AN OVERVIEW OF METHODS FOR SIMULATING AND EVALUATING PIPELINE CORROSION

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SUMMARY: Steel pipelines, buried under the soil and protected by the combination of protective coatings and cathodic protection (CP), are used for oil and gas transportation. These pipelines are one of the critical infrastructures for energy transportation and therefore became lifelines of modern society. The deterioration of the external surfaces of transmission pipelines is a serious problem and is caused mainly by coating and/or CP failure leading to the loss of integrity of pipelines. To avoid such damage, there is a need of techniques which are able to locate active corrosion sites, monitor corrosion, and evaluate corrosion damage. Fundamental understanding of such processes occurring on coated pipelines (with various types of defects in coatings as well as pipe) in complex soil environment is necessary for the development of such techniques. Numerous laboratory techniques, i.e., electrochemical impedance spectroscopy based, polarisation measurements based, mathematical simulations, direct observation etc. have been used to develop fundamental understanding, simulate and evaluate corrosion occurring in oil and gas pipelines under various operating conditions. Given the complex nature of the pipeline corrosion, application of these laboratory techniques in field measurements as well as in understanding the corrosion mechanisms is lacking. This paper presents an overview of investigations, based on electrochemical techniques, for simulation and evaluation of pipeline corrosion in laboratory.

Keywords: Pipeline corrosion, cathodic protection, stray current, cathodic disbondment, electrochemical impedance spectroscopy

1. INTRODUCTION

Most pipeline failures are caused by various forms of corrosion, i.e., general corrosion, crevice corrosion under disbonded coatings, pitting corrosion, stress corrosion cracking (SCC) etc. Due to the electrochemical nature of corrosion, electrochemical techniques can be a very powerful tool not only in monitoring pipeline corrosion but also in developing the life prediction programs for pipelines, understanding mechanistic aspects of corrosion, and possible remedies. Use of electrochemical techniques in monitoring and evaluating external pipeline corrosion is limited. Based on the understanding of electrochemical characteristics of coated pipeline steel and soil, various corrosion models have been developed to predict pipeline corrosion [1-4]. However, these models and electrochemical techniques being used in pipeline industry are at a rudimentary stage, mainly due to:

1) Pipeline systems being very complex involving variables from soil and coating systems that vary not only with geographical locations but also with weather.

2) Lack of extensive and reliable corrosion data.

3) Lack of fundamental understanding of corrosion process occurring in the pipeline.

Development of life prediction programs and electrochemical techniques for corrosion monitoring is possible after rigorous laboratory experiments simulating real life conditions. Such experiments are expected to help in developing fundamental understanding of various forms of corrosion, effect of various variables involved in the process of corrosion damage, effect of environment (i.e., cathodic protection, stray current, soil conditions) etc. Data generated from these experiments can be used as input parameters for calculations of pipeline corrosion. Various electrochemical techniques such as potentiodynamic polarisation, linear polarisation resistance (LPR) measurements and electrochemical impedance spectroscopy (EIS) have been used to investigate the corrosion mechanism and kinetics occurring in pipeline steels [5-8]. For example, polarisation tests and thermodynamic data helped in determining CP parameters [9-11]; linear polarisation method has been used to predict the corrosion resistance [7]; electrochemical impedance spectroscopy has been widely used to understand coating defects and corrosion under disbonded coating [8,12,13]. These techniques could be used to develop further understanding of corrosion processes involved and to quantify corrosion, quality of coating and coating damage. This paper will summarise laboratory investigations, carried out using electrochemical methods, to understand corrosion occurring under applied CP, and to characterise coating properties and coating failure.

2.   CATHODIC PROTECTION AND STRAY CURRENT CORROSION

Pipelines are protected by protective coatings. Various coatings and coating application methods have been developed but none of the coatings are perfect and contain defects which could be inherently present during application of the coating or developed during service conditions [14]. Protection against corrosion at these defects is afforded by impressed current cathodic protection (CP) systems which apply a cathodic current to maintain the metal pipe at potential where the corrosion rate is negligible. Principles of cathodic protection can be found in open literature [15-17]. Most of the standards agree with the applied potential of -850 mV with respect to a copper-copper sulphate (CSE) reference electrode. However, choice of CP potential is controversial and authors suggest that CP potential should be adjusted as per environment/material conditions. Soil chemistry, type of pipeline steel in use, coating type, and influence of stray current etc. must be considered in choosing the CP potential. A very negative applied potential leads to hydrogen generation which may cause hydrogen embrittlement and also enhance coating disbondment, therefore choice of CP potential becomes very important [10,11,18]. With the increasing number of incidents of pipeline corrosion, effect of applied potential on both corrosion rate at the coating defects (exposing metal to soil), and disbondment of coating and corrosion under disbonded coating has to be investigated.

An applied CP potential polarises the steel to bring it into the cathodic region of the Evans Diagram, however, there is always a net corrosion occurring at very slow rate [9.] Determination of corrosion rate under CP conditions is an important issue and has attracted only limited attention. Numeric methods [19-21], based on the knowledge of corrosion current density, open circuit potential (non-polarised state), and understanding of activation polarisation were developed. However, the problem is more complex and concentration polarisation should also be accounted for in these models. There are only limited experimental electrochemical studies to calculate corrosion rate, probably because corrosion rate under CP is considered negligible and poses a minimal threat. Thomson at al. [22] used EIS to investigate the corrosion rate (of bare steel without any coating) under various applied potentials in sand and soil media. EIS analysis suggested diffusion controlled reaction in open circuit potential and charge transfer controlled reaction occurring under cathodic potential. When potential was decreased to very negative values, a decrease in polarisation resistance was noticed. The decrease in polarisation resistance was attributed to increase in cathodic reactions occurring at the surface, but not corrosion. Juchniewicz and Jankowski [23] used EIS to determine impedance as a function of applied potentials (varying from -550 to -1100 mV $_{SCE}$), as presented in Figure 1. Similar to the observation made by Thomson et al. [22], a decrease in impedance was noticed when applied potential was very negative (Figure 1). EIS data was analysed using IMP-CP [24] program and parameters thus obtained were used to calculate the anodic current density. For very high cathodic protection values, determination of anodic current was not possible as the resistance of anodic process exceeds the cathodic process resistance by several orders of magnitude. A critical review on experimental and computational techniques useful for monitoring corrosion rate under CP was given by Jankowski [25,26].

Stray current present in the environment disrupts CP and is reported to cause serious damage on metallic structures subjected to interference even when cathodic protection was applied [27]. Stray current could arise from various sources- both manmade [27] (train or transport lines and electricity transmission lines) and natural [28]. With the development of transportation and the improvement of electrical facilities, the influence of stray current on buried pipelines is becoming more and more serious and with the increasing number of incidents of stray current corrosion, it becomes important to develop techniques to monitor the corrosion by analysing the stray current data [27-29]. At present we have two important challenges: 1) reviewing CP potential to minimise corrosion occurring due to stray currents, and 2) evaluation of corrosion damage caused by stray

currents. Both these challenges require fundamental understanding of corrosion caused by stray currents and laboratory techniques can be very useful in developing understanding which can revise CP criteria.
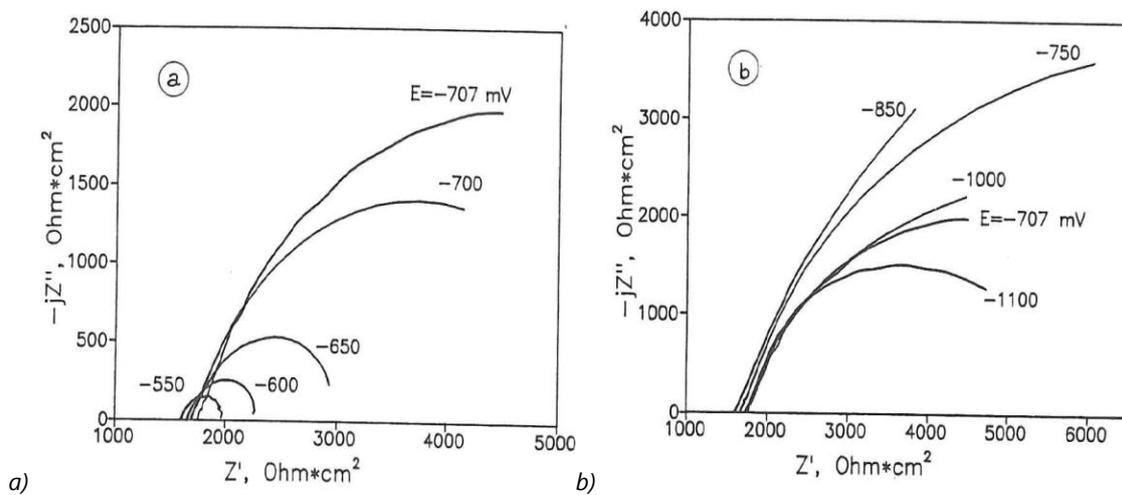

Fig.1. EIS for carbon steel in tap water at various potentials: a) anodic region, b) cathodic region [23]

It is claimed that corrosion induced by stray currents is similar to alternating current (AC)-enhanced corrosion and AC-enhanced corrosion first being recognised at the beginning of the 20th century [27-30]. Gellings [30] was one of the first authors to perform a comprehensive theoretical treatment of the effect of periodic signals on the polarization behaviour of metals. Chin and Venkatesh [31] derived an expression for the normalized corrosion density for a corrosion system where AC was present. Chin et al [32,33] suggested an increase in corrosion rate due to AC. The acceleration of corrosion rate was attributed to the ability of alternating voltage (AV) or AC to reduce both anodic and cathodic polarisations. Lavalani et al [34,35] have presented theoretical model for understanding the effect of AC corrosion and concluded that AC induced corrosion can disrupt passivity.

Experimental investigations on influence of AC current were performed later. Jones [36] investigated influence of AC current on corrosion of low alloy steel and carbon steel in 0.1 N NaCl and concluded that polarisation in cathodic direction was more rapid than that in anodic direction which leads to decrease in anodic Tafel slope and therefore increase in corrosion. Fu and Cheng [37] reported accelerated corrosion caused by applied AC. They performed potentiodynamic polarisation tests under varied AC signal. The presence of AC interference decreased the CP effectiveness to protect the steel from corrosion [38]. Further analysis suggested that when AC current exceeded 100 A/m^2, applied CP of -0.85 V (vs SCE) was not able to protect steel from corrosion [39]. However, a complete protection from AC current was reported when potential was decreased to more negative potential (-1 V vs SCE or less). Godidanich et al [40,41] used potentiodynamic polarisation tests to understand the effect of AC current on corrosion behaviour of various metals including steel. It was found that in presence of AC current, corrosion rate was increased and in general, corrosion potential was shifted in more negative direction. Cheng et al recorded current under variable potentials [42] and it was reported that current obtained under variable potential condition was higher than that at constant potential condition. Localized EIS was conducted to show presence of local microsites with low impedance which were attributed to sources of pitting. Scanning electron microscopy of the specimens after electrochemical tests revealed occurrence of pitting corrosion under variable applied potential conditions, whereas no pitting corrosion under constant applied potential conditions was noticed. These studies show that stray current corrosion can lead to accelerated corrosion and further studies are required to understand, estimate and monitor corrosion occurring due to stray current in catholically protected pipelines. Birbilis et al [43] have presented a comprehensive experimental study to investigate the effect of telluric current on the corrosion of catholically protected pipelines buried under sand. It was concluded that corrosion caused by telluric current in high resistivity soil was too low to be detected. An standard for evaluation of AC corrosion is presented in [44]

3.   COATING CHARACTERISTICS AND DISBONDMENT

Coatings are applied on pipelines to protect them from environmental degradation [14]. These coatings are not perfect and fail during prolonged service conditions due to various reasons, i.e., mechanical damage, holidays, disbondment caused by permeability and/or cathodic reaction on mechanically damage areas. Mechanism of disbondment is not discussed in the present paper. For characterisation of disbondment, a cathodic disbondment

resistance (CDR) test is most frequently used which is a quantitative method. However, it is only a qualitative predictor of corrosion protection performance. More quantitative, reliable and accelerated methods are required for characterisation of pipeline coatings. Electrochemical tests such as EIS and/or potentiostatic polarisation tests could be very useful in investigating coating and coating defects. For instance, Gray et al [45,46] suggested that at an applied frequency of 0.1 Hz, an excellent barrier coating must have an impedance of 1000 MΩ/cm^2 or higher. Impedance value decrease as the number of defects present in the coating increase. Coatings with capillaries have impedance value in between 10 to 1000 MΩ/cm^2 [45-47]. Murray at el [48] investigated coating properties followed by long term immersion of coated steel in sea water and suggested that a good coating should have total resistance more than 100 MΩ/cm^2 and a poor coating shows resistance values less than 1 MΩ/cm^2 [48]. Several EIS based studies, performed over a wide range of frequencies, suggested that coatings with no defect had no real component and this finding could be further used as a method to find out presence of defects/absorbed water in coatings [48-51]. Davis et al [52] suggested an EIS based study to (co-relating change in capacitance due to the difference in dielectric constants of water and coating) calculate water uptake of coatings used in boiler tubers. Margrait and Matos [53] explored possibilities of application of EIS in characterisation of coating under cathodic protection condition and concluded that monitoring change in coating characteristics using EIS is a difficult task. They suggested that presence of defects could be detected but quantification of coating parameters was not possible. However, in a later study with improved experimental design, coating permeability was investigated [54]. These studies were aimed to investigate various coating characteristics of coatings immersed in aqueous electrolytes.

Electrochemical techniques can be very useful in understanding and estimating corrosion occurring under disbonded coating. Dong at el [55] used localised EIS (LEIS) [56] to characterise corrosion at coating defects under applied cathodic potential and it was found that a narrow geometry of coating defect caused cathodic shielding leading to corrosion of the steel surface beneath defect. Chen et al [57] investigated effect of applied cathodic potential on pH, potential, and oxygen concentration by designing special artificial cell. It was shown that IR drop caused CP shielding and sufficiently negative potential was required for complete protection. However, potentiodynamic polarisation tests show that at very negative potentials, hydrogen evolution occurs which is deleterious [57]. Lee et al [58,59] attempted to develop an accelerated EIS based electrochemical technique to evaluate coatings. Pulsed polarisation (alternative cycles of anodic and cathodic polarisation for 3 hours hold time) on a steel sample with defect were used to accelerate coating failure by simultaneous cathodic disbondment and oxide lifting mechanisms. Perdomo and Song [60] designed a special cell to understand chemical and electrochemical conditions under disbonded coating. They concluded CP shielding caused by solution resistivity leads to corrosion. Corrosion was found to also depend upon resistivity, crevice width and holiday size [60-62]. Papavinasam et al. [13] has carried out a comprehensive study to change existing cathodic disbondment resistance tests and evaluated various EIS parameters of coatings under various temperature and applied potential conditions. Further EIS data was compared with disbondment area and found a good correlation with the field data.

Pipeline corrosion is a little more complicated and soil environment imposes high resistance which makes electrochemical measurements challenging. Recent development in electronic devices enabled to make measurements in high resistive systems with an interface resistance of up to 1 TΩ. For example, Macdonald et al [63,64], used EIS to make measurements in high-resistivity media (reinforced concrete structure). Murray and Moran [65] used EIS to investigate the effect of moisture and various soil characteristics on the corrosion of coated pipeline steel in the presence of holiday. Experimental data obtained in the laboratory was in good agreement with field data. Castaneda et al [66] calculated polarisation resistance of buried pipeline by analysing EIS data which was used to calculate corrosion rate using modified Stern-Geary equation. An algorithm was developed to calculate remaining pipeline life and reliability of the method [66]. Murray et al [67] proposed a specific pseudo-capacitance method to determine area of corroding steel surface which could be useful in determining size of holidays, defects cracks etc. Gray and Appleman [46] described several uses of EIS for evaluating critical coating properties (barrier properties and permeability) of protective coatings. They tested six coating with a wide range of properties and EIS was able to detect the subtle differences in the coating properties. They further suggested that comparison of the degree of water permeation of a coating, and pre-existence of water level can be detected by EIS [46].

4. USE OF EIS IN UNDERSTANDING PIPELINE CORROSION

EIS is now a well-established and very powerful tool to understand the electrochemical process occurring at interfaces and can be used to estimate corrosion kinetics and underlying mechanisms. Work mainly pioneered by Mansfield [8,49,51,54], Scully [6,12], Murray [48,65,67,68] etc. suggested that EIS can be used to investigate corrosion occurring in coated metallic materials. In this section an attempt is made to show the relevance of EIS technique in pipeline corrosion, particularly, the manner in which coating impedance decreases. An EIS model which is in general consensus and is widely used in coated metal is presented in

Figure 2. Using EIS, various parameters, i.e., coating capacitance (C_{coat}), double layer capacitance (C_{dl}), polarisation resistance (R_p), pore resistance (R_{coat}) and solution resistance (R_Ω) as shown in the Figure 2 can be determined. Net impedance (Z) can be determined by these parameters which depend upon applied frequencies. At higher frequencies, Z is limited by solution resistance, whereas R_p dominates at lower frequencies. Measuring these parameters various properties of coating and coating defects can be determined. Some of the methods those could be useful for the EIS analysis are discussed below:
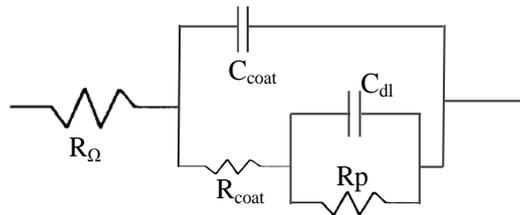

Fig.2. Standard equivalent circuit [13,46]

Method 1 *[13,46]:* After measuring impedance of coatings at 100 mHz, coating can be categorised as following: 1) Impedance of 1000 MΩ/cm^2 indicates to an excellent barrier coating, impedance of 10 to 1000 MΩ/cm^2 indicates to presence of capillaries, coating with pinholes has an impedance from 0.1 to 10 MΩ/cm^2.

Method 2 *[13]:* Capacitance of coating depends upon water intake as dielectric constant of water is about 20 times more than that of polymeric coating. Low volumes of water, υ, can be calculated as:

$$\frac{\varepsilon_t}{\varepsilon_0} = \frac{C_{coat,t}}{C_{coat,0}} = 80^\upsilon$$

Where, ε_t and ε_0 are dialectic constants at time t and 0. $C_{coat,t}$ and $C_{coat,0}$ are capacitance at time t and 0 respectively.

Method 3 *[13]*: Sum of the all resistance ($R_{max} = R_\Omega + R_p + R_{coat}$) can be used to determine coating quality. An excellent coating must have $R_{max} \geq$ 100 MΩ/cm^2 whereas a poor coating possess $R_{max} \leq$ 1 MΩ/cm^2. This method was tested by Papavinsam et al [13,69] but no correlation with real data was established.

Method 4 *[13,46]*: The impedance of a coating with no defect has no real component and therefore a perfect coating should only show capacitance. With the development of defects coating resistance develops and corresponding elements (C_{coat} and R_{coat}) appear in the equivalent circuit presented in Figure 2.

In addition to testing coatings characteristics, progress of disbondment in the presence of coating defect can be monitored by analysing impedance value at regular intervals of time. Impedance value should correlate with the increase in area and reactions occurring under crevice. EIS can be useful in investigating the effect of various CP conditions and its effect on cathodic disbondment.

5.   SUMMARY

This paper has summarised various laboratory investigations (using EIS and polarisation based techniques) carried out to understand and quantify corrosion caused by stray current, evaluate coating characteristics and monitor corrosion under disbonded coatings. These laboratory techniques are very helpful in developing fundamental understanding which is essential for developing electrochemical tools and models for real life applications. For instance, a very negative CP potential prevents corrosion but also enhances coating disbondment due to generation of OH$^-$ (and hydrogen if potential is in water reduction reaction regime). Optimum potential, which can give maximum corrosion protection without causing coating disbondment, can be determined by extensive laboratory experiments and can be further applied in field.

This paper has reviewed various laboratory investigation performed to understand and characterise the coating characteristics, coating defects and corrosion in coated steel. These experimental techniques are promising in developing fundamental understanding of various mechanistic aspects. However, more holistic studies investigating coating characteristics, coating defects, coating disbondment etc. are needed in order to help in modifying current corrosion protection practices and developing new standards. In addition to data generation and understanding mechanism, these techniques, particularly EIS could be used in field to determine coating defects, disbondment, and remaining life of coating. However, dedicated research to develop such techniques for field application and understanding corrosion are required.

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