



Review

Mechanistic Pathways of External Corrosion in Buried Water Pipelines: Integrating Electrochemical Kinetics, Iron Oxide Phase Evolution, and Microbially Influenced Corrosion with Soil Environmental Controls

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Abstract

External corrosion of buried ferrous water mains remains the dominant driver of structural failure in aging water distribution networks, yet the mechanisms linking soil physical and chemical heterogeneity to corrosion kinetics and product phase evolution have not previously been synthesized into a unified critical framework. This review evaluates three partially competing accounts of electrochemical degradation—anodic dissolution coupled to oxygen reduction within porous rust layers, redox cycling of iron oxide phases driven by seasonal soil moisture fluctuations, and microbially influenced corrosion (MIC) mediated by direct extracellular electron transfer (EMIC) and chemical metabolite pathways (M-MIC)—and assesses the weight of evidence for each. We demonstrate that corrosion products retain electrochemical activity long after formation, functioning as dynamic redox mediators that continue the reactions responsible for their own growth: the reduction of lepidocrocite under anoxic conditions regenerates Fe^{2+} ions that sustain anodic dissolution and catalyze oxygen reduction, while repeated soil moisture cycles drive the irreversible transformation of $\gamma\text{-FeOOH}$ to Fe_3O_4 , which fundamentally alters the conductivity and cathodic capacity of the rust layer. The widely cited universal critical-moisture threshold of 65% water-holding capacity (WHC) is evaluated and found to be a single-point approximation contradicted by texture-resolved experimental data that show the critical degree of saturation ranges from $S_r \approx 0.5$ in sand to $S_r \approx 0.8$ in clay. Modern machine learning analyses of field corrosion databases confirm that chloride content, pH, pipe-to-soil potential, and water content are the four highest-ranked predictors of maximum pit depth, consistent with the mechanistic framework developed here. The classical cathodic depolarization model of SRB-driven corrosion is evaluated against EMIC evidence and found insufficient: measured pure-culture SRB corrosion current densities range from 14 to $135 \mu\text{A cm}^{-2}$, not the milliampere-level values reported in some earlier reviews. An explicit research agenda is proposed to address the five most consequential unresolved mechanistic questions.



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Keywords: pipeline corrosion; soil heterogeneity; oxygen reduction reaction; iron oxide phase evolution; microbially influenced corrosion; wet/dry cycling; critical review

1. Introduction

Corrosion-driven failure of municipal water mains imposes economic, operational, and public-health burdens that have not diminished despite decades of research. A com-

prehensive survey of US and Canadian utilities conducted at Utah State University [1] estimated that approximately 260,000 water main breaks occur annually across North America, resulting in roughly USD 2.6 billion in direct and indirect repair costs. Critically, 75% of utilities surveyed reported at least one zone of corrosive soil conditions, and ductile-iron pipe installed in highly corrosive soil exhibited more than six times the break rate of comparable pipe in low-corrosivity soil; a ratio that makes soil environment the single most discriminating site-specific risk variable available to utility asset managers. The total annual direct cost of corrosion across US drinking-water and sewer systems has been assessed at USD 36–79.6 billion, depending on system boundaries [2,3], and the worldwide cost of replacing corroded water and wastewater pipelines has been estimated at USD 2.1 trillion [4]. The American Society of Civil Engineers has rated US drinking-water infrastructure at “C–”, placing an estimated USD 1 trillion investment requirement over the next two decades.

While internal corrosion impacts water quality and hydraulic performance, external corrosion is the primary cause of structural failure in buried metallic pipelines [5]. A systematic ranking of corrosion causes by Hussein Farh et al. [6], employing a fuzzy analytical hierarchy process, indicated that operational factors (relative weight 0.428) are ranked above environmental factors (0.337) and pipe-related factors in contributing to failure. Although this may seem to diminish the mechanistic importance of soil science, this ranking primarily reflects the breadth and controllability of operational variables rather than a true mechanistic hierarchy. The environmental factors identified are those with the least understood mechanistic pathways, which most severely constrain predictive maintenance. Effective pipeline management requires consideration of both dimensions: operational factors influence the likelihood of exposure to corrosive conditions, while the soil-corrosion mechanisms described here determine the severity of damage when exposure occurs.

Prior reviews have addressed these mechanisms in isolation: physically based structural deterioration models [7], qualitative risk-factor rankings [6], internal-scale chemistry [8], and MIC detection methodologies [9] each occupy separate sections of the literature. What is absent is a unified critical narrative connecting electrochemical reaction kinetics, rust-layer phase evolution, soil physical controls, and microbial electron-transfer pathways into a single mechanistic framework. The National Academies of Sciences, Engineering, and Medicine (2023) compendium on the corrosion of buried steel [10] explicitly identifies this integration as the principal barrier to next-generation predictive models.

This critical review addresses this gap in the literature. The specific contributions relative to previous work are threefold. First, the review synthesizes electrochemical and phase-evolution evidence to demonstrate that rust-layer redox cycling is the primary mechanism sustaining corrosion in long-buried pipes, operating independently of bulk dissolved-oxygen availability. This conclusion is supported by iron oxide mineral-transformation experiments under simulated soil redox cycles [11–13] and by quantitative wet/dry cycle modelling [14]. Second, we evaluate and update the critical-moisture-content concept, replacing the universal Gupta and Gupta [15] 65% WHC threshold with the texture-resolved experimental evidence of Azoor et al. [16]. Third, we re-assess MIC kinetics in light of the EMIC framework [17–19], correcting erroneous $\text{mA}\cdot\text{cm}^{-2}$ current densities that appear in earlier reviews with values directly supported by primary experimental data. The paper concludes with an explicit research agenda identifying the five most consequential unresolved mechanistic questions.

2. Corrosion Mechanisms of Ferrous Metals in Soil Environments

2.1. Anodic Dissolution, Oxide Formation, and the Dynamic Rust Layer

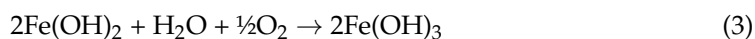
The deterioration of buried ferrous metals begins at discrete anodic sites where metallic iron undergoes electrochemical oxidation:



This step is strongly coupled to cathodic electron consumption and is modified by local pH, dissolved oxygen, chloride content, and soil moisture [5,20,21]. The released Fe^{2+} ions are thermodynamically unstable in neutral or aerated environments and undergo rapid hydrolysis:



The protons produced acidify the local electrolyte, enhancing further dissolution, which is self-reinforcing feedback that is especially consequential within the confined geometry of a developing pit [22]. In the presence of dissolved oxygen, ferrous hydroxide is rapidly oxidized:

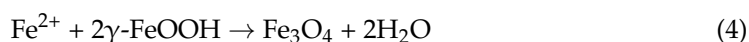


Ferric hydroxide accumulates on the metal surface and matures over time into a suite of iron oxides and oxyhydroxides whose phase composition encodes the electrochemical and environmental history of the burial site [21]. The specific phases that develop depend critically on oxygen availability, pH, chloride concentration, and the frequency of soil wet/dry cycles. Table 1 summarizes the principal phases and their formation conditions.

Table 1. Principal corrosion-product phases in buried ferrous pipelines and their soil-environment conditions of formation.

Phase	Formula	Characteristic Conditions	Conductivity	Protectiveness
Goethite	$\alpha\text{-FeOOH}$	Moderate aeration, neutral pH, stable oxidizing conditions	Low	Moderate–high
Lepidocrocite	$\gamma\text{-FeOOH}$	Moist, aerated, cyclic wetting/drying	Low	Low–moderate
Akaganeite	$\beta\text{-FeOOH}$	High $[\text{Cl}^{-}]$, oxidizing; catalyzed by chloride	Low	Low
Magnetite	Fe_3O_4	Partially reducing; $\text{Fe}^{2+}/\text{Fe}^{3+}$ coexistence	High	Moderate (conductive)
Maghemite	$\gamma\text{-Fe}_2\text{O}_3$	Oxidation of magnetite under cycling	Moderate	Low–moderate
Siderite	FeCO_3	High $[\text{CO}_3^{2-}]$, low O_2 , neutral–alkaline pH	Low	Moderate
Iron sulfide	FeS, FeS_2	Anaerobic, SRB-active; SRB-produced $\text{H}_2\text{S} + \text{Fe}^{2+}$	High (FeS)	Very low (brittle)

A mechanistically critical feature of this phase assemblage is its capacity for redox cycling. Under anoxic conditions, lepidocrocite is reducible below -0.2 V (standard hydrogen electrode, SHE) to regenerate Fe^{2+} ions [23]:



The magnetite produced is electronically conductive and is subsequently re-oxidized during drying or re-aeration events, re-establishing $\gamma\text{-FeOOH}$ and maghemite. This cycle allows corrosion to continue even under oxygen-limited conditions, a central finding that

distinguishes the buried-pipeline environment from bulk immersion and explains why pipe deterioration persists in waterlogged soils. Consistent with this, Mejia et al. [13] demonstrated that magnetite is the dominant product of both lepidocrocite and ferrihydrite reduction under repeated redox cycling, while Schulz et al. [12] showed using ^{57}Fe isotope labelling and X-ray absorption spectroscopy that the soil matrix itself alters the transformation trajectory, diverting lepidocrocite toward goethite and disordered Fe(II)–Fe(III) phases under flood/drainage cycles. The implication for buried pipelines is that the phase distribution within a mature rust layer depends not only on the pipe's electrochemical history but also on the specific soil mineralogy and biological community at the burial site. This process is shown in Figure 1.

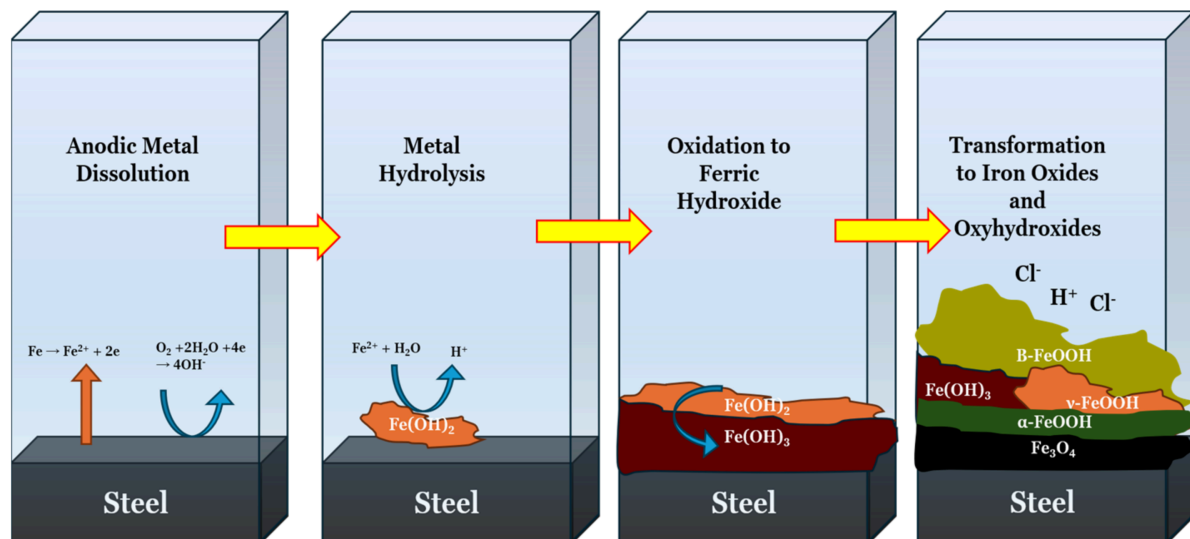


Figure 1. Schematic of anodic reactions in the corrosion process, showing the coupling between Fe dissolution, Fe^{2+} hydrolysis, and the formation of ferrous and ferric hydroxide intermediates.

Field evidence from excavated distribution-system specimens is broadly consistent with these laboratory and soil-science findings, although systematic field characterization of oxide phases on aged water mains remains sparse. Neff et al. [21] characterized corrosion products on buried archaeological iron artefacts using micro-X-ray diffraction (micro-XRD) and Raman spectroscopy, finding that mature corrosion layers are dominated by goethite ($\alpha\text{-FeOOH}$), with magnetite (Fe_3O_4) concentrated at the metal/rust interface where oxygen activity is lowest. Lepidocrocite ($\gamma\text{-FeOOH}$) was largely absent from the innermost layers of long-buried specimens, having transformed to goethite or magnetite over time—a trajectory consistent with the redox cycling sequence in Equation (4). Sancy et al. [24] applied electrochemical impedance spectroscopy to aged cast-iron specimens recovered from service and showed that the effective cathodic resistance of mature rust layers is substantially lower than that of fresh laboratory-formed films, implying a higher density of electroactive Fe^{2+} sites in aged rust. Together, these observations support the mechanistic picture developed here: the phase assemblage in aged rust on buried pipe is predominantly a goethite–magnetite mixture, with a redox-active interface region capable of sustaining cathodic oxygen reduction independently of bulk dissolved-oxygen concentration. Systematic field quantification of porosity and specific surface area in aged pipeline rust by XRD and Mössbauer spectroscopy remains a priority gap and is included in the research agenda (Section 5, Question 2).

Pitting corrosion represents a particularly dangerous form of localized attack. Within a developing pit, accumulation of Fe^{2+} ions drives hydrolysis reactions that release H^+ , sharply lowering local pH [22]:



The resulting acidity prevents re-passivation, promotes selective chloride migration, and maintains the self-sustaining aggressive chemistry that drives pit growth. Acidic, chloride-rich soils are especially susceptible because they simultaneously destabilize protective oxides and sustain a low-pH environment within pits.

Redox cycling evidence contradicts the traditional view that corrosion products progressively passivate the metal surface. In long-buried pipelines, the rust layer functions as a reactive reservoir whose redox state fluctuates in response to seasonal changes in moisture and oxygen availability, periodically regenerating both anodic Fe^{2+} and cathodic Fe^{2+} -bearing oxide sites. Predictive models that treat the rust layer as a static diffusion barrier will systematically underestimate corrosion rates at intermediate pipe ages, when the redox-active lepidocrocite/magnetite fraction is at its peak.

2.2. Oxygen Reduction as the Dominant Cathodic Reaction

In neutral and alkaline soils ($\text{pH} > 4$), the cathodic reaction that balances anodic iron dissolution is the four-electron reduction of oxygen [25]:



Hydrogen evolution ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$) contributes significantly only to acidic soils or under specific EMIC pathways. Oxygen reduction is concentrated within the interior of the porous rust layer, where Fe^{2+} states within partially reduced oxide crystals serve as electron donors, with the bare metal surface playing only a secondary cathodic role. Fully oxidized rust, composed entirely of Fe^{3+} phases, is electronically insulating and suppresses cathodic activity; partially reduced magnetite-bearing rust is semiconducting and sustains it. Stratmann and Müller [25] confirmed, using silver deposition markers and electroactive probe permeation experiments, that electrochemical activity resides within the porous oxide interior, with the metal/oxide boundary playing no significant cathodic role.

The limiting cathodic current density under diffusion control is expressed by Fick's law:

$$i_{\text{lim}} = (D_w n F c_i) / d \quad (7)$$

where D_w is an effective diffusion coefficient $D_w = D_0 \times (\varepsilon / \tau)$; D_0 is the diffusion coefficient of oxygen in the bulk electrolyte (approximately $2.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ in water at 25°C); ε is the rust-layer porosity (typically 0.3–0.5); τ is the tortuosity factor (typically 2–5), yielding D_w in the range of $1\text{--}5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. $n = 4$, $F = 96,500 \text{ C mol}^{-1}$; c_i is the dissolved oxygen concentration; and d is the diffusion layer thickness. Measured oxygen reduction current densities on rust-covered steel frequently reach $0.5\text{--}1.0 \text{ mA cm}^{-2}$, consistent with effective electroactive surface areas of $50 \text{ m}^2 \text{ g}^{-1}$ or greater [24].

Hoërlé et al. [14] modelled the wet/dry cycling of fresh $\gamma\text{-FeOOH}$ -rich rust and identified three mechanistically distinct stages: (i) during wetting, lepidocrocite reduction rather than dissolved O_2 reduction supplies the primary cathodic current, with a modelled cathodic current density of approximately $680 \mu\text{A cm}^{-2}$ for fresh rust (porosity $\varepsilon = 0.3$; internal surface area $S_a = 30 \text{ m}^2 \text{ g}^{-1}$); (ii) during the wet steady-state, oxygen reduction on the partially reduced oxide surface takes over; and (iii) during drying, anodic site blocking extinguishes the electrochemical cell. This three-stage model provides a mechanistic expla-

nation for the non-monotonic relationship between bulk soil saturation and corrosion rate observed in field and laboratory studies.

A recent study of X70 pipeline steel by Xu et al. (2024) [26] adds an important mechanistic nuance: under low dissolved-oxygen conditions, the rate-limiting step in corrosion-product formation is nucleation, which intrinsically favours localized and pitting growth modes; under high dissolved-oxygen conditions, the growth step dominates, producing more uniform corrosion films. This implies that oxygen-starved microenvironments beneath rust tubercles or in waterlogged soils are disproportionately susceptible to deep pitting, which is consistent with field observations linking differential aeration cells to the deepest pipeline corrosion damage.

The internal rust-layer ORR model of [25] is well supported by experimental evidence and should be the baseline framework for any cathodic reaction model applied to long-buried pipe. However, the quantitative [14] model was parameterized for fresh rust; for mature, compacted rust on long-buried pipe, neither porosity nor internal surface area is well constrained by field data. Systematic electrochemical impedance characterization of in situ rust layers on excavated pipe specimens is needed to close this gap.

2.3. Thin Electrolyte Films and Wet/Dry Cycle Effects on Corrosion Kinetics

The thickness of the electrolyte film in contact with the pipe surface governs the transition between three corrosion-control regimes [27,28]. When the film is thick (several millimetres), conditions resemble bulk immersion: ohmic resistance is negligible and oxygen transport is convection-dominated. As the film thins to the order of the natural convection boundary layer (500–1000 μm), transport transitions to diffusion control and the corrosion rate typically increases because the oxygen flux to the cathodic oxide surface improves. At extremely thin films (<10 μm), ionic mobility declines sharply, ohmic resistance rises, and the electrochemical cell becomes self-limiting (Figure 2). The corrosion rate, therefore, peaks at an intermediate film thickness, a trend confirmed experimentally in laboratory thin-film studies [28].

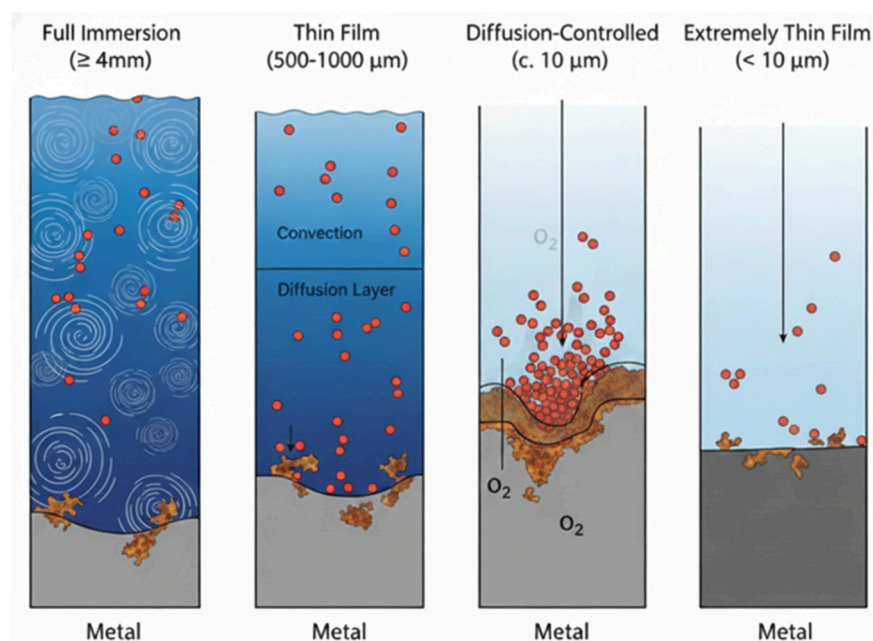


Figure 2. The effect of electrolyte film thickness on corrosion rate, illustrating the transition from bulk-immersion behavior (thick films, convection-dominated transport) through the peak-corrosion diffusion-controlled regime (intermediate films) to the ohmic-limited low-corrosion regime (very thin films).

This progression maps directly onto the soil moisture cycle: infiltration produces the thick-film, high-conductivity regime; partial drainage produces the peak-corrosion, intermediate regime; and extended dry periods produce the ohmic-limited, low-corrosion regime. Non-uniform electrolyte geometry introduces oxygen concentration cells: in sessile droplets, well-oxygenated edges act as cathodes while the oxygen-depleted center acts anodically, producing the pitting and under-deposit patterns characteristic of buried-pipe external damage [24].

Experimental work on carbon steel under cyclic chloride and bicarbonate exposure [29] showed that the oxidation/reduction cycle of iron oxides during wet/dry cycling accelerates the overall corrosion process, and that pitting beneath the corrosion product layer at elevated combined $[\text{Cl}^-] + [\text{HCO}_3^-]$ concentrations is the initiation site for stress corrosion cracking. This directly connects the ionic composition of soil pore water to wet/dry cycle kinetics and underscores that treating moisture cycling and ionic species as independent variables is mechanistically incorrect.

2.4. Microbially Influenced Corrosion: Critical Evaluation of EMIC Versus M-MIC

The MIC of buried pipelines now encompasses two mechanistically distinct pathways whose relative contributions under field conditions remain an active area of research [17,30], and are shown in Figure 3.

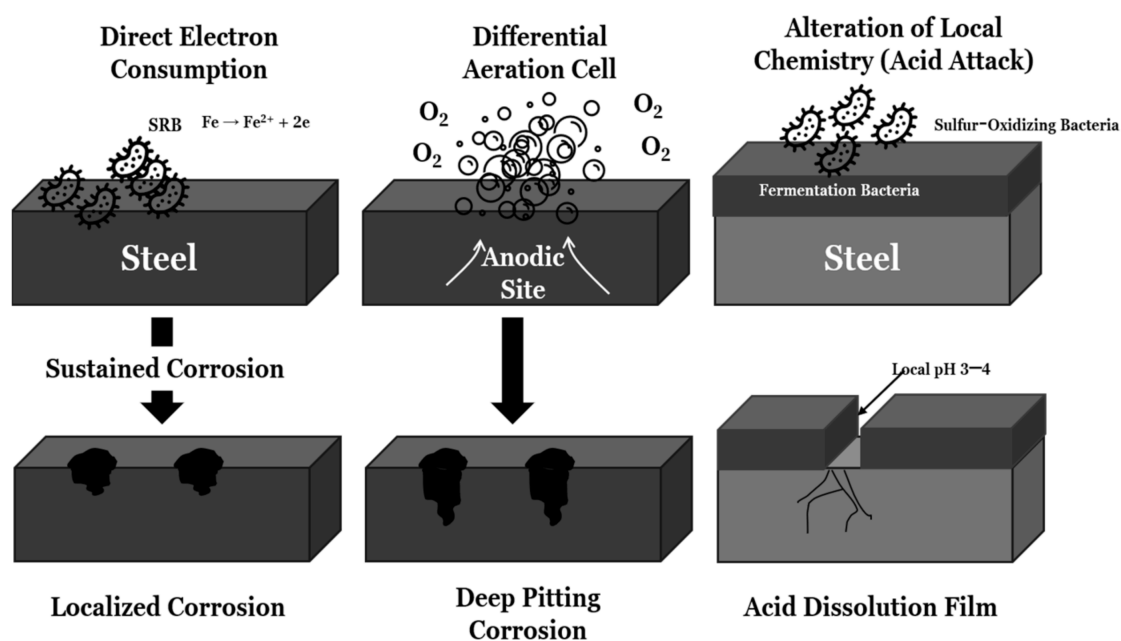
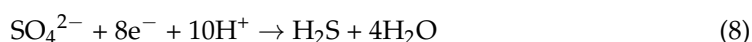


Figure 3. Mechanisms of microbially influenced corrosion showing M-MIC (metabolite-mediated: H_2S production, acid generation, FeS formation) and EMIC (direct electron extraction by SRB via c-type cytochromes and flavin-based electron shuttles).

2.4.1. M-MIC: Metabolite-Mediated Corrosion

Microorganisms produce chemically aggressive metabolites that modify the local electrolyte chemistry and destabilize protective oxide films. Sulfate-reducing bacteria (SRB) reduce sulfate to hydrogen sulfide under anaerobic conditions:



The resulting H_2S reacts with Fe^{2+} to form iron sulfide:



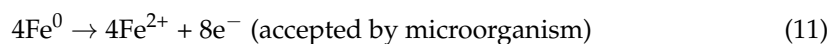
FeS is porous, brittle, and mechanically non-protective; it also reduces local resistivity and facilitates galvanic coupling. Sulfur-oxidizing bacteria generate sulfuric acid that locally depresses pH to 3–4 in otherwise near-neutral soils:



This acidification dissolves protective Fe-oxide phases and maintains the active dissolution state within pits [31]. Carbon dioxide produced by microbial respiration and fermentation further dissolves in pore water to form carbonic acid, compounding the localized pH depression.

2.4.2. EMIC: Extracellular Electron Transfer

Lithotrophic SRB and other anaerobic organisms attach directly to the metal surface or to conductive corrosion deposits and extract electrons from Fe^0 through outer-membrane c-type cytochromes, bypassing the H_2 intermediate entirely [17]. The electron-withdrawal step drives the anodic reaction:



Venzlaff et al. [18] provided decisive experimental evidence for EMIC by demonstrating that a corrosive SRB strain (*Desulfopila corrodens* IS4) markedly accelerates the cathodic polarization curve through direct electron uptake, whereas a hydrogenotrophic control strain that consumes only H_2 produces no such effect. Inactivation of the colonizing bacteria abolished the current enhancement, establishing that the cathodic acceleration was biological in origin and could not be attributed to abiotic surface chemistry.

Wang et al. [19] reported the highest pure-strain SRB corrosion rates yet measured for carbon steel:

D. ferrophilus IS5 produced a weight-loss corrosion rate of 1.03 mm yr^{-1} , rising to 1.57 mm yr^{-1} (pit depth growth rate 2.88 mm yr^{-1}) when 20 ppm riboflavin was added as a flavin-based extracellular electron shuttle. Guan et al. [32] demonstrated corrosion current densities of $14.35\text{--}23.81 \mu\text{A cm}^{-2}$ for X70 pipeline steel under *D. singaporenus* at carbon-limited conditions with redox mediators, representative of nutrient-limited deep soils.

Taken together, these primary data establish that pure-SRB iCCM values under EMIC are in the range of $14\text{--}135 \mu\text{A cm}^{-2}$. Values at the milliamperes-per-square-centimetre level arise only when an external alternating current (AC) synergizes with SRB activity: Qing et al. [33] showed that imposing an AC current density of 10 mA cm^{-2} on X80 steel in SRB-bearing soil-extract solution raised the corrosion current density to approximately nine times the no-AC baseline—a fundamentally different physical configuration from isolated SRB activity. Earlier reviews that cite SRB corrosion currents at the mA cm^{-2} level without the AC qualification should be treated with caution.

Knisz et al. [30] emphasize that MIC is the outcome of interactions between the biofilm extracellular polymeric substance matrix, the metal surface chemistry, abiotic mineral deposits, and environmental drivers (temperature, dissolved O_2 , salinity, and flow). In buried pipelines, conductive phases such as magnetite and FeS within the rust layer act as “microbial–electrochemical bridges” that sustain electron transfer, even during periods of low microbial viability.

A critical assessment indicates that the classical cathodic depolarization model, in which SRB accelerate corrosion by consuming cathodic H_2 , is insufficient as the primary explanation for severe SRB-driven pitting. EMIC, mediated by c-type cytochromes and flavin-based electron shuttles, is the dominant mechanism under strictly anaerobic conditions. However, the quantitative partition between EMIC and M-MIC in mixed-aerobic,

partially saturated soil environments typical of real pipeline burial sites has not been directly measured. Table 2 provides a structured comparison across operating conditions; the weight of evidence suggests EMIC dominates in permanently waterlogged, low-redox environments while M-MIC is more significant in soils subject to aerobic/anaerobic cycling.

Table 2. Comparative summary of metabolite-mediated MIC (M-MIC) and electrical/extracellular MIC (EMIC) pathways under conditions relevant to buried water pipelines.

Feature	M-MIC	EMIC
Primary organisms	SRB, sulfur-oxidizing bacteria, fermenters	Lithotrophic SRB (e.g., <i>D. ferrophilus</i> IS5, <i>D. corrodens</i> IS4)
Electron transfer route	Indirect: via chemical metabolites (H_2S , H_2SO_4 , organic acids)	Direct: $\text{Fe}^0 \rightarrow$ outer-membrane c-type cytochromes $\rightarrow$ organism
Key corrosion products	FeS , H_2SO_4 ; depresses local pH to 3–4	Magnetite, FeS ; conductive phases facilitate further EMIC
O_2 requirement	Facultative; acid production occurs under partial aeration	Strictly anaerobic; suppressed by dissolved $\text{O}_2 > \sim 0.1 \text{ mg L}^{-1}$
Reported icorr range (carbon steel)	Variable; local acid pH sustains dissolution $\gg 100 \mu\text{A cm}^{-2}$	14–135 $\mu\text{A cm}^{-2}$ under pure-culture EMIC [18,19,32]
Dominant soil conditions	Aerobic/anaerobic cycling; sulfate-rich or high-organic soils	Permanently anaerobic, waterlogged, low- E_h ($< +100 \text{ mV vs. SHE}$)
Wet/dry cycle behavior	H_2S reservoir builds during anaerobic phases; re-oxidized to H_2SO_4 during aerobic phases	EMIC rate declines during aerobic phases; re-activates on re-wetting
Cathodic protection interaction	Acid metabolites counteract protective OH^- generated by ORR under CP	Under-protection enables direct electron extraction; over-protection generates H_2 feeding hydrogenotrophic SRB

The interaction between cathodic protection (CP) systems and MIC warrants explicit attention given its engineering relevance. Standard pipeline CP criteria (pipe-to-soil potential $\leq -0.85 \text{ V vs. Cu/CuSO}_4$ per NACE SP0169 [34], incorporated into the corrosivity scoring framework of AWWA C105/A21.5) [35] are calibrated against abiotic corrosion and may be insufficient in MIC-active soils [31]. Under-protection (with a potential that is insufficiently negative) allows EMIC-active SRB to extract electrons directly from the pipe surface, effectively using cathodic current as metabolic energy. Conversely, over-protection (with a potential that is more negative than approximately -1.2 V) generates cathodic H_2 at the pipe surface, which can sustain hydrogenotrophic SRB and accelerate MIC even when nominal protection criteria appear satisfied. AC stray currents from rail transit systems and high-voltage transmission lines compound this problem: Qing et al. [33] showed that AC interference at 10 mA cm^{-2} raises the SRB-associated corrosion current to approximately nine times that of the abiotic baseline, conditions under which standard AWWA C105 CP criteria fail to provide adequate protection. Direct-current (DC) stray currents from impressed-current CP on adjacent structures create additional anodic discharge zones that combine with MIC activity to produce severe localized attack. A comprehensive treatment of CP design, coating integrity, and stray-current mitigation in MIC-active soils (including application of AWWA C105/A21.5 and ISO 15589 criteria [36]) represents a distinct engineering topic that warrants dedicated review and is beyond the mechanistic scope of the present paper.

2.5. Ionic Species and Their Control of Corrosion Product Phase Composition

Soil pore-water ion composition exerts a first-order control on the stability and protectiveness of iron oxide phases, independently of the electrochemical potential and oxygen availability [5,22].

Chloride (Cl^-): Chloride promotes akaganeite ($\beta\text{-FeOOH}$) formation by catalyzing iron dissolution and stabilizing chloride-containing ferric hydroxy complexes. High $[\text{Cl}^-]$ destroys the continuity of goethite-based protective layers by converting them to more porous, more soluble phases. Song et al. [37] confirmed, using SHapley Additive exPlanations (SHAP) analysis of a field corrosion database of 259 pipeline specimens, that chloride content is the single highest-ranked predictor of maximum pit depth (with a mean absolute SHAP value of 0.54), consistent with its mechanistic role as the primary phase-stability disruptor.

Sulfate (SO_4^{2-}): Sulfate is incorporated into corrosion scales and (under anaerobic conditions) is reduced by SRB to sulfide, which forms FeS and H_2S . The combination of FeS (conductive and cathodic with respect to steel) and H_2S (acidifying and complexing Fe^{2+}) constitutes the most severe MIC product combination for localized attack [32]. Aerobic/anaerobic cycling is particularly damaging because sulfate is continually regenerated from H_2S during aerobic periods by sulfur-oxidizing bacteria, maintaining a persistent aggressive sulfur-species reservoir.

Carbonate/Bicarbonate ($\text{CO}_3^{2-}/\text{HCO}_3^-$): At moderate alkalinity, carbonates promote siderite (FeCO_3) and calcareous deposit formation, providing a physical diffusion barrier. At elevated concentrations co-occurring with high $[\text{Cl}^-]$, however, Liu et al. [29] showed that the interaction accelerates stress corrosion cracking initiation from pits beneath the oxide layer, illustrating the non-additive behavior of mixed-ion systems.

When multiple aggressive ions coexist in soil pore water, competitive phase-formation reactions govern the final rust assemblage in ways that single-ion models cannot predict. The co-elevation of $[\text{Cl}^-]$ and $[\text{HCO}_3^-]$ illustrates this clearly: at low $[\text{Cl}^-]/[\text{HCO}_3^-]$ ratios, carbonate activity promotes siderite (FeCO_3) precipitation, providing a moderate diffusion barrier; at high ratios, akaganeite formation dominates, producing a porous, non-protective layer that simultaneously accelerates pitting. This transition is pH-sensitive because carbonate speciation shifts from HCO_3^- at lower pH to CO_3^{2-} at higher pH, altering the thermodynamic stability of FeCO_3 relative to $\beta\text{-FeOOH}$. Liu et al. [29] demonstrated that synergistic $[\text{Cl}^-] + [\text{HCO}_3^-]$ under wet/dry cycling initiates stress corrosion cracking from pits beneath the oxide layer, which is a failure mode not observed in single-ion exposures. When $[\text{SO}_4^{2-}]$ and $[\text{Cl}^-]$ coexist under conditions favourable to SRB activity, FeS precipitation competes with both $\beta\text{-FeOOH}$ and FeCO_3 for available Fe^{2+} . Because FeS is electronically conductive and galvanically cathodic relative to steel, its formation creates an autocatalytic corrosion cycle in which FeS deposition accelerates anodic dissolution, supplying more Fe^{2+} for further FeS growth and ultimately producing the deep pitting morphology characteristic of severe MIC [32]. These interactions underscore the inadequacy of single-ion threshold criteria for phase prediction and corrosivity classification.

It is critically clear that ion competition for phase formation is inadequately treated in most corrosion models, which typically address Cl^- or SO_4^{2-} in isolation. The evidence indicates that phase composition is a multivariate outcome: the same $[\text{Cl}^-]$ produces very different assemblages depending on whether $[\text{CO}_3^{2-}]$ or $[\text{SO}_4^{2-}]$ is co-elevated, whether SRB are active, and whether the local environment is oxidizing or reducing. Single-ion threshold criteria for phase prediction will produce unreliable outputs across the range of real burial environments.

2.6. Summary of Mechanistic Analysis

The mechanistic evidence establishes that buried-pipeline corrosion is sustained by four coupled processes: anodic iron dissolution driven by redox-active rust-layer cycling; cathodic ORR concentrated within the porous oxide interior; MIC mediated by both metabolite production (M-MIC) and direct electron transfer (EMIC); and ionic species competition that determines the phase composition and protectiveness of the developing rust layer. The rust layer is the critical mediator connecting all four processes. Field observations of excavated specimens confirm the laboratory-derived redox cycling trajectory from lepidocrocite toward goethite and magnetite with increasing burial age, although systematic quantification of aged rust properties on in-service water mains remains a priority research gap. Table 2 provides a structured framework for assessing the relative dominance of M-MIC versus EMIC as a function of soil oxygen content and the moisture regime.

3. Soil Parameters and Their Mechanistic Influence on Corrosion Kinetics

3.1. Soil Moisture

Soil moisture is the single most critical prerequisite for electrochemical corrosion of buried pipelines: without adequate moisture to form a continuous ionic electrolyte, neither anodic dissolution nor cathodic oxygen reduction can proceed [5,15]. Its dominant importance is reflected in the field: Barfuss [1] documented that ductile-iron pipe in highly corrosive (typically high-moisture and high-clay) soils exhibits more than six times the break rate of pipe in low-corrosivity soils.

The relationship between moisture content and corrosion rate is non-monotonic, exhibiting a characteristic maximum at an intermediate moisture level. Early work by Gupta and Gupta [15] attributed this maximum to a universal “critical soil moisture content” of approximately 65% of the soil’s water-holding capacity (WHC) (Figure 4). More recent texture-resolved experimental data, however, show that this universal value is an oversimplification. Azoor et al. [16] demonstrated, across sand, silt, and clay soils, that the critical degree of saturation (S_r) at which corrosion current density is maximized is texture-dependent: $S_r \approx 0.5$ for sand, $S_r \approx 0.7$ for silt, and $S_r \approx 0.8$ for clay. The physical explanation is that each soil texture has a characteristic inflection point in its water retention curve at which the pore network transitions from air-continuous to water-continuous; corrosion peaks precisely at this transition because ionic conductivity has increased sufficiently for anodic current to flow while oxygen transport through pores remains adequate for cathodic reactions. The National Academies [10] similarly report a range of 60–85% saturation for maximum corrosion across soil types, consistent with Azoor et al.’s texture-dependent findings.

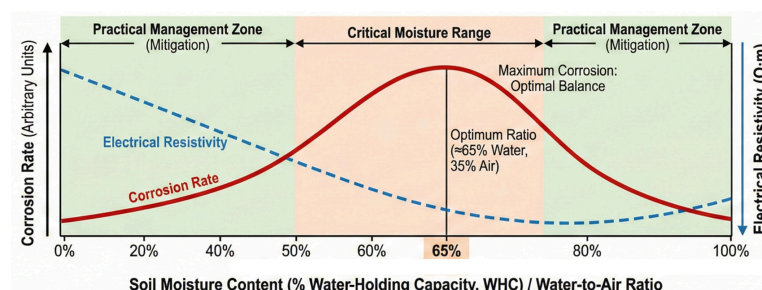


Figure 4. The effect of soil moisture content on corrosion rate, showing the peak at the critical degree of saturation (S_r) and the texture-dependent shift of that peak from $S_r \approx 0.5$ (sand) to $S_r \approx 0.8$ (clay), according to [16]. Key thresholds: $S_r < 0.3$ —minimal corrosion in all textures due to insufficient ionic conductivity; $S_r \approx 0.5$ —peak corrosion in sandy soils; $S_r \approx 0.7$ —peak corrosion in silts; $S_r \approx 0.8$ —peak corrosion in clays; $S_r > 0.9$ —corrosion decreasing in all textures due to oxygen diffusion limitation.

Below the critical S_r , corrosion is restricted by insufficient ionic mobility. Above it, cathodic limitation from restricted oxygen diffusion through water-saturated pores reduces corrosion rates. Clay soils simultaneously retain high moisture and restrict oxygen diffusion, creating conditions conducive to SRB colonization and MIC.

The Gupta and Gupta [15] 65% WHC critical-moisture threshold is historically useful but mechanistically inaccurate for any soil other than the mid-texture soils on which it was calibrated. The evidence supports replacing the universal threshold with Azoor et al.'s [16] texture-dependent S_r framework, which can be parameterized from the soil water retention curve. Integrating water retention curve data into corrosion risk models would improve spatial resolution at negligible additional cost.

The AWWA C105/A21.5 standard classifies soil corrosivity using a point-scoring system incorporating resistivity, pH, redox potential (E_h), sulfide content, and moisture condition. Moisture appears in the AWWA C105 framework as a qualitative descriptor (e.g., “poorly drained” soils score higher), but the standard does not include a quantitative soil saturation criterion linked to soil texture. The texture-dependent S_r framework proposed by Azoor et al. [16] provides a mechanistically grounded quantitative moisture parameter that can be directly aligned with the AWWA assessment categories.

Table 3 maps the approximate AWWA C105/A21.5 corrosivity categories to the corresponding texture-dependent S_r ranges.

Table 3. Approximate mapping of AWWA C105/A21.5 corrosivity categories to texture-dependent critical degree of saturation (S_r) values for three soil textures.

AWWA C105 Category	Resistivity ($\Omega \cdot \text{cm}$)	Moisture Descriptor	S_r Risk—Sand	S_r Risk—Silt	S_r Risk—Clay
Highly corrosive	<1000	Poorly drained, seasonally or permanently saturated	High ($S_r > 0.5$)	High ($S_r > 0.7$)	High ($S_r > 0.8$)
Moderately corrosive	1000–2000	Seasonally wet, moderate drainage	Mod. (S_r 0.3–0.5)	Mod. (S_r 0.4–0.7)	Mod. (S_r 0.5–0.8)
Mildly corrosive	>2000	Well-drained, dry periods predominate	Low ($S_r < 0.3$)	Low ($S_r < 0.4$)	Low ($S_r < 0.5$)

This mapping reveals a critical gap in the AWWA C105 framework: a persistently saturated sandy installation ($S_r \geq 0.5$) may be classified as only “moderately corrosive” based on resistivity alone if its resistivity falls in the 1000–2000 $\Omega \cdot \text{cm}$ range, when mechanistically it is operating at peak corrosivity for its soil texture. Conversely, a seasonally wet clay soil may receive a high-corrosivity score even when its typical S_r remains below the critical 0.8 threshold for most of the year. From a practical standpoint, utility engineers conducting pre-installation soil surveys can estimate S_r from the soil water retention curve—a measurement routinely obtained in geotechnical site investigations. Incorporating S_r relative to the texture-dependent critical value ($S_{r,\text{crit}}$) as an additional scoring parameter in the AWWA C105 framework would yield a more complete corrosivity index with minimal additional field effort.

3.2. Soil Resistivity

Soil electrical resistivity quantifies the ability of the soil electrolyte to conduct ionic current, which is a necessary condition for electrochemical corrosion to proceed at appreciable rates [5]. The AWWA C105/A21.5 standard uses resistivity as a primary soil-corrosivity index, with soils below 1000 $\Omega \cdot \text{cm}$ classified as highly corrosive.

Despite its widespread use, resistivity is an incomplete predictor of actual corrosion damage. Song et al. [37] found that resistivity has a modest independent contribution to maximum pit depth in SHAP analysis compared to chloride content and pH, consistent with multivariate field studies showing that some high-resistivity soils remain highly corrosive when aggressive ion concentrations are elevated. Mechanistically, resistivity's primary role is spatial: in soils of heterogeneous resistivity (everywhere in real burial environments), potential gradients drive long-line galvanic currents that concentrate metal loss at low-resistivity zones. When resistivity changes sharply at soil transitions (clay-to-sand interfaces or disturbed trench backfill boundaries), the resulting microcell currents can produce localized pit depths far exceeding those predicted from bulk resistivity averages.

Resistivity governs where corrosion current concentrates along a pipeline. Its value as a predictor of absolute corrosion rate is considerably weaker, and treating it as such consistently overstates its mechanistic role. Its inclusion as the sole or primary parameter in many legacy corrosion assessment protocols overestimates its mechanistic primacy. Models that treat resistivity as a field-average value will systematically underestimate pit depths at soil heterogeneity boundaries, which are precisely the locations where the most severe failures occur.

3.3. Soil pH

Soil pH directly governs both the kinetics of anodic dissolution and the phase stability of protective corrosion products. In acidic soils ($\text{pH} < 5$), the elevated proton concentration accelerates metal dissolution while the solubility of ferric oxides and hydroxides prevents the formation of stable protective layers [5]. In alkaline soils ($\text{pH} > 7$), cathodic production of OH^- promotes surface passivation, calcareous deposit formation, and the precipitation of compact ferric oxide layers.

Song et al. [37] identified pH as the second-highest SHAP predictor of maximum pit depth (mean absolute value 0.48), behind only chloride content. Peat-rich and industrially influenced soils with pH values of 4.6–5.9 are particularly corrosive because they simultaneously impair oxide formation and support acid-generating microbial populations. Within pits or crevices, the hydrolysis reactions described in Section 2.1 locally depress pH to 3–4, even in bulk-neutral soils, creating a persistent aggressive microenvironment that sustains active dissolution and prevents re-passivation.

The soil's pH and redox potential are mutually dependent: as the soil environment shifts toward more reducing conditions, pH tends to increase. This coupling means that including pH and E_h as independent covariates in corrosion models without accounting for their covariance will produce correlated errors. A Pourbaix diagram framework treating pH and potential jointly would be mechanistically more rigorous and is a practical target for the next generation of soil-corrosivity scoring systems.

3.4. Oxygen and Soil Aeration

Oxygen availability controls the cathodic reaction rate and, therefore, governs overall corrosion intensity in most neutral and alkaline soil conditions. The effective diffusion coefficient of oxygen decreases by approximately one order of magnitude as moisture increases from dry to 65% WHC, and by approximately four orders of magnitude as full saturation is approached [38]. These dramatic reductions in oxygen transport explain the non-monotonic moisture–corrosion relationship discussed in Section 3.1.

Spatial heterogeneity in oxygen availability creates differential aeration cells, which are the primary mechanism for localized corrosion in buried pipelines. Areas of higher oxygen availability (coarse, well-drained, and recently backfilled zones) act as cathodes, while adjacent oxygen-depleted zones (compact clay, permanently saturated low points,

and zones beneath rust tubercles) act as anodes, sustaining active metal dissolution. Xu et al. [26] showed that oxygen depletion at anode sites shifts the corrosion mode toward nucleation-dominated pit growth, intensifying localized attack per unit of dissolved metal (more severe localized attack per unit of dissolved metal) and explaining why oxygen-starved microenvironments beneath existing rust deposits often produce the deepest pits on buried pipe.

Differential aeration is well established as a primary cause of localized corrosion, but its quantification under transient field conditions (where soil moisture and oxygen profiles change with season and precipitation) remains limited. Existing coupled electrochemical–soil models [16,38] treat the soil as a quasi-static medium. Dynamic coupling of precipitation/drainage models with corrosion kinetics is a critical missing capability for infrastructure reliability prediction.

3.5. Redox Potential

Redox potential (E_h) provides the most direct measurement of a soil's tendency to support oxidative or reductive electrochemical reactions. A value below approximately +100 mV vs. SHE indicates highly anaerobic conditions (Figure 5), typically associated with SRB activity and sulfate reduction [22]. The AWWA C105/A21.5 standard explicitly incorporates E_h into its soil-corrosivity scoring system alongside resistivity, pH, and sulfide content. Corrosion rates increase exponentially with decreasing E_h in reducing environments, reflecting both the increasing thermodynamic driving force for anodic dissolution and the expanding ecological niche for SRB.

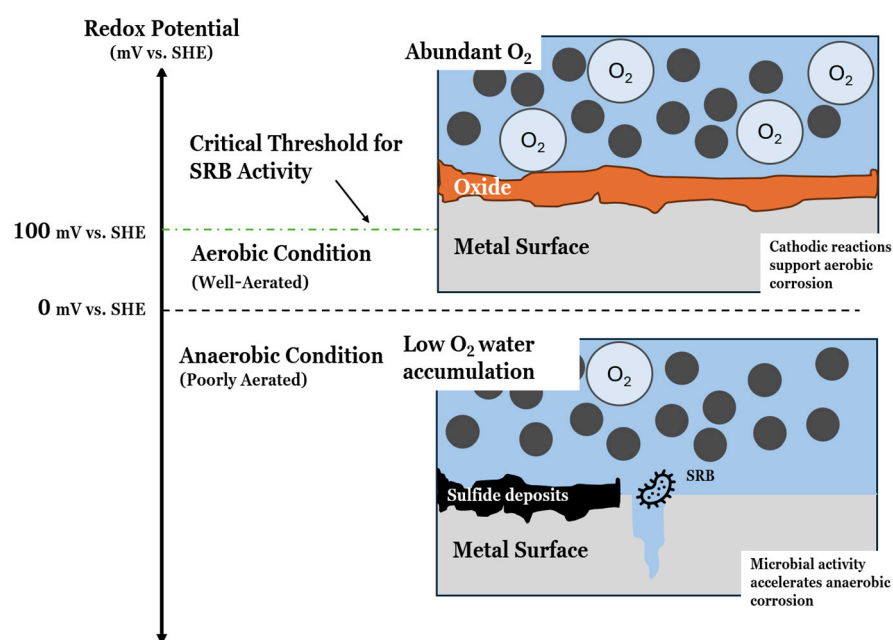


Figure 5. Effect of soil redox potential on external corrosion of buried pipelines, with the transition from aerobic (high E_h) to anaerobic SRB-active (low E_h) conditions. Key thresholds: $E_h > +400$ mV vs. SHE—well-aerated, minimal MIC risk; +100 to +400 mV—moderate aeration; 0 to +100 mV—transitional, early SRB activity possible; <0 mV—anaerobic, high SRB and MIC risk; <-200 mV—strongly reducing, active sulfate reduction and H_2S generation.

Despite its mechanistic relevance, E_h measurement quality in the field is poor: soil disturbance during sampling introduces oxygen, and the measurement fluctuates with seasonal moisture and temperature changes. This has limited the quality of E_h data in historical pipeline corrosion databases. Song et al. [37] confirmed that pipe-to-soil potential (a proxy for E_h when cathodic protection is absent) is among the top predictors of maximum

pit depth in machine learning analysis, with Accumulated Local Effects (ALE) analysis showing that rates increase sharply for pipe-to-soil potential values above -0.8 V.

The mechanistic relevance of E_h (particularly for predicting SRB activity and the redox state of the rust layer) is not matched by the measurement quality in most field datasets. Systematic paired E_h and dissolved-sulfide measurements—both required by AWWA C105 but rarely consistently recorded in utility inspection databases—would substantially improve the predictive value of soil-corrosivity assessments.

3.6. Soil Texture and Particle Size

Soils with high proportions of fine particles are consistently more corrosive toward buried ferrous metals than coarser soils (Figure 6). The mechanisms are coupled: fine soils retain more moisture at a given precipitation level (raising ionic conductivity), restrict oxygen diffusion (promoting anodic conditions beneath rust deposits), present more reactive mineral surfaces (particularly illite and montmorillonite), and create microenvironments that favour SRB growth. Azoor et al. [16] showed that the texture-dependent critical S_r is linked to the soil water retention curve, with clay soils reaching peak corrosivity at the highest saturation levels. These findings place texture mechanistically upstream of moisture in the causal chain.

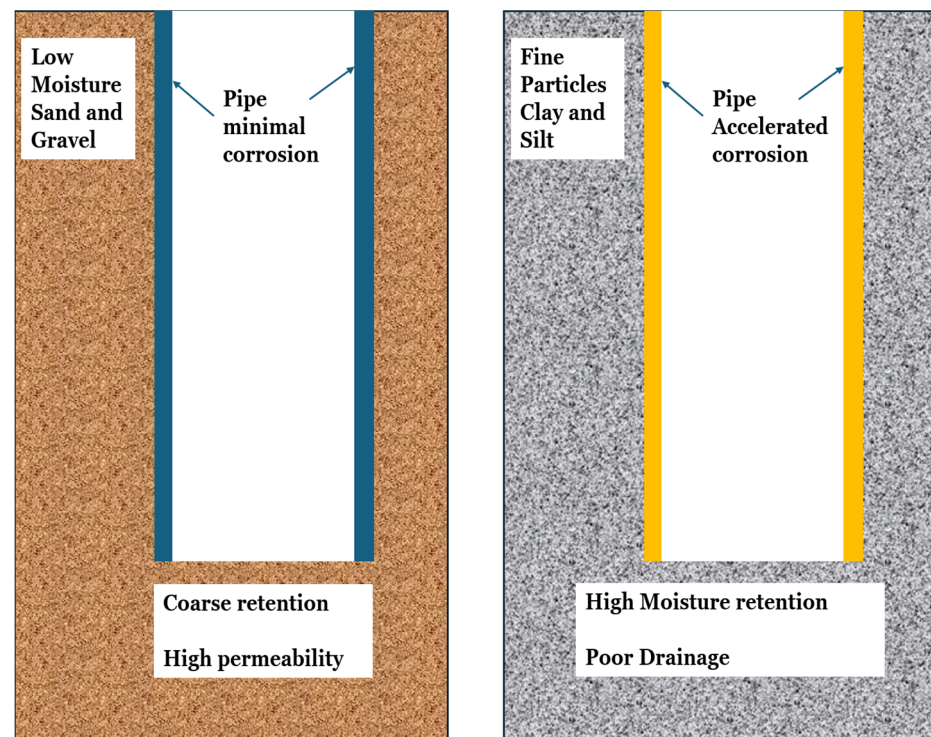


Figure 6. Effect of soil texture on external corrosion of pipelines, showing the differential critical-moisture contents and oxygen diffusion characteristics of clay, silt, and sandy soils. Key thresholds: sandy soils peak at $S_r \approx 0.5$ (approximately 25–30% volumetric moisture content); silt soils peak at $S_r \approx 0.7$; clay soils peak at $S_r \approx 0.8$. At full saturation ($S_r = 1.0$), all textures show reduced abiotic corrosion but elevated MIC risk due to anaerobic conditions.

However, the relationship between clay content and corrosion rate is not invariably monotonic. Some multivariate studies find a low direct correlation between clay fraction and corrosion rate, with soil chemistry and microbial activity emerging as stronger predictors [39]. This could be contradictory as clay soils in well-drained environments may be less corrosive than coarser soils in permanently saturated zones with high saline groundwater. The predictive utility of texture arises from its control over moisture retention,

oxygen diffusion, and microbial habitat, and it should be interpreted accordingly within multi-parameter models.

The proportional fines content (clay + silt fraction) remains one of the most consistently significant covariates in multivariate statistical analyses of pipeline pit depth [40], but its predictive value is best realized within multi-parameter models rather than in isolation. Its principal mechanistic roles (moisture retention, oxygen restriction, and SRB habitat provision) are better captured by explicit moisture, aeration, and redox measurements.

3.7. Soil Temperature

Temperature influences corrosion kinetics through three coupled mechanisms—direct acceleration of electrochemical reaction rates via the Arrhenius dependence of corrosion current density:

$$i_{corr} = i_0 \exp\left(\frac{-E_a}{RT}\right) \quad (12)$$

For unprotected mild and low-alloy steels in near-neutral simulated soil electrolytes, ref. [41] reported activation energy values of 42.96–47.01 kJ mol^{−1} for API 5L X52 over a temperature range of 30–50 °C and a pH range of 4.9–9.0 (values characteristic of mixed charge transfer and diffusion control). Values substantially above 55 kJ mol^{−1} that appear in some of the prior literature derive from inhibited acidic systems (corrosion inhibitor studies) and are not applicable to free-corrosion conditions in soil.

The effect of temperature on resistivity is quantitatively significant: a 20 °C increase in soil temperature typically reduces resistivity by 40–60%, proportionally increasing the corrosion current density under a constant electrochemical driving force [42]. For MIC, biofilm formation rates peak at 35–40 °C for most indigenous soil microbial communities; above 45 °C, thermal deactivation of enzymatic processes reduces biofilm stability and microbial viability. MIC-associated localized corrosion rates at optimal temperature ranges can exceed abiotic rates by factors of 3–8 [31].

The 40–55 kJ mol^{−1} activation energy range for abiotic soil corrosion is well established for reference conditions. In the presence of active SRB biofilms, however, the apparent activation energy will reflect the temperature dependence of biological metabolism, which follows a different functional form from the Arrhenius equation and is not directly captured by i_0 and E_a alone. Combining abiotic kinetic models with temperature-dependent biofilm growth models is needed for realistic corrosion-rate predictions in seasonally variable or warm soil environments.

3.8. Section 3 Summary

Among soil parameters, moisture content and electrical resistivity are the primary determinants of corrosion rate, but neither acts independently. The critical degree of saturation S_r is texture-dependent, ranging from approximately 0.5 in sandy soils to 0.8 in clay soils—a finding that supersedes the universal Gupta–Gupta 65% WHC threshold and can be integrated with existing AWWA C105 corrosivity classification criteria, as described in Section 3.1. Resistivity governs spatial current distribution rather than absolute corrosion rate; pH and E_h determine phase stability and MIC susceptibility; temperature amplifies all kinetic processes and modulates the SRB ecological niche; and ionic composition determines the phase assemblage and the competitive inhibition or promotion of protective layers. Reliable corrosion risk assessment of buried water mains requires integrating all of these parameters rather than relying on any single indicator.

4. Integrated Mechanistic Synthesis: Connecting Soil Environment to Corrosion Kinetics

The preceding sections identify four interacting mechanistic axes that collectively determine external corrosion rates and pit morphology in buried water pipelines: (i) anodic dissolution and its coupling to local electrolyte chemistry; (ii) cathodic oxygen reduction reaction (ORR) kinetics within the rust layer, dominated by the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox state of iron oxide phases; (iii) soil physical parameters (moisture, aeration, temperature, and texture) that govern mass transport and microbial activity; and (iv) MIC pathways (EMIC and M-MIC) that short-circuit the abiotic electrochemical sequence. The central synthesizing insight is that the rust layer is the mechanistic bridge between the soil environment and the corroding metal: its composition (determined by the interaction of all four axes) controls the cathodic current capacity available for ORR, the conductivity pathways enabling EMIC, the permeability to ionic transport, and the susceptibility of the protective layer to dissolution by aggressive ions.

This framework resolves an apparent contradiction between Hussein Farh et al.'s [6] finding that operational factors are the highest-weighted contributors to pipeline corrosion failure (relative weight 0.428, versus 0.337 for environmental factors) and the mechanistic soil-science primacy described throughout this review. The two frameworks are not competing but complementary. Operational management (installation quality, cathodic protection, and inspection frequency) determines the probability of exposure to corrosive conditions; the mechanistic soil-corrosion model determines the severity of damage when operational protection is absent or fails. Optimizing operational practice without understanding the underlying mechanisms is insufficiently reliable, while mechanistic understanding that ignores operational variables will misdirect mitigation investment.

Independent empirical validation of the mechanistic hierarchy comes from Song et al.'s [37] interpretable machine learning analysis of 259 field pipeline specimens, in which SHAP feature importance ranked chloride content (0.54) > pH (0.48) > temperature (0.30) > pipe-to-soil potential (0.27) > water content as the dominant predictors of maximum pit depth. This ranking maps directly onto the ionic-species phase-destabilization mechanism (chloride), the oxide-stability and dissolution-kinetics mechanism (pH), the Arrhenius and MIC temperature dependence (temperature), the cathodic protection and EMIC driving-force mechanism (pipe-to-soil potential), and the moisture-dependent transport mechanism (water content) described in this review.

The mechanistic framework developed in Sections 2 and 3 provides a direct explanation for these relative SHAP values. Chloride ranks first (SHAP 0.54) because it is the only parameter that simultaneously accelerates anodic dissolution through the pitting activation mechanism (Equation (5)), promotes the formation of non-protective akaganeite rather than goethite, and has no inherent self-limiting mechanism (its damaging effect intensifies monotonically with concentration above approximately 20 ppm) [37]. The pH value ranks second (SHAP 0.48) because it governs the thermodynamic stability of the entire oxide phase assemblage (Table 1) across the full pipeline service life, controlling whether rust evolves toward protective goethite or reactive lepidocrocite and akaganeite. Temperature ranks third (SHAP 0.30) because its Arrhenius acceleration of electrochemical kinetics (Equation (12); $E_a = 42\text{--}47 \text{ kJ mol}^{-1}$) is partially offset by the counteracting reduction in dissolved-oxygen solubility at elevated temperatures, limiting its net contribution relative to phase-controlling parameters. Pipe-to-soil potential ranks fourth (SHAP 0.27), reflecting the integrated influence of cathodic protection status: well-protected pipe (potential $\leq -0.85 \text{ V vs. Cu/CuSO}_4$) suppresses both abiotic ORR at the metal surface and EMIC-driven electron extraction by SRB, while inadequately protected pipe allows both pathways to operate simultaneously. Water content, although mechanistically foundational

as the electrolyte carrier, ranks lower because its effect operates indirectly through ionic conductivity and oxygen transport; pathways partially captured by the co-varying resistivity and E_h parameters in the training dataset. This interpretation reinforces that chloride management and pH stabilization provide the greatest leverage for reducing corrosion rates, while moisture control and resistivity management are most effective at reducing the spatial variability of corrosion damage.

The convergence of a mechanism-independent data-driven ranking with a bottom-up electrochemical narrative provides a level of cross-validation absent from previous reviews of this topic.

5. Unresolved Questions and Future Research Directions

Despite the mechanistic progress reviewed above, five consequential questions remain open:

The first unresolved question is how EMIC is quantified in mixed-oxygen soil environments? All published EMIC rate data derive from anaerobic pure-culture experiments. Real burial environments are rarely fully anaerobic; partial aerobiosis may suppress EMIC-active organisms, redirect electron flow to O_2 reduction, or enable syntrophic conglomerate activity with no laboratory analogue. Measuring EMIC current density under controlled partial-pressure O_2 conditions in representative soil microcosms is a prerequisite for incorporating EMIC kinetics into field corrosion models.

The second question is what is the quantitative cathodic capacity of aged rust layers? Hoërlé et al.'s [14] wet/dry model was parameterized for fresh γ -FeOOH-rich rust ($\epsilon = 0.3$; $S_a = 30 \text{ m}^2 \text{ g}^{-1}$). For mature, stratified rust collections on pipes with 30–80 years of service, neither porosity nor internal surface area is known from the systematic field data. Non-destructive electrochemical impedance characterization of in situ rust layers on excavated pipe specimens would directly constrain this parameter and enable calibration of the Hoërlé-type model for aged infrastructure.

The third question is whether the Azoor et al. [16] S_r framework holds for engineered backfills? Most pipeline installations involve engineered granular backfills whose water retention curves differ from the natural soils on which the texture-dependent S_r concept was developed. Extending the framework to engineered and disturbed backfill materials would enable direct integration with geotechnical data from pipeline installation records—data that are commonly available but currently underutilized for corrosion assessment.

The next question is which Fe-oxide phase ratio is diagnostic of impending through-wall corrosion? Systematic phase mapping of excavated pipe specimens at known stages of deterioration (using X-ray diffraction (XRD) and Mössbauer spectroscopy to quantify the goethite/magnetite/lepidocrocite ratio) could identify phase fingerprints that predict structural failure before through-wall perforation. Methods applied to archaeological iron specimens [43] are directly transferable to pipeline specimens.

And the last remaining question is how AC interference and SRB activity interact mechanistically? Qing et al. [33] showed that imposing 10 mA cm^{-2} AC current on SRB-bearing soil-extract solution raises the corrosion current of X80 steel to approximately nine times the no-AC baseline. Whether AC accelerates corrosion by disrupting the passive film, cycling the redox state of the surface oxide, or perturbing biofilm EMIC activity remains unresolved. Given the prevalence of AC stray currents in urban pipeline corridors, this interaction has direct practical relevance for cathodic protection criteria and SRB management protocols.

6. Summary

This critical review provides an integrated mechanistic framework for external corrosion of buried ferrous water pipelines. The principal conclusions, supported by the weight of experimental and field evidence, are as follows.

The rust layer that accumulates on long-buried pipe is an active electrochemical participant. Its redox cycling capacity (lepidocrocite reduction regenerating Fe^{2+} under anoxic conditions, which in turn catalyzes oxygen reduction and sustains anodic dissolution) enables corrosion to continue even in waterlogged, oxygen-limited soils. Repeated wet/dry cycles drive an irreversible lepidocrocite-to-magnetite transformation, increasing the electronic conductivity of the rust layer and expanding the available cathodic surface area. These dynamics are established by Fe-oxide mineral-transformation experiments [11,12], wet/dry cycle modelling [14], and X-ray absorption spectroscopy of field specimens.

The universal Gupta and Gupta [15] 65% WHC critical-moisture threshold is an oversimplification. Texture-resolved data [10,16] show that the critical degree of saturation ranges from $S_r \approx 0.5$ for sandy soils to $S_r \approx 0.8$ for clay soils, which is directly traceable to the inflection point of the soil water retention curve. Corrosion risk assessments should adopt the texture-dependent S_r framework in place of the universal threshold.

EMIC (direct electron transfer from Fe^0 to SRB via outer-membrane c-type cytochromes and flavin-based electron shuttles) is the dominant mechanism for severe SRB-driven pitting under anaerobic conditions, superseding the classical cathodic depolarization model. As established in Section 2.4.2, measured pure-culture SRB corrosion current densities range from 14 to 135 $\mu\text{A cm}^{-2}$; values at the mA cm^{-2} level arise only under combined SRB and AC interference.

Machine learning analysis of field corrosion databases [37] ranks chloride content, pH, pipe-to-soil potential, and water content as the four highest predictors of maximum pit depth, which is an empirical ranking that maps directly onto the ionic phase-destabilization, oxide-stability, EMIC driving-force, and moisture-transport mechanisms developed in this review, providing cross-validation of the integrated framework.

The operational-factor primacy found by Hussein Farh et al. [6] is complementary to, not in conflict with, the mechanistic soil-environment framework: operational management controls the probability of corrosive exposure; the soil environment determines the severity of damage when protection fails. Sustainable management of aging water infrastructure requires both dimensions.

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Nomenclature

Symbol/Abbreviation	Definition	Units/Typical Range
ALE	Accumulated Local Effects (machine learning partial dependence analysis)	—
AWWA	American Water Works Association	—
CP	Cathodic protection	—
EMIC	Electrical (extracellular) microbially influenced corrosion	—
M-MIC	Metabolite-mediated microbially influenced corrosion	—
MIC	Microbially influenced corrosion	—
ORR	Oxygen reduction reaction	—
SHAP	SHapley Additive exPlanations (machine learning feature importance)	—
SHE	Standard hydrogen electrode	—
SRB	Sulfate-reducing bacteria	—
WHC	Water-holding capacity of soil	—
XRD	X-ray diffraction	—
c_i	Dissolved oxygen concentration in electrolyte	mol m^{-3}
D_0	Diffusion coefficient of O_2 in bulk electrolyte	$\approx 2.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 25°C
D_{vv} (or D_e)	Effective diffusion coefficient in porous rust = $D_0 \times \varepsilon / \tau$	$1\text{--}5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$
d	Effective diffusion path length (electrolyte + rust layer)	m
E_a	Apparent activation energy for corrosion (Equation (12))	$42\text{--}47 \text{ kJ mol}^{-1}$ (carbon steel, near-neutral soil)
E_h	Soil redox potential	mV vs. SHE
F	Faraday constant	$96,500 \text{ C mol}^{-1}$
i_{corr}	Corrosion current density	$\mu\text{A cm}^{-2}$
i_{lim}	Limiting cathodic current density under diffusion control	$\mu\text{A cm}^{-2}$
i_0	Pre-exponential factor in the Arrhenius equation (Equation (12))	A cm^{-2}
n	Electrons transferred per ORR step	4 (full O_2 reduction to OH^-)
R	Universal gas constant	$8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
S_a	Internal specific surface area of rust layer	$\sim 30 \text{ m}^2 \text{ g}^{-1}$ (fresh rust); unconstrained for aged rust
S_r	Degree of saturation (vol. water content/porosity)	0–1; critical: 0.5 (sand), 0.7 (silt), 0.8 (clay)
T	Absolute temperature	K
ε	Rust layer porosity	0.3–0.5 (fresh rust)
τ	Tortuosity factor of rust layer pore network	2–5

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