IN-SITU CORROSION MONITORING UNDER FLOWING CONDITIONS; A REVIEW

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ABSTRACT*: Corrosion is a degradation mechanism that affects a wide range of engineering materials because of undesirable interaction of metals with the environment. Corrosion process not only affects the economy but may also lead to catastrophic failures. The pipelines in oil/gas and process industries are often exposed to aggressive environments, making corrosion process unavoidable unless protected by a protection technique. The situation may require costly repairs, replacements loss of material and products. Sometimes corrosion initiates and proceeds unnoticed and not detected until significant damage has occurred. For timely detection of corrosion real-time online corrosion rate measurement is a vital solution. The paper aims to provide a review on in-situ techniques that give real-time corrosion rate measurement in industrial processes. This can help to analyze the life of a pipeline in the prevailed service conditions and keep track on the integrity of the pipeline. Various online corrosion determination techniques have discussed such as (i) mass loss coupons (ii) electrical resistance probe (iii) liner Polarization resistance probes (iv) Zero Resistance Ammetry and (v) Ultrasonic Thickness Measurement.*

Keywords – Corrosion, Corrosion Rate, Industry, In-situ measurement, Probe

1. INTRODUCTION

Corrosion is an electrochemical process resulting from a metal's undesirable interaction with its environment. It is a metal's natural tendency to go back to the most thermodynamically stable form. Considering the extensive use of metals in a wide range of applications, corrosion has become quite problematic. According to a recent NACE IMPACT study carried out in 2016, the global cost of corrosion is estimated to be as high as US$ 2.5 trillion, a major portion of which is utilized by oil and gas industry [1]. By a recent study carried out in Pakistani, the overall cost of corrosion in Pakistan (industrial and domestic) is estimated to be ~USD 2.5-3 billion [2]. Along with economic losses potential loss of life or damage caused to the environment is also unbearable. Some of the losses related to corrosion are catastrophic failure of nuclear reactor, high flow rate pipelines, boilers, pressure vessels, etc.

Rate of corrosion generally depends on both external as well as internal factors. The external factors include working environment, chemistry, moisture, etc. Internal factors contributing to corrosion may include oxygen concentration, the reactivity of the liquids and gases carried in the environment, use of dissimilar metals causing galvanic effects and temperature, flow rate, pressure of fluids and gases [3].

While extensive research has been carried out to protect components susceptible to corrosion and minimize economic, life and environmental losses, it is also important to study the integrity of a component in application and predict its life. Online Corrosion monitoring using probes or coupons is a suitable option for corrosion monitoring of operational plants and machinery. It provides the following information mainly [4]: (i) current state of operational equipment with purpose of avoiding any unplanned shut-downs; (ii) suitable information on interaction of corrosion processes occurring with process variables to allow more efficient use of the plant; (iii) help to prevent any failures leading to disasters; (iv) analyze corrosive contaminants present in the environment.

In this paper, a few useful methods for online corrosion rate determination have been reviewed and discussed. It discusses on Mass Loss Coupons, Electrical Resistance Probes, Linear Resistance Probes, Zero Resistance Ammetry and Ultrasonic Thickness Measurement. These methods can be developed easily and provide an immense advantage to the industry in safety, productivity and economy.

Mass Loss Coupons is the simplest but are more often used with some other technique and are not very applicable for online corrosion rate measurement. Historically it was reported that approximate expenditure made on corrosion monitoring equipment consisted of 50% on fittings for sensing probes, 25% for weight loss coupons and 25% for instrumentation hardware related to the probe setup. Of the 25% expenditure on instrumentation, two-thirds were estimated for Electrical Resistance equipment and the remaining one-third for Linear Polarization Resistance probes [4]. Electrical Resistance Probes are the simplest type with regard to instrumentation and were originally patented by Standard Oil and was used to enhance the efficiency of oil field corrosion inhibitors [5]. An alternate competitive technology to the Electrical Resistance Probe was developed by Petrolite, that is, the Linear Polarization Resistance Probe [6]. Zero Resistance Asymmetry and Ultrasonic Thickness Measurement are less commonly used by the industry which, however, needs further research towards the development of better online monitoring techniques.

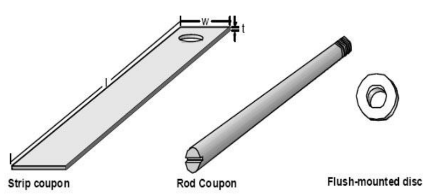
An extremely important principle to consider is to identify components of the plant that might be susceptible to any change in the corrosion environment at a specific location. These might be the introduction of another process stream, a change in the operating pressure or temperature, a change in the construction material of the plant, turbulence, cavitation, particulate impingement or any flow related phenomenon. Appropriate sensors should mostly be positioned at locations susceptible to greatest attack [7]. For example, it is a waste of time and money to install a sensor capable of monitoring only a uniform attack if the cause of corrosion is of localized nature.

2. MASS LOSS COUPONS

Mass loss coupons are the simplest form of corrosion rate monitoring in terms of design, fabrication, and cost. Mass loss is determined of a coupon inserted in an area of interest over a period of several weeks or months. Standardized coupons and related calculations are carried out as per international standards. Since mass loss coupons provide a visual indication of corrosion, pitting and crevice corrosion can also be identified visually. Examples of coupons are shown in Figures 1 and 2. Various shapes of mass loss coupons are available depending on the location where the corrosion rate has to be investigated. The coupons can be either in the form of a strip, rod or flush mounted disk.

Useful data that is reproducible depends largely on surface preparation of coupon before being inserted into the pipeline or any other area to be inspected. Surface preparation techniques include blasting with glass beads or sand, sanding with abrasive belts, surface or double disc grinding using abrasive [8]. Test duration has an important effect on test data. Commonly 24 hours duration is extrapolated to 30 days to up to one year [9]. After Exposure, the coupons should be cleaned and weighed immediately after removal of corrosion product by chemical or mechanical cleaning [10]. Currently, the most common and popular method for cleaning the corrosion products is using an abrasive grit blast [9]. For calculations, initial and final weight loss difference is converted to volume loss using material density and the divided by surface area of coupon exposed and test time.

Figure 1. GMW14872 standard mass loss coupons According to GM9540P, the coupons are eligible to be removed after 8 cycles[13].



(a)

(b)

Figure 1. (a) Mass Loss Coupons (b) before and after of strip type mass loss coupon which has been used to measure corrosion rate inside a pipeline [11].

Calculations of corrosion rate are done using the following formulae:

$$CR = \frac{3.65 \times 10^5 m}{A.d.t}$$

Where,

CR= Corrosion rate (mm/year)

m= Mass loss (g)

A= Surface area of the coupon (mm^2)

d= Metal density (g/cm^3)

t= Exposure time (days)

Standardized coupons and related calculations are carried out with the help of international standards for more accurate and reproducible results. International standards devised for corrosion rate evaluation using mass loss coupons include ASTM-G1, NACE RP0775-99, GMW14872, GM9540P, SAE J2334. Various types of probes have been fabricated and used effectively for varying working conditions. For instance, GMW14872 standard experiment probes are manufactured to provide corrosion rate measurements under several cyclic conditions with varying parameters like salt concentration, temperature, etc. These coupons measure 1x2x0.125 inches and are made of steel with ¼ Inch diameter home in the center as shown in Figure 2 [12].

3. ELECTRICAL RESISTANCE PROBES

Weight-loss coupons give the most reliable results but are time-consuming [9]. Electrical Resistance probes work on the simple principle of dependency of electrical resistance to the cross-sectional area of a conducting element. A wire, tube or strip element is in contact with the corrosive environment under study, backed up by a Wheatstone bridge. The corrosive environment corrodes the element, resulting in a decrease of cross-sectional area. Since the resistance of an element is inversely proportional to cross-sectional area, an increase in resistance is observed. Electrical resistance is measured by the following formula [14]:

$$R = \frac{\rho L}{a} \qquad (1)$$

Where,

ρ= Resistivity of the element material

L= Length of element

a= Cross-sectional area

By plotting metal loss calculated by electrical resistance as a function of time allows corrosion rate to be determined using its slope. Deviations in the slope indicates changes in the corrosion conditions, as shown in Figure 3 [12]. This method is extremely effective for detecting the onset of corrosion in a certain environment due to changes in conditions [13].

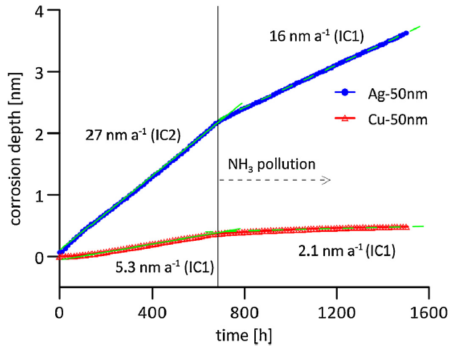


Figure 3. Corrosion depth VS. time for copper and silver[12].

A basic schematic probe design is illustrated in Figure 4.

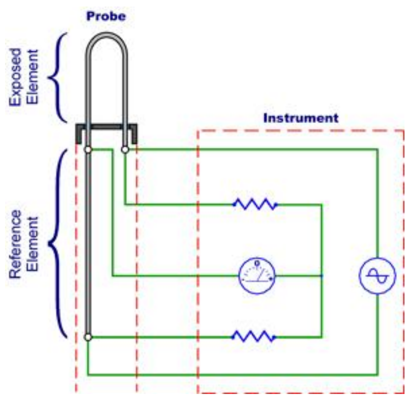


Figure 4. Electrical Resistance Probe [15]

Generally, the electrical resistance probe has the sensing element that is made up of a certain metal/alloy of which the corrosion rate data is to be measured. Like mass loss coupons, electrical resistance probes have been designed for various applications as well. Life of the probe sensing element depends on their thickness. Lower the thickness, higher the sensitivity but shorter is the service life [12].To counter any effect of temperature on element conductivity, two sensing elements are employed in the probe design usually. One element is inside the probe body while the other is exposed to the corrosive environment[16]. Probes are designed and manufactured depending on the application. For example, Probes made by COSASCO Corrosion Monitoring and Chemical Management Systems [17] can be fixed or made retractable. Fixed probes cannot be removed. They may be mounted with a flange or threaded on areas of limitations or to improve the economy. Retractable probes are mounted externally to a valve and can be removed when required. Other probes have been designed to work at high temperatures or underground. Atmospheric electrical resistance probes are a special kind of electrical resistance probes to monitor the corrosive nature of an environment. Examples of electrical resistance probes are shown in Figure 5.

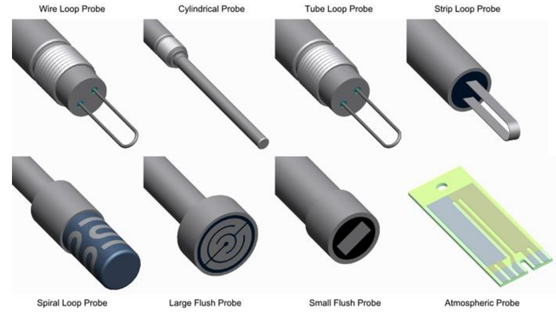


Figure 5. Types of electrical resistance probes[15]

A sample data obtained by electrical resistance probe is graphically represented as shown in Figure 6.

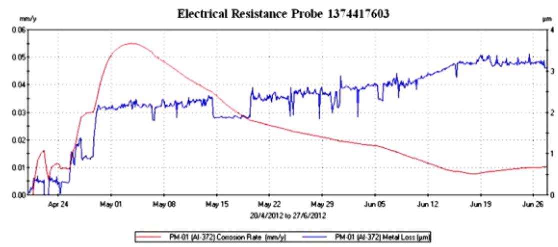


Figure 6. Corrosion rate and loss of material thickness represented against exposure time to corrosive media [18].

Since cross-sectional area is involved, electrical resistance probes are useless when corrosion rate corresponding to pitting or crevice corrosion has to be measured. An advantage of electrical resistance probe is that it does not only need an aqueous environment to give suitable results. Moreover, it can also be used to monitor erosion corrosion.

4. LINEAR POLARIZATION RESISTANCE

The linear polarization resistance (LPR) is a popular electrochemical technique for determining corrosion rates, which provides results in a shorter time compared with other techniques [19, 20]. An extremely important advantage of LPR is that, unlike other techniques, it provides direct information on corrosion rate instead of a mere indication [21]. The probes that work on the principle of LPR require a simple circuit that can be used to study the corrosion rate in any environment. The basic setup involves three electrodes: (i) Working electrode; (ii) Counter electrode and (iii) Reference electrode

The working electrode is made of the material concerned, Counter electrode is usually made of graphite or in some cases gold or platinum. The counter electrode should not result in anodic dissolution if the working electrode works as a cathode. Finally, the Reference Electrode is used to provide a reference for the potential of the working electrode under investigation; however, hardly any current flows through it. Usually, SCE (Standard Calomel Electrode) or SSC (Silver Silver-Chloride Electrode) are generally used for various neutral electrolytes. In fields, since SCE and SSC electrodes are fragile, a reference electrode can be made of the same material as the Working Electrode. Reference electrodes of this sort are termed pseudo- or quasi-reference electrodes (QRE) [22]. The Three electrodes are immersed in an electrolyte and are connected externally through a circuit. A high impedance potentiostat is employed in order to provide the required potential and polarity to the electrodes. Between the counter electrode and working electrode are current measuring device and a source of potential. The current measuring device must be able to measure even smaller magnitudes of the current of the order of nano-or pico-amperes.

When measuring corrosion rates using LPR setup, first any potential difference existing between the reference electrode and the working electrode is nullified. Current will then flow between the counter electrode and the working electrode. This flow of current will increase until the working electrode potential is shifted 10 mV from the reference electrode potential. The current that is needed to sustain the 10 mV potential shift is said to be proportional to the corrosion rate of the working electrode [15]. Linear polarization measurements should be measured using data points that are 5mV from corrosion potential to maintain accuracy. Corrosion tests performed in low conductivity electrolyte may yield erroneous results, if not compensated for IR drop by making use of lugging capillary [23].

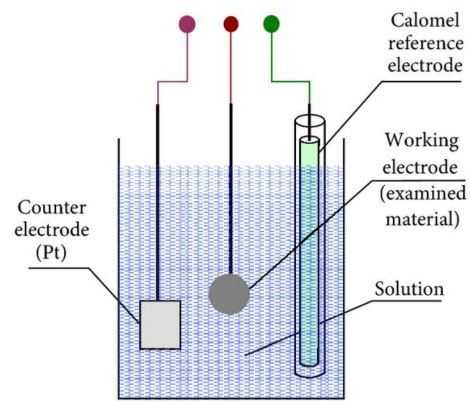


Figure 7. A Sample Three Electrode Cell with Platinum (Pt) Counter Electrode and Calomel Reference Electrode [24].

An example of an LPR probe is shown in Figure 8, in its simplest form. The three electrodes are shown projecting from the probe. These probes are portable, of a different configuration with respect to the media being tested, and provide corrosion rate measurements directly without interrupting the system being evaluated [25].

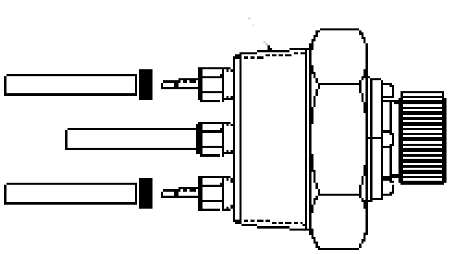


Figure 8. Linear Polarization Resistance Probe[15]

Although this technique is more efficient in terms of data and time, it usually needs more expensive equipment and expertise as compared to the previously discussed techniques[26].

ASTM (American Standard for Testing Materials) has defined several standards for LPR techniques like ASTM G9, G5, G106, G102 [26]. ASTM standard G59 was designed for uniform corrosion study of stainless steel Grade 430 in 1.0 N H_2SO_4 solution while being purged with oxygen free hydrogen gas [27].

5. ZERO RESISTANCE AMMETRY

Zero Resistance Ammetry (ZRA) measures corrosion rate by measuring the galvanic current flowing between two dissimilar metal electrodes usually made of copper and steel. They are built like linear polarization resistance probes with electrodes projecting from the probe body, subject to the corroding environment under study. The electrical circuit diagram of ZRA probe is shown in Figure 10.

For meaningful determination of corrosion rates, it is required that one electrode should be relatively anodic than the other. Another criterion is that the electrodes have to be immersed in an aqueous solution. Zero Resistance Ammetry is applicable in industries for determining the strength of galvanic corrosion occurring due to two dissimilar metals in contact [28].

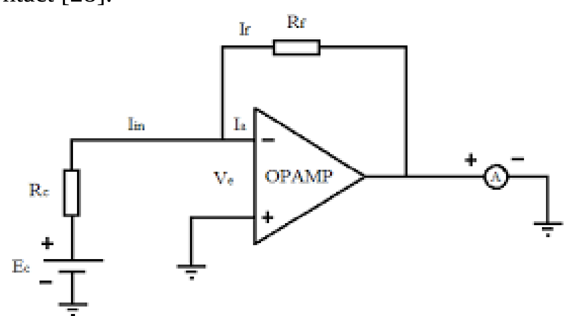


Figure 10. Zero Resistance Ammetry Circuit Diagram [24].

Electrodes of the probe are immersed in an electrically conductive medium. The difference in the electrochemical behavior of two electrodes gives rise to dissimilarity in oxidation-reduction potential of two electrodes. Once the two electrodes are electrically connected via an external circuit, the relatively noble electrode becomes cathodic, while the active electrode becomes anodic. When the anodic reactions are stable as compared to the cathodic reactions, cathodic reactions can be monitored by a galvanic current. However, when the cathodic reactions are more stable, anodic reactions are monitored [29]. ZRA is capable of recording even very small currents between dissimilar electrodes. The galvanic technique is used to study corrosion of dissimilar metals and alloys that are in different galvanic states due to the difference in composition, differential heat treatments like welding, stress relieving, or annealing [29]. A combination of LPR and ZRA has been used by industries and corrosion engineers to measure the rate of localized corrosion, such as pitting and crevice corrosion [30]. The results obtained by ZRA are often plotted with current between electrodes vs. time as shown in Figure 11.

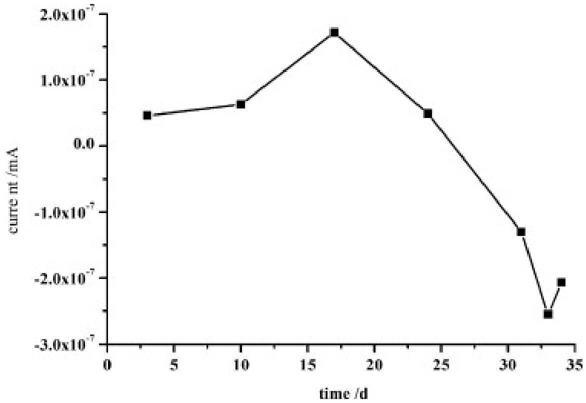


Figure 11. ZRA measurement of copper and iron electrodes [31].

6. ULTRASONIC THICKNESS MEASUREMENT

Uniform or Localized corrosion of a pipeline or any other component results in the reduction of wall thickness. Ultrasonic Thickness Measurement (UTM) is a commonly used non-destructive technique which can be employed for corrosion analysis as well. Erosion and flow assisted corrosion (FAC) can also be effectively studied using this technique [32, 33]. FAC is most pronounced in pipe elbows and is most commonly used in nuclear power plants. This technique is capable of measuring thickness reduction 1/200 of original wall thickness [11]. This method can also indicate thickness increase due to electrodeposition or corrosion product buildup in pipelines [34].

Ultrasound is produced by a transducer in a probe body and is applied to the outer surface of a component under study. The transducer, usually pulse-echo type [35] excites a shear wave which travels across the sample before being reflected back towards the pulse-echo transducer via a back wall of the sample which forms an interface between the material and outside environment [36].

This technique is accurate and more economical for single use in most situations. UTM is advantageous over the previously discussed techniques which have few limitations [37]. Firstly, coupons or probes if installed within the pipe cause pipe's pressure boundary to be affected. Secondly, no direct measure of asset integrity is provided by most of the probes and coupons discussed above, as the actual thickness before corrosion is not being measured. Installation and recovery of the probes and coupons can be risky, and deployment of assessment locations is costly. However, the ultrasonic transducer probe must be applied directly in contact with the external surface of the pipe. This would require repetitive scaffolding, excavation, stripping of coatings or insulation, if any, on the component under study for example pipelines and vessels [31]. Furthermore, ultrasonic transducers fail to work at high temperatures as piezoelectric materials will become ineffective at high temperatures above Curie temperature [32].

Usually, the basic pulse-echo type transducers are used with standards like JIS Z 2355 [38] and ASTM E797 [39]. Once UTM Instrumentation and probes are made applicable, they are permanent or semi-permanent and can be accessed remotely. Once the instrumentation is under use, data can be accessed remotely as well. An example of this technique being used is shown schematically in Figure 12.

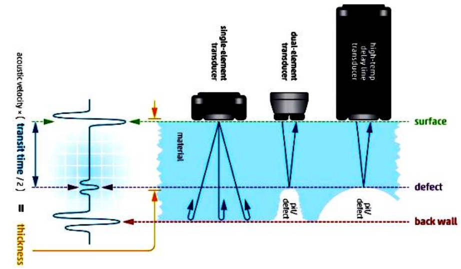


Figure 1 Wall Thickness being measured using ultrasonic transducers [37].

CONCLUSIONS:

Corrosion is a very widespread issue in industries, which has a direct impact on the economy. Corrosion monitoring has become mandatory, in order to diagnose the issue, improve maintenance, prevention from unplanned shutdowns of plants, environmental hazards, and catastrophic failures, etc. The rate of corrosion is important as it tells us how long a certain plant can be safely operated and be useful. Weight Loss Coupons are effective for calculating corrosion rate via weight loss measurements, whereas, the corrosion monitoring probes can be either mechanical, electrical, or electrochemical devices.

The range of instrumentation developed can detect onset along with propagation of both uniform corrosion and localized corrosion. Instantaneous relationship of online corrosion rate data obtained with the process chemistry data and periodic inspection results helps identify severity and duration of the attack to be avoided. Future developments of on-line corrosion monitoring technologies allow real-time control of the problem, with its advantages of safety, reduced operating cost, lesser maintenance, increased service life, lesser contamination, increased productivity and better-quality products.

Various techniques may be involved, alone or in combination to provide data to help to prevent corrosion related problems. A combination of more than one technique is often encouraged to support results and improve accuracy and reproducibility.

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