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Experimental Evaluation of Corrosion Inhibitors for Industrial Metal Protection

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ABSTRACT

Corrosion of industrial metals causes large economic losses, safety hazards and environmental damage, and chemical inhibitors remain one of the most practical means of controlling it in acid cleaning, oil and gas production, cooling water and process equipment. Reliable selection of an inhibitor, however, depends on rigorous experimental evaluation under conditions that reflect service. This article reviews the experimental framework used to assess corrosion inhibitors for metal protection. The principal inhibitor classes and their mechanisms are outlined, followed by specimen preparation and test media, gravimetric measurement, electrochemical polarization and impedance spectroscopy, and surface analysis of protective films. Adsorption isotherms and thermodynamic parameters are discussed as tools for interpreting the mode of interaction, and computational chemistry is presented as a complement to experiment. Finally, environmental considerations, green inhibitors and field validation are examined. The review concludes that no single technique is sufficient, and that agreement among independent methods is the best guarantee of a trustworthy performance claim.

Key words: *corrosion inhibitors, electrochemical impedance spectroscopy, adsorption isotherm, weight loss method, mild steel protection.*

Introduction:

Metals such as carbon steel, stainless steel, copper and aluminum alloys underpin pipelines, boilers, heat exchangers, storage tanks and process plants. When exposed to acids, chlorides, dissolved gases and microbial activity, they deteriorate through uniform attack, pitting, crevice corrosion and other forms of damage. Comprehensive studies have estimated the annual cost of corrosion at a few percent of gross national product in industrialized economies, a burden that includes direct replacement, maintenance, lost production and failures with environmental and human consequences (Koch et al., 2002).Inhibitors are substances that, when added in small concentrations to a corrosive environment, reduce the corrosion rate by interfering with anodic or cathodic reactions, by forming protective films or by modifying the metal surface. Their appeal lies in their flexibility: they can be applied in situ, adjusted to changing conditions and combined with coatings or cathodic protection. Their performance, however, is highly specific to the metal, the medium, the temperature and the flow regime, which makes systematic laboratory evaluation indispensable before any field application.This article describes how inhibitors are evaluated experimentally. It begins with fundamentals and classification, then

presents each major experimental approach, from simple mass loss measurements to advanced electrochemical and surface techniques, and finally discusses interpretation, modeling, sustainability and the translation of laboratory results to industrial practice.

Corrosion Fundamentals and Industrial Impact:

Corrosion is an electrochemical process in which metal oxidation at anodic sites is coupled to a reduction reaction at cathodic sites. In acidic solutions, the dominant cathodic reaction is hydrogen evolution, whereas in neutral and aerated media it is typically oxygen reduction. The rate at which the two half reactions proceed is limited by the kinetics of charge transfer, by the transport of reactants and by the properties of any film that develops on the surface. Thermodynamics indicates whether corrosion is possible, but kinetics determines how fast it occurs, and inhibitors act primarily on the kinetics.Industrial settings present diverse challenges. Acid pickling and descaling expose steel to strong hydrochloric and sulfuric acids, oil and gas systems contain carbon dioxide, hydrogen sulfide and brines, and cooling circuits suffer from dissolved oxygen, scaling and biofouling. Each environment demands inhibitors with different chemistry, solubility and stability, and each influences which evaluation methods are the most informative. Recognizing the dominant corrosion mechanism is thus the first step in designing a meaningful test program.

Classification and Mechanisms of Corrosion Inhibitors:

Inhibitors are commonly grouped according to their mode of action. Anodic inhibitors, such as chromates, nitrites and molybdates, promote passivation of the metal surface and must be used in sufficient concentration, since under-dosing can intensify localized attack. Cathodic inhibitors, including zinc salts and some phosphates, precipitate at cathodic sites and restrict the supply of oxygen or the hydrogen evolution reaction. Mixed inhibitors influence both processes, and organic molecules containing nitrogen, sulfur or oxygen atoms and aromatic rings are the most widely studied examples.Organic inhibitors function mainly by adsorption. Heteroatoms and pi electrons allow the molecule to share electrons with vacant orbitals of the metal, while charged functional groups interact with the surface through electrostatic forces. The resulting adsorbed layer blocks active sites and separates the metal from the aggressive medium (Sanyal, 1981). Volatile inhibitors protect enclosed spaces through vapor-phase transport, and film-forming amines and phosphonates are used in water treatment. Knowledge of the likely mechanism guides which experiments to select and how to interpret their outcome.

Materials, Test Media and Specimen Preparation:

The credibility of every later measurement depends on careful preparation of specimens and solutions. Metal coupons are cut from the same stock, with composition verified by spectrometry, and their surfaces are abraded with successively finer silicon carbide papers, degreased with a solvent, rinsed with distilled water and dried. Dimensions are measured accurately so that exposed area can be calculated, and the edges are sealed or mounted when electrochemical cells are used. Standard practices for preparing, cleaning and evaluating specimens ensure that results can be compared among laboratories (ASTM International, 2017).The test

medium should resemble service conditions as closely as possible. Acid solutions are prepared from analytical-grade reagents, while brines for oilfield studies are saturated with carbon dioxide or purged with oxygen-free gas. Temperature is controlled with thermostatic baths, and the volume of solution per unit surface area is kept sufficiently large to avoid depletion of inhibitor. Hydrodynamic conditions can be reproduced with rotating disc, rotating cylinder or flow loop devices, since shear stress strongly affects film stability. Replicate specimens, blank solutions without inhibitor and documentation of every variable are essential for reproducibility.

Weight Loss Gravimetric Measurements:

The weight loss method is the simplest and most direct way of determining corrosion rate. Pre-weighed coupons are immersed in the test solution for a defined period, withdrawn, cleaned of corrosion products by a prescribed procedure and weighed again. The mass difference is converted into a corrosion rate in units such as millimeters per year, and the inhibition efficiency is computed by comparing the rate with and without inhibitor. Because the technique integrates attack over long exposure times, it captures the net effect of film formation, breakdown and re-formation, including behavior that short electrochemical tests may miss.Gravimetric tests also allow convenient exploration of variables such as inhibitor concentration, immersion time and temperature. Their limitations are equally clear: they provide no direct information on mechanism, they assume uniform corrosion and they require careful cleaning to avoid removing sound metal. Localized attack such as pitting is not reflected in an average mass loss, so visual examination and profilometry should accompany the measurement. Despite these constraints, mass loss data remain the benchmark against which faster techniques are validated.

Electrochemical Techniques: Polarization and Impedance Spectroscopy:

Electrochemical methods provide rapid, sensitive and mechanistically informative measurements. In potentiodynamic polarization, the potential of the working electrode is scanned across a range around the open circuit value and the resulting current is recorded. Extrapolation of the linear regions of the anodic and cathodic branches to their intersection gives the corrosion current density, which is proportional to corrosion rate, and the shift of the corrosion potential and the change in branch slopes reveal whether an inhibitor acts anodically, cathodically or as a mixed inhibitor. Near the corrosion potential, the linear polarization resistance method relates the slope of the potential-current curve to the corrosion rate (Stern & Geary, 1957).Electrochemical impedance spectroscopy applies a small alternating signal over a wide frequency range and models the response with an equivalent circuit. Inhibition usually increases the charge transfer resistance and decreases the double-layer capacitance, because adsorbed molecules replace water at the surface and thicken the dielectric layer. Surface heterogeneity is accounted for by a constant phase element, whose parameters can be converted to effective capacitance (Hsu & Mansfeld, 2001; Macdonald, 2006). Since impedance is non-destructive, it allows continuous monitoring of film formation and degradation over time. Results must be interpreted with caution, since an equivalent circuit that fits the data is not necessarily physically unique.

Surface Characterization of Protective Films:

Electrochemical and gravimetric numbers tell how well a metal is protected, whereas surface analysis shows why. Scanning electron microscopy reveals the morphology of the corroded and inhibited surfaces, contrasting a roughened, pitted blank with a smooth protected one, and energy dispersive spectroscopy maps the elemental distribution of the film. Atomic force microscopy quantifies roughness at nanometer scale and can detect the thickness and uniformity of adsorbed layers.Chemical information is provided by X-ray photoelectron spectroscopy, which identifies the oxidation states of iron and the bonding of nitrogen, sulfur and oxygen in the film, and by Fourier transform infrared and Raman spectroscopy, which detect functional groups of adsorbed molecules and corrosion products. Contact angle measurements indicate whether the surface has become hydrophobic. Combining these methods demonstrates that the inhibitor is truly present on the surface and helps distinguish between a physically adsorbed layer, a chemically bonded monolayer and a precipitated protective deposit.

Adsorption Isotherms and Thermodynamic Analysis:

Most organic inhibitors protect by adsorption, and the relationship between inhibitor concentration and the fraction of surface covered provides insight into the interaction. Surface coverage is estimated from the inhibition efficiency, and the data are fitted to isotherm models, of which the Langmuir model is the most frequently applied. It assumes a fixed number of equivalent adsorption sites, one molecule per site and no interaction among adsorbed molecules (Langmuir, 1918). Other models, such as Temkin and Frumkin, introduce surface heterogeneity or lateral interactions and are used when the Langmuir assumptions fail. In practice, efficiency rises steeply at low dosage and then levels off as the surface approaches saturation, a pattern shown in the figure below.Beyond the knee of the curve, additional inhibitor adds little protection, so the optimal dosage is usually chosen near the onset of the plateau rather than at the highest concentration tested.The fitted adsorption equilibrium constant is converted into a standard free energy of adsorption, and the sign and magnitude of this value are used to classify the interaction. Values of modest magnitude are usually attributed to physical adsorption through electrostatic forces, while larger magnitudes are associated with chemical adsorption through electron sharing. Measurements at several temperatures yield enthalpy and entropy changes, and activation parameters obtained from the Arrhenius and transition-state equations indicate whether inhibition weakens with temperature, as expected for physisorption, or persists, as for chemisorption (Popova et al., 2003). Such conclusions should be treated as indications rather than proofs, since classification thresholds are approximate.

Computational Chemistry and Quantum Descriptors:

Computational methods increasingly accompany experiments and help explain the structure-activity relationships among inhibitors. Density functional theory calculations provide quantum chemical descriptors, such as the energies of the highest occupied and lowest unoccupied molecular orbitals, the energy gap, dipole moment, electronegativity, hardness and the fraction of electrons transferred between molecule and metal. Regions of high electron density identified through Fukui

functions or electrostatic potential maps indicate the atoms most likely to bind to the surface (Obot et al., 2015).Molecular dynamics and Monte Carlo simulations place inhibitor molecules on a model metal surface in the presence of solvent and estimate adsorption energies, orientation and film compactness. These approaches can screen candidate molecules before synthesis and rationalize experimental trends. Their predictions depend on the realism of the surface model, which often neglects oxide layers, defects and the complexity of the electrolyte, so they should be used to support, and not replace, experimental evidence.

Environmental Considerations, Green Inhibitors and Field Validation:

Many traditional inhibitors, including chromates and some organic compounds, are toxic, bioaccumulative or persistent, and regulations increasingly restrict their use. Research has therefore turned to green inhibitors derived from plant extracts, amino acids, biopolymers, expired drugs and ionic liquids, which offer low toxicity and biodegradability along with good protective ability (Raja & Sethuraman, 2008; Sastri, 2011). Plant extracts contain mixtures of phytochemicals, which complicates standardization and reproducibility, while ionic liquids combine tunable structure with strong adsorption but require assessment of their own environmental profile (Verma et al., 2017).Laboratory success does not guarantee field success. Candidate inhibitors should be examined under realistic temperature, pressure, flow and fluid composition, tested for compatibility with other additives, scaling and emulsification behavior, and evaluated for thermal stability. Pilot trials with corrosion coupons, electrical resistance probes and online monitoring on operating equipment provide the final verification. Economic considerations, such as dosage cost and logistics, together with environmental discharge limits, complete the basis for selection.

Summary:

Experimental evaluation of corrosion inhibitors is a multi-step process that links careful specimen preparation, realistic test media and complementary measurement techniques. Weight loss measurements provide a robust benchmark of long-term performance, electrochemical polarization and impedance spectroscopy reveal kinetics and mechanism, and surface analysis confirms the presence and nature of protective films. Adsorption isotherms and thermodynamic parameters connect inhibitor structure with interfacial behavior, while quantum chemical and molecular simulations help rationalize and predict efficiency. Growing environmental constraints are driving the development of green inhibitors, but their promise must be confirmed through standardized testing and field trials. Agreement among independent techniques and transparent reporting of conditions remain the foundation of reliable inhibitor selection for industrial metal protection.

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