Miniaturised Impressed Current Corrosion Protection Systems

AN APPLICATION FOR PLATINUM CLAD NIOBIUM

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The development of platinum coated refractory metal anodes for impressed current corrosion protection will be recorded in the history of technology as an event of extreme importance. The progress recently made in electronics technology has enabled further new developments in corrosion protection, leading now to miniaturised systems.

The need for corrosion protection of metals in aggressive environments is well recognised. One of the important ways of providing this corrosion resistance is by cathodic protection. With impressed current corrosion protection (ICCP), the metal structure to be protected is polarised cathodically by means of an impressed current between the structure and a stable anode. Today, ICCP is used extensively in such applications as ship hulls, oil and gas drill rigs, marine structures such as docks, power plant heat exchangers, buried pipelines and storage tanks, and bridge decks.

The wide range of applications for ICCP is due mainly to the development of platinum clad anodes which perform efficiently in corrosive environments. Initial attempts to use platinum coatings on metals such as lead, copper and silver failed due to corrosion of the substrate. Thicker platinum coatings made to ensure a pinhole-free protective covering for the underlying metal were tried but these anodes were not economical. In 1913, the possibility of using platinum in conjunction with chemically resistant "valve metals" was first recognised (1). Tantalum, niobium and titanium have rectifying characteristics in that when anodised in aqueous environments, an insulating oxide film is formed on the surface. Thus, when surfaced with platinum, these metals will form protective oxide films where exposed, and the anodic electrochemical reaction will occur on the platinum. The development of economic processes for the production of these rectifier metals, combined with the development of ingenious methods of applying thin layers of platinum on them—such as electrodeposition and cladding—led to the development of the stable platinum clad anode. The potential for the use of this anode for ICCP was first recognised by Cotton in 1958 (2). Since that time, the performance and development of various platinum surfaced anodes has been widely covered in the literature (3–11).

Miniaturised Systems

To date, impressed current corrosion protection has been used almost exclusively for the protection of relatively large structures. However, the need for small, economical systems has increased through the years. In the case of hot water storage tanks, potable waters have become more corrosive in recent years due to increased acidity and aggressive ions. Another example involves the more stringent requirements for reliability in water pumps, valves and other plant equipment which has required the use of more expensive materials. An economic miniaturised impressed current corrosion protection system (Mini-ICCP) can now be used in these applications, as well as in a wide range of others (12).

Recent developments in electronics technology for corrosion engineering, along

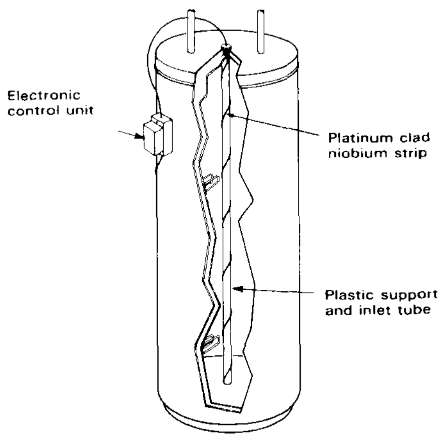


Fig. 1 Glass-lined hot water storage tanks, and through wall heating elements, may be protected by an impressed current corrosion protection system, the tank wall (cathode) and the platinum clad niobium anode being connected to a power source through an electronic control unit. The anode consists of a strip of platinum clad niobium spiralled around a plastic support tube which extends the full length of the tank, and which serves as the water inlet

with the development of platinum clad anodes, have allowed the miniaturisation of ICCP systems (13). These Mini-ICCP systems can now be used in applications where small, controlled currents are required. The miniaturised circuitry has been made possible through the development of sophisticated integrated circuits. The cost of these devices has been reduced so that small controllable power sources can be produced at competitive prices.

Hot Water Storage Tanks

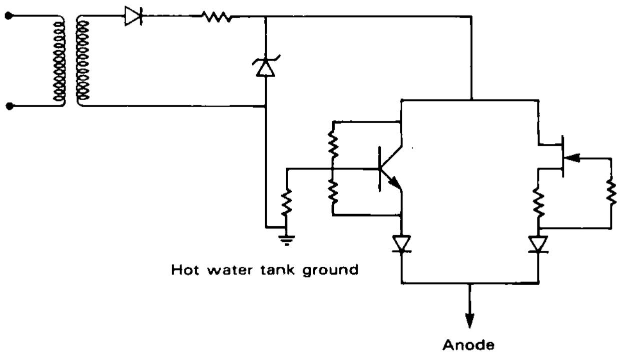
Use of the best available technology has resulted in a hot water storage tank which is constructed of glass-lined, welded steel shell. However, the glass coating is not always free from imperfections, especially in the weld areas. Thus, additional corrosion protection is necessary, normally through the use of magnesium sacrificial anodes (14). In recent years premature failure of the magnesium anodes has led to an increased failure rate of hot water storage tanks. Manufacturers have searched for a universal cathodic protection system that is effective regardless of the corrosivity of the water. This has led to the development of a Mini-ICCP system for hot water storage anks, as well as for a wide range of equipment requiring small protection currents and miniaturised components.

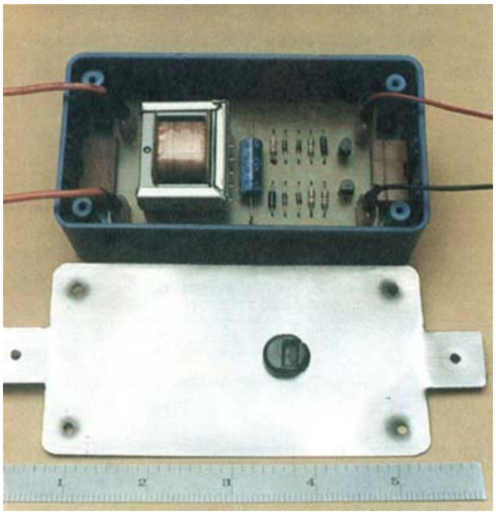
In order to protect the interior surface of a glass-lined steel tank, as shown in Figure 1, the system must be capable of providing uniform protection over the entire surface. Crevices formed by welds at the top and bottom of the shell are the most likely areas for defects in the glass lining, although such holidays may occur in other areas of the tank wall. In electrically heated tanks, the through wall heating elements may also need protection. These factors require that the anode extends over the full length of the tank to provide uniform cathodic protection. In Figure 1, the tank wall (cathode) and the platinum clad niobium anode are connected through a control circuit to the 110 volt or 220 volt AC power source.

The anode must be designed to have a long predictable life in the hot water storage tank environment. Platinum clad niobium has suitable properties for this environment, including high breakdown potential (>120 volts versus the S.C.E.) for the niobium substrate, a uniform platinum cladding, a sound metallurgical bond that prevents platinum spalling, and ease of fabrication (4, 5, 7, 9). The platinum consumption rate is extremely low and predictable in this environment, so that the design of the platinum clad niobium anode is highly reliable (10). The anode consists of a strip of platinum clad niobium, spirally wound on a plastic support tube which extends from the top to the bottom of the tank. The support tube also serves as the water inlet tube.

In order to be universally effective, the Mini-ICCP system must be capable of providing the necessary protection current in corrosive waters while not impressing too much current in less corrosive waters. In addition, an adequate protection current must be maintained regardless of the water resistivity. The key to this is the

Fig.2 The control circuit enables the current supply to vary with the resistivity of the water, thus always providing adequate protection for the tank. Basically, the circuit consists of a constant voltage section, a constant current section and appropriate switching circuitry





development of the control circuit, shown in Figure 2, which provides the protection current

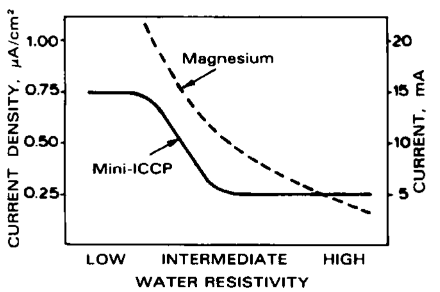


Fig. 3 The tank protection current is plotted here as a function of the water resistivity, for both the Mini-ICCP system and a magnesium anode

as a function of water resistivity, see Figure 3.

For a state-of-the art Mini-ICCP system in a commercial hot water storage tank, the curve of protection current versus water resistivity shown in Figure 3 has three regions. The region of low resistivity and high corrosivity requires maximum protection current. The region of intermediate resistivity exists whereby the current decreases with increasing resistivity. The third region of high resistivity and low corrosivity requires minimum protection current. Included in Figure 3 is the curve for a magnesium anode in the commercial hot water tank. Notice that at low resistivities (high corrosivity) the protection current is extremely high, which can lead to rapid corrosion and premature failure of the magnesium anode. At high resistivities, the current is very low which could possibly lead to under protection.

The regulating nature of the control circuit in Figure 2 provides the output which conforms to the curve in Figure 3. The circuit consists of a constant voltage section, a constant current section, and appropriate switching circuitry.

Field Trials and Service Performance

Field trials have been conducted in areas having documented corrosion failures where tanks had failed in less than three years. They included sites with well waters, waters with high concentration of sulphides or chlorides, and acid waters. Impressed current corrosion protection systems conforming to production specifications were installed at each site. Water conditions, protection currents and tank potentials were measured periodically. Table I gives specific data from selected sites on water resistivity, pH, protection current, and tank potential. These potentials are all in the protection region for steel indicating that the proper protection current is being supplied by the Mini-ICCP system.

A typical potential profile for a hot water storage tank is given in Table II to show that the protection is distributed throughout the inside tank wall. The absence of tank failure after 5 years at sites where failure had previously occurred with magnesium anodes after only three years, provides conclusive evidence of the effectiveness of the Mini-ICCP system in the in-

Table I

Field Evaluation of Mini-ICCP in Hot Water Storage Tanks

Location	Source of water	Water resistivity ohm cm	pH	Protection current mA	Tank potential (volts vs. S.C.E.)
Reheboth, MA	Well	8000	5.5	14	−1.08
Reheboth, MA	Well	3200	4.9	17	−1.13
Attleboro, MA	Reservoir	3500	7.1	9	−0.95
Johnston, R.I.	Well	7100	6.9	15	−0.102
San Diego, CA	Reservoir	1000	8.4	16	−1.32

Table II

Typical Potential Profile of Hot Water Storage Tank with Mini-ICCP Protection*

Tank depth (cm)	Tank potential (volts vs. S.C.E.)
Top	−1.20
10	−1.20
25	−1.31
50	−1.25
75	−1.05
Bottom	−1.03

*1 Year service, 15 mA protection current, 3500 ohmcm water, pH = 5.2

creasingly aggressive hot water storage tank environments now encountered.

Summary

Advances in electronics and materials technologies have led to the development of miniaturised impressed current protection systems. The system described here was developed for the protection of glass-lined steel hot water storage tanks. It consists of a platinum clad niobium anode strip which extends the full length of the tank, and an electronic control unit. The stability of platinum clad niobium has been well documented such that the design of the anode for long life is ensured. The control unit was designed to provide optimum cathodic protection current for the tank in all water conditions. Service performance of the Mini-ICCP system has shown that problems encountered with other protection methods are overcome with this device. The system has applicability in other environments including water pumps, valves, water cooled devices and a wide range of plant equipment where small protection currents and inexpensive miniaturised circuitry is necessary.

References

1 R. H. Stevens, *U.S. Patent* 1,077,920; 1913
2 J. B. Cotton, *Platinum Metals Rev.*, 1958, **2**, (2), 45
3 R. M. Skomoroski, R. Baboian, R. G. Zobbi and E. K. Camp, *Plating*, 1973, **60**, 1115
4 R. Baboian, Chlorine Bicentennial, The Electrochemical Society, Princeton, N.J., 1974, p. 158
5 R. Baboian, Proceedings of the 4th International Congress on Marine Corrosion and Fouling, 1976, p. 51
6 M. A. Warne and P. C. S. Hayfield. *Mater. Perform.*, 1976, **15**, (3), 39
7 R. Baboian, *Mater. Perform.*, 1977, **16**, (3), 20
8 L. L. Shreir, *Platinum Metals Rev.*, 1977, **21**, (4), 110 and 1978, **22**, (1), 14
9 R. Baboian, *Mater. Perform.*, 1979, **18**, (1), 9
10 R. Baboian, *Mater. Perform.*, 1983, **22**, (12), 15
11 R. Baboian, *Mater. Perform.*, 1984, **23**, (9), 31
12 R. Baboian and G. Haynes, *U.S. Patent* 4,407,711; 1983 and *Mater Perform.*, 1983, **22**, (10), 15
13 R. Baboian, L. McBride, R. Langlais and G. Haynes, *Mater. Perform.*, 1979, **18**, (12), 40
14 H. H. Uhlig, "Corrosion and Corrosion Control", 2nd Edn., Wiley, New York, 1971, p. 218

Palladium-Copper Composite Contacts

Electrical contacts form a necessary part of a very wide variety of components used, for example, by the telecommunications and automotive industries. Essential requirements of such contacts are that, on activation, they will consistently close the circuit, carry the current and then break the circuit, for at least the specified number of operations. The reliability of performance depends upon the electrical and mechanical operating conditions, and also upon the chemical and physical properties of the contact.

Although copper-palladium alloys containing 15 or 40 weight per cent copper have been used successfully for electrical contacts for many years, none-the-less work continues to develop materials that combine the different properties in more advantageous ways. A recently published communication from the laboratory of R. Rau G.m.b.H., Pforsheim, and the Institute for Materials Technology of the Technical University Berlin deals with the manufacture of copper/palladium composites, and compares the properties of these new materials with those of conventional copper-palladium contact alloys, (K. Müller, D. Stöckel and H. Claus, *Metall*, 1986, **40**, (1), 33–37).

As the palladium content of a copper-palladium alloy is increased to improve resistance to tarnishing, so the electrical conductivity is decreased and the hardness increased due to solid solution effects. However composite materials can be made from these two metals in ways that hinder solid solution formation. One of the three methods suggested is to draw down bundles of copper-clad palladium wire. By repeated bundling and drawing as many as 5000 wires may be reduced to a diameter of 0.5 to 2mm.

These ductile composite materials can be fabricated in a cost effective manner into bimetallic rivet-headed contacts. Electrical conductivity may be higher by a factor of ten, and contact resistance lower than that of conventional alloy contacts of the same overall composition.