

THE TESTING OF CORROSION INHIBITORS FOR CENTRAL HEATING SYSTEMS

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Abstract—Modern inhibitor formations for protecting central heating systems against corrosion and scaling are complex blends of chemicals, which often act synergistically. They need to protect the mixed-metal system for upwards of 20 years. It is, therefore, important to be able to assess the long-term performance of an inhibitor within a reasonable time period. The present approach is to carry out initially short-term electrochemical studies on a variety of metals at 80°C. Longer-term testing is then carried out using both electrochemical and weight-loss measurements, usually under conditions of thermal cycling. The polarisation resistance of several metals can be measured simultaneously, either in a coupled or uncoupled state, using a multiple offset zero-resistance ammeter technique. Possible adverse effects due to nucleate boiling on boiler surfaces are investigated by subjecting specimens to heat flux of 25 W cm⁻². Other factors which have been taken into account are the water quality, over- and under-dilution with inhibitor and degree of aeration. The paper describes the development of a non-toxic nitrite free inhibitor based on molybdate–borate–phosphate–carboxylate.

INTRODUCTION

CORROSION in central heating systems is promoted due to several factors. Their construction necessitates the use of mixed metals with stressed regions and crevices formed at welds or other contact points in radiators. Microbial corrosion can take place, especially in open-vented systems, which allow organic contamination from outside to occur. Excess use of flux can give rise to high chloride levels. Due to nucleate boiling on the heat exchanger surface, boilers are especially prone to corrosion damage.

The reason why untreated heating systems do not usually fall apart within a very short time is undoubtedly due to the low oxygen content of the recirculating water. Nevertheless, it has been shown that even in very low O₂ containing heating water, significantly <1 ppm, corrosion still continues at an appreciable rate on cast iron,¹ within steel crevices² and on aluminium.³ Oxygen ingress occurs, in open-vented systems, through the feed and expansion tank, especially as the water expands and contracts during the heating cycle. Even in closed systems, oxygen can enter the system through pump seals, plastic pipes or at poor joints on the negative pressure side of the pump.

Modern heating systems are becoming more prone to corrosion.³ This is due to the higher heat flux in boilers and the introduction of aluminium condensing boilers, thinner wall sections on boilers and radiators, and tighter tolerances on pump bearings and automatic valves, which can seize with even small amounts of corrosion debris.

Treatments which are added to recirculating heating systems are complex blends of chemicals which should maintain the integrity of the system for in excess of 20 years. This should prevent not only corrosion but also scaling and growth of bacteria

as well as minimising boiler noise. The factors which influence the formulation and the ideal properties of a water treatment in heating and cooling systems have been discussed by Davies.⁴

The parameters which have to be considered when testing inhibitor formulations have been covered by Mercer.^{5,6} Electrochemical and weight loss tests have been conducted in glassware and simulated near-to-operating conditions using recirculating rigs for automotive coolants,^{7,8} solar heating media⁹ and model heating system water.²

In this work, the test procedures we have used in developing a new non-toxic inhibitor together with examples of results are presented. This inhibitor, which is nitrite-free, is based on a molybdate-phosphate-borate-carboxylate blend.

EXPERIMENTAL METHOD

Initial screening tests on a new product are usually carried out in glass bottles containing steel nails and a copper ring, as shown in Fig. 1. In this way a wide range of concentrations in hard and soft water can be tested quickly to determine if the product is likely to be economically viable at the concentrations necessary to afford full protection. The bottles are placed in an oven at 80°C for several days before inspecting for any signs of corrosion. If attack occurs it is most likely to be seen at the tips of the nails or where the nail contacts the copper ring. Under cupro solvent conditions, the copper ring may also become tarnished or attacked.

Electrochemical testing is carried out using a computer-controlled 'Electrochemical Interrogator' designed and built to our specification by ACM Ltd, Rochdale. All standard d.c. techniques including potentiodynamic polarisation are performed at constant temperature in a short term testing cell. Long term corrosion monitoring is carried out in five other cells either at constant temperature or under temperature cycling. The computer controls the temperature cycle through relays connected to stainless steel immersion heaters or a chilled water supply. For a constant temperature a water-bath set at 80°C is usually used.

The metals used are commercial grades typical of those used in central heating systems and specified in the new BSXXXX. We routinely carry out tests on mild steel, copper, cast iron and, if required, aluminium. The solutions used, for testing our latest product at least, are made using both hard and soft water conforming to BSXXXX. The hard water has a carbonate hardness equivalent to 250 ppm CaCO₃, whilst that of the soft water has 25 ppm CaCO₃. Both waters have the same permanent hardness of 100 ppm. As well as in aerated solutions, tests are also conducted in de-aerated conditions by continually bubbling high purity nitrogen through the solution. The dissolved oxygen concentration can be monitored by using an Ingold oxygen sensor.

A standard cell with electrodes is shown in Fig. 2. This type of cell can have up to four working electrodes either of the 'flag' type or as cylindrical sheaths which enclose the heating element in a push fit.

The surfaces are ground to 400 grit finish before rinsing in methanol, drying, weighing and mounting. The heaters and metal sheaths are designed to give a watt density of 25 W cm⁻² on the surface of the sheath. This is typical of heat flux values in modern boilers. When temperature cycling, the solution is stirred with a magnetic stirrer bar. After testing, the electrodes are inspected for any signs of localised attack or limescale under a low pressure microscope.

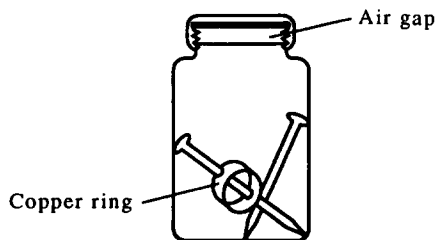


FIG. 1. Nail bottles used for screening inhibitor concentrations.

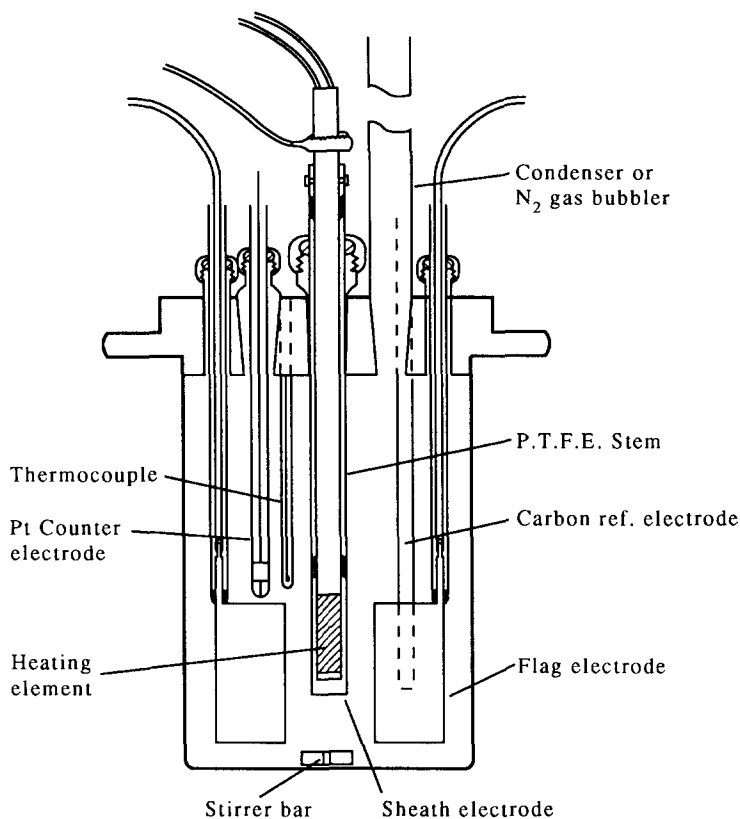


Fig. 2. Glass cell for electrochemical studies showing electrodes used.

EXPERIMENTAL RESULTS AND DISCUSSION

Preliminary screening with nail bottles showed that an inhibitor based on molybdate and carboxylate could offer full protection of mild steel and copper and be economically viable.

Electrochemical testing initially involved monitoring the galvanic current and polarisation resistance values on mild steel/copper couples in both hard and soft water at 80°C for up to 1 week. Previous work has found good correlation between weight loss and LPR measurements for steel, and copper.

The rapid decrease in the galvanic current between a mild steel/copper couple in the new inhibitor can be seen in Fig. 3, in which the inhibitor was thermally cycled between 60 and 90°C over several days. After five days the galvanic current density is for all practical purposes zero even at 90°C. The corrosion rates, as measured by LPR, are shown in Fig. 4 for a portion of the test, which reveals more clearly the actual temperature cycles (temperature cycling is continuous, although electrochemical monitoring is performed only every few cycles). Corrosion rates for mild steel and copper were around 0.001 mm yr⁻¹ indicating that, at least over 6 days, there is no sign of thermal breakdown of the inhibitor (a similar test is still ongoing and will continue for several weeks).

A cast iron heater sheath subjected to 25 W cm⁻² was coupled to a copper flag

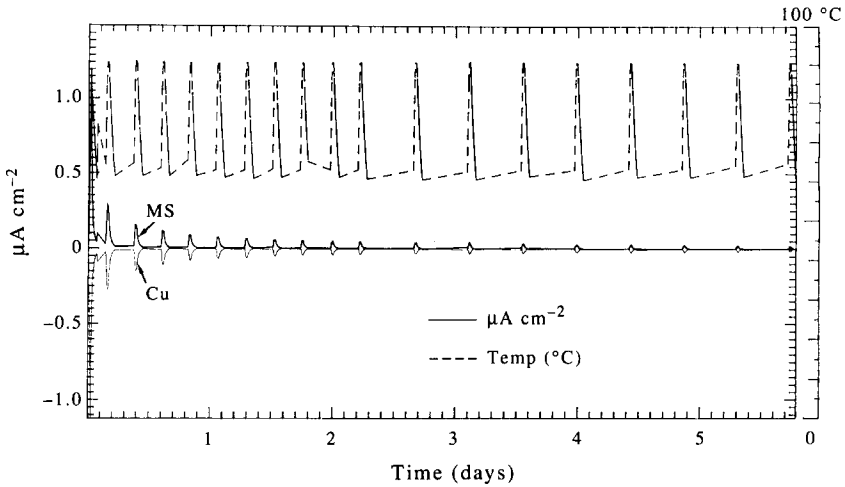


FIG. 3. Galvanic current density for mild steel-copper couple in new inhibitor under thermal cycling.

electrode and thermally cycled for 1 week in the new inhibitor. The galvanic current can be seen in Fig. 5.

High polarisation resistance, $>100 \text{ k}\Omega \text{ cm}^2$, corresponding to a corrosion rate of $\sim 0.002 \text{ mm yr}^{-1}$ were measured for the cast iron at 90°C . Inspection of the sheath after 1 week revealed no sign of pitting corrosion, although some light scaling on the area subject to nucleate boiling was evident. These findings indicate that heat flux on cast iron does not significantly impair the corrosion performance of the inhibitor.

In addition to the above tests carried out at the to-be-recommended 4% concentration of the inhibitor, steel, cast iron and copper have also been tested at 2% in both hard and soft water over 100 h. Similar results were found as before indicating full passivation of steel and cast iron had occurred even at 100% overdilution.

Susceptibility of steel and copper to localised attack in this inhibitor has been

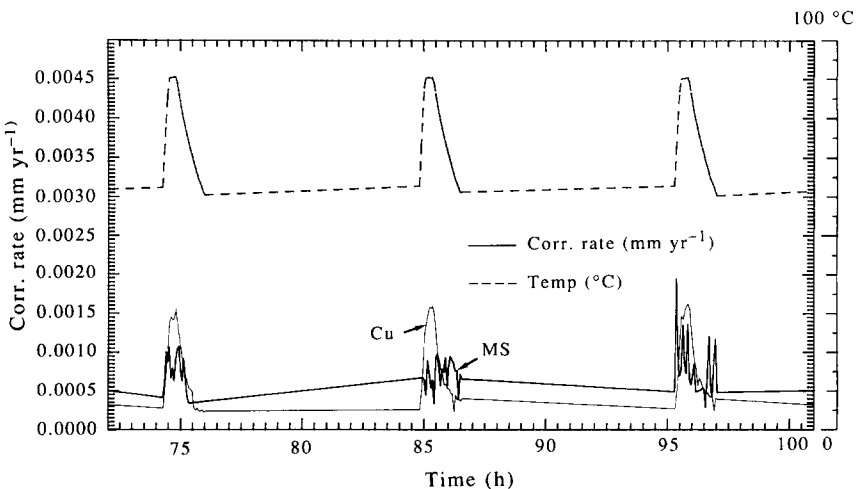


FIG. 4. Corrosion rates derived from LPR for mild steel and copper coupled in new inhibitor under thermal cycling.

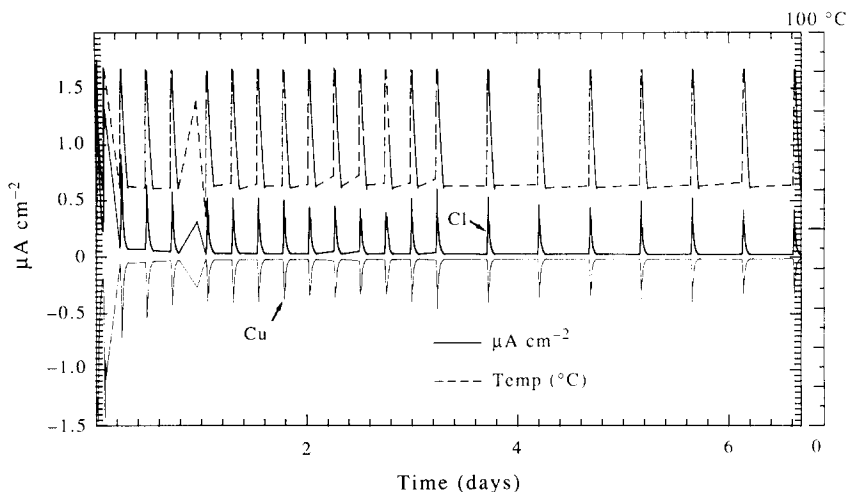


FIG. 5. Galvanic current density for cast iron-copper couple in new inhibitor under thermal cycling. Cast iron subjected to heat flux of 25 W cm^{-2} .

assessed by anodically polarising the specimens from $+200$ to $+1000$ mV above E_{corr} in 50 mV steps of 10 min duration. Even when the overpotential had reached $+1000$ mV the measured current was still found to decay and no localised attack had initiated indicating excellent resistance to pitting corrosion. Other propriety brands of inhibitor we have investigated exhibit much lower breakdown potentials.

All the above tests were performed in glassware under natural aeration. However, in real heating systems, the dissolved oxygen content is much lower, although unlikely to be zero for reasons explained earlier. Even after de-aerating uninhibited hard and soft water with high purity nitrogen for 1 week, the corrosion rates on steel, as measured by weight loss and LPR, were found to be between 15 and $50 \mu\text{m yr}^{-1}$, i.e. up to $50\times$ that of the inhibited solutions. Tests were also carried out on steel/copper couples in de-aerated solutions of the inhibitor in hard and soft water. Any significant galvanic current would indicate that some species in the inhibitor was stimulating the cathodic reaction rate.

In hard water de-aerated conditions, the couple potential remained high and the galvanic current steadily decreased indicating that full passivity had been maintained. On de-aeration with nitrogen gas in soft water conditions, however, a somewhat different behaviour was observed, as shown in Fig. 6. Initially, the couple potential fell by about 200 mV whilst the galvanic current increased, after a slight delay, reaching around $0.5 \mu\text{A cm}^{-2}$ after about 1 h. From then on for the remainder of the test (48 h), the galvanic current decreased steadily whilst the couple potential became more noble than its initial value. Thus, full passivation of the steel was again established. In other formulations in soft water we have tested, however, within 30 min of de-aeration, the couple potential has dropped several hundred millivolts leading to high galvanic currents and active corrosion of the steel.

The above behaviour can be explained knowing the types of chemicals which are in inhibitor formulations for heating systems. These nearly all contain chelating agents such as EDTA or NTA, which prevent scaling by forming complexes with calcium ions in the water. However, these chelating agents also form complexes with

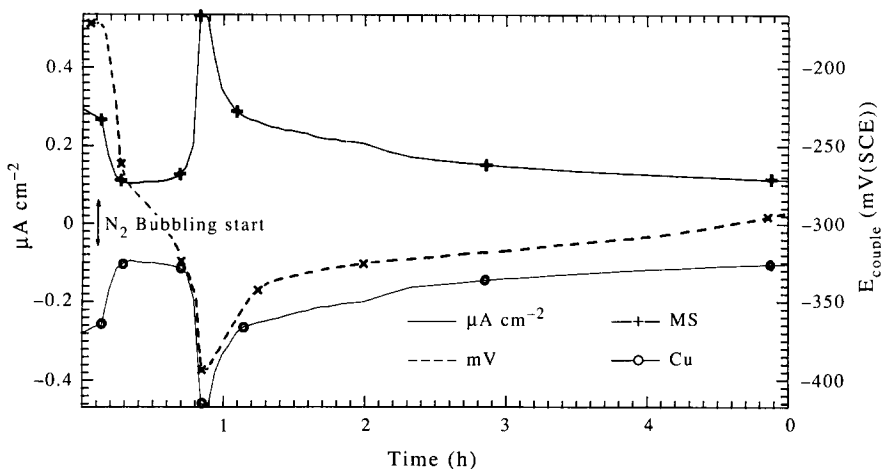


FIG. 6. Galvanic current and couple potential for mild steel/copper in new inhibitor in soft water on de-aerating with N_2 gas.

iron and copper and in the absence of sufficient hardness salts in the water will tend to attack these metals. In soft water oxygenated conditions, the anodic inhibitors possess sufficient oxidising power to maintain passivity. When the dissolved oxygen is removed, however, the chelating agents may be able to interfere with the passivation process sufficient to cause active corrosion. The blend of chelating agent in the new inhibitor have been specially selected to ensure that this phenomenon does not occur.

As with all our previous inhibitors, corrosion inhibition in the new toxic inhibitor is predominantly anodic in character. However, a criticism of anodic-type inhibitors is that where their concentration falls below a critical level due to restricted access, e.g. in crevices or under debris, they can actually accelerate corrosion attack. We are attempting to address this danger by incorporating a cathodic-type inhibitor (a Mg^{2+}/Zn^{2+} blend) into the formulation. Figure 7 shows how the addition of the metal cations has reduced significantly the cathodic current on a steel electrode when polarised to -200 mV overpotential. This rapid decrease in the cathodic current, however, was not observed when the same blend was added to the nitrite-containing formulation. Therefore, it appears, as Qian suggests¹⁰ that metal cations synergise with molybdate to produce a more protective precipitate film at the cathodic sites.

CONCLUDING REMARKS

The development of a new non-toxic nitrite free inhibitor for central heating systems has involved electrochemical testing of steel/copper couples under temperature cycling and of cast iron under nucleate boiling conditions. Tests have been conducted in hard and soft water in both fully aerated and de-aerated solutions. Resistance to pitting attack has been assessed by anodic polarisation.

The possibility of the corrosion of steel changing from passive to active on de-aerating an inhibitor solution in soft water has been found to occur when certain chelating agents are present. The concentration and type of chelating agent in the new inhibitor have been adjusted so that this behaviour does not occur.

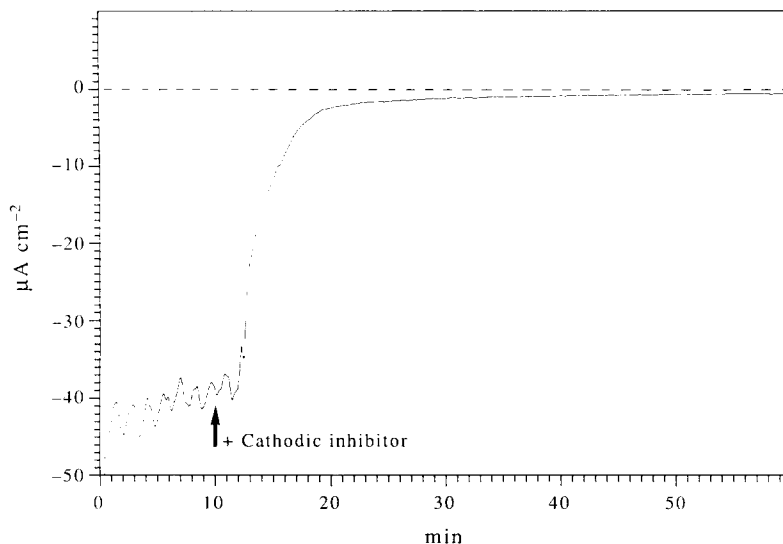


FIG. 7. Effect of addition of cathodic inhibitor on cathodic current of mild steel polarised to -200 mV overpotential in new inhibitor base.

A cathodic inhibitor has been added to minimise any risk of corrosion under debris.

When developing an inhibitor for central heating systems, many other aspects besides corrosion inhibition have been taken into account. These are scale prevention, boiler noise reduction, biocidal activity, compatibility with rubbers and plastics, stability in storage and cost. Therefore many different formulations around a base are tested. Now all the above criteria have been satisfied field trials in real heating systems have commenced.

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