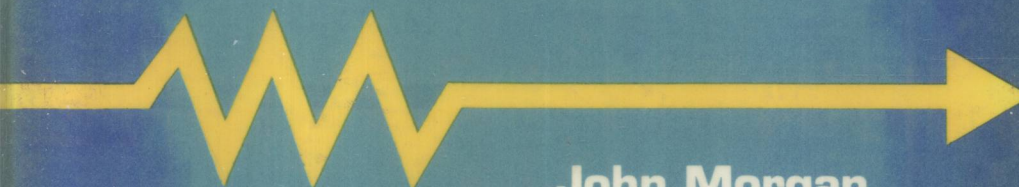


Cathodic Protection

[Second Edition]



John Morgan

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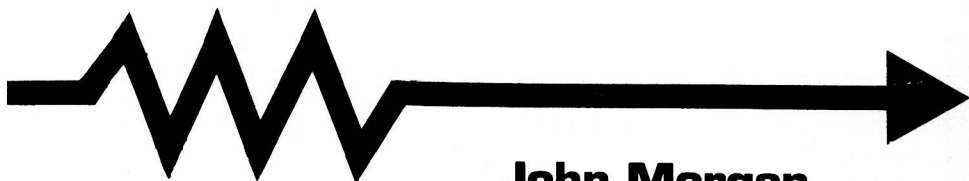
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National Association of Corrosion Engineers

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Preface

Corrosion has been known to man since the earliest metallurgical times and has been a constant drain on his enterprise. It has only comparatively recently received a scientific treatment which can date its foundation less than a century and a half ago and its major developments to the last few decades.

The necessary presence of a corroding fluid has meant that many preventative methods rely upon isolating the metal from the harmful environments either by the use of a foreign coating or by the formation of a resistant corrosion or chemical film upon the metal. The electrochemical theory of corrosion suggests, that in bulk electrolytes at least, an electrical method of corrosion prevention could be used and this method is called cathodic protection.

The object of this book is to explain the techniques employed with this method rather than to establish the electrochemistry of the metal/electrolyte interface. The subject has been broadly divided into two parts, the first of which treats cathodic protection as a technique, while the second considers the methods of achieving protection on a variety of structures. These sections are not exhaustive nor are they intended as a do-it-yourself manual; rather it is hoped to bring to the reader a clearer understanding of how cathodic protection may be used and to give him some critical faculty with which to compare the results of its application and the engineering methods employed.

The criterion of protection has been assumed to be one of achieving a particular potential, or possibly a potential change, between the structure under protection and its local electrolyte. While there may be little theoretical justification for this criterion the ease with which it can be used makes it preferable even when employed only as a secondary criterion. This change in potential is caused by a flow of direct current from the electrolyte on to the metal and the engineer's job is so to arrange this that protection is effective everywhere. As such perhaps he will need more than anything else a training in light electrical engineering.

Metallic corrosion is, almost without exception, solely an economic loss and any method or combination of methods of its prevention must prove to be of economic advantage. To this end cathodic protection will

often find its most acceptable application as a complement to some form of coating. While it is not the answer to every corrosion problem its use can cause great savings but more particularly removing the problem of corrosion from the designer will allow new freedoms, developments and economics in the engineering.

I could not have undertaken to write this book without a great deal of assistance. Much of the information in the book is taken from the original work of my many friends in the cathodic protection industry. Some of that which is my own research work has been stimulated by discussions with these same people, who have always been most helpful, though they are by no means to be held responsible for my heresies and errors. I am grateful to the firms who have supplied the photographs and these sources are acknowledged in the captions. Mr. J. T. Crennell, Dr. V. S. Griffiths and Mr. H. M. Powell have read various parts of the manuscript and I am particularly indebted to Mr. Crennell who has not only read all the proofs but has also written the foreword.

J. H. Morgan
Imber Grove, Esher
July, 1959

Preface to 2nd Edition

On reading the preface for the first edition I am only too aware of the last two paragraphs in which I mentioned my indebtedness to the people I have met in cathodic protection. My acquaintanceship has widened and this has enlarged the debt. Since writing, Mr. Powell has died, Mr. Crennell has left the Admiralty, and Professor Griffiths is now Vice Chancellor at Surrey University. Mr. Crennell has kindly given me permission to reproduce the foreword from the first edition which as appropriate now as it was then. Many of the illustrations and photographs in the book show work which I did when I was Chief Executive at Morgan Berkeley & Company Ltd. and the successors to this company, Corrintec U.K. Ltd., have kindly given me permission to reproduce them. The number of publications in cathodic protection has grown and the excellent abstracts published by NACE would be the most fruitful source of reference for further reading. Some historic papers and some of my own are referred to in the appropriate chapters.

J. H. Morgan

Foreword

Although the first practical application of cathodic protection is of a truly venerable age—long before the first iron-hulled ship—its general recognition and its wide industrial application have been only in the last quarter of a century.

The beautiful simplicity of the principle on which it operates is in contrast to the complexity of the technique, which must be adapted to fit the varying needs of each type of subject.

Whereas all other anticorrosive measures are dealloying rear-guard actions, aimed at saving as much as possible of the main body from destruction for as long as possible, cathodic protection offers the possibility of perfection, of complete freedom from corrosion; and this not merely as a theoretical ideal, but as a practical target.

The justification of any protective measures must be that they save more than they cost. It is sometimes difficult to balance the cost of installing and running a system of cathodic protection against the losses that would have been suffered due to corrosion in its absence; but in many cases the effects of even local corrosion can be so costly, in loss of operating time of plant or ship, that the cost of cathodic protection is a very modest premium to pay for immunity.

To ensure this immunity is the task of the cathodic protection engineer or specialist. Many of his practical problems to-day arise from the need to graft cathodic protection on to structures designed with no thought of its use. The growing practice of planning for cathodic protection at the design stage not only makes protection easier and more certain, but may save its cost by reducing the margin of safety that was left for losses by corrosion, in pipe-thickness, plated piles, underwater ties and the like.

This first publication of an English text-book on cathodic protection will contribute to the informed and effective use of a newly developed and most powerful weapon against the ravages of corrosion.

J. T. Crennell
R.N.S.S., Admiralty

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Electrochemistry, Corrosion and Cathodic Protection

CHAPTER 1

Historical

Corrosion

Corrosion is the degradation of a metal by its chemical combination with a non-metal such as oxygen, sulfur, etc. Generally, this means a return of the metal to the form in which it originally existed as an ore with complete loss of its metallic properties. Most naturally occurring ores are oxides, sulfides or carbonates, and energy must be expended in converting these ores to metal. Corrosion, the reverse process, requires no such supply of energy so that the formation of the sulfide, oxide or carbonate occurs readily, or even spontaneously under certain conditions.

Those metals that are most easily obtained from their ores and require least energy in smelting are generally least prone to corrosion, and those that are won with most difficulty, tend to revert more readily to their natural state. Since the earliest metallurgy was concerned with the metals that could be obtained easily either because they occurred naturally or only required simple smelting, corrosion was very much less a problem than in more recent times. One exception was meteoric iron which was used in the early bronze age, being found in its metallic state in the center of small meteors. This source of iron was quickly exhausted, the available metal was consumed, probably suffering considerable corrosion, and bronze again became the most important metal.

Gold, which is found in its metallic state, does not corrode and silver, which is readily obtainable, enjoys almost equal immunity. Copper and bronze are much more readily won from their ores than iron and so not only did they precede iron chronologically, but they have a much higher corrosion resistance. This does not mean that these metals do not corrode, nor that corrosion was unknown to the ancients. The Romans were aware of it

and Pliny (circa 100 B.C.) mentions methods of preventing the corrosion of bronze and iron, the former being protected by oil or tar and the latter by pitch, gypsum and white lead; red lead was also used by the Romans. About this time copper vessels, particularly those used for the preparation of food, were being tinned and poisoning was reported from the use of lead.

Metallic iron was used extensively in Roman ships and other structural equipment, as well as in tools and arms. Considerable corrosion must have occurred and iron was then being reported as inferior to that produced in the time of Alexander the Great. This is a familiar complaint today, though there is considerable evidence to support a decline in the corrosion resistance of recent iron. Some ancient works, particularly the Delhi Pillar, erected a millenium and a half ago, are in an excellent state of preservation. When considering the corrosion resistance of any archeological specimens, it will be only those which have, possibly by chance, extremely good corrosion resistance that will survive as relics and these cannot fairly be taken as a true cross section.

The introduction of modern smelting techniques using coke instead of charcoal and the contemporary use of coal and oil as the major fuels have led to sulfur contamination of both the iron and the atmosphere. These sulfur additions have now been established as some of the major causes of ferrous corrosion. The Delhi Pillar and several other Eastern iron relics enjoy a dry unpolluted atmosphere and have acquired a highly protective initial corrosion film. Small samples of these relics exposed to the industrial atmosphere of this country have corroded as rapidly as modern iron. Several iron bridges erected in South Wales during the early iron era showed remarkable corrosion resistance in what became a highly polluted atmosphere; their initial corrosion must have occurred before coal was extensively used and a protective, probably pure oxide, film was formed which gave them superior resistance to recently erected steel work. Thus, whether the metal or the atmosphere has deteriorated is questionable but the problem of corrosion has grown with the increased use of metals.

By the mid-eighteenth century the corrosion problem must have become appreciable though it was not until the early nineteenth century that any scientific approach was made towards a solution.

Electrochemistry

Wollaston (circa 1815) regarded corrosion by acids to be an electrochemical process, and a few years later, in 1819, a French writer suggested that rusting was also an electrochemical phenomenon. In 1824, Davy showed that when two dissimilar metals were electrically connected and immersed in water, the corrosion of one was accelerated while the other received a degree of protection. From this work he suggested that the cop-

per bottoms of ships could be protected by attaching iron or zinc plates to them, the earliest example of practical cathodic protection.

In 1681 similar accelerated corrosion was noted and the Navy Board decided locally to remove the lead sheathing from ships' hulls to prevent the rapid corrosion of the rudder irons and bolt heads, Charles II and Samuel Pepys being the instigating experts. In 1830 de la Rive published a paper showing that impure zinc was corroded rapidly by the great number of bimetallic junctions that it contained, the corrosion cells being formed between the zinc and the impurities. This work was followed by the investigations of Faraday into the correlation of electrical and chemical phenomena. Much of Faraday's work could be described as corrosion experiments, and from these he was able to derive his laws of electrochemical action which give the relationship between the current flowing and the associated rate of corrosion.

The metals were arranged in decreasing order of activity by de la Rive who also showed that this order was dependent upon the electrolyte. The generally accepted theory assumed that an electrochemical reaction demanded the presence of two metals or a metal and a metal oxide. Sturgeon (circa 1830) considered that a single metal could have a surface that was 'unequally electrical and consequently electropolar' and Faraday set about to prove this by his experiments involving a single metal. In these he was able to produce potential differences by variations in the electrolyte concentration and temperature.

In 1837, the British Association for the Advancement of Science commissioned Robert Mallet to investigate the effects of 'sea water at various temperatures and of foul river water whether fresh or salt' on cast and wrought iron. During his tests he exposed a great number of specimens to these types of waters all over the British Isles and he observed the differential concentration cell effect on the corrosion of extended iron structures where sea and river water became stratified. At about this time considerable interest was being aroused by Davy's work on the protection of iron by zinc anodes and the development of hot dip galvanizing that followed. Mallet showed that zinc so used became covered with a thick layer of zinc oxide and calciferous crystals 'which retards or prevents its further corrosion and thus permits the iron to corrode.' The variation in the corrosion rate of alloyed zinc reported by de la Rive led Mallet to experiment with zinc alloy anodes. He found that metals cathodic to zinc decreased its efficiency while those which were anodic, notably sodium, tended to increase this and that an addition of mercury was an advantage. A workable anode could be made from zinc when alloyed with mercury and sodium and this produced superior galvanizing.

Towards the end of the century electrochemical corrosion received little attention and the view that two metals were required to produce this

type of corrosion became accepted, the corrosion resistance of metals in aqueous solutions being associated with their purity. The corrosion of two metals in contact was investigated in detail by Heyn and Bauer about 1910. The nobler metal (the cathode) was known to corrode at a slower rate while the more base metal (the anode) corroded more rapidly. The investigators were able to establish that this corrosion increased with the relative separation of the metals in the electrochemical potential table. Other factors played an important part including the relative areas of the metals and the rate of arrival of oxygen at the cathode.

In a paper published in 1924, Evans described several mechanisms which led to the establishment of corrosion currents on a single metal surface and called this 'The Newer Electrochemical View on the Corrosion of Metals.' Some of these principles had been noted earlier, including observations of the differential temperature cell by Walcker (1825), the differential stress cell by Davy (1826), the differential concentration cell by Becquerel (1827) and the differential aeration cell by Marianini (1830). Evans and his colleagues, Hoar, Thornhill and Agar, continued their work at Cambridge and produced direct quantitative evidence of these electrochemical corrosion mechanisms. In 1938 Hoar published a discussion on the basic electrochemical theory of cathodic protection and, independently, a similar theory was suggested by Brown and Mears. Anodic protection of metals that passivate was proposed by Edeleanu in Cambridge in 1955.

Cathodic Protection

Having (in 1823) commissioned Sir Humphrey Davy to investigate the corrosion of the copper sheathing of the hulls of wooden naval ships, the Admiralty were the first users of cathodic protection. Davy experimented with anodes of tin, iron and zinc to protect the copper. The last two metals were used and in a later paper (1824) he favored the use of cast iron because it lasted longer and remained electrically more active than zinc. Zinc remained in use, however, and no doubt gave considerable protection to the copper sheathing. When wooden hulls were superseded by iron and steel, zinc anodes or protectors were still fitted. Though there was every reason to believe that zinc would successfully protect steel, its continued use seems to have rested more on tradition. The zincs were placed close to the stern gear and 'yellow' metal parts, such as circulating pipe inlets, as these areas proved to be the most susceptible to corrosion. The practice became universal in shipping circles and protectors were even placed in boilers, though it is doubtful whether any complete protection resulted. Zincs were reported as being in sound order, that is uncorroded, and this was often regarded as good practice.

Edison tried to achieve cathodic protection of a ship at sea from trailing impressed current anodes but the materials and techniques available to

him in the eighteen nineties proved to be inadequate. Most early users of impressed current in sea water were concerned with attempts to effect antifouling or to prevent the scaling that would occur in boilers which were replenished with sea water. The polarity of this current was often considered unimportant and anticipation of the present cathodic protection trends can hardly be claimed.

Since the beginning of the present century liquid and gaseous fuels have been pumped through underground pipelines made of steel or iron. The extensive networks of oil pipelines that were installed in America in the nineteen twenties presented a vast corrosion problem. To an oil company a single leak from a pipeline can cause numerous losses and may include: loss of commodity, property damage including fire, expensive repairs, service interruptions, contamination of water supplies and loss of livestock, all of which leads to a deterioration of public relations.

By the late twenties leaks were few and could have been tolerated had not the leak frequency curve begun to rise alarmingly. In the early thirties all the major pipeline owners were applying anti-corrosive measures to the external protection of their pipes, including various coatings and cathodic protection. The earliest schemes were applied to the worst sections where the pipes had been laid in corrosive soils, and great success was achieved. The cathodic protection was derived from zinc anodes or from impressed current supplied either by d c wind generators or by transformers and copper oxide rectifiers from a c power supplies.

In 1936 the Mid-Continent Cathodic Protection Association was formed to discuss and exchange information on cathodic protection. This association later became the foundation of the National Association of Corrosion Engineers.

The other area where oil pipelines were used extensively was the Middle East; the first cathodic installation protected a group of sea water loading pipelines at Bahrain in 1939.

There are a great number of patents on methods of preventing the corrosion of buried metals, particularly pipes and cable sheaths. Seventy or so years ago a major cause of corrosion of buried metal pipes was the electrolysis effect, or interference, caused by stray currents from the electric traction systems. The first patents describe the connection of the pipes to the negative pole of the station generator; this method was universally adopted and is still used. The introduction of a further d c generator between the negative return of the electric traction and the structure was claimed to give superior results. In 1911 a German, Herman Geppert, obtained letters patent on 'a method of protecting articles from earth currents' and substantially described cathodic protection. Since then patents have applied to more specific devices such as reverse current switches, anodes, boosters, etc.

From these early beginnings cathodic protection has developed rapidly and its use has become widespread. New materials such as sacrificial alloys of magnesium and aluminum and superior impressed current anodes together with developments in electrical and electronic engineering have allowed great advances in the techniques. Cathodic protection is now established as an essential engineering service with a sound and comprehensive scientific background.

Corrosion

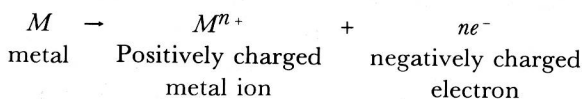
Electrochemical Theory

Modern theory describes the atom as having a massive positively charged central nucleus surrounded by a cloud of negatively charged electrons. The cloud of electrons is divided into a series of shells; the inner ones are filled first and require two, eight, eighteen, or thirty-two electrons to fill them. When the electrons just fill the shells completely with no electrons left over, then the element is very stable.

Usually, however, the atom either has a few electrons left over after filling the last completed shell, or too few to complete the outer shell. The atom tends to obtain a cloud of completed shells by gaining or losing electrons; this loss or gain tendency gives the element its chemical properties. A metal sheds electrons and a non-metal accepts electrons. Thus metals and non-metals will combine to form salts by the metal atom donating electrons and the non-metal receiving them, the molecule so formed having two or more such atoms, each modified to have an electron cloud of completed shells. These modified atoms are called ions.

The common salt molecule consists of an atom of sodium which has given an electron to its associated chlorine atom; this produces a positively charged metal ion and a negatively charged chlorine ion. If the salt is dissolved in water these ions separate and the solution contains a mixture of sodium ions and chlorine ions. The difference, therefore, between the metallic sodium and the sodium ion is one electron, which is little more than a small electric charge, and the difference between a chlorine atom and a chlorine ion is similarly a small electric charge.

The corrosion of a piece of metal may be summarized as the change from the metal to the metal ion or the loss of one or more electrons from the metallic atom. Electrically this can be written.



In the case of iron there are two electrons lost from each atom in forming ferrous ions.