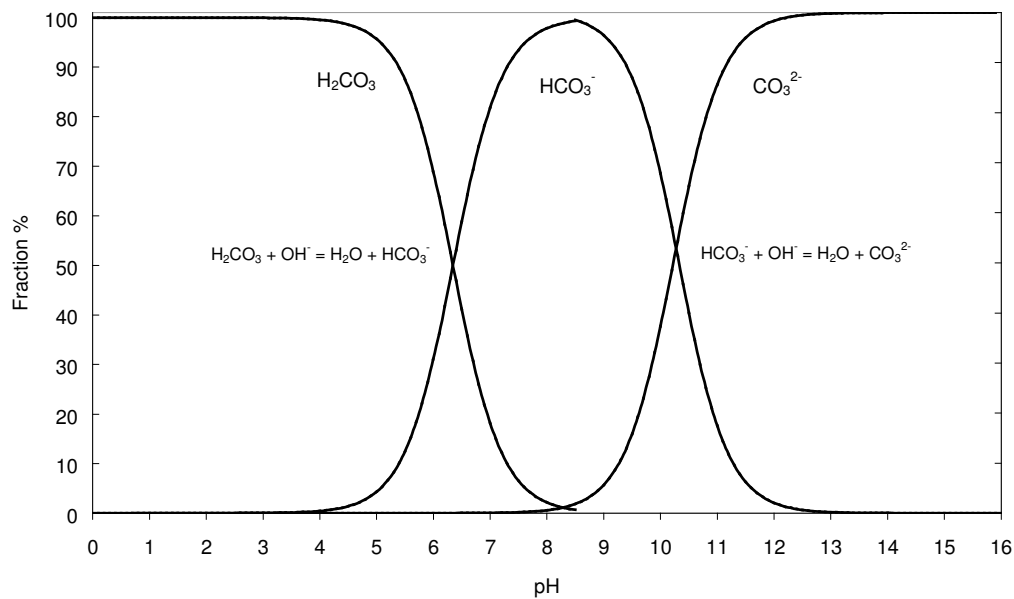

Figure 5. Distribution of carbonate species as a function of the pH.

4. Considerations on Soil Conductivity and Ohmic Resistance

For solutions of simple, pure electrolytes, equivalent molar ionic conductivity (conductivity per unit concentration of charge) is defined as:[5]

$$\Lambda^0 = \lambda_+ + \lambda_- \tag{22}$$

where λ_+ and λ_- are equivalent ionic conductivities of the cation and anion respectively. Hence, for ideal solutions at infinite dilution (no interaction between present ions), the conductivity of the solution can be calculated by:

$$\kappa = \sum_i C_i \cdot \lambda_i \tag{23}$$

where C_i is the concentration of the ion *i*.

At conditions different from "infinite dilution", the molar ionic conductivity may be expressed as:[5]

$$\Lambda(C) = \Lambda^0 - K \cdot \sqrt{C} \tag{24}$$

K is a coefficient that depends on the nature of the dissolved salt (MX, M_2X, etc.).

Table 2 outlines the equivalent ionic conductivity for selected ions.

Cat-ion	Equivalent ionic conductivity λ_+ $S \times cm^2 \times mol^{-1}$	An-ion	Equivalent ionic conductivity λ_- $S \times cm^2 \times mol^{-1}$
H^+	349.6	OH^-	198.0
Na^+	50.1	Cl^-	76.3
K^+	73.5	SO_4^{2-}	160.0
Fe^{2+}	108.0	HCO_3^-	44.5
Mg^{2+}	106.0	CO_3^{2-}	138.6
Ca^{2+}	118.5	NO_3^-	71.4
		HPO_4^{2-}	66.0
		$H_2PO_4^-$	33.0
		$CH_3CO_2^-$	40.9

Table 2. Equivalent ionic conductivities for various ions potentially present in soil solution.[3]

If solid precipitation is caused by increased alkalinity due to CP, the increase in ohmic resistance would be realised only locally at the cathodically protected surface; however, it may significantly contribute to the overall ohmic resistance existing between the pipe and remote earth. Besides the soil resistance and the solid

precipitation, the area of the coating defect is a major parameter in controlling the ohmic resistance.[2] The term "solution resistance" which is usually applied for the ohmic resistance of an electrochemical system accordingly does not cover the present situation, and the term "spread resistance" has been used frequently in relation to AC corrosion.[6,7]

Summary – conclusions

- On a purely theoretical level, this paper dealt with a review of the Pourbaix-diagram for the system $Fe-H_2O$, with possible precipitation of solids at cathodically protected surfaces using calculations of solubility products, with the pH-buffering effect of the carbonate-bicarbonate system, and with considerations on soil conductivity and ohmic resistance.

- The Pourbaix-diagram predicts pH-potential regions in which the steel is either corroding actively, showing immunity to corrosion, or passivating due to formation of protective oxides or hydroxides. Besides the active corrosion domain in the diagram at acidic- or neutral pH, it is emphasised that a small region of active corrosion is predicted at very high pH (>14). It is acknowledged as well that in case aggressive activating ions like chloride are present in the environment, pitting corrosion may occur in the form of an autocatalytic local attack initiating when the passive film is penetrated by said aggressive ions. Both general corrosion in the mentioned pH-potential domains and pitting in the passive domain is relevant in the general "DC-corrosion" case and should accordingly be considered as well in the case of superimposed AC voltage (AC corrosion).

- Local alkalisation of the environment at a cathodically protected steel surface may form solid precipitations of salts. These salts are (besides metal oxides and hydroxides) primarily carbonates, but also sulphates, of the earth alkaline cations Mg^{2+} and Ca^{2+}. Such precipitations are expected to introduce an ohmic resistance which adds to the resistance of the soil solution itself, thus causing an increase in the total pipe to soil ohmic resistance (spread resistance). This scenario is expected to be beneficial in the sense that the risk of AC corrosion decreases.

- The cathodic protection system may cause a local environment at the steel surface, which is strongly alkaline leading to active corrosion as predicted by the high alkaline corrosion region of the Pourbaix-diagram. Alternatively, the CP may lead to a more moderate alkalisation simply creating a situation favouring passivation of the steel surface. Which of the two situations are actually realised may depend on the pH buffer capacity of the ground water chemistry, perhaps in particular the presence of carbonate that usually buffers the system at pH around 10.

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