

Corrosion and Its Inhibition in AISI Stainless Steel: Mechanisms, Electrochemical Evaluation, and Sustainable Approaches

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Abstract

Corrosion of AISI stainless steels is governed by the stability, composition, and reparability of their chromium-rich passive films. Although stainless steels are widely recognized for their corrosion resistance, localized forms of attack, particularly pitting, crevice corrosion, intergranular corrosion, erosion-corrosion, and stress-corrosion cracking, can occur under aggressive chemical, thermal, mechanical, or electrochemical conditions. These processes present significant challenges in petroleum refining, chemical processing, construction, transportation, power generation, food processing, marine systems, and water treatment. Corrosion can cause material failure, economic losses, environmental contamination, and safety hazards. Among the available corrosion-control techniques, corrosion inhibitors can reduce metal dissolution and stabilize protective surface films when their chemistry is compatible with the stainless-steel grade and service environment.

This review discusses the fundamental principles of corrosion inhibition with special reference to AISI stainless steels, including the electrochemical mechanisms of passive-film formation and breakdown, major forms of localized corrosion, classification of corrosion inhibitors, and the physicochemical factors governing inhibitor performance. Particular attention is given to AISI 304 and AISI 316 stainless steels, chloride-induced pitting and crevice corrosion, organic and inorganic inhibitors, adsorption-based protection, repassivation, and environmentally sustainable alternatives derived from plant extracts, biopolymers, and other renewable resources. Methods for evaluating inhibition performance, including gravimetric analysis, open-circuit potential measurements, potentiodynamic polarization, cyclic polarization, electrochemical impedance spectroscopy, critical pitting temperature measurements, and surface characterization, are examined. Thermodynamic adsorption models and computational approaches are also discussed. Finally, the major challenges associated with long-term stability, environmental compatibility, reproducibility, galvanic coupling, and industrial application are identified. The review emphasizes that effective corrosion inhibition of AISI stainless steel requires an integrated understanding of passive-film chemistry, electrochemical kinetics, interfacial adsorption, alloy metallurgy, and environmental conditions.

Keywords: AISI stainless steel; AISI 304; AISI 316; corrosion inhibitors; passive film; pitting corrosion; crevice corrosion; electrochemical kinetics; adsorption isotherms; electrochemical impedance spectroscopy; green inhibitors; corrosion rate.

1. Introduction

Stainless steels are iron-based alloys containing a minimum of roughly 10.5–12% chromium, a level at which a thin, adherent, self-healing oxide film forms spontaneously on exposure to oxidizing environments. Their corrosion resistance is therefore not a matter of thermodynamic nobility, since iron and chromium are both strongly reactive, but of kinetic protection provided by this passive film (Sedriks, 1996; Marcus, 2011). The austenitic grades AISI 304 (approximately 18% Cr, 8% Ni) and AISI 316 (approximately 16–18% Cr, 10–14% Ni, 2–3% Mo) are the most widely used members of the family, and they appear in pipelines, heat exchangers, storage tanks, reactor vessels, surgical and food-contact

equipment, architectural cladding, and marine hardware.

The economic stakes are considerable. A global study estimated the annual cost of corrosion across all materials and sectors at about 3.4% of world gross domestic product (Koch et al., 2016), and a meaningful share of this loss arises from unexpected failure of materials that were selected specifically for their corrosion resistance. Stainless steels seldom corrode uniformly in service. Instead, they fail locally, through pits, crevices, grain boundaries, or cracks, and such damage can progress to perforation or fracture with little warning and with a small overall mass loss (Frankel, 1998; Newman, 2001). This characteristic makes localized corrosion more

dangerous than general dissolution and also makes it harder to predict and to measure.

Several strategies are available for controlling the corrosion of stainless steel, including alloy selection, design that avoids crevices and stagnant zones, surface finishing and passivation treatments, coatings, cathodic or anodic protection, and chemical inhibition. Among these, inhibitors are attractive because they can be applied to existing systems, dosed at low concentrations, and adjusted as conditions change (Sastri, 2011; Dariva & Galio, 2014). Most of the inhibitor literature, however, concerns carbon steel in acidic or carbon dioxide-containing media (Finšgar & Jackson, 2014), and conclusions drawn there cannot be transferred directly to stainless steel, where the metal surface is already covered by an oxide film and where the relevant failure mode is often the breakdown of that film rather than uniform dissolution. This review therefore examines inhibition of AISI stainless steels from first principles, beginning with the structure and breakdown of the passive film, proceeding through the main corrosion forms, inhibitor classes, and mechanisms, and then covering sustainable inhibitors, evaluation methods, adsorption thermodynamics, computational tools, and unresolved challenges.

2. Passive Film Chemistry and Its Breakdown

2.1 Composition and structure

The passive film on austenitic stainless steel is typically 1–3 nm thick and has a duplex character. An inner barrier layer enriched in Cr(III) oxide and hydroxide lies adjacent to the alloy, and an outer layer, richer in Fe(III) oxyhydroxide and in hydrated species, forms toward the electrolyte (Olsson & Landolt, 2003). Nickel does not enter the film

significantly and tends instead to accumulate in the alloy surface layer just beneath it, whereas molybdenum, present in AISI 316, appears as Mo(IV) and Mo(VI) species near the film surface and at the film–metal interface. The film composition and thickness depend on the alloy, the potential, the pH, and the time of exposure, and the film ages and becomes progressively more chromium-rich and less hydrated as it is held in the passive range (Olsson & Landolt, 2003; Marcus, 2011).

2.2 Formation and protective role of alloying elements

Growth of the film is usually described by high-field ion conduction, in which cations and oxygen vacancies migrate through the film under a large internal electric field, and by the point defect model, which relates film thickness and stability to the generation and annihilation of defects at the two interfaces (Macdonald, 1992). Chromium is central to this protection. Brooks et al. (1986) showed that chromium enrichment strengthens the film and shifts the passive range, and the low solubility and low defect mobility of Cr(III) oxide account for much of the barrier function. Molybdenum acts differently. In the bipolar model proposed by Clayton and Lu (1986), Mo(VI) species incorporated in the outer film render it cation-selective and thus hinder inward migration of chloride, while molybdenum dissolved from active sites can also assist repassivation. These features explain why AISI 316 resists chloride attack better than AISI 304, an advantage often summarized by the pitting resistance equivalent number, $PREN = \%Cr + 3.3(\%Mo) + 16(\%N)$, which is approximately 18–20 for AISI 304 and 24–26 for AISI 316 (Sedriks, 1996; Figure 1 and Table 1).

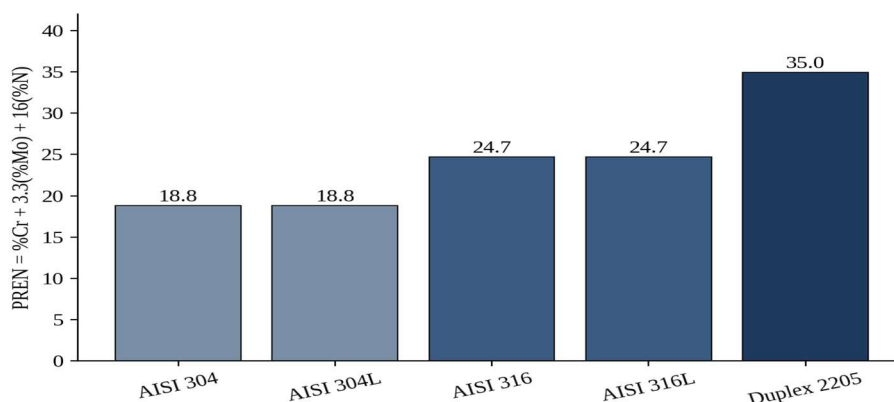


Figure 1. Pitting resistance equivalent numbers (PREN) calculated from typical nominal compositions of common stainless-steel grades (AISI 304: 18% Cr; 316: 17% Cr, 2.1% Mo; duplex 2205: 22% Cr, 3.1% Mo, 0.17% N; nitrogen taken as 0.05% for the austenitic grades). Values are indicative and vary within specification limits.

Table 1. PREN values of common stainless-steel grades plotted in Figure 1

Grade	Cr (wt%)	Mo (wt%)	N (wt%)	PREN
AISI 304	18	–	0.05	18.8
AISI 304L	18	–	0.05	18.8
AISI 316	17	2.1	0.05	24.7
AISI 316L	17	2.1	0.05	24.7
Duplex 2205	22	3.1	0.17	35.0

PREN = %Cr + 3.3(%Mo) + 16(%N), calculated from typical nominal compositions; values are indicative and vary within specification limits.

2.3 Breakdown and repassivation

Breakdown of the passive film is a stochastic process. Several mechanisms have been proposed, including penetration of chloride through the film, adsorption of chloride at the film surface leading to local thinning, and mechanical rupture of the film by stress or defects, with the common outcome of local exposure of bare alloy (Sato, 1971; Frankel, 1998). On stainless steel the initiation sites are strongly linked to microstructural heterogeneities, particularly manganese sulfide inclusions, whose dissolution leaves sulfur-rich residues and a locally aggressive microenvironment (Ryan et al., 2002; Burstein et al., 2004). Many nuclei form and repassivate within seconds, producing the current transients of so-called metastable pitting, but a minority survive and grow to stable pits (Pistorius & Burstein, 1992). Survival requires that the product of pit current density and pit depth exceed a critical value so that the acidic, chloride-rich electrolyte is maintained inside the pit (Galvele, 1976). If the potential is lowered below the repassivation potential, the film re-forms and growth stops. Because inhibitors can act at each of these stages, by hindering initiation, shortening the lifetime of metastable pits, or promoting repassivation, an understanding of the breakdown sequence is essential for rational inhibitor selection.

3. Forms of Corrosion in AISI Stainless Steels

3.1 Pitting corrosion

Pitting is the most frequent localized failure of AISI 304 and 316 in chloride-bearing waters, brines, and process streams. It is characterized by the pitting potential (E_{pit}), above which pits grow stably, and by the critical pitting temperature (CPT), below which pits do not propagate at a given potential and chloride level (Brigham & Tozer, 1973; Frankel, 1998). Increasing chloride concentration, temperature, and acidity lowers E_{pit} , whereas higher molybdenum and nitrogen contents raise it. Pit morphology, depth, and

density matter more than average mass loss for engineering assessment, and a few deep pits may govern the service life of a component.

3.2 Crevice corrosion

Crevice corrosion occurs in narrow gaps formed beneath gaskets, deposits, bolt heads, and fouling layers. Oxygen is depleted inside the gap, so the cathodic reaction is confined to the outer surface while metal dissolution, hydrolysis of metal ions, and migration of chloride acidify and concentrate the crevice solution (Oldfield & Sutton, 1978). Stainless steels are generally more susceptible to crevice attack than to pitting, with a lower critical temperature and a wider range of conditions, and AISI 304 is notably prone to it in seawater (Sedriks, 1996). Inhibitor transport into such a restricted space makes crevice corrosion particularly hard to inhibit.

3.3 Intergranular corrosion and sensitization

When austenitic grades are held or slowly cooled in the range of about 450–850 °C, chromium carbides precipitate at grain boundaries and the adjacent zone is depleted of chromium, so that the local passive film is weakened (Sedriks, 1996). Subsequent exposure to oxidizing acids or other aggressive media then causes selective attack along the grain boundaries. Low-carbon grades such as AISI 304L and 316L and stabilized grades containing titanium or niobium reduce this risk.

3.4 Erosion-corrosion and stress-corrosion cracking

Erosion-corrosion arises where high flow velocity, turbulence, or entrained solids remove or damage the passive film faster than it can be repaired, a situation seen in pumps, impellers, and heat-exchanger tubing. Stress-corrosion cracking of austenitic grades occurs under sustained tensile stress in chloride environments, typically at temperatures

above about 50–60 °C, and produces branched transgranular cracks (Sedriks, 1996). In both cases the interaction of mechanics and chemistry means that an inhibitor can contribute only if it improves the persistence or reformation of the film under the prevailing stress or flow.

3.5 Galvanic and microbiologically influenced corrosion

Stainless steel is noble relative to carbon steel, aluminum, and zinc, and in a galvanic couple it usually acts as the cathode (Revie & Uhlig, 2008). Microbial biofilms, in turn, can create concentration cells, ennoble the open-circuit potential, and produce local acidity or sulfide, so microbiologically influenced corrosion often manifests as pitting at welds and heat-affected zones (Little & Lee, 2007). Both factors will return in Section 9, because an inhibitor that is effective for stainless steel may be ineffective or harmful for another material in the same circuit.

4. Classification of Corrosion Inhibitors

Inhibitors are conventionally classified by their mechanism as anodic, cathodic, or mixed, and by their chemistry as inorganic or organic (Sanyal, 1981; Dariva & Galio, 2014). Anodic inhibitors stifle metal oxidation by promoting or reinforcing the passive film, cathodic inhibitors retard oxygen reduction or hydrogen evolution, and mixed

inhibitors, which include most organic adsorbates, suppress both partial reactions by blocking the surface. For stainless steel the anodic and mixed classes are the more relevant, since the cathodic reaction on a passive surface proceeds at a low rate and since pitting is an anodic process.

Among inorganic species, nitrite, molybdate, phosphate, silicate, and tungstate promote or repair the passive film, whereas chromate, formerly the benchmark, is now strongly restricted owing to its toxicity and carcinogenicity (Sastri, 2011). Early work on 18-8 stainless steel demonstrated that nitrate, sulfate, and hydroxide ions raise the critical potential for pitting in chloride solution, which is consistent with competitive adsorption at sites where chloride would otherwise attack (Leckie & Uhlig, 1966). Anodic inhibitors carry a recognized hazard: if their concentration falls below a critical level, the surface is incompletely protected and anodic dissolution concentrates at the unprotected sites, which may intensify pitting (Sastri, 2011; Dariva & Galio, 2014). Organic inhibitors contain nitrogen, oxygen, sulfur, or phosphorus heteroatoms, aromatic rings, or multiple bonds that supply electrons for adsorption, and they include amines, azoles, Schiff bases, thioureas, carboxylates, and surfactants (Sanyal, 1981; Finšgar & Jackson, 2014). Table 2 summarizes the main classes and their relevance to AISI stainless steel.

Table 2. Principal classes of corrosion inhibitors and their relevance to AISI stainless steels

Class	Representative examples	Main action	Remarks for stainless steels
Inorganic anodic	Nitrite, molybdate, phosphate, silicate, nitrate	Strengthen or repair the passive film; compete with chloride	Effective but dosage-critical; risk of local attack if underdosed; some are environmentally restricted
Inorganic oxidizing	Chromate	Maintains passivity by oxidation	Highly effective historically; now largely excluded because of toxicity
Organic adsorption	Amines, azoles, Schiff bases, thioureas, surfactants	Adsorb through heteroatoms and π -electrons, forming a barrier	Often studied in acids; performance in neutral chloride is less documented
Green extracts	Plant extracts rich in polyphenols, alkaloids, flavonoids, tannins	Multicomponent adsorption and complexation	Biodegradable and low-toxicity; composition varies between batches
Biopolymers and ionic liquids	Chitosan, cellulose derivatives, pectin, gums, amino acids, imidazolium salts	Film formation, chelation, strong adsorption	Renewable or low-volatility; solubility and long-term stability require study

5. Mechanisms of Inhibition and Controlling Factors

Organic inhibitors protect by adsorption at the metal–solution interface, displacing water and

aggressive anions and creating a barrier to charge and mass transfer. Adsorption can be physical, resulting from electrostatic attraction between charged molecules and a charged surface, or chemical,

resulting from donor–acceptor interactions in which lone pairs or π -electrons of the inhibitor are shared with vacant d-orbitals of iron, chromium, nickel, or molybdenum atoms, with the possibility of back-donation from filled metal orbitals into antibonding orbitals of the molecule (Gece, 2008). The hard and soft acid–base principle provides a qualitative guide, since hard donor atoms such as oxygen favor hard Cr(III) centers and softer sulfur or nitrogen donors favor softer metal sites (Pearson, 1963). In practice the two modes often coexist, and many inhibitors adsorb first physically and then reorganize chemically.

On stainless steel the substrate is an oxide-covered surface, not bare metal, so adsorption occurs on hydroxylated Cr(III) and Fe(III) sites whose charge depends on pH and on the point of zero charge of the film. Cationic or protonated molecules therefore adsorb readily at pH values above the point of zero charge, and in acidic media the specific adsorption of halide ions can bridge anionic and cationic species, giving the synergism often reported between organic cations and iodide or bromide (Sastri, 2011; Raja et al., 2016). In neutral chloride solution the central competition is between chloride and inhibitor for surface sites. A successful inhibitor in this setting should either adsorb more strongly than chloride, thicken or stabilize the film, or raise the repassivation potential so that nascent pits cannot continue to grow (Frankel, 1998; Leckie & Uhlig, 1966).

Performance depends on molecular structure, including the number and type of donor atoms, planarity, molecular size, and substituent effects, and on concentration, which typically follows a saturation pattern as surface coverage approaches completion. Temperature has an ambiguous effect. A rise in temperature may desorb physically adsorbed molecules and reduce efficiency, but it may equally promote chemisorption or film formation and enhance it (Finšgar & Jackson, 2014). The medium also matters: pH, chloride concentration, dissolved oxygen, flow, and the presence of oxidants, biocides, or other additives all alter surface chemistry. Finally, the alloy grade, surface finish, welding history, and degree of prior passivation influence both the distribution of weak sites and the ability of the inhibitor to reach them (Olsson & Landolt, 2003; Sedriks, 1996). A result obtained on polished AISI 304 in laboratory solution therefore cannot be

assumed to hold for a rough, welded surface in service.

6. Environmentally Sustainable Inhibitors

Growing regulatory and environmental pressure has accelerated the search for inhibitors that are non-toxic, biodegradable, and derived from renewable resources. Plant extracts have been studied most widely, since they contain phytochemicals such as alkaloids, flavonoids, tannins, terpenoids, and phenolic acids, whose heteroatoms and aromatic structures can adsorb on metal surfaces (Raja & Sethuraman, 2008; Verma et al., 2018). Extracts of leaves, seeds, fruit peels, and roots have reported high inhibition efficiencies for steels and alloys in acidic and chloride media. The multicomponent character of an extract can be an advantage, since different constituents may interact synergistically, but it also complicates the identification of active species and the reproducibility of results.

Biopolymers constitute a second group. Chitosan, cellulose derivatives, starch, pectin, alginate, and plant gums contain hydroxyl, amino, and carboxyl groups that adsorb or chelate surface metal ions and can form protective films, and chemical modification, for instance carboxymethylation or grafting, further improves solubility and surface affinity (Umoren & Eduok, 2016). Amino acids and other small bio-derived molecules, together with ionic liquids designed for low volatility and tunable structure, extend the choice further (Verma et al., 2017). Such compounds are often described as green on the grounds of origin, but this label requires verification, because a renewable source does not guarantee low ecotoxicity, and some ionic liquids and chemically modified polymers are not readily biodegradable.

Two limitations stand out. First, the majority of studies employ acidic media such as hydrochloric or sulfuric acid, where the passive film is dissolved and the situation approaches that of active dissolution, and relatively few examine pitting and crevice behavior of AISI 304 or 316 in neutral chloride, which is the more common service condition (Verma et al., 2018; Finšgar & Jackson, 2014). Second, natural extracts vary with species, harvest, and extraction solvent, are prone to microbial degradation, and may foam or discolor process streams. Standardized extraction, chemical profiling of the active fractions, and long-term exposure testing under realistic chemistry are required before green

inhibitors can be considered reliable for stainless steel.

assessment combines complementary electrochemical, gravimetric, and surface methods. Table 3 summarizes those most widely used.

7. Methods for Evaluating Inhibition Performance

No single technique captures the behavior of inhibitors on a passive alloy, and a credible

Table 3. Techniques used to evaluate inhibition of AISI stainless steels

Technique	Principal parameters	Information obtained	Main limitations
Gravimetric (weight loss)	Mass loss, corrosion rate, inhibition efficiency	Average dissolution over long periods	Insensitive for passive alloys; does not detect pitting
Open-circuit potential	E_{corr} versus time	Passivation, film growth, onset of breakdown	Qualitative; potential shifts are not rates
Potentiodynamic polarization	i_{corr} , Tafel slopes, passive current density	Kinetics; anodic, cathodic, or mixed behavior	Scan-rate and surface-state dependent
Cyclic polarization	E_{pit} , E_{rp} , hysteresis loop	Susceptibility to pitting and repassivation	Aggressive, destructive; poor reproducibility without replicates
Critical pitting temperature	CPT	Temperature limit for stable pitting	Time-consuming; requires controlled cells
Electrochemical impedance spectroscopy	R_{ct} , R_{f} , CPE parameters	Film resistance, capacitance, adsorption	Requires equivalent-circuit interpretation
Surface analysis	SEM/EDS, XPS, AFM, FTIR, Raman, ToF-SIMS	Morphology, film composition, inhibitor presence	Often ex situ; limited sampling area

7.1 Gravimetric methods

Gravimetric testing follows standard immersion practice and specimen cleaning procedures (ASTM G31; ASTM G1). The inhibition efficiency is calculated as $IE\% = [(W_0 - W)/W_0] \times 100$, where W_0 and W are mass losses without and with inhibitor. The method is simple, but because stainless steels corrode at very low general rates and fail locally, mass loss may be below the detection limit while deep pits are developing. Gravimetric data therefore need to be complemented by microscopy and by pit counting and depth measurements.

7.2 Open-circuit potential and polarization methods

Monitoring of the open-circuit potential indicates whether an inhibitor shifts the system toward more passive, noble values and how fast steady state is reached. Potentiodynamic polarization gives the corrosion current density by Tafel extrapolation or by the linear polarization relation (Stern & Geary, 1957), from which corrosion rates are calculated (ASTM G102). Shifts in E_{corr} of more

than about 85 mV relative to the blank are conventionally taken to indicate predominantly anodic or cathodic action, while smaller shifts indicate mixed behavior. For passive stainless steel, the passive current density and the width of the passive region are often more informative than i_{corr} , and anodic polarization procedures are standardized (ASTM G5).

7.3 Cyclic polarization and critical pitting temperature

Cyclic polarization, in which the potential is scanned upward until a defined current density is reached and then reversed, provides E_{pit} , the repassivation or protection potential E_{rp} , and the hysteresis between forward and reverse curves (ASTM G61). An effective pitting inhibitor shifts E_{pit} in the noble direction, raises E_{rp} , and reduces the hysteresis area (Figure 2; Table 4). Because E_{pit} is a statistical quantity, it should be reported as a distribution from replicate measurements and not as a single value (Frankel, 1998). The critical pitting temperature, measured electrochemically at a fixed

potential in a ramped-temperature cell (ASTM G150) or by ferric chloride immersion (ASTM G48), is sensitive to alloy composition and to inhibitors and

gives a metric that can be linked directly to service temperature (Brigham & Tozer, 1973).

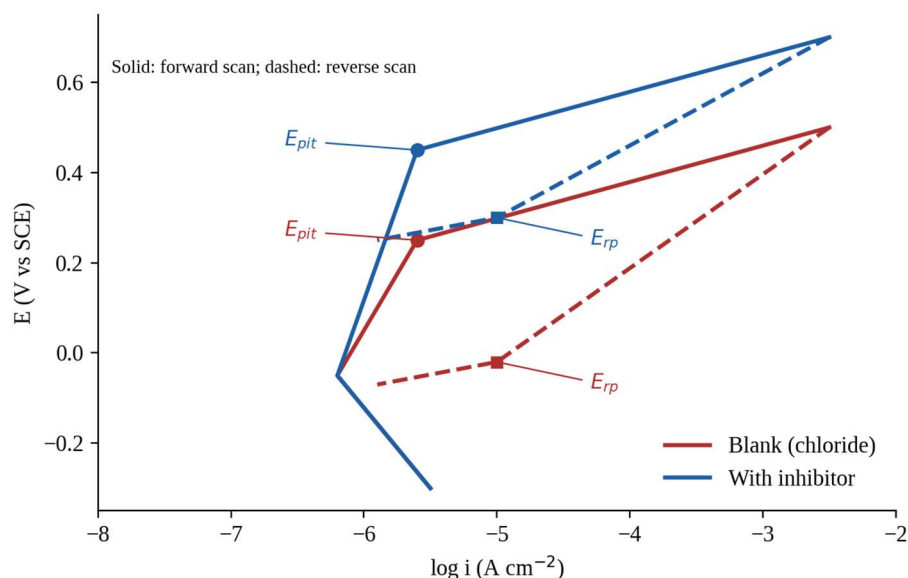


Figure 2. Schematic cyclic polarization curves for AISI 304 or 316 in chloride solution without and with an effective pitting inhibitor. The inhibitor shifts E_{pit} and E_{rp} to more noble values and reduces the hysteresis loop. Illustrative curves only, not experimental data.

Table 4. Characteristic potentials read from the cyclic polarization curves in Figure 2

Parameter	Blank (chloride)	With inhibitor	Change
Corrosion potential, E_{corr} (V vs SCE)	-0.05	-0.05	0
Pitting potential, E_{pit} (V vs SCE)	+0.25	+0.45	+0.20
Repassivation potential, E_{rp} (V vs SCE)	-0.02	+0.30	+0.32
Hysteresis width, $E_{pit} - E_{rp}$ (V)	0.27	0.15	-0.12
Pitting window, $E_{pit} - E_{corr}$ (V)	0.30	0.50	+0.20
$\log i$ at E_{pit} ($A\ cm^{-2}$)	-5.6	-5.6	—
Reverse-scan vertex potential (V vs SCE)	+0.50	+0.70	+0.20

Values are read from the schematic curves and are illustrative only, not experimental data. A positive change in E_{pit} and E_{rp} and a smaller hysteresis width indicate improved resistance to pitting.

7.4 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is a non-destructive method that probes the interface over a range of frequencies with a small perturbation and is thus well suited to following film growth, adsorption, and degradation over time (Mansfeld, 1981; Orazem & Tribollet, 2008). Spectra of passive stainless steel are normally fitted with equivalent circuits that comprise the solution resistance, a film or charge-transfer resistance, and a constant phase element (CPE) in place of an ideal

capacitor to account for surface heterogeneity, with effective capacitance calculated through accepted conversion formulas (Brug et al., 1984; Hsu & Mansfeld, 2001). An increase in the charge-transfer or film resistance and a decrease in capacitance upon inhibitor addition are typically interpreted as evidence of adsorption or film thickening (Figure 3; Table 5). Care is needed because several equivalent circuits can fit the same data, and the circuit must have a physical rationale supported by independent measurements.

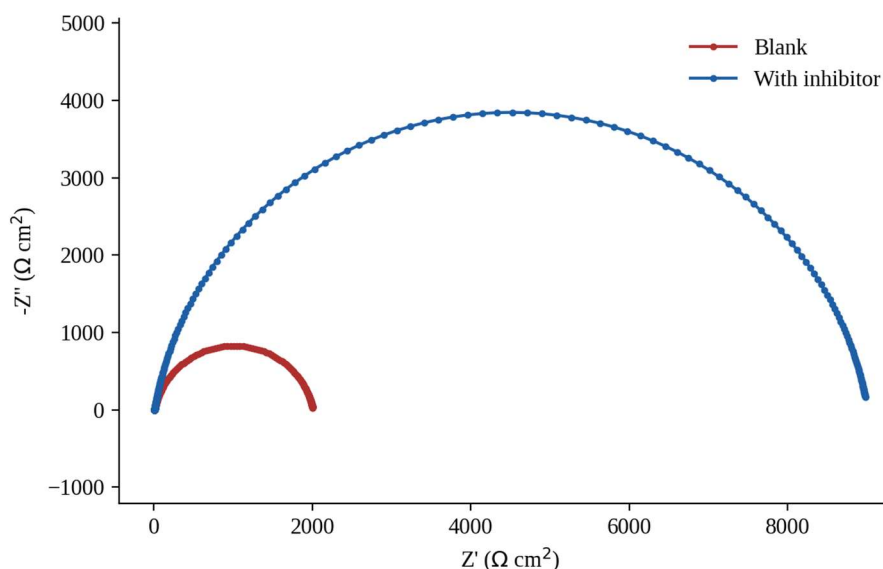


Figure 3. Simulated Nyquist plots for a passive stainless-steel electrode, generated from a simple circuit of solution resistance in series with a parallel charge-transfer resistance and constant phase element. The larger semicircle with inhibitor reflects increased R_{ct} and decreased capacitance. Illustrative values, not experimental data.

Table 5. Impedance parameters read from the simulated Nyquist plots in Figure 3

Parameter	Blank	With inhibitor
Solution resistance, R_s ($\Omega \text{ cm}^2$)	< 50 (near origin)	< 50 (near origin)
Charge-transfer resistance, R_{ct} ($\Omega \text{ cm}^2$)	$\approx 2,000$	$\approx 9,000$
Maximum $-Z''$ ($\Omega \text{ cm}^2$)	≈ 830	$\approx 3,850$
Z' at maximum $-Z''$ ($\Omega \text{ cm}^2$)	$\approx 1,000$	$\approx 4,500$
Inhibition efficiency, η (%)	–	≈ 78

Values are read from the simulated plot and are illustrative only, not experimental data. $\eta = [(R_{ct,inh} - R_{ct,blank}) / R_{ct,inh}] \times 100$. Capacitance cannot be read from a Nyquist plot without the corresponding frequencies.

7.5 Surface characterization

Surface methods link electrochemical response to chemistry and morphology. Scanning electron microscopy with energy-dispersive spectroscopy identifies pit morphology and inclusion-related initiation, atomic force microscopy quantifies roughness changes caused by adsorbed layers, and infrared and Raman spectroscopy identify functional groups. X-ray photoelectron spectroscopy and time-of-flight secondary-ion mass spectrometry give the depth profile of Cr, Fe, Ni, and Mo species in the film and can show whether an inhibitor is incorporated into or merely adsorbed on the oxide (Olsson & Landolt, 2003). Because most of these methods are performed *ex situ* after rinsing and drying, weakly bound layers may be lost and the findings should be read with that limitation in mind.

8. Adsorption Thermodynamics and Computational Approaches

8.1 Adsorption isotherms

Surface coverage (θ) is commonly estimated from inhibition efficiency, and its dependence on inhibitor concentration (C) is tested against isotherm models. The Langmuir isotherm, $C/\theta = 1/K_{ads} + C$, assumes monolayer adsorption on equivalent, non-interacting sites (Langmuir, 1918), and is the most frequently reported fit (Figure 4; Table 6). Temkin, Frumkin, Freundlich, and Flory–Huggins models allow for surface heterogeneity, lateral interaction, or displacement of several solvent molecules. The standard free energy of adsorption is obtained from $\Delta G_{ads}^\circ = -RT \ln(55.5 K_{ads})$, where 55.5 mol L^{-1} is the molar concentration of water. Values near -20 kJ mol^{-1} or less negative are usually taken as physisorption and values near -40 kJ mol^{-1} or more negative as chemisorption, with intermediate values indicating mixed adsorption (Sastri, 2011; Finšgar & Jackson, 2014).

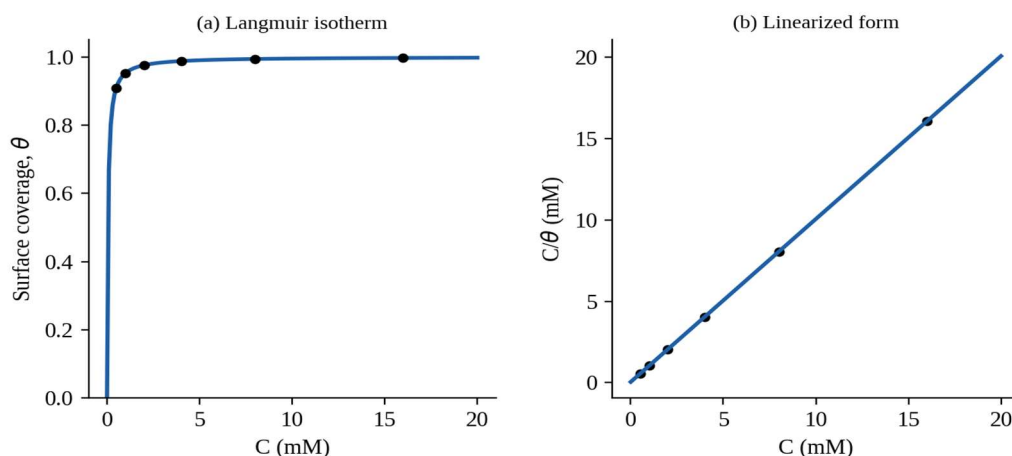


Figure 4. Illustrative Langmuir adsorption behavior: (a) surface coverage versus inhibitor concentration and (b) the linearized plot of C/θ versus C , whose slope near unity and intercept $1/K_{ads}$ are used to estimate the adsorption constant. Simulated for an assumed K_{ads} , not experimental data.

Table 6. Langmuir adsorption data plotted in Figure 4

Inhibitor concentration, C (mM)	Surface coverage, θ	C/θ (mM)
0.5	0.909	0.55
1	0.952	1.05
2	0.976	2.05
4	0.988	4.05
8	0.994	8.05
16	0.997	16.05

Simulated for an assumed K_{ads} , not experimental data. Linear fit of C/θ versus C : slope ≈ 1.00 , intercept $1/K_{ads} \approx 0.05$ mM, giving $K_{ads} \approx 20$ mM⁻¹ (2.0×10^4 L mol⁻¹) and $\Delta G^\circ_{ads} = -RT \ln(55.5 K_{ads}) \approx -34.5$ kJ mol⁻¹ at 298 K.

8.2 Quantum-chemical and molecular simulation methods

Computational chemistry offers a route to relate structure to performance. Density functional theory calculations provide the energies of the highest occupied and lowest unoccupied molecular orbitals, the energy gap, dipole moment, electronegativity, hardness, and local reactivity descriptors such as Fukui functions, which indicate where a molecule is likely to donate or accept electrons (Gece, 2008; Obot et al., 2015). Molecular dynamics and Monte Carlo simulations estimate the adsorption energy and orientation of inhibitor molecules at the interface and include solvent explicitly. A frequent weakness in the published work, however, is the use of a clean Fe(110) surface as a model, which is a poor representation of an austenitic alloy covered by a hydrated Cr–Fe oxide. Models that include Cr₂O₃ or oxyhydroxide surfaces, chloride, and water are more appropriate for stainless steel, though computationally demanding. Data-driven and machine-learning methods, trained on quantitative structure–property relationships, are beginning to

supplement these calculations, but their predictions are limited by the quality and consistency of the experimental data available (Winkler, 2017).

9. Challenges and Future Perspectives

Long-term stability is the first unresolved issue. Most laboratory tests last hours to days, whereas stainless-steel equipment is expected to operate for decades. Inhibitors may be consumed by adsorption, thermal decomposition, hydrolysis, oxidation, or microbial degradation, and the protective layer may thin or desorb during upsets in temperature, flow, or chemistry. Reliable service-life prediction requires extended exposures, replenishment strategies, and monitoring of residual concentration.

Environmental and regulatory compatibility is a second concern. Replacement of chromate and other toxic species must not simply shift the hazard to ecotoxic organic compounds, so toxicity, biodegradability, and bioaccumulation should be assessed together with efficiency (Sastri, 2011; Verma et al., 2017). In food, beverage,

pharmaceutical, and potable-water systems, any inhibitor must also be compatible with contact regulations and must not alter taste, product quality, or downstream processing.

Galvanic coupling is a third. Real systems rarely consist of a single material, and stainless steel is often connected to carbon steel, copper alloys, or aluminum. An inhibitor optimized for one metal can accelerate attack on another or fail to protect it, and a galvanic couple can polarize stainless steel into a potential range where inhibitor adsorption differs from that in isolated tests (Revie & Uhlig, 2008). Evaluation of multi-metal systems should therefore be standard practice.

Finally, translation to industrial practice demands consideration of cost, supply, compatibility with biocides, scale inhibitors, and corrosion monitoring systems, and demonstration under realistic flow, temperature, and crevice geometry. Promising directions include multifunctional formulations that combine film-forming and scale- or biofilm-control properties, hybrid systems that couple inhibitors with coatings or surface treatments, controlled-release carriers that supply inhibitor on demand at damaged sites, in situ and local probes that track film chemistry during exposure, and computational screening based on realistic oxide models (Obot et al., 2015; Winkler, 2017). Progress in each of these areas will depend on a more critical use of stainless-steel-specific metrics, in particular E_{pit} , E_{rp} , and CPT, instead of reliance on mass loss and polarization resistance alone.

10. Conclusion

Corrosion of AISI stainless steels is controlled by a thin chromium-rich passive film whose stability depends on alloy composition, microstructure, and environment. Failure typically occurs by local breakdown of this film, producing pitting, crevice attack, intergranular corrosion, or cracking, and AISI 316 owes its better resistance to molybdenum, which stabilizes the film and aids repassivation. Corrosion inhibitors, whether inorganic film-promoting species or organic adsorbates, can act by competing with chloride, reinforcing the film, and raising the repassivation potential, but their effectiveness is dosage-, medium-, and surface-dependent. Sustainable inhibitors derived from plant extracts and biopolymers offer an attractive alternative to toxic chemistries, although their performance in neutral chloride environments and their long-term reliability

remain insufficiently documented. A sound assessment of any inhibitor requires several complementary methods, including cyclic polarization, critical pitting temperature, impedance spectroscopy, and surface analysis, supported by thermodynamic and computational models that reflect the oxide-covered surface. Advancing the field will require integrated study of passive-film chemistry, electrochemical kinetics, interfacial adsorption, metallurgy, and service conditions, together with standardized testing and validation under realistic industrial conditions.

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