Electrochemical methods for the preservation of masonry clad structural frames

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Abstract

A large number of historic structures incorporate wrought iron or early steel components within the masonry. Generally, these were incorporated at the time of construction or in later refurbishments to enhance the structural integrity or fire resistance of the buildings. With time, and in the presence of moisture and oxygen, the ferrous component starts to corrode and the voluminous corrosion products cause cracking and spalling of the surrounding masonry. The traditional method of dealing with such problems has been to remove the affected masonry and treat or replace the corroded metalwork prior to reinstatement. This is not only expensive, but involves the removal of large amounts of the original masonry, which may have to be replaced with modern equivalents. A more effective and sensitive option is available through the use of electrochemical treatments, specifically cathodic protection which was originally developed by Sir Humphry Davy in the early 19th century for the preservation of naval vessels. This paper discusses the development of this technology from early naval trials to recent development for use on heritage buildings and introduces the numerical methods for modelling of cathodic protection systems that assist in the design optimisation of such systems for protecting historically sensitive structures with the minimum of physical disruption. A number of existing and developing electrochemical approaches to corrosion control are also discussed. This work is being undertaken at the Centre for Infrastructure Management, Sheffield Hallam University with support from the Royal Society.
Keywords: corrosion, masonry, steel frame, cathodic protection, galvanic or sacrificial anodes, impressed current, numerical modelling.

1 Introduction

The identification of "Regent Street Disease" in the United Kingdom in the late 1970's highlighted the problems of the corrosion of iron and steel frames and



other structural components in historically sensitive buildings [1]. This has resulted in serious consequences with respect to serviceability, safety, aesthetics and heritage.

Cathodic protection, originally developed by Humphry Davy and later employed widely on buried and submerged structures, was first considered for reinforced concrete in the late 1950's. It was not until the development of improved anode systems based on catalysed titanium and titanium oxide in the early 1980's and the considerable advances in digital operating systems that it became a serious commercial solution.

The transfer to steel-framed buildings was somewhat slower and it was not until 1997 that the first full structure was protected by such a system. Even now, with several sizeable installations in the UK, there are no formal guidelines for the design, installation and operation of such systems and much of the knowledge is based on empirical observation.

2 Corrosion of iron and steel

Metal corrosion is the destructive result of chemical or electrochemical reaction between a metal or metal alloy and its environment. When moisture and oxygen are present, steel rusts. In its simplest form the corrosion process can be represented by two dissimilar metals in an aqueous electrolyte, joined to allow electrons to pass from anode to cathode. In reality, when a metal corrodes, anodic and cathodic areas can be formed on a single metal surface in contact with the aggressive aqueous environment. As a result, corrosion can occur at a large number of sites over the surface of the metal. Dissolved ions react with hydroxyl ions to form corrosion products [3]. The reactions occurring at anodic and cathodic sites can be represented as follows:

At anodic areas the following oxidation reaction (anodic reaction) takes place:

$$Fe \rightarrow Fe^{2+} + 2e^{-} \tag{1}$$

In well-aerated neutral and alkaline environments, the following reduction reaction (cathodic reaction) takes place at cathodic areas:

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \tag{2}$$

Dissolved iron ions react with hydroxyl ions to form corrosion products. The reaction can be obtained by combining (1) and (2):

$$2Fe + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^{-} \rightarrow 2Fe\,(OH)_2 \tag{3}$$

Ferrous hydroxide precipitates from solution. However, this compound is unstable in oxygenated solutions and is oxidized to the ferric salt, the final product being commonly referred to as rust:

$$2Fe(OH)_2 + H_2O + \tfrac{1}{2}O_2 \rightarrow 2Fe(OH)_3$$
$$\rightarrow Fe_2O_3 \bullet H_2O + 2H_2O \quad (4)$$

The rate and nature of the corrosion process mainly depends on a number of factors including alloy composition, environmental factors and design. The relative humidity of an environment in particular has a profound effect on the rate of corrosion of steel [1].

3 Corrosion of steel framed masonry structures

3.1 Steel frame corrosion and damage mechanism.

There has been increasing awareness over the last 50 years that many high-profile iron and steel-framed masonry structures may be prone to extensive damage as a result of corrosion of the steel frame.

The problems of corrosion of the steel-framed masonry buildings are related to the original designs and the form of construction at a time when the technology of corrosion protection was still largely undeveloped.



Figure 1: Early example of frame corrosion, as reported in 1947. [6].



Figure 2: Cracking of Portland stone resulting from frame corrosion.

The external masonry of the buildings was often tightly packed around the iron or steel frame and cavities in-filled with mortar, brick, or other porous rubble [4]. The porous masonry and in-fill materials allow moisture entering the structures to come into contact with steelwork. Moisture can also enter the structures

through a variety of routes including open joints, cracks or through poorly maintained gutters and pipework. As a result, corrosion becomes inevitable. As expansive corrosion products are formed, the tremendous stresses act on the surrounding mortar and masonry. These result in cracking, spalling and displacement of masonry, further opening up joints and cracks and permitting greater access to water. Thus, the rate of degradation tends to accelerate. Thermal movements that aggravate the opening of joints will also lead to an acceleration of the damage, as typically observed on the weather-exposed corners of such buildings [1].

The time at which corrosion initiates largely depends upon location, aspect and level of previous maintenance. The rate at which corrosion progresses largely depends upon availability to moisture and oxygen, the type of environment, and the variability of the environment. The intimacy of the contact between the corroding steel and the cladding also influences the extent and timing of the damage as gaps between steel and cladding can accommodate extensive corrosion with no visible damage. Corrosion damage not only destroys the integrity of these structures, but also could pose a serious public hazard and liability issue for the owner.

3.2 Types of corrosion in iron and steel framed structures

There are two major types of corrosion that can typically affect masonry clad steel frame buildings; uniform or general corrosion and pitting corrosion.

Uniform attack appears as an even layer of rust on the steel surface. This is the most common form of corrosion that is found in perimeter steel of masonry clad steel framed building. Uniform corrosion is generally due to electrochemical reaction, which occurs from the presence of oxygen and moisture. Under certain conditions the water or moisture that is in contact with the steel, may have extremely low values of pH due to acidic pollutants from rainfall (acid rain) and surveys have shown that acid precipitation at pH of 2 is not uncommon, especially during the initial period of snow or rain.

Carbonation, another contributor to corrosion, is a process by which carbon dioxide enters into the masonry. Carbon dioxide combines with the pore water in the mortar to form carbonic acid, which reduces the pH of the mortar to approximately 8 or 9. At these levels the protective oxide film at the steel surface is no longer stable and, with adequate supply of oxygen and moisture, corrosion will start. The penetration of masonry by carbonation is a slow process, the rate of which is determined by the porosity, permeability and moisture content of mortar.

Pitting corrosion, which is a localized form of attack, can lead to significant loss of steel section. This form of attack is most commonly found in be found in coastal and maritime buildings where air borne salts have penetrated through the porous cladding to the steel surface. The role of chloride ion in inducing corrosion of steel in concrete is well documented. If chlorides are present in sufficient quantity, they disrupt the passive film and subject the iron and steel members to corrosion even when the metal is encased in good quality mortar or concrete (see Figure 3).



4 Cathodic protection of metallic structural components

4.1 Background to cathodic protection

The principles of cathodic protection were identified by Sir Humphry Davy and reported as early as 1824 [5]. Davy was responding to a request from the Royal Navy to problems they encountered with the copper sheathing applied to the wood hulls of ships to prevent marine fouling attack by wood boring organisms. A mechanism, which would later be recognised as galvanic or bimetallic corrosion, resulted in the less noble iron nails corroding preferentially to the more corrosion resistant copper sheet resulting in the sheathing becoming detached. Davy recognised that by attaching a third metal that was more liable to corrosion than either the iron or the copper, then this would corrode preferentially and 'sacrifice' itself thus protecting both the copper and the nails.

This approach, using zinc, aluminium or magnesium as the 'sacrificial' metal, is still widely used today in a wide range of buried and submerged applications. In many ways, Davy's original solution was too successful and prevented the copper from corroding which in turn prevented it from acting as an effective anti-fouling system and it has been suggested that the resulting complaints and ridicule lead to Davy's early death following a stroke.

After Davy’s discovery, Faraday examined the corrosion of cast iron in seawater and found that it corrodes faster near the water surface than deeper down. In 1834 he identified the quantitative connection between corrosion weight loss and electric current. With this discovery he firmly established the scientific foundation of electrolysis and the principles of cathodic protection. There are two basic types of cathodic protection systems commonly used; galvanic and impressed current [6].

4.1.1 Impressed current cathodic protection (ICCP)

Consider iron corroding in well-aerated neutral and alkaline environments. Impressed current cathodic protection works through the provision of a small direct current (DC) from a permanent anode fixed on to the surface or placed into the electrolyte of the protected steel. The anodes employed in the protection of steel-framed structures are generally made from titanium with a mixed metal oxide coating (MMO) or from a titanium oxide ceramic. In either case, the requirement is for the material to a pass a large cumulative current without a significant loss of mass. The DC power supply passes sufficient current from the anode to the protected steel to force the anodic reaction (1) to stop, and to make the cathodic reaction (2) the only one occurring on the protected surface. This would typically be a few tens of milliamps per square metre of metal surface, running at little more than 10 or 12 volts.

4.1.2 Galvanic (sacrificial) cathodic protection

In a galvanic system the protected steel is connected to sacrificial or galvanic anode such as zinc without using a power supply. As in Davy's original system,

the anode corrodes preferentially, liberating electrons with the same overall effect as the impressed current system, for example:

$$Zn \rightarrow Zn^{2+} + 2e^{-} \quad (5)$$

4.1.3 Cathodic protection of reinforced concrete

The first reference of cathodic protection of reinforced concrete is in the 1950's [7]. The work that had been carried out up to the late 1970's emphasized the limitations of the techniques and materials then available but the last few years have seen major anode developments that allowed a significant expansion of these methods of corrosion prevention. In 1973 and 1974 the first commercial cathodic protection system for reinforced concrete was applied to the top deck of Sly Park Crossing Bridge Deck in California, USA [8].

Since those first systems were applied in the 1970s systems have been developed and applied to bridge deck, substructure and other elements, buildings, wharves, and every conceivable type of reinforced steel. Anodes have been developed in the form of conductive coatings, conductive meshes embedded in concrete overlays, conductive concrete overlays and probes drilled into concrete.



Figure 3: Corrosion of rolled steel section, circa 1900.



Figure 4: Example of conservation of a listed heritage structure by cathodic protection (1997).

4.1.4 Cathodic protection of iron and steel framed masonry

Cathodic protection systems for iron and steel-framed masonry buildings have only been developed relatively recently [1]. The first cathodic protection system for the prevention of steel corrosion in a masonry structure was installed in 1991. The system protects the entrance colonnade at Royal College of Science, Dublin;

a limestone structure containing two parallel structural 'I' beam members. Regular remote monitoring and annual visual inspections have confirmed corrosion has been arrested. Further applications in the early 1990s involved historically protected sites, with the protection of iron cramps in the Inigo Jones Gateway, Chiswick House, London, and iron staircase supports embedded in the brickwork of Kenwood House, Hampstead.

It was not until 1997 that the first full steel-framed structure was protected by a cathodic protection system (Gloucester Road Underground Station, see figure 4). At the present time more than twenty systems have been completed in the United Kingdom. Examples include Lloyds Bank, Lombard Street, London; Arkwright House and House of Fraser in Manchester; St Andrew House, Edinburgh and Putney Boathouse, London. However, despite several sizeable installations in the United Kingdom and considerable overseas interest, there remain no formal guidelines for the design, installation and operation of such systems.

4.2 Numerical methods for modelling of cathodic protection systems

4.2.1 Background and mathematical model

The employment of an appropriate current and potential distribution is one of the important parameters determining the effectiveness of cathodic protection systems. Both under–protection and over-protection are undesirable. Under-protection of a structure clearly does not adequately prevent corrosion while over-protection can significantly reduce the life of the system components and result in other undesirable side effects. To avoid these problems, proper anode location to produce uniform current and potential distributions is essential. This can also help minimise the current required to achieve the protection criterion, thus reducing the cost and improving the life of the system components.

To determine the optimum anode distributions, the current and potential distributions of cathodically protected structures need to be calculated as part of a design. Traditionally, such designs have mainly relied on empirical methods and experience. These methods have been used for a long time and have been an adequate tool for most conventional applications. However, for new applications of cathodic protection, the accuracy of these methods becomes uncertain. Hence, the current and potential distribution prediction of cathodic protection systems is not only useful but also necessary when extending the technique to more sensitive or technically challenging applications.

For a uniform isotropic electrolyte, the flow of current can be shown to obey the Laplace equation. The equation is written in term of the electrical potential [9],

$$k \nabla^2 E(p) = 0 \qquad p \in \Omega \tag{6}$$

where E is the potential at any p(x, y, and z) of domain, k is the conductivity of electrolyte and Ω is the problem domain together with the following relationship between the current density and potential:

$$i=-k\frac{\partial E}{\partial n} \tag{7}$$

where i is current density at the electrode surface, n is the normal vector to the electrode surface. This is the governing partial differential equation for potential distributions in electrochemical cells. The problem in cathodic protection is to solve the above Laplace equation subject to certain boundary conditions. They can be presented in Table 1 [10]:

Table 1: Boundary conditions.

Type	Boundary Condition	Comment
Anodically polarized electrode	$-k\frac{\partial E}{\partial n} = i_0 f(E-E_{eq})$	Anodic branch if experimental polarization curve used
Cathodically polarized electrode	$-k\frac{\partial E}{\partial n} = i_0 f(E-E_{eq})$	Cathodic branch if experimental polarization curve used
Painted surface	$\frac{\partial E}{\partial n} = 0$	
Non-polarized	E = fixed value	For E consult EMF series
Impressed current	$-k\frac{\partial E}{\partial n}$ = fixed value	Current density output

Combining the boundary conditions, the Laplace equation is solved and the potential distributions in electrochemical cells are given.

4.2.2 Numerical solutions

Except for some special problems, it is widely accepted that such a system in practice cannot be solved solely by analytical methods. The numerical methods have therefore been employed. The three major numerical approaches used for cathodic protection analyses are the finite difference method (FDM), finite element method (FEM) and boundary element method (BEM). Comprised with the finite difference method and the finite element method, the advantages of boundary element method for analysis of cathodic protection are as follows [11]:

- The meshes are only on the surface, hence only one or two-dimensional elements are required. It therefore reduces the number of nodes required to model a particular system and minimises data preparation.
- Boundary element methods give the solutions on the boundary and, only if required, at specified internal points. Since for analysis of cathodic

protection the solution is only required on the surfaces, it is far easier to analyze the results than the finite element method which automatically gives results for all nodes (internal or boundary).

- Boundary element methods are very effective and accurate for modelling infinite domains.

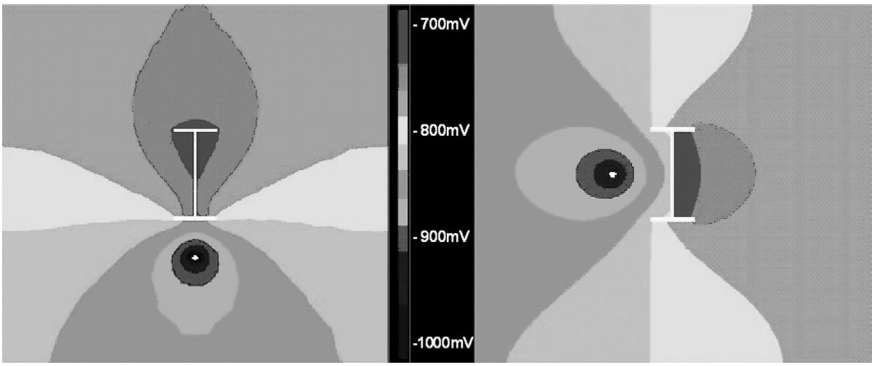


Figure 5: Numerical modelling of potential distribution between discrete anode (white dot) and stanchion (H-section) for two anode configurations.

Therefore, it is this approach that is considered most applicable for the modelling and optimisation of cathodic protection systems for the preservation of iron and steel elements in masonry structures. Using this method it is possible to predict potential distributions for the different anode locations, as shown in Figure 5.

5 Alternatives to cathodic protection

In addition to cathodic protection a number of alternative approaches are available for the treatment and control of corrosion to iron and steel structural elements encased within masonry. Corrosion inhibitors, generally based on amino alcohols, have been used extensively for the short to medium term protection of exposed surfaces and hollow sections. They can be incorporated in to protective wax coatings or blown as powder into enclosed spaces and have the advantage of being totally reversible.

More recently, low viscosity liquids have been developed that can be painted or sprayed onto the surface of concrete and masonry, allowing the active inhibitor group to permeate through the cover and attach to the surface of buried metal components [3].

It is also possible to employ temporary cathodic protection systems that take advantage of the side effects of the treatment and are optimised to either remove chloride ions from the surrounding masonry (chloride extraction) or enhance the level of alkalinity in the vicinity of the buried metal (re-alkalisation) [6]. Such treatments have been employed for reinforced concrete but should be equally

applicable to iron or steel components within masonry. The advantage of this approach from a heritage viewpoint is that once the treatment is completed, all the equipment is removed. Further techniques in use on reinforced concrete such as electro-osmosis are currently under evaluation for masonry applications.

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