

# Platinum Provides Protection for Steel Structures

## PART II—PERFORMANCE IN SERVICE

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*The first part of this article considered the principles of cathodic protection and described ways in which platinum could be utilised economically as an electrode material. This article examines how such electrodes perform in service, in a variety of applications and under differing conditions.*

Although platinum is relatively inert it does corrode at a very slow rate when anodically polarised in natural water, and except at very high current densities the extent of corrosion is proportional to the quantity of electrical charge transferred across the metal/solution interface. Up to  $1000\text{A/m}^2$  the maximum corrosion rate is about  $1\mu\text{g/A-h}$  ( $2.8 \times 10^{-4}\mu\text{g/C}$ ) and is about twice that value for current densities up to  $5000\text{A/m}^2$ . It follows that the higher the current density and the longer the projected life the thicker the coating required for the anodes. Charts have been produced by Marston Excelsior showing the various relationships between service life, current density, coating thickness and corrosion rates, in which only 85 per cent of the coating thickness is taken into account to allow for uneven corrosion. Thus whereas a coating thickness of  $2.5\mu\text{m}$  may suffice for a relatively small installation with a contemplated life of say 10 years, as much as  $50\mu\text{m}$  may be required for a very large system where the anodes have to operate at high current densities and the contemplated life may be as much as 30 years.

It should also be noticed that under certain

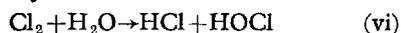
circumstances attack may occur on the titanium substrate through the pores in the electrodeposited platinum with consequent loss of adhesion and exfoliation of the latter; hence clad coatings and niobium substrates have many advantages. This loss of platinum by both anodic dissolution and exfoliation is perhaps more appropriately referred to as "wear" rather than corrosion.

Surprisingly, solid platinum appears to have a slightly higher corrosion rate than electrodeposited platinum, and even more surprising is the fact that platinum anodes in fresh water corrode, or wear, at a rate that is about five times the rate in sea water (6). This may be associated with the different electrode reactions, and with the high overpotential required to oxidise water to oxygen as compared with low overpotential for chlorine evolution.

Laboratory studies by Juchniewicz (15) on the effect of superimposed alternating current ripple of 50Hz on direct current showed that the ripple caused a marked increase in the corrosion rate of platinum anodes. This, in the early days of platinised titanium, was regarded as a serious limitation and Marston Excelsior issued a precautionary instruction to the effect that when platinised titanium was used as an anode the maximum permissible ripple should not exceed 5 per cent. Subsequently, further investigations by Juchniewicz and Hayfield (16) showed that this enhanced corrosion was critically dependent on ripple frequency, and that fortuitously the most detrimental frequencies were 50Hz or lower. Furthermore, it was established that negligible

effects on the corrosion rates are obtained, providing the frequencies from commercial three-phase or single-phase full-wave rectifiers are 100Hz or higher. These considerations apply also to the various "automatic-type" thyristor-controlled current supplies, which are used to vary the current with changing corrosiveness of the environment, resulting from changes in velocity, temperature or salinity.

The electrolysis of water results in the formation of equivalent amounts of hydroxyl ions at the cathode and hydrogen ions at the anode, Eqns. iii and iv, Part I, but the water will remain neutral providing these reactions' products are allowed to mix one with the other or are dispersed in a large volume of water. However, in certain circumstances this is prevented with a consequent decrease in the pH of the water in the vicinity of the anode, and although platinum corrodes only slowly in near-neutral waters it corrodes at a significantly higher rate in acids (17-19). This acidification of the anolyte may result from the chlorine evolution reaction (Equation v) followed by



and/or the oxygen evolution reaction (Equation iv).

Acidification of the anolyte can occur in practice if the anode is immersed in silt or inserted in steel bore holes, conditions that inhibit ready mixing of the anode products with the bulk water. This occurred with the long rod platinised titanium anodes used for the cathodic protection of a jetty at Thameshaven (19). These anodes, which were coated with a thickness of platinum well above  $2.5\mu\text{m}$  and operated at comparatively low current densities, became covered with silt at their lower ends and the acidification of the water resulted in the complete stripping of the platinum from these areas. Anodes placed in bore holes to protect the land-based foundation to the approach to a jetty suffered a similar fate owing to percolation of sea water into the ground, and it was observed that the platinum had been removed by corrosion and by exfoliation owing to attack

on the titanium substrate. Another interesting example (19) is provided by an installation in which the anodes were placed at the base of a steel-cased bore hole and were inadvertently in electrical contact with the casing prior to the application of the polarising e.m.f. Enhanced bimetallic corrosion of the steel occurred (Fig. see 1 (b)) and the acid ferric chloride formed attacked the platinised titanium when it was subsequently made anodic.

Acid attack under silt deposits has been demonstrated (19) in laboratory experiments on platinised titanium polarised at  $500\text{A}/\text{m}^2$  in 3 per cent sodium chloride mixed with a fine limestone mud, and it was observed that not only was the corrosion rate of the platinum six times greater than in a limestone-free solution but that attack on the titanium had resulted in exfoliation of the coating. The sodium chloride solution under the deposit was found to have a pH of 1. The MA form of platinised titanium, recently developed by Marston Excelsior, as compared with the conventional material, is claimed to have ten times the resistance to acid attack. This is achieved by applying a platinum electrodeposit of low porosity, and by interposing an acid-resisting layer between the platinum and the titanium; both reduce the tendency of the titanium to corrode in acid solutions.

## **Anodes Incorporating Platinum Wires**

The anodes described above are characterised by the use of platinum applied as a coating—electrodeposited or clad—to a substrate of titanium or niobium. However, there are two other types of anodes, based on different principles, that utilise platinum in the form of fabricated wire.

### **Lockheed Anode**

Studies of the anodic evolution of gases on platinum by Littauer (20) have shown that the ohmic resistance of gas films and bubbles make a considerable contribution to the total anode polarisation, particularly at high current densities where transport of reactants

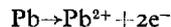
to and reaction-products away from the platinum electrode result in excessive anode polarisation (transport overpotential). Determinations of the overpotential versus log  $i$  relationships using platinum wires of 0.75mm diameter or greater and sheet electrodes of the same surface areas showed that the curves were very similar. However, with thinner wires a marked decrease in transport overpotential was observed, which means that finer wires are more economical and can be operated at higher current densities with less polarisation than thicker wires or sheet of the same surface area. The Lockheed anode consists of a niobium rod around which a fine platinum wire, 0.05 to 0.25mm diameter, is tightly wound to form a helix, the spacing of the turns of the wire being 4.5 to 7.5mm; the wire is spot-welded to the niobium rod at intervals. It is claimed that the anode can operate at 20,000A/m<sup>2</sup>, and that a single anode of about 1.5m in length can provide 200A. This anode, which is highly stable and guaranteed for a 20-year life, is considered to be the most suitable for cathodic protection systems that are subjected to the severe environmental conditions that prevail in Alaskan waters.

#### Lead-Platinum Bielectrodes

The anodic behaviour of lead in sulphuric acid is characterised by the formation of a thin layer of brown lead dioxide, which has an electronic conductivity that is approximately 20 per cent that of the metal. Thus once the film is formed further reaction is confined to oxidation of water to oxygen. The presence of chloride ions, as might be anticipated, results in film breakdown and corrosion of underlying lead, and it is for this reason that chloride-free water must be used in the lead-acid accumulator. In the light of the above it is remarkable that lead can be used as an inert anode in sea water.

The behaviour of lead when anodically polarised in sodium chloride solutions is highly complex, and its study is complicated by the comparatively high solubility of lead

chloride (the solubility product of PbCl<sub>2</sub> is  $2.4 \times 10^{-4}$  compared to  $2.3 \times 10^{-8}$  for PbSO<sub>4</sub>). The primary reaction product is the plumbous ion



and this is followed by crystallisation of PbCl<sub>2</sub> from solution, providing the solubility product is exceeded. The position of formation of the PbCl<sub>2</sub> will depend on the concentration of Cl<sup>-</sup> ions in solution and the current density, and providing these are sufficiently high the lead chloride deposits as an adherent coating on the surface of the lead. Since these crystals are non-conducting the active surface area of the lead will decrease, and if the applied current is maintained constant the potential of the lead/solution interface will increase to a value at which Pb<sup>2+</sup> ions in solution are oxidised to PbO<sub>2</sub>. For the equilibrium

$$\text{PbO}_2 + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Pb}^{2+} + 2\text{H}_2\text{O}, \quad E = 1.45 - 0.1182\text{pH} - 0.030 \log a_{\text{Pb}^{2+}} \text{ V (7)}$$

and in a neutral chloride solution oxidation of Pb<sup>2+</sup> to PbO<sub>2</sub> will occur at  $\sim 0.6\text{V}$  (vs S.H.E.).

Initially only a small proportion of the PbO<sub>2</sub> formed adheres to the lead, since it is constantly undermined and detached by the formation of PbCl<sub>2</sub>. However, with passage of charge the PbCl<sub>2</sub> is slowly replaced by PbO<sub>2</sub>, which gradually consolidates and forms a continuous, adherent conducting film. The Pb/PbO<sub>2</sub> now behaves as an inert electrode and the predominant reaction is the oxidation of Cl<sup>-</sup> ions to Cl<sub>2</sub>.

Lead has been used as anode in extractive metallurgy since the beginning of the century, but the use of lead alloys for cathodic protection of steel in marine environment dates from 1955 when Crennel and Wheeler (21) used Pb-1Ag for the protection of naval ships, and demonstrated that its performance was far superior to the best grades of graphite. In 1959 Barnard, Christie and Gage (22) after studying a number of lead alloys concluded that Pb-2Ag had optimum anodic properties, and this alloy found extensive use in protecting ships of the Royal Canadian Navy. At about the same time Morgan (23) developed a ternary alloy Pb-6Sb-1Ag which prior to

*Fig. 8 Lead-platinum bielectrodes (2.5cm diameter  $\times$  2.5 cm long and 1.0cm diameter  $\times$  4.0cm long) on test in a waterbox of a sea water cooling system to determine the rate of corrosion of different lead alloys (27)*

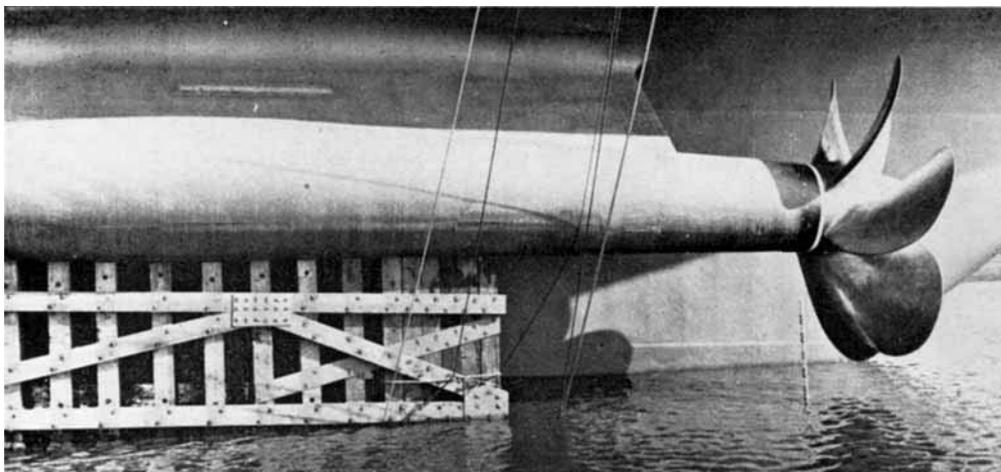


the advent of platinised titanium was widely used for protecting marine structures.

The ability of alloying additions of silver to promote the formation of lead dioxide and to decrease its tendency to breakdown in chloride environment has been well established, and although this phenomenon has been subjected to laboratory studies the role of silver is still far from clear (24). However, the formation of a Pb-Ag eutectic (2.5 wt per cent silver) suggests that the crystallites of silver might be an important factor, and this prompted a study of the effect of micro-electrodes of platinum, which were found to have a remarkable influence on the stability of the PbO<sub>2</sub> in chloride solutions (25, 26).

The lead-platinum bielectrode consists of lead, or a lead alloy (frequently extruded rod 25 to 48mm diameter) into which are inserted platinum pins (wire 0.5mm diameter  $\times$  12mm) at intervals of approximately 0.3m. This is achieved by drilling holes in the lead, inserting the pins so that the ends are flush with the lead surface, and then peening to ensure good electrical contact.

Tests carried out by Peplow (27) (see Figure 8) on lead-platinum bielectrodes in high velocity sea water at 2000A/m<sup>2</sup> for a period of six months to one year showed that the rate of conversion of lead to lead dioxide was 0.0163 kg per year, and this figure has been quoted widely. However, this current



*Fig. 9 This strip-type platinised titanium anode mounted on a propeller bracket of the Cunard liner Queen Elizabeth II forms part of the ten anode fully automatic impressed current protection system, which was designed, engineered and installed by F. A. Hughes using Marston Excelsior Anodes.*  
 Photographed by courtesy of Marston Excelsior Limited

density was excessively high, and the anodes are normally operated in the range 200 to 750A/m<sup>2</sup>; one of the first systems using these anodes, which was installed 15 years ago, is still performing satisfactorily, and there is little evidence of significant conversion of lead into lead dioxide even though it has been operating at 700A/m<sup>2</sup>.

The lead-platinum bielectrode is inexpensive, readily fabricated into a variety of shapes and is mechanically robust, and although it cannot be operated at such high current densities as platinised titanium it is often an advantage to use an anode of large surface area to reduce the metal/water resistance. It has been used for protecting a variety of structures in sea water, and its most important application has been for the cathodic protection of the San Francisco Bay Rapid Transit System, the system being installed by the Lockheed Co (28).

Although the role of the platinum in stabilising the lead dioxide at high current densities has been investigated the precise mechanism is still not clear, but it is appropriate here to outline a possible explanation. Localised attack on the lead following breakdown of the film manifests itself as a gradual increase in potential, which is due to the

formation of lead chloride at the site of breakdown and its propagation over the surface of the lead. Under these circumstances the lead dioxide is insulated from the lead with a consequent increase in potential. This can be demonstrated in a spectacular manner by forming PbO<sub>2</sub> on a lead-platinum bielectrode at constant current density, and then removing the platinum pin when the potential will rise in a few minutes to 10 to 20V (26).

However, when breakdown of the PbO<sub>2</sub> film occurs at the surface of a lead-platinum bielectrode the potential of the lead/solution interface cannot exceed that of the platinum, and since this polarises only slightly even at very high current densities the potential will be maintained at approximately 2.5V (vs. S.H.E.). Under this circumstance continued propagation of lead chloride is inhibited, and any lead chloride already formed on the surface of the lead will be converted to lead dioxide. The platinum microelectrode may be regarded, therefore, as acting as an internal potentiostat, which controls the potential of the lead/solution interface in a similar manner to a coating of platinum on titanium.

Its use is confined to saline waters of appreciable chloride content, and it will corrode with the formation of a film of high

resistance when used in natural fresh waters. Laboratory studies (29) of the oxidation of  $Pb^{2+}$  ions to  $PbO_2$  in sodium chloride solutions shows that this occurs only in the range 0.1 to 1.2M NaCl, and it would appear that the chloride concentration of sea water (19 per cent) is about the optimum for the formation of a stable  $PbO_2$  film; this is also facilitated by the presence of sulphates and bicarbonates. Deposits on the surface, such as silt and sand, which result in the formation of acid at the surface of the electrode, cause corrosion. Deposits of calcareous salts formed at the cathodically protected steel surface can cause a similar effect, and may arise if the anode is placed too close to the protected structure.

Hollandsworth and Littauer (30) have carried out laboratory studies of the behaviour of the bielectrode in sea water under pressure in order to simulate the effect of depth of immersion. They observed that severe corrosion occurred when the pressures were equivalent to a depth of 30m or greater.

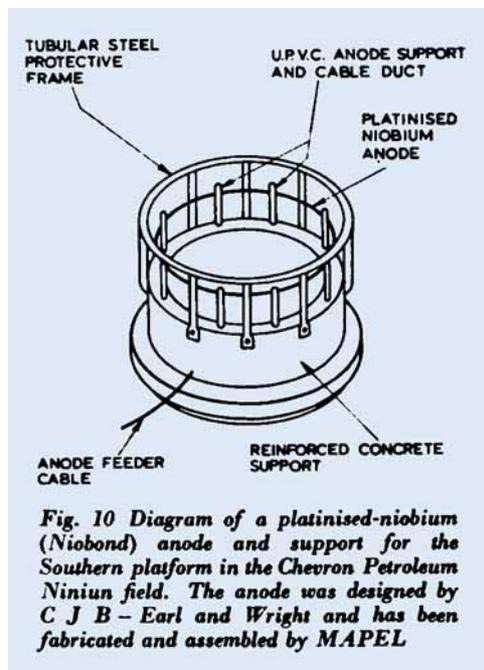
## Applications

The use of platinum-containing anodes for the cathodic protection of structures immersed in sea water is now well-established, and details of the protection of ships hulls, Figure 9, jetties, cooling-water systems, and the like are well documented in the literature. However, since the protection of North Sea oil platforms is highly topical it merits further discussion.

In cathodic protection there are two principles that are normally adopted:

- (a) the structure is given a protective coating and cathodic protection is used to prevent steel exposed at discontinuities from corroding, and
- (b) impressed current systems are considered to be more economical than sacrificial anodes for protecting large structures.

However, in the case of North Sea platforms there are certain difficulties, and in the majority of cases protective coatings are not used because of the incidence of damage



*Fig. 10 Diagram of a platinised-niobium (Niobond) anode and support for the Southern platform in the Chevron Petroleum Ninium field. The anode was designed by C J B - Earl and Wright and has been fabricated and assembled by MAPEL*

during installation and total reliance is placed on cathodic protection; British Petroleum appears to be an exception, and all their platforms are provided with a high-quality coating (31). Another difficulty is that impressed current systems require a source of direct current, and this may not be available for some months after installation of the platform in the sea, and during this time it will not be protected. For these reasons, sacrificial anodes of zinc or aluminium, attached to selected parts of the platform during its fabrication, have the advantages that protection is provided immediately and current distribution is uniform. On the other hand, to give protection to the large immersed area of the platform for a period of 25 to 30 years a tremendous mass of anode is required.

Even so, impressed current systems are becoming increasingly important, and once again platinum in various forms is being used as anodes for this purpose. Platinised titanium anodes, suspended from the structure, have been used for protecting the mobile drilling platforms "Sea Quest" and the "Ile de France", and lead-platinum bielectrodes

have been used for protecting a number of Philips Petroleum platforms located in the southern North Sea.

The use of Niobond (see Figure 6) to protect the Southern platform in the Chevron Petroleum Ninian field is described in a recent press report. The system has twelve sets of anodes, Figure 10, placed on the sea bed circumferentially around the platform at a distance of several hundred meters from the platform, and these are connected to a transformer rectifier on the platform by cables that lie on the sea bed. This location of anodes ensures that the current distribution will be far more uniform than if they are attached to the structure. The total current required for protection is 7200A operating at up to 35V, and this will provide a current density on the immersed part of the platform of 100 to 150mA/m<sup>2</sup>. Aluminium anodes are to be installed during the construction of the platform to protect critical areas from corroding during the initial launching period and prior to the application of the impressed current, which will come into operation a few months after the rig has been towed into position; these critical areas will also be given a protective coating. Although the cost of this protective system will be high, the dangers of corrosion of North Sea platforms are such that the initial expenditure on Niobond anodes, which will have a projected life of 30 years, is economically justified.

Another method of avoiding scouring or silting of the anode, when located on the sea bed, has been developed by Solus Schall in the form of a buoyant anode (32). This "Solanode" consists of a buoyant float fabricated from a syntactic foam resin with an external strength capable of withstanding the levels of pressures encountered at depths in the ocean, and in service it floats about 3m above the sea bed to which it is moored by a steel and concrete support. Thus both the Niobond anode and the connector to the cable float in the sea and are out of contact with the sea bed. The effectiveness of this anode has been proved by trials carried out on the

Indefatigable K platform, operating on behalf of Shell U.K. Ltd. and Esso Petroleum Ltd. The platform, which was illustrated in Part I of this article, is already being protected by aluminium anodes. It has been demonstrated that a single Solanode with an output of 400A placed 100 metres from the platform gives full and uniform protection to the platform, as established by measurements of potential, and reduces the current output from the aluminium anodes to zero.

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