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Formation of iron oxide and iron sulfide at high temperature and their effects on corrosion

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ABSTRACT

Recent high temperature H₂S corrosion study reported that a thermodynamically less stable iron oxide layer can also form in addition to iron sulfide. In this work, H₂S corrosion experiments were conducted at 120 °C for different exposure times, ranging from 1 to 21 days. The inner layer was identified by Transmission Electron Microscopy (TEM) as Fe₃O₄ (magnetite); Fe₃O₄ was always present over time despite it being less stable than iron sulfide. The observed formation sequence of iron sulfide at high temperature was mackinawite → troilite → pyrrhotite → pyrite. The role of the different corrosion product layers in corrosion is discussed.

1. Introduction

As exploration and drilling conditions for petroleum involve ever higher pressure and temperature (HPHT) in combination with high H₂S content, development of adequate asset integrity management practices (associated with technology development, regulation, and corrosion mitigation) brings many new challenges [1–5]. In 2008, it was reported that at least 11% of wells to be drilled were expected to be at temperatures exceeding 177 °C [1]. HPHT wells are now very common worldwide, from the North Sea and the Gulf of Mexico to Southeast Asia, Africa, and South America [6]. The likelihood of encountering H₂S corrosion also correlates with the increase of temperature in these wells [7]. H₂S corrosion at lower temperatures (< 80 °C) has been extensively studied over the past several decades [8–10], and significant progress has been made related to the understanding of the associated mechanisms. However, research related to H₂S corrosion mechanisms at higher temperatures (> 80 °C) has, so far, been limited. Laboratory experiments at temperature below 80 °C are typically conducted in a glass cell, while autoclaves are used when the temperature is above 80 °C.

In our previous high temperature H₂S corrosion study [11], iron oxide was observed as an inner corrosion product layer. A thin layer (~5 μm) was detected near the metal surface starting at 80 °C, and it became thicker (~25 μm) at higher temperatures (120 °C, 160 °C, and 200 °C). However, according to thermodynamic predictions (Pourbaix diagrams), as shown in Fig. 1, iron oxide should not be present in an aqueous H₂S environment since it is less stable than any of the various iron sulfides that can form. There it is seen that Fe₃O₄ is the most stable species in a pure H₂O-Fe system (see Fig. 1(a)), while iron sulfide is

more thermodynamically favored in the presence of aqueous H₂S (Fig. 1(b)). The red rectangular region represents the typical bulk pH and potential range seen in brines encountered in oil and gas transportation. While the bulk pH is often between 4 and 6, the pH at the steel surface, *i.e.*, the surface pH, is often approximately one unit higher than it is in the bulk [12], especially under low flow or in quiescent conditions. In the region of interest, at a high temperature, 120 °C for example, in a solution without H₂S, only Fe₃O₄ can form (Fig. 1(a)). With the addition of 0.1 bar H₂S, the Fe₃O₄ stability zone is completely replaced by a more thermodynamically favored mackinawite. In this graph, mackinawite is chosen as a meta-stable iron sulfide because it is most kinetically favored. However, other compounds such as pyrrhotite and pyrite can also be included in the analysis, as they are even more thermodynamic stable and would replace mackinawite. Pourbaix diagram determinations are based on bulk brine chemistry, *i.e.*, they can only predict the outer most thermodynamical stable corrosion product in contact with the bulk fluid. However, whether and what other corrosion product can form under the iron sulfide layer is still unknown, because the H₂S concentration underneath the iron sulfide layer can be much lower than that in the bulk solution. Indeed, iron oxide was clearly identified beneath the iron sulfide layer in a short-term (4 days exposure time) experimental study conducted by Gao, et al. [11]. Therefore, further research was warranted to investigate whether the unexpected iron oxide layer would keep growing or, as thermodynamics predicts, it is eventually converted into iron sulfide as the exposure time increases (research question #1).

The growth and phase transitions of polymorphous iron sulfides, with different stoichiometric ratios and structures, are complex. Direct observations are difficult to perform as some of these phases are

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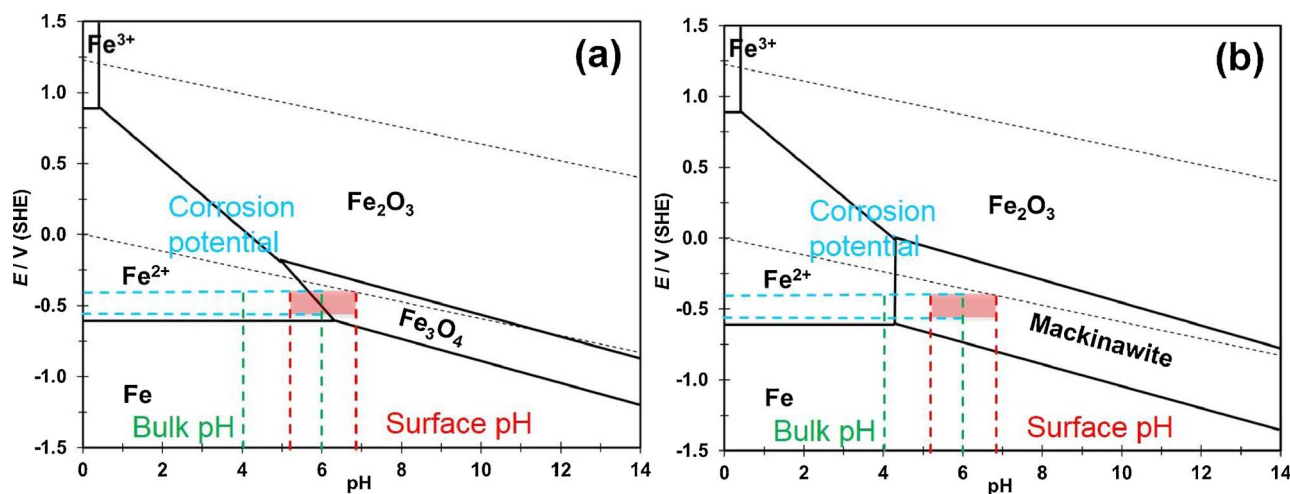


Fig. 1. Pourbaix diagrams for (a) H_2O -Fe system, (b) H_2S - H_2O -Fe system (only mackinawite is considered), $T = 120^\circ\text{C}$, $p_{\text{H}_2\text{S}} = 0.1$ bar.

Table 1

Iron sulfides typically encountered in H_2S corrosion environment [8].

Name	Formula	Crystal Structure	Properties
Mackinawite	FeS	Tetragonal; stacked layers of “2D” FeS sheets	Metastable, primarily precipitates from aqueous solution, initial corrosion product.
Cubic FeS	FeS	Cubic	Unstable, transforms into mackinawite, troilite or pyrrhotite. Does not form in the presence of oxygen or chlorides.
Troilite	FeS	Hexagonal	Stoichiometric member of the Fe_{1-x}S group ($x = 0$). Needle-like, flower-like, and beam-shaped morphologies.
Pyrrhotite	Fe_{1-x}S ($x = 0 \sim 0.17$)	Hexagonal $\text{Fe}_{10}\text{S}_{11}$, Monoclinic Fe_7S_8 or Orthorhombic	With vacancies, p-type semiconductor. Can co-exist with troilite, both are thermodynamically stable.
Greigite	Fe_3S_4	Cubic	Metastable $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$ sulfide, associated with fresh water system.
Pyrite	FeS_2	Cubic	Stable iron(II) disulfide, cubic and framboidal (and raspberry-like) morphologies. Pyrite and pyrrhotite are the most stable iron sulfides.

unstable in certain environments and act as transition states. The typical iron sulfide encountered in H_2S corrosion environment are given in Table 1. Transformations among iron sulfides at 21°C were summarized by Shoosmith, et al. [13]. At low temperature, the reported sequence of the reaction products with time is mackinawite \rightarrow cubic FeS \rightarrow troilite \rightarrow pyrrhotite \rightarrow greigite (transition state) \rightarrow pyrite [14]. Bai, et al., [15] stated that troilite was the final corrosion product at 50°C after 96 h exposure time, but also found greigite and pyrite after 21 h under the same conditions [16]. This is somewhat contradictory to Shoosmith’s findings. The most likely reason are the different experimental conditions such as pH and $p_{\text{H}_2\text{S}}$ are often not well controlled or even properly defined during the tests, which makes the results difficult to reproduce. Considering that the formation/transformation and properties of iron sulfides are highly dependent on water chemistry, controlling the operating parameters is of prime importance. This problem can be addressed by first developing a comprehensive water chemistry prediction model [11] that can be used to calculate the desired operating conditions at any given temperature and then by closely monitoring those conditions. At elevated temperatures ($> 80^\circ\text{C}$), no work has yet been reported on the transformation sequence of iron sulfide (research question #2). In addition, the high temperature is fully expected to have a significant effect on the transformation kinetics.

As it pertains to the corrosion of steel, the protectiveness of iron sulfide layers is generally governed by pH, temperature, $p_{\text{H}_2\text{S}}$, time, and brine chemistry. Sardisco, et al., [17] found that the protectiveness of the sulfide layer changed at different pH values. Between pH 6.5–8.8, mackinawite was the least protective layer, compared to troilite and pyrite. Ren, et al., [18] observed that when the partial pressure of H_2S increased, fine grains of pyrrhotite formed that made the layer more compact and continuous, leading to a decrease of the general corrosion rate and a lower pitting tendency. Ning, et al., [19] have found that the

appearance of pyrite can initiate and sustain localized corrosion on steel. In summary, little is known about the protectiveness of the various iron sulfide polymorphs found in the corrosion product layer at high temperature (research question #3).

In order to address the three research questions stated above, H_2S corrosion tests were performed on carbon steel at 120°C with exposure times of 1, 4, 7, and 21 days. X-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-ray spectroscopy microanalysis (SEM/EDS), and linear polarization resistance (LPR) methods were employed to investigate the time-dependent formation of iron oxide, the transformation of iron sulfide polymorphs, and consequently, their roles in corrosion at elevated temperature. The corrosion product layer was also characterized by selected area diffraction (SAD) measurements, conducted in conjunction with transmission electron microscopy (TEM).

2. Experimental procedure

Experiments were conducted in a 7 L autoclave made from Hastelloy C276, shown in Fig. 2. A conventional three-electrode setup was used to conduct LPR measurements. The working electrode was a cylindrical API 5L X65 carbon steel sample. The chemical composition of this ferritic-pearlitic steel is shown in Table 2. A Pt-coated Nb cylinder was used as the counter electrode and a commercial Zr/ZrO₂ high temperature, high pressure pH probe was used as a pseudo reference electrode. While the exact potential was still unknown, this pseudo reference electrode served its purpose as long as its potential was stable under the operating conditions [11]. Additional flat samples were also suspended using a PTFE-coated 304 stainless steel wire. A centrally mounted impeller on a rotating shaft was used to keep the solution well mixed during each experiment.

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