Designation: G205 – 10

Standard Guide for
Determining Corrosivity of Crude Oils[1]

1. Scope

1.1 This guide presents some generally accepted laboratory methodologies that are used for determining the corrosivity of crude oil.

1.2 This guide does not cover detailed calculations and methods, but rather a range of approaches that have found application in evaluating the corrosivity of crude oil.

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

1.4 This guide does not address the change in oil/water ratio caused by accumulation of water at low points in a pipeline system.

1.5 This guide is intended to assist in the selection of methodologies that can be used for determining the corrosivity of crude oil under conditions in which water is present in the liquid state (typically up to 100°C). These conditions normally occur during oil and gas production, storage, and transportation in the pipelines.

1.6 This guide does not cover the evaluation of corrosivity of crude oil at higher temperatures (typically above 300°C) that occur during refining crude oil in refineries.

1.7 This guide involves the use of electrical currents in the presence of flammable liquids. Awareness of fire safety is critical for the safe use of this guide.

1.8 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.9 *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 appro-priate safety and health practices and determine the applica-bility of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D96 Test Method for Water and Sediment in Crude Oil by Centrifuge Method (Field Procedure) (Withdrawn 2000)[3]

D473 Test Method for Sediment in Crude Oils and Fuel Oils by the Extraction Method

D665 Test Method for Rust-Preventing Characteristics of Inhibited Mineral Oil in the Presence of Water

D724 Test Method for Surface Wettability of Paper (Angle-of-Contact Method) (Withdrawn 2009)[3]

D1125 Test Methods for Electrical Conductivity and Resistivity of Water

D1129 Terminology Relating to Water

D1141 Practice for the Preparation of Substitute Ocean Water

D1193 Specification for Reagent Water

D4006 Test Method for Water in Crude Oil by Distillation

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4377 Test Method for Water in Crude Oils by Potentiometric Karl Fischer Titration

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

G31 Guide for Laboratory Immersion Corrosion Testing of Metals

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

G170 Guide for Evaluating and Qualifying Oilfield and Refinery Corrosion Inhibitors in the Laboratory

G184 Practice for Evaluating and Qualifying Oil Field and Refinery Corrosion Inhibitors Using Rotating Cage

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G193 Terminology and Acronyms Relating to Corrosion
G202 Test Method for Using Atmospheric Pressure Rotating Cage

2.2 *ISO Standard:*[4]

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

2.3 *NACE Standard:*[5]

TM0172 Standard Test Method Determining Corrosive Properties of Cargoes in Petroleum Product Pipelines

3. Terminology

3.1 *Definitions*—The terminology used herein, if not specifically defined otherwise, shall be in accordance with Guide G170, Terminology and Acronyms G193, and Terminology D1129. Definitions provided herein and not given in Guide G170, Terminology and Acronyms G193, and Terminology D1129 are limited only to this guide.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *emulsion, n*—two-phase immiscible liquid system in which one phase is dispersed as droplets in the other phase.

3.2.2 *emulsion-inversion point, n*—percentage of water at which a water-in-oil (W/O) emulsion converts into an oil-in-water (O/W) emulsion.

3.2.3 *wettability, n*—tendency of a liquid to wet or adhere on to a solid surface.

3.3 *Acronyms:*

CO_2	=	Carbon dioxide
EIP	=	Emulsion inversion point
H_2S	=	Hydrogen sulfide
KOH	=	Potassium hydroxide
NaCl	=	Sodium chloride
Na_2CO_3	=	Sodium carbonate
$NaHCO_3$	=	Sodium bicarbonate
NaOH	=	Sodium hydroxide
Na_2S	=	Sodium sulfide
O/W	=	Oil-in-water
W/O	=	Water-in-oil

4. Summary of Guide

4.1 This guide describes methods for determining the corrosivity of crude oils by a combination of three properties: *(1)* the emulsion of the oil and water, *(2)* the wettability of the steel surface, and *(3)* the corrosivity of water phase in the presence of oil.

4.2 Conductivity of emulsion can be used to determine the type of emulsion: oil in water (O/W) or water in oil (W/O). The conductivity of the O/W emulsion (in which water is the continuous phase) is high. The conductivity of the W/O emulsion (in which oil is the continuous phase) is low.

4.3 The wettability of a steel surface is determined using two methods: *(1)* contact angle method and *(2)* spreading method.

4.4 The corrosiveness of water phase in the presence of crude oil can be determined using several methods.

5. Significance and Use

5.1 In the absence of water, the crude oil is noncorrosive. The presence of sediment and water makes crude oil corrosive. Test Methods D96, D473, D4006, and D4377 provide methods for the determination of the water and sediment content of crude oil.

5.2 The corrosivity of crude oil containing water can be determined by a combination of three properties (Fig. 1) (**1**)[6]: the type of emulsion formed between oil and water, the wettability of the steel surface, and the corrosivity of water phase in the presence of oil.

5.3 Water and oil are immiscible but, under certain conditions, they can form emulsion. There are two kinds of emulsion: O/W and W/O. W/O emulsion (in which oil is the continuous phase) has low conductivity and is thus less corrosive; whereas O/W (in which water is the continuous phase) has high conductivity and, hence, is corrosive (see ISO 6614) (**2**). The conductivities of various liquids are provided in Table 1(**3**). The percentage of water at which W/O converts to O/W is known as the emulsion inversion point (EIP). EIP can be determined by measuring the conductivity of the emulsion. At and above the EIP, a continuous phase of water or free water is present. Therefore, there is a potential for corrosion.

5.4 Whether water phase can cause corrosion in the presence of oil depends on whether the surface is oil wet (hydrophobic) or water wet (hydrophilic) (**4-8**). Because of higher resistance, an oil-wet surface is not susceptible to corrosion, but a water-wet surface is. Wettability can be characterized by measuring the contact angle or the conductivity (spreading method).

5.4.1 In the contact angle method, the tendency of water to displace hydrocarbon from steel is measured directly by observing the behavior of the three phase system. The contact angle is determined by the surface tensions (surface free energies) of the three phases. A hydrocarbon-steel interface will be replaced by a water-steel interface if this action will result in an energy decrease of the system. To determine whether the surface is oil wet, mixed wet, or water wet, the angle at the oil-water-solid intersection is observed and measured.

5.4.2 In the spreading method of determining wettability, the resistance between steel pins is measured. If a conducting phase (for example, water) covers (wets) the distance between the pins, conductivity between them will be high. On the other hand, if a nonconducting phase (for example, oil) covers (wets) the distance between the pins, the conductivity between them will be low.

5.5 Dissolution of ingredients from crude oils may alter the corrosiveness of the aqueous phase. Based on how the corrosivity of the aqueous phase changes in its presence, a crude oil can be classified as corrosive, neutral, inhibitory, or preventive

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[4] Available from the American National Standards Institute, 25 W. 43rd St., New York, NY 10036.

[5] Available from the National Association of Corrosion Engineers, 1440 S. Creek Dr., Houston, TX 77084-4906.

[6] The boldface numbers in parentheses refer to a list of references at the end of this standard.
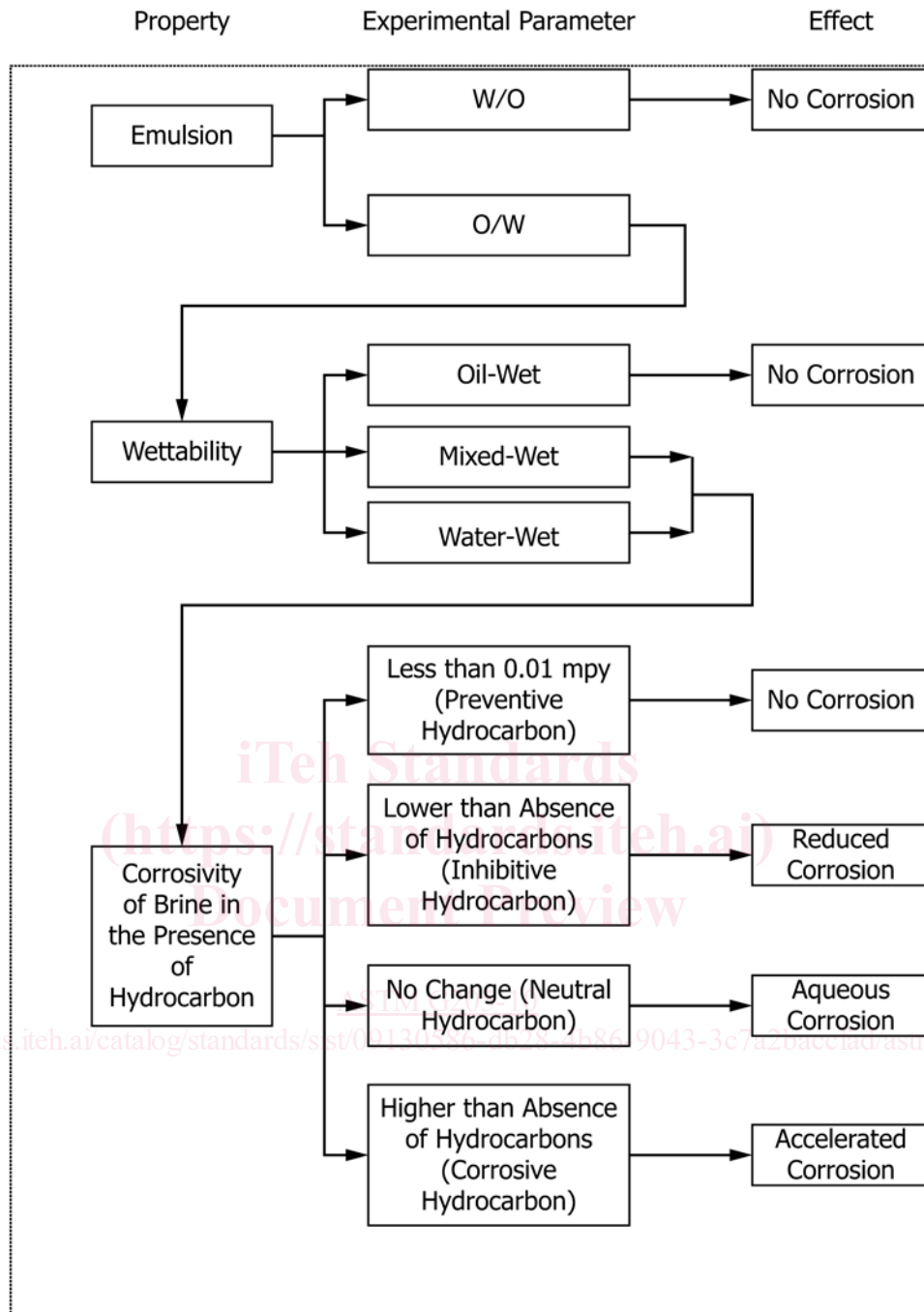
FIG. 1 Predicting Influence of Crude Oil on the Corrosivity of Aqueous Phase

crude. Corrosiveness of the aqueous phase in the presence of oil can be determined by methods described in Test Method D665, Guide G170, Practice G184, Test Method G202, and NACE TM0172.

6. Materials

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

6.2 The coupons/probes should be made of the field material (such as carbon steel) and have the same metallographic structure as that used in the service components. The probes for wettability and EIP measurements should be ground to a

TABLE 1 Conductivities of Selected Hydrocarbons and Aqueous Phases (3)

Liquid	Temperature, °C	Conductivity[A]
Acetic acid	0	5×10^{-9}
Aniline	25	2.4×10^{-8}
Benzene	...	7.6×10^{-8}
Formic acid	25	6.4×10^{-5}
Glycerol	25	6.4×10^{-8}
Glycol	25	3×10^{-7}
Heptane	...	$<1 \times 10^{-13}$
Hexane	18	$<1 \times 10^{-18}$
Kerosene	25	$<1.7 \times 10^{-8}$
Pentane	19.5	$<2 \times 10^{-10}$
Sulfur	115	1×10^{-12}
Sulfur dioxide	35	1.5×10^{-8})
Sulfuric acid	25	1×10^{-2}
Sulfuryl chloride, SO_2Cl_2	25	3×10^{-8}
Water	18	4×10^{-8}
KOH	18	234^{B}
NaCl	18	106.5^{B}
NaOH	18	208^{B}
$1/2 Na_2S$	18	104.3^{B} (N= 1.0)
$NaHCO_3$	25	93.5^{B}
$1/2 Na_2CO_3$	18	112^{B}

[A] Electrical conductivity is the reciprocal of the ac resistance in ohms measured between opposite faces of a 1-cm cube of an aqueous solution at a specified temperature (in accordance with Test Methods D1125). The unit of electrical conductivity is Siemens per centimetre (S/cm). The previously used units of mhos/cm are numerically equivalent to S/cm. At low concentrations to obtain the conductivity of electrolyte the conductivity of pure solvent should be subtracted from that of the solution.

[B] Equivalent conductivity of an electrolyte, Λ ($\Omega^{-1} \cdot cm^2 \cdot equiv^{-1}$) – the sum of contributions of the individual ions; $\Lambda = \kappa/C$, where C is concentration in equivalents per litre. The volume of the solution in cubic centimetres per equivalent is equal to $1000/C$, and $\Lambda = 1000 \kappa/C$. The values are taken at 0.001 concentration (N), except where specified otherwise.

surface finish of 600 grit. Preparation of coupons for corrosion measurements is described in Guide G170, Practice G184, and Test Method G202.

7. Preparation of Test Solutions

7.1 Oil should be obtained from the field that is being evaluated. Practice D4057 provides guidelines for collecting crude oil. It is important that live fluids do not contain externally added contaminants, for example, corrosion inhibitors, biocides, and surfactants. A water sample should also be obtained from the field. A synthetic aqueous solution could be used; the composition of which, however, should be based on field water analysis. Alternatively, standard 3 % brine or synthetic brine (of a composition provided in Practice D1141) may be used. Their composition should be specified in the work plan and recorded in the laboratory logbook. The solutions should be prepared following good laboratory practice. The solutions should be prepared using reagents (in accordance with Test Method G202) and deionized water (in accordance with Specification D1193).

7.2 The solutions (oil and water phases) should be deaerated by passing nitrogen (or any other inert gas) and kept under deaerated conditions. Solutions should be transferred with minimal contact with air. Procedures to transfer the solutions are described in Test Method G202.

7.3 Procedures to deoxygenate and saturate the solutions with acid gases are presented in Test Method G202. To simulate field operating conditions, the solution is often re-quired to be saturated with acid gases such as hydrogen sulfide (H_2S) and carbon dioxide (CO_2). H_2S and CO_2 are corrosive gases. H_2S is poisonous and shall not be released to the atmosphere. The appropriate composition of gas can be obtained by mixing H_2S, CO_2, and methane streams from the standard laboratory gas supply. Nitrogen or any other inert gas can be used as a diluent to obtain the required partial pressures of the corrosive gases. Alternatively, gas mixtures of the appropriate compositions can be purchased from suppliers of industrial gases. The composition of gas depends on the field gas composition. The oxygen concentration in solution depends on the quality of gases used to purge the solution. The oxygen content of nitrogen or the inert gas should be less then 10 ppm by volume. Leaks through the vessel, tubing, and joints should be avoided.

7.4 The test vessels should be heated slowly to avoid overheating. The thermostat in the heater or thermostatic bath should be set not more than 20°C above the solution temperature until the test temperature is reached. 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.

7.5 A general procedure to carry out experiments at elevated pressure and elevated temperature is described in Guide G111. For elevated temperature and elevated pressure experiments using individual gases, first the autoclave is pressurized with H_2S to the required partial pressure and left for 10 min. If there is a decrease of pressure, the autoclave is repressurized. This process is repeated until no further pressure drop occurs. Then, the autoclave is pressurized with CO_2 by opening the CO_2 gas cylinder at a pressure equal to the $CO_2 + H_2S$ partial pressure and left for 10 min. If there is a decrease in pressure, the autoclave is repressurized with CO_2 gas. This process is repeated until no further pressure drop is observed. Finally, the autoclave is pressurized with an inert gas (for example, methane) by opening the appropriate cylinder at the total gas pressure at which the experiments are intended to be carried out.

8. Laboratory Methodologies

8.1 *Determination of Emulsion Type:*

8.1.1 A schematic diagram of the equipment used for determining the emulsion type is presented in Figs. 2 and 3. The apparatus consists of an experimental section (Fig. 3), a reservoir, a circulating pump, and a flow controller.

8.1.2 The experimental section (Fig. 3) is a 15-cm-long horizontal pipe section of 2.5 cm in diameter containing two vertically placed measuring pins (typically made from carbon steel). The distances between the pins can be varied with a screw arrangement. For optimal measurements, a pin distance of 0.25 cm is suggested.

8.1.3 The reservoir (typically 7-L capacity) may be an autoclave (for higher pressure measurements) or a glass
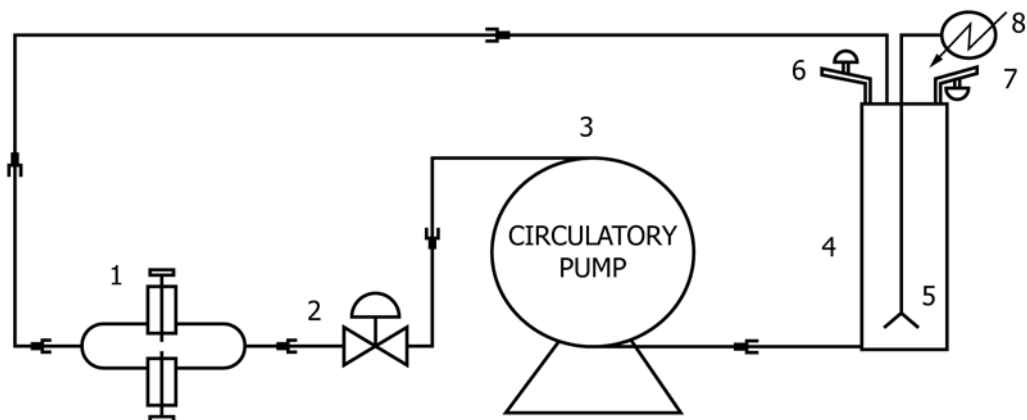
1—Experimental section (see Fig. 3)
2—Flow controller
3—Circulatory pump
4—Reservoir (volume = 7 L)
5—Impeller
6—Gas inlet
7—Gas outlet
8—Power source to operate the impeller

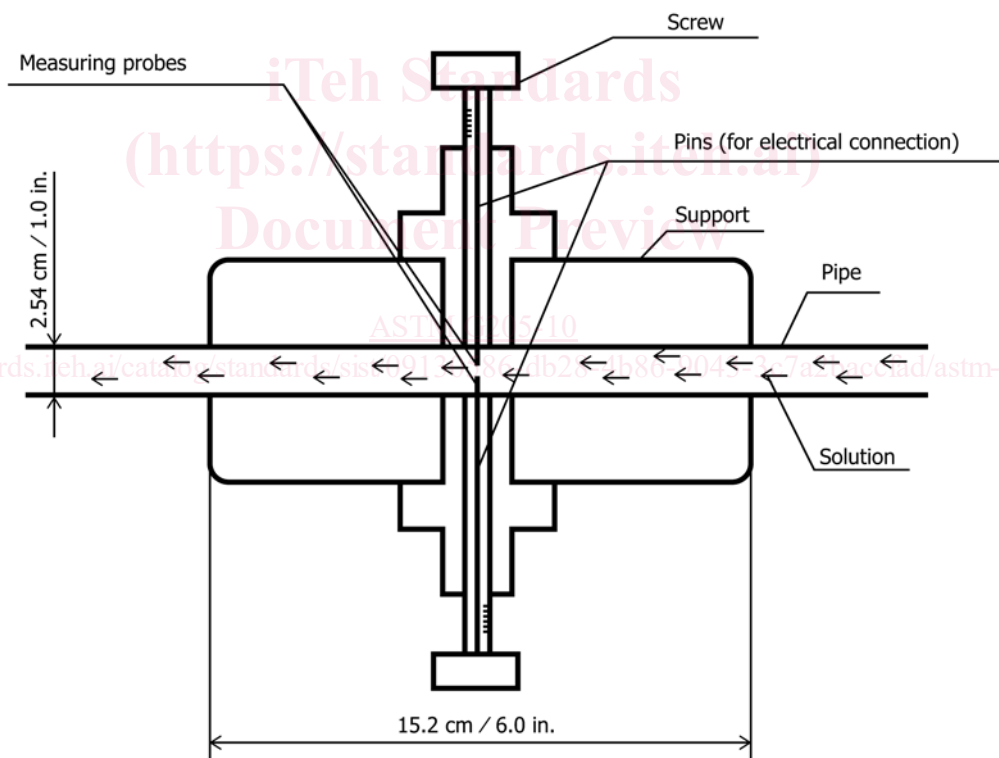**FIG. 2 Schematic Diagram of a Flow Loop of an EIP Apparatus**

FIG. 3 Schematic Diagram of the Experimental Section of the EIP Apparatus

container (for atmospheric pressure measurements). The top cover of the reservoir is fitted with an inlet, an outlet, and an impeller. For higher pressure experiments, the reservoir is also fitted with a pressure gauge to monitor the pressure. The impeller should be capable of rotating at annular rotation speeds higher than 1000 rpm.

8.1.4 The circulating pump is used to circulate the emulsion between the reservoir and the experimental section. The pump should be capable of pumping fluids up to a speed of 50 cm/s.

8.1.5 The flow controller controls the velocity of the fluids through the experimental section. The flow controller should be capable of controlling fluids up to a speed of 50 cm/s.

8.1.6 The apparatus should be cleaned before each experiment. The measuring pins should be washed as described in Practice G1 to remove any corrosion products.

8.1.7 An appropriate volume of oil (typically 4 L) is poured into the reservoir and the entire EIP apparatus is deoxygenated using an inert gas (and presaturated with gases (typically CO_2, H_2S, and methane) when necessary), as described in Section 7 as well as Test Method G202. Note that proper deoxygenation of the apparatus may be critical for fire safety.

8.1.8 The impeller is started to mix the fluids thoroughly. The rotation speed of the impeller and the duration of rotation depend on the characteristics of oil. To ensure formation of stable emulsion of most crude oil, a minimum impeller speed of 1000 rpm and rotation for up to 30 min is sufficient.

8.1.9 Once the stable emulsion is formed, the circulating pump is started and the flow controller is adjusted. For most crude oil-water systems, a velocity of about 20 cm/s at the experimental section provides reproducible results.

8.1.10 The electrical resistance of the solution passing through the experimental section is measured using the two probes as described in Test Method D1125.

NOTE 1—The dc method of measuring electrical resistance may be used. However, special care should be taken to avoid electrolysis by restricting the duration of the measurement (typically 5 s) and by taking several measurements (typically three) at regular intervals (with at least 1 min between (during which time the dc power source is turned off) each measurement).

8.1.11 After measuring the electrical resistance of 100 % oil, the circulating pump and impeller are stopped. Of the oil, 400 mL (10 % of the original volume) is pumped out and replaced with 400 mL of 3 % NaCl and 8.1.3 to 8.1.9 are repeated. After measuring with 90 % oil the water and oil are allowed to separate and 400 mL of the oil is removed (10 % of the volume) to be replaced with 3 % NaCl solution. This process is repeated until 100 % water is reached or until it becomes impossible to remove oil without also removing water/oil emulsion. If the oil cannot be removed in 10 % aliquots then separate mixtures will need to be prepared and inserted in the apparatus.

NOTE 2—Procedures for converting the measured resistance to resistivity are described in Test Methods D1125. Resistivity (in ohms-cm) is numerically the inverse of conductivity (in Siemens per cm).

8.1.12 The emulsion inversion point is determined from a plot of conductivity versus oil-water ratio as being the first point on the graph at which the conductivity starts to increase significantly.

8.2 *Determination of Wettability:*

8.2.1 *Contact Angle Method:*

8.2.1.1 The contact angle of the water-oil system on steel can be measured using two different sequences: adding water first and the oil drop next (Sequence 1; 8.2.1.4 – 8.2.1.7) or adding oil first and the water drop next (Sequence 2; 8.2.1.8 and 8.2.1.9) is experimentally easier but does not simulate the sequence in an oil and gas pipeline (in which the surface will be first contacted with oil and then with water). 8.2.1.8 is more relevant to the pipeline operating conditions, but measuring the contact angle through a dark oil background is relatively difficult (such measurements require illumination).

8.2.1.2 Contact angles reported depend on whether the water phase is advancing or receding over the steel surface. This phenomenon is known as contact angle hysteresis and is caused by surface roughness or absorption of surface active agents on the surface (9). In order to account for this phenomenon the oil drop volume (Sequence 1; 8.2.1.4 – 8.2.1.7) or water drop volume (Sequence 2; 8.2.1.8 and 8.2.1.9) needs to be varied in order to determine the maximum and minimum contact angles. Average of both contact angles should be determined and reported.

8.2.1.3 The contact angle can be measured as interior angle or exterior angle.

Sequence 1

8.2.1.4 In Sequence 1, the steel surface is first in contact with water, a drop of oil is then added, and the contact angle is measured through the water phase. A water-steel interface will be replaced by an oil-steel interface if the energy of the system decreases as a result of this action. In order to account for contact angle hysteresis the minimum and maximum contact angles need to be determined by increasing and decreasing the size of the oil droplet. The average of minimum and maximum contact angles should be determined and reported.

8.2.1.5 Figs. 4 and 5 provide examples of different contact angles of oil drop and water on a steel surface. In Fig. 4, σ_{os}, σ_{ow}, and σ_{ws} are surface tensions of oil-steel, oil-water, and water-steel interfaces, respectively. In Figs. 4 and 5, θ is the contact angle. If σ_{ws} is much larger than σ_{os}, θ will approach 180°, and the surface will be completely oil wet (4, 5). Different methods of measuring and reporting the contact angle are provided in Table 2.

8.2.1.6 The steel sample is placed horizontally in a beaker. The beaker is filled with aqueous phase (distilled water or 3 % NaCl) so as to immerse the steel surface completely. A drop of oil is then injected using a needle (typical diameter 21G (0.8 mm)). The photograph of the oil droplet on the steel surface is taken. On a printed photograph, a horizontal line is drawn at the base of the droplet. At the point of contact of the droplet with the steel surface, two tangents to the curve are drawn at the two points of contact with the baseline. The two exterior angles between the base and the tangents are measured with a protractor. Alternatively, the tangent can be drawn using the tools in software.

8.2.1.7 The angle is measured exterior to the oil droplet on the metal surface; the surface is considered oil wet when the contact angle is more than 120°, mixed wet when the contact angle is between 60 and 120°, and water wet when the contact angle is less than 60° (Table 2, Figs. 4 and 5).

Sequence 2

8.2.1.8 In Sequence 2, the steel surface is first in contact with oil, a drop of water is then added, and the contact angle is measured through the oil phase. Determining the contact angle through the oil phase with a dark oil background is difficult experimentally. Therefore, the surface is illuminated. Test Method D724 provides the procedure to measure the contact angle using Sequence 2. In order to account for contact angle hysteresis the minimum and maximum contact angle need to be determined by increasing and decreasing the size of the water