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The Role of Rusts in Corrosion and Corrosion Protection of Iron and Steel

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Abstract

The processes of atmospheric corrosion of iron and steel and the properties of corrosion products (rusts) are modeled based on a quantitative evaluation of the chemical reactions pertaining to corrosion to elucidate the conditions with which corrosion-protective rust films form. Based on the model, it is suggested that in the initial stage of corrosion, in the rusts, the pH of the aquatic system is maintained at 9.31 owing to an equilibrium with iron(II) hydroxide and the rate of air-oxidation at this pH is very fast, and that dense, self-repairing rust films form, protecting the underlying iron and steel. However, after corrosion stops, the rust film deteriorates due to the dissolution and shrinkage by aging, and the deteriorated rust film separates the anode and cathode reaction products (Fe^{2+} and OH^- ions) to cause crevice corrosion. The air-oxidation of iron(II) in anode channels without the presence of OH^- ions results in strongly acidic solutions (pH 1.41), causing acid corrosion. It is proposed that good catalysts (e.g. copper(II) and phosphate ions) accelerate the air-oxidation at low pH, delaying the crevice- and acid-corrosion stages. Further, it is argued that iron compounds with negative charges due to the non-stoichiometric proportions of the lattice oxide ions and metal ions (solid oxoanions of iron) exhibit stable cation-selective permeability even with a drop in pH. Rust films including such compounds would stop the passage of aggressive anions and act to protect iron and steel.

Keywords: Iron, Low alloy steel, Modeling studies, Atmospheric corrosion, Rust

1. Introduction

“Weathering steels” have been developed with the idea that rusts formed by corrosion shield the metal from environments and inhibit further corrosion. This is represented by the saying that “rusts stop rusting”, which stands for the inhibition of corrosion by the corrosion products. It is considered that well working weathering steels require little maintenance, and recently extensive application of weathering steels is planned for bridges, buildings, and in other construction. However, there are cases where rusts accelerate corrosion as suggested by the saying that “rusts invite rusting” where rusts are not corrosion protective but corrosion promoting. The loss of the protective abilities of rusts is very unfavorable and fatal for weathering steels. To improve the performance and reliability of weathering steels, it is important to elucidate the role of rusts in corrosion and to ensure the development of protective properties of rusts in a wide range of environmental conditions.

1.1. Passive oxide films

The idea of corrosion protection by corrosion products can be traced back to the discovery of “passivation” of iron, where iron keeps its metallic luster without corroding in concentrated nitric acid solutions. Dipping iron in chromate solutions or the application of appropriate anodic potentials to iron also leads to passivation. Passivation of iron requires strongly oxidizing environments, and passivity is attributed to protective oxide films formed by oxidation of iron as first proposed by Faraday. In passivation of iron, iron is oxidized instantaneously in strongly oxidizing conditions to form oxides containing iron(III) with very low solubilities, and this oxide is assumed to be directly formed in close connection with the crystal structure of the metal [1]. This little soluble oxide film isolates the metal surface from corrosive environments and prevents further corrosion. When a film in an oxidizing environment is imperfect or broken, iron exposed to the solution through the film defects is immediately turned into the little soluble oxides containing iron(III) at the defect sites and the film is repaired. As a result, the passive oxide film is not merely a static physical barrier that is formed only once at a certain stage of passivation, but it is a self-maintaining dynamic barrier that is constantly repaired and renewed.

The dimensions, chemical compositions, and crystal structures of the passive oxide film have been the object of studies. Nagayama and Cohen [2] proposed that passivated iron is covered with a thin film of $\gamma\text{-Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ in a cubic system with a thickness of 1-3 nm. The suggested characteristics of the passive oxide film have generally been supported by subsequent detailed studies with spectroscopic, microscopic, diffraction, and other techniques. However, not all studies have agreed, indicating that the film characteristics depend on the treatment of iron and the kind of solution in which the iron is passivated.

1.2. Characterization of rusts and rust formation

In atmospheric corrosion, steels in ordinary structures, not necessarily in strongly oxidizing environments, corrode to form rusts. These rusts are generally coarse, porous, and flaky substances without the properties necessary to shield the steel from environments, and so do not have protective and self-maintaining properties like passive oxide films.

Corrosion resistance in weathering steels indicates the formation of special types of rusts, and studies have been made of the characteristics and properties of rusts. It has been reported that α -, β -, $\gamma\text{-FeOOH}$, $\gamma\text{-Fe}_2\text{O}_3$, Fe_3O_4 , and amorphous oxyhydroxides are included in the rusts [3-8]. It is assumed that small rust particles are packed densely to form a tightly adherent film that acts as a barrier protecting the steel from further corrosion, and nano-sized $\alpha\text{-FeOOH}$ and amorphous oxyhydroxides of iron(III) are considered protective [4, 5]. However, rust components show some solubility to water, and if a protective rust film forms and further corrosion stops, then without the supply of iron ions and hydroxide ions due to corrosion, the protective film deteriorates with time forming defects by dissolution. The rust film is not permanently maintained as protective, and corrosion will start again through the defect sites. Rusts providing just a mechanically dense and tightly adherent film do not seem adequate to develop into a long-lasting film to shield iron and steel from water and oxygen.

1.3. The purpose of this investigation

In this investigation, it is pointed out that for rusts to develop into a long-lasting

protective film, constant self-repairing of the film by fusing particles together, by filling up defect spaces, or by other means is necessary, like the passive oxide film that is self-maintained by repairing defects. The atmospheric corrosion of iron and steel is composed of several reactions, e.g., formation of hydroxide ions at the cathode, dissolution of iron(II) and alloying metal(II) ions at the anode, air-oxidation of iron(II) to iron(III), iron(III) hydroxo-complex formation, precipitation and dissolution of iron(III) hydroxide, magnetite, and ferrites, transformation of these compounds to rusts by aging, ion adsorption on rusts, and other reactions. As a result, an atmospheric environment that brings about the corrosion of iron and steel can be regarded to constitute an aquatic system. It is important to assess these reactions proceeding in aquatic systems quantitatively to elucidate the characteristics and properties of rusts necessary to form a long-lasting protective film. Kinetic and equilibrium calculations are made for the reactions occurring during the rust formation, and the composition of aquatic systems around the corroding region at different stages of corrosion is obtained. A scenario of the corrosion process is deduced based on the calculated results, and the observed results for the atmospheric corrosion are explained from the scenario. Further, the conditions where a self-maintaining protective rust film develops are discussed. For the formation of an adherent dense rust film, it is pointed out that the acceleration of air-oxidation of iron(II) during corrosion is important. With rapid air-oxidation, the deposition of iron(III) hydroxide completes within the film before iron(II) ions can leak out from the film, which results in the plugging of rust defects and hence the densification and self-repair of the film. Possible mechanisms to enhance the oxidation rate during corrosion are suggested. For rusts where defects remain, it is noted that cation-selective permeability of the rusts brings about protective properties because corrosive anions are prevented from penetrating through the defects. The conditions with which the cation-selective permeability develops in rusts are discussed, and several compounds that are cation-selective over a wide range of conditions are suggested as potential protective components in rusts.

This paper studies the role of rusts in corrosion and corrosion protection of iron and steel by analyzing the related chemical reactions in aquatic systems based largely on the author's previous work. In the previous individual works, the chemical reactions themselves were the interest of the studies, and the relation to the corrosion of iron and steel was explored only superficially. However, the investigation in this paper aims at the

elucidation of corrosion phenomena by integrating the author's previous works and offers insights into the mechanism of corrosion and the role of rusts in corrosion and corrosion protection. The results obtained advance the knowledge of corrosion and can be applied to develop weathering steels.

2. Observed results for rust formation

“The Research Group of Rust Chemistry” (Chairman: Prof. T. Ohtsuka) of the Japan Society of Corrosion Engineering has carried out the characterization of rusts formed on weathering steels and inspected sites of corrosion in weathering-steel bridges. The results of these activities as well as the findings for the corrosion of iron and steel obtained so far [3-8] can be summarized as,

- a) In wet environments containing chlorides, iron and steel corrode forming rusts with brownish colors.
- b) Occasionally rust surfaces are stained yellow and it appears that “rust fluids” have leaked out, and the new yellow rust formed is called “flowing rust”. The “flowing rust” indicates that corrosion is not a static process, but that dynamic changes occur during rusting.
- c) Rusts develop into a layer structure with repeating dense and coarse layers.
- d) The chloride ions are concentrated at layer boundaries, the most notably at the rust/substrate interface.
- e) The application of wet pH-test paper to rust surfaces exposed by removing the surface layers clearly indicates the presence of acidic ($\text{pH} < 3$) and alkaline ($\text{pH} > 10$) regions.
- f) Microscopically, many cracks form along the layer planes as well as in the direction vertical to the layer planes, and voids are also found in rusts.
- g) On steels constantly exposed to water, rusts keep growing and finally detach as flakes or even as slabs at the substrate/rust interface.
- h) Rusts formed on heavily corroded steels contain approximately 25% of Fe_3O_4 , 10% of $\alpha\text{-FeOOH}$, 5% of $\beta\text{-}$ and $\gamma\text{-FeOOH}$ respectively, with the balance amorphous components.

3. Scenario of atmospheric corrosion

According to the calculated compositions of the aquatic system of the corroding region to be discussed here, a scenario of the corrosion process will be deduced, and the observed results of corrosion described above are explained based on the scenario.

3.1. Initial corrosion and development of protective rust films

3.1.1. Formation of iron(II) and hydroxide ions by corrosion

Iron and steel surfaces are covered with a thin oxide layer of Fe_3O_4 or $\gamma\text{-Fe}_2\text{O}_3$ from the very beginning due to exposure to air. In the presence of water and oxygen, metallic iron is thermodynamically unstable as apparent from the Pourbaix diagram [9], and corrosion proceeds according to the electrochemical mechanism as shown in Fig. 1. Iron is oxidized at the anode to dissolve Fe^{2+} ions, dissolved oxygen is reduced at the cathode to form OH^- ions, and these are combined to deposit iron(II) hydroxide solid, $\text{Fe}(\text{OH})_2(\text{s})$, when the solubility is exceeded. This corrosion is enhanced by the presence of electrolytes, e.g., NaCl, (Section 2, a); the electrolyte anions Cl^- compensate the positive charge of Fe^{2+} , resulting in FeCl_2 at the anode, and the electrolyte cation Na^+ compensates the negative charge of OH^- , generating NaOH at the cathode. With electrolytes, $\text{Fe}(\text{OH})_2(\text{s})$ also forms by the reaction between FeCl_2 and NaOH, because the OH^- ions have a larger mobility than other anions and are more reactive to Fe^{2+} ions. The presence of NaCl in environments is assumed throughout this paper.

The $\text{Fe}(\text{OH})_2(\text{s})$ deposited by corrosion shows solubility to water, and the Fe^{2+} ions dissolved tend to hydrolyze weakly. The composition of an aquatic system including $\text{Fe}(\text{OH})_2(\text{s})$ can be obtained by equilibrium calculations, and the reactions and equilibrium constants reported in [10] are shown below. The solubility product of $\text{Fe}(\text{OH})_2(\text{s})$, $K_{\text{s,II}}$, is given as:

$$\text{Fe}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Fe}^{2+} + 2\text{OH}^-, \quad K_{\text{s,II}} = [\text{Fe}^{2+}][\text{OH}^-]^2 = 10^{-14.5} \text{ mol}^3 \text{ dm}^{-9} \quad (1)$$

The stability constants of Fe(II) hydroxo complexes, $\beta_{1,\text{II}} \sim \beta_{3,\text{II}}$, are:

$$\text{Fe}^{2+} + \text{OH}^- \rightleftharpoons \text{FeOH}^+, \quad \beta_{1,\text{II}} = [\text{FeOH}^+]/([\text{Fe}^{2+}][\text{OH}^-]) = 10^{4.5} \text{ mol}^{-1} \text{ dm}^3 \quad (2)$$

$$\text{Fe}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Fe}(\text{OH})_2^0, \quad \beta_{2,\text{II}} = [\text{Fe}(\text{OH})_2^0]/([\text{Fe}^{2+}][\text{OH}^-]^2) = 10^{7.4} \text{ mol}^{-2} \text{ dm}^6 \quad (3)$$

$$\text{Fe}^{2+} + 3\text{OH}^- \rightleftharpoons \text{Fe}(\text{OH})_3^-, \quad \beta_{3,\text{II}} = [\text{Fe}(\text{OH})_3^-]/([\text{Fe}^{2+}][\text{OH}^-]^3) = 10^{11.0} \text{ mol}^{-3} \text{ dm}^9 \quad (4)$$

where the $\text{Fe}(\text{OH})_2^0$ species is the dissolved zero charge hydroxo complex of iron(II). The ionic product of water, K_w , is:

$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-, K_w = [\text{H}^+][\text{OH}^-] = 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \quad (5)$$

The solubility of $\text{Fe}(\text{OH})_2(\text{s})$, S_{II} , is the sum of the concentrations of all iron(II) ions dissolved in the water, and is transformed with the constraints of the solubility product in Eq. (1) as:

$$\begin{aligned} S_{\text{II}} &= [\text{Fe}^{2+}] + [\text{FeOH}^+] + [\text{Fe}(\text{OH})_2^0] + [\text{Fe}(\text{OH})_3^-] \\ &= K_{s,\text{II}} \{1 + \beta_{1,\text{II}}[\text{OH}^-] + \beta_{2,\text{II}}[\text{OH}^-]^2 + \beta_{3,\text{II}}[\text{OH}^-]^3\} / [\text{OH}^-]^2 \end{aligned} \quad (6)$$

The solubility S_{II} calculated as a function of pH with Eq. (6) is drawn in Fig. 2.

The proton reference level of this system (a level at which no protons are released or taken to/from a solution [11]) is the moment when $\text{Fe}(\text{OH})_2(\text{s})$ is put (formed) in water before dissociation, and the proton balance equation is:

$$[\text{H}^+] = [\text{OH}^-] + [\text{Fe}(\text{OH})_3^-] - 2[\text{Fe}^{2+}] - [\text{FeOH}^+] \quad (7)$$

Expressing the concentrations of the iron(II) ions in Eq. (7) as functions of the proton concentration with the equilibrium constants results in:

$$2K_{s,\text{II}}[\text{H}^+]^3 + K_w(K_w + K_{s,\text{II}}\beta_{1,\text{II}})[\text{H}^+]^2 - K_w^3(1 + K_{s,\text{II}}\beta_{3,\text{II}}) = 0 \quad (8)$$

Solving Eq. (8) leads to a proton concentration corresponding to pH 9.31. The solubility of $\text{Fe}(\text{OH})_2(\text{s})$ at pH 9.31 is $1.27 \times 10^{-5} \text{ mol dm}^{-3}$ from Eq. (6) as apparent from Fig. 2. The pH is slightly alkaline, suggesting that the basicity of dissolved OH^- is slightly higher than the acidity of dissolved Fe^{2+} .

3.1.2. Air-oxidation of iron(II)

The solubility of the $\text{Fe}(\text{OH})_2(\text{s})$ formed is relatively high as calculated above, and dissolved iron(II) ions are oxidized by air. The overall stoichiometry can be described with iron(II) aqua ions by:

Equation (9) indicates that no additional alkali is required for the formation of iron(III) hydroxide, $\text{Fe}(\text{OH})_3(\text{s})$, because the two hydroxide ions are provided from $\text{Fe}(\text{OH})_2(\text{s})$ and the one additional hydroxide ion necessary for the formation of $\text{Fe}(\text{OH})_3(\text{s})$ is generated by the reduction of oxygen. As a result, the air-oxidation of iron(II) derived from $\text{Fe}(\text{OH})_2(\text{s})$ would not affect the pH.

The rate of air-oxidation of iron(II) in aquatic systems has been reported to change depending on pH as shown in Fig. 3 [12], where the log of the initial oxidation rate for $[\text{Fe}(\text{II})] = 0.01 \text{ mol dm}^{-3}$ and saturated air with $[\text{O}_2] = 2.8 \times 10^{-4} \text{ mol dm}^{-3}$ at 20°C is plotted against pH. The log oxidation rate in the neutral to alkaline region has a

second-order dependence on pH (Fig. 3), as the reaction rate has been reported to obey the following rate equation [12-18]:

$$-d[\text{Fe(II)}]/dt = k_0[\text{Fe(II)}][\text{O}_2][\text{OH}^-]^2 \quad (10)$$

where $[\text{Fe(II)}]$ stands for the concentration of all iron(II) ions dissolved in water and k_0 is the rate constant with a value of $2.3 \times 10^{14} \text{ mol}^{-3} \text{ dm}^9 \text{ s}^{-1}$ at 25°C [15, 16]. In Fig. 3, the rates in the neutral to alkaline region were calculated for the specified iron(II) and oxygen concentrations at 25°C with the rate equation (10), and converted to 20°C . In the course of the air-oxidation of iron(II), the pH is 9.31 as described above, and with this pH the half-life of iron(II) can be calculated as $9.1 \times 10^{-3} \text{ s}$ from Eq. (10). This oxidation rate is very fast, and the $\text{Fe(OH)}_2(\text{s})$ formed by corrosion is likely to turn into $\text{Fe(OH)}_3(\text{s})$ immediately at the site of corrosion. The deposition of $\text{Fe(OH)}_3(\text{s})$ at the corrosion sites would lead to good adherence of the precipitates to the corrosion sites.

The 9.31 pH obtained above is a value attained for pure water in equilibrium with $\text{Fe(OH)}_2(\text{s})$, and neutralization by carbon dioxide from the air can be ignored by the following reasons: The hydration of carbon dioxide to carbonic acid is a slow process taking tens to hundreds of seconds to complete [19], while the rate of air-oxidation of iron(II) ions at pH 9.31 is very rapid with a half-life of $9.1 \times 10^{-3} \text{ s}$ as shown above. As a result, before carbon dioxide transforms to carbonic acid, the air-oxidation of iron(II) ions with the two hydroxide ions from $\text{Fe(OH)}_2(\text{s})$ completes without being neutralized by carbonic acid to form iron(III) hydroxide, and the pH can be maintained at 9.31 throughout the air-oxidation. The formed iron(III) hydroxide does not react with carbon dioxide or carbonic acid, and carbonate rusts do not form. However, when the air-oxidation is slow or has stopped by a blockage of the oxygen supply or for some other reason, the iron(II) hydroxide may turn into carbonate according to: $\text{Fe(OH)}_2(\text{s}) + \text{H}_2\text{CO}_3 \rightarrow \text{FeCO}_3(\text{s}) + 2\text{H}_2\text{O}$. Carbonate rusts may be formed under such circumstances.

3.1.3. Solubilities of compounds containing iron(III)

3.1.3.1. Iron(III) hydroxide. Some of the formed $\text{Fe(OH)}_3(\text{s})$ dissolves in water and releases Fe^{3+} ions that are stronger acids than Fe^{2+} ions together with hydroxide ions. The effect of the dissolution of $\text{Fe(OH)}_3(\text{s})$ on pH can be evaluated by equilibrium calculations, and the reactions and equilibrium constants reported in [10] are:

$$\text{Fe}^{3+} + 2\text{OH}^- \rightleftharpoons \text{Fe}(\text{OH})_2^+, \beta_{2,\text{III}} = [\text{Fe}(\text{OH})_2^+]/([\text{Fe}^{3+}][\text{OH}^-]^2) = 10^{22.3} \text{ mol}^{-2} \text{ dm}^6 \quad (13)$$

$$\text{Fe}^{3+} + 3\text{OH}^- \rightleftharpoons \text{Fe}(\text{OH})_3^0, \beta_{3,\text{III}} = [\text{Fe}(\text{OH})_3^0]/([\text{Fe}^{3+}][\text{OH}^-]^3) = 10^{30.0} \text{ mol}^{-3} \text{ dm}^9 \quad (14)$$

$$\text{Fe}^{3+} + 4\text{OH}^- \rightleftharpoons \text{Fe}(\text{OH})_4^-, \beta_{4,\text{III}} = [\text{Fe}(\text{OH})_4^-]/([\text{Fe}^{3+}][\text{OH}^-]^4) = 10^{34.4} \text{ mol}^{-4} \text{ dm}^{12} \quad (15)$$

where $K_{s,\text{III}}$ is the solubility product of iron(III) hydroxide, the $\text{Fe}(\text{OH})_3^0$ species is the dissolved zero charge hydroxo complex of iron(III), and $\beta_{1,\text{III}} \sim \beta_{4,\text{III}}$ are the stability constants of iron(III) hydroxo complexes. The solubility of $\text{Fe}(\text{OH})_3(\text{s})$, S_{III} , is:

$$\begin{aligned} S_{\text{III}} &= [\text{Fe}^{3+}] + [\text{FeOH}^{2+}] + [\text{Fe}(\text{OH})_2^+] + [\text{Fe}(\text{OH})_3^0] + [\text{Fe}(\text{OH})_4^-] \\ &= K_{s,\text{III}} \{ 1 + \beta_{1,\text{III}}[\text{OH}^-] + \beta_{2,\text{III}}[\text{OH}^-]^2 + \beta_{3,\text{III}}[\text{OH}^-]^3 + \beta_{4,\text{III}}[\text{OH}^-]^4 \} / [\text{OH}^-]^3 \end{aligned} \quad (16)$$

The solubility S_{III} calculated as a function of pH with Eq. (16) is drawn in Fig. 2, and it is apparent that the solubility of $\text{Fe}(\text{OH})_3(\text{s})$ is much smaller than that of $\text{Fe}(\text{OH})_2(\text{s})$ at low pH values.

The proton reference level of this system is the moment of the formation of $\text{Fe}(\text{OH})_3(\text{s})$ from $\text{Fe}(\text{OH})_2(\text{s})$ by the reaction in Eq. (9) in water before dissociation, and the proton balance equation is:

$$[\text{H}^+] = [\text{OH}^-] + [\text{Fe}(\text{OH})_4^-] - 3[\text{Fe}^{3+}] - 2[\text{FeOH}^{2+}] - [\text{Fe}(\text{OH})_2^+] \quad (17)$$

This is transformed with the equilibrium constants to:

$$\begin{aligned} 3K_{s,\text{III}}[\text{H}^+]^4 + 2K_{s,\text{III}}\beta_{1,\text{III}}K_w[\text{H}^+]^3 + K_w^2(K_w + K_{s,\text{III}}\beta_{2,\text{III}})[\text{H}^+]^2 \\ - K_w^4(1 + K_{s,\text{III}}\beta_{4,\text{III}}) = 0 \end{aligned} \quad (18)$$

By solving Eq. (18), a proton concentration corresponding to pH 7.00 is obtained, and hence the solubility S_{III} is $1.20 \times 10^{-8} \text{ mol dm}^{-3}$ as apparent from Fig. 2. This indicates that the solubility of $\text{Fe}(\text{OH})_3(\text{s})$ is small and does not affect the pH. As described above, the pH of 9.31 caused by $\text{Fe}(\text{OH})_2(\text{s})$ is maintained during the oxidation to $\text{Fe}(\text{OH})_3(\text{s})$, and after the completion of the oxidation, the pH would change to 7.00. The very small effect of $\text{Fe}(\text{OH})_3(\text{s})$ on pH suggests that the acid strength of dissolved Fe^{3+} is balanced by the base strength of released OH^- .

3.1.3.2. Iron(III) oxyhydroxides The aging of $\text{Fe}(\text{OH})_3(\text{s})$ leads to dehydration even in the presence of water and forms oxyhydroxides, FeOOH [20]:

where no acid or base is consumed or generated, and there would be no change in pH during the aging. Synthetic beaker experiments have shown that α - FeOOH (Goethite) with yellow to brownish color and γ - FeOOH (Lepidocrocite) with orange color form in neutral to alkaline solutions [21], and these are incorporated in the rusts (Section 2, h). It

has been considered that in the corrosion products on weathering steel, γ -FeOOH is dominant at the early stages of exposure, followed by a gradual transformation of γ -FeOOH and an amorphous oxyhydroxide to α -FeOOH [4, 5].

The oxyhydroxides with different crystal structures may be developed by the particle-particle interactions during aging. The surfaces of hydroxide, oxyhydroxide, and oxide particles in water are charged depending on pH; at low pH the surface charge is positive due to protonation of surface hydroxyl groups, at high pH the charge is negative due to deprotonation of surface hydroxyl groups, and at a certain pH the net charge is zero [22-25]. This specific pH giving a zero charge to the oxide surface is called the point of zero charge (pzc), which is characteristic of oxide specimens. The reported pzc values for α -FeOOH range from 7.5 to 9.38 [26], close to the initial corrosion pH of 9.31, and the surface charge of α -FeOOH would be small. As a result, the α -FeOOH rusts formed in the initial stage of corrosion would be tightly aggregated due to the small repulsion between particles.

The oxyhydroxides of iron(III) dissolve in water to some extent and the solubility product of α -FeOOH, $K_{s,\alpha}$, reported in [10] is:

The form of the solubility product $K_{s,\alpha}$ is the same as $K_{s,\text{III}}$ for $\text{Fe}(\text{OH})_3(\text{s})$ in Eq. (10), but the numerical value is five orders of magnitude smaller. The solubility of α -FeOOH, S_α , calculated as a function of pH from an equation obtained by replacing S_{III} and $K_{s,\text{III}}$ in Eq. (15) with S_α and $K_{s,\alpha}$ is drawn in Fig. 2. The solubility at pH 9.31 is $1.51 \times 10^{-13} \text{ mol dm}^{-3}$, also five orders of magnitude smaller than $\text{Fe}(\text{OH})_3(\text{s})$. For β -, γ -, and other types of oxyhydroxides of iron(III) and non-hydrated iron(III) oxides incorporated in the rusts, similar calculations can be made.

3.1.3.3. Magnetite. At the early part of the initial stage of corrosion, magnetite and ferrites may also form from a thick $\text{Fe}(\text{OH})_2(\text{s})$ gel due to an insufficient supply of oxygen. When corrosion is rapid and $\text{Fe}(\text{OH})_2(\text{s})$ is produced faster than it is consumed by dissolution, the $\text{Fe}(\text{OH})_2(\text{s})$ gel may oxidize directly. The air-oxidation of $\text{Fe}(\text{OH})_2(\text{s})$ gel is complex and it forms “green rusts” as intermediates before finally forming magnetite, Fe_3O_4 [27-30], and this magnetite is incorporated in the rusts (Section 2, h). However, the overall stoichiometry is simply described by:

It is apparent from the reaction in Eq. (21) that this partial oxidation of $\text{Fe}(\text{OH})_2(\text{s})$ does not produce or consume any acid or base, like the oxidation in Eq. (9) that was shown not to affect pH. For the formation of magnetite, either a reducing condition near the metal surface or an insufficient supply of oxygen due to a thick $\text{Fe}(\text{OH})_2(\text{s})$ gel that is provided by rapid corrosion is necessary. As a result, magnetite is more likely to form in the early part of this initial stage of corrosion in contact with metal surfaces.

The solubility of magnetite can be obtained by equilibrium calculations, and the solubility product, $K_{\text{s,II/III}}$, is defined as:

$$\text{Fe}_3\text{O}_4 + 8\text{H}^+ \rightleftharpoons \text{Fe}^{2+} + 2\text{Fe}^{3+} + 4\text{H}_2\text{O}, K_{\text{s,II/III}} = [\text{Fe}^{2+}][\text{Fe}^{3+}]^2/[\text{H}^+]^8 \quad (22)$$

There is no reported value of $K_{\text{s,II/III}}$ available, and here it was calculated from the thermodynamic data as follows. The standard Gibbs free energy change of the dissolution ΔG° is given as:

$$\Delta G^\circ = \Delta G^\circ_{\text{f,Fe}^{2+}} + 2\Delta G^\circ_{\text{f,Fe}^{3+}} + 4\Delta G^\circ_{\text{f,H}_2\text{O}} - \Delta G^\circ_{\text{f,Fe}_3\text{O}_4} - 8\Delta G^\circ_{\text{f,H}^+} \quad (23)$$

where the $\Delta G^\circ_{\text{f}}$ terms express the standard free energy of formation of the respective species. According to the published data in [31], $\Delta G^\circ_{\text{f,Fe}^{2+}} = -78.9 \text{ kJ/mol}$, $\Delta G^\circ_{\text{f,Fe}^{3+}} = -4.7 \text{ kJ/mol}$, $\Delta G^\circ_{\text{f,H}_2\text{O}} = -237 \text{ kJ/mol}$, $\Delta G^\circ_{\text{f,Fe}_3\text{O}_4} = -1015.4 \text{ kJ/mol}$, $\Delta G^\circ_{\text{f,H}^+} = 0$, and hence $\Delta G^\circ = -21.4 \text{ kJ}$. As a result, $K_{\text{s,II/III}} = \exp(-\Delta G^\circ/RT) \text{ mol}^{-5} \text{ dm}^{15} = 5.66 \times 10^3 \text{ mol}^{-5} \text{ dm}^{15}$ [32].

From the dissolution stoichiometry in Eq. (22), the solubility of magnetite, $S_{\text{II/III}}$, is given as: $S_{\text{II/III}} = [\text{Fe}^{2+}] + [\text{FeOH}^+] + [\text{Fe}(\text{OH})_2^0] + [\text{Fe}(\text{OH})_3^-]$, and hence

$$[\text{Fe}^{2+}] = S_{\text{II/III}} / \{1 + \beta_{1,\text{II}}[\text{OH}^-] + \beta_{2,\text{II}}[\text{OH}^-]^2 + \beta_{3,\text{II}}[\text{OH}^-]^3\} \quad (24)$$

Also, $2S_{\text{II/III}} = [\text{Fe}^{3+}] + [\text{FeOH}^{2+}] + [\text{Fe}(\text{OH})_2^+] + [\text{Fe}(\text{OH})_3^0] + [\text{Fe}(\text{OH})_4^-]$, and hence

$$[\text{Fe}^{3+}] = 2S_{\text{II/III}} / \{1 + \beta_{1,\text{III}}[\text{OH}^-] + \beta_{2,\text{III}}[\text{OH}^-]^2 + \beta_{3,\text{III}}[\text{OH}^-]^3 + \beta_{4,\text{III}}[\text{OH}^-]^4\} \quad (25)$$

When Eqs. (24) and (25) are substituted into Eq. (22),

$$S_{\text{II/III}} = \{K_{\text{s,II/III}}[\text{H}^+]^8(1 + \beta_{1,\text{II}}[\text{OH}^-] + \beta_{2,\text{II}}[\text{OH}^-]^2 + \beta_{3,\text{II}}[\text{OH}^-]^3) \times (1 + \beta_{1,\text{III}}[\text{OH}^-] + \beta_{2,\text{III}}[\text{OH}^-]^2 + \beta_{3,\text{III}}[\text{OH}^-]^3 + \beta_{4,\text{III}}[\text{OH}^-]^4)^2/4\}^{1/3} \quad (26)$$

The solubility $S_{\text{II/III}}$ calculated as a function of pH with Eq. (26) is drawn in Fig. 2, where it was assumed that iron(II) ions dissolved remain without oxidizing. The solubility at pH 9.31 is $1.10 \times 10^{-13} \text{ mol dm}^{-3}$, somewhat lower than that for $\alpha\text{-FeOOH}$ obtained above as $1.51 \times 10^{-13} \text{ mol dm}^{-3}$. Magnetite may also serve as a component that sustains a protective rust film from a solubility point of view.

3.1.3.4. Ferrites. For steels containing transition metals, M, as alloying elements, the transition metals are also oxidized to hydroxides, $\text{M}(\text{OH})_2(\text{s})$, by corrosion similarly to

iron, and would become constituents of the rusts. Beaker experiments have shown that when transition metal ions, M^{2+} , are added to the $Fe(OH)_2(s)$ gel and aged in slightly alkaline and weakly oxidizing solutions at tens °C, transition metal ferrites, MFe_2O_4 , are formed [33-35]. These conditions of ferrite formation are very similar to those of rapid wet corrosion of steels where $Fe(OH)_2(s)$ gel is formed, and it may be assumed that transition metal ferrites form in the early part of this corrosion stage according to:

The reaction in Eq. (27) also does not consume or produce acids or bases and does not affect pH. The amount of ferrites in rusts may be small because of the low content of alloying elements, but minor components do not necessarily play a minor role in the corrosion protection as very thin passive oxide films are strongly protective. The importance of transition metal ferrites as corrosion products has been reported elsewhere [36].

The solubility product of one such ferrite, zinc ferrite, $K_{s,Zn/Fe}$, is defined as:

The value of $K_{s,Zn/Fe}$ can be evaluated from the thermodynamic data like for magnetite. The standard Gibbs free energy change of dissolution ΔG° is given as:

$$\Delta G^\circ = \Delta G^\circ_{f,Zn^{2+}} + 2\Delta G^\circ_{f,Fe^{3+}} + 4\Delta G^\circ_{f,H_2O} - \Delta G^\circ_{f,Zn/Fe} - 8\Delta G^\circ_{f,H^+} \quad (29)$$

where $\Delta G^\circ_{f,Zn^{2+}} = -147$ kJ/mol [31] and $\Delta G^\circ_{f,Zn/Fe} = -1063.5$ kJ/mol [37], the other terms are the same as those for magnetite, and hence $\Delta G^\circ = -40.9$ kJ. As a result, $K_{s,Zn/Fe} = \exp(-\Delta G^\circ/RT) \text{ mol}^{-5} \text{ dm}^{15} = 1.47 \times 10^7 \text{ mol}^{-5} \text{ dm}^{15}$ [38].

The zinc hydroxo complex formation and the stability constants of the respective zinc species, $\beta_{1,Zn} \sim \beta_{4,Zn}$, reported in [10] are:

where $Zn(OH)_2^0$ is the dissolved zero charge hydroxo complex of Zn(II). Then, the solubility of zinc ferrite, $S_{Zn/Fe}$, is expressed as: $S_{Zn/Fe} = [Zn^{2+}] + [ZnOH^+] + [Zn(OH)_2^0] + [Zn(OH)_3^-] + [Zn(OH)_4^{2-}]$, and hence

$$[Zn^{2+}] = S_{Zn/Fe} / \{1 + \beta_{1,Zn}[OH^-] + \beta_{2,Zn}[OH^-]^2 + \beta_{3,Zn}[OH^-]^3 + \beta_{4,Zn}[OH^-]^4\} \quad (34)$$

Also, $2S_{Zn/Fe} = [Fe^{3+}] + [FeOH^{2+}] + [Fe(OH)_2^+] + [Fe(OH)_3^0] + [Fe(OH)_4^-]$, and hence

$$[Fe^{3+}] = 2S_{Zn/Fe} / \{1 + \beta_{1,III}[OH^-] + \beta_{2,III}[OH^-]^2 + \beta_{3,III}[OH^-]^3 + \beta_{4,III}[OH^-]^4\} \quad (35)$$

When Eqs. (34) and (35) are substituted into Eq. (28),

$$S_{\text{Zn/Fe}} = \{K_{\text{s,Zn/Fe}}[\text{H}^+]^8(1 + \beta_{1,\text{Zn}}[\text{OH}^-] + \beta_{2,\text{Zn}}[\text{OH}^-]^2 + \beta_{3,\text{Zn}}[\text{OH}^-]^3 + \beta_{4,\text{Zn}}[\text{OH}^-]^4) \times (1 + \beta_{1,\text{III}}[\text{OH}^-] + \beta_{2,\text{III}}[\text{OH}^-]^2 + \beta_{3,\text{III}}[\text{OH}^-]^3 + \beta_{4,\text{III}}[\text{OH}^-]^4)^2/4\}^{1/3} \quad (36)$$

The solubility $S_{\text{Zn/Fe}}$ calculated as a function of pH with Eq. (36) is drawn in Fig. 2. The solubility at pH 9.31 is $4.84 \times 10^{-12} \text{ mol dm}^{-3}$ as small as those of the other rust compounds described above. While some thermodynamic data are not available, similar calculations can be made for Ni-ferrite, Cu-ferrite, and other transition metal ferrites with similar results, and these ferrites would also serve as components that sustain a protective rust film.

3.1.4. Mechanism of initial stage of corrosion

The corrosion processes occurring in the initial stage can be summarized as: When $\text{Fe}(\text{OH})_2(\text{s})$ is formed by corrosion, the pH becomes 9.31, and a thick $\text{Fe}(\text{OH})_2(\text{s})$ gel formed at the early part of the initial stage is oxidized to magnetite and transition metal ferrites.

With decreasing corrosion rate, the air-oxidation takes place through iron(II) ions dissolved from $\text{Fe}(\text{OH})_2(\text{s})$ to form $\text{Fe}(\text{OH})_3(\text{s})$ very quickly at this pH. The hydroxide, $\text{Fe}(\text{OH})_3(\text{s})$, is a gel, and water and oxygen easily penetrate and transfer into the gel phase. The anode and cathode reaction products (Fe^{2+} and OH^-) can also move easily in the gel phase and are subsequently oxidized to $\text{Fe}(\text{OH})_3(\text{s})$ by dissolved oxygen, even below the already formed hydroxides. As a result, the corrosion would proceed consecutively throughout the gel phase with the intermediation of coexisting electrolytes at pH 9.31. The hydroxide layer continues to grow, but is not stable, because the hydroxide particles are not strongly aggregated. Sometimes these hydroxide layers may be washed away by exposure to the elements or may be newly formed along the passage of water flows, as is apparent from the non-uniform yellowish stains of “flowing rusts” observed on recently constructed steel structures (Section 2, b).

With further aging, the dehydration and crystallization of $\text{Fe}(\text{OH})_3(\text{s})$ gel rust proceed and the outer part of the rust layer (that was formed earlier) transforms to a tightly aggregated and little soluble $\alpha\text{-FeOOH}$ solid rust film. In the case where corrosion occurs through film defects, the $\text{Fe}(\text{OH})_3(\text{s})$ gel rust forms by rapid air-oxidation immediately at the corrosion site, and fills up voids and vacancies in the

film. As a result, a dense, adherent rust film with self-maintaining properties forms, serving as a barrier to the penetration and transfer of water and oxygen.

Overall, the rust film formed in the initial stage of corrosion described so far may be visualized schematically as in Fig. 4. The innermost layer of the rust film adjacent to the steel surface is the magnetite/transition metal ferrite rust formed at the beginning of corrosion, the next layer is the $\text{Fe}(\text{OH})_3(\text{s})$ gel rust, and the outer layer facing the outside environment is the $\alpha\text{-FeOOH}$ solid rust transformed from the $\text{Fe}(\text{OH})_3(\text{s})$ gel rust. With the progress of corrosion, the corrosion rate decreases due to the increase in the thickness of the $\alpha\text{-FeOOH}$ solid rust layer which is resistant to the mass transfer, and the rate of formation of new $\text{Fe}(\text{OH})_3(\text{s})$ gel rust slows down. However, the transformation of the $\text{Fe}(\text{OH})_3(\text{s})$ gel rust into the $\alpha\text{-FeOOH}$ solid rust by aging proceeds continuously, and as a result the $\alpha\text{-FeOOH}$ solid rust becomes the whole of the rust layer, completing the formation of the protective rust film. The rust compounds formed here show very low solubilities, favorable for sustaining the protective rust film.

3.2. Deterioration of protective rust films and crevice corrosion

3.2.1. Development of rust channels

After completing the protective rust film formation in the initial stage of corrosion, the corrosion stops and the protective rust film will be sustained for some time owing to the very small solubility of the rust film compounds. However, eventually, the film will be broken according to the following processes: Some portions of the film will dissolve away depending on the solubilities as rains and condensates wash the film, without the supply of iron and hydroxide ions due to corrosion. Further dehydration and crystallization of rusts will take place, and some iron(III) oxyhydroxides in the rusts may transform into non-hydrated oxides, like hematite $\alpha\text{-Fe}_2\text{O}_3$. The result of these processes is cracks and voids in the film as observed in mature rusts (Section 2, f). The cracks and voids may develop into channels connecting the metal surface and the outside environment, through which water and oxygen reach the metal surface. A new stage of corrosion may start, but the Fe^{2+} and OH^- ions (the anode and cathode reaction products) cannot react directly because the remaining rusts hinder their approach to each other as indicated in Fig. 5. Electric neutrality is attained with the intermediation of an electrolyte, and the coexisting electrolyte NaCl plays a major role in the corrosion (Section 2, a). The positive charge of dissolved Fe^{2+} is counter balanced by the electrolyte anions Cl^- to form

FeCl₂ in the anode channel, and the negative charge of OH⁻ is counter balanced by the electrolyte cation Na⁺ to form NaOH in the cathode channel. This corrosion under thick rust layers may be regarded as crevice corrosion [39].

3.2.2. Air-oxidation of iron(II) in anode channels

The pH of the FeCl₂ solution formed in the anode channel can be obtained by equilibrium calculations with Eqs. (2) ~ (4). For a 1 mol dm⁻³ FeCl₂ solution, the pH is calculated as 4.75 and iron(II) hydroxide does not precipitate because its solubility at this pH is far higher than 1 mol dm⁻³ as is apparent from Fig. 2. The FeCl₂ solution is only weakly acidic (pH 4.75) because iron(II) ions hydrolyze weakly as described above, and the dissolution of iron(II) ions as FeCl₂ alone does not cause the region of crevice corrosion to become strongly acidic.

The FeCl₂ will be oxidized by air transported through the anode channels as:

The salts NaCl and FeCl₂, the acid HCl, and the alkali NaOH are all ionized in water, but the molecular reaction type expressions are used here to demonstrate the role of electrolyte anions and cations in the reaction. The reaction in Eq. (37) suggests that the air-oxidation of FeCl₂ generates hydrochloric acid, and this formation of acid by the air-oxidation is different from the initial stage of corrosion. The acid is formed because the NaOH in the cathode channels and the FeCl₂ in the anode channels do not react directly, and because the air-oxidation of FeCl₂ in the anode channels produces protons due to the subsequent hydrolysis of the formed iron(III) ions. In the narrow anode channels, the pH decrease with the formed acid would be steep, and the deposition of iron(III) hydroxide within the anode channels will be difficult due to both the decrease in the rate of air-oxidation of iron(II) (Fig. 3) and the increase in the solubility of iron(III) hydroxide (Fig. 2). Iron ions dissolved leak out the rust layer, depositing iron hydroxide outside the channel, and as a result, the protective, self-repairing properties of the rust film will deteriorate.

The decrease in pH also results in a decrease in the slope of the log of the oxidation rate vs. pH (Fig. 3). It decreases from two in the neutral to alkaline region (pH > 5), via one in the slightly acidic region (2 < pH < 5) [40], to zero in the strongly acidic region (pH < 2) [41]. The rate equations for pH values below 5 are:

$$2 < \text{pH} < 5 \quad -\text{d}[\text{Fe}(\text{II})]/\text{d}t = k_1[\text{Fe}(\text{II})][\text{O}_2][\text{OH}^-] \quad (38)$$

$$\text{pH} < 2 \quad -d[\text{Fe(II)}]/dt = k_2[\text{Fe(II)}]^2[\text{O}_2] \quad (39)$$

where the order of reaction with respect to iron(II) has increased to two in the strongly acidic region, and the initial oxidation rates for the slightly acidic and strongly acidic regions plotted in Fig. 3 were obtained by converting the original data [40, 41] to values for the specified common iron(II) and oxygen concentrations at 20°C.

Tamura *et al.* reported that the reaction product of the air-oxidation, iron(III) hydroxide, has a catalytic effect, and the rate of air-oxidation of iron(II) increases with the progress of the reaction, autocatalytically [42]. The oxyhydroxides of iron(III), α -, β -, and γ -FeOOH, also act as catalysts [43], and the air-oxidation of iron(II) in the anode channels at strongly acidic pH could proceed by the catalysis of the rust compounds as heterogeneous catalysts, although the rate of homogeneous air-oxidation decreases with decreasing pH as described above.

3.2.3. Composition of aquatic system in anode channels

The pH and composition after the air-oxidation of FeCl₂ has completed are assessed as follows: The reaction in Eq. (37) is an over-all expression comprising several processes, like air-oxidation of iron(II), formation of hydroxo complexes of iron(III), and deposition of iron(III) hydroxide. For the process of the air-oxidation, the reaction, $\text{Fe}^{2+} + (1/4)\text{O}_2 + (1/2)\text{H}_2\text{O} \rightarrow \text{FeOH}^{2+}$, may be selected as a reference since no protons are consumed or generated. Then, equilibrium calculations can be made for the transformation of the formed FeOH^{2+} ions into various iron(III) aqua and hydroxo complexes as well as solid hydroxide precipitates, by consuming or generating protons. As a result, the proton reference level of this system is the moment of the formation of FeOH^{2+} ions in water before dissociation, and the proton balance equation is obtained as:

$$[\text{H}^+] = [\text{OH}^-] + [\text{Fe}(\text{OH})_2^+] + 2[\text{Fe}(\text{OH})_3^0] + 3[\text{Fe}(\text{OH})_4^-] + 2[\text{Fe}(\text{OH})_3(\text{s})] - [\text{Fe}^{3+}] \quad (40)$$

With the solubility product of $\text{Fe}(\text{OH})_3(\text{s})$, $K_{\text{s,III}}$, and the stability constants of iron(III) hydroxo complexes, $\beta_{1,\text{III}} \sim \beta_{4,\text{III}}$, Eq. (40) becomes:

$$3K_{\text{s,III}}[\text{H}^+]^4 + 2K_{\text{s,III}}\beta_{1,\text{III}}K_{\text{w}}[\text{H}^+]^3 + K_{\text{w}}^2(K_{\text{w}} + 2K_{\text{s,III}}\beta_{2,\text{III}})[\text{H}^+]^2 - 2[\text{Fe}]_{\text{T}}K_{\text{w}}^3[\text{H}^+] - K_{\text{w}}^4 = 0 \quad (41)$$

where $[\text{Fe}]_{\text{T}}$ is the total concentration of iron ions in the system (originally FeCl₂). The concentration of hydroxide precipitate $[\text{Fe}(\text{OH})_3(\text{s})]$ in Eq. (40) was equated with the difference between this total concentration $[\text{Fe}]_{\text{T}}$ and the sum of the concentrations of

dissolved iron(III) ions, equal to the solubility S_{III} . For $[\text{Fe}]_{\text{T}} = 1 \text{ mol dm}^{-3}$, the pH is calculated as 1.41 with Eq. (41), and hence the solubility S_{III} is $0.686 \text{ mol dm}^{-3}$ ($\text{Fe}^{3+} 0.590 \text{ mol dm}^{-3}$, $\text{FeOH}^{2+} 0.096 \text{ mol dm}^{-3}$). These calculated results confirm that the air-oxidation of FeCl_2 generates HCl as well as $\text{Fe}(\text{OH})_3(\text{s})$, FeCl_3 , and FeOHCl_2 as dominant species. The regions in rusts with pH lower than 3 detected by pH test paper where high concentrations of chloride ions are contained (Section 2, d, e) would be these anode channels. The regions with pH higher than 10 would then be the cathode channels.

3.2.4. Mechanism of crevice corrosion under rust layers

The calculated results for the aquatic composition in anode channels indicate that 30% of the corroded iron deposits as iron(III) hydroxide $\text{Fe}(\text{OH})_3(\text{s})$ in the strongly acidic condition with pH 1.41. The pzc of $\text{Fe}(\text{OH})_3(\text{s})$ particles has been reported as 8.5 [44], and the $\text{Fe}(\text{OH})_3(\text{s})$ particles at pH 1.41 would have a large positive charge. Such charged hydroxide particles do not coagulate, they disperse in water, easily leak out from the anode channels and do not fill out the defects. The $\text{Fe}(\text{OH})_3(\text{s})$ staying in the anode channels may turn into $\beta\text{-FeOOH}$ (Akaganéite) appearing as a yellow precipitate, which is incorporated in the rust (Section 2, h), as it has been shown that the formation of $\beta\text{-FeOOH}$ is facilitated by strongly acidic solutions containing high concentrations of chloride ions [45]. The $\beta\text{-FeOOH}$ rust would not aggregate due to the large positive surface charge caused by the strongly acidic conditions. The yellow stains occasionally observed on the surface of rusts appearing like it has leaked from the deeper parts of the rust (Section 2, b), the “flowing rusts” above, may be $\beta\text{-FeOOH}$.

The remaining 70% of the corroded iron is aqua and hydroxo complexes of iron(III), these ions diffuse to the bulk solution with higher pH, and are hydrolyzed to deposit as $\text{Fe}(\text{OH})_3(\text{s})$. The decrease in pH outside anode channels due to hydrolysis would be slow because of the large volume of bulk water provided by rains and condensates and because some NaOH diffuses from the cathode channels. The formed iron(III) hydroxide particles continuously settle as precipitates from the bulk solution on the already formed rusts. These precipitates are coarse, porous, and flaky substances, and would also appear as stains with colors like yellow on the already formed brownish rusts, without protective properties due to weak aggregation and little ability to plug film defects as described above.

The corrosion processes under thick rust layers as described here is proposed to occur

in the following manner: The protective rust film formed in the initial stage of corrosion will deteriorate with the formation of cracks and voids; because of the film dissolution by washing with fresh environmental water and because of film shrinkage due to dehydration and crystallization of the rusts. Under the remaining rusts and in the presence of NaCl, a new stage in the corrosion (crevice corrosion) starts with water and oxygen transported through channels due to the defects in the rust, causing formation of FeCl₂ in the anodic channels and NaOH in the cathodic channels. The air-oxidation of FeCl₂ generates HCl, iron(III) ions, Fe(OH)₃(s), and also β-FeOOH. The strongly acidic condition reduces the rate of air-oxidation of iron(II) and increases the solubility and the surface charge of formed Fe(OH)₃(s) and β-FeOOH particles. As a result, in this stage a rapid deposition of strongly aggregated corrosion products in the rust film defects is impossible, and the corrosion products leak out of the film to become non-protective rust precipitates.

3.3 Acid corrosion and corrosion stage alternations of iron and steel

3.3.1. Corrosion with protons and iron(III) aqua ions

The strongly acidic HCl solution in the anode channel is saturated with Fe(OH)₃(s) as described in the previous section, and would not be able to dissolve the remaining rusts (Fig. 5), because these rusts have much smaller solubilities than the fresh Fe(OH)₃(s) formed at this stage. However, steel surfaces in contact with this strongly acidic solution will be subject to acid corrosion by protons from HCl and iron(III) aqua ions from FeCl₃ in the solution as shown in Fig. 6 according to:

where HCl and FeCl₃ are provided by the air-oxidation of iron(II). The site where hydrogen evolves (Fig. 6) is the new cathode, and the new cathode and anode reaction products are not separated. The consumption of acid by the reaction in Eq. (42) results in an increase in pH; this increase in pH in turn accelerates the air-oxidation of FeCl₂ by Eq. (37), resulting in a decrease in pH due to the generation of hydrochloric acid. These reactions balance each other and the apparent result is a steady-state with corrosion proceeding at an acidic constant pH. A similar process occurs when iron powder is put in a sulfuric acid solution with air bubbling, this is known as the Penniman process, and is

used to produce a yellow pigment (Yellow Ochre) consisting of α - and γ -FeOOH [33, 46]. At the stage of corrosion discussed here, the conditions are similar to those of the pigment production except that the coexisting anions are chloride ions, and the yellow “flowing rusts ” (Section 2, b) may also contain α - and γ -FeOOH, in addition to the β -FeOOH suggested above.

3.3.2 Tunneling below the rust layers

The acid corrosion under the rust layer described in 3.3.1 would spread progressively (Fig. 6), invading neighboring corroding regions, and the cracks and voids observed along layer planes (Section 2, f) may be a result of such acid corrosion. At this stage rust remains on the substrate metal over un-corroded metal areas. At the end of this stage the regions of acid corrosion tunnel into the previous cathode region where NaOH is concentrated, and the acidic solution containing iron(II), iron(III), and alloying metal(II) ions mixes with the NaOH, resulting in an increase in pH. At this point the acid corrosion stops because of the pH rise, and the regenerated steel surface exposed under the rust becomes covered with a mixture of thick hydroxide gels. The hydroxide gels will undergo the following reactions: A thick iron(II) hydroxide gel formed at the beginning is partially oxidized by air to magnetite as described by Eq. (21). A mixture of iron(II) hydroxide gel and alloying metal(II) hydroxide gel is oxidized by air to form transition metal ferrites according to the reaction described by Eq. (27). Magnetite and ferrites also form with the participation of iron(III) without air-oxidation [47]. Iron(II) ions dissolved from iron(II) hydroxide are oxidized by air to iron(III) hydroxide according to Eq. (9). These processes can be regarded to occur at pH 9.31 as long as iron(II) hydroxide keeps formed and air-oxidized as discussed in Section 3.1. Now the metal surface under the rust layer is in the same state as in the initial stage of corrosion, and corrosion may be assumed to resume with the formation of a tightly aggregated, self-maintaining, protective rust film. In due course this protective rust film will disintegrate by crevice- and acid-corrosion and complete this cycle.

3.3.3. Mechanism of corrosion stage alternations

For severely corroding steels in wet conditions, there is a speed up of corrosion by rusts, and the colors, textures, adherence to the substrate, and other properties of the rusts change visibly with the progress of the corrosion, as described in Section 2. These

dynamic aspects of corrosion have not been explained so far, and this paper proposes the alternating corrosion-protective and corrosion-promoting stages with different chemical reactions at the different stages to explain the role of rusts in the progress of corrosion more generally. In the corrosion-protective stage, the steady development of the rust layer due to oxidation and aggregation inhibits further corrosion, while in the corrosion-promoting stage the rust film causes crevice- and acid-corrosion. These corrosion-protective and corrosion-promoting stages alternate due to the changes in the accessibility of the anode and cathode reaction products by the surrounding rusts, resulting in periodically and spatially different structures and properties of the rust layer. The layer structure in the rust (Section 2, c) may be due to these cycles. The dense layers would correspond to the corrosion-protective stage where a tightly aggregated, self-maintaining rust film forms at pH 9.31, and the coarse layers would correspond to the corrosion-promoting stage where dissolved iron ions and charged, non-aggregated rust particles formed in acidic conditions (pH 1.41) leak and precipitate outside the rust film. The daily and yearly cycles of temperature and humidity, the wet-dry-wet cycles of the environment, would also affect the structure and properties of rusts, like in the case of the dehydration by aging progressing more rapidly in dry periods than in wet periods. With repeated cycles the weight of rusts increases, and the rusts may detach as flakes or slabs of rust from the rust/substrate metal interface (Section 2, g) in the stage of acid corrosion.

4. The Evans model

Differently, it has been suggested that the formation of corrosion-protective α -FeOOH rust is stimulated by wet-dry-wet environmental cycles [4, 5]. Also Evans [48, 49] proposed an effect of wet-dry-wet cycles on the growth of rusts, and assumed the following reactions to occur depending on the dry or wet conditions for a steel with inner magnetite Fe_3O_4 and outer iron(III) oxyhydroxide FeOOH layers as shown in Fig. 7. In the wet condition, the anodic oxidation of iron combined with the cathodic reduction of FeOOH to magnetite proceeds according to:

where Fe^{2+} ions and electrons formed by oxidation of iron transfer through the magnetite

layer and reduce FeOOH to magnetite. Thus iron and FeOOH are consumed, while magnetite forms. In dry conditions, the magnetite is oxidized to FeOOH by air with water transported through the FeOOH layer from the outside environment as:

where the FeOOH grows at the expense of the magnetite. If, as a result of the wet-dry-wet cycles, the inner magnetite layer maintains a constant thickness by a balance between formation and transformation, there is no net change in the amount of magnetite, and a summation of Eqs. (44) to (46) leads to:

This total reaction suggests that the outer FeOOH layer would increase steadily, likely with uniform properties, to become a barrier to the penetration of water and oxygen. Overall, the Evans model explains the decreasing corrosion rates of weathering steels with rust growth. A modification of this model has been proposed where $\text{Fe}\cdot\text{OH}\cdot\text{OH}$, a reduced surface layer of FeOOH, is assumed to take the place of the magnetite layer [50, 51], and this would also explain the progressively increasing protection by rusts in the same way as the Evans model.

However, the dynamic aspects of corrosion pointed out in this paper are not considered in the Evans model. The model proposed in this paper explains the role of rusts in corrosion of steels as including not only protective but also promoting roles, more generally than the Evans model. The following section will detail the conditions necessary for rusts to be protective based on the model proposed in this investigation.

5. Formation and maintenance of protective rusts

5.1. Self-repairing film maintained by rapid air-oxidation

The previous sections proposed that in the initial stage of corrosion the anode and cathode reaction products of corrosion (Fe^{2+} and OH^-) react without obstacles to form $\text{Fe}(\text{OH})_2(\text{s})$. In this stage, the pH of the corroding region in contact with $\text{Fe}(\text{OH})_2(\text{s})$ becomes 9.31 as calculated in Section 3.1, and the air-oxidation of iron(II) at this pH is very rapid, generating and depositing rust compounds on the metal surface. Due to the rapid air-oxidation of iron(II), the rusts formed at this stage plug voids and vacancies in the rusts, and result in a dense, adherent rust film. During corrosion in the initial stage,

the underlying steel is well protected by this dense, adherent rust film with self-repairing properties. Thus, the very rapid air-oxidation of iron(II) at the high pH is the governing factor for the formation of the protective rust film.

This high pH environment is realized when there is good accessibility between the anode and cathode reaction products during the corrosion. Evans discussed the possibility of a “pure chemical corrosion”, where the anode and cathode reactions take place at the same site [3]. With pure chemical corrosion, $\text{Fe}(\text{OH})_2(\text{s})$ would always form, resulting in the maintenance of the 9.31 pH of the initial corrosion stage throughout, but such pure chemical corrosion did not occur according to experimental data [3]. However, the negative result that pure chemical corrosion did not occur was obtained empirically, and as pure chemical corrosion does not violate the basic principles of natural science, devising steels that corrode through pure chemical corrosion processes is still a possibility.

If the air-oxidation of iron(II) is accelerated with some catalysts, then a protective rust film would be formed even in acidic conditions. It is known that steels containing copper and phosphorus are resistant to atmospheric corrosion, and weathering steels incorporating these elements have been developed. When copper and phosphorus are oxidized, copper(II) ions and phosphoric acid are formed, and these are good catalysts for the air-oxidation of iron(II). Tamura *et al.* [52-54] made a kinetic analysis of these catalysts with regard to the effect of pH and catalyst concentration, and it was shown that iron(II) can be air-oxidized in acidic conditions. When the initial stage of corrosion is finishing and the solution pH is declining, these catalysts would enable air-oxidation of the formed iron(II) leading to the self-repair of the protective rust film in the newly acidic conditions. As a result, the dissolution of FeCl_2 by crevice-corrosion would stop with these catalysts. The corrosion resistance of steels containing copper and phosphorus can be ascribed to the acceleration of the air-oxidation of iron(II) by copper(II) and phosphate ions as the corrosion products. Fluoride ions also accelerate the air-oxidation of iron(II) [52, 53, 55], and could help the rust film formation in acidic conditions. However, high concentrations of fluoride do not seem to promote the formation of a protective-rust film, because this ion forms water soluble complexes with iron(III), like FeF_6^{3-} . To maintain a protective-rust film, low solubility to water is important as described in Section 3.1.

5.2. Formation of dense protective film with fine particles

Alloying elements in weathering steels are important to the protective properties of rusts as described above, and the effect of copper(II) ions on the crystal growth and colloid and surface chemical properties of rusts has been investigated [56-59]. The results showed that the growth and crystal structure development of rust particles is inhibited by copper(II) ions. With other ions, similar results were obtained: With cobalt(II) ions, the particle size of cobalt-ferrite was smaller than that of magnetite formed under corresponding conditions without cobalt(II) ions [34]. The addition of titanium(IV), chromium(III), or nickel(II) ions to a hydrolyzing iron(III) solution resulted in poorly crystalline nanosized synthetic-rust particles, while without the addition of foreign ions larger ferrihydrite particles were obtained [60, 61]. These results indicate that coexisting ions interfere with the growth and crystal structure development of rust particles. It is believed that an aggregate of fine rust particles constitutes a dense rust layer serving as a good barrier to the mass transfer and that the alloying elements contribute to form fine particle rusts. However, it would be difficult for the rust film to completely stop the permeation of water and oxygen only by mechanical exclusion as a physical barrier, because openings at colloidal dimensions far larger than molecular sizes develop in the rust film. Other processes like “self-repairing by air-oxidation” suggested above would also take part in the complete shielding of steel surfaces by weathering steel rusts, where alloying elements may accelerate the air-oxidation.

5.3. Ion-selective film formation

5.3.1. Development of ion-selective permeability

A rust film with electrically charged surfaces would be a barrier to the mass transfer of charged species even with openings in the film. Aggressive ions for corrosion, generally anions, are repelled by negatively charged rust surfaces, and cannot penetrate through the film to the steel surface under the rust. This property of the rust, termed cation-selective permeability, has been regarded as important for the protective ability of rusts [62-66]. A rust film with cation-selective permeability may be visualized as shown in Fig. 8, where rust channel surfaces are negatively charged and the negative charges adsorb sodium ions in solution as counterions, forming an electrical double layer. If the electrical double layers on opposite channel walls overlap, only cations can be

accommodated in the channel, and due to the electric repulsion from the negative walls, anions cannot enter the channel to neutralize the positive charge of Fe^{2+} ions generated by corrosion. However, if, after the generation of Fe^{2+} ions by corrosion, excess cations transfer to the bulk solution by cation-selective permeation, the anode channel recovers electric neutrality, and Sato [66] suggested protons as the mobile cations. The dissolved Fe^{2+} ions are hydrolyzed to produce protons, and these protons escape from the anode channel much more quickly than the sodium ions present in the channel as counter ions, owing to their very large mobility. As a result, Fe^{2+} ions precipitate as iron(II) hydroxide and become iron(III) hydroxide by air-oxidation, plugging the anode channel. A rust film with cation-selective permeability would, therefore, be corrosion protective.

A bipolar rust film where the top half of the film facing the outside environment is cation selective as in Fig. 8 and the lower half adjacent to the steel is anion selective would stop both entering anions and exiting cations. The performance of a bipolar rust film has been examined and it was shown that the corrosion current was low [65, 66].

The development of ion-selective permeability in rusts would depend on the dimensions of rust channels because the overlap of electrical double layers is necessary as described above. If the channel radius is larger than the double layer thickness, the central regions of the channels are not affected by the rust surface charge, and nonselective ion passage would be possible. For a 1-1 electrolyte the double layer thickness is about 1 nm for a $10^{-1} \text{ mol dm}^{-3}$ solution, about 10 nm for a $10^{-3} \text{ mol dm}^{-3}$ solution, and the thickness increases with decreasing electrolyte concentration [67]. A rust film with channel diameters less than a few tens of nm would satisfy the dimensional requirements for the development of ion-selective permeability.

5.3.2. Charging of rusts and development of cation-selective permeability

The cation-selective permeability of rusts develops with the negative charge of rust surfaces. The charging of metal oxides is commonly due to: 1) protonation and deprotonation of surface hydroxyl groups with nonspecific adsorption of monovalent anions and cations, 2) specific adsorption of multivalent ions by non-stoichiometric exchanges with surface hydroxyls, and 3) non-stoichiometric proportions of lattice metal and (hydr)oxide ions, and these causes of charging of metal oxides will be discussed independently below.

5.3.2.1. *(De)protonation of surface hydroxyl groups* The surface hydroxyl groups are formed by hydration of the surface oxide ions, $-O$, on oxides as [68, 69]:

The two types of hydroxyl groups (a) and (b) are acids and bases, respectively. The base hydroxyl group, $-OH(b)$, is a deprotonated water molecule, attracted by a lattice metal ion. The acid hydroxyl group, $-OH(a)$, is a protonated surface lattice oxide ion, adjacent to neighboring lattice metal ions. Hydroxyl groups subject to strong electrostatic effect from lattice metal ions are acidic, and hydroxyl groups subject to small electrostatic effect are basic.

The surface charge formation due to 1) (de)protonation of surface hydroxyl groups is [23-25]:

In the presence of an electrolyte, NaCl here, the acid hydroxyl group $-OH(a)$ releases an H^+ ion to create a negative site $-O^-$ where an Na^+ ion is adsorbed. The base hydroxyl group $-OH(b)$ releases an OH^- ion (accepts an H^+ ion) to create a positive site $-OH_2^+$ where a Cl^- ion is adsorbed. Monovalent ions in solution are weakly adsorbed by the charged sites of oxides to satisfy the electric neutrality, and form electrical double layers as indicated by the dots ($\bullet$) in Eqs (49) and (50) (this type of adsorption is termed “nonspecific”). These reactions would be responsible for the charging of rust surfaces that determines the pzc of rust particles as described in Section 3.1.3.2. The surface (de)protonation is pH dependent and the polarity of surface charge changes with solution pH. The negative surface charge is reversed to positive in acidic conditions below pzc because of the enhancement of both the backward reaction in (49) and the forward reaction in (50), and cation-selective permeability would be lost at pH values below pzc.

As a result, the cation-selective permeability of rusts due to the deprotonation of acid hydroxyl groups is not sustainable over the full pH range.

5.3.2.2. *Specific adsorption of multivalent ions* The surface charging due to 2) above, the specific adsorption of divalent metal ions M^{2+} on acid hydroxyl groups in the presence of NaCl is [24, 25]:

The interaction of divalent metal ions with negative charged sites is very strong and forms complexes with oxide surfaces, and the positive charge of adsorbing ions is donated to the oxide phase (this type of adsorption is termed “specific”). The exchange between M^{2+} and H^+ in (52) is stoichiometric and there is no net surface charge formed. However, the exchange in (51) is non-stoichiometric, leaving a net 1+ charge on the oxide surface, and the 1+ charge here is counterbalanced by nonspecific adsorption of a chloride ion. As a result, the specific adsorption of divalent metal ions extends the range where the oxide surface is positively charged to a higher pH and the pzc shifts to a higher value. Conversely, the specific adsorption of multivalent anions on basic hydroxyl groups creates negative charges, and the pzc shifts to a lower value, extending the pH range where oxides show cation-selective permeability. There has been research into the effect of oxyanions as multivalent anions on the development of cation-selective permeability of rusts, with chromates, phosphates, molybdates, tungstates, and sulfates [62-66]. It was shown that the adsorption of these oxyanions on rusts brought about cation-selective permeability. The role of phosphorus as an alloying element in weathering steels may be explained by the phosphate ions formed by oxidation of phosphorus resulting in a negative charge on the rust surfaces, providing cation-selective permeability (70). The reaction may be expressed as:

However, at the pH in the crevice- and acid-corrosion stages described in Sections 3.2 and 3.3, the protonation of oxyanions of weak acids occurs, and the formed oxyacids with zero charge would be liberated from the rusts. Such cation-selective permeability due to the specific adsorption of multivalent anions would be absent in strongly acidic conditions.

5.3.2.3. Non-stoichiometric structures A third cause of surface charge is the structural one due to non-stoichiometric proportions of lattice metal and (hydr)oxide ions. As an example, hydrotalcite, a naturally occurring clay mineral, is a layered double hydroxide of magnesium and aluminum ions with the crystal structure of $Mg(OH)_2$ (brucite). The hydroxide layers have positive charges owing to the extra positive charge of Al^{3+} ions as $[Mg_{1-x}Al_x(OH)_2]^{x+}$, and the layer positive charges are compensated by the negative charges of interlayer anions X^- to form the layered compound with the general formula of $[Mg_{1-x}Al_x(OH)_2]X_x \cdot mH_2O$ [71]. When this compound is put in water, the anion X^- leaves

the solid to form an electrical double layer with the positive layer charge, and anion-selective permeability would be developed due to the positive surface charges. Tetratitanates as another example are layered compounds of titanium oxide with the general formula of $M^I_2[Ti_4O_9]$ where M^I is alkali metal ions. The oxide layer here has a negative charge because the negative charge due to oxide ions is larger than the positive charge due to titanium(IV) ions as $[Ti_4O_9]^{2-}$, and the layer negative charge is compensated by the positive charges of interlayer cations M^+ . In water, the interlayer cations leave the oxide, and the resulting negative surface charges would develop cation-selective permeability:

This type of charge of structural origin is characteristic of (a) very large charge densities and (b) very wide pH ranges where the same polarity is sustained. For (a), layered compounds have much larger surface area than ordinary solids with only outer surfaces, due to interlayer internal surfaces, and as a result, the number of charging sites is larger. The maximum possible charge density of tetratitanates as layered compounds is $5.63 \times 10^{-3} \text{ mol g}^{-1}$, while that of titania as a corresponding compound with only outer surfaces is $2.34 \times 10^{-5} \text{ mol g}^{-1}$, and more than two orders of magnitude different [72, 73]. For (b), the pH range, tetratitanates clearly showed negative charges at pH as low as 3 [72, 73], while the pzc of titania is 5.36 [23, 24], and at pH below this value titania shows positive charges. Surface hydroxyl groups are amphoteric in nature, and the surface charge due to the (de)protonation of surface hydroxyl groups changes their polarity depending on pH.

The negative charge of tetratitanates decreases with decreasing pH because interlayer alkali metal ions are exchanged with protons to form tetratitanic acid with zero charge, but the polarity does not change. To exchange interlayer alkali metal ions with all protons and for the negative charge to disappear, very strong acidic conditions are necessary, as follows. To prepare tetratitanic acid, potassium tetratitanate is dispersed in 1 mol dm^{-3} hydrochloric acid with stirring for 24 hours, and the hydrochloric acid is replaced with new solution three times to ensure the complete exchange [72, 73]. The negative charge of structural origin is sustained over strongly acidic conditions, and would show cation-selective permeability, stably against a pH drop. Iron compounds with such properties are promising as components of a corrosion protective rust film.

Ferrites ($M^I[Fe^{III}O_2]$), other ferrites than the transition metal ferrites $M^{II}Fe^{III}_2O_4$

described in Section 3.1, are formed by the solid phase reaction of iron(III) oxide with a little excess of alkali by calcination, and these ferrites are very difficult to dissolve in water.

Replacement of iron(III) ions with ions having a lower charge (transition metal ions M^{II} as alloying elements or Fe^{II}) in the Fe_2O_3 structure would result in $M_x^I[M_x^{II}Fe_{2-x}^{III}O_3]$ or $M_x^I[Fe_x^{II}Fe_{2-x}^{III}O_3]$ with the inclusion of alkali metal ions for the charge compensation. These compounds are compositionally similar to magnetite and the transition metal ferrites described in Section 3.1, possibly with correspondingly low solubility to water.

The iron compounds $M^I[Fe^{III}O_2]$, $M_x^I[Fe_x^{II}Fe_{2-x}^{III}O_3]$, and $M_x^I[M_x^{II}Fe_{2-x}^{III}O_3]$ suggested here may be formed just above the steel surfaces in the corrosion stage described in Section 3.3 where the acid solution containing Fe^{3+} , Fe^{2+} , and M^{2+} ions is mixed with the NaOH solution on the steel surfaces under the rust layer. If this innermost layer of rusts containing these compounds show stable cation-selective permeability due to the release of alkali metal ions to water, in addition to the resistance of mass transfer by the outer layer constituted of dense α -FeOOH rusts described above, perfect corrosion protection would be possible.

The formation and presence of $M^I[Fe^{III}O_2]$, $M_x^I[Fe_x^{II}Fe_{2-x}^{III}O_3]$, and $M_x^I[M_x^{II}Fe_{2-x}^{III}O_3]$ in rusts have not been reported so far, and it is necessary to explore the potential of these compounds as components of corrosion protective rusts.

6. Summary and conclusions

The final paragraph of the introduction described the thrust and aims of the paper and the conclusions may be summarized as follows:

1. At the initial stage of corrosion, $Fe(OH)_2(s)$ forms, and this is dissolved and air-oxidized very rapidly at pH 9.31. With aging of the oxidation products, a rust film forms, and the voids and vacancies in the film are plugged by rapid air-oxidation of iron(II). As a result, a dense self-repairing protective rust film is formed.
2. After completing a protective rust film, eventually, the film deteriorates by further aging and dissolution to form channels through which water and oxygen migrate to the metal surface from the outside environment. Under the remaining rusts, crevice corrosion starts to occur, forming $FeCl_2$ in the anode channel and NaOH in the cathode channel.

The air-oxidation of FeCl_2 in the anode channel produces hydrochloric acid with a pH of 1.41, leading to acid corrosion. Corrosion products here are dissolved iron ions and non-aggregated “flowing” rusts due to a large surface charge at a low pH. In this stage, corrosion products leak out and become coarse, porous, flaky, non-protective rusts outside the film.

3. The regions of acid corrosion tunnel into the previous cathode region, and the acidic solution containing iron(II), iron(III), and alloying metal(II) ions mixes with the NaOH solution, attaining a pH of 9.31. Then the state of the metal surface is in the initial stage of corrosion, and a dense self-repairing protective rust film forms. The corrosion-protective and corrosion-promoting stages alternate, resulting in a layer structure in the rust film.

4. To form a long-lasting protective rust film with self-repairing properties, it was pointed out that an acceleration of the air-oxidation of iron(II) at low pH is important. Copper and phosphorus as weathering steel components were suggested to play roles as catalysts when these are oxidized to copper(II) and phosphate ions. Fine particles of rusts are considered to form a dense rust film that is a good physical barrier to the mass transfer of water and oxygen. The addition of foreign ions results in small rust particles, and some alloying elements may serve to form a dense rust film composed of fine particles. Cation-selective permeability of rusts can prevent corrosive anions from penetrating to the metal surface, and the conditions to develop the cation-selective permeability are discussed. For the dimension of an ion passage in cation-selective rusts, it was proposed that the diameter should be less than a value at which the electrical double layers of opposing surfaces overlap (several tens nm), within this distance there is a repulsion from the negatively charged rust wall to entering anions. As negatively charged potential rust compounds with cation-selective permeability, layered iron oxides (ferrites) were suggested, of which negative charge arises from the non-stoichiometry of lattice metal and oxide ions and is kept stably negative even in very acidic conditions without changing the polarity.

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Figure legends

Fig. 1 Electrochemical mechanism of corrosion of iron

Fig. 2 Solubilities of corrosion products as functions of pH

Fig. 3 Initial rate V_0 of air-oxidation of iron(II) as functions of pH

$[\text{Fe(II)}]_0 = 0.01 \text{ mol dm}^{-3}$, saturated air with $[\text{O}_2] = 2.8 \times 10^{-4} \text{ mol dm}^{-3}$, 20°C

Fig. 4 Processes of the initial stage of corrosion

Fig. 5 Crevice corrosion under rust

Fig. 6 Acid corrosion under rust

Fig. 7 Evans model of corrosion

Fig. 8 Anode channel with cation-selective permeability

Fig. 1 Electrochemical mechanism of corrosion of iron

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$[\text{Fe(II)}] = 0.01 \text{ mol dm}^{-3}$, saturated with air $[\text{O}_2] = 2.8 \times 10^{-4} \text{ mol dm}^{-3}$, 20°C

Fig. 4 Rust film formed in the initial stage of corrosion

Fig. 5 Crevice corrosion under rust

Fig. 6 Acid corrosion under rust

Fig. 7 Evans model of corrosion

Fig. 8 Anode channel with cation-selective permeability