Standard Guide for
Evaluating and Qualifying Oilfield and Refinery Corrosion Inhibitors in the Laboratory[1]

1. Scope

1.1 This guide covers some generally accepted laboratory methodologies that are used for evaluating corrosion inhibitors for oilfield and refinery applications in well defined flow conditions.

1.2 This guide does not cover detailed calculations and methods, but rather covers a range of approaches which have found application in inhibitor evaluation.

1.3 Only those methodologies that have found wide acceptance in inhibitor evaluation are considered in this guide.

1.4 This guide is intended to assist in the selection of methodologies that can be used for evaluating corrosion inhibitors.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory requirements prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1141 Practice for the Preparation of Substitute Ocean Water

D4410 Terminology for Fluvial Sediment

G1 Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens

G3 Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing

G5 Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements

G15 Terminology Relating to Corrosion and Corrosion Testing (Withdrawn 2010)[3]

G16 Guide for Applying Statistics to Analysis of Corrosion Data

G31 Guide for Laboratory Immersion Corrosion Testing of Metals

G46 Guide for Examination and Evaluation of Pitting Corrosion

G59 Test Method for Conducting Potentiodynamic Polarization Resistance Measurements

G96 Guide for Online Monitoring of Corrosion in Plant Equipment (Electrical and Electrochemical Methods)

G102 Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements

G106 Practice for Verification of Algorithm and Equipment for Electrochemical Impedance Measurements

G111 Guide for Corrosion Tests in High Temperature or High Pressure Environment, or Both

2.2 *NACE Standards:*[4]

NACE-5A195 State-of-the-Art Report on Controlled-Flow Laboratory Corrosion Test, Houston, TX, NACE International Publication, Item No. 24187, December 1995

NACE-ID196 Laboratory Test Methods for Evaluating Oil-Field Corrosion Inhibitors, Houston, TX, NACE International Publication, Item No. 24192, December 1996

NACE-TM0196 Standard Test Method "Chemical Resistance of Polymeric Materials by Periodic Evaluation," Houston, TX, NACE International Publication, Item No. 21226, 1996

2.3 *ISO Standards:*[5]

ISO 696 Surface Active Agents — Measurements of Foaming Power Modified Ross-Miles Method

ISO 6614 Petroleum Products — Determination of Water Separability of Petroleum Oils and Synthetic Fluids

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *atmospheric pressure experiment*—an experiment conducted at the ambient atmospheric pressure (typically less than 0.07 MPa (10 psig)), using normal laboratory glassware.

3.1.2 *batch inhibitor*—an inhibitor that forms a film on the metal surface that persists to effect inhibition.

3.1.3 *batch treatment*—a method of applying a batch inhibitor. Batch inhibitors are applied as a plug between pigs or as slugs of chemical poured down the well bore. The batch inhibitor is dissolved or dispersed in a medium, usually hydrocarbon and the inhibited solution is allowed to be in contact with the surface that is to be protected for a fixed amount of time. During this period, the inhibitor film is formed on the surface and protects the surface during the passage of multiphase flow, for example, oil/water/gas.

3.1.4 *continuous inhibitor*—an inhibitor that is continuously injected into the system in order to effect inhibition. Since the surface receives full exposure to the inhibitor, the film repair is continuous.

3.1.5 *emulsification-tendency*—a property of an inhibitor that causes the water and hydrocarbon mixture to form an emulsion. The emulsion formed can be quite difficult to remove and this will lead to separation difficulties in the production facilities.

3.1.6 *film persistency*—ability of inhibitor film (usually batch inhibitor) to withstand the forces (for example, flow) that tend to destroy the film over time.

3.1.7 *flow loop*—an experimental pipe that contains various corrosion probes to monitor corrosion rates. A flow loop can be constructed in the laboratory or attached to an operating system.

3.1.8 *foaming tendency*—tendency of inhibitor in solution (water or hydrocarbon) to create and stabilize foam when gas is purged through the solution.

3.1.9 *gas to oil ratio (GOR)*—ratio of the amount of gas and oil transported through a pipe over a given time.

3.1.10 *high-pressure*—a pressure above ambient atmospheric pressure that cannot be contained in normal laboratory glassware. Typically, this is greater than 0.07 MPa (10 psig).

3.1.11 *high-temperature*—temperatures above ambient laboratory temperature where sustained heating of the environment is required.

3.1.12 *laboratory methodology*—a small laboratory experimental set up, that is used to generate the corrosion. Examples of laboratory methodologies include rotating cylinder electrode (RCE), rotating cage (RC), and jet impingement (JI) under flowing conditions.

3.1.13 *live water*—aqueous solution obtained from a pipeline or well. Usually live water is protected from atmospheric oxygen.

3.1.14 *mass transfer coefficient (k, m/s)*—the rate at which the reactants (or products) are transferred to the surface (or removed from the surface).

3.1.15 *measuring technique*—technique for determining the rate of corrosion and the inhibitor efficiency. Examples of measuring techniques are mass loss, linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS), electrical resistance (ER), and potentiodynamic polarization (PP) methods.

3.1.16 *multiphase flow*—simultaneous passage or transport of more than one phase, where the phases have different states (gas, liquid, and solid) or the same state (liquid), but different fluid characteristics (viscosity, density, and specific gravity).

3.1.17 *synthetic water*—a synthetic solution prepared in the laboratory using various chemicals. The composition is based on the composition of fluid found in an oil production system.

3.1.18 *Schmidt Number (Sc)*—a measure of the ratio of the hydrodynamic boundary layer to the diffusion boundary layer. This dimensionless parameter is equal to kinematic viscosity divided by diffusion coefficient.

3.1.19 *wall shear stress (τ, N/m^2)*—a force per unit area on the pipe due to fluid friction.

3.2 The terminology used herein, if not specifically defined otherwise, shall be in accordance with Terminology D4410 or G15. Definitions provided herein and not given in Terminology D4410 or G15 are limited only to this guide.

4. Summary of Guide

4.1 Inhibitor evaluation in the laboratory consists of two steps (*1*) evaluation of inhibitor efficiency and (*2*) evaluation of secondary inhibitor properties.

4.2 Four laboratory methodologies, flow loop, rotating cylinder electrode (RCE), rotating cage (RC), and jet impingement (JI) are available to evaluate the inhibitor efficiency in the laboratory. All four methodologies can be operated at atmospheric and high pressure conditions. The corrosion rates can be measured using mass loss or electrochemical methods. Using the methodologies, several variables, compositions of material, composition of environment (gas and liquid), temperature, pressure, and flow, that influence the corrosion rate in the field can be simulated in the laboratory. Rotating cylinder electrode (RCE), rotating cage (RC), and jet impingement (JI) methodologies are compact, inexpensive, hydrodynamically characterized, and scalable; that is, can be carried out at various flow conditions.

4.3 Several secondary properties of the inhibitor are evaluated before the inhibitor is applied in the field. They are water/oil partitioning, solubility, emulsification tendency, foam tendency, thermal stability, toxicity, and compatibility with other additives/materials. Laboratory methods to evaluate the secondary properties are described.

5. Significance and Use

5.1 Corrosion inhibitors continue to play a key role in controlling internal corrosion associated with oil and gas production and transportation. This results primarily from the industry's extensive use of carbon and low alloy steels, which, for many applications, are economic materials of construction that generally exhibit poor corrosion resistance. As a consequence, there is a strong reliance on inhibitor deployment

for achieving cost-effective corrosion control, especially for treating long flowlines and main export pipelines (**1**).[6]

5.2 For multiphase flow, the aqueous-oil-gas interphases can take any of an infinite number of possible forms. These forms are delineated into certain classes of interfacial distribution called flow regimes. The flow regimes depend on the inclination of the pipe (that is, vertical or horizontal), flow rate (based on production rate), and flow direction (that is, upward or downward). The common flow regimes in vertical upward flow, vertical downward flow, and horizontal flow are presented in Figs. 1-3 respectively (**2**, **3**).

5.3 Depending on the flow regime, the pipe may undergo various forms of corrosion, including general, localized, flow-induced, and erosion-corrosion. One of the predominant failure mechanisms of multiphase systems is pitting corrosion.

5.4 The performance of a corrosion inhibitor is influenced primarily by the nature of inhibitor, operating conditions of a system, and the method by which it is added. Two types of inhibitors are used in the oil field, continuous and batch. Water-soluble and oil-soluble, water-dispersible inhibitors are added continuously. Oil-soluble inhibitors are, in general, batch treated. The test methods to evaluate the inhibitors for a particular field should be carried so that the operating conditions of the system are simulated. Thus during the evaluation of a corrosion inhibitor, an important first step is to identify the field conditions under which the inhibitor is intended to be

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[6] The boldface numbers in parentheses refer to the list of references at the end of this standard.
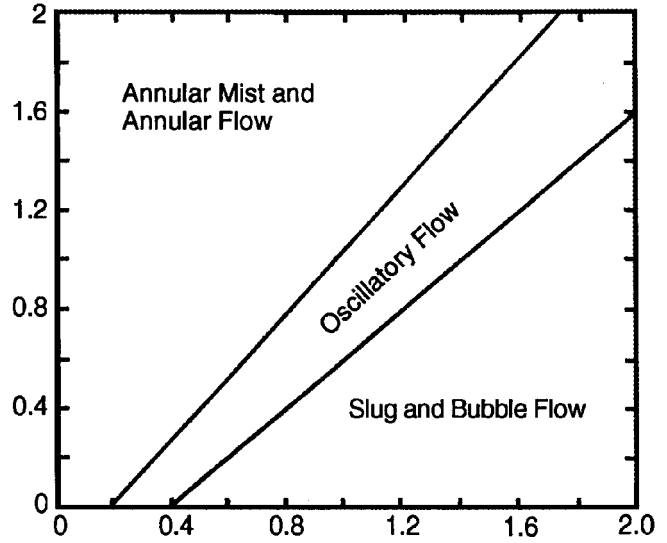

FIG. 2 Flow Regimes for Vertical Downward Flow (**2**)

used. The environmental conditions in the field locations will dictate the laboratory conditions under which testing is carried out.

5.5 Various parameters that influence corrosion rates, and hence, inhibitor performance in a given system are (*1*) composition of material (*2*) composition of gas and liquid (*3*) temperature (*4*) flow and (*5*) pressure.

5.5.1 In order for a test method to be relevant to a particular system, it should be possible to control the combined effects of
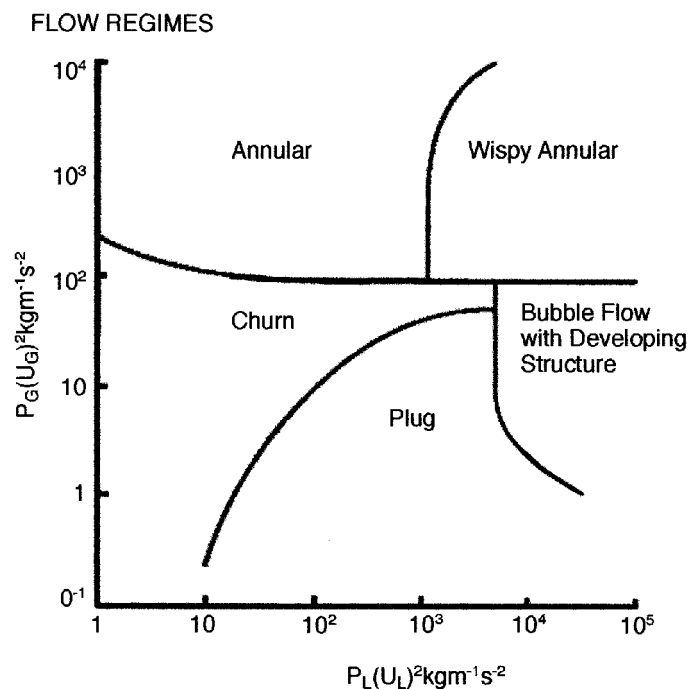
FLOW REGIMES

NOTE 1—ρ_G and ρ_L are gas and liquid densities and U_L and U_G are superficial velocities or the volume of flow rates of the liquid and gas per unit cross-sectional area of the channel (**2**).

FIG. 1 Flow Regimes for Vertical Upward Multiphase Flow
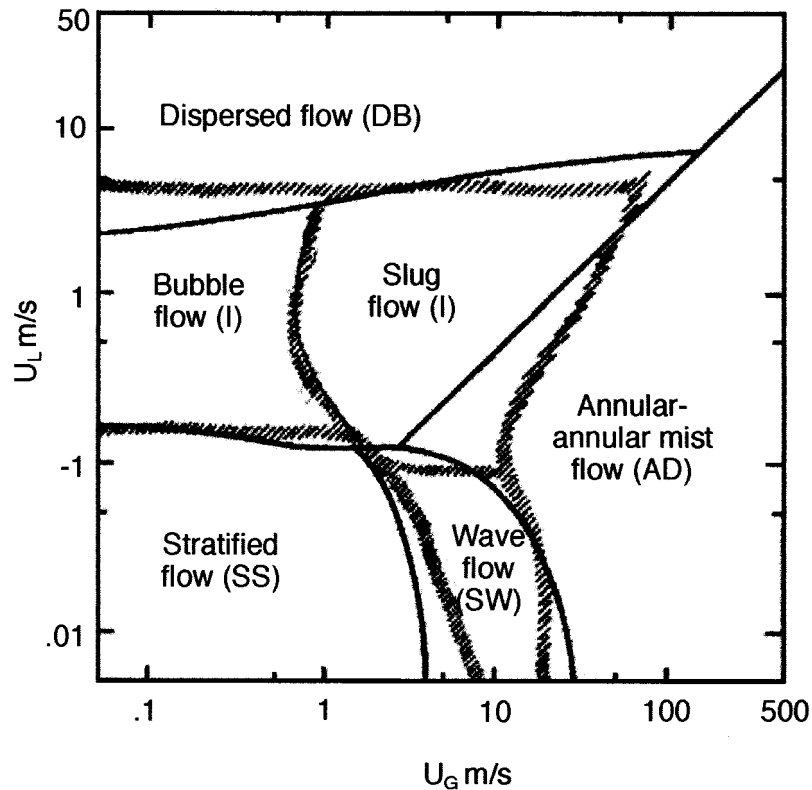
NOTE 1—Boundary conditions given by two studies are presented.(2)
FIG. 3 Flow Regimes for Horizontal Flow

various parameters that influence corrosion in that system. A test method is considered to be predictive if it can generate information regarding type of corrosion, general and localized corrosion rates, nature of inhibition, and life of inhibitor film (or adsorbed layer). Rather than try to perfectly reproduce all the field conditions, a more practical approach is to identify the critical factors that determine/impact inhibitor performance and then design experiments in a way which best evaluates these factors.

5.6 Composition of material, composition of gas and liquid (oil and water), temperature, and pressure are direct variables. Simulation of them in the laboratory is direct. Laboratory experiments are carried out at the temperature of the field using coupons or electrodes made out of the field material (for example, carbon steel). The effect of pressure is simulated by using a gas mixture with a composition similar to the field for atmospheric experiments and by using partial pressures similar to those in the field for high pressure experiments.

5.7 In multiphase systems there are three phases, oil, aqueous (brine water), and gas. Corrosion occurs at places where the aqueous phase contacts the material (for example, steel). The corrosivity of the aqueous phase is influenced by the composition and the concentration of dissolved gases (for example, H_2S and CO_2). In evaluating corrosion inhibitors in the laboratory, aqueous phase is usually used with a positive pressure of gas mixture to simulate the gaseous phase. The oil may have a major effect on the corrosion rate and inhibitor efficiency. The presence of oil phase in the test environment

can have significantly different effects (4). The primary effect of the oil phase is apparently on the protectiveness of the corrosion inhibitor. The oil phase may have the following effects: (1) partitioning of inhibitor between phases (2) changing the contact time of the aqueous phase on the pipe (3) changing the wetting behaviour of the pipe surface (4) introducing protective compounds that are naturally occurring in the oil.

5.7.1 Inhibitor evaluation in the absence of the oil phase cannot give an accurate picture of the behaviour of steel in multiphase environments. Ideally, the oil phase should be present when testing the inhibitor in the laboratory.

5.8 Flow is an indirect variable, and simulation of flow in the laboratory is not direct. For this reason, the hydrodynamic flow parameters are determined, and then the laboratory corrosion tests are conducted under the calculated hydrodynamic parameters. The fundamental assumption in this approach is that, when the hydrodynamic parameters of different geometries are the same, then the corrosion mechanism will be the same. Under these conditions, the corrosion rate and the efficiency of corrosion inhibition in the laboratory and in the field are similar. The commonly used hydrodynamic parameters are wall shear stress, Reynolds number, and mass transfer coefficient (3, 5).

5.9 Neither the flow rate (m/s) nor dimensionless parameters can be directly related to the local hydrodynamic forces at the material surface that may be responsible for accelerated localized attack. Local hydrodynamic forces are influenced by

several factors including pipe inclination, position (that is, 3, 6, 9 o'clock), presence of bends, deposits, edges, welds, expansion, and contraction. The flow rate and dimensionless parameters describe only bulk, or average, properties of the dynamic system. Thus the wall shear stress and mass transfer coefficient can be calculated only as averages at the surface with an average surface roughness.

5.10 Inhibitors are first screened in the laboratory, then evaluated in the field, and finally used in engineering operations. The laboratory methodologies, therefore, should be carried out in a compact system with the capacity to evaluate various products quickly with the flow pattern and regime characterized. The results obtained should be relevant to field operation, should be predictive of field performance in terms of inhibitor efficiency, and should be scalable, that is, the experiments can be carried out at various hydrodynamic conditions.

5.11 Flow loops are used to evaluate corrosion inhibitors either in the laboratory or by attaching to a live pipe. The loop simulates the flow regime, but the apparatus is relatively sophisticated, and experiments are expensive and time consuming. The loop is considered sophisticated to be an ideal laboratory methodology under the scope of this guide.

5.12 This guide discusses test facilities and considers the necessary elements which need to be built into a laboratory strategy for testing corrosion inhibitors for multiphase systems. The emphasis is on those methodologies that are compact and scalable, hydrodynamically well characterized, and relatively inexpensive to use. The laboratory methodologies are (1) rotating cylinder electrode (RCE) (2) rotating cage (RC) and (3) jet impingement (JI). These methodologies can be used under both atmospheric and high pressure conditions. Detailed description of RCE and JI are presented in NACE-5A195.

5.13 Laboratory tests for inhibitor evaluation consist of two main components–laboratory methodology and measurement technique. The combinations of laboratory methodology and measurement technique for inhibitor evaluation for multiphase systems are presented in Table 1.

5.14 To develop an inhibitor selection strategy, in addition to inhibitor efficiency, several other key performance factors need to be evaluated: (1) water/oil partitioning, (2) solubility, (3) emulsification tendency, (4) foaming tendency, (5) thermal stability, (6) toxicity, and (7) compatibility with other additives/materials.

6. Preparation of Test Solutions

6.1 Ideally, all solutions (oil and aqueous) should be obtained from the field for which the inhibitor is being evaluated. It is important that live fluids do not already contain corrosion inhibitor. In the absence of live fluids, synthetic solutions should be used, the composition of which, however, should be based on field water analysis. Alternatively, standard brine (in accordance with Practice D1141) should be employed. The solutions should be prepared following good laboratory practice. Their composition should be specified in the work plan and recorded in the laboratory logbook. Test solutions should be prepared using analytical grade reagents and deionized water, unless otherwise specified. If other grades of chemicals are used, their purity or grade should be recorded in the laboratory logbook.

6.2 The solutions should be deaerated by passing nitrogen (or any other inert gas) or carbon dioxide and kept under deaerated conditions. The solution pH before and after testing should be measured and recorded. If possible, the solution pH should be monitored continuously during the test. Solutions should be transferred from the preconditioning vessel to the test vessel under positive nitrogen pressure to minimize air contamination during the transfer operation.

6.3 The appropriate composition of gas can be obtained by mixing H_2S and CO_2 streams from the standard laboratory gas supply. Nitrogen can be used as a diluent to obtain the required partial pressures of the corrosive gases. Alternatively, gas mixtures of the required compositions can be purchased from suppliers of industrial gases. The concentrations of impurities, particularly oxygen, should be kept as low as technically possible (below 5 ppb, preferably under 1 ppb oxygen in solution). The solution oxygen concentration depends on the quality of gases used to purge the electrolyte.

6.4 Measure Inhibitor concentrations and report in % weight/volume or ppm w/v (percentage or parts per million, weight in volume basis). The method of injecting the inhibitor into the test solution should reflect the actual field application that is being tested. Water-soluble inhibitors may be injected neat (as-received) into the test solution (aqueous phase). To avoid the errors associated with handling small volumes of solution, an inhibitor stock solution may be prepared by diluting the as-received chemical in an appropriate solvent. The type of solvent and the concentration of the stock solution will depend on the characteristics of the inhibitor and on the specified test conditions.

6.5 Oil-soluble, water-dispersible inhibitor solutions are prepared by the partition method. Place the required amounts of crude oil, or condensate, and brine in the partitioning vessel (usually a separation funnel). The relative volumes of hydrocarbon and aqueous phases reflect the water cut to be tested. If actual field condensate is not available, heptane, kerosene, or any suitable hydrocarbon can be used as a substitute for the oil phase. Add the corrosion inhibitor to the oil phase. Vigorously

TABLE 1 Laboratory Methodologies and Measurement Techniques for Corrosion Inhibitor Evaluation

Laboratory Methodology	Measurement Technique	Aqueous/Oil/ Gas Phase	Remarks
RCE	mass loss, electrochemical	aqueous phase	specimen is a cylinder
RCE	mass loss	aqueous/oil phase	specimen is a cylinder
JI	mass loss, electrochemical	aqueous phase	specimen is a disc
JI	mass loss	aqueous/oil phase	specimen is a disc
JI	electrochemical measurements	aqueous phase	specimen is a ring
RC	mass loss	aqueous phase or aqueous/oil phase	electrochemical measurements cannot be carried out

shake the vessel to mix both phases thoroughly and allow the phases to separate. Heating to the minimum expected field temperature may help in the separation and will also provide more meaningful results; remove the aqueous phase and use as the test solution.

6.6 Oil-soluble inhibitors (usually as batch inhibitors) are applied in a separate procedure and the corrosion test is carried out after this. The inhibitor is dissolved in the oil phase to form an inhibited oil-phase. The corrosion coupon or electrode is exposed to this solution for a certain amount of time (usually 30 min). The coupon or electrode is then removed and introduced into the experimental vessel for the corrosion test.

6.7 Depending on the size of experimental vessel, heating unit (mantle, bath, or wrapper around the vessel), difference between room and experimental temperatures, a range of temperature may prevail within the vessel. Exercise precaution to avoid or minimize the temperature differentials. The test vessels should be heated slowly to avoid overheating and, in the case of glass autoclaves, to prevent high thermal stresses between the inner and outer walls. The exact protocol followed will depend on the controller, the size and output of the heater, and parameters such as vessel size, amount of liquid, thermal conductivity of liquid, and agitation. The pressure in the vessel should be monitored during heating to make sure it does not exceed the relief pressure. If necessary, some of the gas in the vessel may be bled off to reduce the pressure. The test temperature should be maintained within 2°C of the specified temperature. Once the test temperature is reached, the test pressure should be adjusted to the predetermined value. The pressure should be maintained within ±10 % of the specified value for the duration of the test.

6.8 For high-temperature, high-pressure experiments, using a pre-mixed gas composition, pressurize the autoclave using the specified gas composition, and depressurize to approximately 0.2 bar above atmospheric pressure. Repeat this cycle of pressurizing/depressurizing at least twice to ensure that the gas cap has the required composition. Finally, pressurize the autoclave to the test pressure.

6.9 For high-temperature, high-pressure experiments (**6**) using individual gases, first pressurize the autoclave with H_2S to the required partial pressure. Leave it for 10 min. If there is a decrease of pressure, repressurize the autoclave again. Repeat the process until no further pressure drop occurs. Then, pressurize the autoclave with CO_2, by opening the CO_2 gas cylinder at a pressure equal to the $CO_2 + H_2S$ partial pressure. Leave it for 10 min. If there is a decrease of pressure, repressurize the autoclave again with CO_2 gas. Repeat the process until no further pressure drop is observed. Finally, pressurize the autoclave with the inert gas, by opening the inert gas cylinder at the total gas pressure at which the experiments are intended to be carried out.

7. Materials

7.1 Methods for preparing specimens for tests and for removing specimens after the test are described in Practice **G1**. Standard laboratory glassware should be used for weighing and measuring reagent volumes.

7.2 The specimen should be made of the material (for example, carbon steel) for which the inhibitor is being evaluated. Corrosion rates and inhibitor performance change by several orders of magnitude as surface roughness changes from rough to fine. The surface roughness should be kept the same during inhibitor screening and, if possible, the surface roughness of specimens used in the laboratory experiments should be related to that of field pipe. The specimens should be ground to a specified surface finish. The grinding should produce a reproducible surface finish, with no rust deposits, pits, or deep scratches. All sharp edges on the specimen should be ground. All loose dirt particles should be wiped off using tissue paper.

7.3 Rinse the specimens with distilled water and then degrease the specimens by immersing in acetone (or methanol) and ultrasonically cleaning for 1 min; dry the specimens with a paper towel. Do not touch the surface of the specimens with bare hands; and weigh the specimens to the nearest 0.1 mg. Measure the dimensions of the specimens to the nearest 1 mm, and calculate the area of each specimen.

7.4 In general, specimens are held in an insulating specimen holder; the type of holder varies with the test. Install the freshly prepared specimens in the synthetic materials holder and tighten them. Place the specimen holder in the vessel, and close the lid. Fill the vessel with the preconditioned (deaerated) test solution and continue deaerating for at least 1 h using nitrogen.

8. Laboratory Methods for Evaluating Inhibitor Efficiency

8.1 *Rotating Cylinder Electrode (RCE):*

8.1.1 The RCE test system is compact, relatively inexpensive, and easily controlled (**7**). It operates in the turbulent regime over a wide range of Reynolds numbers. The apparatus operates under known and controlled hydrodynamic conditions. The experiments require small amounts of fluid, and mass loss and electrochemical measurements can be made. General procedures for specimen preparation, methods of cleaning, corrosion rate measurements and evaluation of results are described in detail in Guide **G16**, Practices **G31**, **G102**, and **G106**, Test Method **G59**, and NACE-1D196.

8.1.2 At very low electrode rotation speeds, the flow around the RCE is laminar and occurs in concentric circles around the cylinder. At higher rotation speeds this simple flow pattern becomes unstable. Cellular motion is imposed on the flow producing toroidal Taylor vortices containing a radial component of velocity, but the bulk of the flow remains essentially laminar. As rotational speeds increase further, the flow becomes fully turbulent and eddies increasingly break up the regular flow pattern. The transition to fully turbulent flow occurs at about Re 200. In the turbulent flow region, the RCE can be applied to simulate flow behavior by hydrodynamic analysis.

8.1.3 A typical RCE apparatus consists of a rotating unit driven by a motor that is attached to a sample holder. A system with a range of rotational speeds from 100 to 10 000 rpm with an accuracy of ±2 rpm is typical. It is essential to be able to rotate the electrode at both low and high speeds and to be able to measure the speed and maintain it constant. At the side of the sample holder, electrical connections to the electrodes are

made by a brush or mercury contact. The cylinder geometry is usually defined in terms of the length-to-diameter ratio. Both low and high ratios are used, with ratios varying between 0.3 and 3.0. The corrosion rates are measured using conventional electrochemical instruments. Detailed procedures are described in Practices G3, G102, and G106, Reference Test Method G5, Test Method G59, and Guide G96. The rotating cylinder can also be used as a mass loss coupon when the mass loss is sufficiently large to be accurately measured using a conventional balance (with accuracy 0.1 mg).

8.1.4 In many designs, two electrodes, inner (rotating) and outer (stationary) electrodes are used. The outer electrode is usually the counter electrode. Below the mass-transfer-limited conditions, the current distribution is uniform if the electrode and the electrical isolation planes are at right angles, as shown in Fig. 4. If the electrodes are not placed in this way (as shown in Fig. 5), the current distribution is not uniform (7). When designing the rotating cylinder apparatus, the outer concentric electrode must be placed several inner-cylinder diameters away from the inner concentric electrode for Eq 1 to be valid (see 8.1.6).

8.1.5 For RCE, the reaction rates may be mass transport controlled. Provided the IR drop is constant in the cell, the current distribution over the electrode surface may be uniform, and concentration (of reactants or product) 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 $Re_{crit} \sim 200$, 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 have to be simulated on a smaller scale or when mass transport must be maximized.

8.1.6 The limiting current density (i_L) for turbulent flow in RCE is described as (7-9).

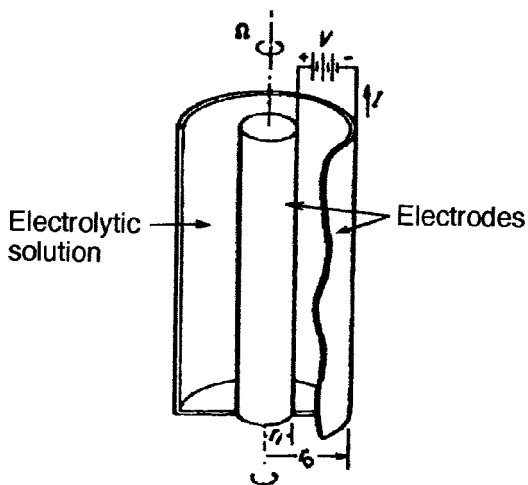$$i_L = 0.0791 nFC(\omega r)^{0.7}(r/v)^{-0.3}(v/D)^{-0.644} \quad (1)$$

FIG. 4 Schematic Representation of RCE for Uniform Current and Potential Distribution (Below the Mass-Transfer-Limiting Current) (7)
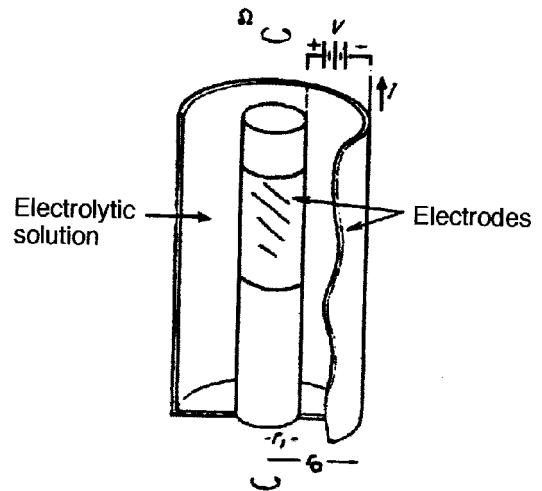
FIG. 5 Schematic Representation of RCE for Nonuniform Current and Potential Distribution (Below the Mass-Transfer-Limiting Current) (7)

where:
n = number of electrons,
F = Faraday constant,
C = concentration of the reactant,
ω = angular velocity,
r = radius of the electrode,
v = kinematic-viscosity, and
D = diffusion coefficient.

8.1.7 When the wall shear stresses are equal in the two geometries (that is, the RCE and the pipe), then similar hydrodynamic conditions, for example, turbulence, are maintained. Under these conditions, the corrosion mechanism (not the rate) is hypothesized to be the same in the two geometries.

8.1.8 The wall shear stress of RCE, τ_{RCE} is given as (10).

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

where:
Re = Reynolds number,
ρ = density,
ω = angular velocity, and
r = radius of the cylinder.

8.1.9 Eq 2 can be used as a first approximation to establish the appropriate RCE velocity for modelling the desired system when evaluating corrosion inhibitors by single-phase flow. There may be instances in which Eq 3 does not provide a good approximation. Equality of shear stress in RCE and pipe systems does not result in equal mass-transfer coefficients, but relationships exist between mass-transfer coefficients and wall shear stress.

8.2 *Rotating Cage:*

8.2.1 The rotating cage (RC) provides higher flow velocities than can usually be obtained simply by stirring the solution (11, 12). Fig. 6 shows the schematic diagram of the rotating cage system. The vessel should be manufactured from an inert material. Glass and acrylic have been used. A typical rotating cage system is described below. A base is fitted at the bottom of the container. At the center of the TFE-fluorocarbon base, a
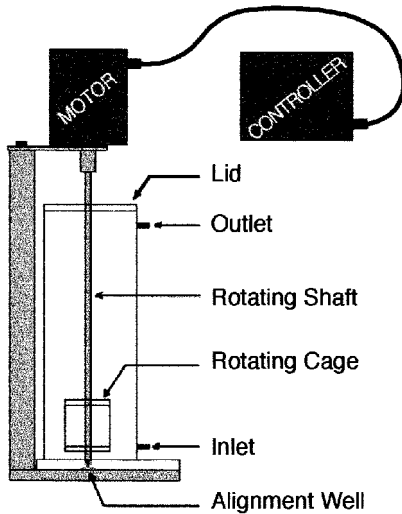
FIG. 6 Schematic Diagram of Rotating Cage (13)

hole is drilled into which the lower end of the stirring rod is placed. This arrangement stabilizes the stirrer and the coupons. Eight coupons (each of surface area about 36 cm²) are supported between two TFE-fluorocarbon disks mounted 76 mm apart on the stirring rod of the autoclave. Holes (diameter 1 cm) are drilled in the top and bottom TFE-fluorocarbon plates of the cage to increase the turbulence on the inside surface of the coupon. This experimental setup can be used at temperatures up to 70°C and rotation speeds up to 1 000 rpm. The corrosion rates are determined by mass loss.

8.2.2 Rotating cage experiments need relatively inexpensive facilities that can be easily duplicated to save investigation time. The tests are relatively simple to conduct. The flow intensity is probably highest in the gap (grooves) between the coupons (Fig. 7). The grooves in the RC contribute to different types of corrosion artifacts. Local high turbulence at the leading and trailing edges of the grooves increases localized corrosion rates. Procedures for examining and evaluating pitting corrosion are described in Guide G46. A decrease in corrosion may be observed inside the groove where the coupon is protected from the turbulent flow.

8.2.3 Depending on the rotation speed, the volume of the container, and the fluids used, the flow pattern can be divided into four zones (Fig. 8):

8.2.3.1 *Homogeneous Zone*—Vortex dimensions that have been observed (length and width) increase with rotation speed.

8.2.3.2 *Side-wall Affected Zone*—Vortex length increases, but the width has reached the side and collides with the wall.

8.2.3.3 *Turbulent Zone*—Vortex length penetrates into the rotating cage unit and creates turbulent flow.

8.2.3.4 *Top-cover Affected Zone*—The liquid level oscillates and rises to the top, pushing the flow pattern due to the backward movement of the fluids, and changing the flow pattern (the rate of vortex length increases at a lower rate).

8.2.4 The wall shear stress can be calculated using Eq 3 (13):

$$\tau_{RC} = 0.0791\, Re^{-0.3} \rho r^2 \omega^{2.3} \qquad (3)$$

where:

r = the radius of the rotating cage.

8.2.5 Eq 4 can be used to calculate the wall shear stresses in the homogeneous zone only. In the turbulent zone, the wall shear stress may be higher than predicted by Eq 4; on the other hand, in the side-affected and top-cover affected zones, the wall shear stress may be less than that predicted by Eq 4, because of the movement of a portion of the fluid in the opposite direction by the vortex-driven flow.

8.2.6 The approach to correlate hydrodynamic relationships between RC and another system (for example, pipe) is the same as that used for RCE. When the wall shear stresses are equal in the two geometries (for example, RC and pipe), then similar hydrodynamic conditions, for example, turbulence, are maintained.

8.3 *Jet Impingement (JI):*

8.3.1 Jet impingement is a widely used technique to study flow-induced corrosion. The high turbulence associated with jet impingement is considered to simulate the turbulence encountered at threaded joints, bends, valves, welds, and so forth in tubulars, flowlines, and pipelines (14).
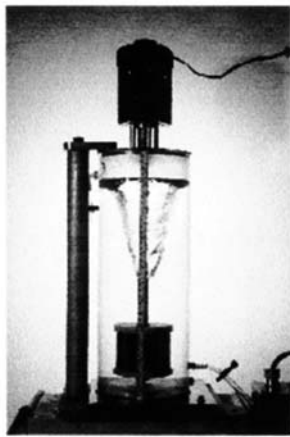
8.3.2 Jet impingement is a widely used test methodology to study flow-accelerated corrosion and is a relatively new
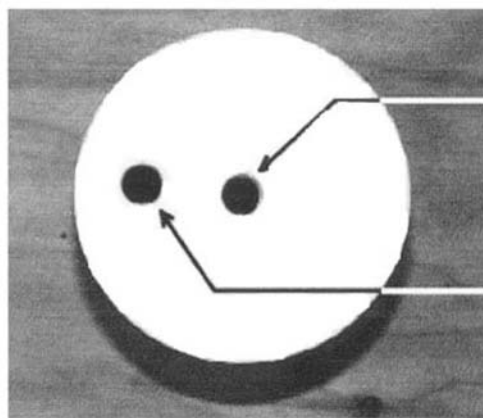
Note 1—The gap between the coupons (A) and the hole (B) introduce localized turbulence.
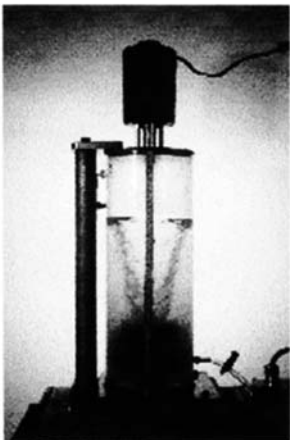**FIG. 7 Photo of Rotating Cage Containing Coupons**

A. Homogeneous Flow

B. Top-cover Affected Zone
(compare with A, the
Vortex width decreases)

C. Turbulent Flow

D. Side Wall Affected Zone

FIG. 8 Flow Patterns in a Rotating Cage

methodology for evaluating the performance of corrosion inhibitors. The jet impingement test can simulate reliably and reproducibly high turbulence conditions in multiphase systems (for example, oil, water and gas). It requires relatively small volumes of test fluids and is controlled easily.

8.3.3 Jet impingement systems can be used to study the effects of differential mass-transfer cells if the electrode diameter is more than five times larger than the diameter of the jet nozzle. Alternatively, a configuration or geometry of the probe/electrode can be designed to account for a specific shear stress region.

8.3.4 The advantage of using an impinging jet is that the flow profile produced by an impinging jet is mathematically well defined and expressed. By changing the jet velocity, the nozzle diameter, and the distance between nozzle and test coupon, the flow profile inside an impinging jet can easily be adjusted over a wide range to simulate various flow conditions.

8.3.5 The typical flow field established by a jet impinging on a flat plate with central axis normal to the plate is illustrated in Fig. 9 (**15**). Under these conditions, a stagnation point exists at the intersection of this axis with the plate and the flow is symmetric about the axis. Because the flow is axis-symmetric, only the flow and fluid properties in the radial plane normal to the disk are considered.

8.3.6 Region A is the region in which the flow is essentially laminar near the plate and the principal velocity component changes from axial to radial, with a stagnation point at the center. Region A extends from the central axis to the point of maximum velocity and minimum jet thickness at approximately $r = 2r_o$. The local velocity field is complex, but is mathematically definable. Because the flow vector is changing rapidly as radial distance increases, this region is of little use for correlation to field conditions.

8.3.7 Region B is a region of rapidly increasing turbulence, with the flow developing into a wall jet; that is, the primary flow vector is parallel to the solid surface. This region extends
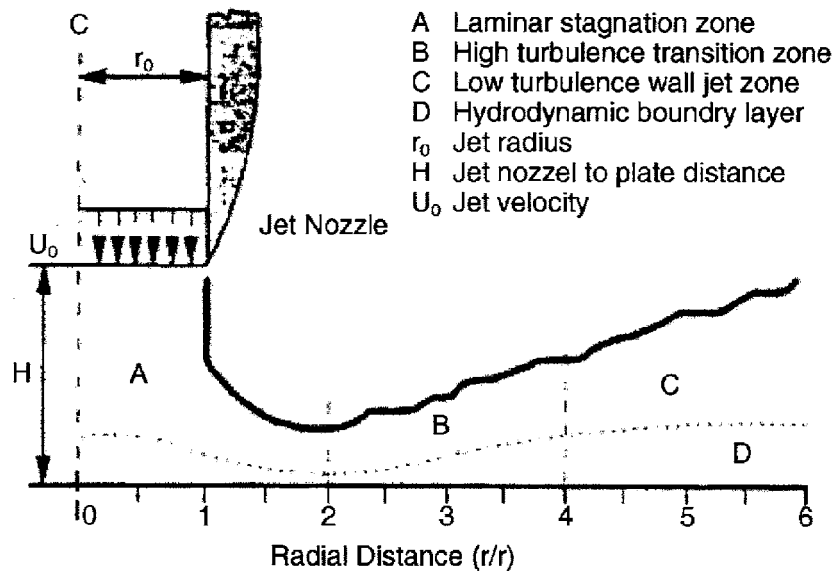

A   Laminar stagnation zone
B   High turbulence transition zone
C   Low turbulence wall jet zone
D   Hydrodynamic boundry layer
r_0 Jet radius
H   Jet nozzel to plate distance
U_0 Jet velocity

FIG. 9 Different Flow Regions on a Jet Impingement

radially to approximately $r = 4r_o$. The flow pattern is characterized by high turbulence, a large velocity gradient at the wall, and high wall shear stress. Region B is of primary interest for studying fluid flow effects on corrosion in high turbulence areas and areas of flow disruption. The equation for the wall shear stress in this region is:

$$\tau_w = 0.1788 \times \rho \times U_0^2 \times Re^{-0.182} \left(\frac{r}{r_0} \right)^{-2.0} \quad (4)$$

where:
τ_w = wall shear stress (N/m^2),
ρ = density (kg/m^3),
U_0 = velocity (m/s) of the flow at the position of leaving the nozzle,
r = distance from stagnant point, m,
r_0 = jet nozzle radius, m, and
Re = Reynold's number.

8.3.8 The jet Reynolds number is defined as:

$$Re = \frac{2r_0 \times U_0}{\nu} \quad (5)$$

where:
ν = the kinematic viscosity of the testing liquid, (m^2/s).

$$(\nu = \mu/\rho) \quad (6)$$

where:
μ = viscosity, and
ρ = density.

8.3.9 In Region C, 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 correlate to field conditions, since momentum transfer and fluid entrainment in this region are in the opposite direction from pipe flow.

8.3.10 One design of JI consists of a central cell with four arms containing the nozzles. The impeller is housed in the cell body and is driven by a motor magnetically coupled to the impeller shaft. Fluid from the cell is forced by the impeller through the nozzles and is recirculated to the cell, as shown in Fig. 10. In this compact design, all moving parts of the pump are located in the closed compartment of the cell. Up to four multiple samples can be used simultaneously.

8.3.11 The efficiency of an inhibitor in JI and in the field can be correlated using wall shear stress, as for RCE and RC.

8.4 *High Pressure Experiments:*

8.4.1 In order to simulate the effects of partial pressures of corrosive gases (CO_2, H_2S), experiments should be carried out under high pressure (see Guide G111). All laboratory methodologies used in atmospheric pressure tests can also be pressurized to simulate high-pressure pipeline operation. The methodologies are high-temperature, high-pressure rotating cylinder electrode (HTHPRCE); high-temperature, high-pressure rotating cage (HTHPRC); and high-temperature, high-pressure jet impingement (HTHPJI).

8.4.2 The analysis of corrosion inhibitors in high-pressure experiments should be performed using an autoclave. The autoclave is equipped with various measuring and regulating devices. Corrosion rates can be determined by mass loss (in HTHPRC and HTHPJI) and electrochemical methods (HTHPRCE and HTHPJI).

8.4.3 A high-temperature, high-pressure system for electrochemical measurements should possess an electrically isolated electrode system, an electrically isolated motor for rotating the electrode, and a vessel that can withstand high pressure without leakage.

8.4.4 The design of a vessel that can be used under pressurized conditions is shown in Fig. 11 (16, 17). The stirring rod of an autoclave can be modified by drilling a hole in the rod into which an insulator, for example, can be inserted. O-rings
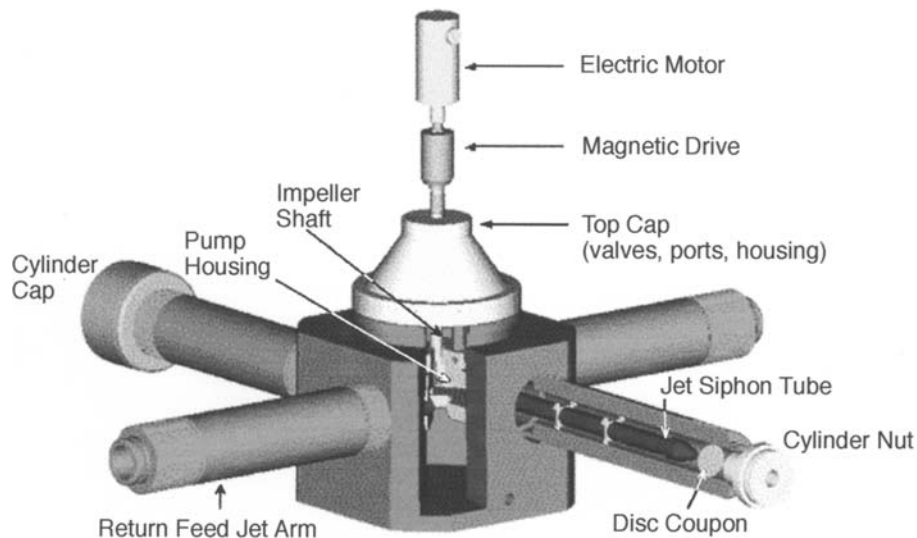
FIG. 10 Schematic Diagram of Jet Impingement
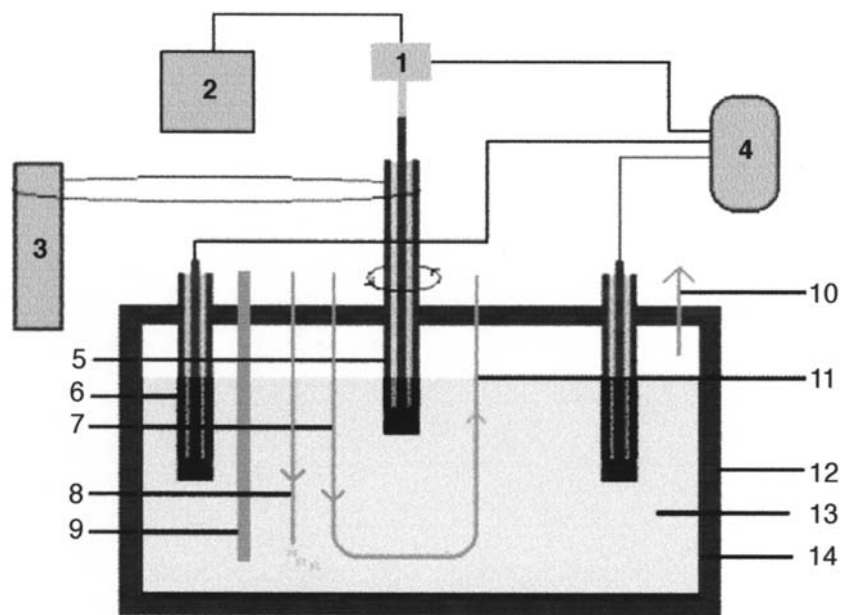
NOTE 1—Legend:

1. Electrical contact unit
2. Techometer (rotation speed display)
3. Rotation controller
4. Electrochemical instruments
5. Rotating electrode units (working electrode)
6. Reference electrode
7. Water cooler coil

8. Inlet (gases and solution)
9. Thermocouple
10. Outlet (gases and solutions)
11. Counter electrode
12. Autoclave body
13. Solution
14. TFE-fluorocarbon liner

FIG. 11 Schematic Diagram of HTHPRE System (13)

are used to prevent leakage. Inside the TFE-fluorocarbon insulator, a metal rod is introduced (Fig. 12). One end of the metal rod is threaded so that cylindrical (RCE) specimens can be attached (Fig. 13). The other end of the rod, projecting slightly above the motor unit, is attached directly to the rotating unit, through which the electrical connection is made. The

stainless steel rod is rotated by a separate motor connected to the rod using a belt. The counter and reference electrodes are inserted inside the autoclave. The corrosion rates can be determined using conventional electrochemical measurements.

8.4.5 The experimental setup similar to the one used for atmospheric pressure RC and JI can be used to carry out
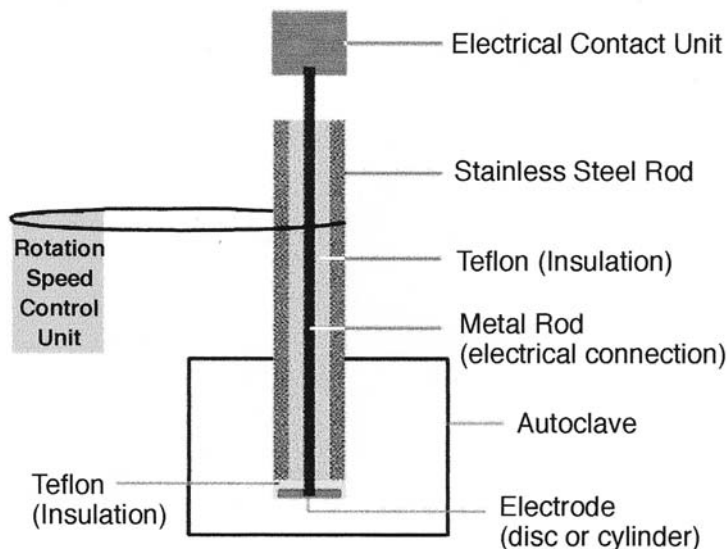

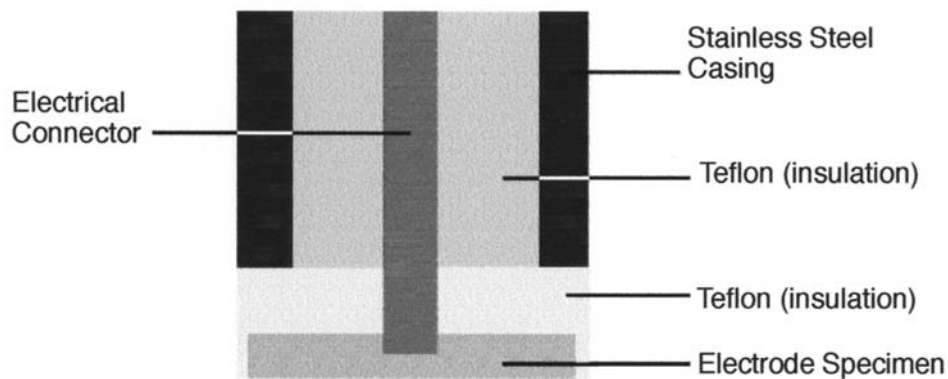**FIG. 12 Rotating Units of HTHPRE System**

FIG. 13 Schematic Diagram of Rotating Electrode Tip
(Where a cylinder or disc can be attached.)

HTHPRC and HTHPJI except that an autoclave is used. The hydrodynamic calculation of elevated pressure experiments is the same as that for atmospheric experiments.

9. Laboratory Methods for Determining Secondary Inhibitor Properties

9.1 *Oil Water Partitioning:*

9.1.1 In oil and gas production, corrosion-related problems are invariably attributed to the presence of aqueous phase. Therefore, in order to prevent corrosion, the inhibitor must be present in the aqueous phase. This is achieved by partitioning or dispersion of the inhibitor from the hydrocarbon and is enabled by the inhibitor being water dispersible or, more commonly, water soluble. Irrespective of the water solubility of the inhibitor, many factors influence the ability to partition efficiently. Because of the need to address the performance of an inhibitor in a given environment, it is most appropriate to test the partitioning characteristics based on a direct performance measure. This is achieved by measuring the corrosivity of an aqueous phase following partition of a corrosion inhibitor from the hydrocarbon. Information gained from partitioning studies can be used as a guide to obtain accurate dosing levels to achieve the desired degree of protection in areas of water drop.

9.1.2 A known amount of corrosion inhibitor is allowed to distribute between a crude oil and an aqueous phase over a period of up to 24 h. Typically, a range of water/crude oil ratios (1:9, 1:1, 8:2 V/V) and corrosion inhibitor concentrations are used. During each test, the fluids are visually examined to ensure that the corrosion inhibitor does not cause formation of a stable emulsion or any excess foaming. These can be costly problems to control in the field if they require extra demulsifier or anti-foam chemicals over and above the levels normally used in the fluids processing.

9.1.3 After the desired time has elapsed, the aqueous phase is separated from the crude oil and its corrosivity measured using one of the laboratory methodologies described in Section 8. The corrosion rates are then compared to the graphs of inhibitor efficiency versus concentration obtained by injecting the inhibitor directly into the test solution.

9.1.4 It is important to undertake baseline partitioning tests without any corrosion inhibitor present to identify if the crude oil has any inherent inhibitory properties.

9.1.5 The aqueous phase (of composition corresponding to that in the field) is prepared using AnalaR grade salts. The crude oil should be a representative sample (dry, stabilized, additive-free) obtained from the field where the candidate inhibitor is to be deployed.

9.1.6 The test fluids are conditioned as follows prior to partitioning. Deaerate with corrosive gas mixtures, H_2S, CO_2 (less than 10 ppm oxygen in the gas) for 1 h. The partial pressures of CO_2 and H_2S should be the same as in the field with the balance made up with N_2. Continue sparging with gases during the test. The cleanliness of the partitioning vessel (Fig. 14) is important to obtain reproducible and reliable data. The following cleaning procedure is recommended after each
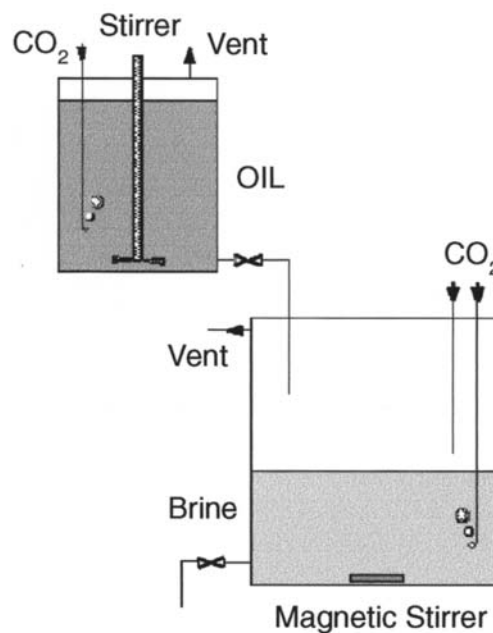

FIG. 14 Partition Vessel

partitioning run: deionized water rinse; toluene rinse; petro-leum ether (70 to 90°C fraction) rinse; acetone rinse; and deionized water rinse (five times).

9.1.7

$$C_o V_o + C_w V_w = C_t \qquad (7)$$

$$P = C_w C_o \qquad (8)$$

where:

C = concentration,
V = volume fraction,
w = the water phase,
o = the oil phase,
t = total fluids, and
P = the partitioning co-efficient (water/oil).

$$C_w = C_t P/(V_o + PV_w) \text{ and } C_o = C_t/(V_o + PV_w) \qquad (9)$$

9.1.8 It is not possible to obtain an accurate partition coefficient directly from corrosion rate data. However, information can be obtained on its partitioning characteristics. If the inhibitor is preferentially water soluble, then, for a given inhibitor concentration, the corrosion rate of the separated aqueous phase should increase with increasing water cut. For a preferentially oil soluble inhibitor, the corrosion rate should decrease with increasing water cut. Based on the corrosion rate data, an estimate of the required dose rate on total fluids can be made. This estimate is achieved by comparing the data obtained from the separated aqueous phase with data obtained when the same concentration of inhibitor is dosed directly into aqueous phase only. The time taken to reach maximum inhibition is also important.

9.2 *Solubility:*

9.2.1 The solubility of corrosion inhibitors in carrier fluids (aqueous or liquid hydrocarbons) should be assessed at the prospective storage temperature, often ambient temperature to -20°C. The main concerns are: loss of solubility of the active ingredients, with the formation of solids or *gunks*, and phase separation due to changes in solubility.

9.2.2 In a 100-mL graduated cylinder, make a solution of the appropriate concentration of the corrosion inhibitor in the recommended carrier (aqueous or hydrocarbon). Keep the solution at temperature for at least two weeks. Disqualify the product if a deposit or a separate liquid phase forms within that period. Report any cloudiness or change in appearance of the liquid. Since the solubility of inhibitors can vary drastically depending on the chemical composition of the water and hydrocarbon phases, it is recommended that this test be repeated with actual field fluids if at all possible.

9.3 *Emulsification Tendency:*

9.3.1 The emulsions formed can be quite difficult to remove and can lead to separation difficulties in the production facilities. Shake flask tests are used to evaluate whether the inhibitor will cause the water/hydrocarbon mixture to form an emulsion.

9.3.2 Volumes of 100-mL (or other suitable volume) mixtures of oil phase and water phase are tested. Different ratios can be used depending on the system, for example, 95:5, 75:25, 50:50, and so forth, of condensate/oil to synthetic water.

9.3.3 The mixtures are injected with various concentrations of test chemical usually at a higher level than that recommended, to act as a worst case. Blanks are also used along with the inhibited samples.

9.3.4 Each bottle is then given 100 hard shakes by hand and then left to settle. The clarity and color of the hydrocarbon and aqueous layers, and the appearance of the interface are observed over a period of time, for example, 1, 2, 5, and 10 min. Comparisons are then made with the blank.

9.3.5 Report the appearance (clear or hazy) and the volume of the aqueous and hydrocarbon phases in the bottle after 5, 15, 30, and 60 min, as outlined in Table 2. Report the time needed for full separation of the two phases. Use the appearance of the two phases (that is, clear/hazy) to evaluate solubility or dispersibility of the product.

9.3.6 The formation of a precipitate or a third liquid phase during this test should be considered as a warning sign of possible instability of the formulation.

9.3.7 Stirring the fluids in a defined cylinder with a defined stirrer and using a standard procedure to evaluate respective phases and interphase represents another method to evaluate emulsion properties of a given inhibitor (ISO 6614).

9.4 *Foaming Tendency:*

9.4.1 The method employs sparging gas through a glass frit into a solution of chemical in either waters or hydrocarbons. The foam height and the stability of the foam are used to assess the degree of foaming. The effect is compared to a blank.

9.4.2 One hundred millilitres of synthetic water or hydrocarbons (heptane may be used to simulate condensate) is placed in a 500-mL measuring cylinder. The fluid is sparged with gas mixture at a constant rate. The foam produced is measured and recorded as a function of column height, and its time to collapse is also measured. The foaming tendency of the samples dosed with chemical is then compared to that of the blank.

9.4.3 Alternatively, a specified volume of solution can be flowed through a defined pipe (nozzle) into a measuring cylinder. The foam height is recorded versus time (ISO 696).

9.4.4 The high shear foaming test requires the use of a small, high pressure (rated to at least 100 bar) sampling bottle or autoclave. The bottle should be fitted with a pressure relief valve, with a gas inlet dip tube that reaches to the bottom of the bottle, with a manual shut-off valve to depressurize the contents of the bottle quickly, and with a gas outlet tube to allow gas bubbling through the liquid mixture in the bottle. An example of this equipment is shown in Fig. 15.

9.4.5 Prepare 100 mL of a 50:50 v/v mixture of hydrocarbon and aqueous phase with the prescribed composition. Pour the mixture into a 100-mL high pressure autoclave. Bubble gas of

TABLE 2 Example of Presentation of Emulsion Test Results

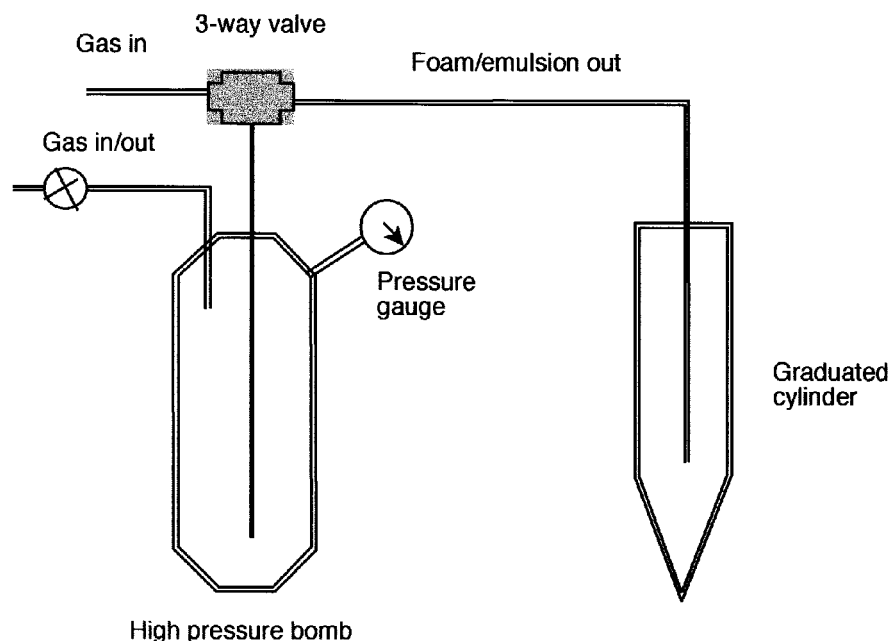| Time, min	Aqueous Phase		HC Phase		Interface
	Appearance	Volume	Appearance	Volume	
5	hazy	10 mL	hazy	10 mL	5 cm
15	hazy	25 mL	hazy	20 mL	1 cm
30	hazy	35 mL	clear	45 mL	firm
60	hazy	40 mL	clear	45 mL	firm
>1 day	clear	50 mL	clear	50 mL	firm

**FIG. 15 Test Apparatus for a 100-mL Pressure
(High-Shear Foaming Test)**

the appropriate composition through the mixture. Pressurize the autoclave to the required test pressure. Depressurize slowly to about 5 bar, avoiding liquid carry-over with the gas. Repeat the pressurization/depressurization step at least three times. Pressurize the autoclave once more to 100 bar, and allow to equilibrate for 5 min. Disconnect the dip-tube from the pressure bottle, and direct its end to the bottom of a 200-mL graduated cylinder. Suddenly open the shut-off valve, allowing all the contents to flow into the graduated cylinder. Record the height of liquid and foam with time for at least 1 h, or until the foam pad disappears.

9.5 *Thermal Stability:*

9.5.1 The effect of the pipeline or flowline inlet temperature on the efficiency of the inhibitor formulation should be evaluated. If the corrosion inhibitor formulation is to be blended with methanol or glycol, and possibly other chemical additives, and stored prior to injection, the stability of this mixture should be investigated, as well as the stability of the inhibitor formulation itself. Even if the corrosion inhibitor formulation is introduced into the methanol or glycol immediately before injection, it is important to test that the resultant mixture viscosity does not increase substantially, and thus, impede pumping. The first two tests described in this section are intended specifically for downhole applications. The last three tests are intended for transport lines in which glycol is used to prevent hydrate formation.

9.5.2 *Sticky Deposits Test*—This test evaluates the tendency of inhibitors to form undesirable sticky deposits. Sticky deposits might form, for example, due to thermal decomposition of the corrosion inhibitor or another component of the formulation, or due to flashing of the solvent at high temperatures. Prepare a solution of inhibitor in at least 150 mL of the prospective carrier. Mix 75 mL of this solution with 15 g mixture (1:1) of formation sandstone and bentonite. The

solutions with and without the mixture are heated in an oven for three days at the operating temperature. After this period, the mixtures are cooled to room temperature. A comparison is made by observing the appearance (consistency, settling, viscosity). Any deposits that are observed are studied to determine whether they re-dissolve by adding 75 mL carrier.

9.5.3 *Downhole Stability*—To perform the test, prepare a solution of inhibitor in the appropriate carrier fluid (hydrocarbon or aqueous). Heat and maintain the solution at the desired temperature for a period of four days in an autoclave, preferably glass or glass-lined to prevent contamination of the inhibitor solution with corrosion products. After completion of this period, evaluate the performance of the inhibitor using standard laboratory techniques described in Section 8. Alternatively, the inhibitor solution may be analyzed, using for example gas or liquid chromatography, infrared spectroscopy, mass spectroscopy, or other suitable analytical techniques, to detect any decomposition products of the CI. The formation of a separate liquid or solid phase should be considered a warning sign of instability of the formulation at high temperatures. This test is not necessary if the inhibitor will not be exposed to downhole temperatures for extended periods, for example, if downhole injection takes place using a capillary tube.

9.5.4 *Glycol Test*—Prepare a 50/50 v/v solution of glycol and aqueous phase with an inhibitor concentration of 1000 mg/L (based on total volume), or 20 times the recommended dosage, whichever is greater. Pour approximately 100 mL of this solution into a 250-mL flask connected to an aqueous-cooled condenser in a reflux (vertical) position. The flask should be continuously purged with gas mixture (depending on the field conditions, H_2S, CO_2) at a rate of approximately 100 cm^3/min. Heat the flask using a regular laboratory heating mantle or hot plate. The boiling temperature of the glycol/aqueous solution is expected to be around 135°C. Reflux the

solution under the gas purge for 5 days and then evaluate the performance of the corrosion inhibitor in a standard foam test, described in Section 8. This can be accomplished by adding 50 mL of the refluxed solution to 1 L of test solution.

9.5.5 *Stability of Inhibitor Formulation at Ambient Temperature*—The formulation is exposed, under stagnant conditions, to three temperatures, 5, 20 and 50°C, in a closed vessel blanketed with a slowly flowing stream of air. A test period of three weeks is recommended. The viscosity of the formulation, or phases that may separate, should be measured at the test temperature before and after the test. At the conclusion of the tests, the formulation should be examined to determine if separate phases or solid materials have formed. If separate phases form, the viscosity of each phase should be measured. Samples of each phase should be saved for further analysis, if necessary.

9.5.6 *Stability of Corrosion Inhibitor + Methanol/Glycol at Ambient Temperature*—If the corrosion inhibitor formulation is to be blended with methanol or glycol, and possibly other chemical additives, and stored prior to injection, the stability of this mixture should be investigated, as well as the stability of the inhibitor formulation itself. Even if the corrosion inhibitor formulation is introduced into the methanol or glycol immediately before injection, it is important to test that the resultant mixture viscosity does not increase substantially, and thus, impede pumping.

9.5.7 To test for compatibility problems involving the mixture, the corrosion inhibitor formulation should be introduced into the methanol or glycol along with the other chemical additives in the proportions that are representative of the mixture to be stored and pumped down the umbilical. The viscosity of the mixture should be measured after combination and compared to the viscosity of the individual components, to obtain data on short term changes in mixture viscosity. It is recommended that this test be carried out at 5 and 20°C. If the mixture is to be stored for a longer term, stability tests of the type described above should be carried out.

9.6 *Toxicity:*

9.6.1 A further factor of growing importance is the toxicity of corrosion inhibitors and indeed other production chemicals. Awareness and concern for the environment will inevitably demand more stringent legislation to regulate discharges into coastal and offshore waters. Environmental concerns worldwide are increasing and are likely to influence the choice of corrosion inhibitors in the future. Environmental requirements are still being developed, but some elements have been established.

9.6.2 The biodegradation, or biological oxygen demand (BOD), should be at least 60 %, and inhibitors should be nontoxic (**18**). The BOD is a measure of how long the inhibitor will persist in the environment. Toxicity is measured as LC_{50} or EC_{50}. LC_{50} is the concentration of the inhibitor needed to kill 50 % of the total population of the test species. The results are quoted as milligrams of chemical per litre of fluid (or LD_{50}, mg/kg) for exposure times of 24 and 48 h. The EC_{50} is the effective concentration of inhibitor to adversely affect 50 % of the population. In general, EC_{50} values are lower than LC_{50}

values because the former are the concentrations required to damage the species in some way without killing it.

9.7 *Compatibility with Other Additives/Materials:*

9.7.1 *Effect of Inhibitor on 316 SS Transfer Lines*—A series of tests should be carried out utilizing the corrosion inhibitor formulation and a variety of specimens, including stainless steel, welded coupons and crevice coupons. For crevice corrosion testing, samples with metal-to-metal crevices and crevices with elastomeric seal materials should be fabricated. For stress corrosion cracking tests, a stressed sample, such as a C-ring, should be used. Testing should focus first on the highest expected temperature to assess possibility of attack in the most aggressive environment. A slow purge with air should be maintained during the test.

9.7.2 *Effect of Inhibitor Formulation on Elastomeric Seals*—Both amines and different solvents in the inhibitor formulations are known to cause swelling and embrittlement of some elastomers. The problems may not be observed unless the elastomers are subjected to rapid decompression. Autoclave exposure tests are recommended where multiple samples of the elastomers are exposed to the corrosion inhibitor formulation. Periodically, samples are removed and examined for change in mass and tensile strength as well as being visually examined. See also NACE-TM0196.

9.7.3 *Effect on Flexible Umbilicals*—If flexible umbilicals are to be used, it is recommended that short-term exposure tests be conducted to assess compatibility of the liner material with the individual components in the mixture carried by the umbilical, including the corrosion inhibitor, and with the mixture itself. Exposure times of 1 to 3 weeks are recommended. Although the subsea umbilical temperature is low, approximately 4°C for many deepwater prospects, tests may be carried out at elevated temperatures to accelerate effects.

9.7.4 *Compatibility of the Corrosion Inhibitor with Production Tree and Flowline Materials*—When the mixture containing the corrosion inhibitor is mixed with the produced fluid stream, all components are substantially diluted. In general, this dilution would be expected to reduce concerns about compatibility. One possible concern is the impact of the corrosion inhibitor on flexible flowlines. If the flowline contains a flexible section, it is recommended that exposure tests of the flowline liner be carried out with concentrated solutions of all components of the mixture to be injected, as well as the mixture itself. The tests should be conducted at the subsea tree temperature. Tensile tests should be used to assess changes in properties as well as mass gain.

9.7.5 *Injection Point—Flashing of Solvents*—Solubility tests can be used to establish the least amount of solvent required to keep the inhibitor components in solution. The behavior of the inhibitor formulation at the injection point can be experimentally measured, for example, by heating a small volume of inhibitor to the injection temperature in a larger volume autoclave, letting the system stabilize, measuring the viscosity of the resulting product, and observing the formation of any solids.

15

10. Keywords

10.1 emulsion tendency; foaming tendency; high-temperature, high-pressure; inhibitor evaluation; jet impingement; laboratory methodologies; multiphase; rotating cage; rotating cylinder

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