CHAPTER (2)
LITERATURE REVIEW

2-1 Introduction

In this chapter a review concerning corrosion in general and methods of corrosion prevention with particular emphasizes on cathodic protection is given. The review is classified in related subdivisions starting with a historical background.

2-2 History and Background

Technologies by which corrosion, in general, can be controlled or prevented include:

a) Proper materials selection,

b) Proper design,

c) Coatings,

d) Inhibitors (not applicable, of course, for open sea water exposures),

e) Modified operating conditions, and

f) Cathodic protection (CP).

The last of these, (CP), was first conceived and studied for more than 160 years ago, as reported by the classic papers of Davy [2-4], and remains today the primary corrosion mitigation technology for the submerged portion of marine structures.

Because of its relatively high strength, good fabrication ability, and low cost, steel has, for the past century, been the most utilized material of construction for marine as well as on land structures. However, corrosion of steel in most submerged sea water service proceeds at an unacceptably high rate unless protective measures are taken. Of the different corrosion control options mentioned above, cathodic protection is now generally recognized as the most cost effective and reliable for corrosion mitigation. Hallmark accomplishments in the evolution of CP are summarized in Table 2.1 [5].

Table 2.1 Historical development of cathodic protection technology

Time	Accomplishments
1820's	Classical experiments of Davy and introduction of cp.
1940's-1950's	Experimental programs by Canadian and U.S. Navies'
1960's-1970's	Development of improved galvanic anodes (aluminum base in particular)
1980's	Introduction of Mixed Metal Oxide (MMO) impressed current anodes.
1980's	Incorporation of Rapid Polarization into design practice.
1980's-1990's	Research studies on calcareous deposits.
1980's-1990's	Development of Boundary Element Modeling methods.
1990's	Development of a first principles based unified design equation.
1990's	Development of improved potential attenuation models.

Particularly noteworthy are developments over the past two decades, which include:

a) Development of improved materials for impressed current anodes,

b) Recognition of the benefits of rapid polarization, and

c) Development of a unified design equation.

A fundamental aspect of CP for any application is the criterion for design if the level of cathodic protection is adequate. Several of these are available; however, a requirement of polarization to at least -0.80 $V_{Ag/AgCl}$ has evolved as prevalent for steel in sea water. It is generally accepted that such a potential criterion for protection corresponds to polarization of cathodic sites to the reversible value for the anodic reaction; and theoretical considerations, subject to certain assumptions, have shown this to be approximately the case [6].

Typical values for three design current densities are listed in Table 2.2 [7]

Table 2.2 Cathodic protection design current densities

Production Area	Typical Design Current Density, mA/m^2		
	Initial	Mean	Final
Gulf of Mexico	110	55	75
U.S. West Coast	150	90	100
Cook Inlet	430	380	380
Northern North Sea	180	90	120
Southern North Sea	150	90	100
Arabian Gulf	130	65	90
Australia	130	90	90
Brazil	180	65	90
West Africa	130	65	90
Indonesia	110	55	75

2-3 Corrosion Protection

Marine structure models were constructed in 1974 to study new corrosion protection systems over a long term [8]. The results based on 12 years exposure indicate that excellent systems for splash and tidal zones were polyethylene, rubber, epoxy mastic and metal wrappings with cathodic protection. The laboratory tests showed that the minimum rupture energy of a sprayed urethane coating was proportional to the square of coating thickness and gave minimum coating thickness required. This paper also reviews new corrosion control measures applied later to the gigantic maritime structures, which are desired to possess 50 to 100 years durability. The protective coatings using in atmospheric zone are fluororesin and acrylic silicone resin paints with excellent weather ability. In the splash and tidal zones super heavy duty epoxy mastic and corrosion resistant metal (SUS 316 L, Ti) wrapping are preferably listed in the specification in combination with cathodic protection.

The rapid advances in technologies in various fields have also recorded significant progresses in the field of newer materials as the reliability and effective performance of industrial equipment as well as the associated components mostly depends upon their integrity over specified period [9]. Though the basic methods of protection of materials like use of corrosion-resistant alloys, application of surface coatings, modification of the environment and application of cathodic protection have largely remained the same, the approaches and techniques adopted in each of these fields have been so advanced that one could today advocate appropriate protection systems with high reliability and performance. The author presents some of his contributions along with his colleagues in the fields of cathodic protection of vital structures, development of newer coatings for specific applications and new approaches to corrosion monitoring techniques, besides highlighting the corrosion behaviour of some of the heat-treated alloys which are specifically used in such strategic areas as space and defense. The presentation would also cover briefly some of the techniques that have been employed by the author for better understanding of corrosion and passivation of metals and alloys.

The cathodic protection has been applied to steel structures located in submerged zone of sea wave environments [10]. The purpose of this study is to examine the protective effectiveness of cathodic protection and steel potential behavior of steel affected by sand erosion at sea bottom. The study described in this paper was carried out by using existing steel pipe pile structure and test pieces. From the test results, it was found that protective effectiveness of cathodic protection was recognized even for the steel under sand erosion. Also, it was found that the behavior of steel potential was affected by the sand drift at sea bottom caused by (significant) wave.

This program investigated the requirements for extremely long duration (more than one hundred years), special corrosion resistance to sea water for a floating structure hull [11].

A combination of corrosion resistant, metal clad plate for the splash zone and painting with cathodic protection for the submerged area of the hull was identified, considering long-term durability and construction and maintenance costs. Verification that clad plates would be a rational choice for corrosion prevention and structural member application in spite of possible difficulties in welding at sea still remained. This study attempted to demonstrate the practicality of using clad steel plates for not only corrosion protection, but also for the structural steel of floating structures by the construction of 2 meter high, 60 meter wide by 300 meter long prototype floating model.

Twenty years experience with corrosion protection of metallic and reinforced concrete structures at the Kislogubsk tidal power plant is described[12]. The use of paint coatings was found to be inexpedient due to short service life. Cathodic protection was accomplished using scrap-steel anodes" in the form of welded structures submerged to a depth of 5m.

The reinforced concrete exposed to marine atmosphere deteriorates very fast resulting in the corrosion of reinforcement. Corrosion of reinforcement reduces the life of the structure [13]. It is impossible to estimate accurately the loss resulting from corrosion. In 1925, FRANKN Speller estimated roughly that the renewal of iron and steel products such as roofing, wire, tubes and pipe, oil-well equipment, steel coal cars and many other steel or iron structures subject to corrosion because of inadequate or no protection amounted annually to about 2 percent of the total tonnage of such products in use. In this paper, the facts were established with respect to the nature and mechanism of corrosion, typical chemical reactions of the corrosion process; corrosion measurements, corrosion control methods: cathodic protection methods, protective coatings, admixtures and incubations. Corrosion measurement techniques are also presented and examples are given wherever possible. The corrosion in the Tuticorin marine environment is described.

2-4 Cathodic Protection Monitoring

Several methods were developed for corrosion protection monitoring, some of which are rather sophisticated for large scale floating structures, the pseudo-noise inverse analysis method for the estimation of the electro-potential distribution on the surface of floating structures based on the measured potential data in sea water is proposed [14].

For analyzing the galvanic corrosion of a long underground structure such as a pipeline and an oil well casing a new boundary element method was developed.

A long underground structure is often buried in soil with non-uniform electric conductivity [15]. In case where the conductivity change is distinct, the conventional multi-region method is useful, while it gives an unrealistic solution with discontinuous jumps for gradual change of conductivity. To overcome the difficulty, the fundamental solution for a field with linear change of conductivity was introduced by using the Fourier transform technique, and the polarization characteristics were formulated to express its continuous change. A few example problems were solved with this method to demonstrate its applicability and usefulness.

The measurement of corrosion in hot, hostile and inaccessible locations, both within process plants and on remote pipelines, and the collection of data from widely-separated measurement points to a single location for monitoring and assessment have been automated using a type of ultrasound transducer, called an Ml [16]. For data collection, there is the DTS 2000 communication system which used the metal structure of the pipeline as a transmission path for an electromagnetic signal. This technique has to co-exist with the pipeline's cathodic protection (CP) regime, together with sources of external electrical noise. A 15-year power supply is provided for the instrument and the communication module.

It is generally accepted that a buried steel structure is protected if its potential is more negative than minus 850 mV [17] relative to $Cu/CuSO_4$ electrode. Gaz de France has developed a numerical integrator called Corva, this new device is really user-friendly and easy to manipulate. The collected data stored in histograms is quickly analyzable. This paper also discusses PC Tel, an innovative method of monitoring the efficiency of a cathodic protection system of a large urban gas network.

The approach consists in defining significant criteria, as well as choosing a reduced number of measurement points representative of the protection level. The PC Tel, cathodic protection remote monitoring system is made of two components. On the site, a Field Satellite Station (FSS) is made up of a PC Tel, which measures, classifies, stores, and restitutes the cathodic protection data. It is connected via modem to the telephone network. In your office, a non-dedicated microcomputer, called a Central Surveillance Station (CSS), allows data storage and the alarm transmissions coming from the connected FSS.

2-5 Design of Cathodic Protection Systems

The current required to protect various components in a complex plant structure varies dramatically, depending on the associated structures nearby and the specific environment [18]. The cathodic protection design should supply current where needed rather than attempt to provide a uniform current density throughout the plant. A review of the plant construction drawings is useful in identifying the areas of possible high current densities. Current requirement tests in major process facilities provide meaningful and useful data and can be used to locate an ideal ground bed and predict resultant potential readings. This method can be used to upgrade existing facilities and design the optimum location for a ground bed in pipeline gathering systems.

A successful design of CP systems underground structures should consider, besides current and voltage calculations, other factors that may arise such as interference with neighboring metallic facilities, shielding phenomenon .... etc.

Cathodic protection is most efficiently and uniformly applied with the primary structure is electrically isolated [19]. For pipe lines, cathodic isolation is a form of electrical isolation that maintains stringent electrical grounding requirements and confines the DC protective current at the surface of the structure. It provides all the advantages of electrical isolation by blocking the DC protective current at the electrical isolating device, while maintaining an effective grounding path to ensure personnel and equipment remain safely protected during all types of electrical disturbances, including AC fault currents, lightning, AC induction and power switching surge current.

With cathodic isolation, uniform cathodic protection can be safely achieved at a greatly reduced cost.

According to the author [20], problems that develop with the use of cathodic protection indicate the need for confirmation of principal fundamentals. The value of the protective potential and other cathodic protection conditions can be established by laboratory investigations. If various corrosion systems are formed on the structure being protected, attention must be focused on this situation in designing cathodic protection.

Cathodic protection is essential for long-term corrosion protection of steel in submerged service, but it adds cost and weight to offshore structures. With proper design optimization savings of 0.12 to 5.0% can be achieved while increasing reliability [21].

The optimization approach presented in this work tailors the sacrificial anode number, shape, dimensions, core diameter and alloy to the given design criteria (current density requirements and design life) and environmental conditions. A program for a personal computer has been developed to determine the optimum design for a given structure. The program provides automatic consideration of a myriad of possible designs by varying the different anode parameters and ranking the designs according to cost or weight. Length and cross-sectional area are shown to be the most important anode parameters. Results indicate that the optimum design varies significantly with the design criteria and environmental conditions.

2-6 Monitoring of Cathodic Protection

A unique probe configuration which incorporates a salt bridge and a fixed steel ring coupon to assist in making potential measurements on cathodically protected structures with consideration of voltage drop error is described [22].

The successful and efficient cathodic protection (CP) survey of a deep water structure using a remotely operated vehicle (ROV) has remained an enigma to many corrosion engineers in oil companies [23]. The location of the corrosion group within the company structure often plays a major role in the success of the project. Operators locate their corrosion departments in different groups, some in the offshore/onshore operations and others in the design group. This location often has a bearing on the financial and operational approach to the project. A successful CP survey is both an achievable and exciting project with experienced preplanning and selection of the correct equipment

Coupons are utilized mainly for conducting on-line corrosion monitoring of metals in plant equipment under operating conditions by the use of electrical or electrochemical methods [24]. Within specified limitations, these test methods can be used to determine cumulative metal loss or instantaneous corrosion rate, intermittently or on a continuous basis, without removal of the monitoring probes from the plant.

2-7 Computer Modeling

Computer modeling is gaining popularity in the design and verification of cathodic protection (CP) systems for offshore structures [25]. The work presented in this article expands the use of CP simulation to consider the metallic electrical resistance of risers/tendons used with tension leg platforms where anodes are mounted on the hull or sub sea structure. The SEACORR/CP computer system was used to perform a parametric study to identify the limitations of CP and coatings in providing corrosion protection. The effect of using a titanium riser instead of a steel riser was also considered.

The electrochemical impedance for a two-electrode cell consisting of a buried metallic structure and a small non-polarizable disk electrode is discussed on the basis of a computer simulation considering the distribution of ac signal current [26]. Since interfacial impedance decreases with increasing ac frequency, the electrochemical impedance at high and low frequencies correspond to those for the primary and secondary current distributions, respectively. The complex plane plot of the simulated electrochemical impedance for a buried structure exhibits a deformed semicircle, the intercept of which on the real axis is not proportional to the true transfer resistance. The impedance diagrams for buried structure in the presence of a local corrosion deviate from those in the absence of local corrosion below a certain frequency which is determined mostly by the distance between the local corrosion site and the probe electrode. This break-point frequency serves as a reliable tool for detecting the location of a local corrosion of a buried structure.

Computer applications demonstrate the importance of expert systems for corrosion control of metallic structures [27]. Significant considerations for coating selection, corrosion-monitoring, and protection evaluation are summarized. Effective insulating coatings display good electrical performance, require minimal current densities for structure protection, and are synergistic with cathodic protection systems even after many years of service. Computerized database programs can be employed to evaluate structure protection potentials and corrosion probe data. Computerized ON/OFF potential data can be used to assess IR drop and polarization effects for cathodic protection evaluation. Corrosion probes connected to cathodically protected structures verify adequacy of protection levels and support existing protection criteria. Computerized survey and historical analyses can help assess cathodic protection system changes due to coating damage, electrical shorts, and stray-current interference.

A paper [28] describes the PROCAT computer system, under development by the Civil Engineering Department of COPPE/UFRJ for Cenpes/Petrobras. The main objective of PROCAT is to assist in design of cathodic protection systems for underwater or buried pipelines and offshore structures. The program makes use of a numerical formulation based on the boundary element method and can be applied to two-dimensional, axisymmetric or fully three-dimensional problems. The cathodic protection system may be of galvanic or impressed current type. The boundary conditions of the problem can be linear or nonlinear, based on the cathodic polarization curve.

A numerical modeling of cathodic protection for both submarine and underground structures has been developed [29]. This modeling can aid and double check the design of cathodic protection system for the corrosive environment. The polarization resistance, the relation of specific conductivity, and the remote distance of anode system in semi-infinite structure are the major variables used in designing this model. The computer prediction has been found in good agreement with scale down test and real size measurements. This multipurpose numerical model can aid the cathodic protection engineer in the design of the optimum anode size and location. As a result, the protection efficiency and the cost can be improved dramatically.

Cathodic protection (CP) is a corrosion prevention technique which uses electrochemical properties of metals to insure that the structure to be protected becomes the cathode of an electrolytic cell [30]. The technique is commonly used for protecting metallic structures placed in aggressive environments, e.g. ship hulls, offshore structures and underground pipelines. Mathematical models of CP problems require appropriate boundary conditions given by a polarization curve, which is a non-linear relationship between the electrochemical potential and current density. However, information on the polarization curve is not always available and strongly depends on the time history of the system. Another important problem in corrosion engineering is the identification of coating holidays, i.e. parts of the structure which have lost their protective coating and became anodic and prone to strong localized corrosion. The purpose of this paper is to present a boundary element methodology coupled to genetic algorithms for inverse problems in corrosion engineering. The problems studied include the identification of parameters characterizing the polarization curve, the identification of coating holidays and the optimization of anode positioning and their-impressed current. Several results of applications are discussed, including

CP studies of practical three-dimensional engineering problems.

2-8 Solar Photovoltaic

The cathodic protection (CP) system objective is to protect metallic structures against corrosion caused by chemical reaction between metallic structures and surrounding mediums, such as soil or water [31]. To overcome such a problem, a sacrificing anode is connected to the protected structure (which acts as a cathode) through a DC power supply. As a result, a current passes from the sacrificing anode to the protected cathode. This leads to anode corrosion rather than causing the cathode (protected structure) corrosion. To stop the corrosion, the protected structure requires a constant current.

Impressed current cathodic protection is increasingly becoming the preferred method for protecting inaccessible structures that are vulnerable to corrosion [32]. Solar generators are the obvious choice to supply power to these installations and the "intelligent output controller has overcome many of the problems associated with previous systems.

The disadvantages of existing technology led to the development of the intelligent output controller designed especially for solar generators. This energy efficient device is capable of automatic metering and monitoring of system performance. The level of protection can be automatically adjusted by manipulating the potential difference between the structure and the sacrificial anode.