

INSPECTION STANDARD
FOR
CORROSION SURVEY
AND
INHIBITOR EVALUATION

GENERAL REQUIREMENTS

0. INTRODUCTION

This inspection Standard which is contained in 2 parts deals with monitoring internal corrosion as follows:

Part 1: Gives guidance for on-line monitoring internal corrosion in plants associated with Oil, Gas and Petrochemical Industries.

Part 2: Gives guidance for laboratory monitoring concerning evaluation of corrosion inhibitors.

Additional specific guidance on corrosion monitoring is given in Appendix A.

Appendix B deals with an experiment for corrosion behavior of high alloy tubular materials in inhibited acidizing conditions.

1. REFERENCES

Throughout this Standard the following standards and codes are referred to. The editions of these standards and codes that are in effect at the time of publication of this Standard shall, to the extent specified herein, form a part of this Standard. The applicability of changes in standards and codes that occur after the date of this Standard shall be mutually agreed upon by the Company and the Vendor/Consultant/Contractor.

ASTM (AMERICAN SOCIETY FOR TESTING AND MATERIALS)

D 88	"Test Method for Saybolt Viscosity"
D 97	"Test Methods for Pour Point of Petroleum Oils"
D 482-87	"Standard Test Method for Ash from Petroleum Products"
D 1121	"Test Method for Reserve Alkalinity of Engine Antifreeze, Antirust and Coolants"
D 1076	"Test Methods for Acidity or Alkalinity in Rosin"
D 1217	"Test Method for Density and Relative Density (Specific Gravity) of Liquids by Bingham Pycnometer"
D 1298	"Test Method for Density, Relative Density (Specific Gravity) or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method"
D 1384-65	"Corrosion Test for Engine Antifreezes in Glassware"
D 1881	"Test Method for Foaming Tendencies of Engine Coolants in Glassware"
D 2162	"Method for Basic Calibration of Master Viscometers and Viscosity Oil Standard"
D 2550	"Test Method for Water Separation Characteristics of Aviation Turbine Fuels"
D 2570-66T	"Simulated Service Corrosion Testing of Engine Antifreezes"
D 2688-69 (23)	"Corrosivity of Water in the Absence of Heat Transfer (Weight-Loss Method)"
D 2776-69T (23)	"Corrosivity of Water in the Absence of Heat Transfer (Electrical Method)"
G 46-76	"Recommended Practice for Examination and Evaluation of Pitting Corrosion"

API (AMERICAN PETROLEUM INSTITUTE)

API RP 38	"Recommended Practice for Biological Analysis of Subsurface Injection Waters"
API RP 45	"Recommended Practice for Analysis of Oilfield Waters"

IPS (IRANIAN PETROLEUM STANDARDS)

IPS-E-EL-110	"Electrical Area Classifications and Method of Safeguarding"
--------------	--

NACE (NATIONAL ASSOCIATION OF CORROSION ENGINEERS)

TM0173	"Methods of Determining Water Quality for Subsurface Injection Using Membrane Filters"
RP0775	"Recommended Practice for Preparation and Installation of Corrosion Coupons and Interpretation of Test Data in Oil Production Practice"

2. DEFINITIONS AND ABBREVIATIONS

Auxiliary Electrode

An electrode commonly used in polarization studies to pass current to or from a test electrode. It is usually made of noncorroding material:

CUI	Corrosion Under Insulation
DLA	Double Layer Activation
ER	Electrical Resistance
HAZ	Heat Affected Zone
LPR	Linear Polarization Resistance

Corrosion Engineer

The person or persons responsible for carrying out the corrosion monitoring and interpretation of data produced.

PTFE	Polytetra-Fluorethyline
-------------	-------------------------

Potentiostat

An electronic device which maintains an electrode at a constant potential; used in anodic protection devices or to draw E Log I curves:

3. UNITS

This Standard is based on International System of Units (SI), except where otherwise specified.

CONTENTS :

PAGE No.

PART ONE: ON-LINE CORROSION MONITORING

1. SCOPE	3
2. REFERENCES	3
3. DEFINITIONS & ABBREVIATIONS.....	3
4. UNITS	3
5. GENERAL	3
5.1 The Concept of Corrosion Monitoring.....	3
5.2 Use of Corrosion Monitoring Data.....	3
5.3 Corrosion Monitoring Techniques.....	4
5.4 Selecting a Technique for Corrosion Monitoring.....	6
6. CORROSION MONITORING.....	8
6.1 General.....	8
6.2 Equipment.....	8
6.3 Safety	9
6.4 Techniques	9
6.5 Design Requirements	21
6.6 Automated System.....	25

PART TWO: EVALUATION OF CORROSION INHIBITORS

1. SCOPE	30
2. REFERENCES	30
3. DEFINITIONS & ABBREVIATIONS.....	30
4. UNITS	30
5. GENERAL	30
6. REASONS FOR INHIBITOR TESTING.....	30
7. INHIBITOR PROPERTIES.....	30
8. TEST CONDITIONS.....	31
9. DETECTION OF CORROSION.....	32
10. METHODS INVOLVING LOSS OF METAL.....	33
11. INDIRECT MEASUREMENTS FOR CORROSION DETECTION.....	34
11.1 Hydrogen Evolution.....	34
11.2 Current-Voltage Relationships	35

12. UTILIZATION OF FILM MEASUREMENTS.....	35
13. MISCELLANEOUS CORROSION TESTS.....	36
14. RESULTS OF THE TEST METHOD.....	36
15. FIELD TESTING OF INHIBITORS.....	38
16. ILLUSTRATIONS OF COMPLEX TESTING PROCEDURES NECESSARY TO SIMULATE FIELD CONDITIONS	38
16.1 Antifreeze for Internal Combustion Engines.....	39
16.2 Clear Packer Fluids for the Annulus of An Oil or Gas Well.....	39
16.3 "Wheel Test" Alternate Immersion in Two Mutually Insoluble Phases.....	39
16.4 Recirculating Cooling Water Test.....	43
17. INHIBITOR PROPERTIES OTHER THAN EFFECTIVENESS IN MITIGATING CORROSION	43
17.3 Influence of Density.....	43
17.4 Influence of Solubility.....	47
17.5 Surface-Active Characteristics	47
17.6 Testing for Solubility, Dispersibility, Emulsion Foaming.....	47
17.7 Formation of Sludges or Precipitates.....	48
17.8 Ecological Effects	48
17.9 Effects of Temperature	48

APPENDICES:

APPENDIX A MONITORING OF CORROSION INHIBITORS	50
APPENDIX B AN EXPERIMENT FOR CORROSION BEHAVIOR OF HIGH ALLOY TUBULAR MATERIALS IN INHIBITED ACIDIZING CONDITIONS	52

PART ONE

ON-LINE CORROSION MONITORING

1. SCOPE

This Part one of inspection standard gives guidance for on-line monitoring internal corrosion in plants associated with Oil, Gas and Petrochemical Industries.

2. REFERENCES

See general requirements.

3. DEFINITIONS & ABBREVIATIONS

See general requirements.

4. UNITS

See general requirements.

5. GENERAL

5.1 The Concept of Corrosion Monitoring

The concept of corrosion monitoring has developed from two distinct areas, plant inspection techniques (see Clause 6 of this Standard), and laboratory corrosion testing techniques (see Part 2), with the original aim of assessing or predicting corrosion.

5.2 Use of Corrosion Monitoring Data

5.2.1 To monitor the effectiveness of a solution

A logical extension of the diagnostic application is to use corrosion monitoring techniques to establish whether a solution has been effective. This can be done simply by continuing the original investigation, but more permanent installations are being used to an increasing extent to provide long term assurance. Such equipment is likely to be more sophisticated, since the information is recorded with other operational data and interpreted, in the first instance at least, by staff with a more limited corrosion knowledge.

5.2.2 To provide operational or management information

Corrosion can often be controlled by maintaining a single operational variable (e.g., temperature, pH, humidity) within limits determined by prior monitoring or other investigations. If the significant variable is measured for other reasons, this measurement can be used directly for corrosion control. If the variable is not otherwise measured, or in more complex cases where several variables interact, corrosion monitoring information can be used by plant operators to control plant operation so as to control corrosion. Any process change may have significant effects on corrosion, and corrosion monitoring techniques allow full scale trials to proceed with a minimum of risk to plant.

5.3 Corrosion Monitoring Techniques

A wide range of corrosion monitoring techniques is now available allowing determination of total corrosion, corrosion rate, corrosion state, analytical determination of corrosion product or active species, detection of defects or changes in physical parameters. Associated costs can be small where simple instrumentation and a few measurements are appropriate but in some cases may be extremely costly and require expert skills.

Much of the progress which has been made in the past few years has been due to advances in electronics which have allowed multiprobe measurement and recording at a tolerable cost. Instantaneous feedback of corrosion information can be obtained from various parts of the plant, which can be fed to the plant control room and/or plant computer to permit control of the necessary process variable to provide corrosion control. Table 1/1 indicates corrosion monitoring techniques available some of which is described in more detail. (See Clause 6 Part 1 and Part 2).

TABLE 1/1 - METHODS AND TECHNIQUES FOR CORROSION MONITORING

METHOD	MEASURES OR DETECTS	NOTES	USE
Linear polarization (polarization resistance)	Corrosion rate is measured by the electrochemical polarization resistance method with two or three electrode probes.	Suitable for most engineering alloys providing process fluid is of suitable conductivity. Portable instruments at modest cost to more expensive automatic units are available.	Frequent
Electrical resistance	Integrated metal loss is measured by the resistance change of a corroding metal element. Corrosion rates can be calculated.	Suitable for measurements in liquid or vapor phase on most engineering metals and alloys. Probes as well as portable and more expensive multichannel units are available.	Frequent
Potential monitoring	Potential change of monitored metal or alloy (preferably plant) with respect to a reference electrode.	Measures directly state of corrosion of plant, e.g., active, passive, pitting, stress corrosion cracking via use of a voltmeter and reference electrode.	Moderate
Corrosion coupon testing	Average corrosion rate over a known exposure period by weight loss or weight gain.	Most suitable when corrosion is a steady rate. Indicates corrosion type. Moderately cheap method with corrosion coupons and spools readily made.	Frequent
Analytical	Concentration of the corroded metal ions or concentration of inhibitor.	Can identify specific corroding equipment. Wide range of analytical tools available. Specific ion electrodes readily used.	Moderate
Analytical	pH of process stream	Commonly used in effluents. Standard equipment available through robust pH responsive electrodes such as antimony, platinum, tungsten can be preferable to glass electrodes. Solid Ag/AgCl is useful reference electrode.	Frequent
Analytical	Oxygen concentration in process stream.	Useful where oxygen control against corrosion using oxygen scavengers such as bisulfite or dithionite is necessary. Electrochemical measurement.	Moderate
Radiography	Flaws and cracks by penetration of radiation and detection on film.	Very useful for detecting flaws in welds. Requires specialized knowledge and careful handling.	Frequent
Ultrasonics	Thickness of metal and presence of cracks, pits, etc. by changes in response to ultrasonic waves.	Widely used for metal thickness and crack detection. Instrumentation is moderately expensive but simple jobs contracted out at fairly low cost.	Frequent
Eddy current testing	Uses a magnetic probe to scan surface.	Detects surface defects such as pits and cracks with basic instrumentation of only moderate cost.	Frequent
Infrared imaging (thermography)	Spot surface temperatures or surface temperature pattern as indicator of physical state of object.	Used most effectively on refractory and insulation furnace tube inspection. Requires specialized skills and instrumentation is costly.	Infrequent
Acoustic emission	Leaks, collapse of cavitation, bubbles vibration level in equipment. b) Cracks: by detection of the sound emitted during their propagation.	A new technique capable of detecting leaks, cavitation, corrosion fatigue pitting and stress corrosion cracking in vessels and lines.	Infrequent
Zero resistance ammeter	Galvanic current between dissimilar metal electrodes in suitable electrolyte.	Indicate polarity and direction of bimetallic corrosion. Useful as dewpoint detector of atmospheric corrosion or leak detection behind linings.	Infrequent
Hydrogen sensing	Hydrogen probe used to measure hydrogen gas liberated by corrosion.	Used in mild steel corrosion involving sulfide, cyanide and other poisons likely to cause hydrogen embrittlement.	Frequent in petrochemical industry
Sentinel holes	Indicates when corrosion allowance has been consumed.	Useful in preventing catastrophic failure due to erosion at pipe bends, etc. Leaking hole indicates corrosion allowance has been consumed.	Infrequent

5.4 Selecting a Technique for Corrosion Monitoring

Many techniques have been used for corrosion monitoring (see Table 1/1), it is clearly possible to develop others. Consequently when a possible new application is being considered, a problem arises in choosing the most appropriate technique. Each has its strong points and its limitations, and none is the best for all situations.

Any monitoring technique can provide only a limited amount of information, and the techniques should be regarded as complementary rather than competitive. Where more than one technique will give the information required, the information is obtained in different ways; a cross-check can be valuable and differences in detail can add meaning.

A corrosion monitoring technique rarely gives wrong information, unless the equipment used is faulty. "Nonsense" results arise because the information is correct, but irrelevant in the corrosion sense. The polarization resistance method, for example, measures the combined rate of any electrochemical reactions at the surface of the test sample. If the main reaction are the corrosion ones, the rate measured is the corrosion rate. If however, other reactions are possible at rates that are comparable or greater, the measured rate includes the other reactions. Useful deductions can still be made provided it is recognized that the corrosion rate has not been measured. The choice of a monitoring technique is a complex problem requiring expert knowledge. The first essential is to establish what type of information is needed. This necessarily involves an input from the management of the plant in question. The information below will give general guidance.

5.4.1 Where the primary objective is diagnosis in a new situation

Typically the nature of the corrosion processes involved and the controlling parameters are uncertain. It may be difficult to decide on the most appropriate technique, but it is in any case often advantageous to use more than one. The factors that actually prove to be significant are not always those which would have been expected.

One approach is to undertake a laboratory study to determine which parameters are likely to be important, the information being used both to decide which techniques should be used on the plant and to aid interpretation of the results obtained on the plant.

Alternatively, monitoring can be undertaken directly. The choice between these approaches depends on the availability of suitable laboratory facilities and staff with the necessary experience, and on the extent to which the problem is understood. In either case, it is sensible to check the information obtained by monitoring; by inspection before and after, or other means. Expert help is often necessary in interpretation of the results and may be desirable in planning the work and selection of techniques. However successful interpretation require knowledge of the plant and process in question as well as expertise in monitoring techniques and knowledge of corrosion.

5.4.2 Where the primary objective is to monitor the behavior of a known system

Applications of this type often follow one of the diagnostic type; alternatively the problem resembles other cases where monitoring has been used successfully. In either case, the choice of technique is based on past experience. Expert assistance may well be unnecessary even in interpretation of the results, unless unusual features appear.

In addition to choosing the technique, it is necessary to decide the degree of complexity that is appropriate. The basic monitoring equipment for most techniques is relatively simple, comprising a probe (the sensing element) and a measuring instrument. The equipment cost is relatively modest, as is the labor cost if only a few readings are required. The amount of information that can be obtained by this approach is limited, but may be sufficient. If not, additional probes can be installed and or more complex instrumentation introduced to enable automatic scanning, automatic recording or regular readings from one or more probes and control panel displays.

5.4.3 Criteria for selection of technique

Eight criteria on which the choice of a technique depends are summarized in Table 2/1 for the various corrosion monitoring methods and described as follows:

5.4.3.1 Time for individual measurement

Some techniques provide information that is effectively instantaneous, while others are necessarily slower in this respect.

5.4.3.2 Type of information obtained

Some techniques provide a measurement of corrosion rate, others measure total corrosion, or the remaining thickness, which is not exactly equivalent; yet others provide information on the distribution of corrosion on the corrosion regime.

5.4.3.3 Speed of response to change

Techniques which do not provide an individual measurement quickly are obviously unsuitable for situations where a fast response is required. Not all techniques that provide effectively instantaneous information are however capable of a fast response. Where the measurement is of rate, of corrosion regime, a fast response can be obtained, but if the measurement is of total corrosion, remaining thickness or distribution of corrosion, the speed of response is limited by the ability of the technique to discriminate between successive readings.

5.4.3.4 Relation to plant behavior

Many of the more effective techniques provide information on the behavior of a probe inserted into the plant, which does not necessarily reflect the behavior of the plant itself. The information obtained is in fact a measure of the corrosivity of the environment, from which plant behavior can be inferred. Other techniques provide an indication of the total corrosion in the system, with little or no indication of its distribution. Others give an accurate picture of a local corrosion pattern of the plant itself, but no information on what is happening elsewhere.

5.4.3.5 Applicability to environments

A fast response is most readily obtained from electrochemical measurements which require that the environment is an electrolyte; a high electrolytic conductivity is not always necessary however. Non-electrochemical measurements can be used in gaseous environments, or nonconducting fluids, as well as in electrolytes.

5.4.3.6 Type of corrosion

Most corrosion monitoring techniques are best suited to situations where corrosion is general, but some provide at least some information on localized corrosion.

5.4.3.7 Difficulty of interpretation

Interpretation of the results is often relatively straightforward if the technique is used within its limitations. The interpretation of the results obtained by some techniques is however, more difficult, and this is true of all techniques if they are used near the limits of their applicability.

5.4.3.8 Technological culture

Some techniques are inherently technically sophisticated; this tends to limit their use to organizations with a strong technological culture. Most others are much less demanding in this respect.

5.4.4 In principle, the available techniques could be ranked in an order of merit for each of these eight criteria. In practice, the relative merits change with circumstances so that a formal treatment of this type is potentially misleading. The most useful general approach is therefore, to consider the strengths and weaknesses of the techniques individually and Table 2/1 provides a reasonable starting point.

6. CORROSION MONITORING

6.1 General

6.1.1 Strategy

6.1.1.1 A comprehensive review of the process plant materials, corrosion allowances and operating conditions should be carried out to identify all areas which could be susceptible to significant corrosion within the projected lifespan of the plant. An assessment of the consequences of a corrosion failure occurring will be an integral part of the review. The identification of the specific corrosion processes likely to occur is essential to the selection of particular on-line corrosion monitoring devices to be used. The review should also identify those parameters which are instrumental in causing corrosion and which are likely to influence the corrosion rate. The results of the review should be used to develop a corrosion monitoring strategy encompassing the following:

- Identification and location of monitoring devices and their location.
- Prescribed monitoring frequencies.
- Agreed monitoring procedures.
- The allocation of responsibilities for:
 - a) ensuring that monitoring is carried out in accordance with the defined procedures,
 - b) the interrogation, storage and retrieval of the information recorded,
 - c) the presentation of detailed reports at the required frequency.

6.1.1.2 For new projects the corrosion monitoring requirements shall be established during the early development of the design.

6.2 Equipment

The selection of the specific on-line corrosion monitoring devices will be determined by the known or perceived corrosion processes taking place.

Individual corrosion monitoring devices provide only a limited amount of information. A minimum of two techniques should be used to monitor corrosion in order to provide complementary data. In addition the information provided by the corrosion monitoring devices should be supplemented by detailed operational data covering the monitoring period, chemical analysis of process fluids and equipment inspection records.

On-line internal corrosion monitoring should be undertaken using proprietary access fittings which permit the installation and removal of probes and coupons without the need for plant shutdown. The design and mechanical properties of such fittings must meet the requirements of the appropriate Standard(s) and Code(s) used for the design and construction of the plant being monitored

TABLE 2/1 - CHARACTERISTICS OF CORROSION MONITORING TECHNIQUES

TECHNIQUE	TIME FOR INDIVIDUAL MEASUREMENT	TYPE OF INFORMATION	SPEED OF RESPONSE TO CHANGE	RELATION TO PLANT	POSSIBLE ENVIRONMENTS	TYPE OF CORROSION	EASE OF INTER- PRETATION	TECHNOLOGICAL CULTURE NEEDED
Electrical resistance	Instantaneous	Integrated corrosion	Moderate	Probe	Any	General	Normally easy	Relatively simple
Polarization resistance	Instantaneous	Rate	Fast	Probe	Electrolyte	General	Normally easy	Relatively simple
Potential measurement	Instantaneous	Corrosion state and indirect indication of rate	Fast	Probe or plant in general	Electrolyte	General or localized	Normally relatively easy but needs knowledge of corrosion. May need expert	Relatively simple
Galvanic measurements (zero resistance ammeter)	Instantaneous	Corrosion state and indication of galvanic	Fast	Probe or occasionally plant in general	Electrolyte	General or unfavorable conditions localized	Normally relatively easy but needs knowledge of corrosion	Relatively simple
Analytical methods	Normally fairly fast	Corrosion state, total corrosion in system item corroding	Normally fairly fast	Plant in general	Any	General	Relatively easy but needs knowledge of plant	Moderate to demanding
Acoustic emission	Instantaneous	Crack propagation and leak detection	Fast	Plant in general	Any cavitation	Cracking, cavitation and leak detection, pitting	Normally	Crack propagation specialized, otherwise relatively simple
Thermography	Relatively fast	Distribution of attack	Poor	Localized on plant	Any. Must be warm or sub-ambient	Localized	Easy	Specialized and difficult
Optical aids (closed circuit TV, light tubes, etc.)	Fast when access available, otherwise-slow	Distribution of attack	Poor	Localized on plant	Any	Localized	Easy	Relatively simple
Visual, with aid of gages	Slow. Requires entry on shutdown	Distribution of attack indication of rate	Poor	Accessible surfaces	Any	General or localized	Easy	Relatively simple but experience needed
Corrosion coupons	Long duration of exposure	Average corrosion rate and form	Poor	Probe	Any	General or localized	Easy	Simple
Ultrasonics	Fairly fast	Remaining thickness or presence of cracks and pits	Fairly poor	Localized on plant	Any	General or localized	Easy	Simple
Hydrogen probe	Fast or instantaneous	Total corrosion	Fairly poor	Localized on plant or probe	Nonoxidizing electrolyte or hot gases	General	Easy	Simple
Sentinel holes	Slow	Go/no go remaining thickness	poor	Localized on plant	Any, gas or vapor preferred	General	Easy	Relatively simple
Radiography	Relatively slow	Distribution of corrosion	poor	Localized on plant	Any	Pitting possibly, cracking	Easy	Simple but specialized radiation hazard

6.3 Safety

Statutory and safety considerations relevant to the specific hazardous areas as cited in IPS-E-EL-110, where corrosion monitoring activities are being carried out, must be followed.

6.4 Techniques (see Table 3/1)

6.4.1 Weight loss coupons

Coupons may be used to determine the average fluid corrosivity by measurement of weight loss. Susceptibility to pitting, bimetallic corrosion, stress corrosion cracking, crevice corrosion, corrosion in weldments or Heat Affected Zones (HAZ), hydrogen embrittlement, scaling, erosion and cavitation may also be determined. The method facilitates an assessment of the corrosivity of an environment with respect to the specific material of construction of that part of the plant in which the corrosion monitoring is taking place.

The chemical composition and metallurgical condition of the coupon material should be as close as possible to that of the plant material. The results may be influenced significantly by the monitoring location within the plant and the position of the coupon(s) in the process stream, see NACE RP0775.

Careful consideration shall be given to the proposed monitoring location and coupon position during the development of the corrosion monitoring strategy.

The two most common types of weight loss coupon are strip and flush disc, although rods and rings may also be used in certain circumstances. Guidance on coupon selection, handling exposure times and evaluation are given in NACE RP0775.

Each coupon shall carry its own individual identification mark and be degreased and uniformly grit blasted prior to exposure. Where considered appropriate 'as finished' metal surfaces may be evaluated but these are likely to give inconsistent results.

For purposes other than weight loss from a single metal or alloy, (e.g. bimetallic corrosion, weldment corrosion, stress corrosion cracking) novel coupon designs will be required, appropriate to the corrosion phenomena being evaluated.

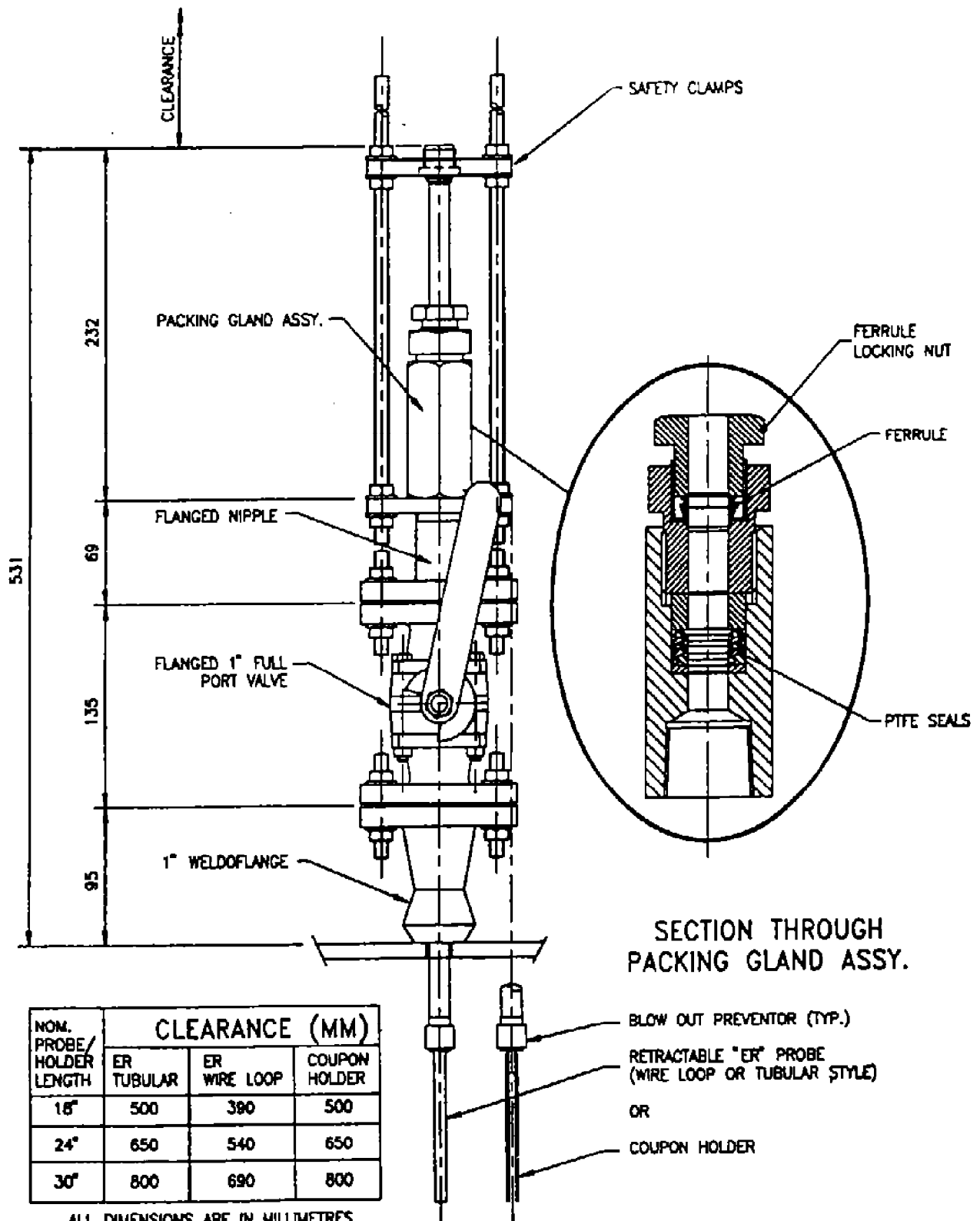
Coupons shall be attached to holders suitable for installation in low pressure or high pressure (50 mm) access fitting systems as appropriate (see Figs. 1/1 and 2/1).

Exposed coupons should always be visually examined for the type and uniformity of the attack both before and after chemical cleaning. Samples of corrosion product should be removed for detailed chemical analysis. Where pitting is the predominant form of attack the extent and type of pitting may be evaluated in accordance with ASTM G46-76.

6.4.2 Spool pieces

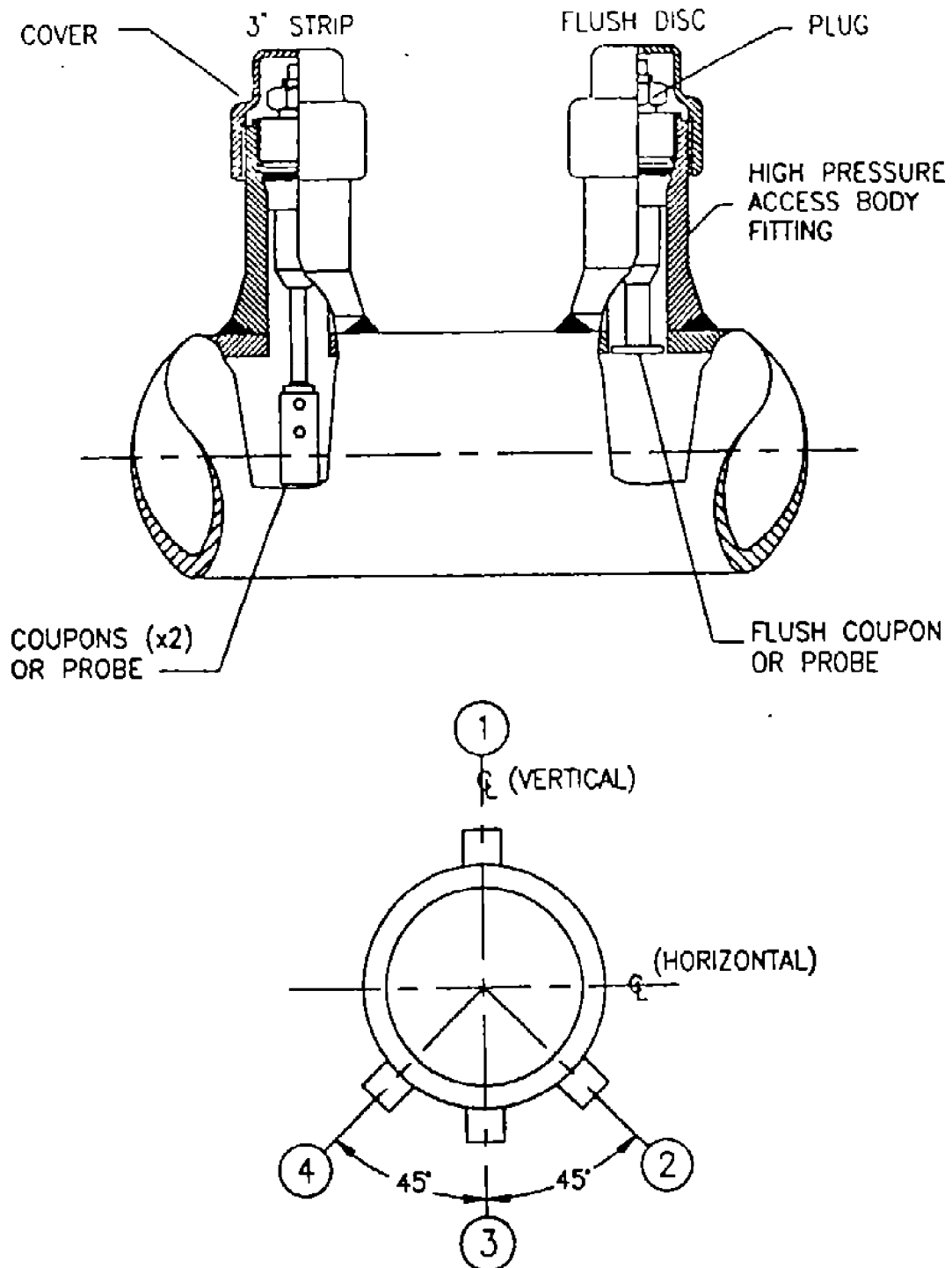
To obtain a direct assessment of the corrosivity of a process stream the piping system may be configured to include short lengths of flanged pipework (0.3 to 1.0 m) which can be removed periodically for internal inspection. These spool pieces should be fabricated from an identical piping material to the adjacent pipework.

Where spool pieces with different piping materials are to be evaluated, the extent of any galvanic couple between adjacent piping and spools must be assessed and electrical insulation requirements established as appropriate.



LOW PRESSURE ACCESS FITTING SYSTEM

Fig. 1/1



ARRANGEMENT OF COUPON AND PROBES INSTALLED IN HIGH PRESSURE ACCESS FITTINGS

Fig. 2/1

The piping spools shall be cleaned prior to exposure and may also be weighed, where the measurement of weight loss is considered practical. If weight loss is to be determined then the spools must be protected from external corrosion or mechanical damage while in service.

After exposure, the spool piece shall be cleaned internally using the methods described for corrosion coupons in NACE RP0775 and, where appropriate, re-weighed in order to calculate the overall corrosion rate. Sectioning will be required to enable a detailed visual assessment of the metal loss to be made. Localized corrosion shall be evaluated in accordance with ASTM G46-76.

6.4.3 Field signature method (electric fingerprint)

This comprises the measurement of the changes in an applied electric field within a pipe spool, caused by the loss of material from the inner wall due to internal corrosion. Field signature methods are commercially available.

Thin contact pins typically up to 64 in number are welded or cemented to the outside of the pipe wall in a configuration which will be determined by the position and the pattern of internal corrosion expected. Each pin is connected to a data acquisition unit which monitors the potential difference generated between individual pairs of pins as a consequence of the application of an external current between two auxiliary pins spanning the measurement pin configuration. Using appropriate software the change in the 'fingerprint coefficient' with time for each pair of pins enables a graphical representation of the corrosion pattern to be developed with quantitative estimates of the loss in wall thickness across the area covered by the pin array.

The technique has the advantage that it measures the actual corrosion taking place within the process system regardless of process fluid type and with a high degree of sensitivity without the need for access fittings, intrusive probes and retrieval operations.

Removal of the spool piece for confirmation of the pattern and extent of corrosion being indicated is recommended. This will normally have to coincide with a plant shutdown.

Careful thought must be given to the overall pattern and the individual spacing of the pins in order to generate the optimum information from the data recorded.

The magnitude of the current applied between the auxiliary pins is dependent upon wall thickness and needs to be adjusted accordingly to maximize the accuracy of the data.

6.4.4 Electrical resistance probes

Electrical Resistance (ER) probes measure the change in electrical resistance of a sacrificial element exposed to the process fluid relative to a reference element sealed within the probe body. If the probe corrodes uniformly the change in resistance of the exposed element over a fixed time period is directly proportional to the average corrosion rate for that period.

Successive readings must be compared in order to determine fluid corrosivity over the intervening period. Electrical resistance probes may be used to measure the corrosivity of both conductive and non-conductive liquids and vapours. There are three main types:

- Tubular element
- Wire loop
- Flush

Of the three types the tubular element is the most commonly used. Wire loop probes are less robust than their tubular element counterparts and are more susceptible to mechanical damage. Flush mounted probes can suffer preferential crevice attack at the steel element/potting compound interface which can give rise to unrepresentative corrosivity data.

Under high velocity process conditions tubular element and wire loop probes may require velocity shields for protection. However, velocity shields are prone to debris accumulation with attendant spurious results from the probe and their use should be limited accordingly.

Wire loop or tubular element electrical resistance probes, fitted with velocity shields which extend the full length of the probe body, shall not be used in conjunction with low pressure access fittings on hydrocarbon, or other hazardous duty.

There is a risk that an uncontrolled fluid release could occur on retracting the probe, should the velocity shield fail by a corrosion related or other mechanism.

6.4.5 Electrochemical probes

The Linear Polarization Resistance (LPR) technique is based upon the measurement of the “apparent resistance” of a corroding electrode when it is polarized by a small voltage of the order of 10 millivolts. The ‘apparent resistance’ is determined from the current flowing as a consequence of the small applied voltage and is inversely proportional to the corrosion rate. LPR probes have the advantage over electrical resistance probes in that they provide an instantaneous measurement of fluid corrosivity. However, they can only be used to measure the corrosivity of “clean” low resistivity process fluids under conditions of continuous immersion.

The limits of operation of the technique are also governed by the expected corrosion rate and advice should be sought from the probe supplier.

As the electrochemical characteristics of LPR probe elements may change with corrosion of the elements, probes should be replaced on a more frequent basis (than for electrical resistance probes) in order to ensure that consistent data is being produced.

LPR probes may also suffer from “shorting out” due to the accumulation of debris or corrosion products bridging the gap between the electrodes.

LPR probes are available in the form of two or three rod like electrode assemblies with the rods protruding into the process stream. Three electrode assemblies are used where a high corrosion rate is anticipated in a low conductivity fluid and where there would be a significant contribution to the measured polarization resistance from the electrolyte resistance. Three electrode probes are normally used where the fluid conductivity is less than 100 micro mhos (fluid resistivity greater than 10^4 ohm cm). Flush mounted versions are also available in various two electrode configurations. As with electrical resistance probes the flush mounted versions can be susceptible to crevice corrosion at the electrode/potting compound interface and may give unrepresentative corrosivity values.

6.4.6 Electrochemical noise

This technique of corrosion monitoring utilizes three electrode linear polarization probes but is more sensitive than LPR measurement. It records the random fluctuations in current and/or potential (electrochemical noise) generated by corrosion reaction taking place at the surfaces of the probe elements. Unlike the LPR method the electrodes are not polarized but allowed to corrode freely in the process stream. The technique is very sensitive to changes in processing conditions which affect the corrosivity of the fluids and is particularly useful for optimizing corrosion inhibitor/chemical treatment programs.

However, as the same probe configuration is used for the measurement of electrochemical noise as in the LPR method the technique suffers from the same disadvantages.

6.4.7 Solid particle impingement probes

Sensors for the evaluation of solids entrained in fluid systems are available in two versions, intrusive and non-intrusive as follows:

Intrusive solid particle impingement probes are available which can be located within standard 5.08 cm (2") high pressure access fittings. These probes work on a similar principle to electrical resistance probes in that the change in electrical resistance with time due to the abrasive wear of the probe element is taken as proportional to the solids concentration of the fluid.

Derived formulas which include the average particle size, the flow velocity and, where applicable, gas liquid ratio enable a measure of the solid particle concentration to be made. In general this type of probe suffers from problematic sensitivity-lifespan relationship. Probes sensitive enough to give useful data require frequent change out due to their finite lives.

Non-intrusive solid particle impingement probes comprise a sensor which is strapped to the outside of the pipe wall in an area where particle impingement is judged to be greatest. Two types of sensor can be used to detect particle impacts; ultrasonic and stress wave.

Ultrasonic sensors record the magnitude of the noise generated by the particle impacts and appropriate computer software is used to convert the ultrasonic signals to give a measure of solid particle content. In the alternative technique stress wave sensors in acoustic contact with the pipe wall count the number of acoustic pulses generated by the particle impacts on the inner wall of the pipe. The acoustic pulses or stress waves generated have a typical frequency of 500 kHz. Stress wave sensors have the advantage that the pulse counting method suppresses the influence of erroneous signals produced by, for example, pipe vibration, which can be a significant problem with ultrasonic sensors.

6.4.8 Hydrogen probes and patch monitors

Hydrogen is the product of corrosion reactions in many systems, but most significantly where the process streams contain water and H_2S , HCN or HF .

The combination of hydrogen atoms to form hydrogen gas at the corroding metal surface is retarded by certain anions, the most common being sulphide, cyanide and fluoride. These anion thereby promote the diffusion of atomic hydrogen into the steel substrate.

Methods of measuring the rate of diffusion of atomic hydrogen into structural materials are available in two forms, either as thin walled tubular probes inserted directly into the process stream through standard 5.08 cm (2") high pressure access fittings or as patch detectors clamped or welded to the outer pipe or vessel wall.

Intrusive thin-walled hydrogen probes collect the hydrogen diffusing through the wall of the probe element. An integral pressure gage is used to monitor the pressure build up arising from arrival of atomic hydrogen at the inner wall of the probe element where the atoms combine to form hydrogen gas. The rate of pressure build up can be related to the potential for hydrogen damage occurring in the vessel or piping materials. A period of stabilization is required to enable the tubular element to saturate with atomic hydrogen before meaningful data can be accumulated.

There are two types of non-intrusive hydrogen patch probes. The first comprises a carbon steel patch contoured to fit the outside of the vessel or pipe and welded to it.

The patch is fitted with temperature and pressure gages and the quantity of hydrogen diffusing directly through the vessel or pipe wall is measured by logging the rate of increase in pressure within the patch envelope in an analogous manner to the tubular element hydrogen probe. The second type of patch probe is mounted directly onto the vessel or pipe wall using mechanical straps.

The probe comprises a small electrochemical cell with one electrode, a thin inert metal foil, usually palladium, in direct contact with the pipe wall. As the hydrogen diffuses through the vessel or pipe wall and the metal foil it is electrochemically oxidised on the inner face of the foil which is in contact with the cell electrolyte. The current flowing in the cell is directly proportional to the rate of hydrogen permeation through the wall of the equipment and provides a direct measure of hydrogen activity.

As with the other types of hydrogen probes described above the electrochemical patch probe requires an initial stabilization period. In addition it requires regular maintenance in the form of electrolyte replenishment and/or renewal.

6.4.9 Galvanic probes

Probes comprising two dissimilar metals may be used to assess the corrosivity of a conductive process fluid. The natural current flow between the two metals is measured using a zero resistance ammeter and the magnitude of the current gives a measure of fluid corrosivity.

Direct correlations between the corrosivity of the fluid measured by a galvanic probe and the performance of the less noble constituent of an equivalent bimetallic couple which exists within the process plant should be made with care as the surface area ratio between the two metals is critical in determining the magnitude of the galvanic effect.

Conventional galvanic probes comprising a brass cathode and mild steel anode are sensitive to the concentration of oxidizing species in conductive fluids and may be used to monitor the level of dissolved oxygen and the effectiveness of oxygen scavengers in water injection and cooling water systems.

Galvanic probes comprising parent metal, weld metal and heat affected zone combinations may be used to assess the potential for preferential weldment corrosion within the process streams.

Such probes may comprise either 5 or 6 elements with the galvanic current between the various combinations of electrodes being recorded using a zero resistance ammeter.

Care is required in the manufacture of the probe elements to ensure that the welding processes used are comparable with those used in plant fabrication. Such probes are able to indicate the effect of changes in composition of the process fluids on the relative susceptibility of parent metal, heat affected zone and weldment to internal corrosion.

6.4.10 Electrical potential monitoring

The measurement of the electrical potential between the piece of process equipment (or a probe of the same material) and a fixed reference electrode will provide information on the corrosion risks. The technique requires that the process fluid be conductive and the electrochemistry of the system well understood. Potential monitoring does not give a measure of the corrosion rate, but will indicate the onset of active corrosion from an otherwise passive state due to changes in the processing conditions where a clearly defined active-passive transition exists.

For practical purposes a robust and stable reference electrode must be selected. The location of the test probe and the reference electrode may be critical to the provision of reliable information and require careful consideration.

High impedance voltmeters (> 1 megohm) should be used to record potentials in combination with a chart recorder.

6.4.11 pH probes

In aqueous process streams where the control of pH is critical either to the efficiency of the process or the resistance of the plant materials to corrosion, pH measurements may be used in conjunction with chemical treatment programs.

The removal of process fluid samples to a laboratory for pH measurement is not a reliable method of determining the system pH since the pH of the sample may alter considerably as a consequence of the sampling procedures. For many applications on-line monitoring using pH probes is the only reliable method of monitoring unit or system pH.

The distance between the off-take point and the probe location should be kept as short as possible to minimize pressure drops which will affect the reliability of the pH measurement. The flow control and flow monitor should be placed downstream of the probe location to avoid sudden pressure drops which will encourage the release of gas from solution, the formation of gas pockets and gas blocking of the probe element. For similar reasons long and tortuous sidestreams should be avoided. High flow rates through the sidestream will be beneficial in preventing the fouling of the probe element.

pH probes are prone to fouling, require frequent cleaning and calibration and are more suited to installation in sidestreams or off-take lines rather than in a main process line or vessel.

6.4.12 Measurement of dissolved gases

Electrochemical probes are available which measure the concentration of dissolved oxygen in both conducting and non-conducting media. Care has to be taken in the selection of probe type as with some the elements are easily poisoned by certain species within the process fluid.

The more reliable probes comprise a thin membrane which is porous to oxygen. The oxygen diffuses through the membrane and dissolves in the small body of electrolyte within the probe. The oxygen within the electrolyte is electrochemically reduced at an inert electrode and the corresponding current which flows between this and an auxiliary electrode gives a measure of the concentration of dissolved oxygen in the process fluid.

Dissolved oxygen probes should not normally be inserted directly into the process stream but fitted into a small flow chamber connected to a sidestream or a process fluid off-take point.

Proprietary kits may be used for the rapid on site determination of oxygen, carbon dioxide and hydrogen sulphide levels in aqueous process fluids.

The kits employ vacuum sealed glass ampoules containing chemical reagents. Breaking the glass tip on the ampoule while the tip is submerged in a process fluid test sample admits a small volume of the sample into the tube where a chemical reaction occurs resulting in the development of a characteristic color. The intensity of the color is used to determine the concentration of dissolved gas in the sample either by using a multifilter photometer and calibration chart or directly using a series of comparators.

6.4.13 Pipeline inspection tools

The corrosivity of fluids being transported along subsea or buried onshore pipelines can be assessed using standard monitoring techniques at accessible locations, which are usually limited to each end of the pipeline. However, detection of localized corrosion of the pipe wall requires the use of intelligent pigs.

There are two principle types of inspection vehicle used to survey the internal and/or external condition of steel transmission pipelines. The first involves the direct measurement of wall thickness by ultrasonics. The second uses an induced magnetic flux in the pipe wall to assess the defect size from the perturbation caused by defects. Both techniques require the pipe internals to be thoroughly cleaned and free of deposits for them to function successfully.

Ultrasonic pigs have the advantage that they measure wall thickness directly. There is also no practical limit to the pipe wall thickness that can be measured and the results are not affected by the proximity of girth welds.

They have the disadvantage that as with all ultrasonic measurements a couplant is required between the sensing head and the pipe wall. This means that for successful use in gas lines ultrasonic pigs require to be run in slugs of a couplant such as methanol or glycol, or behind a gel pig.

In older pipelines where significant internal wastage has occurred the reliability of ultrasonic pigs is questionable due to the reduced intensity of the reflected signal from the non-planar surface.

Magnetic flux pigs can be run in liquid and gas lines, but rely upon previous wall thickness calibrations taken by direct measurement using ultrasonics, or by reference to pipe manufacturer's data sheets. The maximum wall thickness capabilities for the more sophisticated designs are typically 15 mm for 10 inch ID pipe and 30 mm for 30 inch ID pipe.

The assessment of the material thickness in the weld area is affected by changes in the profile and the thickness of the pipe material and accuracy is therefore reduced at these locations. In addition the results are also affected by external welded attachments.

For new pipelines a base line survey should be considered during the pre-commissioning phase to enable construction defects to be discounted in future surveys.

Surveys using intelligent pigs should be carried out throughout the life of a pipeline. More frequent surveys are to be expected during the early part of the life of a pipeline, becoming less frequent once a level of confidence has been established regarding the corrosivity of the fluids and/or the effectiveness of any corrosion inhibitor treatment program.

Before a pipeline is surveyed using an intelligent pig for the first time, the feasibility of the pipeline for pigging must be assessed. This must include a review of pig launcher and receiver suitabilities and pipeline contours along the full length.

A comprehensive cleaning program will normally be essential prior to the survey for optimum data capture internal gaging may also be justified.

6.4.14 Ultrasonic thickness measurement

Conventional compression wave ultrasonics may be used to measure the residual wall thickness in pipework and vessels handling potentially corrosive fluids. The measurement accuracy depends upon the actual wall thickness and the condition of the outer surface of the pipe or vessel in contact with the probe, but will typically be ± 0.5 mm.

Correlations of actual pipe wall wastage can be made with data from the installed intrusive corrosive monitoring devices, but care has to be taken in deriving corrosion rates from ultrasonic wall thickness data in view of the limited accuracy of the technique.

The precise locations on the pipe or vessel being examined should be permanently marked in order to ensure that successive ultrasonic readings are always taken at the same location.

In critical situations where high corrosion rates are anticipated over a small area, solid coupled probes may be welded directly onto the pipe or vessel at the suspect locations in order to permit continuous monitoring of wall thickness. The proposed welding procedures shall be submitted for approval prior to the probe attachment.

One commercial solid coupled probe is available from AGA Technology. Where internal metal loss occurs over a wide area, automated and manual ultrasonic scanning techniques are available to develop visual displays of the extent and depth of the metal loss.

6.4.15 Radiography

As an alternative to ultrasonics, radiography may be used to examine the internal condition of process pipework and supplement the information on fluid corrosivity received from other monitoring methods.

It is particularly useful for the examination of preferential corrosion at weldments and erosion at bends, but the limited accuracy renders it suitable only for the detection of significant changes in pipe wall thickness.

Due to the absorption of the incident radiation by liquids as well as the pipe wall, its use on-line is limited to small diameter process streams containing vapors or gases. Under normal circumstances radiography is impractical for examining pipework larger than 8" diameter.

6.4.16 Sidestream monitoring

Sidestream monitoring encompasses the temporary use of a by-pass spool or off-take from the main process stream being monitored to provide supplementary information to that produced by the on-line monitoring devices. Sidestream monitoring may be used to examine the short term effect of chemical additives or process changes upon the electrochemistry of the plant material-process fluid system.

The sidestream equipment should comprise one or more probe or coupon holders and flow control and metering devices. It should be used to supplement on-line corrosion monitoring methods and should not be used in isolation unless on-line methods are not practical.

6.4.17 Visual inspection

The visual inspection of vessel and equipment internals during periods of plant shutdown should be used to supplement information from on-line corrosion monitoring activities.

6.4.18 Failure analysis

All plant and equipment failures should be thoroughly investigated, documented and reviewed in conjunction with the results of on-line corrosion monitoring activities.

6.4.19 Bacterial methods

In order to measure the propensity for microbial corrosion in a process system it is necessary to quantify both the mobile (planktonic) bacteria and the surface adhering (sessile) bacteria. The mobile bacteria may be enumerated by removing a sample of liquid from the process stream into a clean sterilized container and carrying out a serial dilution test in the laboratory.

The tendency for sessile population development within a system should be assessed by using a bioprobe exposed to the process stream through a standard 5.08 cm (2") high pressure access fitting. Biofilms may also be removed from standard strip coupons protruding into the process stream.

As bacterial corrosion relies upon the development of bacterial colonies upon the metal surface it is the determination of sessile populations which is most important in deciding whether or not a problem exists. Bioprobes typically carry 6 removable studs on which the biofilms are allowed to develop. Removal of the studs from the bioprobe enables the growth of sessile populations to be quantified and may provide additional information on the morphology of the corrosion to be expected in the system. Typical exposure times for bioprobes for development of biofilms is 2 to 4 weeks.

The corrosion of mild steel as a consequence of the growth of sulphate reducing bacterial populations is characterized by the formation of iron sulphide scale, which can be fairly easily detached to reveal shiny, almost hemispherical confluent pits. As sessile microbial populations tend to develop predominantly in areas where flow rates are very low, probes should be fitted into deadlegs or other stagnant locations.

The recommended method for examining water samples for evidence of sulphate reducing bacteria in the laboratory is described in API RP 38. In the field a technique known as serial dilution testing may be used to determine order of magnitude concentrations of mobile microbial populations in water samples.

The serial dilution method uses the same media to culture bacterial populations as does the method described in API RP 38. The technique may be modified slightly to interrogate surface deposits removed from bioprobe studs.

The serial dilution test for a liquid sample is as follows:

A sample of water is removed from the process stream into a clean sterilized and stoppered borosilicate glass container. A 1 ml sample of this liquid is introduced into a sterilized syringe and injected into a sealed bottle of a selected culture medium (serial bottle). Following vigorous shaking a 1 ml sample is taken from the serum bottle and introduced into a second serum bottle using a fresh sterilized syringe. This procedure is repeated with a sample from the second serum bottle introduced into a third bottle, and so on until 5 serum bottles have been inoculated. The 5 bottles are then incubated at a temperature within 5°C (41°F) of the process stream for a 28 day period. Bottles indicating bacterial growth will discolor. The data relating to the concentration of bacteria is dependent upon the number of bottles that have discolored and is reported as the number of colonies over a range from 10/ml to 100,000/ml if a 5 bottle series is used.

The main drawback with the serial dilution method is the time taken to incubate the colonies. The serial dilution test should be carried out at least twice on each sample of water or surface deposit.

More rapid semi-quantitative techniques are available in kit form for detecting bacteria responsible for corrosion where their presence within a process stream or storage area is suspected.

These techniques are as follows:

A test using the enzyme hydrogenase is available to measure the activity in the bacterial population. In this test sulphate reducing bacteria employs the hydrogenase in a microbially induced corrosion reaction.

Samples of corrosion product or sludge from bioprobes or the internal surface of the process equipment are exposed to an enzyme extracting solution. After filtering, the enzyme is chemically reduced in an anaerobic chamber. The hydrogenase activity and hence the level of bacteria is assessed by the intensity of color from an indicator dye in the enzyme extracting solution.

Results are available within 24 hours. The results obtained from this test cannot be compared directly with results from other test methods.

Another indirect test measures the bacterial population density by determination of the enzyme adenosine phosphosulphate reductase, present in the bacteria.

Measurement of this enzyme, is again by color intensity, but uses a color interpretation card. The approximate population density can be determined with a detection threshold of 10^3 sulphate reducing bacteria per ml of liquid sample.

Test results can be available within 15 minutes of sampling and show reasonable correlation with those from serial dilution tests.

Enumeration of sessile bacteria begins with the removal of the bacteria from the monitoring stud. This may be accomplished on site by scraping with a scalpel, or by swabbing. A sterile field water solution should be used to collect the removed bacteria for enumeration by one of the above methods.

Sampling for bacterial populations should be accompanied by the following:

Recording of the date, time and sampling location. Measurement of the sample temperature, pH, dissolved oxygen and H_2S in the sample. Recording of the concentration of any production chemicals present. Recording of the appearance of the sample in particular the presence of slimes, turbidity, color, and smell.

Since bacterial populations may undergo quantitative changes within sample bottles, samples should be analyzed with minimum delay to obtain reliable information.

6.4.20 Measurement of dissolved solids

The measurement of process fluid corrosivity should be supported by measurements of the chemical composition of the different fluid phases present since fluid composition can have an important influence upon corrosion rates, hydrogen damage, stress corrosion cracking, etc.

In aqueous solutions the determination of ions such as Fe^{++} , Cu^{++} , Zn^{++} , Al^{+++} , Ca^{++} , Cl^- , SO_4^{--} , S^{--} , CO_3^{--} may be carried out either by spectrophotometry, colorimetry or by conventional analytical techniques.

The quantitative analysis of non-aqueous samples should be carried out after first ashing the sample in accordance with ASTM D482.

Samples of liquid for analysis shall be taken from the process stream into clean, stoppered borosilicate glass container(s). Reagents shall be used so that the ions under test form stable suspensions or complexes. The resulting turbidity or intensity of color change shall be determined by photoelectric colorimeter or spectro-photometer and compared to a curve prepared from standard solutions.

Care shall be taken to ensure that other dissolved ions do not interfere with the formation of the suspension(s) or complex(es), giving rise to spurious results.

Detailed test methods and procedures are given in ASTM Publication "Water and Environmental Technology" Section II, Volumes 01 and 02 and API RP45.

6.4.21 Measurement of suspended solids

The measurement of suspended solids should be carried out where necessary as part of a water quality assessment.

In oilfield water injection systems for example, where plugging of a tight formation could result, suspended solids must be kept to a minimum. The measurement may also be used as an indication of deteriorating water quality due to bacterial action and/or corrosion in the system.

The measurement of suspended solids may be undertaken by filter analysis, turbidity meter or other instruments measuring size and density of particles. Membrane filters are the most suitable for carrying out suspended solid determinations on water which is allowed to flow directly from the process stream.

Methods of determining oilfield water injection quality are described in NACE Standard TM0173.

6.4.22 Corrosion product analysis

The measurement of fluid corrosivity using probes and coupons should be supplemented by the chemical analysis of any corrosion products or deposits which are found either on the probes and coupons or on the internals of the process equipment during plant inspections.

The following techniques may be used to examine corrosion products.

- Visual examination
- Magnetic examination
- Microscopy
- Wet chemical analysis
- Spectroscopy
- X-ray diffraction and elemental analysis.

The collection, handling and storage of corrosion products should be in such a manner as to avoid contamination and/or degradation of the sample. Detailed examination should be carried out as soon as possible after removal from the system.

Recommended procedures for the collection and identification of corrosion products are given in NACE Standard RP0173.

6.5 Design Requirements

6.5.1 General

A corrosion monitoring philosophy shall be established based upon a detailed review of the process conditions and plant materials. The potential corrosion problems arising from both routine and non-routine operation of the plant shall be assessed in order to determine areas which may be affected. The actual process streams to be monitored and the monitoring devices to be used shall be based on this assessment.

6.5.2 Access fitting location

As far as practical access fittings should be installed on horizontal process lines in a vertical aspect as shown in Position 1 in Fig. 2/1.

Bottom of the line access fittings show a tendency to accumulate debris which may give unrepresentative monitoring results. It can also result in galling of the threads on the monitoring device and/or the fitting which could ultimately render the fitting unusable.

Where bottom of the line fittings are unavoidable, flanged access fittings may be used in place of flare weld fittings to enable the fitting to be replaced should problems be encountered.

In sour systems iron sulphide deposits may cause galling problems regardless of the position of the access fitting and flanged fittings should always be used on such service.

Access fittings should be located a minimum distance of 7 pipe diameters downstream and a minimum of 3 pipe diameters upstream of any changes in flow caused by bends, reducers, valves, orifice plates, thermowells, etc. Where access fittings are installed in pairs there should be a minimum distance of 1 meter between each fitting. Where the monitoring devices are intrusive and comprise a probe and a coupon holder, the probe should be located in the upstream fitting to minimize turbulence around the second monitoring device.

TABLE 3/1 - GENERAL GUIDE TO THE APPLICATION OF CORROSION MONITORING TECHNIQUES

	Weight Loss Coupons/ Spool Pieces	Corrosion Product Analysis	Electrical Resistance Probes	Electrochemical (LPR) Probes	Galvanic Probes	Bacterial Monitoring	Suspended Solids	Dissolved Solids	Dissolved Gases	pH	Potential Measurement	Hydrogen Probes Patch
Seawater Injection and Cooling Systems	✓	✓	✓	✓	✓	✓	✓3	✓	O ₂ only	✓	x	x
Produced Water Treatment and Injection Systems	✓	✓	✓	x	x	✓	✓4	✓	CO ₂ , H ₂ S	✓	x	x
Aquifer Water	✓	✓	✓	1	x	✓	✓	✓	CO ₂ , H ₂ S	✓	x	x
Unstabilized Crude Oil	✓	✓	✓	x	x	x	x	x	x	x	x	✓6
Hydrocarbon Gas	✓	✓	✓	x	x	x	x	x	x	x	x	✓6
Crude Distillation Units & Associated Pipework	✓	✓	✓	x	x	x	x	x	x	✓	x	✓7
Fluidised Catalytic Cracker Unit, Fraction- ation and Light Ends	✓	✓	✓	x	x	x	x	x	x	x	x	✓7
Effluent Water	✓	✓	✓	x	2	✓	x	✓	O ₂ , H ₂ S	✓	x	x
Process Units Reactor Columns Pipework	✓	✓	✓	x	x	x	x	x	x	Aqueous Systems Only	✓5	x
Storage Vessels with Separated Water Bottom	✓	✓	✓	x	x	✓	x	x	H ₂ S	✓	x	x

1. Depends on water quality. LPR unavailable where there is a strong scaling tendency or other form of electrode contamination is possible.
2. May be used where oxygen content is high.
3. Sea Water injection systems only.
4. Produced Water injection systems only.
5. Where plant materials display a pronounced active to passive transition.
6. Where fluids are sour, in accordance with BP Group GS 136-1.
7. For sulphur containing feedstocks.

Intrusive monitoring devices aimed principally at the measurement of fluid corrosivity should not be located in high velocity process streams where vortex shedding could result in fatigue of the probe or coupon holder. For the same reason the length of the probe or coupon holder should be kept as short as possible, particularly in large diameter lines.

The positioning of corrosion monitoring fittings should be such as to allow routine access for probe interrogation and coupon and probe retrieval.

Ideally fittings should be located in pipework situated at floor level or immediately adjacent to permanent walkways.

The locations of all monitoring points should be marked on the process flow diagrams, materials selection diagrams and isometric piping drawings.

6.5.3 Access fitting design

For operating pressures up to 137 barg (2000 psig) on-line internal monitoring shall be undertaken using proprietary 2" high pressure access fittings which permit the installation and removal of probes and coupons without the need for plant shutdown. Typical high pressure access fitting assemblies with coupon holders and coupons fitted are shown in Fig. 2/1.

Where on-line retrieval and installation of monitoring devices installed in 2" high pressure access fittings is required, the fittings shall be located where adequate clearance is available for installation and operation of a service valve and retriever attached to the access fitting body. The following clearances are recommended based upon the use of fully extended telescopic retrievers.

RETRIEVER STROKE		CLEARANCE (FROM TOP OF ACCESS FITTING)	
mm	in	mm	in
660	26	1880	74
1270	34	2290	90
1070	42	2670	105
1270	50	3100	122

The required clearance with respect to the outer wall of the pipe in which the fittings are located will be determined by the type of fitting, i.e. flareweld or flanged. For a flareweld fitting the additional clearance will be typically 150 mm (6") and for a flanged fitting 380 mm (15").

Low pressure access fittings should consist of a weldoflange, a flanged full port valve, a threaded nipple welded into a slip-on flange and a stuffing box, see Fig. 1/1. For this system the maximum recommended operating pressure is 10 barg (146 psig). See Clause 6.4.4 with regard to the selection of electrical resistance probes for use with low pressure access fittings.

The nipple between the valve and the stuffing box should be the same length or longer than the probe element or coupon to facilitate removal of the monitoring device clear of the ball within the valve. The stuffing box should be fitted with a ferrule and locking nut and chevron PTFE seals. A 25 mm (1 inch) full port valve will normally be large enough to permit the probe or coupon holder to pass freely through the valve body, in fouling duties a 37.5 mm (1.5") valve is recommended.

Fig. 1 shows approximate dimensions of a typical low pressure access fitting assembly and gives guidance on the clearance required for retrieval operations based upon probe or coupon holder length.

The exact dimensions of the assembly should always be confirmed before checking that adequate clearance exists.

All probes and coupon holders to be used in low pressure access fittings shall be fitted with a blow out preventer to limit the extent of slide out of the monitoring device through the stuffing box during installation and retrieval operations on-line.

Safety clamps shall be used with low pressure access fittings to secure retractable probes and coupon holders while on line.

The maximum operating temperature for each of the two access systems will be governed mainly by the performance of the non-metallic components of the pressure sealing devices utilized within the various parts of the fitting assemblies and probes.

The suitability of the non-metallic seals for pressure containment at the requisite operating temperature shall be confirmed prior to procurement.

All 2" high pressure access fittings shall be fitted with heavy duty covers to protect the access fitting threads from damage and contamination. Each cover should have an integral pressure gage and relief valve so that any leaks between access fitting body and the monitoring device can be readily identified.

Sample points for the collection of process fluids for chemical/bacterial analysis shall include two isolating valves in series. In horizontal pipework sample point shall be installed at positions 2 and 4 shown in Fig. 2/1.

6.5.4 Materials selection

Material selection for access fitting bodies shall conform to the requirements of the piping specification for the process line being monitored.

Solid and hollow plugs used in 50 mm (2") high pressure access fittings shall be fabricated from a material which is resistant to corrosion under the process conditions within the line being monitored. In most circumstances Type 316 stainless steel will be suitable, but the final choice shall be approved by Company.

The elastomeric components used for pressure sealing shall be demonstrated to have satisfactory performance in the expected process fluids.

Access fittings shall be welded onto the process pipework in accordance with approved welding procedure. The inspection and testing of the attached fitting shall comply with the appropriate piping fabrication code. On successful completion of the pressure test the access hold shall be cut in the pipe wall centrally within the access fitting using a 38 mm ($1\frac{3}{8}$ inch) milling cutter. Proprietary drilling machines mounted on the access fitting may be used for this purpose. The flame cutting of access holes prior to the attachment of the fitting is not permitted.

6.6 Automated System

6.6.1 General

Methods for the interrogation of corrosion probes range from hand held analogue or digital meters to multichannel data-loggers linked directly to microprocessor driven data analysis units. The selection of the data collection method will be governed by the following considerations:

- The number, range and distribution of corrosion monitoring devices.
- The required frequency of data collection.
- The availability of manpower for data retrieval.
- A comparison of the capital and operating costs associated with the various options.

6.6.2 Manual methods

Hand held instruments for the interrogation of corrosion probes range in versatility from simple direct reading meters dedicated to one probe type and with no data storage facility to multifunction meters with direct read out, data storage and retrieval and computer interface capabilities for optimum data recording and data analysis.

Rack mounted instruments providing direct analogue or digital read out of the corrosivity readings from a number of probes are also available.

6.6.3 Data loggers/collection units

Data logging instruments hard wired to the monitoring devices may be single or multichannel. Single channel instruments have the advantage that they may be mounted local to the monitoring point to minimize the length of the cable run.

Removable memory modules allow manual transfer of the recorded data to the office where it is downloaded to a personal computer for interrogation.

6.6.4 Transmitter units

Individual or multi-probe transmitter units are available which are mounted local to the probe and used to receive, process and transmit the probe signals to a remote interrogation unit. The interrogation unit may be either a dedicated chart recorder, a digital display unit or a process computer.

6.6.5 Computers

Computers dedicated to corrosion monitoring may be used to receive data from corrosion probes either via transmitter units or multiplexers. The computer facilities enable selection of recording frequency and alarm setting. Sequential scanning through the active channels provides a display of “real time” probe values. They are primarily concerned with data collection and display and data storage capabilities vary according to manufacturer, but are generally limited. Further data analysis and permanent storage of data is catered for by interfacing with a personal computer, programmed using dedicated software.

6.6.6 Data analysis and reporting

The methods used to analyze the corrosion monitoring data will be determined by the number, location and variation in monitoring devices used and the method of data collection.

Suitable computer software may be available commercially for this purpose or may be modified to suit the particular application.

In selecting computer software consideration should be given to the inclusion of plant process data and plant inspection results.

The frequency and format of reporting the results shall be determined by Company Corrosion Engineer. The reports should make reference to significant processing parameters and any chemical treatment programs carried out during the time interval covered and highlight any significant change in fluid corrosivity. Detailed corrosion monitoring reports should be issued annually, but may be required more frequently where on-line monitoring is used to assist in plant control.

6.6.7 Guidelines for safe on-line installation and retrieval of corrosion monitoring devices

6.6.7.1 Low pressure systems

These guidelines should be read in conjunction with Fig. 1/1.

6.6.7.1.1 Probe/coupon removal procedure

- a)** Loosen and remove the nuts holding the upper safety clamp plate. Remove the plate taking care to ensure that the safety clamp rods are supported.
- b)** Loosen the ferrule locking nut taking care in case the probe or coupon holder stem is forced up through the packing gland assembly by the line pressure.
- c)** Slide the probe or coupon holder stem out through the packing gland assembly until the probe element or coupons clear the valve ball or gate. There should be a mark or label on the stem to indicate when this position has been reached.
- d)** Close the valve.
- e)** Slowly release the pressure contained within the assembly above the valve by loosening the bolts on the upper flange of the valve.
- f)** Remove the bolts from the upper flange on the valve and lift off the flanged nipple, clamp and packing gland assembly with the probe or coupon holder.
- g)** Fully withdraw the probe or coupon holder from the packing gland. Complete removal of coupon holders may not be necessary. The coupons may be removed, the holder cleaned and new coupons fitted with the packing gland, etc. still in place.

6.6.7.1.2 Probe/coupon installation procedure

- a)** Slide the coupon holder or probe stem through the flanged nipple and into the stuffing box having first checked that the bottom plate of the safety clamp is in place around the nipple. If this is not the case then the nipple and packing along assembly will need to be split, the plate fitted and the two reconnected.
- b)** Adjust the position of the probe or coupon holder so that the bottom of the probe element or the coupons will be clear of the valve ball or gate when the assembly is in place above the valve. Mark the stem of the probe or coupon holder where it emerges from the top of the ferrule locking nut to record the 'clear of the valve' position.
- c)** Check that the flange faces on the flanged nipple and upper valve flange are clean and the gasket in good condition.
- d)** Mount the assembly on top of the valve and bolt up the mating flanges securely.
- e)** Partially open the valve and check for leaks. If a leak is evident at the top of the packing gland, tighten the packing retaining nut until the leak stops.
- f)** Once the assembly is leak free, open the valve fully and slide the probe or coupon holder through the valve and into the process stream. The distance of travel of the probe should be checked to ensure that the monitoring position is correct and that the probe element or coupons are not damaged by contact with the opposite wall of the pipe.
- g)** Where coupons are being installed ensure that they are correctly orientated parallel with the direction of flow of the process stream.

- h) Tighten the ferrule locking nut securely with a wrench or spanner while preventing the packing retaining nut from moving with a second tool.
- i) Assemble the safety clamp ensuring that the upper clamp plate fits securely over the top end of the probe or coupon holder and prevents any upward movement of the same.

6.6.7.2 High pressure systems

The following constitutes guidelines for the installation and retrieval of on-line corrosion monitoring devices using a high pressure telescopic retriever and pressure test valve. On-line retrieval/installation of corrosion monitoring devices shall only be carried out by operators skilled in use of the equipment. The owner of retrieval tools and service valves used in retrieval operations shall be in possession of valid certificates confirming that tests have been carried out which demonstrate that the equipment is suitable for the pressures and temperatures at which it will be used.

6.6.7.2.1 Valve integrity test: Fittings without integral service valve installed

- a) If a pressure gage is fitted, check and note the pressure gage reading. Bleed off any pressure and monitor the rate of subsequent pressure build up. Notify the plant operator if there is a significant leak on the fitting and abort the retrieval operation. Where no pressure gage is fitted gradually remove the threaded heavy duty cover from the fitting, carefully noting any obvious leakage. Notify the plant operator if there is evidence of significant leakage and abort the retrieval operation, replacing the cover. Where no leakage is found remove the cover completely, clean the access fitting threads and install the service valve.
- b) Install the retrieval tool; pressure up the entire assembly with the service valve open to 110% line pressure. This checks the connection between service valve and access fitting.
- c) Close the service valve, depressurize and remove the retrieval tool, keeping the service valve closed.
- d) Check that the service valve is not passing, if nitrogen is used as the test medium, use soap solution to check for leaks.
- e) If no leakage is observed, bleed off the pressure using the by-pass valve and proceed to 6.6.7.2.3.

6.6.7.2.2 Valve integrity test: Fittings with integral service valve installed

- a) Remove the threaded heavy duty cover and clean the threads. Check the integrity of the plug fitting by cracking open the by-pass valve.
- b) Install the retrieval tool and pressure up the entire assembly with the service valve open. (To 110% line pressure.)
- c) Close the service valve; depressurize and remove the retrieval tool, keeping the service valve closed.
- d) Check that the service valve is not passing, if nitrogen is used as the test medium use soap solution to check for leaks.
- e) If no leakage is observed bleed off the pressure using the by-pass valve and proceed to 6.6.7.2.3. If leakage is observed, suspend operations.

6.6.7.2.3 Coupon/probe retrieval

- a) Make up the retrieval tool to the service valve and open the service valve.
- b) Pressure test the entire assembly to 110% line pressure.
- c) Engage the retriever mandrel in the plug fitting.

- d) Back-off the plug until a small product bleed is observed, allow pressure in the retriever to equalize to line pressure.
- e) Unscrew the plug completely and withdraw into the retriever body.
- f) Close the service valve (ensure mandrel is clear of valve).
- g) Remove the retrieval tool and change out the probe/coupon as required.

6.6.7.2.4 Coupon/probe installation

- a) Make up the retrieval tool (with the probe/coupon holder installed) to the service valve.
- b) Pressurize the tool to 100% line pressure. Check for leaks.
- c) Crack open the by-pass valve to allow line pressure into the retrieval tool. Allow pressure to stabilize and check for leaks.
- d) Fully open the service valve.
- e) Insert the probe/coupon holder into the fitting and screw home.
- f) Depressurize the retrieval tool and check for any pressure build-up. This checks the integrity of the plug seal.
- g) Disengage the tool from the plug.
- h) Remove the retrieval tool-ensure pressure is zero.

Note:

If coupons are being installed, their final orientation may have to be adjusted at this stage, use the retrieval tool or a socket wrench.

- i) Clean the plug top, service valve, etc. and replace the threaded cover. On completion the retrieval tool should be stripped down, cleaned and re-greased prior to storage.

PART TWO

EVALUATION OF CORROSION INHIBITORS

1. SCOPE

Part 2 of Inspection Standard gives guidance on laboratory corrosion monitoring. It deals with techniques for evaluation and testing of corrosion inhibitors.

2. REFERENCES

See general requirements.

3. DEFINITIONS & ABBREVIATIONS

See general requirements.

4. UNITS

See general requirements.

5. GENERAL

In order to determine the effect of chemical additives on corrosion, an actual corrosion process must be taking place, so that the inhibitor test and the corrosion test are inseparable. The fact that many variables affect a corrosion process means that numerous different inhibitor tests are available. Although additive concentration is generally low, the type of system, whether once-through or recirculating, or the method of treatment, continuous or batch-wise, will determine not only the test method, but also inhibitor concentration required.

6. REASONS FOR INHIBITOR TESTING

Inhibitors may be tested in many ways or for different reasons, but basically, the objective is to determine the effectiveness of a chemical additive in slowing down the overall corrosion process. Evaluation of new additives is necessary as chemicals are developed for new systems or for existing applications. Then, when an inhibitor looks promising or is ready for field use, it is necessary to judge its performance under field conditions. Associated with the effectiveness of an inhibitor, however, are other inherent properties necessary to carry it to the metal surface where it does its job. These properties often directly contrary to properties considered ideal for corrosion inhibitors, also must be included in an evaluation.

It is the purpose of this Part 2 of standard to describe the variables that affect the properties and performance of an inhibitor and the tools and techniques necessary to measure them both in the relatively controllable conditions of a laboratory and in the practical, usually more difficult conditions in the field.

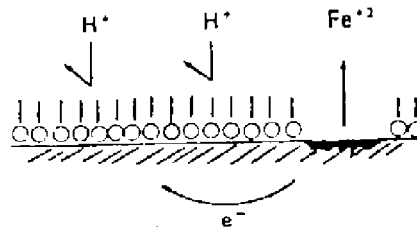
7. INHIBITOR PROPERTIES

7.1 Desirable properties of a corrosion inhibitor formulation include:

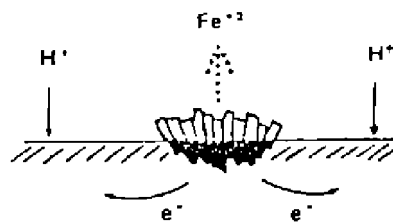
- a)** That the formulation stifle or reduce the corrosion process;
- b)** that transport of the active ingredient to the metal surface be promoted; and
- c)** that no undesired side effect results.

7.2 Because effectiveness as well as many other physical properties must be considered for each application, evaluation may involve many unrelated tests.

7.3 As illustrated in Fig. 1/2, the inhibitor may interfere with either the anodic or cathodic reaction. The effect of inhibitor on the corrosion rate is essentially a measure of the integrity or tightness of the barrier formed on the metal surface. In an evaluation for effectiveness, one is interested in the integrity or tightness of the barrier and the amount of additive necessary to form it. In certain cases, when inhibitors are applied batchwise, the tenacity or permanence of the barrier film is important. This property is called persistency. Persistency involves a time factor; it is a measure of time between batch additions over which the inhibitor maintains a protective barrier in the uninhibited environment.



a) Barrier at Cathodic Surface



b) Barrier at Anodic Surface

A CORROSION INHIBITOR FORMS A BARRIER AT A CATHODIC:
a) SURFACE OR ANODIC
b) SURFACE WHICH INTERFERES WITH ELECTROCHEMICAL REACTIONS
Fig. 1/2

7.4 Inhibitor concentrations vary from a few parts per million in continuous injection applications to several thousand parts per million in closed systems, to batch treatments of the "neat" or undiluted inhibitor. Concentrations used influence test conditions and often determine whether or not undesirable side effects are encountered. The relationship between additive concentration and corrosion rate raises the question of just what can be accomplished in reducing corrosion. Should complete stifling of corrosion be the goal? If some small amount of corrosion is acceptable, is this then in the form of increased pitting, compared to the untreated system, thus making the situation worse than without the inhibitor? This consideration is particularly important when working with anodic type inhibitors such as chromate.

8. TEST CONDITIONS

8.1 Before undertaking a program of evaluating inhibitors for effectiveness in mitigating corrosion, one must review the overall problem and determine what is required of the inhibitor, that is, exactly what parameters are to be tested and what factors affect test results. These questions and their answers will help in obtaining meaningful data for selection of the most efficient inhibitor in the environment of interest. The first step is to select the critical environmental conditions of interest and to incorporate them in the test.

If the corrosion problem is stress cracking, it is of little value to design a test which mainly involves general corrosion. Unfortunately, many tests consider only the overall loss of metal, a measure of uniform corrosion and attempt to read into the data information that cannot be or is not measured.

8.2 In designing a laboratory test, it is important to simulate physical field conditions and to select corrodent(s) important to the field conditions.

8.2.1 Some important corrodents dissolved in aqueous systems are listed below. In some cases, combinations of these will be common.

- Oxygen
- Carbon dioxide
- Hydrogen sulfide
- Ammonia
- Acids, bases
- Acid salts
- Oxidizing agents
- Dissolved solids and scale formers.

8.2.2 The physical parameters of the test include the following:

- Temperature
- Pressure
- Velocity or agitation
- Surface-to-volume ratio
- Dual phases immersion
- Presence immersion
- Presence of crevices.
- Presence of stresses

8.3 Since the corrosion process directly involves a metal, the mechanical and metallurgical properties of the metal are important. The content of alloying or secondary constituents, heat treatment and method of forming determine the characteristics of the metal. If stress is involved, one must keep in mind the applied and residual stress as well as the effect of notches as stress raisers. If more than one metal is involved, galvanic corrosion is a possibility and the ratio of areas of the metals will dictate intensity of attack on the anodic metal. Surface preparation of the specimens may be effected in different ways. Some investigators sandblast coupons, while others polish them with 400 grit or other abrasives. In any case, the surface of the metal must be clean, uniform, reproducible, and oil-free so that meaningful corrosion results may be obtained. This is necessary even though the condition of the metal surface may not be typical of metals exposed under field conditions.

9. DETECTION OF CORROSION

One of the most important aspects of an inhibitor test is the actual measurement of changes that reflect the degree of corrosion. In all cases, the metal of interest comprises the specimen, but the actual changes measured may not necessarily involve the metal directly. The detection of corrosion can be described by the three classifications illustrated in Fig. 2/2.

9.1 Measurements directly related to actual metal loss occurring during the corrosion process.

9.2 Measurements utilizing a related part of the overall electrochemical corrosion process; and

9.3 Measurements not involved in the electrochemical process, such as time, or surface film thickness.

10. METHODS INVOLVING LOSS OF METAL

10.1 Most direct measurements of corrosion utilize the weight loss of metal over a period of time on a small sample such as a coupon, wire or strip. Dimensions of the coupon are important for several reasons. The ratio of surface area to coupon weight should be as high as possible to facilitate detection of small weight losses. This permits the shortest possible exposure period between weightings. Selection of the maximum surface-to-weight ratio, however, may still result in a relatively long test.

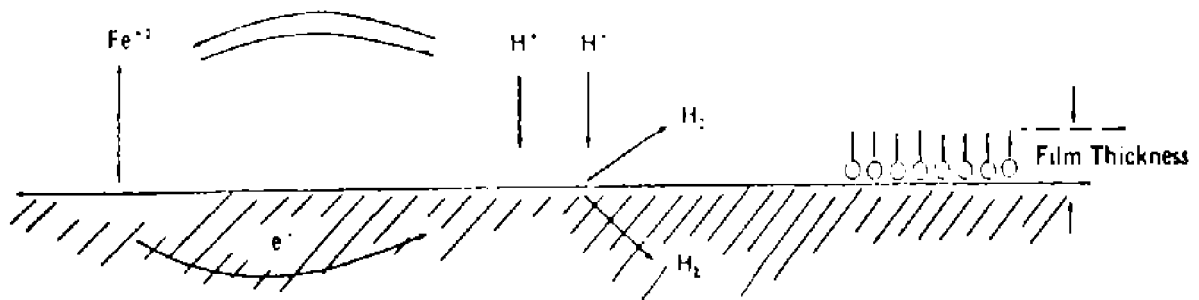
10.2 A long time between weightings is disadvantageous because it averages weight loss over the interval so rate of attack fluctuations are missed. However, a large specimen has the advantage of being able to detect and measure pitting attack. Thus, in many cases, the coupon weight loss method must be a compromise between the length of test, the sensitivity of the weight measurements and the importance of observing pitting corrosion. The coupon technique is by far the most common and most inexpensive method in current use. The preparation of coupons is discussed in some texts in general terms, and some standards have been set up for specific tests.

10.3 Standard Coupon Projected

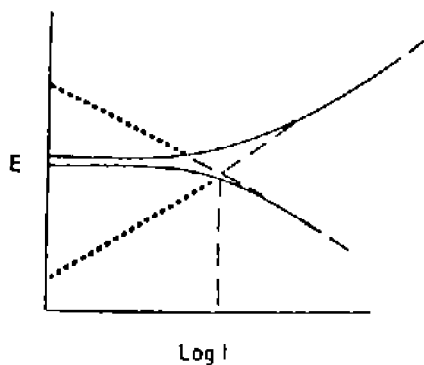
10.3.1 A standard coupon that may be used for many inhibitor test programs is scheduled to be issued by NACE Committee T-3-P. This coupon, developed by and used for many years by NACE Committees in testing inhibitors in products pipelines has the advantages of being made of homogeneous material of specific analysis, uniform surface preparation and controlled size and weight. Reproducibility of either static or dynamic tests can be improved by using this coupon and it is especially valuable when comparisons need to be made among results achieved by several different laboratories.

10.3.2 The disadvantage of lengthy test times has been decreased by the development of the Corrosometer, a device that measures metal loss directly in periods as short as one hour. The Corrosometer detects the change in electrical resistance of a small specimen resulting from loss of metal. Another advantage of the Corrosometer is that the electrical measurements can be made while the specimen is in place, without disturbing the system or the corrosion products. The Corrosometer technique can be used in aqueous liquids, nonaqueous liquids, gaseous or solid systems. Because specimens are small, pitting is not always detected and if the specimen does pit, instrument response is not linear with respect to the metal lost.

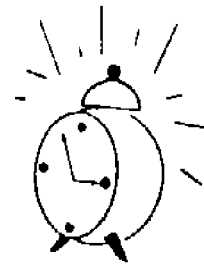
10.3.3 The analytical measurement of iron or other soluble metal content in the corrodent stream is another method directly related to metal loss. This technique can give poor results if the corrosion products are insoluble or adherent to the metal surface. If the method is used in a two-phase system, either both phases must be analyzed for metal ions, or particular care must be taken to put the dissolved metal into the aqueous phase. Quantitative measurements of dissolved metals are used frequently in acidic systems or in special cases where the corrosion products are known to be soluble. There are inexpensive colorimetric tests available for measuring iron, copper, and other metals in solution.



a) Direct Measurements of Metal Loss, Linear, Volumetric or Indirectly as by Hydrogen Evolution or Film Thickness



b) Indirect Measurements Such as Polarization and Polarization Resistance



c) Measurements Related to Time, i.e., Time to Break

THREE TYPES OF MEASUREMENTS OF CORROSION AND THEIR RELATIONSHIP TO ELECTROCHEMICAL PROCESSES

Fig. 2/2

11. INDIRECT MEASUREMENTS FOR CORROSION DETECTION

Indirect methods of corrosion rate measurement involve aspects of the electrochemical process other than metal dissolution. These measurements involve cathodic reactions such as the evolution of hydrogen or consider current-potential relationships such as polarization curves or polarization resistance values.

11.1 Hydrogen Evolution

Hydrogen evolution can be used where reduction of hydrogen ions is the cathodic reaction, e.g., in acidic solutions. The method can be cumbersome, because the solubility of hydrogen in the solution and hydrogen absorption into metals must be considered. The method can be most practical at high rates of corrosion in acids, but is not too commonly used. In one case, the technique has been used for rapid screening of acid inhibitors. An interesting variation of the hydrogen evolution technique is that in which hydrogen from corrosion enters the steel and is then measured. The build-up of hydrogen pressure in a "volumeless cell" is a measure of potential hydrogen blistering which may be caused by certain

environments containing chemicals such as sulfides or cyanides that interfere with the normal evolution of molecular hydrogen and make it enter the metal in atomic form. The environment may be either acidic or basic. A technique using the effects of diffused hydrogen on current flow between electrodes in a vacuum has been used to study corrosion mechanisms and should be valuable for inhibitor studies, because sensitivity of this method is considerably better than that of the pressure build-up technique.

11.2 Current-Voltage Relationships

11.2.1 Current-voltage relationships are commonly used as measurements of corrosion and are consequently of value in evaluating inhibitors. The technique is used in two ways as illustrated in Fig. 3/2. The first determines the potential vs current curves for both the anodic and cathodic reactions. Data are plotted on a semi-logarithmic current scale and are extrapolated backward toward the low current direction until the anodic and cathodic curves intersect, the current density at that point representing the rate of corrosion. The second method uses polarization resistance, which is the slope of the polarization curves at the point of corrosion. This method has practical use both in the laboratory and in the field. Instruments for polarization resistance-type corrosion measurements are commercially available as the "Corrater" and the "Pairmeter". The instruments translate polarization resistance data into corrosion rates and are known as instantaneous corrosion rate meters. The polarization resistance method is also reviewed in an NACE Task Group report with a complete bibliography.

11.2.2 Another type of rate meter is one which uses the complete electrochemical circuit in the form of a galvanic cell. While the galvanic cell may not simulate the actual corrosion cell, it does generate its own current and voltage; the cathodic and anodic reactants can be the same as those of the corrosion cell and the current generated is proportional to the corrosion rate. This system forms an inexpensive qualitative instrument for field use and can be used to monitor and evaluate corrosion inhibitors.

11.2.3 Instantaneous corrosion rate meters all have the advantages of detecting very rapid changes in the rate of corrosion without disturbing the corrosion process. The measurements can be made at locations distant from the location of the electrodes. A disadvantage, as in the case with all current-voltage methods, is that the measurements must be taken in liquid, aqueous phase which has a reasonable electrical conductivity.

12. UTILIZATION OF FILM MEASUREMENTS

12.1 A relatively new method of inhibitor evaluation directly measures film thickness on the metal surface by a technique known as ellipsometry. This method is an optical one in which a change in the character of a polarized light beam reflected from a surface is used to measure film thickness. Refined equipment is necessary to generate and measure the reflected light beam. Surface conditions are also critical. Although this may be an interesting tool for mechanistic studies in the laboratory, it is not presently useful for rapid laboratory or field evaluation of inhibitors.

12.2 Similar methods directly related to surface films are involved in "double layer capacitance", "differential capacitance" and "nuclear magnetic resonance" techniques described in the recent literature. As with ellipsometry, advantages are sensitivity in measurements but equipment requirements limit these techniques to laboratory use and there mostly for highly theoretical, mechanistic studies.

12.3 The copper ion displacement test is another method which measures directly the barrier effect of an inhibitor film. In this technique, steel coupons are immersed in the inhibited solution to develop a protective film formed under the condition of the environment. Then on a "go-no-go" basis, the coupon is removed and immersed in an acidified copper sulfate solution. If the inhibitor film is not protective, copper plates out on the steel surface and is readily seen. The method has some disadvantages in that the inhibitor film must be resistant to the acid conditions of the plating solution and that correlations for each particular environment should be checked.

One evaluation of the method indicates that it works well under strong filming conditions where hydrogen sulfide is present but does not work well in a carbon dioxide environment. The method has been used as a laboratory screening test for determining inhibitor persistence. When the method is applicable, it can be a useful tool for field evaluation of inhibitor treatment.

12.4 The last method in which the adsorbed film is involved is one in which tagged radioactive molecules expose photographic film and reveal a "picture" of the areas they cover. The technique is qualitative and may be useful for laboratory studies. In a more practical vein, radioactively tagged molecules also can be a very useful field tool. This technique has been used to measure areas covered by an inhibitor and the inhibitor persistency time.

13. MISCELLANEOUS CORROSION TESTS

13.1 Several tests are not related to any particular part of the corrosion process but involve only a specific test specimen that responds to corrosion by complete failure.

These tests are used in the measurement of certain forms of corrosion involving factors such as stress. Examples are: Corrosion fatigue, stress corrosion cracking and hydrogen embrittlement. In designing such corrosion tests, the variety of test specimens parallels the number of applications.

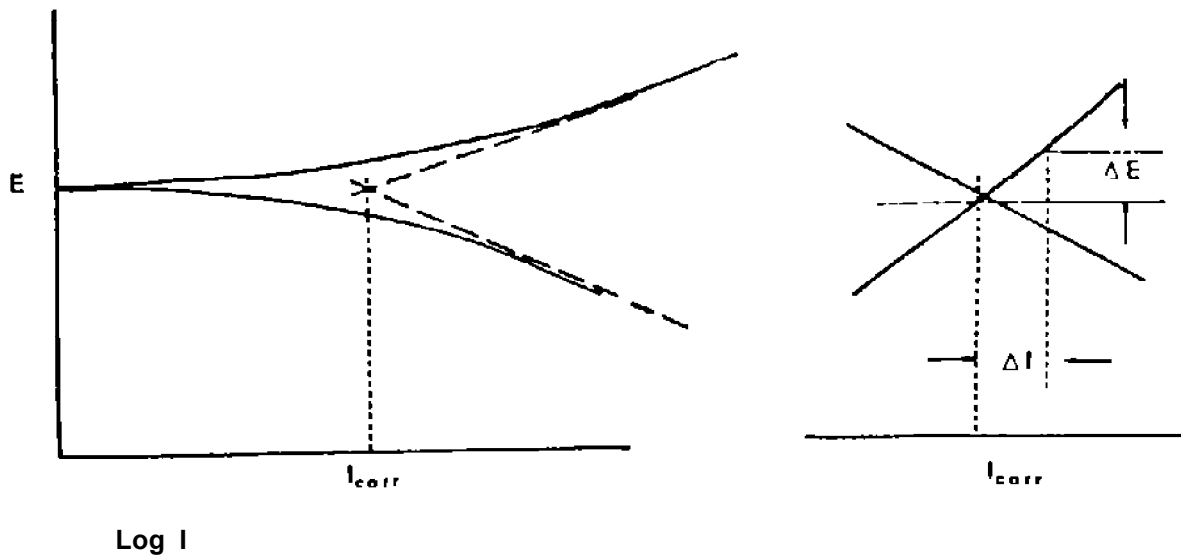
13.2 Stress corrosion tests may use a constant applied stress or one that changes as the crack progresses. Two commonly used test specimens are shown in Fig. 4/2. Corrosion fatigue tests may vary in the way cyclical stresses are applied: Tensile only, or tension-compression. The commonly used test for caustic embrittlement employs an applied stress along with a technique to concentrate dissolved solids at the critical area. When complete failure of the specimen is involved (e.g., breaking), the measured variables can be:

- a) Time to failure,
- b) Stress to cause failure, or
- c) Concentration of the corrodent to cause failure, all other variables being held constant.

13.3 In summary, any corrosion test can be used to evaluate corrosion inhibitors as long as it detects a difference in corrosion with and without the inhibitor. The most meaningful test is one that closely simulates field conditions. Sensitivity of measurements may not always produce the most useful results and requirements of the test method can vary widely depending on whether it is used in the laboratory or in the field.

14. RESULTS OF THE TEST METHOD

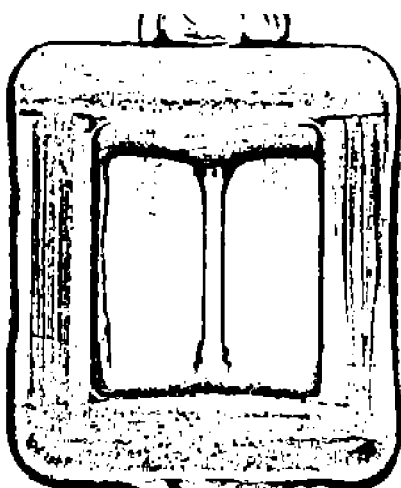
14.1 Despite strenuous efforts, duplicating field conditions may be difficult or impossible, this objective being subject to the additional difficulty that conditions actually are unknown. Many times, an evaluation test may be altered to develop a more corrosive condition or to "accelerate" the test. In such cases, the combination of corrodents should remain the same but it may be necessary to increase concentrations. The question then arises concerning interpretation of data. If the test is accelerated, the absolute corrosion rates may be higher than those resulting under field conditions.



a) A Polarization Diagram Plotted on a Semi-Logarithmic Current Scale. Data from the Anodic and Cathodic Reactions are Extrapolated Backwards in the Low Current Direction to an Intersection.

b) Plotting Rates by Using Polarization Resistance Plots. This Technique is Described in Numerous References.

MEASUREMENTS USING CURRENT-VOLTAGE RELATIONSHIPS
Fig. 3/2



a) A jig that puts tension on the tension bar (center is coated to prevent corrosion effects).



b) A C-ring tension specimen has micarta bushings electrically insulating the tension bolt from the specimen for the same reason. (Fig. 1 - Susceptibility of Aluminum alloys to Stress Corrosion. D. O. Sprowls and H.C. Rutenmiller. Mat. Pro., 2, No. 6, 63-65 (1963) June.)

TWO OF THE MANY CONFIGURATIONS OF SPECIMENS FOR CORROSION TESTS
Fig. 4/2

14.2 However, it must be assumed that the same corrosion mechanism is taking place and if an inhibitor is effective at high corrosion rates, it will be effective also under milder conditions. Testing using comparative data under accelerated conditions will permit identification of the better inhibitors. Then, under field conditions, the actual dosage of the inhibitor may have to be determined in some other manner.

14.3 In a laboratory test, the question always arises as to when an inhibitor is effective. Must the corrosion rate be stopped completely or can it be slowed to some degree and still be effective? In the field, the decisive factor will be whether the inhibitor eliminates failures. A complicating factor in both laboratory and field is the fact that corrosion products (or other surface-active particles) will adsorb the inhibitor and either keep it from the metal surface or lower its available concentration. Still another factor to consider in interpreting data is the wide statistical band over which test results will vary until a minimum necessary concentration of inhibitor is exceeded. Quite often, the individual test method, while stimulating field conditions accurately, will not give reproducible results because of variables such as surface preparation, velocity and adsorption of inhibitors on solid particles, and other factors, some of which are indeterminate. Several investigators have reported the use of statistical methods in the evaluation of test results.

15. FIELD TESTING OF INHIBITORS

15.1 The most reliable test apparatus is field equipment itself. However, it is the most expensive because of the cost of the equipment and because testing in fullscale equipment is time consuming. No source of information should be ignored, though, in evaluating additives or process variables and much valuable data can be obtained if careful day-to-day records are kept on equipment performance. A simple tabulation of failures vs time can show improvement resulting from inhibitor treatment. The records can be made even more sophisticated by identifying various parts of the equipment that fail and by deciding whether wear or stresses or other factors have been involved.

15.2 A method of record keeping that has been used in treated water systems is to plot logarithm of cumulative leaks against time. A plot of this type will approximate a straight line, indicating that the number of leaks increases with time. As a treatment becomes effective, the slope of such a line will be reduced.

15.3 Field testing usually is performed by means of coupons exposed to the test environment. The coupons can be installed on a holder in the full flow of a process line of interest. Another method is to use a test pipe nipple in the flow line to simulate more closely velocity conditions. When either of these techniques is used, however, inhibitor treatment of the complete stream is necessary for relatively long times needed for coupon exposure. To minimize the test times, electrical resistance probes, polarization resistance electrodes, or iron counts can be used when applicable reducing test times to days instead of weeks.

15.4 A further refinement is to use a slip stream off of the actual process lines. In this method, small amounts of the actual process fluids are passed over the metal specimen so only small amounts of inhibitors are needed for evaluation. If electrical resistance probes or polarization resistance electrodes are used, many additives can be checked in a short time.

16. ILLUSTRATIONS OF COMPLEX TESTING PROCEDURES NECESSARY TO SIMULATE FIELD CONDITIONS

An inhibitor evaluation test often will involve more than merely exposing a sample of metal to a corrosive environment. In this sub section, four laboratory tests will be described to illustrate the complex conditions or the specific properties that can be encountered in designing a test to meet certain applications. Table 1/2 summarizes the conditions of each of the four tests and the other requirements peculiar to the application. Tests also are discussed below in detail to elaborate on the reasons which make them different from others.

16.1 Antifreeze for Internal Combustion Engines

16.1.1 The cooling system for an internal combustion engine contains a variety of metals, plastics and rubber in contact with the aqueous coolant. The coolant has a relatively low volume for the area contacted and remains essentially unaltered except for makeup over a period of one to five years depending on the maintenance program. An additive must not accelerate degradation of any of the structural materials in the cooling system. The principal corrodents are oxygen from the atmosphere and hydrogen ions from degradation of ethylene glycol, commonly used as an antifreeze. Because the system contains a minimum of dissolved chlorides and sulfates, this minimizes the problem of corrosion and the requirements of the inhibitor. In time, however, as makeup water is added, dissolved solids will increase in concentration.

16.1.2 The main requirement of a test to evaluate inhibitors for such systems is providing several representative galvanic couples exposed in an aerated, hot, agitated mixture of water and antifreeze. The ASTM D1384 test describes the method, solution composition and coupon size and coupling for a glassware test. Steel, cast iron, aluminum, solder, brass and copper coupons are galvanically coupled in the test method as illustrated in Fig. 5/2. Another paper describes a test procedure on several common inhibitors and their effectiveness on the various individual metals and galvanic couples.

16.1.3 Other properties of the inhibitor formulation are important to insure optimum performance of the coolant. Foaming should be prevented so heat transfer is not impeded in any part of the engine. ASTM D-1881 test describes a technique for evaluation of foaming characteristics. Reserve alkalinity is a property required to provide a reasonably long period of constant pH conditions. Degradation of glycol antifreezes can lower the pH to the acid range. ASTM D-1121 test describes a method for determining reserve alkalinity of an antifreeze formulation.

16.2 Clear Packer Fluids for the Annulus of an Oil or Gas Well

Fig. 6/2 illustrates construction of a well using a packer fluid.

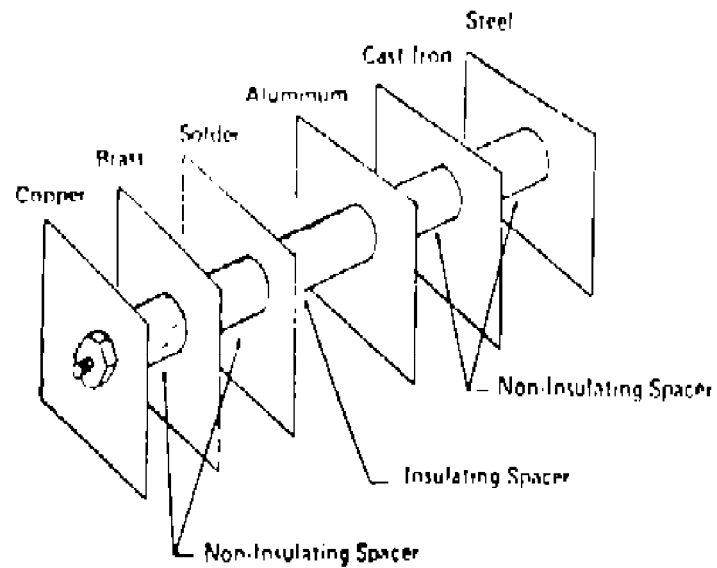
16.2.1 The packer fluid system, similar to the automotive coolant, contains a large area of metal in relation to the volume of fluid. However, the system differs in that the packer fluid is deaerated, static and contains a high concentration of dissolved solids.

16.2.2 The evaluation test requires a static system with the proper surface-to-volume ratio. Since the required temperature is high and air must be eliminated, a pressurized bomb with a glass liner makes a suitable test vessel. Because a relatively large area is needed, coupons are the simplest and most logical detection technique, although others can be used. The deficiency of the test is that uniform corrosion is measured even though localized pitting is quite often the mode of failure in oil or gas well tubing. However, because of its large area, the coupon can be inspected for pitting. Because the deaerated system alone does not produce a very high uninhibited corrosion rate, in this case an accelerated test is achieved by adding carbon dioxide or hydrogen sulfide to the system.

16.2.3 Organic inhibitors are often used in a packer fluid at high concentrations, so solubility becomes a problem. Solubility tests must be carried out at an elevated temperature because some organic inhibitors become less soluble as temperature is increased. The pH value at the high concentration should be checked because some highly soluble formulations are acidic. Furthermore, other additives such as bactericides often are included in the packer fluid system, so compatibility tests also must be considered.

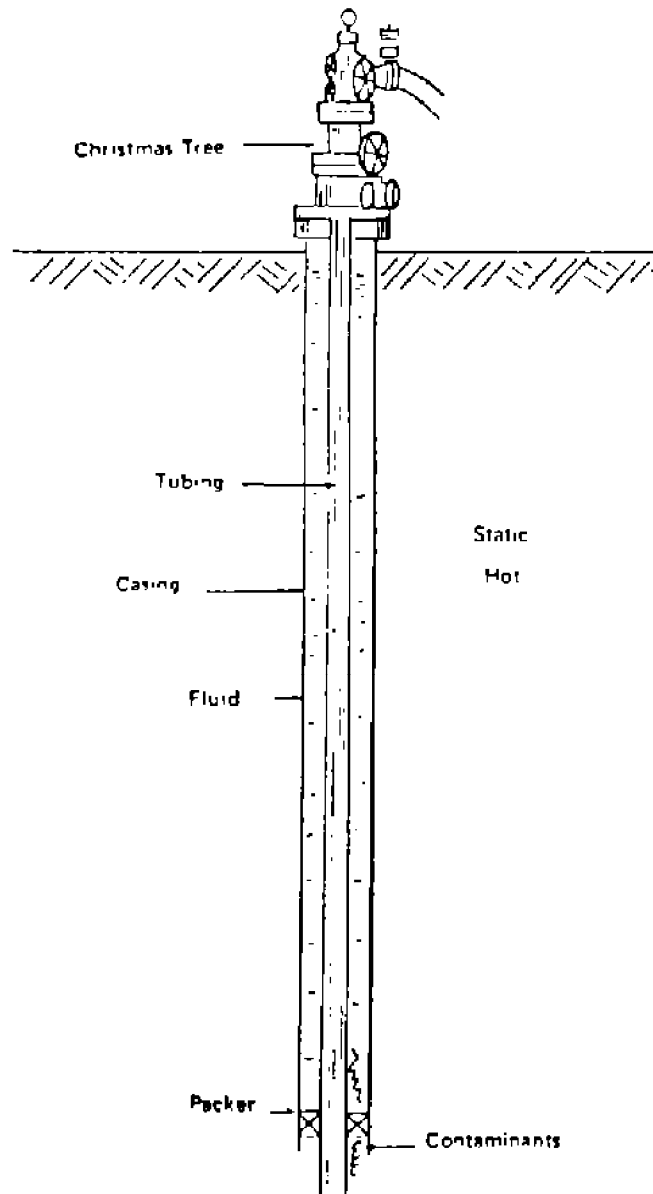
16.3 "Wheel Test" Alternate Immersion in Two Mutually Insoluble Phases

16.3.1 Contacting the metal specimen with the proper mixture and for the proper time in each phase is difficult in laboratory testing, particularly when the inhibitor may have preferential solubility in one of the phases.



TEST SPECIMENS ASSEMBLED ON SPOOL FOR INSERTION IN FLOW STREAM
Fig. 5/2

* Note Provision to evaluate galvanic effects through use of non-insulating spacers and to prevent galvanic effects by insulating spacers.



**DIAGRAM SHOWING ENVIRONMENTS AND CHARACTERISTIC MATERIALS
IN A PRODUCING OILWELL, ILLUSTRATING SOME OF THE
FACTORS INVOLVED IN DEVISING AND INHIBITIVE SYSTEM
FOR PETROLEUM PRODUCTION EQUIPMENT**

Fig. 6/2

16.3.2 The aqueous phase can be either a condensate such as exists in fuel product pipelines or it can contain moderate amounts of solids such as is the case in refinery crude distillation overheads or it can be strong brine as in the aqueous phase produced in an oil well. The hydrocarbon phase can vary among aromatic, aliphatic, saturated and unsaturated compounds, all of which can affect the solubility and the effectiveness of the inhibitor. Both fluids may be saturated with gases, such as carbon dioxide, hydrogen sulfide or air that will be factors in determining corrosiveness and the requirements of the inhibitor. Temperatures may range between ambient and 205°C (400°F).

16.3.3 Because a dual phase system may be treated with an inhibitor continuously or batchwise, the properties of the inhibitor should be selected to correspond with the treatment method. The "wheel test," however, measures only the actual effectiveness of the inhibitor in minimizing corrosion. Persistency (long term effectiveness by a strongly adsorbed film in an uninhibited environment) and solubility determinations are supplementary tests used to evaluate desirable properties for the batch treatment method. Although the "wheel test" is used sometimes in persistency testing, care must be taken to minimize an increase in inhibitor concentration in the uninhibited fluids through carryover from the treated metal sample. A good review of this method and its results is given in a report of a cooperative test carried out by an NACE Task Group T-ID-2 on evaluation of film persistency.

16.3.4 The "wheel test" attempts to simulate the time and frequency of specimen immersion in both phases of the dual system. Exposure to both phases is accomplished either by rotating or by oscillating bottles containing the fluids and metal specimen as shown in Fig. 7/2. With the coupons or electrodes at one end of the bottle, the heavier aqueous phase will cover the specimen once in every cycle. The frequency of rotation or oscillation determines the time in each phase and the degree of agitation in the system. When the rotating bottle assembly is installed in an oven to provide elevated temperatures, it is installed in an oven to provide elevated temperatures, it is necessary to use vessels capable of withstanding pressure.

16.3.5 The total volume and the ratio of the two phases must be taken into account for two reasons:

- a) Determination of inhibitor concentration, and
- b) Effects of corrosion Products.

If the inhibitor is soluble in only one phase, the effective concentration can be determined directly. However, if the inhibitor distributes itself between the two phases, the relative volumes as well as the distribution coefficient will determine the concentration in each of the phases. The amount of corrodent in the aqueous phase will determine changes occurring in soluble and/or insoluble products as a result of corrosion.

If corrosion is completely stifled by the inhibitor there will be no changes. However, the formation of either soluble or insoluble corrosion products and the depletion of the corrodent can change the corrosivity of the aqueous phase, particularly if this phase has but a small volume. Insoluble corrosion products also can provide a large surface area on which the inhibitor can adsorb, thus depleting inhibitor available to the metal.

The "wheel test" requires two phases closely approximating the actual environment of interest (the actual fluids, if possible) and a clean specimen of metal in the form of coupons, Corraters electrodes or Corrosometer probes. Use of the Corraters or Corrosometer permits the use of prerusted surfaces if these are necessary in the evaluation of the inhibitor. The inhibitor is added before the metal contacts either phase and in some cases, the metal specimen is soaked for a short period in the inhibited hydrocarbon phase prior to alternate immersion. Quite often, the test is accelerated by saturating the fluids with carbon dioxide or hydrogen sulfide, using a much higher concentration of the acid gases than is encountered in the field. While the use of Corraters electrodes and Corrosometer probes in laboratory testing is described in the literature, these sensing methods are more useful under field conditions where rapid evaluation in the actual environment is desired rather than laboratory testing under accelerated conditions.

16.3.6 Because of the wide variety of two-phase systems and because of the potential problems related to inhibitor treatment, other properties of the inhibitor formulation become quite important; each application will have its specific problems and requirements. Inhibitor solubility is an important factor and usually will be dictated by the major phase present. In certain cases, such as in batch treating oil wells, dispersibility of an oil-soluble inhibitor into an aqueous phase is necessary merely to carry the inhibitor throughout the system. Dispersibility is also necessary for the same reason in using the relatively insoluble inhibitors for long-term persistency in batchwise treatment.

16.3.7 In most applications involving dual phase systems, inhibition against corrosion is only one of the problems. Anti-scale inhibitors, bactericides or other additives may be added along with the inhibitors. In such cases, supplementary tests must be carried out to determine their mutual interaction. The different chemicals may be synergistic in their desired effects, but most likely they will interfere with each other.

16.4 Recirculating Cooling Water Test

The surface-to-volume ratio is relatively low in such systems so that little effect on the bulk fluid can be expected from the corrosion process. In many cases, metals other than carbon steel are used for heat exchanger tubing, including Admiralty brass, cupronickel, stainless steels and to some extent, aluminum and titanium. Fig. 8/2 shows one of several ways to test the effectiveness of inhibitors in recirculating cooling water systems.

17. INHIBITOR PROPERTIES OTHER THAN EFFECTIVENESS IN MITIGATING CORROSION

17.1 In many applications, properties of the inhibitor other than its effectiveness in inhibition are equally important in obtaining maximum efficiency with a minimum of undesirable side effects. Some of these properties have been discussed in previous sections illustrating the importance of solubility, compatibility, portability and other characteristics in the four examples of inhibitor evaluation. In this Section, the properties listed in Table 2/2 will be discussed, showing their relationship to inhibitor effectiveness or their undesirable side effects on the system. When known, a method of evaluating the property of interest will be described.

17.2 The properties of the "neat" inhibitor formulation (i.e., as received from the formulators) are important mainly from the standpoint of handling the material. Low viscosity is necessary to provide adequate pumping rates or flow rates. For example, when an oil well is treated batchwise, the time to reach the bottom and the hangup on the surfaces depends on viscosity which accordingly affects the shut-in period. Downtime costs money. Often, the inhibitor may be diluted just prior to injection to improve its mobility. Pour point is related to viscosity and is mainly important during cold weather. The inhibitor must flow at the lowest temperature expected at the location of use. Often the active ingredient of an inhibitor formulation is only 20% of the bulk, in order that the proper viscosity and pour point can be achieved through dilution.

17.3 Influence of Density

17.3.1 Density is important in achieving proper mixing of the inhibitor in the corroding stream. High density inhibitors have been developed for batch treating a two-phase system such as an oil well, where getting the inhibitor to the proper location is a particular problem. These inhibitors consist of very tight emulsions containing high-density materials. The emulsions break slowly to release the inhibitor after the formulation has reached the greatest depth in the system. These formulations cannot be diluted when added to the system.

17.3.2 The effects of mixing the inhibitor, either concentrated or dilute, with the environment of the treated system can be related to inhibitor efficiency and to treatment techniques and are frequently the cause of undesirable side effects.

TABLE 1/2 - SUMMARY OF CONDITIONS AND SPECIFIC REQUIREMENTS OF FOUR DIFFERENT TEST EXAMPLES

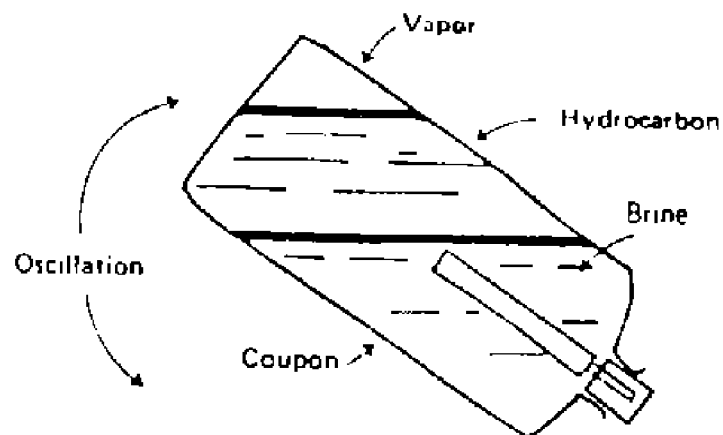
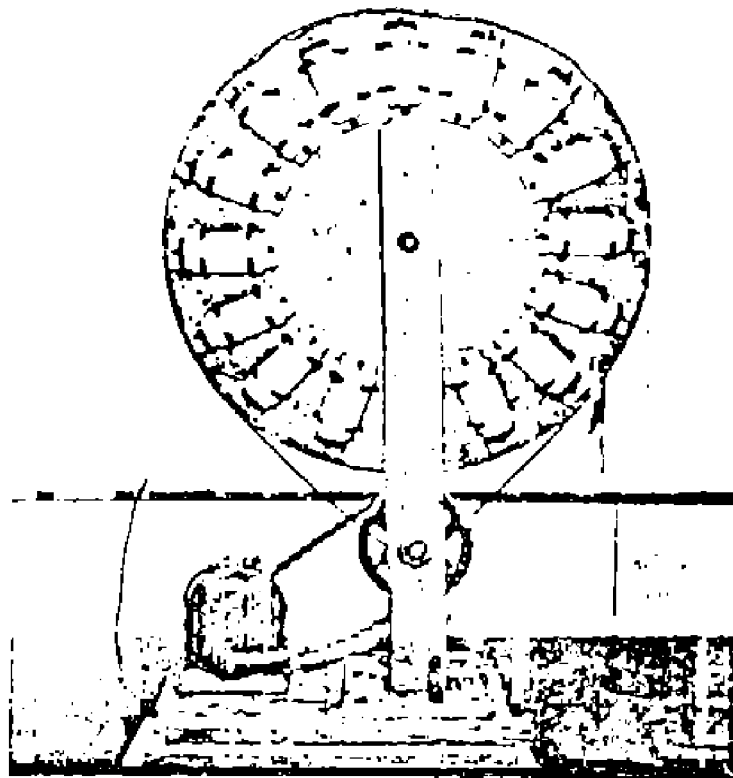
	1	2	3	4
Reference to Standard Tests	Antifreeze for Internal Combustion Engine ASTM D1884 D2570 D1881 D1121	Clear Packer Fluid for Annulus of Oil or Gas Wells Bottle Tests for Solubility and Compatibility	"Wheel Test" Alternate Immersion for Two Phase Systems Bottle Tests ASTM D1935, D2550	Recirculating Water for Cooling Towers ASTM D2688 D2776
Environment	Water and Freeze Point Depressant: - Low dissolved solids - Air-saturated - 71°C to 82°C Agitated	Brine, Weighted with High Concentration of NaCl, CaCl ₂ or ZnCl ₂ : - Deaerated - Contaminated with H ₂ S or CO ₂ - 66°C to 177°C - Static	Two Phases ⁽¹⁾ : - Saturated with Air, CO ₂ or H ₂ S - Ambient to 93°C - Mild Agitation	Water, with Moderate Dissolved solids: - Air-saturated - 49°C to 60°C - Agitated
Metal of Interest	Steel, Al, Cu Brass, Cast Iron	Steel	Steel	Steel, Cu Alloys
Specific Requirements	1. Galvanic coupling 2. Reserve alkalinity 3. No foaming 4. High surface to-volume ratio	1. Solubility at elevated temp. 2. High surface to volume ratio 3. No reaction with CO ₂ or H ₂ S 4. Compatibility with bactericides	1. Solubility 2. Dispersibility 3. Water tolerance in oil 4. Detergency 5. Foaming 6. Compatibility with other additives 7. Pour point	1. Heat transfer 2. Compatibility with other additives 3. Non polluting 4. Non foaming
Method Detection	Coupon Galvanic Current	Coupon	Coupon Corrosometer Polarization Resistance	Heat Exchanger Coupon (Tube)

1) Hydrocarbon may have high or low viscosity, may contain straight chains or aromatics, quite often taken from field installation. Aqueous phase may have high or low dissolved solids.

TABLE 2/2 - IMPORTANT PROPERTIES OF INHIBITOR FORMULATION OTHER THAN EFFECTIVENESS IN MITIGATING CORROSION

	BROAD CLASSIFICATION	SPECIFIC PROPERTY OF INTEREST	TEST METHOD
1	Property of Neat Inhibitor Formulation	Viscosity Pour Point Density	ASTM D2162 and D88 ASTM D97 ASTM D1217 and D1298
2	Effect of Mixing with Environment of Interest	Solubility Water Tolerance Emulsion Formation Foam Formation	Bottle Tests ASTM D2550 ASTM D1935 and Bottle tests ASTM D1881
3	Reactions with other Additives	Compatibility with: Bactericides Scale Inhibitors Dispersants	Bottle Tests Effectiveness Tests
4	Effect on Animal Life	Portability	1)
5	Miscellaneous Effects of Temperature	Drying Solubility changes Release of Weighted Inhibitors	Drops applied to hot plate Bottle Tests Bottle Tests

1) Tests not within scope of this chapter. See government regulations covering specific material.



(TOP)
SHOWING ONE CONFIGURATION OF A "WHEEL" TEST DESIGNED TO EVALUATE
INHIBITORS EXPECTED TO FUNCTION IN EITHER LIQUID OR VAPOR PHASES
IN BOTH.

(BOTTOM)
DIAGRAM SHOWS HOW BOTTLES PROVIDE EXPOSURES
IN WATER, OIL AND VAPOR PHASES FOR EVALUATIONS IN THESE
THREE ENVIRONMENTS

Fig. 7/2

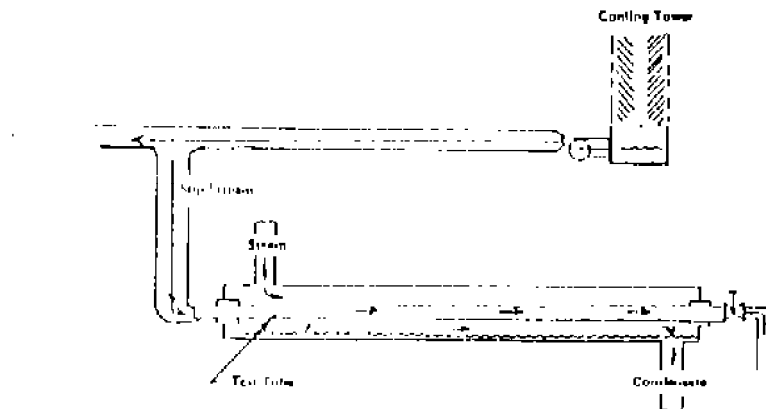


DIAGRAM SHOWING SIDE STREAM TECHNIQUE FOR EVALUATION OF INHIBITORS ON HEAT TRANSFER SURFACES. REMOVABLE TUBE CAN BE WEIGHED AND EXAMINED TO DETERMINE RESULTS

Fig. 8/2

17.4 Influence of Solubility

17.4.1 Solubility in the environment is necessary if the inhibitor is to reach the metal surface. However, in some cases, the degree of solubility can be related to the inhibitor's effectiveness. Borderline solubility along with polar properties is thought to be an important feature in promoting the effectiveness of a particular molecule as a corrosion inhibitor. However, as solubility decreases, the amount of inhibitor available is decreased and the ease with which the material reaches the metal surface is diminished. In many cases, it is necessary to disperse the additives so it will be diluted in the process stream sufficiently to dissolve. Thus, along with effectiveness, solubility and dispersibility become important properties in the evaluation of an inhibitor formulation.

17.4.2 Solubility in a two-phase system becomes even more complex. It is necessary to decide into which phase the inhibitor must be dissolved or if it should be distributed between both phases.

17.5 Surface-Active Characteristics

The surface-active properties of an inhibitor, in many instances, are inherent in the particular inhibitor molecule but in some formulations are enhanced by the addition of other chemicals. Surface activity, in addition to influencing inhibitor effectiveness, determines dispersibility and detergency which in turn affect emulsion and foaming properties of the system. Detergency, the ability to clean a surface or keep a surface clean, is desirable because of the need for a clean surface onto which the corrosion inhibitor can be adsorbed. Foam or emulsion formation can seriously affect equipment operation and in a two-phase system can impede separation of the phases when it is necessary to do so. An example of the severe restriction placed on a corrosion inhibitor regarding a foam or emulsion formation is that concerning water tolerance of jet fuel. Water pickup in the fuel must be limited so that fuel lines will not freeze and plug during low temperature operation.

17.6 Testing for Solubility, Dispersibility, Emulsion Foaming

17.6.1 Solubility, dispersibility and emulsion-forming properties of an inhibitor may be determined in simple bottle tests. Either the actual fluids of interest or some closely simulating them may be used. The inhibitor is added to bottles at varying concentrations and the bottles are shaken and then observed for total solubility or dispersibility and the time

for the dispersion to separate. If two-phase systems are involved, both should be included in the bottle to find the effects of emulsion formation. For example, for oil field use, the bottle tests may include either high or low molecular weight hydrocarbons, aromatic or aliphatic hydrocarbons, brine and mixtures of brine and hydrocarbons.

17.6.2 More elaborate equipment is required to determine certain other properties. The ASTM D-2550 test describes a method to determine water tolerance in jet fuels in which the fuel is emulsified, filtered, separated and the remaining entrained water is measured as turbidity by a photocell. A less stringent test for water pickup is described in ASTM D-2550 where steam is sparged into the hydrocarbon phase and time of cloudiness is measured. Detergency is difficult to evaluate in equipment other than that being treated. In the petroleum industry, detergency of fuels is evaluated in small-scale engines.

17.6.3 Foaming occurs usually where gas evolution or pressure changes occur. The ASTM D-1881 test describes a method for evaluating foaming characteristics in an automotive antifreeze mixture in which a gas is bubbled at a fixed rate through the fluid of interest and the height of the generated foam is measured. A similar test can be used for any single fluid or mixed phase system.

17.7 Formation of Sludges or Precipitates

The use of corrosion inhibitors is often accompanied by treatment with other additives such as scale inhibitors, dispersants, or bactericides. These additives may react with the inhibitor to produce sludges or precipitates that have no protective properties and which may consume the inhibitor, thereby reducing its concentration in the solution. Two kinds of tests should be carried out to determine the effects of mixing if the chemical structure of each additive is not already known. A bottle test should be carried out in which relatively concentrated solutions of the two additives are mixed and observed for gross reactions such as the formation of a precipitate. The second test is one in which each of the additives was originally evaluated. In this test, the additives are mixed at the low concentrations used in treating and the test results of the mixture are compared with the results using the additive alone. If a significant loss of effectiveness is observed with the mixture, the materials should be considered incompatible.

17.8 Ecological Effects

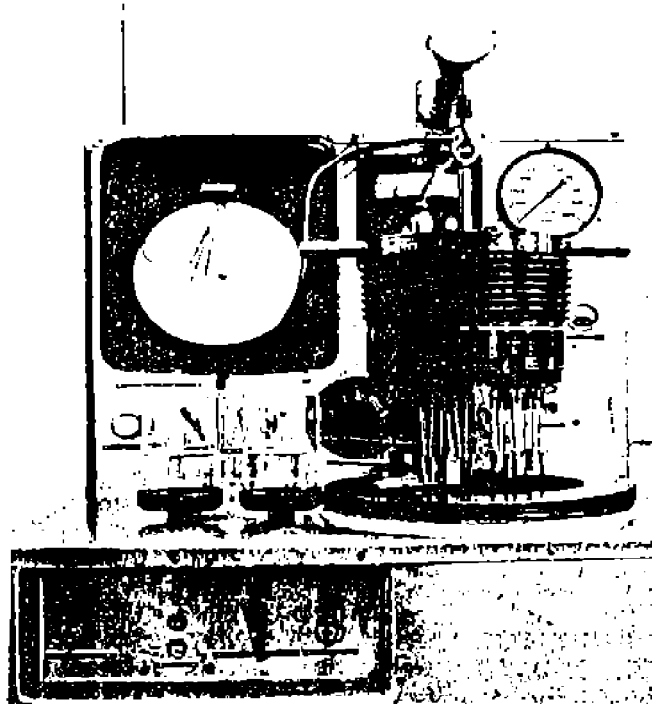
If the treated system is to be ingested by human beings or animals, the additives must have no toxicity. When disposal is to the sewer or to natural water streams, the effect on the environment must be minimal. It is also the responsibility of both the supplier and the user to be aware of government regulations regarding the use of specific chemicals in applications where potential pollution exists.

17.9 Effects of Temperature

17.9.1 The use of a corrosion inhibitor at elevated temperatures sometimes requires more tests than the evaluation of inhibitor efficiency alone. Solubility may be affected in an unexpected way as the temperature increases. For example, some organic inhibitors have a lower solubility in brine at elevated temperatures than at ambient temperatures. In a static system requiring relatively high concentrations of inhibitor (see description of packer fluid application), it is essential that the solubility of inhibitor be unaffected by temperatures to which the solution is exposed. Bottle tests can easily evaluate these properties. Drying and the properties of the resulting film can be important in hot gaseous systems where the carrier solvent will be evaporated. The film should flow at the temperature of the system, should not dry to form flakes which could be abrasive and should be readily soluble in some easily available solvent. Simple tests can be devised to evaluate these properties, e.g., by applying the neat inhibitor to a hot metal plate and observing the degree of evaporation, the degree of fluidity and the changes of the film with exposure time.

17.9.2 Fig. 9/2 shows laboratory test equipment designed to evaluate inhibitors under heat, pressure and velocity conditions.

17.9.3 High density (weighted) inhibitors are designed to reach the bottom of oil wells by being heavier than oil or brine phases in the well. Contact with brine at the elevated temperature at the bottom of the well causes the emulsion carrying the inhibitor to break and release it to the system. A bottle test has been devised in which the inhibitor is dropped through the hot brine and the time for completed breakdown of the emulsion observed. The characteristics of the released phase should also be noted.



SHOWING AUTOCLAVE USED TO TEST INHIBITORS UNDER HIGH TEMPERATURE, PRESSURE AND VELOCITY CONDITIONS. GROUPS OF SPECIMENS (RIGHT) ARE LOWERED INTO SOLUTIONS (LEFT) AFTER SOLUTIONS HAVE BEEN PLACED INSIDE THE AUTOCLAVE. AFTER PRESSURES AND TEMPERATURES ARE BROUGHT UP, MOTORS ROTATE THE SPECIMENS IN THE SOLUTIONS. (FIG. 10. LABORATORY APPARATUS TESTS PRESSURE AND VELOCITY EFFECTS ON CORROSION OF OIL FIELD TUBING IN INHIBITED HYDROCHLORIC ACID. W.E. BILLING. J.A. KNOX AND DAVID MORRIS. MAT. PRO., 2, No. 8, 59-62 (1963) AUG.)

Fig. 9/2

APPENDICES

APPENDIX A MONITORING OF CORROSION INHIBITORS

A.1 General

Assessment of the performance of corrosion inhibitors applied either by batch or continuous techniques requires a field monitoring program. A well-designed monitoring program shall be supported by normal field records and annual (turn-around) inspections. Field monitoring methods for producing wells include caliper surveys, visual inspection of pull rods and tubing strings and other techniques designed to indicate the condition of the production tubing. Flow lines and junctions may be inspected on an annual basis by techniques such as X-ray ultrasonic testing, Lin-a-log and other surveys.

A.2 Water Samples

Samples are collected at wellheads, inlet separators or intermediate points in the system. Waters are normally analyzed for manganese levels and total iron. Most produced water associated with oil and gas production has extremely low natural manganese levels. Thus, a finding of significant manganese levels in the water sample is usually indicative of corrosion because any manganese has originated from the steel in the system. Comparison of manganese levels between wellheads and inlet separators, making allowances for the contribution of each water source to the fluid reaching the separator, can give a measure of the protection achieved along the flow lines. Similar comparisons of iron levels at wellheads and inlet separators can be made.

Where a downhole protection program is in use for producing oil or gas wells, monitoring of the iron and manganese levels in wellhead or field separator samples is an extremely valuable tool in indicating when renewal of inhibitor in a batch program is required.

It should be noted that many produced waters have a significant level of iron originating from the formation. Since the normal manganese content of steel used in oil and gas production is approximately 1%, an iron to manganese ratio that is significantly in the excess of 100:1, particularly in well head samples, is a strong indication of iron originating from the formation.

Iron to manganese levels may fall significantly below 100:1 in the case of sour gas fields as the hydrogen sulfide present converts the iron to insoluble iron sulfide which may not be carried forward to the inlet facilities.

A.3 Data from laboratory analysis is compared with prior values from the same location. These comparisons alter the user to trends and changes in the system monitored.

A.4 Corrosion Coupons

Installation of corrosion coupons changed quarterly, semi-annually or annually in wellheads and at suitable points in a gathering system provides very valuable information that good protection is being provided by the corrosion inhibitor used in the system. Some manufacturers can supply coupons, bull plugs, coupon holders and assist with the installation and coupon changes and carry out analyses reporting weight changes, pitting rates and qualitative identification of deposits on coupons installed in the system. Inhibitor manufacturer fully supports all monitoring programs involving coupons with reports giving not only basic data on the coupons but full discussions of the results obtained with comparisons for the previous exposure period. This additional information has proven very valuable to many customers in giving indications of changes occurring in a system.

(to be continued)

APPENDIX A (continued)**A.5 Inhibitor Residuals**

Quantitative data, when appropriate, on inhibitor residuals measured in fluid samples collected at suitable points in the field such as dehydrators, intermediate sample points and inlet separators shall be provided. Knowledge of the residual inhibitor levels as well as the iron and manganese levels allows the most economic rates to be established for full protection of a particular system.

A.6 Electric Resistance Probes and Corrosion Monitoring Probes

Results obtained on field probes can be correlated with chemical analysis data, residual inhibitor data and corrosion coupon monitoring data.

Successful corrosion control programs depend both on proper application techniques of the protective chemicals and good monitoring. Consistent record keeping by both the supplier and the customer is an essential part of a successful monitoring program.

APPENDIX B

AN EXPERIMENT FOR CORROSION BEHAVIOR OF HIGH ALLOY TUBULAR MATERIALS IN INHIBITED ACIDIZING CONDITIONS

B.1 General

The use of corrosion resistant alloys to fight bottomhole corrosion due to the presence of H_2S and CO_2 has led to the need of testing such alloys in all expected conditions, typically during acidizing stimulation jobs, which determine very severe corrosion either in terms of general or localized attacks.

While the behavior of carbon and low alloy steels in inhibited stimulation conditions are well known, few data are available on the corrosion behavior of corrosion resistant alloys, primarily at high temperatures.

This Appendix B deals with corrosion behavior of duplex stainless steel, some high austenitic stainless steels and a nickel-base alloy in 28% HCl acidizing solutions either in inhibited or uninhibited conditions, at 130°C.

Weight loss, crevice corrosion and stress corrosion cracking tests were carried out for 6 and 24 hours, with amine-base commercial corrosion inhibitors, originally formulated for carbon steel.

B.2 Experimental Procedure

The depletion of easy oil and gas fields has led, in recent years, to the exploitation of both new deep reservoirs and already discovered fields which very often produce H_2S and CO_2 at high temperature and pressure, showing, consequently, very severe corrosion conditions. Traditional completion type, i.e. carbon or low alloy steels, associated with corrosion inhibitors, does not represent a reliable solution from the corrosion point of view.

These alloys shall resist corrosion not only at bottomhole conditions, but also at all expected conditions, typically during acidizing stimulative operations where high concentrated mineral acids are used, such as HCl or HCl/HF mixtures.

Currently available corrosion inhibitors were formulated for carbon and low alloy steels and their performance with standard materials is sufficiently known. Recently some data on the corrosion behavior of corrosion resistant alloys during acidizing job and using standard corrosion inhibitors, became to be available. However, only few data have been published and restricted to low or medium temperatures, and medium acid concentration.

B.3 Materials

Present laboratory investigation regarded four high austenitic stainless steels and a duplex stainless steel. The low alloy steel was tested since the corrosion inhibitors used were formulated for carbon and low alloy steels.

Chemical compositions (% by weight) and relevant mechanical properties in as received conditions are respectively reported in Tables B.1 and B.2.

(to be continued)

APPENDIX B (continued)

TABLE B.1 - CHEMICAL COMPOSITIONS (% BY WEIGHT)
OF THE MATERIALS EXAMINED

ELEMENT ALLOY	C	Cr	Ni	Mo	Mn	Si	Cu	S	P	N	OTHERS	
Duplex S.S	0.040	23.3	6.0	3.0	1.51	0.33	0.07	0.004	0.013	0.166	Al	0.022
High austenitic S.S.1	0.017	21.6	36.3	4.5	0.53	0.45	0.50	0.001	0.020	N.D.	Ti	0.27
											W	0.48
High austenitic S.S.2	0.015	25.0	38.1	4.0	0.62	0.18	1.00	0.001	0.21	0.029		
High austenitic S.S.3	0.018	27.1	31.1	3.5	1.84	0.82	0.75	0.002	0.015	N.D.		
High austenitic S.S.4	0.020	26.3	31.9	4.0	1.60	0.03	1.00	0.003	0.019	N.D.		
IN718	0.046	19.0	52.9	3.0	0.07	0.14	0.04	0.002	0.007	N.D.	Al	0.060
											Ti	1.02
											Nb+Ta	5.4
Low alloy steel	0.24	1.03	0.15	0.16	1.28	0.29	0.10	0.007	0.012	N.D.	Al	0.049
											Ti	0.045
											Sn	0.011

TABLE B.2 - MECHANICAL PROPERTIES OF THE MATERIALS EXAMINED

EXP. COND. ALLOY	Yield Strength TYS (MPa)	Elongation %	Hardness HR _C
Duplex S.S.	980	9	29
High austenitic S.S.1	875	15	29
High austenitic S.S.2	800	14	26
High austenitic S.S.3	800	20.8	27
High austenitic S.S.4	770	13	28
IN718*	1320	15	43
Low alloy steel	780	18	27.8

* Thermal treatment: 1 hr at 955°C; A.C. + 8 hrs 720°C; F.C. at 55°C/hr to 620°C; held 8 hrs; A.C.

B.4 Specimens

Potentiodynamic test specimens were disks of 16 mm in diameter, prepared by machining, water grinding and final polishing with diamond pastes up to 1 µm.

All specimens, before and after testing, were degreased by ultrasonic dipping in trichloroethylene first and then followed by acetone and distilled water.

Weight loss specimens were coupons of about 30 cm² in area. Machined surfaces were water grinded with abrasive papers up to 220 mesh.

Crevice corrosion specimens were tailored as Anderson's assembly (12). For specimens obtained from tubulars, a milling operation was carried out. Surface preparation regarded machining, followed by wet grinding up to 600 mesh. Crevice sites were 16 (only one side) for specimens obtained from tubulars, and 32 (two sides) for other materials.

SCC specimens were C-ring in accordance with ASTM G3079, loaded at 100% yield strength. As far as high austenitic stainless steel N.3 is concerned, also U-bend specimens were used, in accordance with ASTM G38-73. Bolts and nuts were made of Hastelloy C-276.

(to be continued)

APPENDIX B (continued)

B.5 Test Solution

Tests were carried out in 28% HCl solution, in both inhibited and uninhibited conditions. Two commercially available acid inhibitors for low alloy steels were taken into account, whose basic compositions were as follows:

- **Inhibitor A:** Proprietary blend of aliphatic and cycloaliphatic amines, acetylenic alcohols and surfactants. Concentration used were both 1% and 2% by volume. Intensifier, when used, was added at same concentrations.
- **Inhibitor B:** Proprietary blend of acetylenic alcohols, heterocyclic amines, surfactants and inorganic copper salt. Concentration used was 1% by volume.

B.6 Test Procedures

Potentiodynamic tests for anodic polarization curves were carried out at $80 \pm 1^\circ\text{C}$ at a scanning rate of 1,200 mV/h, starting from -250 mV vs rest potential. The inhibitor concentrations used were 1% for both inhibitors. The experimental apparatus was the one reported in ASTM G5-82 standard practice.

Before starting the test, samples were left in contact with the acid solution for 15 minutes, in order to attain stable corrosion potential values.

All potentials were measured against a saturated calomel electrode, maintained at room temperature. The interliquid junction was minimized by using an agaragar bridge saturated with KCl. The thermogalvanic effect was not taken into consideration.

B.7 Autoclave Tests

Weight loss, crevice corrosion and SCC tests were carried out at following conditions:

- temperature $130 \pm 1.5^\circ\text{C}$;
- exposure time, both 6 and 24 hours.

The autoclaves, internally clad with tantalum, had a capacity of 1.5 liters. The volume of test solution was 1.3 L, leading to a volume/surface sample ratio ranging from 5.9 to 7.2 mL/cm².

Taking into consideration also the autoclave surface, the ratio became 1.7-1.8 mL/cm², which is similar to the volume/surface ratio for a 73 mm ($2\frac{7}{8}$ in) tubing.

Special care was taken in order to avoid galvanic contact between samples and tantalum autoclave surface, by hanging the specimen into suitable glass devices.

Oxygen was not removed from the HCl solution and autoclave gas cap, at test start up, was air. Some tests were carried out on the duplex stainless steel also at 80°C in a glass cell.

TABLE B.3 - CORROSION INHIBITOR EFFICIENCIES
AT 80°C $Z = (i_{un} - i_{in}) / i_{un}$

ALLOY	CORROSION CURRENT DENSITIES (mA / cm ²)			INHIBITOR EFFICIENCY	
	Uninhibited	Inhibitor A	Inhibitor B	Z _A	Z _B
Low alloy steel	46	0.78	0.018	98.30	99.96
Duplex S.S.	56.1	0.136	0.030	99.95	99.96
High austenitic S.S.1	0.15	0.036	0.0042	76	97.2
High austenitic S.S.2	0.48	0.033	0.0024	93.1	99.5

(to be continued)

APPENDIX B (continued)

B.8 Potentiodynamic Tests

Typical potentiodynamic polarization curves of tested materials are reported in Figs. B.1, B.2 and are reported in Figs. B.1, B.2 and B.3. The aim of test was primarily the establishment of a mechanism of the corrosion inhibitors.

Accordingly it resulted that, at 80°C, both inhibitors move the rest potential of all tested materials toward more noble potential values more and show a strong influence on the Cathodic curve, giving rise to a decrease of circulating current of two decades on average.

Inhibitor efficiencies were calculated from potentiodynamic tests by determining the corrosion current densities (Table B.3). Results confirmed good efficiencies at 80°C of corrosion inhibitors for all the materials.

B.9 Weight Loss

All results are reported in Table B.4. In Figs. B.4 and B.5, same results are conveniently showed by histograms, where weight losses are reported and compared with the maximum accepted practical value, which is 0.244 kg/m² (0.05 lb/ft²) for each single acidizing operation; calculated corrosion rates are also reported.

The results at 1% inhibitor A concentration are not reported in the histograms, because of the recommended concentration at test operating temperature is 2%, that was confirmed by experimental results (Table B.4).

TABLE B.4 - CORROSION RATES (mm/YEAR) IN 28% HCl AT 130°C

Exp. cond. Alloy	Not inhibited (6 hours)	Inhibitor A 1%		Inhibitor A 2%		Inhibitor A 1%+ Intensifier 1% (24 hours)	Inhibitor A 2%+ Intensifier 2%		Inhibitor B 1%	
		6 hours	24 hours	6 hours	24 hours		6 hours	24 hours	6 hours	24 hours
Duplex S.S.	2900	405	540	1250	1150*	595	2260	570	500	90
High austenitic S.S.1	250	2.8	2.0	1.2	1.7	1.2	4.8	2.0	0.4	0.25
High austenitic S.S.2	440	3.0	2.5	2.5	2.0	1.6	6.2	2.2	0.5	0.23
High austenitic S.S.3	1470	20	14	3.6	12.2	13	4.8	1.6	0.5	0.42
High austenitic S.S.4	1340	4.4	13	2.5	2.5	23	7.5	3.0	0.7	0.25
IN 718	180	3.4	8	2.0	2.0	50	4.2	2.0	12	0.25
Low alloy steel	2500*	545	650*	420	650*	2500*	1090	650*	250	25

* Specimen totally corroded after test.

**TABLE B.5 - WEIGHT LOSSES AND CORROSION RATES FOR
DUPLEX STAINLESS STEEL AT 80°C**

EXPOSURE TIME (h)	WEIGHT LOSSES (kg/m ²)			CORROSION RATES (mm/y)		
	Uninhibited	Inhibitor A 1%	Inhibitor B 1%	Uninhibited	Inhibitor A 1%	Inhibitor B 1%
6	—	0.0097 0.0097	0.029 0.039	—	1.80 1.95	5.42 7.15
24	13.86	0.068	0.244	531	3.39	11.15

(to be continued)

APPENDIX B (continued)

TABLE B.6 - RESULTS OF THE CREVICE CORROSION TESTS IN 28% HCl AT 130°C

Exp. cond. Alloy	Uninhibited	Inhibited (6 hours)			Inhibited (24 hours)		
		Inhibitor B 1%	Inhibitor A 1%	Inhibitor A 1% + Intensifier 1%	Inhibitor B 1%	Inhibitor A 1%	Inhibitor A 1% + Intensifier 1%
Duplex S.S.	Very high dissolution	C.C.	Very high dissolution	Very high dissolution	//	//	//
High austenitic S.S.1	Protection	Very light C.C.	light C.C.	C.C.	C.C.	C.C.	C.C.
High austenitic S.S.2	Protection	No C.C.	Very light C.C.	light C.C.	light C.C.	C.C.	C.C.
High austenitic S.S.3	Protection	Very light C.C.	light C.C.	C.C.	C.C.	C.C.	C.C.

TABLE B.7 - RESULTS OF STRESS CORROSION TESTS IN 28% HCl AT 130°C

EXP. COND. ALLOY	Uninhibited*	Inhibited**
Duplex S.S.	Very high dissolution	No S.S.C.
High austenitic S.S.1	S.S.C.	No S.S.C.
High austenitic S.S.2	S.S.C.	No S.S.C.
High austenitic S.S.3	S.S.C.	No S.S.C.

* 6 hours exposure tests.

** 6 and 24 hours exposure tests.

B.10 Low Alloy Steel

Although data reported by suppliers on technical information brochures, low alloy steels, exposed to inhibited solutions, exhibited in laboratory test conditions severe corrosion rates, higher than maximum allowed. Most likely this is primarily due to the high temperature and relatively long exposure time. Of the two corrosion inhibitors tested, that designated B showed a better effectiveness in all experimental conditions.

B.11 Crevice Corrosion

High austenitic stainless steels in the presence of corrosion inhibitors suffers crevice corrosion attacks occurring in all locations. All result of SCC tests are reported in Table B.7.

B.12 Conclusions and Recommendations

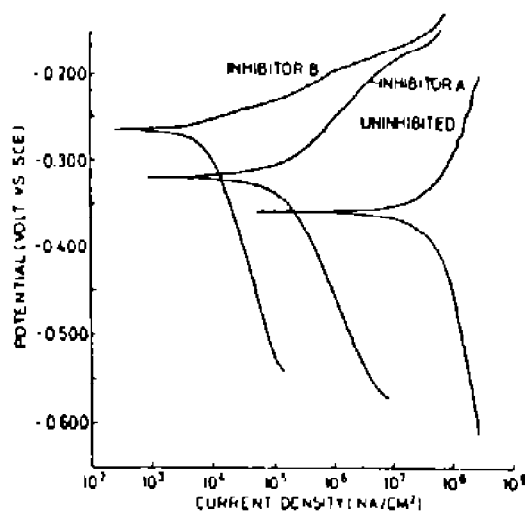
Laboratory tests, carried out in 28% HCl solution at 130°C, showed the following results:

- Commercial corrosion inhibitors, formulated for low alloy steels, showed good effectiveness, when used with high austenitic stainless steels and nickel-base alloys.

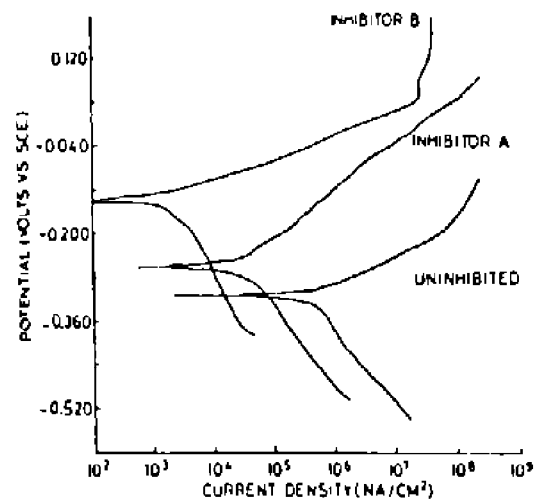
(to be continued)

APPENDIX B (continued)

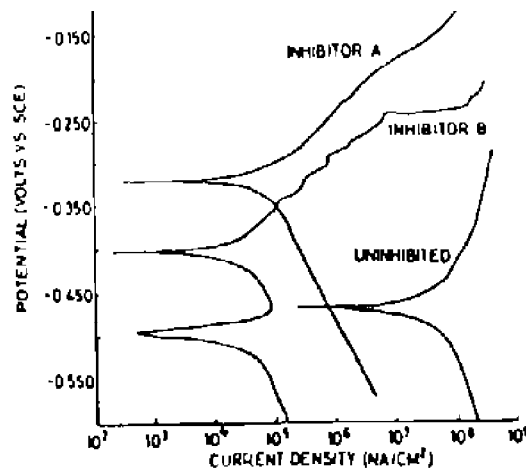
- Low alloy steels, exposed to inhibited solutions, exhibited under laboratory test conditions, severe corrosion rate, higher than the maximum allowed.
- The behavior of duplex stainless steel, also in the inhibited solution, was very poor at 130°C: At this temperature, although in the presence of inhibitor, the galvanic coupling was operating; however at 80°C the behavior was acceptable. As a consequence for high operation temperatures, there is a need for better inhibitors.
- Crevice corrosion tests revealed the susceptibility to corrosion attack in the presence of corrosion inhibitors, while in their absence no preferential attack in crevice sites was observed.
- SCC, in the presence of commercial inhibitors, never occurred for all tested materials; in the absence of corrosion inhibitors, transgranular microcracks were present at the bottom of pits on high austenitic stainless steel.



**POLARIZATION CURVES OF THE
DUPLEX STAINLESS STEEL IN 28%
HCl AT 80°C**
Fig. B.1



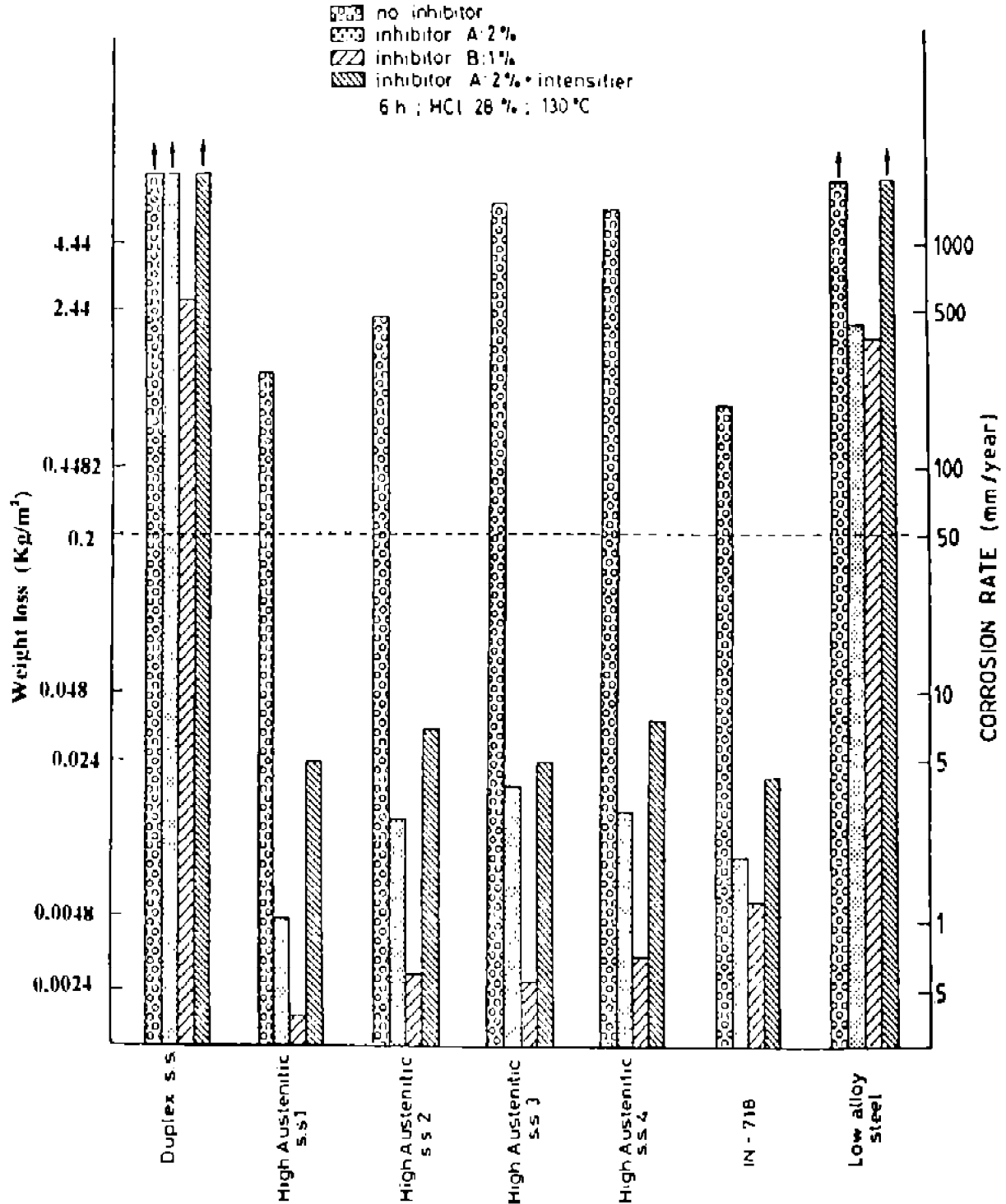
**POLARIZATION CURVES OF THE
HIGH AUSTENITIC STAINLESS
STEEL No. 2 IN 28% HCl AT 80°C**
Fig. B.2



POLARIZATION CURVES OF THE LOW ALLOY STEEL API G105 IN 28% HCl AT 80°C
Fig. B.3

(to be continued)

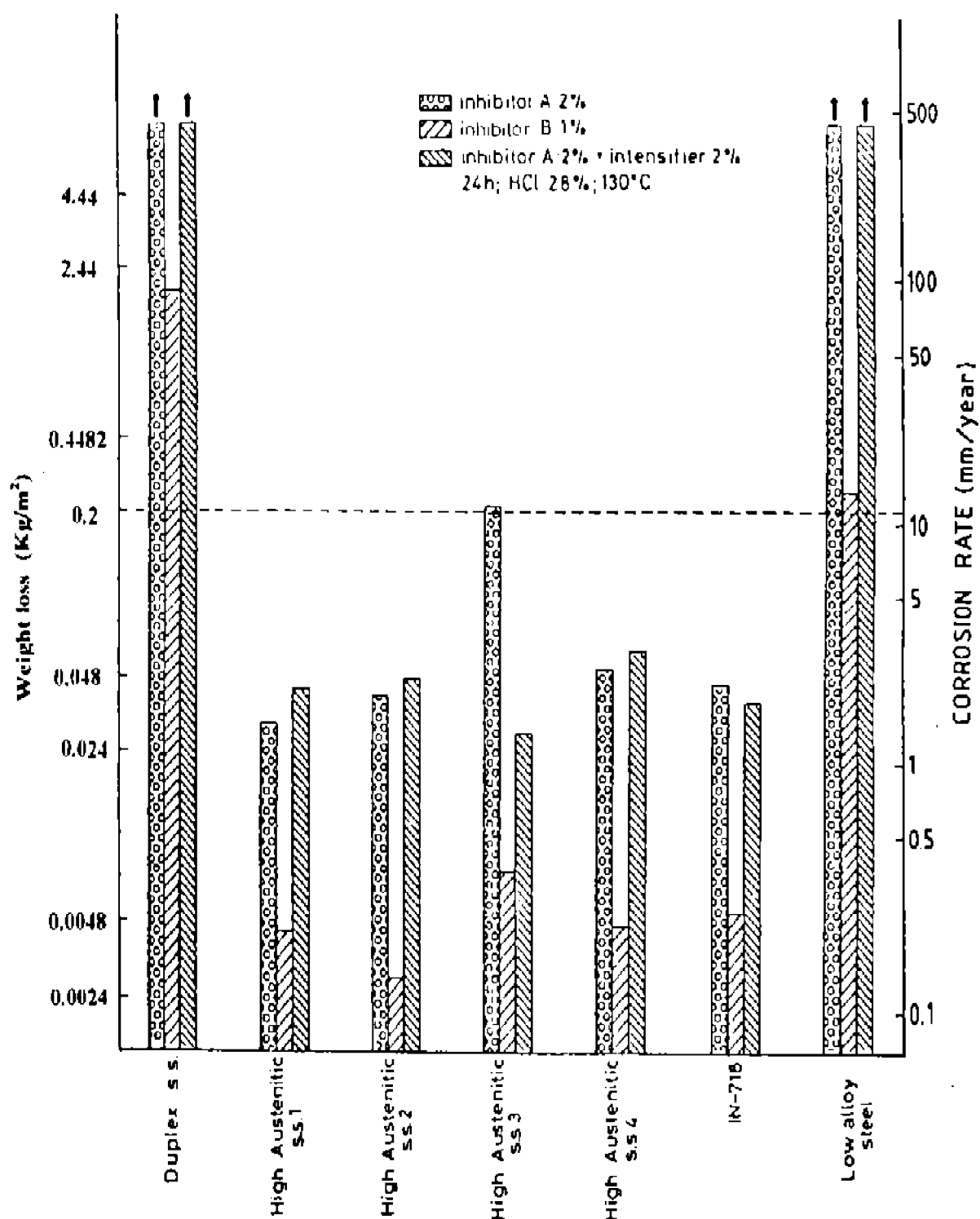
APPENDIX B (continued)



WEIGHT LOSSES IN 6 HOURS AUTOCLAVE TESTS OF EXAMINED MATERIALS
Fig. B.4

(to be continued)

APPENDIX B (continued)



WEIGHT LOSSES IN 24 HOURS AUTOCLAVE TESTS OF EXAMINED MATERIALS
Fig. B.5