

International Journal of Engineering Sciences & Research Technology

(A Peer Reviewed Online Journal)
Impact Factor: 5.164



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**INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH
TECHNOLOGY****A REVIEW ON CORROSION OF LOW CARBON STEELS IN AQUEOUS
HYDROGEN SULFIDE****I.A. Fioravante, J.F. Macedo, R. Z. Nakazato, H.A. Acciari & E.N. Codaro***

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DOI: 10.5281/zenodo.3577181

ABSTRACT

Sour corrosion has been a problem for the oil exploration and extraction industry for many decades. It can manifest itself in different ways and one of which is the formation of a scale on the inner walls of pipelines. Although the consequences of corrosion are well known, the combination of factors that determine the composition and physicochemical characteristics of the scale remains unclear. This one is initially composed of mackinawite, which is relatively stable in the absence of oxygen. At high partial pressures of hydrogen sulfide and/or temperatures, other more stable sulfides such as troilite and pyrrhotite are formed. Thus, the protectiveness of the scale is enhanced by the formation of these new compounds. An undesirable entry of air in pipelines during drilling and oil recovery operations changes scale composition and therefore polysulfides, oxides and oxyhydroxides can also be found as corrosion products. The degree of oxygen contamination determines the relative proportions of these compounds, so low concentrations favor the formation of polysulfides, while high concentrations favor the formation of oxides. In this context, this paper discusses the effects of partial pressure of hydrogen sulfide, dissolved oxygen and water chemistry on scale formation. Particular attention is paid to the nature and stability of the aqueous species formed during the corrosion process, as well as the thermodynamic and kinetic aspects lead to scale formation. The main objective is to enhance the understanding of the formation and precipitation conditions of mackinawite and pyrrhotite and their effects on corrosion processes involving low carbon steels.

KEYWORDS: Sour corrosion; Iron monosulfide layers; Mackinawite; Pyrrhotite; Low carbon steels; Hydrogen sulfide.**1. INTRODUCTION**

In the last few decades, the world has witnessed a growing demand for fossil fuels. Despite efforts by international organizations to diversify energy resources, current projections indicate greater demand for oil and natural gas over the next 20 years. Once many countries aspire to achieve energy autonomy, new oil reserves have been exploited in areas of difficult geological access (e.g. deep waters or Arctic regions) [1]. Due to the extraction of more acid fluids, there have been increasingly frequent and severe corrosion problems, thus reducing the lifespan of pipelines in just a few years [2]. Low carbon steel materials are widely used in the oil and gas production industry because of their availability, malleability, and ductility and relatively low cost. But once there is hydrogen sulfide and brine in oil, this medium becomes so aggressive that it leads to corrosion of these materials [3-5]. Among the types of localized corrosion, hydrogen embrittlement stands out as the most serious form of corrosion. In this process, an amount of hydrogen that is reduced during the corrosion reaction diffuses through steel, thus accumulating in crystalline defects and microstructural discontinuities such as inclusions, pores, etc. [6-8]. Then, hydrogen pressurization leads to the formation of cracks and eventual pipeline failure [9-11]. General corrosion is commonly manifested by the formation of a scale of iron monosulfides and polysulfides on the inner walls of pipelines (Figure 1) and valves, which can cause problems in pumping systems [12,13]. Although corrosion consequences are known, causes and mechanisms by which each phenomenon occurs are still not well understood. There are two contributing factors to this situation, which are: a correlation of multiple parameters that influence corrosion and the limitations of laboratory test systems to reproduce the actual internal conditions of pipelines [14,15].



Many petroleum experts have studied the corrosive processes of carbon steels in sour environments. Their hands-on experience combined with scientific research allowed discerning which corrosion products were formed during oil extraction and production operations. Generally, a carbon steel pipeline contains a relatively continuous layer of iron oxide and oxyhydroxide (hematite α -Fe₂O₃, maghemite γ -Fe₂O₃, magnetite Fe₃O₄, lepidocrocite γ -FeOOH, and goethite α -FeOOH) formed spontaneously in air [16,17], which is not removed before installation. As oil passes, hydrogen sulfide can react with these compounds to form either monosulfides or polysulfides. Different iron sulfides have been identified in corrosion products within pipelines [18-20]. The most frequently cited monosulfides are tetragonal mackinawite (FeS) and hexagonal/monoclinic pyrrhotite (Fe_{1-x}S with x = 0 to 0.17), both relatively stable in oxygen-free acid media. Polysulfides such as greigite (Fe₃S₄) and pyrite (FeS₂) are formed by partial oxidation of monosulfides, probably on account of air being introduced during drilling or secondary oil recovery [21,22]. Research using different corrosion techniques in aqueous media have made a significant contribution in this sense. Synthetic sea water and other saline solutions containing hydrogen sulfide have often been used as corrosive media, probably due to these media having a similar chemical composition to emulsified water in oil [23,24]. However, results obtained in relatively short exposure times at room temperature have led to one or two types of iron sulfides, mackinawite and pyrrhotite. Thus, the present work aims to broaden understanding about the conditions of formation and precipitation of these phases and their effects on corrosion processes involving low carbon steels.

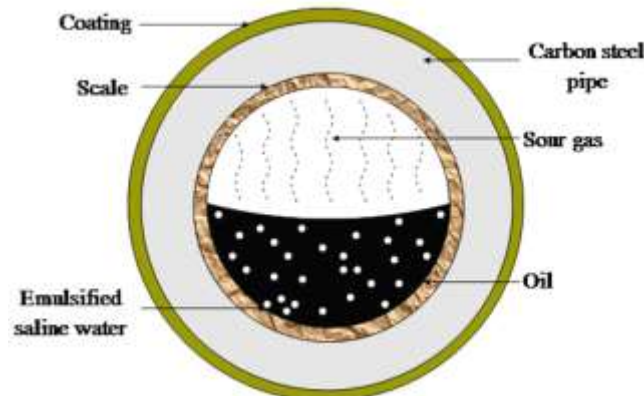
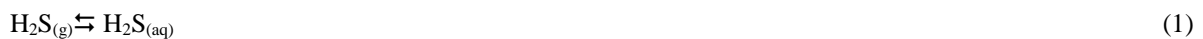


Figure 1: Illustration of the cross section of an oil pipeline showing the scale formed by sour corrosion

2. REVIEW AND DISCUSSION

Hydrogen sulfide in aqueous solution

Hydrogen sulfide (H₂S(g)) is a relatively water-soluble gas at room temperature. When it is dissolved, it forms a very weak diprotic acid, also known as hydrosulfuric acid (H₂S(aq)) (equations 1 to 3). In literature, there are multiple dissociation constants for such acid (K_{a1} and K_{a2}), particularly for the second dissociation which involves very low concentrations of ionic species [25,26].



In this study, intermediate values for K_{a1} = 1.0 x 10⁻⁷ and K_{a2} = 1.0 x 10⁻¹⁴ were used to calculate the equilibrium concentrations. Given the low values of these constants and a broad difference between them, the pH of an aqueous solution can be determined by the first dissociation. Since the analytical concentration of H₂S is higher than its effective concentration, it is more appropriate to write an equilibrium expression involving the partial pressure of H₂S (pH₂S). Although Henry's law is strictly aimed at gases that do not interact with the solvent, it

requires low p_{H_2S} (≤ 1.0 atm) and room temperature conditions. From Henry's law expression for H_2S in water at 25 °C ($K_H = 0.1013 \text{ mol L}^{-1} \text{ atm}^{-1}$) [27], it is possible to obtain an equation relating pH and p_{H_2S} (equation 4).

$$pH = 4.0 - 0.5 \log p_{H_2S} \quad (4)$$

Figure 2 shows a graphical representation of equation 4. It reveals two characteristics of this gas in aqueous solutions: i) saturated solutions are slightly acid at ordinary pressures; ii) in order to increase pH by one unit, it is necessary to decrease p_{H_2S} by two orders of magnitude. In Figure 2, a dashed region formed by different pH and p_{H_2S} conditions that are considered as not being sour stands out. Petroleum and natural gas industries, through established standards, have determined an empirical value of 0.003 atm for p_{H_2S} , i.e. below this value the acidity of aqueous phase in oil does not affect the lifespan of pipelines [28]. For a given p_{H_2S} in this region, pH mainly varies according to the relative concentration of formic, acetic and carbonic acids present in produced water [29,30]. In this sense, water chemistry can be a major contributor to better understand pipeline corrosion.

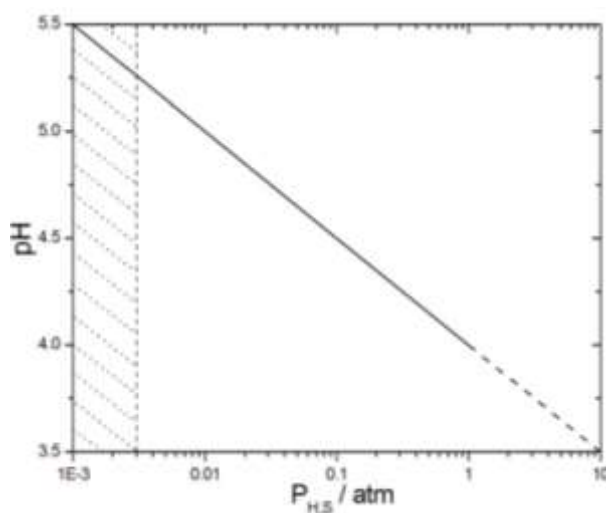


Figure 2: Effect of p_{H_2S} on pH at 25 °C. Dashed region shows non-sour conditions

If pH is changed at constant p_{H_2S} and temperature, equilibrium will be disturbed and a new sulfide species ratio will be established for the solution. The relation between sulfur-containing species and pH can be calculated using Henderson-Hasselbalch equation [31] by the dissociation constant expression (K_{a1}) for pH values that are less than 7.0 and the hydrolysis constant expression ($K_h = 1.0$) for pH values greater than or equal to 7. Figure 3 shows $H_2S_{(aq)}$, $HS_{(aq)}^-$ and $S^{2-}_{(aq)}$ concentrations as a function of pH for total concentration of sulfur-containing species at 0.1 mol L^{-1} , which has been determined for $p_{H_2S} = 1.0$ atm at 25 °C.

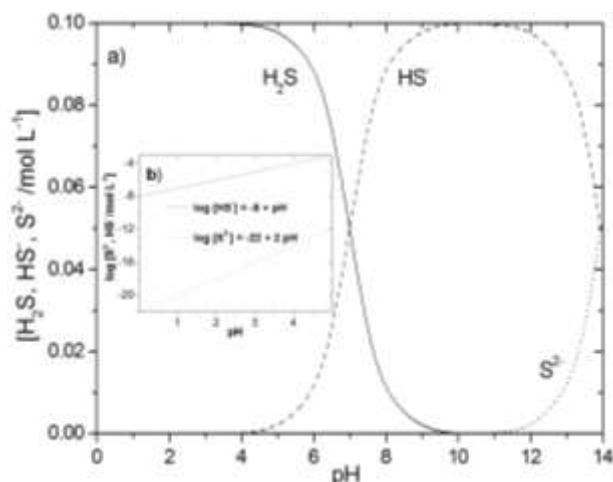


Figure 3:(a) Sulfur-containing species as a function of pH and (b) $\text{HS}^-_{(\text{aq})}$ and $\text{S}^{2-}_{(\text{aq})}$ species in an acid medium

Figure 3a indicates that for pH values below 4.0, $\text{H}_2\text{S}_{(\text{aq})}$ is present mainly in its molecular form, but there are small concentrations of $\text{HS}^-_{(\text{aq})}$ and $\text{S}^{2-}_{(\text{aq})}$ that are ready to react, even in this pH range. These concentrations can be estimated from K_{a1} and $K_{a1}K_{a2}$ (total dissociation) expressions, respectively, by assuming that $[\text{H}_2\text{S}_{(\text{aq})}] = 0.1 \text{ mol L}^{-1}$. Figure 3b shows the variation of ionic species concentration in an acid pH range in greater detail. It is observed that in highly acid solutions, only the most insoluble transition metal sulfides can precipitate. In the Pourbaix diagram depicted in Figure 4, stability regions of sulfur-containing species are indicated between the lines representing redox and acid-base reactions between species that can be in equilibrium [32].

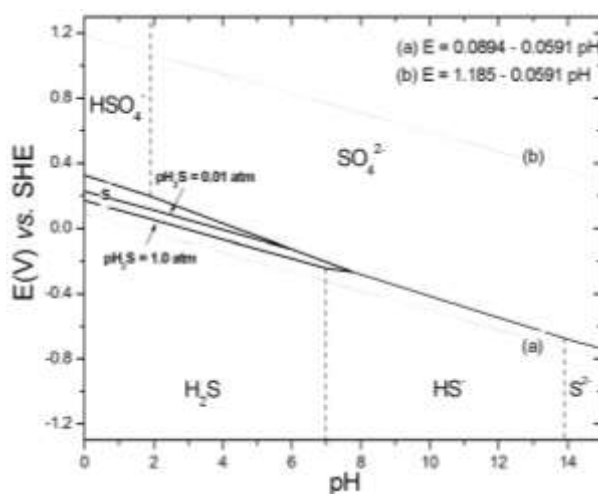


Figure 4: Simplified Pourbaix diagram for the S- H_2O system at 25 °C showing the effect of pH_2S on sulfur formation

Dashed lines at $\text{pH} = 7.0$ and 14.0 represent the same concentration ratios of molecular and ionic species, as shown in Figure 3a. Two dotted lines were added to the diagram in order to indicate the water stability region. In lines (a) and (b), hydrogen and oxygen partial pressures were assumed to be equal to 0.001 atm at $25 \text{ }^\circ\text{C}$, but the higher the partial pressure, the higher the water stability region. The species within this region do not react with H_2O , whilst those outside are able to do so. Therefore, it is verified that: i) $\text{HSO}_4^-_{(\text{aq})}$ and $\text{SO}_4^{2-}_{(\text{aq})}$ are stable in aqueous solutions throughout the pH range; ii) $\text{S}_{(\text{s})}$ is stable in acid or neutral aqueous solutions; iii) $\text{H}_2\text{S}_{(\text{aq})}$, $\text{HS}^-_{(\text{aq})}$ and $\text{S}^{2-}_{(\text{aq})}$ are stable throughout the pH range in the absence of dissolved oxygen; iv) oxidation of $\text{H}_2\text{S}_{(\text{aq})}$ into $\text{S}_{(\text{s})}$ can only occur in an acid medium in the presence of oxygen [33] and, as the latter is much less soluble

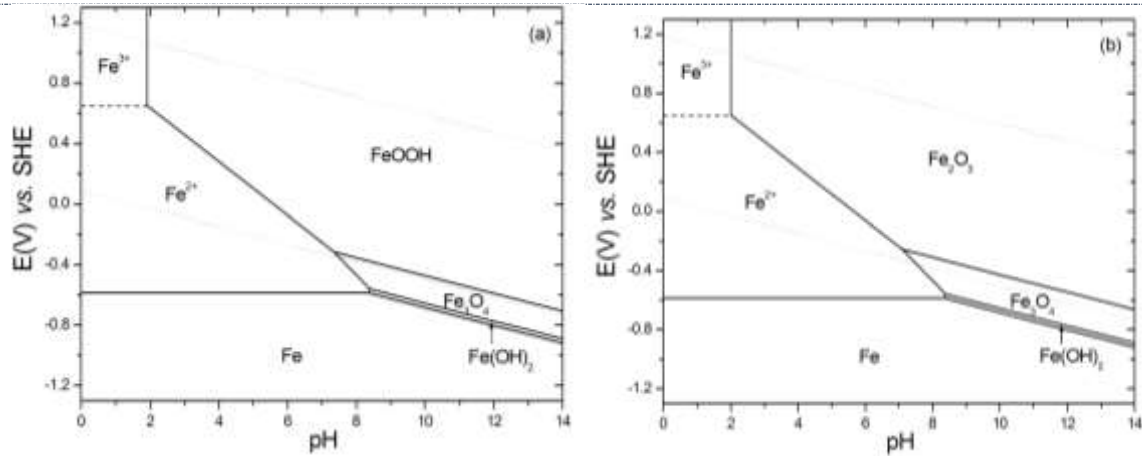


Figure 6: Simplified Pourbaix diagrams for the Fe-H₂O system at 25 °C with passivity domain formed by (a) Fe(OH)_{2(s)}, Fe₃O_{4(s)} and FeOOH_(s), and (b) Fe(OH)_{2(s)}, Fe₃O_{4(s)} and Fe₂O_{3(s)}

According to the diagrams, it should be noted that iron may be oxidized throughout this pH range, but the oxidation product will depend on the oxidizing agent. At pH < 8.4, the anodic reaction product is Fe²⁺_(aq) (shorthand notations for [Fe(H₂O)₆]²⁺ or [FeOH]⁺), and Fe(OH)_{2(s)} and Fe₃O_{4(s)} for 8.4 ≤ pH ≤ 14. It is worth mentioning that Fe(OH)_{2(s)} is not necessarily a precursor of Fe₃O_{4(s)}, the latter can also be formed at lower pH values. In the presence of oxygen, the medium becomes more oxidizing and Fe(II)-containing species can be oxidized into Fe³⁺_(aq) (shorthand notations for [Fe(H₂O)₆]³⁺ or [FeOH]²⁺), FeOOH_(s) (Figure 6a) or Fe₂O_{3(s)} (Figure 6b) depending on pH conditions. Three domains can be differentiated through these diagrams: corrosion (composed of iron cations), immunity (consisting of pure iron) and passivity (consisting in a layer that supposedly protects iron). These regions represent theoretical conditions in which corrosion may, cannot and does not occur, respectively. In practice, a source of oxygen contamination is the key factor relating to fluids used in secondary and tertiary oil recovery. In saline solutions such as produced water [39,40], dissolved oxygen concentration greatly depends on salinity, that is, the higher the salinity, the lower the dissolved oxygen concentration [41]. According to Craig [19], if there is not much dissolved oxygen in produced water, a mixed scale consisting principally of iron oxyhydroxides and magnetite is formed on carbon steel, but if the water is nearly saturated with dissolved oxygen, the hematite is almost always present in this scale. Moller et al. [42] performed corrosion test on SAE 1006 (UNS G10060) in natural and synthetic seawaters. They concluded that the composition and physicochemical characteristics of the scale depend on the chemical composition of the saline solution. By comparing Figures 6 and 4, oxides and oxyhydroxides of iron (III) can react with H₂S to form sulfur species which include elemental sulfur, sulfate and polysulfides. In addition to changing the nature of corrosion products, the oxygen contamination in brines containing H₂S can also result in drastic increases in corrosion rates by as much as two orders of magnitude [23,24,33,43].

Iron and hydrogen sulfide in aqueous solution

When iron is exposed to an aqueous solution containing hydrogen sulfide, a corrosion reaction occurs whose consequence may be iron sulfide precipitation. As the concentration of ionic species in this medium is directly linked to pH conditions, whether sulfides will precipitate or not also depends on pH. There are different expressions in the literature that determine the solubility equilibrium and several constants for these equilibria [25,26,44,45]. In this study, the expressions of the solubility products of Fe(OH)₂, FeS_{mackinawite} and FeS_{pyrrhotite} described by equations 5, 6 and 7 were used, respectively.

$$K_{\text{hydroxide}} = [\text{Fe}^{2+}] [\text{OH}^-]^2 = 6.3 \times 10^{-16} \quad (5)$$

$$K_{\text{mackinawite}} = \frac{[\text{Fe}^{2+}] p_{\text{H}_2\text{S}}}{[\text{H}^+]^2} = 1.6 \times 10^4 \quad (6)$$

$$K_{\text{pyrrhotite}} = \frac{[\text{Fe}^{2+}] \text{ pH}_2\text{S}}{[\text{H}^+]^2} = 7.1 \times 10^3 \quad (7)$$

By rearranging equations 5, 6 and 7, it is possible to obtain equations 8, 9 and 10, which can clarify the influence of pH on solubility equilibria.

$$\log [\text{Fe}^{2+}]_{\text{hydroxide}} = 12.8 - 2 \text{ pH} \quad (8)$$

$$\log [\text{Fe}^{2+}]_{\text{mackinawite}} = 4.19 - \log \text{pH}_2\text{S} - 2 \text{ pH} \quad (9)$$

$$\log [\text{Fe}^{2+}]_{\text{pyrrhotite}} = 3.85 - \log \text{pH}_2\text{S} - 2 \text{ pH} \quad (10)$$

Figure 7 shows a graphical representation of these equations, which reveals that $\text{Fe}^{2+}_{(\text{aq})}$ concentration in equilibrium with $\text{Fe}(\text{OH})_{2(\text{s})}$ or $\text{FeS}_{(\text{s})}$ decreases as pH of the medium increases. Each line divides the graph into a couple of regions: the dissolution region on the left and the precipitation region on the right. It is also evident that when pH_2S is increased, lower concentrations of $\text{Fe}^{2+}_{(\text{aq})}$ are sufficient to precipitate FeS. FeS precipitation will start when $\text{Fe}^{2+}_{(\text{aq})}$ concentration and pH are the same as those on the line. Then, the ionic product $[\text{Fe}^{2+}][\text{S}^{2-}]$ value will be the same as that of $K_{\text{mackinawite}}$ or $K_{\text{pyrrhotite}}$. Since $\text{OH}^{-}_{(\text{aq})}$ and $\text{S}^{2-}_{(\text{aq})}$ concentrations are defined according to Figure 3b, the ionic product $[\text{Fe}^{2+}][\text{OH}^{-}]^2$ is always less than $[\text{Fe}^{2+}][\text{S}^{2-}]$, and thus there is no precipitation of $\text{Fe}(\text{OH})_2$ in an acid environment containing H_2S .

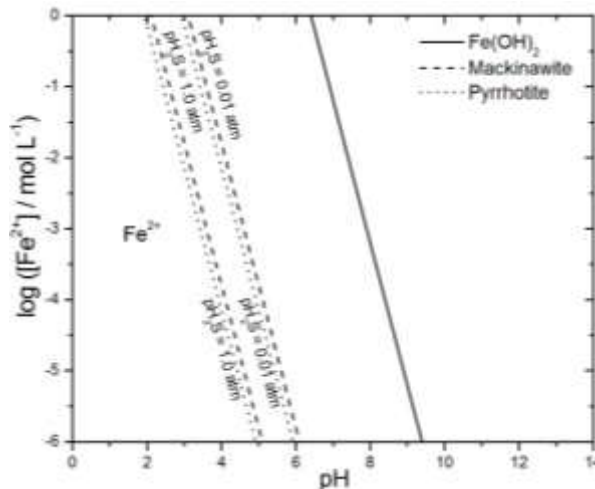
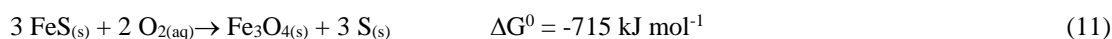


Figure 7: Influence of pH on solubilities of FeS and $\text{Fe}(\text{OH})_2$ at 25 °C

Mackinawite has been more widely studied than pyrrhotite (Fe_{1-x}S with $x = 0$ to 0.17), or troilite. This one is the stoichiometric form of pyrrhotite with $x = 0$ (FeS). Mackinawite is rapidly formed over a wide range of pH, pressure and temperature. On the other hand, pyrrhotite needs a complex combination of factors for its precipitation. In a deaerated acid medium, pyrrhotites are preferably formed at higher pH_2S and/or temperatures than mackinawite [18,46]. It is noteworthy that the increase in temperature and partial pressure have opposite effects on pH [47], so it is difficult to associate pyrrhotite formation with pH. When local conditions at the metal/electrolyte (or mackinawite layer/electrolyte) interface are favorable for pyrrhotite nucleation and growth, mackinawite is probably not formed and the layer stops growing [48]. This usually occurs when ionic concentration in equilibrium with a solid phase is much smaller than that required to precipitate the other one. Although this assumption is difficult to verify, mackinawite is a metastable phase and a precursor in the formation of polysulfides (equations 11 and 12) [19,45,49], so that at some stage of the corrosion process of carbon steel, the mackinawite layer would stop growing.



Pourbaix diagrams of iron in the presence of $\text{H}_2\text{S}_{(aq)}$ are shown in Figure 8. For constructing these diagrams, equations 9 and 10 were used to represent chemical equilibria. Nernst equations 13 to 18 were obtained from $\Delta G_f^0(\text{FeS}_{\text{mackinawite}}) = -100 \text{ kJ mol}^{-1}$ and $\Delta G_f^0(\text{FeS}_{\text{pyrrhotite}}) = -102 \text{ kJ mol}^{-1}$ [38].

$$E(\text{FeS}_{\text{mackinawite}}/\text{Fe}) = 0.345 + 0.0296 \log \text{pH}_2\text{S} - 0.0591 \text{ pH} \quad (13)$$

$$E(\text{FeOOH}/\text{FeS}_{\text{mackinawite}}) = 0.505 + 0.0591 \log \text{pH}_2\text{S} - 0.0591 \text{ pH} \quad (14)$$

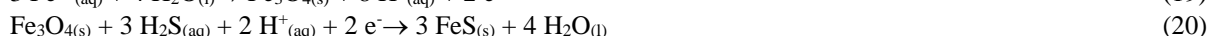
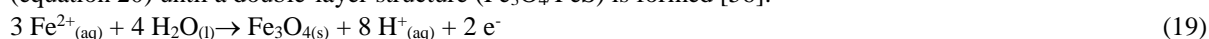
$$E(\text{Fe}_2\text{O}_3/\text{FeS}_{\text{mackinawite}}) = 0.520 + 0.0591 \log \text{pH}_2\text{S} - 0.0591 \text{ pH} \quad (15)$$

$$E(\text{FeS}_{\text{pyrrhotite}}/\text{Fe}) = 0.355 + 0.0296 \log \text{pH}_2\text{S} - 0.0591 \text{ pH} \quad (16)$$

$$E(\text{FeOOH}/\text{FeS}_{\text{pyrrhotite}}) = 0.526 + 0.0591 \log \text{pH}_2\text{S} - 0.0591 \text{ pH} \quad (17)$$

$$E(\text{Fe}_2\text{O}_3/\text{FeS}_{\text{pyrrhotite}}) = 0.540 + 0.0591 \log \text{pH}_2\text{S} - 0.0591 \text{ pH} \quad (18)$$

By comparing Figures 8 and 6, it can be concluded that the former shows a larger passivation domain due to iron monosulfide formation in each case. A more detailed analysis of Figure 8a,b reveals that for $\text{pH}_2\text{S} = 1.0 \text{ atm}$ and $\text{pH} < 4.1$, for example, conditions are not favorable for mackinawite layer formation. Research indicates that mackinawite precipitation can start at pH values as low as 2.7 and layers formed at $\text{pH} \leq 4.0$ are discontinuous or porous [48-51]. However, these values may vary depending on the presence of complexing agents and ionic strength of the medium. When pyrrhotite precipitation occurs, the region of passivation becomes larger and there is less corrosion (Figure 8c,d) as a consequence of smaller metal active area due to the formation of a relatively more protective layer. Similar Pourbaix diagrams were constructed by other authors [52,53] who also had demonstrated that an increase in pH_2S , temperature or exposure time favors the formation of crystalline monosulfides, particularly pyrrhotite. Other studies indicate that the higher the pH_2S , the higher pyrrhotite/mackinawite ratio, which is in turn increases with exposure time, thus making the layer more compact [18,46,54,55]. A recent high-temperature study showed that a layer of magnetite is initially formed on API 5L X65 in an oxygen-free aqueous H_2S medium (equation 19) and then it is slowly converted into mackinawite (equation 20) until a double-layer structure ($\text{Fe}_3\text{O}_4/\text{FeS}$) is formed [56].



The presence of iron oxides as corrosion products in an oxygen-free and H_2S -containing acid environment is a matter of discussion. Incomplete deaeration of the test solution, entry of oxygen during and after the test and oxidation of the corrosion products during their chemical analysis are the main causes of oxide formation. When it happens, magnetite is often found among corrosion products because it is the most stable iron oxide and a very low oxygen concentration is sufficient for its formation [20,57].

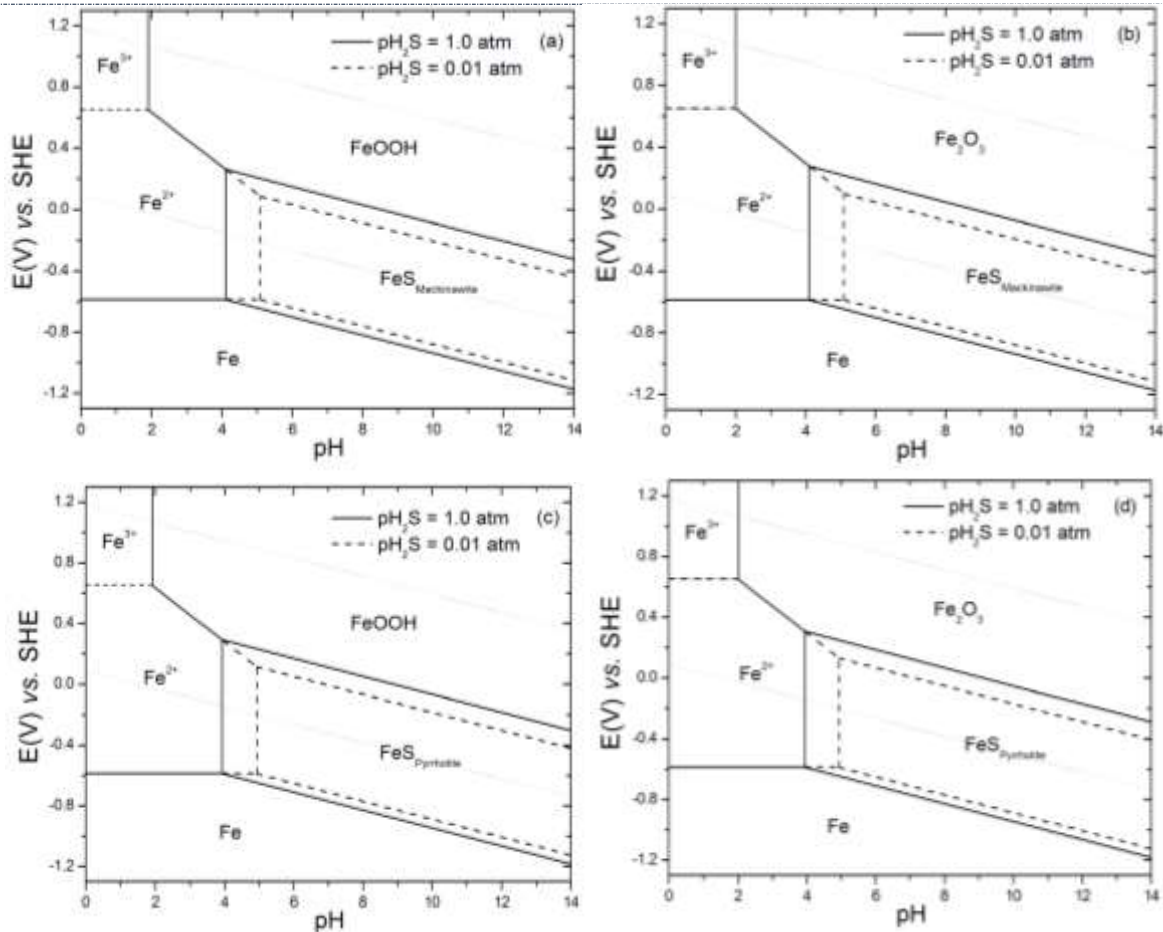


Figure 8: Simplified Pourbaix diagrams for the Fe-H₂O-H₂S system at 25 °C considering the effect of pH₂S on mackinawite (a, b) and pyrrhotite (c, d) formation

A few iron sulfide complexes have been reported, some of which do not have well-defined stoichiometry. Figure 9 shows the distribution of iron- and sulfur-containing species in terms of pH. The total concentration of Fe(II) and S(-II) species was assumed to be equal to 0.0001 and 0.1 mol L⁻¹, respectively. In acid media, predominantly ionic Fe²⁺_(aq) and HS⁻_(aq) species can form FeHS⁺_(aq) and shift the solubility equilibrium towards higher pH values. Although all equilibrium conditions in a complex system must be satisfied simultaneously, it is often possible to make some approximations so as to quantify the complexing action of HS⁻_(aq). From the formation constant of FeHS⁺_(aq) ($K_f \approx 22000$) [45,58], it is possible to demonstrate [59] that the concentration of free Fe²⁺_(aq) decreases by about twenty times at pH = 5.0 and two hundred times at pH = 6.0. Hence, Fe²⁺_(aq) will be practically in the form of complex ions at higher pH values. In alkaline media, however, FeS_(aq) cluster was proposed to be a more stable species than FeHS⁺_(aq) [60]. This Figure also suggests that if the total concentration of S(-II) species was lower than the total concentration of Fe(II), Fe(II)-hydroxyl species would be the dominant species in alkaline media.

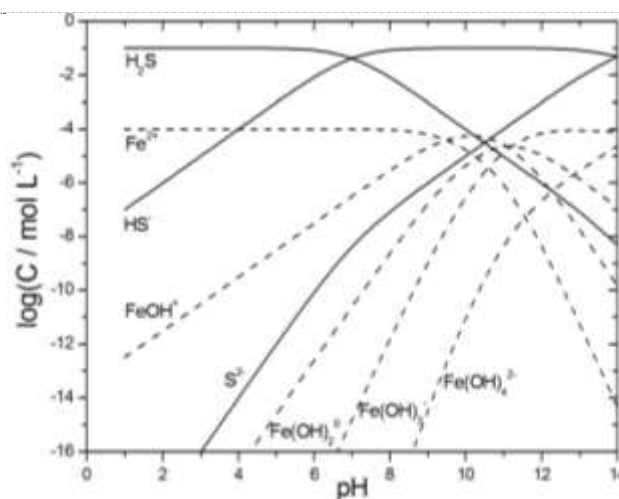


Figure 9: Distribution of species containing iron and sulfur in aqueous solution

In produced water there are several complexing agents (e.g. Cl^- , HCO_3^- and SO_4^{2-}) [73] that can react with iron and increase the solubility of iron sulfide. FeCl^+ ($K_f \approx 0.33$) is one of the most important complexes in the pH range between 4.0 and 8.0 [74-76]. Despite the low K_f value, the high chloride concentration in produced water [29,39,40,77] shifts the ionic equilibrium, favoring the formation of the complex. Figure 10 reveals that this one becomes the predominant species when chloride concentration is higher than 3.0 mol L^{-1} . In addition, the solubility of an iron compound may be markedly increased if chloride is available to react with the iron of this compound. Using mass balance equations, it is possible to calculate species concentrations under equilibrium conditions [59,78]. Thus, the solubility of mackinawite ($K_{sp} = 1.62 \times 10^{-18}$) can be increased by $\sim 8.5\%$ in a seawater-like NaCl solution and $\sim 73\%$ in saturated NaCl solution.

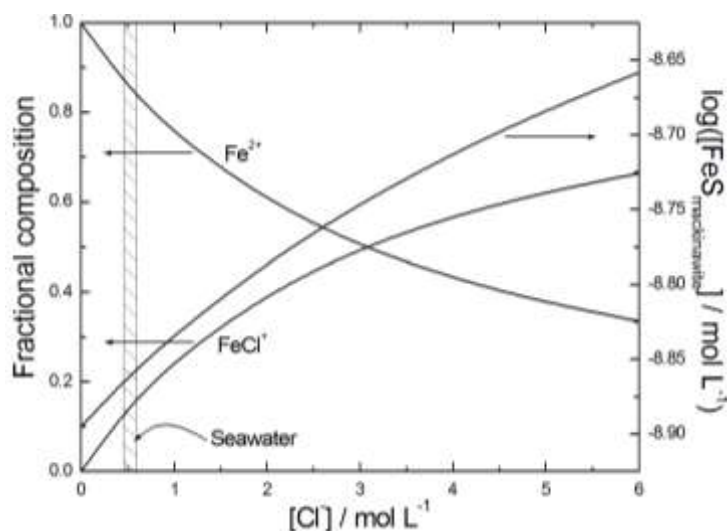


Figure 10: Iron-containing species distribution and mackinawite solubility as a function of chloride concentration

Low carbon steel corrosion

When low carbon steel is exposed to an oxygen-free and H_2S -containing acid environment, it is initially corroded and $\text{Fe}^{2+}_{(\text{aq})}$ and $\text{H}_{2(\text{g})}$ are the main corrosion products. Secondary phases such as cementite or other carbides can act as cathodes, while iron dissolution occurs in ferrite grains [61]. In strongly acid media, iron corrosion probably occurs by means of an adsorbed Fe(II)-hydroxo complex and the oxidation this species is deemed to be the rate-determining step (rds) (equations 21, 22, 23 and 24) [62].

[Codaro, *et al.*, 8(12): December, 2019]
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A similar mechanism involving chemisorbed sulfide species was proposed by Shoosmith *et al.* (equations 25 and 26) [50].



$\text{FeSH}^+_{(\text{ad})}$ may be hydrolyzed to yield soluble species (equation 27), or it may be incorporated directly into a growing layer of mackinawite (equation 28), depending on the pH value of the solution. Then, the iron dissolution may be promoted at lower pH values or it may be inhibited at higher pH values [63].



FeS_{1-x} is a non-stoichiometric form of mackinawite, according to the old understanding that prevailed until 2006 [64].

As pH increases, a very thin layer of mackinawite is formed rapidly. This layer appears to be formed through a direct mechanism from adsorbed species at the metal/electrolyte interface. This is based on a certain similarity between unit cells of tetragonal mackinawite and the body-centered cubic ferritic structure of carbon steel [48]. Due to its high electrical conductivity [65], $\text{H}^+_{(\text{ad})}$ or $\text{HS}^-_{(\text{ad})}$ ions can be reduced on the layer surface, thus causing iron oxidation, iron sulfide formation and layer growth. A rapid layer growth coupled with the high ratio of volume of unit cell of formed iron sulfide to volume of unit cell of consumed iron (~ 2.6) can generate unbalanced internal stresses that lead to cracking of layers and new paths to the steel surface. Fe(II) ions released in the metal/electrolyte interface can precipitate with the adsorbed sulfides within the cracks or they can diffuse out of these to the layer/electrolyte interface. Since the local composition of the electrolyte can change along the entire length of the crack, another phase can nucleate and grow within the cracks of the mackinawite layer. At an early stage of corrosion of carbon steel, the cubic phase of FeS has been reported as a secondary crystalline product following mackinawite [61,66], but it is a metastable phase which appears to be converted by a dissolution and recrystallization process into mackinawite, troilite or pyrrhotite during the corrosion process [67,68]. As there is no experimental evidence of solid-state transformation of mackinawite into troilite (or pyrrhotite) at least in the medium and low-temperature range [69], the latter will be formed when the medium conditions are favorable for its nucleation and growth. After successive cracks, crystals of the new phase multiply across the surface of the mackinawite and they will continue to be formed until the growth of a layer hinders the diffusion of ionic species involved in the process. Since pyrrhotite is the most stable phase, its layer will provide greater protection against corrosion. Although monosulfides may initially inhibit corrosion, the evolution of the physicochemical properties of the layer (adhesion, compactness, thickness and conductivity) during the exposure time will determine the protectiveness of the layer [46,51,54,70-72].

3. CONCLUSION

A corrosion process is initiated when low carbon steel is exposed to an oxygen-free and H_2S -containing acid environment. Partial pressure of hydrogen sulfide and water chemistry are two of the main contributors to this process. In strongly acid media, iron is preferably dissolved from the predominant phase and general corrosion occurs. Hence, the steel surface becomes richer in cementite and other insoluble carbides. In moderately acid media, a brittle mackinawite layer is formed, which is relatively stable in the absence of dissolved oxygen. As the thickness of the layer increases, it breaks more easily and the formation of cracks promotes the nucleation

and growth of troilite or pyrrhotite. The protective characteristics of this layer are improved by the subsequent formation of a more compact layer of pyrrhotite, which is favored at higher partial pressures of hydrogen sulphide (higher temperatures and/or longer exposure times).

Despite the limitations of potential-pH diagrams, the present thermodynamic approach supports a dissolution-recrystallization mechanism for monosulfides layer growth at room temperature. Other solid species such as ferrous hydroxide and magnetite should not be formed during corrosion in an oxygen-free and H₂S-containing acid environment. If they are present before oil passes through the pipeline, they will react with hydrogen sulfide to form mackinawite and greigite, respectively. Oxides and oxyhydroxides of iron (III), elemental sulfur, sulfites, sulfates and thiosulfates should also not be among its corrosion products, as they arise as a consequence of an amount of oxygen present in the medium. The degree of oxygen contamination will determine the relative proportions of these compounds, thus low concentrations favor the formation of polysulfides, while high concentrations favor the formation of oxides. Although these conclusions can enhance the understanding of sour corrosion, there are still several unclear aspects that require more attention. It is well-known that iron sulfide precipitation does not occur at low partial pressures of H₂S_(g) and/or low pH values at room temperature, but what is the set of parameters that actually decreases the corrosion rate by forming a layer of mackinawite? How do native oxides and oxyhydroxides affect the formation of the mackinawite layer? What are the necessary conditions for the nucleation and growth of pyrrhotite? and which of them lead to the formation of a protective layer? To what extent do the protective characteristics of these films change in the presence of dissolved carbon dioxide?

4. ACKNOWLEDGEMENTS

This work was supported by the São Paulo Research Foundation (Grant No. 2017/11361-5)

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