

Corrosion Prevention in Concrete

THE CATHODIC PROTECTION OF REINFORCING STEEL BARS USING PLATINISED-TYPE MATERIALS

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The cathodic protection of steel reinforcing bars in concrete to prevent their corrosion, brought on principally by de-icing salts used on roadways, is at the interesting stage where technology is barely keeping pace with practical demand. It already seems likely that platinum and other noble metals, used in conjunction with titanium and niobium, will play a vital role in several of the protection systems that appear to be the forerunners in a rapidly developing industry.

Reinforced concrete is used in numerous ways, some of the larger and better known uses including roadways, bridges, car parks, residential buildings and in industry; for example it is widely used in nuclear power plant. It is in general an excellent construction material (1). Concrete alone is good in compression, but reinforced concrete greatly increases the scope for making structures required to withstand other forms of mechanical force.

In a small percentage of instances reinforced concrete may deteriorate prematurely, but so widespread is the use of the material that problems can be encountered in a wide range of individual applications. It is reliably reported that in North America there are now some 300,000 concrete bridges requiring repairs, with costs estimated in terms of billions of dollars, in addition to the roadways and car parks requiring remedial attention. There are also lesser but significant problems with reinforced concrete in Europe and the Middle East. From a financial aspect the future costs over the next few decades for repairs and replacement throughout the world are likely to be staggeringly high.

One is tempted to ask why, if reinforced concrete has been used for so long, is it only now that problems are arising, predominantly, though not exclusively, associated with corrosion of the reinforcing steel bars, or rebars as they are commonly called. While it is

dangerous to make generalities, the reasons would seem to be that since World War II the volume of reinforced concrete has greatly increased and so also has the amount of salt used on roads, salt being a major cause of rebar corrosion. For example, in the U.S.A. from 1955 to 1970, the amount of de-icing salt used increased by an order of magnitude, and it continues to increase. Such is the insidious nature of salt in concrete that it requires an ingestion period of 10 to 20 years for the damage to make itself evident.

Degradation of reinforced concrete shows up in a variety of ways. Corrosion of rebars produces a bulky reaction product that puts pressure on the surrounding concrete cover which first cracks and eventually spalls. Spalling of the cover gives rise to possible injury, particularly for example in the case of high rise flats or bridges, but extensive corrosion of the rebar itself will lead to mechanical weakening of the reinforced structure. The ultimate result can be collapse of the structure, and disquieting examples have, in fact, occurred.

While the commonest cause of rebar corrosion arises from the use of de-icing salts on roadways, chloride contamination can also arise from setting additives such as calcium chloride put into the concrete during mixing, or by the accidental use of contaminated make-up water. Most salt corrosion problems occur in the so-



Fig. 1 Reinforced concrete is widely used as a constructional material for structures that are required to withstand more than simple compressive forces. This section of motorway viaduct in the English Midlands is just one example of the many crucially important uses of the material



Fig. 2 Premature deterioration of concrete can result from corrosion of the steel reinforcement bars. Commonly this is due to the action of de-icing salts on finished structures, but it may also be caused by chloride-containing setting additive or contaminated make-up water. Bulky reaction products can result in spalling of the concrete cover and mechanical weakening of the whole structure

called Northern Hemisphere snow belt area. However, problems are also rife around the Arabian Gulf, for example, in hot humid conditions where sea-water laden winds deposit salt on roadways and buildings, and where water supplies are also high in chloride, the higher environmental temperature accentuating the rate of rebar corrosion.

Porosity in Concrete

Most concrete is porous, this being in the form of interconnecting micropores, and in consequence pore water will have access to embedded rebars. Due to the chemistry of concrete, pore water is usually highly alkaline at pH 12 to 13 and this high alkalinity is responsible for the inertness generally exhibited by rebars in concrete, steel under such conditions forming a stable protective oxide film (2). When reinforced concrete is being made up, it is not uncommon to observe that the rebars are already rusted. Provided the rust is adherent, it is said that this helps to promote a good bond between rebar and concrete. Exposing the surface of a rebar that has been embedded in concrete for some time shows that the rust layer on the steel has transformed to a hard, shiny, dark, protective film which renders the steel perfectly stable from a corrosion viewpoint.

With concrete exposed to humid or wet conditions, and with salt contamination, a situation eventually arises where the steel, irrespective of the high pH, is exposed to oxygenated chloride-contaminated water. These are conditions that can give rise to corrosion of steel, often by localised pitting attack (3). That this is the case can be judged by measuring the electrode potential of the rebar (4), but because of the concrete cover this cannot be done directly. None the less, indications of the so-called 'mixed' potential of the rebar can be obtained by measurements taken on the outer surface of the material. Indeed, electrode potential mapping of concrete structures is now commonly used to reveal corrosion in a structure at locations where it might be expected to occur preferentially, and sometimes to detect corrosion in areas where its presence was not anticipated.

It will not be possible to overcome rebar corrosion by introducing a non-porous form of concrete on a large scale so the use of more corrosion resistant materials such as galvanised or stainless steel rebars, is being considered. Some countries, including Sweden, have banned the use of de-icing salts on roads, and Austria seems likely to follow.

Salt contamination of existing structures, however, is now an immense problem. On a practical scale there is no ready possibility of expelling chloride or other activating ions. Several years ago research was carried out to show that, on a pilot scale, salt contamination could be removed electrochemically (5), but so far it has proved impractical to apply this technique in the field; thus the engineer is still left with the unenviable task of deciding what to do with salt contaminated porous concrete containing corroding rebars (6-13).

Solutions to the Problem of Corroding Steel Reinforcement

There are a number of options for resolving the problems. The structures could be rebuilt and steps taken to ensure no further salt contamination, but applied to a motorway, for instance, this could be far too expensive. Another option is to uncover the corroding rebar, remove the corrosion product, or even weld in new reinforcement, and then repair with a low porosity concrete, all of which can be difficult and expensive work. Yet another option is to seal the outer surface of the concrete, for example with silicones or polymer concretes, so that no further oxygen, chloride ion or water is permitted into the structure, any activating products inside eventually stifling themselves; but even this is considered impractical on a large scale.

The consensus view seems to be that the only real practical option left is to arrest rebar corrosion electrochemically by the application of cathodic protection.

Cathodic protection has been described several times in past articles in this journal (14-16). It is a corrosion prevention method based upon the fact that iron held at a specified

negative electrode potential is immune from corrosion, for all practical purposes. There is a long history of the successful application of cathodic protection to steel structures such as oil rigs, oil well casings, oil pipelines and storage tanks, the hulls of ships and buried pipelines.

Impressed Current Cathodic Protection

The cathodic protection of rebars, on any scale, is unlikely to be based upon the use of consumable zinc, aluminium or magnesium electrodes which make use of the principle that the galvanic difference between these metals and iron will allow sufficient depression of the iron electrode potential for cathodic protection to occur. This is because the available driving force in terms of volts is too small to cope with the resistance of the concrete cover. In contrast impressed current cathodic protection, using non-consumable anodes, allows whatever cell voltage is necessary to drive the required current density of reaction.

However, impressed current cathodic protection to concrete raises special problems including:

- (1) The resistivity of the concrete, which will depend upon concrete type and quality. Sea-water has a resistivity of $30\Omega\text{cm}$ whereas concrete might possess values up to $20,000\Omega\text{cm}$ or more. Also, because the mobility of electrolyte in concrete is limited, some areas of the concrete may have high salt contamination while others have almost none; thus large differences of resistivity can occur in the pore water electrolyte of even relatively small concrete items.
- (2) The location of the counter electrode anodes is limited. They need to be applied either to the surface or at only a shallow depth. A fundamental problem arises because anodes operating in aqueous systems produce H^+ ions or acidity through decomposition of the water. In most environments acidity would dissipate without problem, but in concrete such acidity is almost certain to react with the free alkaline content of the concrete. Thus the very real possibility exists that acid attack around anodes might lead to as much damage to the concrete

as cathodic protection of the rebars is helpful in preventing corrosion.

There is little prior art relating to anodes in or on concrete which the cathodic protection engineer can turn to for guidance. Perhaps the closest experience is in electro-damp-proofing where small anodes are embedded in brickwork or masonry. Anodes have been observed to produce high acidity in the mortar immediately surrounding them, usually necessitating the use of specially developed forms of acid-resisting platinum electroplated titanium anodes, and an appropriate fixing technology.

In the cathodic protection of rebars in concrete, the cathode reaction is fairly predictable with some slow evolution of hydrogen accompanying the lowering of the electrode potential to values which will protect the steel. There has been concern that hydrogen evolution might lead to embrittlement of the steel or break-up of the steel/concrete bond, but this does not seem to be a major problem area.

Reactions at the anode counter electrode are more difficult to forecast, and will depend upon the level of salt contamination, current density and electrochemical characteristics of the anode. The major reactions will be chlorine and oxygen gas evolution, the latter being accompanied by H^+ ion production or acidity. What happens to the acidity is debatable.

The Practical Application of Cathodic Protection to Rebars

How cathodic protection of rebars is applied in practice is determined more by what is practicable than by design. By this is meant that in most cathodic protection systems careful consideration is given to the siting of the anodes to give the throwing power required for effective protection.

In contrast the way that the problems of reinforced concrete have been tackled has been to cover the available surface with as much anode as possible, irrespective of the positioning and depth of the underlying rebars. Inevitably with such systems that part of the anode blanket coverage nearest to a rebar and separated by the most conductive concrete is

the part most likely to operate at highest current density, giving rise to the greatest acid attack of the underlying or adjacent concrete, which has a bearing on the life of the system.

The Indirect Use of Noble Metals

The majority of systems proposed to-date use carbon (or graphite) as the primary anode material, which is usually called the ground bed. This can be a coke/asphalt mix, a paint or in some other form. To this ground bed are attached electrical connections, which may be carbon fibre strands, lumps of silicon iron or some form of platinised titanium or platinised niobium. Often these are misleadingly named secondary anodes, but the terminology may not be too inapt if the network does not make con-

tinuous contact to the carbon, because then it becomes the primary anode and needs to have appropriate durability to contend with such an eventuality.

Some examples illustrating techniques that involve platinised materials are now given.

The Saw-Cut Method

For concrete roads without an asphalt cover, grooves are cut into the surface at intervals of approximately 300mm, the cross-section of the grooves being about 25mm × 25mm (17-19). This separation is selected on the basis of a rule of thumb figure of 150mm for the throwing power of an anode in concrete, though clearly this figure will depend upon the many factors that can affect the electrical conductivity of

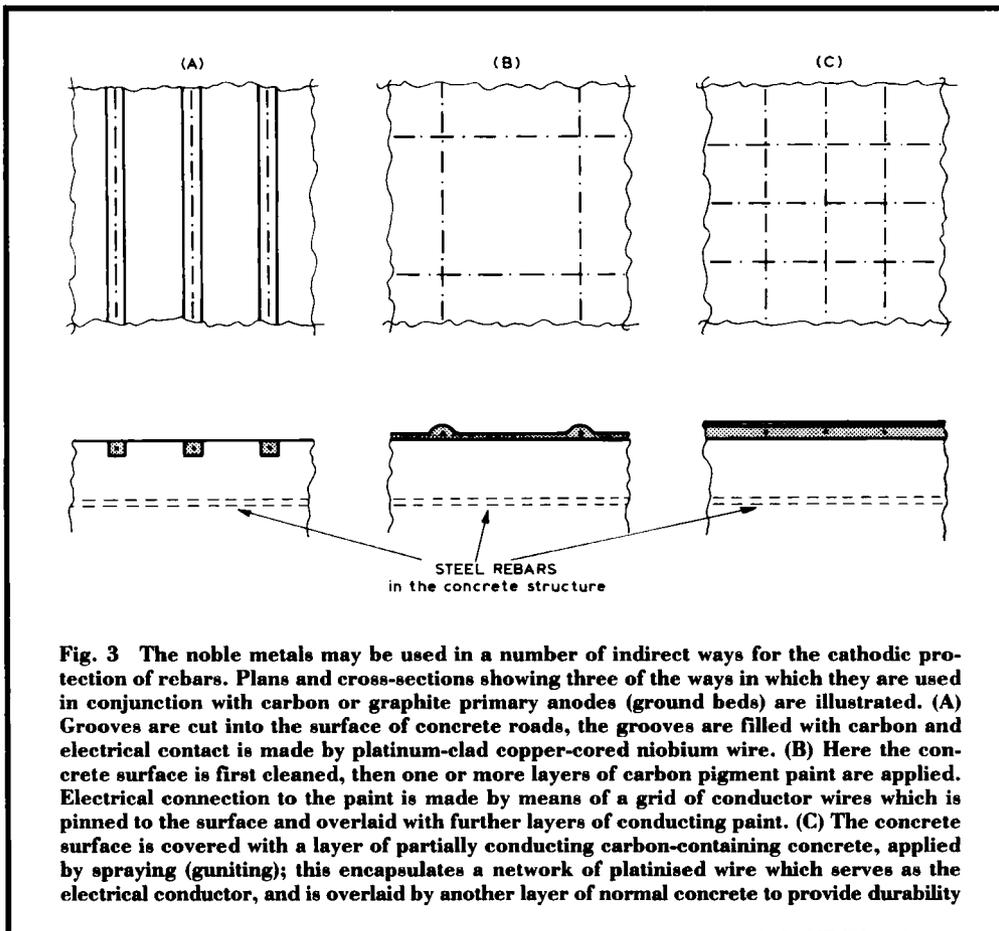


Fig. 3 The noble metals may be used in a number of indirect ways for the cathodic protection of rebars. Plans and cross-sections showing three of the ways in which they are used in conjunction with carbon or graphite primary anodes (ground beds) are illustrated. (A) Grooves are cut into the surface of concrete roads, the grooves are filled with carbon and electrical contact is made by platinum-clad copper-cored niobium wire. (B) Here the concrete surface is first cleaned, then one or more layers of carbon pigment paint are applied. Electrical connection to the paint is made by means of a grid of conductor wires which is pinned to the surface and overlaid with further layers of conducting paint. (C) The concrete surface is covered with a layer of partially conducting carbon-containing concrete, applied by spraying (guniting); this encapsulates a network of platinised wire which serves as the electrical conductor, and is overlaid by another layer of normal concrete to provide durability

concrete. Into each groove is placed the carbon-based ground bed, and electrical connection is achieved using metallurgically co-processed platinised copper-cored niobium wire (20). Because the roadway is used without further cover over the slots, there is a risk that the backfill will work out of the grooves due to the constant movement of vehicles, and to prevent this the U.S. Federal Bureau of Highways has developed a suitable backfill formulation.

For this application the predominant type of anode is platinum-clad copper-cored niobium wire 1 to 2mm in diameter which is produced in coils of hundreds of metres by a process developed by IMI Titanium Ltd. (20). The material begins as a metal billet 10cm or more in diameter by 20cm or more in height; this is composed of a copper core, with first a niobium sleeve and then an outer coating of wrought platinum (20). Subsequently these billets are hot extruded to take the form of the massive anodes used in North Sea Oil platforms, and illustrated in Figs. 5, 6 and 7 of Shreir's article (15). Such material can also be further reduced to form fine wire coated with a pore-free layer of wrought platinum, perhaps 0.5 μ m thick. Should any breaks occur in the coating due to scratching or bending, the underlying niobium provides high corrosion resistance to any adjacent acidity which may possibly develop during use, and it is also able to withstand high electrical stress in the presence of chloride ions.

High Carbon Paint

The saw-cut method is applicable to roadways (pavements in American terminology) and also to other concrete forms such as crossbeams and pillars, but there are other more appropriate techniques of which the paint method is proving a popular choice (21). In this technique the concrete to be protected is first cleaned down, say by grit blasting, any urgent repairs to the cover effected, and then one or more layers of an 80 per cent carbon (graphite) pigment paint are applied. To achieve electrical connection to the paint, a grid of conductor wires is then pinned to the surface. The grid may take the form of a mixture of carbon fibres or

platinum electroplated titanium (22) or metallurgically co-processed forms of wire (20). The connection to the paint is enhanced by further layers of electrically conducting graphite paint which are applied so that the wire current distribution network becomes embedded in the paint layer. High carbon/graphite containing products are black, and because a coating of black paint is aesthetically undesirable on many structures, particularly public buildings, the black electrically conductive paint is overlaid with a more attractive, lighter-coloured, conventional electrically non-conductive paint.

Carbo-Concrete

This material is partially electrically conducting due to the high percentage of carbon with which the concrete is loaded. Generally the electrical connection is made by means of a platinised titanium conductor wire.

The Direct Use of Noble Metals and Noble Metal Oxides

In the previous section reference has been made to the use of platinised titanium or platinised niobium conductors for the distribution of electricity to the electrocatalyst, which is essentially carbon, and that if the contact between carbon and feeder arrangement fails for any reason, such as slow conversion of the carbon to carbon monoxide/dioxide in the anodic reaction, then the platinised material takes over as the primary anode. It is logical to think that if a network of platinised wires could be arranged, at an economically attractive price, then it should be possible to dispense with the carbon. This is precisely what has happened, and it seems to be the developing trend. The material, which might be likened to wire netting, is a very open form of titanium mesh, typically having a metal cross-section of 1mm² with holes of 100mm by 50mm. Such a mesh is included in Figure 4.

The mesh requires a special coating designed not only to accommodate an appropriate electrocatalyst, but also to make the overall product acid resistant. The wire and netting illustrated in Figure 4 is coated with an iridium-based



Fig. 4 These are some examples of the platinised titanium-type materials used in the cathodic protection of reinforcing bars in concrete. The coil of wire at the front right is metallurgically co-processed platinum-clad copper-core niobium (courtesy of IMI Titanium Ltd.). The coil of wire front left is platinum electroplated titanium wire, while the centre coil of wire and the rolls of netting are iridium-based coated titanium (courtesy of Marston Palmer Ltd.)

material which is a preferable electrocatalyst to platinum in respect of durability under oxygen evolution conditions. There are now at least two other similar products commercially available using alternative electrocatalysts.

The wire netting type of product can be used for most applications. For example it can be laid down on roadways, on the floors of car parks, and wrapped around columns or cross beams. The coated mesh is attached by clips to the concrete and is then overlaid with a concrete cover which is applied by spraying.

Methods Not Involving the Noble Metals or Their Oxides

For the sake of completeness other methods that are being proposed are now mentioned, even though they do not involve platinum, other noble metals, or their compounds.

Electrically Conducting Titanium Oxide.

The anode is a porous electrically conductive ceramic looking much like graphite but in fact composed of a particular form of titanium oxide (23, 24). Localised anodes of this material are mounted at approximate 30cm intervals at positions midway between underlying rebars, and are connected to each other, and to the electrical supply, by a means of a network of thin titanium strip or wire.

Coke/Asphalt/Silicon Iron. To cathodically protect the steel mesh rebar over a road surface, the road surfacing is removed to expose the underlying concrete and allow repairs to be made to any exposed damaged cover. Onto this is placed a layer of coke/asphalt. The electrical connection to the coke is made by flat pancake anodes of silicon iron with conventional electrical lead connections. The silicon iron is overlaid with further ground bed and the normal road surface applied (25).

Carbon Loaded Polymer. Yet another method based upon carbon involves a copper conductor wire which is covered with a thick coating of a carbon-loaded plastic. In terms of metals, the carbon loaded plastic is not very electrically conductive, but it is entirely adequate for passing the low currents required in the cathodic protection of rebar. This rope-like anode is attached over the surface of the concrete to be protected by means of suitable fixings and it is then embedded in a few centimetres depth of sprayed on concrete (26).

Discussion

There are now a number of competing impressed current cathodic protection systems for arresting the corrosion of rebars in concrete; some of these have been under trial for a number of years while others have only recently been introduced. Specifications are being updated continuously to ensure that the most updated technology is invoked in new systems (27). But just as it may take a number of years for salt corrosion of rebars to result in significant degradation of reinforced concrete, so it takes several years to prove not only the effectiveness of cathodic protection systems but also

their long term durability in actual service.

Most cathodic protection of rebars in concrete systems have been installed and operated in North America, with no more than a few examples in the U.K., mainly to protect buildings. The deterioration of reinforced concrete roads and bridges is less of a problem in the U.K. because of the more widespread use of asphalt-type coverage, especially over bridges. This acts as a membrane to keep de-icing salts from seeping into the reinforcement of the roadways and any supporting structures. However, problems exist with salt contamination of some crossbeams and pillars in concrete motorway viaducts, and it has recently been announced on behalf of the U.K. Department of Transport that trials of several methods will shortly take place on parts of a motorway viaduct in the Midlands (28).

It has been estimated that over the next twenty-five years many millions of square metres of reinforced concrete will be fitted with impressed current cathodic protection systems. This application looks certain to become a significant new outlet for both noble metals and for refractory oxide base metals, principally titanium.

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Some Platinum Group Metals Cluster Catalysts

Contribution of Clusters Physics to Materials Science and Technology

EDITED BY J. DAVENAS AND P. M. RABETTE, Martinus Nijhoff, Dordrecht, 1986, 646 pages, Dfl. 250,000/£69.25

Clusters and small particles have a large area to volume ratio and can therefore be considered as an intermediate state of matter at the interface between atomic or molecular chemistry and the physics of condensed matter. Discussion at the NATO Advanced Study Institute held in France in 1982, where the papers in this book were given, centred on the critical size at which the change to bulk properties occurs.

The book includes a chapter on catalysis by molecular clusters and many of the examples given contain platinum group metal systems. Following a description of the reactivity of molecular clusters, the reactions catalysed by these systems are described. The rhodium and ruthenium catalysed synthesis of ethylene glycol from carbon monoxide and hydrogen under high pressure conditions has been studied in detail by workers at Union Carbide and has been shown to involve anionic clusters such as $[\text{Rh}_3(\text{CO})_9]^-$, and $[\text{HRu}_3(\text{CO})_{11}]^-$ and $\text{Ru}(\text{CO})_3\text{I}_3^-$; but other examples showing unambiguous catalysis by clusters are still rare. Two examples of homogeneous catalysis given are the isomerisation of olefins catalysed by $\text{H}_2\text{Os}_3(\text{CO})_{10}$ and catalysis of the water gas shift reaction by $\text{Ru}_2(\text{CO})_{12}$. Olefin hydrogenation has been shown to be catalysed by silica supported $\text{HOs}_3(\text{CO})_{10}$, and the water gas shift reaction is catalysed by $\text{Rh}_6(\text{CO})_{16}$ on alumina.

Molecular clusters can be used as starting materials for the preparation of heterogeneous catalysts, and for ruthenium systems cluster derived catalysts display enhanced activity for the hydrogenation of straight chain aliphatic hydrocarbons. The increased activity superficially correlates with the smaller metal crystallite sizes reproducibly obtained with metal cluster compounds as catalyst precursors.

The study of the organometallic chemistry of

surfaces could prove to be a significant area for future investigations. For example, the oxidative addition of hydrogen onto a coordinately unsaturated rhodium atom on the surface of alumina has been described.

The book gives many examples of the surface characterisation of supported platinum metals catalysts and, for example, links product selectivity in catalysis to platinum particle size in platinum on alumina catalysts produced by the evaporation of a range of platinum film thicknesses followed by various treatments in hydrogen and oxygen. There are many surface methods available for the characterisation of metal supported catalysts and examples of the use of ESCA, EXAFS, EELS and other techniques are given throughout the book.

Cluster science has relevance to a large number of solid state sciences including metallurgy, magnetism, and defects in solids and alloys, in addition to inorganic chemistry and catalysis. Interrelating results from all these fields is still in its infancy, but this book has helped to focus attention on the value of considering the relevance of cluster phenomena to them all.

D.T.T.

Commodity Meeting on Platinum

The Institution of Mining and Metallurgy is to hold its Annual Commodity Meeting on December 4th, 1986 at The Geological Society, Burlington House, London. The programme will include presentations on platinum as a strategic metal, exploration targets and guidelines, the UG2 platinum reef, processing of platinum metals, developments in the platinum market, trends in industrial applications, and its use in the control of gaseous environmental pollutants.