

67 Evaluation and Selection of Corrosion Inhibitors

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A. INTRODUCTION

In principle, any method to determine the corrosion rate can be used to test a corrosion inhibitor. The primary criterion for evaluation is the inhibitor efficiency. Inhibitors having sufficiently high efficiency are tested for "side effects," which include environmental compatibility, emulsion formation, viscosity and pour point density. Finally, the inhibitor formulation is tested in the field. In general, the process of evaluation and selection of corrosion inhibitors involves three steps: (1) laboratory evaluation, (2) evaluation of compatibility (including cost), and (3) field evaluation.

B. LABORATORY METHODOLOGIES

The laboratory test methods should be carried out under conditions that simulate operational conditions in the field, including composition of material and environment, temperature, flow, pressure, and the method by which the inhibitor is added, continuous or batch. Screening of inhibitors in the laboratory requires two parts: methodology and measuring techniques. Methodology is defined as an experimental setup to generate corrosion, and measuring techniques are used to determine the corrosion rate and inhibitor efficiency.

The laboratory methodology should simulate the variables that influence inhibitor performance. These variables are classified into two categories: direct and indirect. The direct variables include composition (environment and metallurgy), temperature and pressure. If the direct variables of a system are known, then the laboratory experiments can be carried out under these conditions. On the other hand, simulation of indirect variables in a laboratory experiment is not straightforward. One common indirect variable is flow. To simulate flow effects in laboratory experiments, hydrodynamic parameters, including mass transfer coefficients, wall-shear stress, and Reynolds number, are used, as described in Chapters 14 and 15. The merit of a laboratory methodology is generally judged by the ability to control and determine these hydrodynamic parameters. Some of the laboratory methodologies to evaluate inhibitors are discussed in the following sections.

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1. Wheel Test

The wheel test is performed by adding the corrosive fluids and inhibitor to a $\sim 7\text{-oz}$ ($\sim 207\text{ cm}^3$) bottle with a metal coupon, purging with a corrosive gas, and capping the bottle [1]. The bottle is then agitated for a period of time by securing it to the circumference of a “wheel” and rotating it. In the high-temperature, high-pressure wheel test, autoclaves substitute for the conventional bottle and allow different partial pressures of corrosive gases, such as CO_2 and H_2S , to be used. The wheel test is best regarded as a screening test in a preliminary stage of inhibitor evaluation because it may discriminate poor inhibitors from good ones, but not necessarily the best inhibitor among several good ones [2]. There is no theoretical or hydrodynamic method to determine the flow patterns in a wheel test.

2. Bubble Test

The bubble test is also known as the stirred corrosion test or as the kettle test. It is a flexible laboratory procedure for monitoring corrosion rates and inhibitor performance. The test is performed in a 1-L glass beaker or conical flask. The glass lid of the vessel has access ports for the working, counter, and reference electrodes, thermometer, and gas inlet and outlet tubes (Fig. 1 [3]). In the bubble test, the composition and temperature of the field can be simulated. The only fluid movement is generated by the bubbles of the purging gas. No hydrodynamic equation exists to describe the flow conditions in bubble test.

3. Static Test

The static test is used to evaluate inhibitor performance in the absence of flow. The apparatus described for the bubble test can also be used for the static test. The corrosion rates can be measured by weight loss or by electrochemical methods.

4. Rotating Disk Electrode

The rotating disk system is simple and provides information quickly and inexpensively. For these reasons, the rotating disk electrode (RDE) is very popular in electrochemical studies [4–6]. A typical

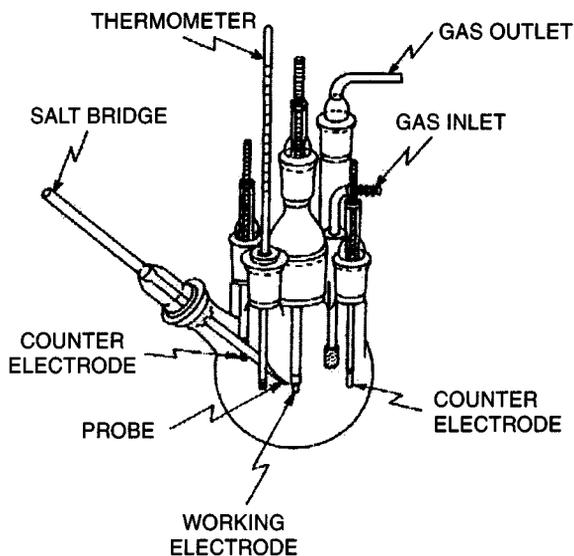


FIGURE 1. Apparatus for the bubble test [3]. Copyright ASTM. Reprinted with permission.

RDE apparatus consists of a rotating unit driven by a motor that is attached to a sample holder. Electrochemical connections to the electrodes are made using brush contacts. The corrosion rates are measured using conventional electrochemical instruments.

The RDE surface is uniformly accessible. It is one of the few convective systems for which the equations of fluid mechanics have been solved rigorously for steady-state conditions. The limiting current density, i_d , at the RDE is given by [7]

$$i_d = 0.62n\mathcal{F}CD^{2/3}\nu^{-1/6}\omega^{1/2} \quad (1)$$

where n is number of electrons; \mathcal{F} is the Faraday constant; C is concentration of reactant (or product); D is the diffusion coefficient of the reactant (or product); ν is the kinematic viscosity; and ω is the angular velocity.

Equation (1) can be applied only under conditions of laminar flow. At higher rotation speeds, the flow at the RDE changes from laminar to turbulent. Hydrodynamic relationships have been derived to correlate RDE and other systems, for example, pipe flow [5] [Eq. (2)]. The relation between the RDE under laminar conditions and under pipe conditions is

$$\text{Re}_p = 79(d/r_o)(e/d)^{-0.15}\text{Sc}^{-1/6}\text{Re}_D^{1/2} \quad (2)$$

where Re_D is the Reynolds number for the rotating disk; Re_p is the Reynolds number for pipe; d is the diameter of pipe; e is the roughness of the pipe wall; r_o is the radius of the rotating disk; Sc is the Schmidt number. Only a few experimental verifications of this equations have been performed, and, for this reason, RDE has not been widely used for inhibitor evaluation. Rotating electrode systems are now available for studies under flowing conditions at elevated temperature and pressure [8].

5. Rotating Cylinder Electrode

The rotating cylinder electrode (RCE) test system is compact, relatively inexpensive, and easily controlled [9]. It provides stable and reproducible flow in relatively small volumes of fluid. It operates in the turbulent regime over a wide range of Reynolds numbers. The design of the RCE has several features in common with the RDE including control of the rotation speed that is continuously variable at high and low speeds.

For RCE, the reaction rates may be mass transport controlled. Provided the ohmic polarization (IR drop) is constant in the cell, the current distribution over the electrode surface may be uniform, and concentration changes may be calculated even though the fluid flow is generally turbulent. Laminar flow is limited because, in the conventional arrangement the RCE, is enclosed within a concentric cell and $\text{Re}_{\text{crit}} \sim 200$, corresponding to rotation speeds of < 10 rpm. Notwithstanding the instability of turbulent motion, the RCE has found a wide variety of applications, especially when naturally turbulent industrial processes must be simulated on a smaller scale or when mass transport must be maximized.

Dimensionless group correlation for turbulent flow in RCE has been described [10–14]. When the wall shear stresses are equal in the RCE laboratory test and in the pipe in the fluid, then similar hydrodynamic conditions (e.g., turbulence) are maintained. Under these conditions, the corrosion mechanism (not the rate) is hypothesized to be the same in two geometries (e.g., RCE and pipe).

The wall shear stress of RCE, τ_{RCE} is given as [10–12]

$$\tau_{\text{RCE}} = 0.0791\text{Re}^{-0.3}\rho r^2\omega^2 \quad (3)$$

where Re is the Reynolds number; ρ is the density; ω is the angular velocity; and r is the radius of the cylinder.

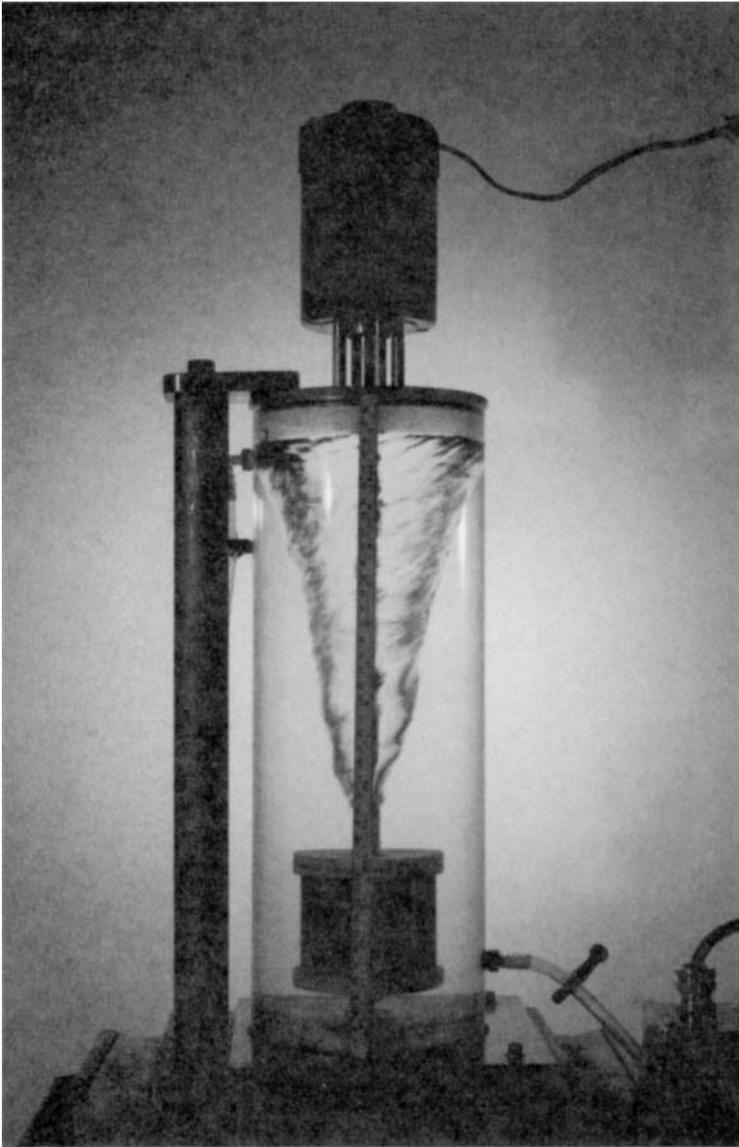


FIGURE 2. Photograph of rotating cage (note the vortex formation).

In the absence of other correlations, Eq. (3) can be used as a first approximation to establish the appropriate RCE velocity for modelling the desired system when trying to examine corrosion accelerated by single-phase flow.

6. Rotating Cage

The rotating cage (RC) has been reported in the literature as one of the promising laboratory methodologies to evaluate corrosion inhibitors [15–17]. Several results have been reported using this methodology, but methods to calculate the hydrodynamics of this system, to optimize apparatus dimensions, and to assess their effects on flow have not been clearly defined.

Figure 2 shows a rotating cage system. Several coupons (8 or 10) are supported between two Teflon disks mounted at a fixed distance apart on a stirring rod.

When the rod is rotated, a vortex is formed and the dimensions of the vortex (both length and width) increase with rotation speed until the width reaches the side walls of the container. The flow patterns in the rotating cage can be qualitatively divided into four zones that depend on the rotation speed and on the volume of the solution and of the container [18]:

1. Homogeneous zone: Vortex dimensions (length and width) increase with rotation speed.
2. Side wall affected zone: Vortex length increases, but the width has reached the side and collides with the wall.
3. Turbulent zone: Vortex length penetrates into the rotating cage unit and creates turbulent flow.
4. Top cover affected zone: The liquid level oscillates and rises to the top cover which restricts the development of the vortex.

The rotating cage illustrated in Figure 2 is in the homogeneous zone. As a first approximation, rotating cage wall shear stress can be calculated using Eq. (4)

$$\tau_{RC} = 0.0791 \text{Re}^{-0.3} \rho r^2 \omega^{2.3} \quad (4)$$

where r is the radius of the rotating cage.

7. Jet Impingement

The jet impingement (JI) test can simulate reliably and repeatedly high-turbulence conditions at high temperature and pressure for gas, liquid, and multiphase turbulent systems. It requires relatively small volumes of test fluids and is controlled easily. Jet impingement is a new methodology to evaluate corrosion inhibitors.

For a circular jet impinging on a flat plate with the central axis of the jet normal to the plate, a stagnation point exists at the intersection of this axis with the plate, and the flow is axisymmetric. Only the flow and fluid properties in the radial plane normal to the disk are considered (Fig. 3) [19–21].

Region A in Figure 3 is the stagnation zone. The flow is essentially laminar near the plate, and the principal velocity component is changing from axial to radial, with a stagnation point at the centre. Region A extends from the central axis to the point of maximum velocity and minimum jet thickness at $r/r_o = 2$.

Region B in Figure 3 is a region of rapidly increasing turbulence, with the flow developing into a wall jet (i.e., the primary flow vector is parallel to the solid surface). This region extends radially to $r/r_o = 4$. The flow pattern is characterized by high turbulence, a large velocity gradient at the wall, and high wall shear stress. Thus, Region B is of primary interest for studying fluid flow effects on corrosion in high-turbulence areas. This region has not been rigorously characterized mathematically, but results of some research indicate that wall shear stress is proportional to the velocity squared [11].

$$\tau_j = 0.179 \rho U_o \text{Re}^{-0.182} (r/r_o)^{-2.0} \quad (5)$$

$$\text{Re} = 2r_o U_o / \nu \quad (6)$$

where τ_j is the wall shear stress of the jet; ρ is the density of the fluid, U_o is the flow rate; Re is the Reynolds number; r is the jet radius; r_o is the radial distance; and ν is the kinematic viscosity.

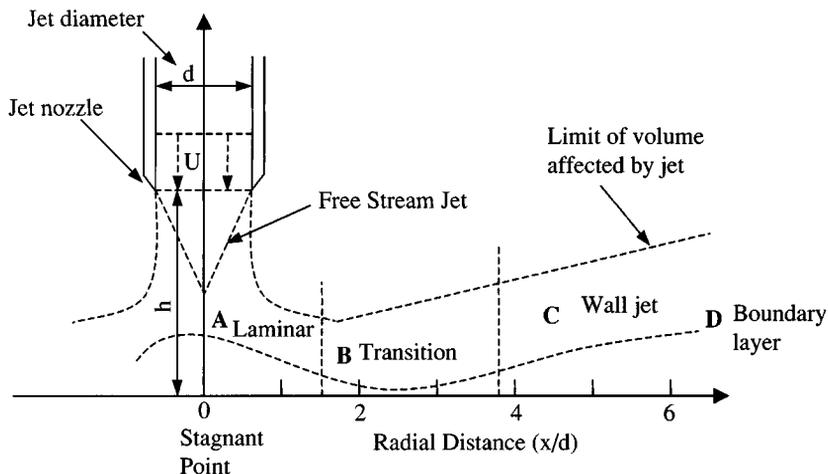


FIGURE 3. Schematic representation of fluid flow characteristics of jet impingement. Adapted from [11].

In Region C in Figure 3, the bulk flow rate and turbulence decay rapidly as the thickness of the wall jet increases, momentum is transferred away from the plate, and the surrounding fluid is entrained in the jet. This region is amenable to mathematical characterization, but the flow cannot be related to other flow conditions (e.g., pipe flow), because momentum transfer and fluid entrainment are in the opposite direction from pipe flow.

8. Humidity Chambers

Inhibitors to prevent corrosion in the vapor phase (vapor-phase inhibitors, VPI) are tested in humidity chambers in which wet-dry cycles are carried out and parameters such as temperature and relative humidity are measured. Various accelerated procedures have been developed to simulate different conditions (e.g., tropical, marine, and industrial [22–25]). Observations are made after a predetermined time or number of cycles (for wet-dry tests). Corrosion of ferrous metals is assessed in terms of the percentage of the surface area covered by rust, whereas corrosion of non-ferrous metals is assessed from changes in the state of the surface, as reflected by color changes.

C. MEASURING TECHNIQUES

The measuring techniques used to determine corrosion rates can be broadly classified into two categories: nondestructive and destructive. A measuring technique is destructive if it alters the corrosion process during the measuring process (e.g., potentiodynamic polarization) or if the material is physically removed from the environment (e.g., weight loss measurements). Non-destructive techniques, including linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS), and electrochemical noise, can be used to make repeated measurements at different time intervals.

1. Weight Loss

Determination of weight loss of the coupons in a corrosion experiment is one of the common methods to calculate corrosion rates. The coupons are cleaned and weighed before and after the experiments to remove the surface and/or corrosion products. Corrosion rates in wheel tests and in rotating cage experiments can be determined only by weight loss methods. This method can, in

principle, be used in all laboratory methodologies, and for monitoring corrosion rates in the field using coupons.

From the weight loss measurements, the corrosion rates are calculated using Eq. (7).

$$\text{Corrosion rate (mm/year)} = (w \times 10^4/a)(0.365/\rho) \quad (7)$$

where w is weight loss (gm); a is the surface area (cm²); and ρ is the density (g/cm³).

The inhibitor efficiency is usually given as percentage inhibition (% P). Percentage inhibition can be calculated as

$$\%P = \frac{X_o - X_i}{X_o} \times 100 \quad (8)$$

where X_o and X_i are weight loss (or corrosion rate or corrosion current) in the absence and presence of inhibitor, respectively.

2. Electrochemical Methods

Linear polarization resistance, EIS, electrochemical noise (all nondestructive), and potentiodynamic polarization (destructive) are all used in measurements to assess inhibitors. These methods are discussed in detail in Chapters 68 and 69.

3. Solution Analysis

In this method, determinations are made of changes with time in the content of metal ions measured in the process liquid resulting from the corrosion process; inhibition will be reflected in the analytical data. The method is clearly of most use when the corrosion products are soluble, and is of less value when the corrosion, or inhibition, process leads to the formation of insoluble products.

A recent variation of this method is the technique of thin film activation analysis. In this technique, metal components or special test coupons are irradiated to produce a thin layer of radioactive isotopes on the metal surface. The extent of inhibition can then be determined from changes in the radioactivity of the medium or the specimen [26].

D. EVALUATION OF COMPATIBILITY

1. Cost

A philosophy for using corrosion inhibitors is to define the benefits in terms of reduced costs of operation, shutdown, inspection, reliability, and maintenance, by using a cheaper material with inhibitor versus using a costly corrosion resistant material without inhibitor. Economic considerations and factors such as plant life dictate the material chosen and the corrosion prevention strategies used. Various methods (e.g., discounted cash flow discussed in Chapter 2), can be used to determine the benefits of using corrosion inhibitors.

2. Environmental Issues

There has been increasing concern about the toxicity, biodegradability, and bioaccumulation of inhibitors discharged into the environment. Standardized environmental testing protocols are being developed [27–29].

3. Quality Control

Spectroscopic techniques, including carbon-13 nuclear magnetic resonance (¹³C NMR) and Fourier transform–infrared spectroscopy (FT–IR), are used as quality control methods to ascertain whether

the correct inhibitor ingredients are blended into the product and whether the ingredients are added in the correct proportions [30].

4. Emulsion Formation

The effect that an inhibitor has on the emulsion forming tendency of well fluids is critical in the selection of the proper inhibitor. Test methods available to determine emulsion formation include the Setzer bottle test and the high pressure cell test [31].

E. FIELD EVALUATION

Corrosion inhibitor monitoring in a field may be needed at several points to ensure that the inhibitor has reached all locations, has formed films and/or adsorbed, is persisting and, more importantly, has reduced the corrosion rates. Techniques for the field should satisfy the following requirements: high-resolution/short response time; high reliability; no regular maintenance or long maintenance intervals (years); and simple signal collection, processing and transmission. Techniques for field monitoring are discussed in the following sections.

1. Weight Loss Coupons

Corrosion monitoring using weight loss coupons is one of the common practices in many industries. Preweighed coupons are exposed for a fixed duration and then retrieved. Equipment is now available to place and remove coupons without shutting down the plant or reducing pressure, temperature or flow. However, coupon measurements are used to calculate only time-averaged values of corrosion rate and may not adequately represent corrosion rates throughout the entire system.

2. LPR Probes

The presence of a conducting solution (e.g., NaCl solution) is necessary for LPR probes. In systems where there is no water or the probe is not exposed to water, LPR probes do not give meaningful results.

3. Mass Counts

Historical metal count data are useful for determining corrosion trends. The method of collecting metal count data is difficult to apply as a tool for controlling the day-to-day dosage of inhibitors.

4. Pipeline Integrity Gauge (PIG)

Internal inspection of pipelines with intelligent (containing sensors) pigs defines the corrosion status of the pipeline for scheduling the inhibitor treatment frequency. This method is relatively expensive and, for this reason, cannot be used frequently [32].

5. Field Signature Method (FSM)

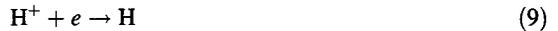
FSM technology is a relatively new, nonintrusive electrical resistance method for measuring wall thickness on a semicontinuous basis [33]. In this method, a large number of electrical resistances measured on a short section of the equipment are used to generate a map of the monitored area in terms of the changes in wall thickness over time as compared to the original readings. Even though this technique does not directly measure inhibitor efficiency, it can be used to monitor corrosion, erosion, and cracking.

6. Visual Inspection

Visual inspection by permanently installed video cameras is now a possibility. A very small color video camera for borehole inspection that can operate at temperatures up to 150°C and at pressures up to 10,000 psi (69 MPa) is available. For certain critical equipment, for example, subsea oil production equipment, and at critical locations such an internal visual monitoring system can be valuable.

7. Hydrogen Permeation

One of the common cathodic reactions during corrosion in acid solution is hydrogen reduction:



The atomic hydrogen that can form, for example, inside a pipeline carrying wet sour gas can diffuse and recombine on the outside to form molecular hydrogen. Monitoring of this hydrogen gas on the outside surface can provide an indirect measurement of the corrosion inside the equipment [34]. This principle is used in assessing corrosion and inhibitor efficiency using externally mounted hydrogen foils. Two different types of hydrogen monitoring probes are used: electrochemical and vacuum probes [35–38].

8. Electrochemical Techniques

Electrochemical techniques are reviewed in Chapters 68 and 69.

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