

Standards for Evaluating Oil Field Corrosion Inhibitors in the Laboratory

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ABSTRACT

The success of a corrosion inhibitor in controlling internal corrosion depends on (1) when the application of it has started, (2) efficiency of it, (3) interference of it with other chemicals and processes, and (4) presence of intact inhibitor film on the surface to be protected. Several standards and industry best practices are available to evaluate these properties. They include:

- ASTM^(A) G170, “Standard Guide for Evaluating and Qualifying Oilfield and Refinery Corrosion Inhibitors in the Laboratory”
- ASTM G184, “Standard Practice for Evaluating and Qualifying Oil Field and Refinery Corrosion Inhibitors using Rotating Cage”
- ASTM G185, “Standard Practice for Evaluating and Qualifying Oil Field and Refinery Corrosion Inhibitors using Rotating Cylinder Electrode”
- ASTM G202, “Standard Test Method for Using Atmospheric Pressure Rotating Cage”
- ASTM G205, “Standard Guide for Determining Corrosivity of Crude Oils”
- ASTM G208, “Standard Practice for Evaluating and Qualifying Oil Field and Refinery Corrosion Inhibitors using Jet Impingement”
- NACE 1D182, “Wheel Test Method Used for Evaluation of Film-Persistent Corrosion Inhibitors for Oil Field Applications”
- NACE 1D196, “Laboratory Test Methods for Evaluating Oil Field Corrosion Inhibitors”
- European Federation of Corrosion (EFC)^(B), “Test Methods for Corrosion Inhibitors”, Working Party Report #11 (1985)
- EFC, “Corrosion Inhibitors for Oil and Gas Production”, Working Party Report #39, 2004

This paper describes these standards, explains hierarchy of standards, and provides guidelines to obtain reliable and relevant data on corrosion inhibitors from laboratory.

Key words: corrosion inhibitors, standards, rotating cage, rotating cylinder electrode, jet impingement, wheel test, kettle test

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INTRODUCTION

Addition of corrosion inhibitors is a time-tested and proven methodology to control internal corrosion of oil production infrastructures, transmission pipelines, and refineries¹. Corrosion inhibitors are used to control general corrosion, pitting corrosion, under-deposit corrosion (UDC), and top-of-the-line corrosion (TLC). The ability of the inhibitors to control specific type of corrosion must be evaluated in the laboratory before they can be used in the field.

Success of inhibitor in controlling internal corrosion depends on (1) when during the operation, the application of it has started, (2) efficiency of it, (3) interference of it with other chemicals and processes, and (4) presence of intact corrosion inhibitor film on the surface to be protected.

Industry normally assumes that corrosion conditions do not exist if the percentage of water is less than 30, i.e., percentage oil is 70 (or above) and water is 30 (or below). Under these conditions, corrosion inhibitors are not normally applied. This practice, however, does not consider the properties of oil and water phases. Field experiences have indicated that corrosion may occur even with 1% water or may not occur even in the presence of 99% water. For this reason, the ability of crude oils and other hydrocarbons (e.g., condensates) in inhibiting corrosion must be evaluated. ASTM G205 provides guidelines to determine the ability of crude oils to inhibit corrosion based on three properties: emulsion tendency, wettability, and influence of oil-phase on water-phase corrosivity².

Efficiency of corrosion inhibitors depends on several parameters including flow, pressure, temperature, as well as compositions of material (e.g. carbon steel), oil phase, water phase, and gas phase. Standards and industry guidelines to evaluate the efficiency of corrosion inhibitors include ASTM G184³, ASTM G185⁴, ASTM 202⁵, ASTM 208⁶, NACE 1D182⁷, NACE 1D196⁸, EFC WP Report #11⁹, and EFC WP Report #39¹⁰.

The corrosion must be compatible with other chemicals (e.g., biocides and scale inhibitors), must meet environmental regulations, and must not cause any side effects (e.g., foaming and emulsion). ASTM G170 describes several secondary corrosion inhibitor properties and laboratory methodologies to evaluate them¹¹.

Even the best corrosion inhibitor would fail, if it was not applied properly. For this reason, the inhibitor must be properly applied so as to form intact film on the surface to be protected.

This paper describes standards to evaluate corrosion inhibitors, explains hierarchy of different standards, and provides guidelines to obtain reliable and relevant data from the laboratory.

STANDARDS FOR PREDICTING CONDITIONS TO APPLY CORROSION INHIBITORS

For corrosion to take place, water (or any other conducting electrolyte) phase must be in contact with the metallic surface. Corrosion may not take place, if the water is prevented from contacting with the metallic surface. This situation occurs when the water is emulsified with oil or when the metallic surface has greater affinity towards crude oil, i.e., oil-wet.

Crude oils cannot dissolve ionic water because of their non-polar nature. But they can form emulsion with water. Type of emulsion and its stability depends on type of crude oil, composition of water, operating pressure, temperature, and flow rate.

There are two kinds of emulsion: water-in-oil and oil-in-water. In water-in-oil emulsion, non-ionic (non-conducting) oil is continuous phase in which ionic water is dispersed. Therefore, corrosion does

not occur in the presence of water-in-oil. On the other hand, ionic (conducting) water is continuous phase in oil-in-water emulsion. Therefore, corrosion can occur in the presence of oil-in-water. The percentage of water at which water-in-oil emulsion inverts into oil-in-water is known as “emulsion inversion point (EIP)”². The EIP depends on several parameters including the physical interactions between oil and water phases, constituents of oil and water phases, flow velocity, and pipeline profile.

ASTM G205 describes a methodology to determine the EIP under atmospheric pressure conditions (Fig.1)². This methodology measures the conductivity of the emulsion under flowing conditions to determine the type of emulsion. Though the EIP apparatus can be operated at elevated pressure conditions, ASTM G205 does not provide guidelines for performing tests at high-pressure conditions.

Probability of corrosion in the presence of oil-in-water emulsion or free water depends on the wettability. When oil phase preferentially wets the surface (oil-wet), corrosion does not take place; when water phase preferentially wets the surface (water-wet), corrosion takes place; and when no phase preferentially wets the surface (mixed-wet), corrosion may or may not take place.

ASTM G205 describes two methodologies to determine the wettability: contact angle method and spreading method. Figure 2 presents a schematic diagram of the spreading method². This methodology measures conductivity between two steel pins to determine the wettability of the surface. The test can be carried out both under atmospheric and elevated pressure conditions.

Contact angle method is extensively used to determine the wettability of various liquids both on metallic and on non-metallic surfaces. During contact angle measurement, oil and water may be added in two sequences: oil-first, water-next sequence or water-first, oil-next sequence. The first sequence represents the case of oil transmission pipelines but measuring contact angle using this sequence is relatively difficult. Due to the dark background of the oil, the apparatus should be illuminated. For this reason, the contact angle is normally measured following water-first, oil-next sequence. However, this sequence does not truly represent oil transmission pipeline operating conditions. Further, the contact angle method cannot be easily used under elevated pressure conditions.

The spreading method overcomes these difficulties. However, boundary to differentiate different wettability, i.e., oil-wet, water-wet, and mixed-wet, is arbitrary. Though the apparatus can be operated at elevated pressures, procedures to carry out tests under flow conditions are not described in ASTM G205.

It should be pointed out that emulsion and wettability are two different properties. The emulsion depends on the interaction between two phases: water phase and oil phase whereas wettability depends on three phases: water phase, oil phase, and solid phase (e.g., pipeline steel). For these reasons, a crude oil may have high EIP, i.e., may hold water in the water-in-oil phase, but as soon as the EIP is exceeded, water may drop out and wet the surface. On the other hand, the crude oil may have low EIP, i.e., water drops out of emulsion at low concentration, but metallic surface may continue to be oil-wet.

In the presence of oil-in-water emulsion or in the presence of free water phase, on a water-wet surface, corrosion may take place. The crude oil phase surrounding the water phase may influence corrosion rate by partitioning water-soluble species (Fig.3)²:

- If the water soluble species in oil phase is inhibitory in nature, then corrosivity of the aqueous phase would be less than that observed in the absence of oil phase. Under this condition, addition of corrosion inhibitor may not be necessary.

- If there is no water soluble species in present in the oil phase or the water soluble species does not have any influence of corrosivity of aqueous phase, then corrosivity of aqueous phase would be unaffected by the presence of oil phase. Under this condition addition of corrosion inhibitors may be necessary.
- If the water soluble species in oil phase is corrosive in nature, then the corrosivity of the aqueous phase would be more than that observed in the absence of oil phase. Under this condition the addition of corrosion inhibitors is necessary.

STANARDS FOR DETERMINING CORROSION INHIITOR EFFICIENCY

One of the primary criteria for selecting a chemical as corrosion inhibitor is its efficiency to control corrosion. Several laboratory methodologies are available for determining the efficiency of corrosion inhibitors.

Based on the comparison of laboratory and field data, a study ranked rotating cage (Fig. 4) as the most appropriate methodology to simulate field operating conditions¹². This study found that the rotating cage simulated both general as well as localized pitting corrosion observed in the field.

The method uses a well-defined rotating cage setup and determines the corrosion rates from mass loss measurements. ASTM Standard Practice G184 provides step-by-step procedures for evaluating corrosion inhibitor efficiency in a rotating cage apparatus³. Separate procedures for conducting the tests at atmospheric pressure and elevated pressure are provided in the standard.

ASTM G202 presents detailed procedure for conducting rotating cage test at atmospheric pressure. As part of developing this standard, ASTM coordinated round robin tests. Ten laboratories from Canada, India, USA, and Venezuela participated. All ten laboratories conducted the tests using rotating cage manufactured to the same specification, at same operating conditions, and for same duration of time. Each laboratory repeated the tests at least four times. Based on statistical analysis of more than 400 data points, ASTM established uninhibited general corrosion rate of carbon steel as 23 ± 2 mpy (0.58 ± 0.05 mm/y)⁵.

Rotating cylinder electrode (RCE) uses a well-defined rotating specimen setup and mass loss and/or electrochemical measurements to determine corrosion rates. Measurements can be made at a number of rotation rates to evaluate the inhibitor performance under increasingly severe hydrodynamic conditions. ASTM Standard Practice G185 provides detailed step-by-step procedures for evaluating corrosion inhibitor efficiency in a RCE apparatus (Fig.5)⁴. Separate procedures for conducting the tests at atmospheric pressure and elevated pressure are provided in the standard.

Jet impingement (JI) uses a well-defined impinging jet set up and mass loss and/or electrochemical measurements to determine corrosion rates. Figure 6 presents schematic diagram of flow pattern in a JI apparatus⁶. There are three different designs of JI. ASTM Standard Practice G208 describes details of these three designs and provides procedures for evaluating corrosion inhibitor efficiency in a JI apparatus.

Kettle (bubble) and wheel tests are used to evaluate corrosion inhibitor efficiency under low or no flow conditions. NACE report 1D196 describes procedures to carry out the kettle (bubble) and wheel tests. During the development of 1D196, NACE coordinated round-robin tests using kettle and wheel tests⁸. Most repeated ranking of three inhibitors was obtained in 5 out of the 9 laboratories for the wheel test and by 6 out of the 8 laboratories for kettle test. These results indicate that better reproducibility was

obtained in the kettle test (75% reproducibility) than the wheel test (55% reproducibility). NACE report 1D182 presents additional procedures for performing wheel test.⁷

EFC working party reports describe wheel test, bubble test, RCE, flow loop, jet impingement, and rotating cage methodologies to evaluate corrosion inhibitor efficiency.^{9, 10} These reports suggest bubble tests for preliminary screening, and RCE, flow loop, rotating cage, and jet impingement methodologies for final evaluation of corrosion inhibitors.

STANDARDS FOR EVALUATING SECONDARY CORROSION INHIBITOR PROPERTIES

Several other properties (commonly known as secondary inhibitor properties) are evaluated, before a chemical is used in the field as corrosion inhibitor. These properties include water/oil partitioning, solubility, emulsification tendency, foam tendency, thermal stability, toxicity, and compatibility with other additives/materials. ASTM Standard G170 describes methodologies and procedures to evaluate these properties¹¹. NACE Task group 330 is currently developing another report for providing guidelines to evaluate secondary properties of corrosion inhibitors.

STANDARDS FOR ELUSIDATING INHIBITOR AVAILABILITY

It is important to ensure that the inhibitor reaches the surface where corrosion takes place and forms protective film on it. This may not happen for several reasons; some of which are described in the following paragraphs.

Inhibitor film may not adequately form on the surface due to “logistic issues”, e.g., improper working of inhibitor injection pumps, inhibitor tank is not timely refilled, etc. No laboratory methodologies can be developed to provide solutions for logistic issues. They can only be overcome by implementing appropriate best practices in the field. Papers describing some industry best practices to overcome logistics issues are available³⁻¹⁵.

There are at least two types of corrosion mechanisms for which traditional methods of applying corrosion inhibitors would not ensure intact inhibitor film on the surface where corrosion takes place. They are “top-of-the line corrosion (TLC) and under-deposit corrosion (UDC). Though several laboratory methodologies have been developed, none of them adequately simulate the field conditions¹⁶⁻²⁰. Consequently, no consensus standard for evaluating corrosion inhibitors to control TLC and UDC currently exists; however, NACE TG 380 is currently developing a standard for simulating UDC.

HIERARCHY OF STANDARDS

Standards are developed by technical associations, such as NACE International, when practical knowledge has sufficiently matured and when the industry, regulatory body, and other stakeholders require them. Standards are developed so that methodologies/best practices can be uniformly adopted and implemented throughout the industry.

Standards are developed based on inputs and participation of many people who are knowledgeable of subject matter. They are mutually agreed upon minimum procedures/best practices with which suppliers, users, producers, third-party laboratories, academicians, and scientists are comfortable. They are based on the current state of knowledge on a particular subject matter. Standards have a fixed lifetime, i.e., they must be reapproved periodically (typically every 4, 5, 7, or 10 years).

Standards may be developed under various categories. With respect to inhibitor evaluation there are three categories of standards:

- Test Method (Gold)
- Standard Practice (Silver)
- Guide or Report (Bronze)

Table 1 presents various categories of standards available to evaluate corrosion inhibitors in the laboratory.

Test Methods (Gold) are the highest level of standards. They provide clear direction for using a methodology, step-by-step procedure, conditions of using the standard, and, more importantly, anticipated test result, i.e., the user must reproduce the anticipated results to demonstrate that they met the requirements of the standard. The anticipated results are determined based on round-robin tests conducted in several laboratories. The round-robin tests are completed before the Standard Test Method is published or within a short-duration after the standard is first published.

The Standard Test Methods present “repeatability” value, i.e., what is the variation in the result if the same operator repeats the same test following the same procedure. Normally four independent test data are used to establish the “repeatability.”

The Standard Test Methods also present “reproducibility” value, i.e., what is the variation in the result if different operators repeat the same test following the same procedure. Normally the reproducibility value is higher than the repeatability value, i.e., variation of the results is high when different operators are involved. For example, the uninhibited corrosion rate of (carbon steel in CO₂ saturated brine solution) 23 ± 2 mpy (0.58 ± 0.05 mm/y) presented in ASTM G202 is the reproducibility data. This data confirms that the reliable test data can be produced using rotating cage by different operators.

Because the corrosion rate in uninhibited conditions has been established in ASTM G202 Test Method, the users may simply specify a two-step procedure for evaluating corrosion inhibitors in commercial (third party) laboratories:

- Ensure that the ASTM G202 baseline general corrosion rate of 23 ± 2 mpy (0.58 ± 0.05 mm/y) is obtained under uninhibited conditions
- Identify an inhibitor that produces “XX%” of efficiency at “XX” ppm concentration with respect to the ASTM G202 baseline general corrosion rate.

It should be noted that the uninhibited general corrosion rate may vary if the conditions prescribed in the ASTM G202 are changed. Under this condition, the user may change the requirements as follows:

- Ensure that the ASTM G202 baseline general corrosion rate of 23 ± 2 mpy (0.58 ± 0.05 mm/y) is obtained under uninhibited conditions (This step may be used to qualify the laboratory, personnel, and apparatus)
- Repeat the test using the modified conditions prescribed
- Identify an inhibitor that produces “XX%” of efficiency at “XX” ppm concentration when tested under modified condition.

Standard Practices (Silver) present specific aspects of a methodology, step-by-step procedures to conduct tests using the methodology, and specific limitations of the methodology. However they do not provide anticipated results, i.e., the user of the standard should determine if all aspects of the standard are properly and adequately followed.

Guides or Reports (Bronze) are just state-of-the-art documents providing general guidelines on various aspects of the methodologies. They present general aspects of a methodology, general procedures to conduct test using the methodology, and general limitations of the methodology.

SUMMARY

1. Standards for evaluating corrosion inhibitors in the laboratory have been reviewed.
2. The hierarchy of various standards has been presented.
3. ASTM G202 on rotating cage methodology is currently the top-level (Gold) standard for evaluating the efficiency of corrosion inhibitors for oil field application.
4. Using ASTM G202 standard the most reliable corrosion inhibitor to control internal general and pitting corrosion can be selected.
5. Currently no Standard Test Method is available for any other laboratory methodologies to evaluate efficiency of corrosion inhibitors.
6. Currently no standard is available to evaluate corrosion inhibitors to control top-of-the line corrosion and underdeposit corrosion.

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TABLE 1: Categories of Standards to Evaluate Corrosion Inhibitors in the Laboratory

Evaluation of	Application	Standard category		
		Report/Guide (Bronze)	Practice (Silver)	Test Method (Gold)
Conditions to add corrosion inhibitor	To control general and pitting corrosion	<ul style="list-style-type: none"> • ASTM G205 		
Inhibitor efficiency	To control general and pitting corrosion	<ul style="list-style-type: none"> • NACE 1D182 • NACE 1D196 • EFC WPR 11 • EFC WPR 39 	<ul style="list-style-type: none"> • ASTM G184 • ASTM G185 • ASTM G208 	<ul style="list-style-type: none"> • ASTM G202
Secondary inhibitor properties	To avoid side effects from adding corrosion inhibitors	<ul style="list-style-type: none"> • ASTM G170 		
Inhibitor availability	To control top-of-the-line corrosion and under-deposit corrosion	No standard is currently available		

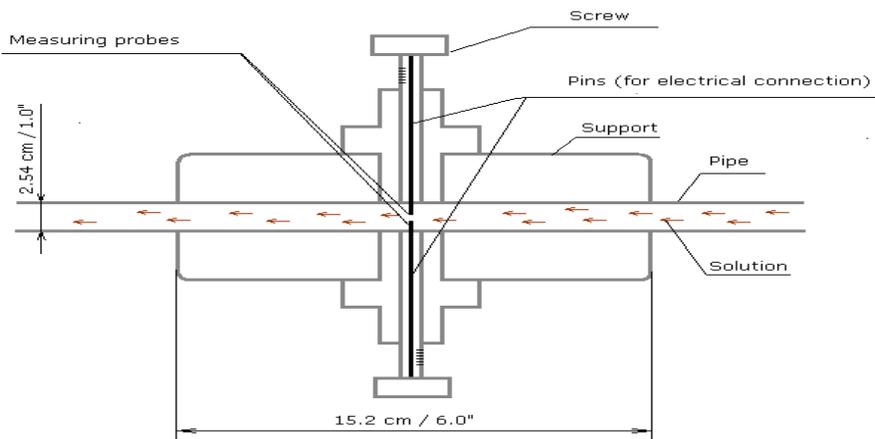


Fig. 1: Schematic Diagram of the Experimental Section of Emulsion Inversion Point Apparatus (ASTM G205)

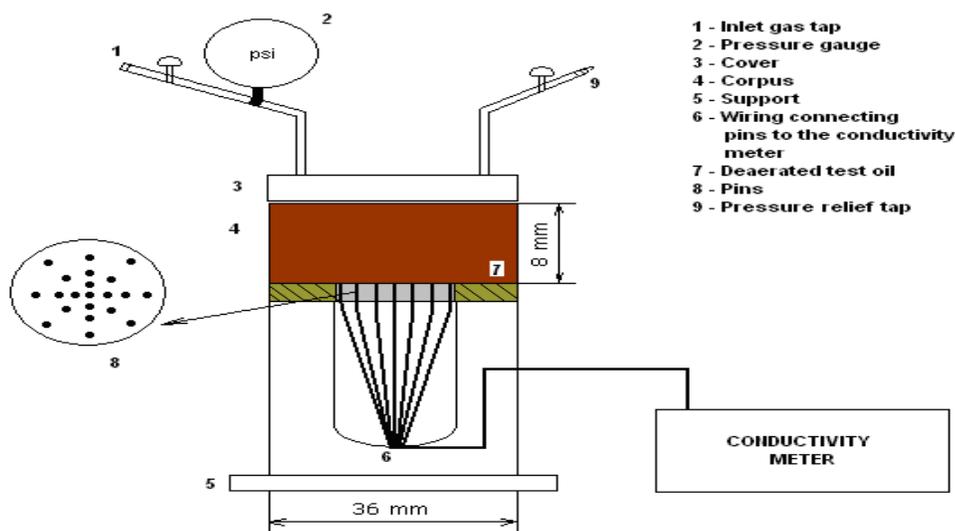


Fig. 2: Schematic Diagram of an Apparatus to Determine Wettability by Spreading Method

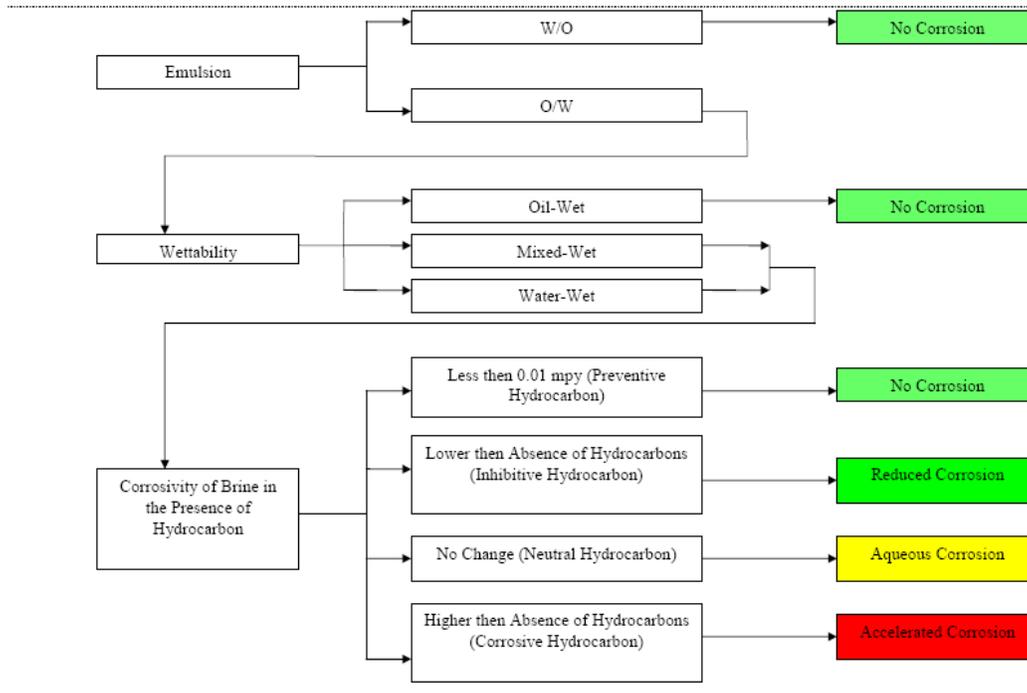


Fig. 3: Flow Chart to Determine the Condition to Apply Corrosion Inhibitor (ASTM G205)
 (Addition of corrosion inhibitors may not be necessary in the presence of preventive and inhibitor hydrocarbons but is necessary in the presence of neutral and corrosive hydrocarbons)

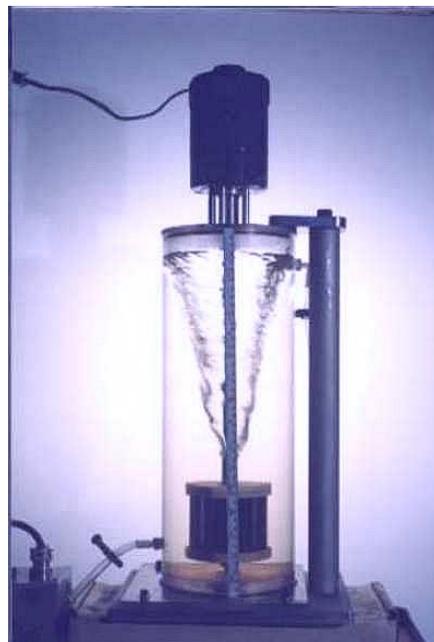


Fig. 4: Rotating Cage (ASTM G184)

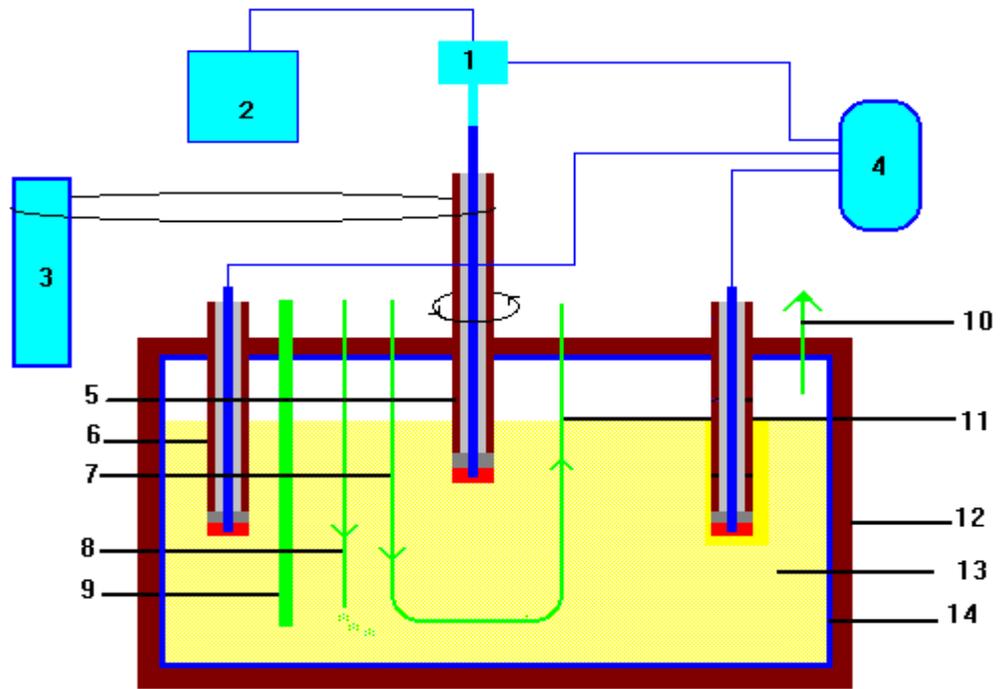


FIG.5: Schematic of a High-Temperature, High-Pressure RCE System: 1. Electrical Contact Unit; 2. Techometer (Rotation Speed Display) ; 3. Rotation controller; 4. Electrochemical Instruments; 5. Rotating electrode units (working electrode); 6. Reference Electrode; 7. Water Cooler Coil; 8. Inlet (Gases and Solution); 9. Thermocouple; 10. Outlet (Gases and Solutions); 11. Counter Electrode; 12. Autoclave Body; 13. Solution; and 14. TFE-fluorocarbon Liner (ASTM G185).

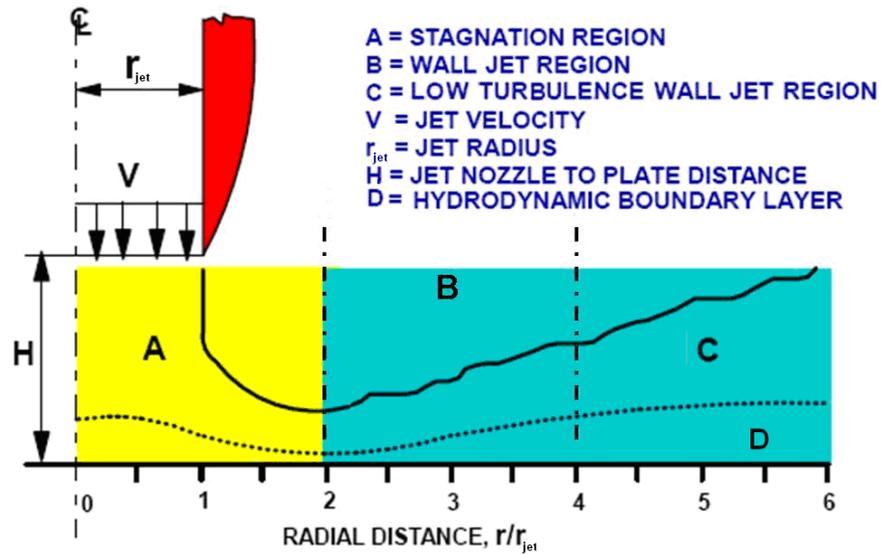


Fig. 6: Hydrodynamic characteristics of jet impingement on a flat plate showing the characteristic flow regions (ASTM G208)