

Iron Oxides and Their Role in Oxygen-Influenced Internal Pipeline Corrosion in the Oil and Gas Industry

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ABSTRACT

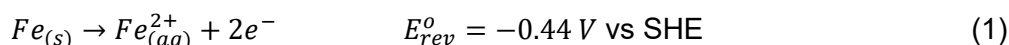
This review examines the fundamental relationship between iron oxides and corrosion mechanisms associated with internal pipeline corrosion in oil and gas infrastructure exposed to oxygen contamination. Through comprehensive analysis of existing literature, this study explores how various iron oxides, including ferrous oxide (FeO), ferric oxide (Fe₂O₃), and mixed-valence magnetite (Fe₃O₄), influence corrosion processes based on their physical and electrochemical properties. The review systematically evaluates the stability, electrical conductivity, and formation conditions of these oxides as depicted in Pourbaix diagrams and correlates these properties with corrosion behavior. Particular attention is given to magnetite's superior electrical conductivity (10²-10³ S/cm) compared to other iron oxides, which creates pathways for electron transfer that potentially accelerate localized corrosion. The analysis identifies distinct iron oxidation pathways (catalytic and non-catalytic) and their theoretical correlation to polarization curve regions, providing insights into how these mechanisms may interact with dissolved oxygen. This review highlights critical knowledge gaps regarding oxygen's role in corrosion processes, particularly in systems containing weak acids like CO₂ and H₂S, and proposes areas requiring further investigation to develop more effective corrosion prediction models and mitigation strategies for oil and gas infrastructure.

Keywords: Iron oxides; oxygen corrosion; electrochemical properties; oilfield applications; weak acid systems; corrosion mechanisms.

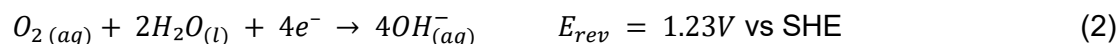
INTRODUCTION

Most pipelines in oil and gas production systems are constructed using carbon steel. Due to the contents flowing through them and the internal conditions, these mild steel pipelines are vulnerable to internal corrosion. Although a common assumption exists that hydrocarbon production and transmission systems contain no oxygen, its presence represents an important risk factor to asset integrity. While no oxygen is contained in hydrocarbon reservoirs, oxygen can enter these systems as a contaminant.¹ Several reasons account for oxygen ingress, including leaks, maintenance procedures, equipment failures, chemical injections, and improper operating protocols.¹ From parts per billion (ppb) to parts per million (ppm), oxygen can be introduced into these systems, accumulating in stagnant areas and resulting in localized corrosion. Infrastructure corrosion and possible alteration of hydrocarbon composition make the presence of oxygen a concern.²

Most infrastructure in the oil and gas industry is constructed of carbon steel, which is primarily composed of iron. Consequently, the main anodic reaction in the corrosion of these materials is iron oxidation. The oxidation half-reaction for iron dissolution is shown in Reaction 1 with a standard reduction potential (E°) of -0.44V compared to the standard hydrogen electrode (SHE).



Oxygen (O_2), having high electron affinity and the ability to form compounds with most metals, makes studying its corrosion implications of great importance (Reaction 2). When oxygen enters pipeline systems it creates conditions that significantly modify the electrochemical processes occurring at the steel surface. In aqueous solutions under standard conditions, the oxygen reduction reaction (ORR) has a reversible potential of 1.23 V (vs SHE):



With the difference of these two potentials being positive, the corrosion of iron by oxygen is thermodynamically spontaneous. The presence of oxygen leads to the formation of various iron oxides and oxyhydroxides, each with distinct physical and electrochemical properties that can either accelerate or inhibit further corrosion.

Understanding the fundamental relationship between iron oxides and corrosion mechanisms remains critical for developing effective corrosion prediction models and mitigation strategies. This matters especially in the oil and gas sector, where corrosion poses a major problem, worsened by weak acids such as carbonic acid (H_2CO_3) from hydrated carbon dioxide (CO_2), hydrogen sulfide (H_2S), and organic acids (acetic, formic) in aqueous systems.

This review analyzes how various iron oxides, including ferrous oxide (FeO), ferric oxide (Fe_2O_3), and mixed-valence magnetite (Fe_3O_4), affect corrosion processes based on their physical and electrochemical properties. The paper evaluates the stability, electrical conductivity, and formation conditions of these oxides shown in Pourbaix diagrams and connects these properties with observed corrosion behavior. Magnetite deserves special attention for its superior electrical conductivity compared to other iron oxides, which creates pathways for electron transfer that may have the potential to accelerate localized corrosion.

BACKGROUND

Iron Oxidation Mechanisms

To understand the influence of oxygen on the corrosion of steel infrastructure in the oil and gas industry, it is essential to review the mechanisms of iron oxidation. Iron oxidation occurs through two parallel pathways in corrosion-relevant conditions: catalytic and non-catalytic routes.³

The non-catalytic pathway involves only Fe(I) intermediates, while the catalytic pathway includes both Fe(I) and Fe(II) intermediates.³⁻⁶ These pathways have a direct correlation to the currents observed on an anodic polarization of iron, as illustrated in Figure 1 and Table 1.

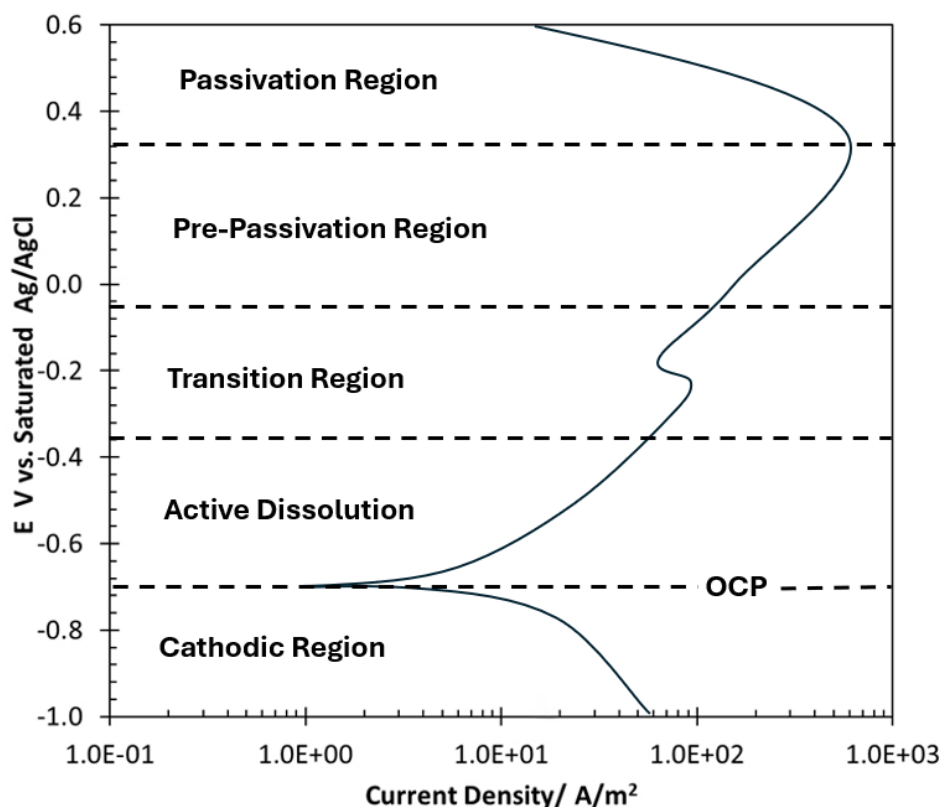


Figure 1. Illustration for a polarization curve for pure iron simulated at pH 5 (25 °C) showing the open circuit potential (OCP) and different regions corresponding to various iron dissolution mechanisms^{3,7}

Starting from the open circuit potential, as the electrode is polarized in the anodic direction, a linear increase in current is observed, indicating the active dissolution region. This active dissolution region is mainly governed by the non-catalytic pathway with Fe(I) being the intermediate.³ As the electrode is polarized further to higher overpotentials, an S-shape is observed in the polarization curve which indicates the transition region. The catalytic pathway with Fe(I) and Fe(II) intermediates is the governing mechanism in this transition region. Further anodic polarization of the electrode results in a linear increase in currents which indicates the pre-passivation region. The pre-passivation region is again influenced by the non-catalytic pathway.³

Table 1. Tabulated correlation between the observed regions on polarization and the corresponding pathways³

Region	Characteristic feature	Dominant pathway
Active dissolution	Linear increase in current	Non-catalytic
Transition	S-shape	Catalytic
Pre-passivation	Increasing currents observed at more positive overpotentials beyond the transition region	Non-catalytic

Table 2. Overview of Reaction Pathways for Anodic Dissolution of Iron, Including Non-Catalytic and Catalytic Mechanisms, Intermediates, and References (Adapted from Hariri)³

Reaction Mode	Reaction Scheme Pathway	Intermediates Found	References
Non-Catalytic Pathway	$Fe \rightarrow Fe(I)_{ads} + e^{-}$ $Fe(I)_{ads} \rightarrow Fe(II)_{sol} + e^{-}$	$Fe(I)_{ads}$	3,4
Catalytic Pathway	$Fe \rightarrow Fe(I)_{ads} + e^{-}$ $Fe(I)_{ads} \rightarrow Fe(II)_{ads} + e^{-}$ $Fe + Fe(II)_{ads} \rightarrow Fe(II)_{sol} + Fe(II)_{ads} + 2e^{-}$	$Fe(I)_{ads}$ $Fe(II)_{ads}$	3,6

In systems with mild steel (overwhelmingly Fe), like most oil and gas industry infrastructure, the presence of O₂ leads to iron oxide/oxyhydroxide formation. The interaction between dissolved oxygen and these iron oxidation pathways can affect the corrosion behavior of steel, particularly through the formation of various iron oxides with different properties and stability characteristics.

Pourbaix Diagrams and Stability of Iron Oxides

Pourbaix diagrams map thermodynamic stability regions of different species as functions of pH and electrochemical potential, offering insights into iron oxide formation and stability in aqueous environments.⁸

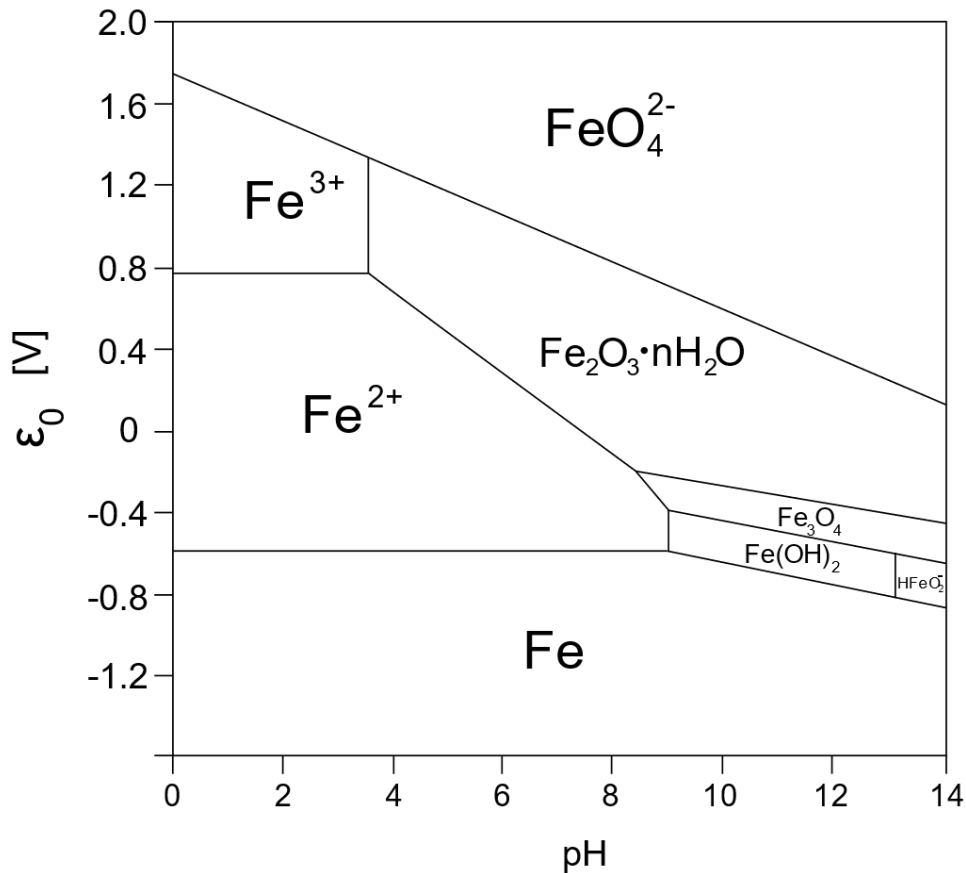


Figure 2. Pourbaix diagram of iron at $[Fe]^{2+} = [Fe]^{3+} = 10^{-6}$ mol/L, $T = 25$ °C⁹

As shown in Figure 2, the Pourbaix diagram for iron illustrates the stability domains of various iron species across different pH and potential conditions. In systems with mild steel, like most oil and gas industry infrastructure, the presence of O_2 leads to iron oxide/oxyhydroxide formation. These oxides can exist in different oxidation states with ferrous (FeO , $Fe(OH)_2$ [Fe(II)]), ferric (Fe_2O_3 , $FeO(OH)$ [Fe(III)]), and mixed-valence (Fe_3O_4 [Fe(II)& Fe(III)]) forms being common.¹⁰ As indicated in the Pourbaix diagram, most iron oxides are stable in neutral to alkaline pH ranges but are less stable in acidic conditions. This is of relevance in corrosion environments containing strong acids or weak acids, which prevent the formation of protective oxide layers and thus potentially causing aggravated corrosion.

IRON OXIDES AND THEIR PROPERTIES

Ferrous Oxide (FeO) and Ferrous Hydroxide (Fe(OH)₂)

FeO (wustite) forms in conditions with limited oxygen availability and higher temperatures. Fe(OH)₂ (ferrous hydroxide) can be described as a hydrated form of FeO, tending to exist in aqueous conditions at elevated pH values.^{10,11} FeO isn't very stable and readily oxidizes into magnetite (Fe₃O₄) in O₂ rich environments¹⁰. The Pourbaix diagram for iron shows FeO and Fe(OH)₂ being stable at elevated pH levels (pH>8).⁸ However, they tend to transform into more stable oxides or hydroxides in oxidizing environments.

FeO has a simple cubic halite-type (NaCl) characteristic crystal structure and is typically observed with a black/dark grey color. It can possess lattice gaps because of iron vacancies, which has an adverse impact on its overall stability.¹⁰ Fe(OH)₂ is a pale green solid and has a layered structure that affects how it reacts.¹⁰ FeO has low electrical conductivity compared to other iron oxides. In its non-stoichiometric structure (Fe_{1-x}O), the iron vacancies necessitate the presence of some Fe³⁺ ions to maintain charge balance. Electrical conduction primarily occurs through electron hopping between these Fe²⁺ and Fe³⁺ sites¹¹. Low electrical conductivity has an impact on how it performs in corrosion processes.

Ferric Oxide (Fe₂O₃) and Ferric Oxyhydroxide (FeOOH)

Hematite (Fe₂O₃) forms in high temperature O₂-rich environments and is thermodynamically more stable than FeO and Fe₃O₄.^{8,10} Goethite (α-FeOOH) typically forms in aqueous conditions¹⁰. (It is noteworthy that Fe₂O₃ and FeOOH have polymorphs that can also be encountered in corrosion environments, specifically maghemite and lepidocrocite, respectively; their presence tends to be less common. This paper will limit itself to the more commonly encounter ferric polymorphs). The Pourbaix diagram for iron indicates stability of hematite over a wide range of pH values and relatively high potentials.⁸ Hematite has a reddish-brown color, whereas goethite's color is yellowish-brown. Hematite forms with a rhombohedral crystal structure, whereas goethite is orthorhombic.¹⁰ Hematite's electronic configuration and wide band gap leads to its low electrical conductivity impacting electron transfer in corrosion processes.¹¹

Mixed Valence Oxides (Fe₃O₄ - Magnetite)

Magnetite (Fe₃O₄) possesses both Fe(II) and Fe(III) ions in its cubic lattice.¹⁰ The Pourbaix diagram indicates that Fe₃O₄ remains stable across a range of neutral to alkaline pH values under potentials linking the stability zones of FeO and Fe₂O₃.⁸ Magnetite is black and exists with the spinel-type characteristic crystal structure with iron ions of different valencies spreading out in tetrahedral and octahedral sites.¹⁰

Magnetite exhibits conductivities several magnitudes higher as compared to other iron oxides,^{10,12} primarily due to electron transfer between the Fe(II) and Fe(III) ions within its structure.¹¹ This electron transfer process lets electrons move through the crystal structure enabling electrical flow. The mixed-valence structure creates a path for transfer of charge, which plays a key role in electrochemical corrosion processes. Figure 3 illustrates the single unit cell structures for the discussed iron oxides and hydroxides, giving a better insight into their structural properties. Better conductivity facilitates cathodic reactions, like oxygen reduction or hydrogen evolution, by offering a pathway for electrons to flow. It also has an impact on anodic reactions impacting the dissolution of iron. The conductive magnetite layer can be hypothesized to lead to pitting-type localized corrosion, by enabling separation of anodic and cathodic sites and promoting galvanic coupling. Thus, electrical conductivity is a key property in electrochemical corrosion as it facilitates charge transfer and redox reactions.

Rare and Unstable Iron States (Fe(I), Fe(IV), Fe(IV))

Fe(I) and Fe(IV) oxidation states are short-lived because they are highly reactive and unstable; consequently, they don't play a crucial role in corrosion as their effects are overshadowed by the more stable Fe(II), Fe(III) (in single/mixed valence products).¹⁰

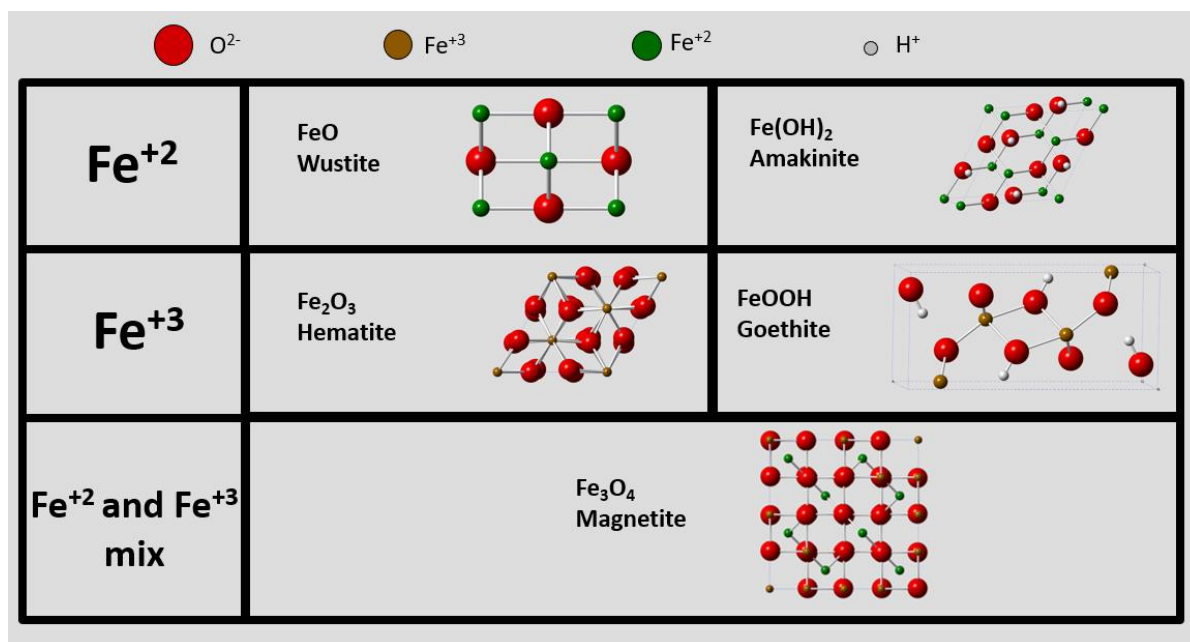


Figure 3. Single unit cell structures of iron oxides and hydroxides, illustrating the arrangement of their constituent atoms: brown (ferric ions), green (ferrous ions), red (oxygen), and white/gray (hydrogen). These structural properties highlight the atom organization within each structure discussed in the review, providing insight into their stability and electrochemical behaviors.^{13–17}

Physical Properties

Table 3 summarizes the relevant physical properties of iron oxides and hydroxides that are relevant to corrosion. Most iron oxides are poor conductors of electricity, which can lead to inhibited rates of electrochemical reactions on the metal surface. This property has been particularly observed in iron oxides with reddish-brown to yellow colors and with an Fe(III) oxidation state. The Fe(III) oxidation state is the most stable oxidation state of iron, the orbital configuration does not facilitate free electron mobility making this oxidation state a bad conductor of electricity. However, with Fe(II) and Fe(III) mixed oxidation states the electrons have been reported to follow a hopping mechanism, resulting in improved electronic conductivity¹¹.

Poor electrical conductivity limits electron transfer processes, which slow when protective oxide layers form. Iron oxides are stable in neutral to alkaline pH ranges but are less stable in acidic conditions. This is of relevance in corrosion environments containing strong acids or weak acids, like hydrated carbon dioxide (H₂CO₃ formed from aqueous CO₂), hydrogen sulfide (H₂S), or acetic acid. These acidic environments prevent the formation of protective oxide layers and thus potentially causing aggravated corrosion.

Table 3. Iron oxides and their properties.

Name	Oxidation State	Physical Appearance	Electrical Conductivity	Stability pH Range
Ferrous Oxide (FeO)	Fe(II)	Black or dark grey	Low; semiconductor type ¹⁰	Stable at high pH ⁸
Ferrous Hydroxide (Fe(OH)₂)	Fe(II)	Pale green	-	Stable at high pH ⁸
Ferric Oxide (Fe₂O₃)	Fe(III)	Reddish-brown	10 ⁻⁵ - 10 ⁻⁷ S/cm, low; semiconductor type ^{10,12}	Stable in acidic (higher potentials) to alkaline pH ⁸
Goethite (α-FeOOH)	Fe(III)	Yellowish-brown to ochre	10 ⁻⁹ S/cm, slightly better than Fe ₂ O ₃ in aqueous media ¹⁰	Stable in neutral to alkaline pH ⁸
Magnetite (Fe₃O₄)	Mixed Fe ²⁺ and Fe(III)	Black	10 ² - 10 ³ S/cm, higher due to electron transfer between Fe ²⁺ and Fe ³⁺ (¹⁰⁻¹²)	Stable in neutral to alkaline pH ⁸
Rare/Unstable Iron States	Fe(I), Fe(IV), Fe(V)	Not commonly observed	Very low, transient and unstable ¹⁰	Generally unstable ¹⁰

Influence of Iron Oxide Properties on Corrosion Processes

Iron oxide physical and electrochemical properties significantly impact their role in corrosion processes. Electrical conductivity stands out among these properties as especially influential in electrochemical corrosion. Most iron oxides conduct electricity poorly, which inhibits electrochemical reaction rates on metal surfaces. Most iron oxides are classified as semi-conductors due to their orbital energy difference between the conduction and valence band being less than 5 eV.¹⁰ This property appears particularly in reddish-brown to yellow iron oxides with Fe(III) oxidation states. Hematite (Fe₂O₃), for example, exhibits low electrical conductivity (10⁻⁵ - 10⁻⁷ S/cm) due to its electronic configuration and wide band gap, which affects electron transfer during corrosion.¹⁰

Unlike other iron oxides, magnetite (Fe₃O₄) possesses conductivity that is several magnitudes higher (10² - 10³ S/cm).¹⁰ primarily from electron transfer between Fe(II) and Fe(III) ions within its structure.¹¹ These conductivity differences potentially create significant implications for corrosion processes. Higher conductivity would enable cathodic reactions like oxygen reduction or hydrogen evolution by providing pathways for electron flow. It would also affect the anodic reaction involving iron dissolution. The conductive magnetite layer can be hypothesized to cause pitting-type localized corrosion by allowing separation of anodic and cathodic sites and promoting galvanic coupling.¹⁸ Electrical conductivity thus serves as a key property in electrochemical corrosion by allowing charge transfer and redox reactions.

CONCLUSIONS AND IMPLICATIONS

The relationship between iron oxides and corrosion mechanisms in oil and gas infrastructure exposed to oxygen contamination was reviewed. The analysis revealed several key findings about how iron oxide properties affect corrosion processes.

1. Physical and electrochemical properties of various iron oxides, specifically ferrous oxide (FeO), ferric oxide (Fe₂O₃), and mixed-valence magnetite (Fe₃O₄), can be hypothesized to directly affect whether they protect against or accelerate corrosion. Electrical conductivity stands out among these properties, with magnetite's relatively high conductivity (10²-10³ S/cm) potentially creating pathways for electron transfer that can accelerate localized corrosion through galvanic coupling.
2. Iron oxides show varying stability across different environmental conditions. Pourbaix diagrams demonstrate that most iron oxides remain stable in neutral to alkaline pH ranges but become unstable in acidic environments.
3. Iron oxidation occurs through parallel pathways, catalytic and non-catalytic routes, which correlate with specific regions observed in polarization curves. Dissolved oxygen interacts with these iron oxidation pathways and affects steel corrosion behavior by forming various iron oxides with different stability characteristics.

These findings matter directly to the oil and gas industry. Understanding iron oxide properties formed during oxygen contamination can improve corrosion prediction models and mitigation strategies. Corrosion inhibitor formulations could target specific oxide formation conditions, and monitoring protocols could detect early signs of oxygen ingress before significant corrosion damage occurs. This knowledge can also inform material selection and design for infrastructure where oxygen contamination poses a risk, potentially extending asset lifetimes and reducing maintenance costs across the oil and gas sector.

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REFERENCES

1. Deshmukh Shrirang, Brown Bruce, Young David. Investigating Oxygen Ingress in the Oil and Gas Industry. In: AMPP CORROSION 2024-20995. 2024.
2. Ishii Y, Sakaguchi S, Iwahama T. Innovation of hydrocarbon oxidation with molecular oxygen and related reactions. *Adv Synth Catal*. 2001;343(5):393–427.
3. Hariri MB. Mechanism of Anodic Dissolution of Iron and Steel in CO₂ Environments. Ohio University; 2023.
4. J.O. B, Drazic D, Despic AR. The electrode kinetics of the deposition and dissolution of iron. *Electrochim Acta*. 1961;4(2–4):325–61.
5. J.O. B, Drazic D. The kinetics of deposition and dissolution of iron: effect of alloying impurities. *Electrochim Acta*. 1962;7(3):293–313.
6. Heusler KE. Encyclopedia of Electrochemistry of the Elements. Vol IX-A Marcel Dekker, New York. 1982;229–381.
7. El Miligy AA, Geana D, Lorenz WJ. A theoretical treatment of the kinetics of iron dissolution and passivation. *Electrochim Acta*. 1975;20(4):273–81.
8. Pourbaix M. Atlas of electrochemical equilibria in aqueous solutions. NACE. 1966;
9. Andel Fröh. Pourbaix Diagram of Iron. https://commons.wikimedia.org/wiki/File:Pourbaix_Diagram_of_Iron.svg. Wikimedia Commons Diagram licensed under CC BY-SA 2.5; 2006.
10. Cornell RM, Schwertmann U. The iron oxides: structure, properties, reactions, occurrences, and uses. Vol. 664. Wiley-vch Weinheim; 2003.
11. Tannhauser DS. Conductivity in iron oxides. *Journal of Physics and Chemistry of Solids*. 1962;23(1–2):25–34.
12. Hrubia AB, Kotsyubynsky VO, Moklyak V V, Ostafiyshuk BK, Kolkovsky PI, Fedorchenko S V, et al. The electrical conductivity and photocatalytic activity of ultrafine iron hydroxide/oxide systems. *Molecular Crystals and Liquid Crystals*. 2018;670(1):97–111.
13. Mookherjee M, Stixrude L. High-pressure proton disorder in brucite. *American Mineralogist*. 2006;91(1):127–34.
14. Haavik C, Stølen S, Fjellvåg H, Hanfland M, Hausermann D. Equation of state of magnetite and its high-pressure modification: Thermodynamics of the Fe-O system at high pressure. *American Mineralogist*. 2000;85(3–4):514–23.
15. Fjellvåg H, Hauback BC, Vogt T, Stølen S. Monoclinic nearly stoichiometric wustite at low temperatures. *American Mineralogist*. 2002;87(2–3):347–9.
16. Gualtieri AF, Venturelli P. In situ study of the goethite-hematite phase transformation by real time synchrotron powder diffraction. *American Mineralogist*. 1999;84(5–6):895–904.
17. Blake RL, Hessevick RE, Zoltai T, Finger LW. Refinement of the hematite structure. *American Mineralogist: Journal of Earth and Planetary Materials*. 1966;51(1–2):123–9.
18. Song GD, Jeon SH, Son YH, Kim JG, Hur DH. Galvanic effect of magnetite on the corrosion behavior of carbon steel in deaerated alkaline solutions under flowing conditions. *Corros Sci*. 2018;131:71–80.