The Use of Cathodic Protection for Copper Alloys in Seawater Cooling Systems

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Historical

In the very early days of coolers and condensers, the water box was normally made from carbon steel or cast iron. It was a heavy component as the wall thickness was generous in order to provide a corrosion allowance and was not coated. The water box served as a sacrificial anode and therefore formed a type of cathodic protection system for the copper alloy tubes and tube plate as well as dosing iron ions into the water. The result was excellent and corrosion problems were very limited. The units at this time tended to be small and the water flow was low.

The next development was to bigger units and coated water boxes. It was at this time that erosion corrosion started to be observed at the tube plate and tube inlets as the galvanic protection was lost. In 1912, the Cumberland US patent led to the use of impressed current cathodic protection to protect against this. Iron blocks were used as anodes which had the added advantage of providing ferrous ion dosing for the protection of the inner surfaces down the tubes. Other methods of providing ferrous ions such as ferrous sulphate dosing and sacrificial anodes followed.

Internationally, the era of building large power plants and steamships took off in the 1950s and 60's through to 1980. Many large power plants had their own expert in this area and a number of theories developed in offsetting corrosion issues, particularly as conditions in the plants differed. These were related to materials, design, type of cooling water, salinity, content and type of sand/mud, flow velocity and operating conditions. For the greater part of this time, the copper alloy tube material often used had been aluminium brass and experience grew relating to safe shut downs, filling with fresh water, fast cleaning and controlled flow regimes.

In some plants, ferrous ions from ferrous sulphate dosing or iron anodes, cleaning regimes and cathodic protection systems worked well. However, with time it was appreciated that care was needed to form a protective layer on the alloy surface. Rate of surface layer formation depended on the temperature and time of year; formation rates are faster in warmer waters. In general, and unless there were polluted conditions, ferrous ion dosing was not so necessary in summer time and iron anodes could be removed. If the film became too thick, spalling might occur which could affect flow conditions. During shut downs, if the film dried out, it was necessary to clean and remove the layers with low concentrations of acid .Acid cleaning combined with iron dosing and cathodic protection were successfully used to provide good service at the Danish plant of Aasnes at Kalundborg for many years. The efficiency of surface layers forming in the tube was checked by measuring the change in outlet water copper content.

Below 3-4^{o}C, problems were experienced in achieving the protective layers. This was studied in several Swedish nuclear plants for several years in all kinds of combinations. Using cathodic protection in the water box, it was possible to prevent inlet and outlet tube erosion totally; the tubes being protected internally for approximately 0.5m from the tube plate. The water box, tube plate, rolled ends and inlet and outlet lengths of tube were successfully protected. The longer tube lengths of around 10m needed to form the protective layer and this was difficult for aluminium brass in Scandinavia in wintertime and was eventually solved by changing material.

Today, condensers and cooling systems still use a lot of copper alloys for shipping and offshore oil/gas production because of cost and also advantages relating to biofouling resistance. The design advantages related to heat transmission can also be important. From around 1990, copper-nickels became more widely used for condenser tubing. Ferrous ions are not so necessary for copper-nickel as aluminium brass. Often, it is sufficient for impressed current cathodic protection (ICCP) and iron anodes to be used in the inlet water and inert anodes only in the turn chamber and outlet water box. Such combinations have been used for a large number of installations with very good results.

Cleaning

Cleaning is always important for optimising heat transfer whatever the material combinations used. Today, even if sophisticated automatic pressure regulated filters are available, they might not be used for smaller installations or sufficient filtering might not be carried out. In some cases, it is necessary to employ additional antifouling measures, such as copper ion dosing, as biofouling can be compromised in copper alloys by applying cathodic protection. Particular problems arise if larger sizes of shells get stuck in the system, collect silt, and block the tubes causing turbulent flow and corrosion.

For larger power plants as opposed to shipping, a ball cleaning system is often used for regular tube cleaning. In the past, soft balls with a layer of carborundum were used which quickly scratched the aluminium brass surface. Today, too, sometimes heavy manual cleaning with metal brushes are used and cause problems. Soft nylon brushes would normally be preferred instead. Automatic brush cleaning systems are available but often the work is performed using manual brushes and pressurised water and air. It is important to adhere to instructions given by the heat exchanger or system supplier as well as methods used for cleaning, and that these are specific to the actual tube material to be cleaned.

Material Developments and Protection

Materials and alloys have been developed and their performance improved over the years. Tube materials have changed from copper to aluminium brass to copper-nickel alloys whereas the stainless steels have changed to higher alloyed alternatives. Titanium is now used as well. The materials have advantages and disadvantages and they all have a place in achieving technical and economical solutions.

Cathodic protection of stainless steels or copper-nickel with ICCP can work very well. Both materials are easy to protect by applying cathodic current and, with clean surface conditions, only a minor negative polarisation is required to achieve protection (ie 50-100mV for stainless and even less for copper-nickel). It is more important with lower grades of stainless steels to have a surface which is clean and free from marine fouling than for copper-nickel. In general, the current distribution and potential influence can reach further into stainless steel tubes due to the better oxide resistance than for copper alloys. Nevertheless good protection results have been achieved for copper-nickel tubes.

For copper-nickels, it not always necessary, unless the waters are cold or polluted, to have additional ferrous ions in the sea water to provide protection; it is often used as a carry over from aluminium brass practice. If used, it is important to keep the protective layer as thin as possible to reach the optimum corrosion protection and this is good for heat transfer too. Warmer water (> 15-20^{o}C) might cause an excessive floc in ordinary sea water, ferrous additions are normally unnecessary as the material will readily form a protective layer anyway and will show good corrosion resistance naturally. The addition of an ICCP system will protect the water box and tube plate from galvanic corrosion or deposit corrosion and the inlet and outlet ends of the tubes from turbulence or erosion corrosion caused by localised high flow rates. Evaluations by electrochemical means are not so straight forward or as well understood with copper alloys as with stainless steel as the protective film formations are different and the two cannot be compared. Any future development of alternative short term methods of evaluation suitable for copper alloys to predict the onset of localised corrosion by erosion or sulphides, would be a bonus.

Past Cathodic Protection Systems

The Cumberland US Patent from 1912 was an important development and this type of cathodic protection combined with electrolytic iron dosing has been used a lot over the years mostly in condensers with aluminium brass tubing.

From 1960-1985, a large number of the systems were supplied for both on-shore power plants and shipping. Many of the big tankers during this period used steam turbines with large condensers and over a 1000 ships had this type of system. In Europe, they were often known as BERA systems which was an old trade mark of the Danish Bergsoe group. The author was involved over a number of years with the design, supply and service of several hundred of these. The older system used ICCP and a rectifier unit that supplied a constant voltage or constant direct current output. To begin with a constant voltage was used but later this changed to a constant current. Both are possible as the sea water resistivity is normally fairly constant. In some applications, the system was potentiostatically controlled as well which means reference electrodes are required leading to increased complexity and more examination.

However, in practice, the use of reference electrodes in ship installations led to problems of electrode maintenance. Most of the systems supplied had two current output settings; one for normal operations and one for stagnant flow which was about 20% of the normal current. Control of the two settings was often by a relay function with the main cooling water pump. The reason for reducing the current was to avoid unnecessary consumption of the iron anodes, as well as reducing the amount of calcareous deposit caused by too low a cathode potential. These white alkaline deposits can be high in sea water at low potentials and may even block the tubes. The iron anodes were designed for 1-2 years life. According to Faraday's Law, the iron is consumed at approximately 10 kgs per amp.yr. The normal design "rule of thumb" is that a direct current output of around 1-3amps/m^2 of tube plate (depending on flow and materials) is required to reach a current density to protect the tube in/outlets from erosion. For example, for a 1m diameter copper-nickel tube plate, a rectifier with a capacity of 2 amps would be used. As aluminium brass is more sensitive to erosion, copper-nickel can have the lower current density. Normally, this results in a potential at the tube plate surface of approx. 1V vs. SCE. Over the years, many studies and data collection were performed on these installations by ABB/BBC, Stal Laval, EPRI and others[1,2,3,4].

Sacrificial anodes of so called “soft iron” have been used and continue to be so, particularly in rubber lined water boxes with titanium tubing. Experience where these ceased to work were when they were completely insulated with a plastic holder and where steel sheet was used which became passivated by corrosion products. On other occasions they have been positioned disrupting flow and causing erosion corrosion or turbulence.

Impressed Current Cathodic Protection Systems Today.

The need for higher water velocities and optimum performance of coolers and their design has influenced material selection. Today, copper-nickel is frequently selected and the tubes are rolled tight into the tube plate which may itself be clad with copper-nickel. In general copper alloys, especially copper-nickel, are very easy to protect by cathodic protection and only a small cathodic polarisation is required; in normal favourable conditions this would be about 50mV minimum. Cathodic protection systems in general are known to be over designed and often too much direct current output is experienced resulting in heavy alkaline deposits which can increase when a system is stagnant for part of the time. Different methods have been used to solve this problem with a variety of success. For more than 10 years an automatic (interrupter potentiostat) rectifier system has been used in several hundred installations with good success.

A popular automatic rectifier system uses an interrupter potentiostat and a titanium mixed oxide coated (activated) anode. The interruption is controlled to less than a microsecond and the potential (voltage) is read and recorded. In this way, the titanium oxide anode acts as a reference electrode without a normal reference electrode being used. This is possible because the noble oxide* coating/activation layer of the titanium rod versus the water potential is very stable in the first microseconds. This measurement gives a potential free of voltage (IR) drop. The advantage of this system is that for periods of stagnant water, the current output is automatically controlled. Contamination and use of special reference electrodes is avoided as well. The anodic reaction of oxygen and chlorine gas evolution keeps the anode surface clean.

As these impressed current cathodic protection systems protect the water boxes and tube inlets and outlets, it is still important that efficient cleaning regimes are practiced for the bulk length of tubes. Even with a cathodic protection system, it is important to clean and keep the surfaces free from mud, deposits and fouling. Formation of the protective layer, commissioning and standby practices need particular attention. Cathodic protection systems cannot reverse corrosion that has already occurred and often corrosion of condensers and coolers develops under deposits when the unit is out of operation and perhaps partially empty of water so that the cathodic protection cannot function properly. In fact, a standby unit can suffer more from corrosion than when the unit is under full flow. Standby systems are normally filled with water with the cathodic protection system on. The water should be periodically circulated, and replaced with fresh water at least once every week, or drained down and dried. Each

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* the type of metal oxide used is dependant on application and whether seawater or brackish water is used.

manufacturer will have their own recommendations and it is important that these are followed, especially the procedures for unit start up and shut down.

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