Pergamon

CORROSION OF CENTRAL HEATING SYSTEMS

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Abstract—This paper begins by summarizing the main mechanisms by which components in central heating systems can corrode, and indicating the factors which can increase or decrease the rates of corrosion. The basic principles are then applied to the analysis of three case studies of corrosion failure in heating systems: rusting through of mild steel radiators after only 2 years in service; premature pitting corrosion of aluminium heat-exchanger tubes; and external corrosion of mild steel water pipes. © 1997 Elsevier Science Ltd

1. BACKGROUND

Figure 1 is a schematic diagram of a typical closed recirculating heating system. The heat-exchange medium (water) is circulated between the heat source (boiler) and the heat sink (radiators). The maximum water temperature at the exit from the boiler is typically 80 °C. A typical radiator is made from two separate sheets of mild steel 1–2 mm thick, which are press-formed to produce the shapes of the waterways, and joined by electrical-resistance welding (Fig. 2). The water pipes are generally made from thin-walled copper tube. The heating modules in the boiler are made from steel, copper or aluminium alloy. Fittings such as valves are usually made from brass.

2. OXYGEN REDUCTION—BASIC MECHANISMS

Mild steel has a strong tendency to rust when exposed to water and oxygen. Because the mains water which is used to fill the system is saturated with air, one might think that mild steel was an unwise choice of material for radiators and heat exchangers. As shown in Appendix A, the conditions under which a metal corrodes in water can be summarized using the electrochemical equilibrium (or Pourbaix) diagram [1]. Figure 3 shows the Pourbaix diagram for iron at 25 °C. Mains water usually
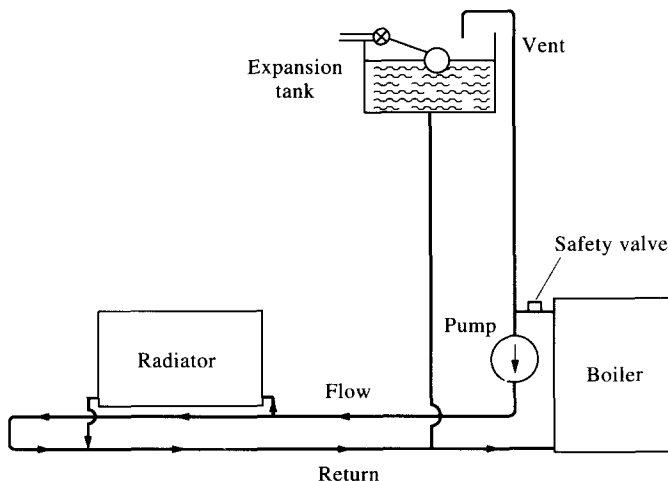

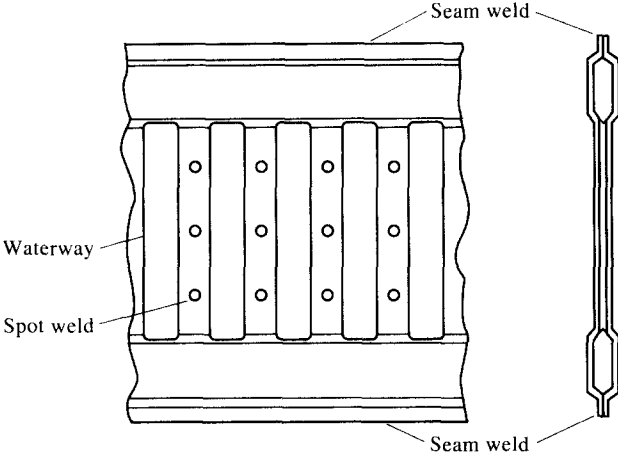Fig. 1. Schematic diagram of a closed recirculating heating system.

Fig. 2. Construction of a typical mild-steel radiator.

has a pH of 6.5–8 [2], so as long as the potential of the iron is kept below −0.6 V (standard hydrogen-electrode scale) the iron will be immune from corrosion. The Pourbaix diagram also shows the line for the oxygen-reduction reaction. The open-circuit potential for this reaction in mains water is ≈ 0.8 V. This means that if iron is immersed in mains water saturated with oxygen the voltage difference available to drive the corrosion process will be $0.8 - (-0.6) = 1.4$ V.

In practice, the oxygen content of the water in the heating system rapidly falls towards zero. The water is only saturated with air when the system is first filled. The solubility of oxygen in water decreases as the temperature increases: it is $8 \, \text{mg} \, \text{l}^{-1}$ at 25 °C [2], but only $3 \, \text{mg} \, \text{l}^{-1}$ at 80 °C [3]. When the water is heated to the operating temperature, air is driven out of solution: it escapes through the vent and is bled off through the valve at the top of each radiator. The steel only has to corrode to a small extent to consume the remaining oxygen, and the water becomes de-aerated. It takes typically 75 days for this to happen; at steady state the oxygen concentration is only $0.3 \, \text{mg} \, \text{l}^{-1}$ [4]. The oxygen-reduction reaction effectively stops, and further corrosion is negligible. Under these conditions, mild steel radiators and heat exchangers can last for well over 30 years without rusting through. However, if fresh oxygen gets into the system in any quantity it is possible for radiators to perforate after only 2 years in service.
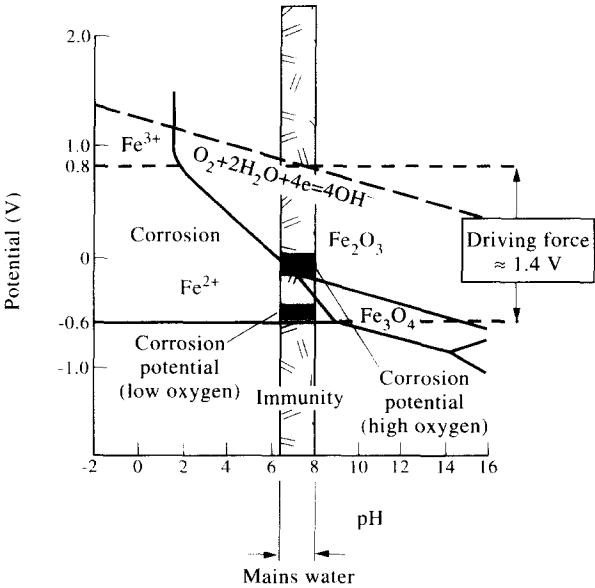

Fig. 3. The Pourbaix diagram for iron at 25 °C, showing the oxygen-reduction reaction.
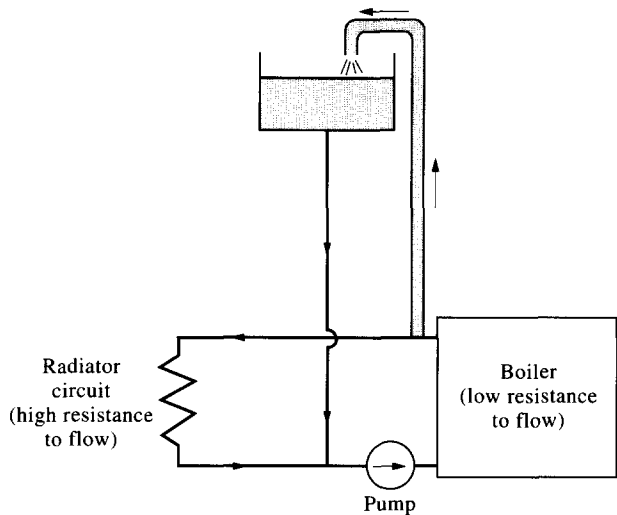
Fig. 4. Design fault 1—pumping water through the expansion tank.

2.1. *Oxygen pick-up*

There are a number of ways in which the water can pick up oxygen. Obviously, some air will get in when the circuit is drained down (e.g. for repairs, or when there is a risk of freezing) and then refilled. A limited amount of fresh water is taken into the system to compensate for evaporation from the expansion tank or losses due to leaks, and this, too, is a source of oxygen. But a major intake of oxygen is usually caused by design faults in the pipework.

A typical fault is shown in Fig. 4 [4]. If the flow resistance of the radiator circuit is large compared to that of the boiler, then, depending on the location of the pump, water can be forced up the vent and discharged into the expansion tank. A particularly bad location for the pump is shown in Fig. 4—in the return line between the cold feed and the boiler. It is easy to see that, when a large pressure drop is needed to get the water to flow around the radiator circuit, then the water will tend to take the easier route, and there will be a circulation loop between the boiler and the expansion tank. Naturally, as the water pours out of the vent it continually picks up air. This "pumping over" would not have happened if the pump had been positioned to the *left* of the cold feed instead of to the right. Figure 1 shows the standard position for the pump in a modern installation—in the flow line after the vent. When the pump is put in this position pumping over cannot occur.

Figure 5 shows another fault—when air is drawn in down the vent pipe [4]. In order to pull water through the boiler the pump must generate a low pressure in the flow line from the boiler. This low pressure depresses the head of water in the vent pipe. If the expansion tank is not high enough, the surface of the water in the vent pipe will be pulled down to the level of the flow line, and bubbles of air will be swept into the circuit. Oxygen concentrations of ≈5 ppm have been found in systems
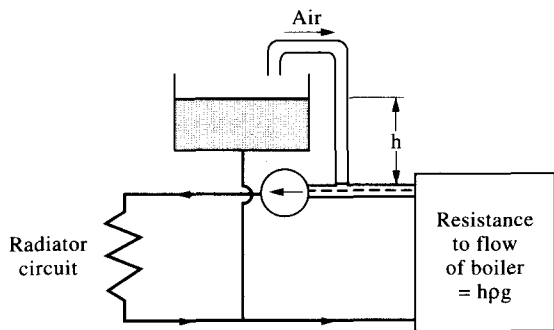

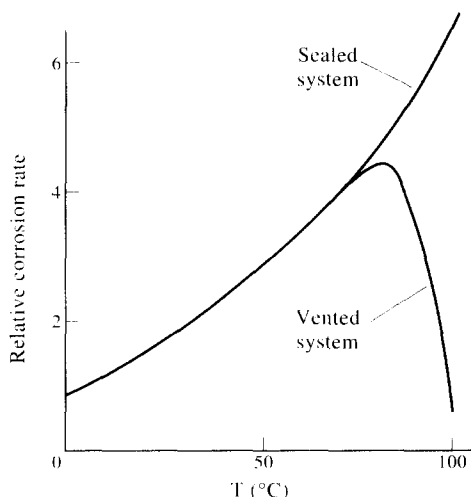Fig. 5. Design fault 2—drawing air in through the vent.

Fig. 6. Rate of corrosion of mild steel in aerated mains water as a function of temperature.

suffering from this defect [4]. To avoid air intake, the static head h must be greater than the flow resistance of the boiler by a suitable safety margin; a typical value for h is 1.5 m.

In order to guarantee that oxygen is excluded from the system, the trend in most modern installations has been to replace the traditional open expansion tank with a sealed air cushion expansion tank. The system water expands into a polymeric bag which is contained in an outer tank of pressurized air.

2.2. Corrosion rates

When the water is saturated with oxygen, the steel will corrode rapidly. The rate of corrosion is controlled by the oxygen-reduction reaction, which is in turn controlled by the rate at which oxygen diffuses through the water to the surface of the steel. Because diffusion is a thermally-activated process, the rate of diffusion will increase exponentially with temperature. So also will the corrosion rate, as shown by the rising curve in Fig. 6. As one approaches 80 °C, the curve divides into two branches [3, 5]. If the system is pressurized (so none of the dissolved oxygen can escape), the curve carries on upwards. But if the system is vented (as most central heating systems are), the oxygen can come out of solution as the water warms up. As the oxygen concentration falls below $3 \, \text{mg} \, \text{l}^{-1}$, the oxygen-reduction reaction slows considerably, and at 100 °C the steel is corroding no faster than it would have done in aerated water at 25 °C.

2.3. Diagnosis

It is relatively easy to find out whether excessive oxygen has been getting into a heating system. When oxygen is plentiful, the iron corrodes rapidly at a relatively high potential. The reaction takes place in the Fe_2O_3 field of the Pourbaix diagram (see Fig. 3), and a red sludge of hydrated ferric oxide collects at the bottom of the radiators. When oxygen is scarce, the iron corrodes slowly at a relatively low potential. The reaction generates ferrous ions, and a thin black coating of hydrated magnetite (magnetic iron oxide) forms instead. Both oxides are 5 times as dense as water: although oxide particles can be carried around with the circulating water, most of the sludge remains in the radiators. Contrary to the view commonly held by many heating engineers, oxide sludge cannot be removed by flushing water through the radiators (although it can be removed by circulating a warm solution of inhibited phosphoric acid through the system).

3. OXYGEN REDUCTION—SOME COMPLICATIONS

There are several things which can make steel corrode faster in the presence of oxygen. These are summarized as follows.

3.1. *Galvanic corrosion*

The mixture of copper pipes and steel radiators makes up a galvanic couple. The Pourbaix diagram for copper is shown in Appendix A. Copper will be immune from corrosion in mains water as long as its potential is kept below 0 V. This is 0.6 V higher than the corrosion potential of iron. The copper is in excellent electrical contact with the steel through soldered joints or compression fittings. Because of this, the iron corrodes in preference to the copper, and acts as a sacrificial anode. The copper is protected by cathodic protection and provides an inert surface at which the cathodic oxygen-reduction reaction takes place. In practice, the extent of galvanic corrosion is limited by the ionic conductivity of the water. If the conductivity is low, the electrical resistance of the galvanic cell is high, and the steel will only corrode galvanically near to a copper surface. On the other hand, if the conductivity is high galvanic attack will occur some distance away from the copper. The solution conductivity can be decreased considerably if insoluble corrosion products form.

There is another way in which the copper pipes can lead to galvanic corrosion. The bore of the tubes corrodes slowly, and releases copper ions into the circulating water. At steady state, it is quite common to find concentrations of Cu^{2+} of 0.1–$0.2 \, mg \, l^{-1}$ [4]. Because steel is more reactive than copper, the following reaction takes place where the water passes over the steel surfaces:

$$Cu^{2+} + Fe = Fe^{2+} + Cu. \tag{1}$$

The copper metal produced by the reaction deposits on the surface of the steel as an extremely thin layer. Galvanic cells are then set up between the islands of deposited copper and the steel in between [3, 6]. However, opinions vary as to how important this mechanism really is.

3.2. *Dissolved ions*

Mains water typically contains approximately $50 \, ppm \, Cl^-$ and SO_4^{2-} in association with Na^+, Ca^{2+} and Mg^{2+}. The ions increase the conductivity of the water, and help the corrosion processes. The metal ions migrate to the cathodic surfaces where they neutralize the OH^- ions produced by the oxygen-reduction reaction. The Cl^- ions are small and highly mobile: they migrate rapidly to the anodic areas, and neutralize the Fe^{2+} ions produced when the iron dissolves. When mains water enters the system to make up for evaporation, it brings dissolved ions with it, and over time the concentration of the ions in the circulating water will increase. Both Cl^- and SO_4^{2-} are aggressive ions: they help to stop passive oxide films forming on the surface of steel, and this encourages corrosion even more.

3.3. *Pitting*

The surface of the steel tends to divide itself into anodic areas (where the iron corrodes) and cathodic areas (where the oxygen-reduction reaction takes place). This separation is encouraged by anything which makes the environment of the steel non-uniform. In most places, the metal is exposed to the flowing water (and the oxygen it contains), and behaves cathodically. However, steel in crevices has almost no exposure to oxygen, and behaves anodically. Crevices are present in many places: under deposits of sludge, next to welds, and in screwed connections. Obviously, the current of electrons produced by the anodic areas must balance the current of electrons delivered to the cathodic area. Since the anodes are small compared to the cathodes, the current density at the anodes will be large compared to the current density at the cathodes. The steel will corrode rapidly over a small area, and localized pits will form.

4. REDUCTION OF HYDROGEN

Figure 7 shows the line for the hydrogen-reduction reaction superposed on the Pourbaix diagram for iron. The open-circuit potential for the hydrogen-reduction reaction in mains water is $-0.4 \, V$. The voltage difference available to drive the corrosion process is $-0.4 - (-0.6) = 0.2 \, V$. The hydrogen-reduction reaction *polarizes* rapidly: an "overvoltage" is needed to make the reaction go at a reasonable rate. The extent of the polarization depends strongly on the metal or alloy concerned,
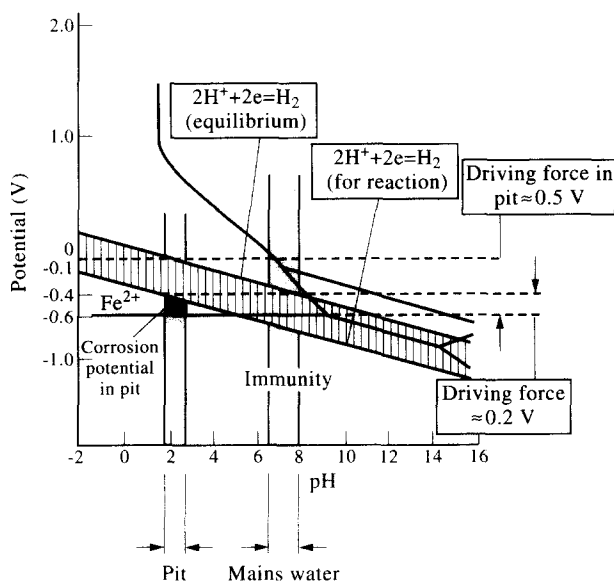
Fig. 7. The Pourbaix diagram for iron at 25 °C, showing the hydrogen-reduction reaction.

the condition of the surface, and the nature of the environment. Polarizations of $\approx 0.2–0.3$ V are common when hydrogen is reduced on the surface of iron. As shown in Fig. 7, the practical line for the hydrogen-reduction reaction probably lies below the corrosion potential of iron in mains water. In theory, therefore, steel radiators should not corrode by the hydrogen-reduction reaction.

In spite of this, hydrogen is often given off in central heating systems. The usual symptom is that one or more of the radiators suddenly goes cold for no apparent reason. This is because hydrogen gas has collected at the top of the radiator, and has blanketed the top ends of the vertical waterways. Heating engineers often claim that this is caused by dissolved air coming out of solution. In fact, when the gas is vented off it can usually be lit with a match! Provided there is no risk of explosion, having to vent radiators in this way is just a nuisance. However, the corrosion process produces magnetite, which can deposit in the waterways and clog the pumps.

Why does this hydrogen reduction occur? If the temperature is high enough, a reaction called the Schikorr reaction can take place [4, 7]. This has two steps as follows.

$$Fe + 2H_2O = Fe(OH)_2 + H_2, \tag{2}$$

$$3Fe(OH)_2 = Fe_3O_4 + 2H_2O + H_2. \tag{3}$$
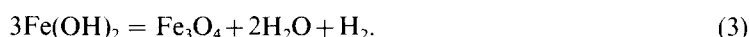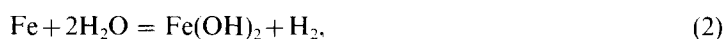
The Schikorr reaction is catalysed by copper ions: when these are present, it can take place above 60 °C. In systems where the water is aggressive to copper, the concentration of Cu^{2+} which is released into the circulating water can be large enough to provide the required catalyst. A survey carried out on one central heating system gave the results shown in Fig. 8. Below 63 °C, there was no detectable evolution of hydrogen. However, at 70 °C, the radiators had to be vented every week; and at 80 °C they had to be vented every day. An obvious way of suppressing the reaction, therefore, is to keep the temperature in the system below 60 °C.

4.1. Hydrogen and bacterial corrosion

Heating systems can become contaminated by bacteria [3, 8]. The most common are the anaerobic sulphate-reducing bacteria (SRB) such as *Desulfovibrio* which live in oxygen-starved conditions. As part of the metabolic cycle, the organisms convert sulphate ions into sulphide ions. Sulphide greatly speeds up the hydrogen-reduction reaction, and this allows steel to corrode even in neutral oxygen-free solutions. *Desulfovibrio* grows in the pH range 5–10, and the temperature range 5–50 °C. Some SRB can survive to even higher temperatures. If aerobic bacteria are present, these can colonize deposits and produce anaerobic conditions under the deposit where SRB can thrive under nominally aerobic conditions. The bacteria require nutrients, which are usually present in the form of hydro-
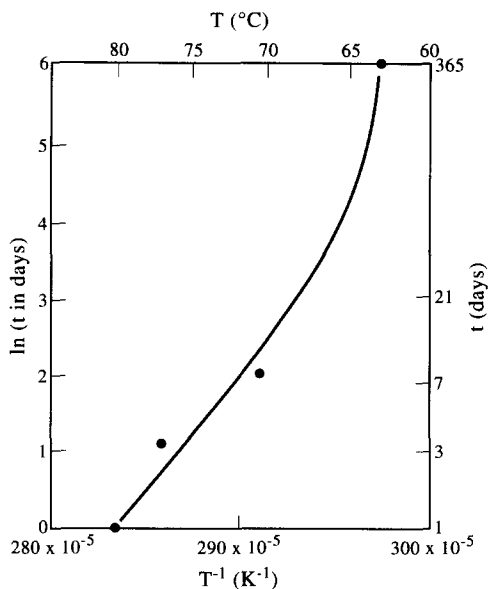
Fig. 8. Rate of hydrogen evolution as a function of temperature. Radiators have to be vented after a time interval t. Typical data only [4].

carbons. The usual way of preventing bacterial corrosion in heating systems is to add a biocide to the water.

4.2. Hydrogen and pitting corrosion

Once pitting has started, it is unlikely to stop. In order to maintain electrical neutrality in the pit, the Fe^{2+} ions attract Cl^- ions from the water outside. The pit becomes concentrated with $FeCl_2$, and this hydrolyses according to the reaction [2]

$$FeCl_2 + 2H_2O = Fe(OH)_2 + 2HCl. \tag{4}$$
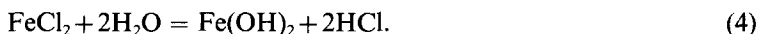
The corrosion product forms a crust which covers the mouth of the pit, and isolates it from the water outside. The HCl which is trapped inside the pit lowers the pH to ≈ 2 [5]. At this low value of pH, the hydrogen-reduction reaction gives a voltage differential of $\approx 0.5\,V$ (see Fig. 7), and this is enough to make the iron corrode quite rapidly. Hydrogen gas is given off inside the pit, and the crust bursts to let it escape. Of course, the new Fe^{2+} produced by this attack will suck in fresh Cl^- ions, and the cycle of events will repeat itself. The pitting process is therefore said to be *autocatalytic*. Because the corrosion is intense and localized, it can perforate the radiator wall after only a short time. Hydrogen evolved at low temperatures (where the Schikorr reaction is suppressed) is almost certainly a sign of rapid pitting corrosion.

5. USING INHIBITORS

These problems can be avoided by using *inhibitors* [3, 9]. A common inhibitor for steel is sodium nitrite, which is dissolved in the water to give a concentration of $\approx 800\,mg\,l^{-1}$ of NO_2^- ions. The nitrite functions as an *oxidizing agent* [10]. It increases the potential at the surface of the steel, and if the concentration is high enough the steel is moved up into the Fe_2O_3 field on the Pourbaix diagram (see Fig. 3). A thin stable film of γ-Fe_2O_3 forms, and this acts as a very effective barrier to further corrosion. The pH is kept above about 9 in order: (a) to avoid the corrosion field on the diagram, and (b) to reduce the potential at which the Fe_2O_3 field starts. Because sodium nitrite interferes with the anodic reaction (the oxidation of Fe to Fe^{2+}), it is called an *anodic inhibitor*.

It is very important to have a large enough concentration of nitrite in the water. Figure 9 shows how the rate of corrosion is affected by the nitrite concentration [9]. Above a critical concentration, there is no corrosion at all. However, as the concentration is decreased the corrosion rate increases
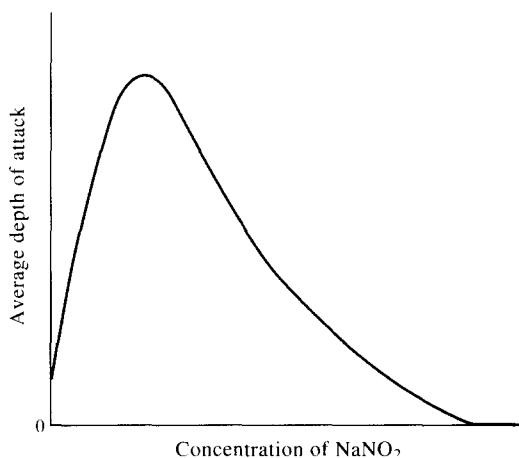
Fig. 9. Schematic effect of sodium nitrite concentration on the rate of corrosion of mild steel in mains water.

enormously; the maximum corrosion rate is much greater than it is when there is no inhibitor present at all. When the concentration is below the critical level, the surface of the steel is not fully passivated. The electron current taken by the cathodic reaction is concentrated at the weak points in the film, and these are subjected to rapid localized attack. The nitrite also increases the ionic conductivity of the water, and this increases the corrosion rate even more. Sodium nitrite is therefore classified as a *dangerous* inhibitor.

The actual value of the critical concentration depends on several factors. It is difficult for the nitrite to get at the steel when it is covered by deposits or shielded inside crevices: the concentration of inhibitor in the bulk of the water has to be increased considerably to stop the shielded areas corroding. Cl^- and SO_4^{2-} ions attack the passive film, so the concentration of the inhibitor must be increased to compensate. The minimum amount of extra sodium nitrite is given by [3]

$$(\text{weight } NaNO_2)/(\text{weight } NaCl + \text{weight } Na_2SO_4) \approx 1. \tag{5}$$

Because it is so important to keep the concentration safely above the critical level, the water in the system must be analysed at regular intervals, and topped up with extra inhibitor as required. Inhibitor will obviously be lost if the system leaks or if it is drained down. What is less obvious is that sodium nitrite can also be removed by the action of bacteria such as *Nitrobacter* which are very efficient at oxidizing nitrite to nitrate [3, 8]. Because of this, it is particularly important to use a biocide in any system which relies on sodium nitrite for its protection.

The best inhibitors for copper are specific organic chemicals such as benzotriazole [3, 7]. These react with the copper at the surface of the metal to produce a uniform adherent film. Benzotriazole is classed as a *cathodic* inhibitor because it interferes with the cathodic oxygen-reduction reaction. Around 5 mg l^{-1} is usually required to stop the copper corroding. Benzotriazole can also deactivate (chelate) copper ions which have already dissolved in the water. The Schikorr reaction cannot occur (because there are no active copper ions to catalyse it), and galvanic attack is inhibited (because copper ions are not reduced at steel surfaces). Finally, benzotriazole is a *safe* inhibitor. Because it is an organic compound, it cannot increase the ionic conductivity of the water. In addition, because it inhibits the *cathodic* reaction it does not cause pitting.

6. CASE STUDY 1—RAPID RUSTING OF STEEL RADIATORS

6.1. *Background*

The subject of this case study is a large central heating system in an office block. When the system was about 20 years old, the radiators started to leak and had to be replaced. However, because of the age of the system it was decided not to clean the existing pipework with a chemical descaling agent. The new radiators had a wall thickness of only 1.25 mm, and it was decided to protect them against rusting by adding a corrosion inhibitor to the water. The inhibitor was supplied as a concentrated solution of sodium nitrite and sodium borate. The solution was added to the system
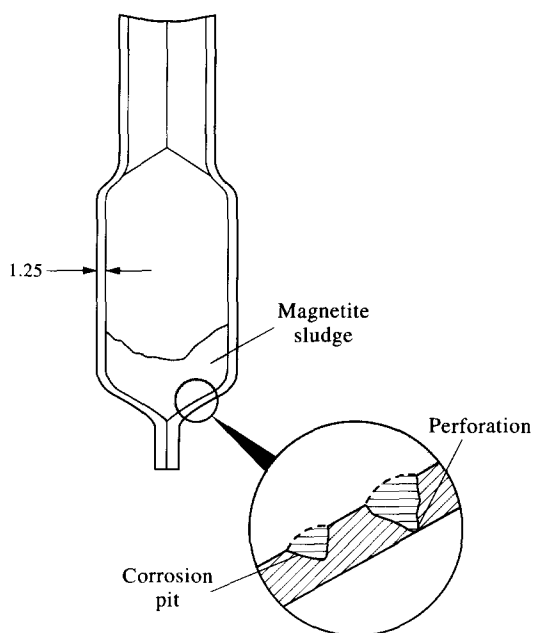
Fig. 10. A layer of magnetite sludge had formed in the water space at the bottom of the radiator. Pitting corrosion had occurred where the sludge covered the steel. Dimensions in mm.

until the concentration of sodium nitrite in the water was 1300 ppm (parts per million, or $mg\,l^{-1}$). The sodium nitrite was the active ingredient in the inhibitor package; the sodium borate was added as a buffer to keep the pH of the water at about 9. However, after only 2 years the new radiators started leaking. The offending radiators were removed, and one was cut open. As shown in Fig. 10, a layer of black sludge had formed in the water space at the bottom of the radiator. The corrosion had originated beneath this deposit, and had developed into deep pits. One of these had penetrated right through to the outside surface. However, there was no evidence of any pitting above the sludge.

The water had been analysed every 2 months to make sure that the inhibitor concentration was up to the recommended level. In most cases, it was found that the concentration had fallen significantly since the previous service, and extra inhibitor had to be put in to make up the shortfall. The average concentration reading was ≈ 500 ppm. However, on several occasions the nitrite level was as low as 100 ppm. An analysis of the mains water gave: $pH \approx 8$; $Cl^- \approx 500$ ppm; $SO_4^{2-} \approx 100$ ppm; high hardness. However, samples of water taken from the system itself gave: $pH \approx 10$; $Cl^- \approx 250$ ppm (max); $SO_4^{2-} \approx 300$ ppm (max); strong indications of nitrite-oxidizing bacteria.

6.2. Failure analysis

The first thing that one notices about the system is the high concentration of Cl^- and SO_4^{2-}. The minimum concentration of sodium nitrite which must be added to compensate for these aggressive ions can be estimated from Eqn (5). The ionic mass of Cl^- is 35, and the molar mass of NaCl is 58. The 250 ppm of Cl^- is therefore equivalent to $(58/35) \times 250 = 414$ ppm of NaCl. The ionic mass of SO_4^{2-} is 96, and the molar mass of Na_2SO_4 is 142. The 300 ppm of SO_4^{2-} is therefore equivalent to $(142/96) \times 300 = 444$ ppm of Na_2SO_4. The combined mass of NaCl and Na_2SO_4 is 858 ppm. Equation (5) shows that this must be balanced by at least 858 ppm of $NaNO_2$. As seen earlier, the average concentration of inhibitor was ≈ 500 ppm, and the minimum concentration was ≈ 100 ppm. These levels are far below the minimum requirement, so it is hardly surprising that the radiators corroded rapidly. The situation was still worse in practice because the sludge would have screened the metal from the inhibitor. The routine analyses show that the inhibitor level regularly fell from the recommended dose of 1300 ppm to as little as 100 ppm after only 2 months. Presumably nitrite was consumed by the nitrite-oxidizing bacteria. This would have been avoided if a biocide had been added to the water when the system was first filled.

7. CASE STUDY 2—HOLES IN ALUMINIUM HEAT-EXCHANGER TUBES

7.1. *Background*

Figure 11 is a simplified drawing of a heat exchanger from a large gas-fired central heating boiler. It consists of a number of externally finned aluminium tubes arranged concentrically around a tubular gas burner. The tubes are enclosed by a perforated sleeve of stainless steel; this is meant to spread the hot gases out uniformly as they flow away from the burner. Figure 12 shows a cross-section through one of the heat-exchanger tubes. The ends of the tubes are expanded into headers cast from eutectic aluminium–silicon alloy LM6. The cover plate on the return header is also cast in LM6. The cover plate on the inlet/outlet header is cast in grey cast iron, and so too are the pair of curved elbows. The boiler contains between two and six of these units depending on the heat output required. Technical data for a single heat exchanger are as follows.

Maximum heat output $= 100\,\text{kW}$.
Heat flux at bore of tube $\approx 230\,\text{kW m}^{-2}$.
Flow rate $\approx 2\,\text{l min}^{-1}$.
Flow velocity inside tube $\approx 0.5\,\text{m s}^{-1}$.
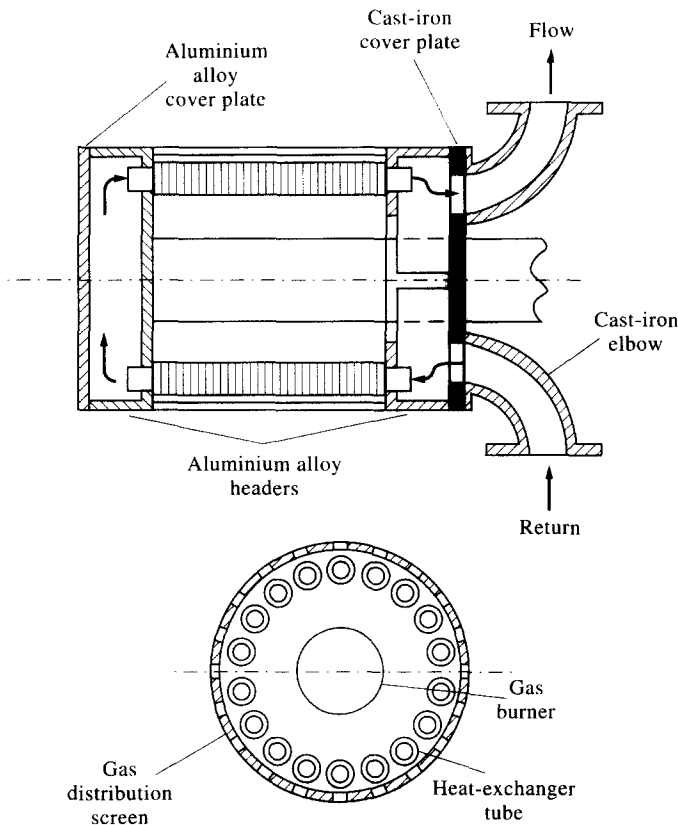Maximum temperature at return elbow $\approx 80\,^{\circ}\text{C}$.

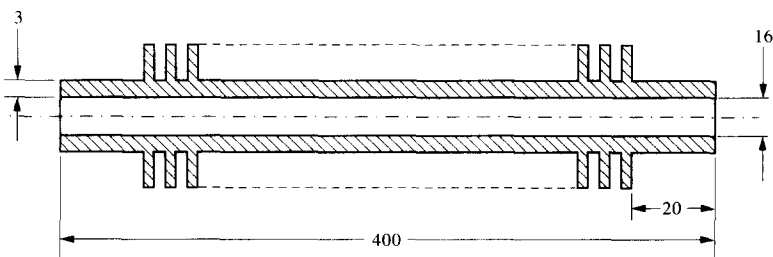Fig. 11. Simplified drawing of the heat exchanger. Not to scale.

Fig. 12. Cross-section through the heat-exchanger tube. Dimensions in mm. Not to scale.

Maximum temperature at flow elbow $\approx 90\,^{\circ}C$.
Maximum temperature drop across tube wall $\approx 10\,^{\circ}C$.
Reynolds number at $80\,^{\circ}C \approx 20,000$ (fully turbulent).

The tubes were made from wrought aluminium–magnesium–silicon alloy 6063. The specified composition is shown in Table 1.

A number of failures were reported where the heat-exchanger tubes had perforated from the inside. The water had been treated with a liquid inhibitor package containing sodium nitrite, sodium borate, sodium silicate, sodium hydroxide, and "organic scale and corrosion inhibitors". When the water contained less than $50\,\text{mg}\,l^{-1}$ of chloride, the recommended dose of sodium nitrite was $1250\,\text{mg}\,l^{-1}$. This was achieved by adding 5 parts by volume of the inhibitor liquid to 1000 parts by volume of water. The organic corrosion inhibitor was presumably added to protect any copper in the system; it could well have been benzotriazole. The neat inhibitor had a pH of 11.5, so the pH of the diluted solution was probably around 9.

7.2. Failure analysis

7.2.1. Corrosion resistance of aluminium. The Pourbaix diagram for aluminium is given in Appendix A. It shows that a protective film of aluminium oxide can form on the surface of the metal as long as the pH of the water is between 4 and 8.5. The diagram does not give any information about the effectiveness of this barrier layer. When aluminium is exposed to oxygen in the atmosphere, it immediately forms a thin invisible film of aluminium oxide [11–13]. The film is bonded firmly to the surface, and is an excellent electrical insulator. Because of this, aluminium (a very reactive metal which would otherwise oxidize very rapidly) is widely used as a corrosion-resistant material. Even when the surface is damaged by mechanical abrasion, the oxide film reforms immediately. Although this repaired film is very thin to begin with, it is still a good barrier to corrosion. On further exposure to the air, the film thickens, typically by 100 times, and the barrier becomes more effective. Because of this film, aluminium does not corrode in water where the pH is in the range 4–8.5.

Outside this pH range, the oxide film is unstable, and the aluminium corrodes: the rate of uniform corrosion increases by roughly 10 times for every unit increase in pH above 8.5 [1]. The film can, however, be stabilized by adding chemicals to the water. At low pH, aluminium is hardly affected by dilute or concentrated nitric acid or dilute sulphuric acid because the oxidizing action of these chemicals provides a strong film-forming tendency [14]. At high pH, the film is stabilized by *silicates* [6, 15, 16]—compounds having the variable composition $n\text{Na}_2\text{O}.m\text{SiO}_2$. These are most effective on aluminium when the *module* of the silicate (the ratio m/n) is high (typically ≈ 3–3.5) [9]. But even sodium disilicate ($\text{Na}_2\text{Si}_2\text{O}_5$; module $= 2$) can stop uniform corrosion at a pH of ≈ 11.5 [12].

7.2.2. Aluminium alloy 6063. 6063 alloy is one of a series of wrought aluminium alloys containing silicon and magnesium. They have good corrosion resistance, especially in alkaline solutions [11]. Alloying elements, mainly iron and copper, can lead to local weaknesses in the oxide film, and can cause pitting [10, 17]. 6063 resists corrosion well because the concentration of the alloying elements (silicon and magnesium) is small, and the harmful elements (iron and copper) are present only as low-level impurities. In contrast, the corrosion resistance of the 2000 series alloys (which contain 2–7% copper as an alloying element) is relatively poor. Minute particles or films of copper can deposit on these alloys as a product of corrosion, and the galvanic cells which are created attack the film [12]. 6063 alloy was therefore a good choice for the heat-exchanger tubes. High-purity aluminium would have been better still, although it might not have had the neccessary mechanical properties.

Table 1. Composition of aluminium alloy 6063

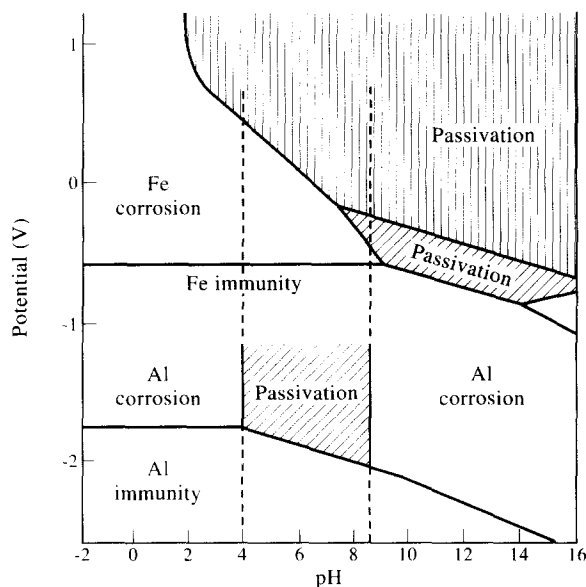| Element	Weight %	Element	Weight %	Element	Weight %
Silicon	0.20–0.6	Magnesium	0.45–0.9	Tin	0.05 maximum
Iron	0.35 maximum	Zinc	0.10 maximum	Lead	0.05 maximum
Copper	0.10 maximum	Chromium	0.10 maximum	Aluminium	Balance
Manganese	0.10 maximum	Titanium	0.10 maximum		

Fig. 13. Superposition of the Pourbaix diagrams for iron and aluminium at 25 °C.

7.2.3. Function of inhibitor package. It is not easy to get the optimum protection of both steel and aluminium in the same system. The situation is summarized in Fig. 13. To protect the steel best, the pH needs to be buffered to at least 9, so that it misses the corrosion field on the Pourbaix diagram. However, this is above the pH at which the oxide film on aluminium breaks down. The approach which was adopted here was presumably to protect the steel in the usual way with sodium nitrite and an alkaline solution, but to add sodium silicate to stop the film of aluminium oxide breaking down. An alkaline pH is also compatible with any copper in the system: the Pourbaix diagram for copper (see Appendix A) shows that a protective oxide film can form in the pH range 7–12.5. The protection of the copper can be completed by adding benzotriazole.

The Pourbaix diagrams show that iron is a more reactive metal than copper. Because of this, copper ions can be reduced to copper metal by a steel surface [see Eqn (1)]. Aluminium is more reactive than both copper and iron. When water containing dissolved copper flows over an aluminium surface, there is a tendency for copper metal to precipitate out [12, 15]. If the water contains dissolved iron, there is a tendency for metallic iron to precipitate out as well [12]. It has already been seen that metallic copper and iron are likely to damage the aluminium oxide film. It is therefore necessary to keep the concentration of copper and iron in the water as low as possible when there is aluminium about. This is another (and very important) function of the inhibitors.

7.2.4. Conclusions. The most straightforward explanation of the failures is an inadequate concentration of inhibitor. The situation is made critical by the special environment of the heat-exchanger tubes. As was seen earlier, the bore of the tube is subjected to conditions of high heat flux and temperature ($230\,kW\,m^{-2}$ and $90\,°C$). For comparison, conditions at the surface of the heating element in an electric kettle are $\approx 130\,kW\,m^{-2}$ and $100\,°C$. The chemical environment at the aluminium surface (pH, concentration of ionic species) may be significantly different from that in the bulk of the water. The oxide film can also be worn away by suspended particles of corrosion product circulating with the water. When the rate of mechanical damage becomes greater than the rate of chemical healing, rapid corrosion will result.

8. CASE STUDY 3—EXTERNAL CORROSION OF STEEL WATER PIPES

8.1. *Background*

In the final case study, we look at a central heating system which failed from corrosion on the *outside*. The system was installed in 1970 in a large new student residence. The building was made from columns and slabs of reinforced concrete. The water pipes were made from mild steel, and
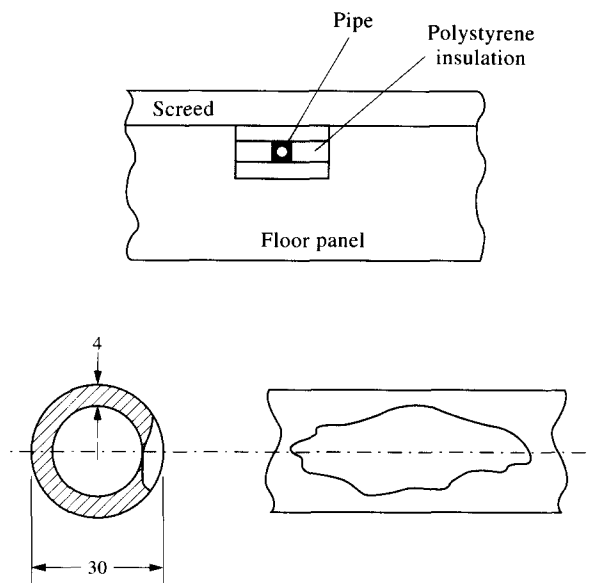
Fig. 14. The corroded steel pipe. Dimensions in mm.

were laid in the concrete during the construction. By 1985, the pipes had started to leak. A typical failure is shown in Fig. 14. The pipe had an outside diameter of ≈ 30 mm, and a wall thickness of ≈ 4 mm. It had been cast into the floor panel of one of the student rooms, and was insulated with slabs of expanded polystyrene. When the floor was dug up, it was found that the pipe had rusted from the outside. The wall of the pipe had perforated, and the water inside the heating system had started to leak out. The corrosion deposits were reddish-brown in colour.

8.2. Failure analysis

The roof of the building consisted of a series of horizontal pre-cast concrete slabs. These had started to take in rain-water at the joints. The structure of the building was complex, and the rain-water travelled large distances before leaking into the rooms or the public areas. It was concluded that the most likely explanation for the corrosion was that the pipes had come into contact with the leaking rain-water. The horizontal runs of piping on each floor were connected by vertical runs laid in open ducts, and it was thought that these could have channelled the rain-water from one floor to another.

Since air was able to get to the surface of the pipe, the cathodic oxygen-reduction reaction would have taken place easily. In addition, the incoming rain-water would have been saturated with oxygen. The corrosion product was presumably red rust (hydrated Fe_2O_3). The Pourbaix diagram for iron (see Appendix A) shows that this oxide is produced when the oxygen content is high. Rain-water is also saturated with carbon dioxide: it contains ≈ 1300 mg l^{-1} of the gas [3]. The carbon dioxide converts to carbonic acid, and the pH falls to ≈ 4.5 as a result [2]. As can be seen from the Pourbaix diagram, rain-water is aggressive to mild steel: iron cannot start to produce an oxide film at a pH of 4.5 unless the potential is taken up to $+0.4$ V. A strong oxidizing agent would be needed to get the potential this high.

Mild steel typically corrodes at the rate of 0.05–0.15 mm/year in slowly moving soft water saturated with air at 15 °C [16]. However, the pipes were not always at 15 °C: when the heating system was operating they were closer to 70 °C. Figure 6 shows that the corrosion rate should go up by ≈ 2.7 times over this temperature interval. The heating system was generally used only for 6 months out of each year; on average the corrosion rate was probably ≈ 1.8 times greater than it would have been at 20 °C. This would give a corrosion rate of ≈ 0.09-0.27 mm/year. If it is assumed that rain-water had been leaking into the building for ≈ 7 years, the depth of attack would be ≈ 0.6–1.9 mm. If the steel develops pitting corrosion, the rate of attack in the pit can be up to 10 times the rate of general corrosion [16]. In this case, the pits would easily be capable of perforating the wall

of the pipe after 7 years. Localized attack of this sort would have been encouraged by the wet crevices which probably formed between the polystyrene and the outside of the pipe.

9. DESIGN IMPLICATIONS

Many central heating installations function perfectly well without corrosion inhibitors. But what must be done to avoid corrosion when inhibitors are not used? The first requirement is to make sure that a uniform, stable film of oxide forms on the metal to act as a barrier to corrosion. The pH of the water must be in the range where a passive layer is thermodynamically possible. pH ranges can be estimated from the Pourbaix diagrams (see Appendix A): they are 7–12.5 and 9–14 for copper and iron, respectively. Hard water ($pH \approx 8$) is less aggressive to copper and steel than soft water ($pH \approx 6.5$). The initial condition of the system has an important influence on the state of the protective films. It is bad to test a system with water and then leave it drained down. Corrosion will occur in the aerated pool of water at the bottom of each radiator, and the film may be penetrated by corrosion pits. It is best to put the system into working order straight away, and to keep it filled with water. Because chloride and sulphate ions attack the oxide films, the water should be as free from them as possible. Copper pipes are sometimes attacked by residues of soldering flux or graphite, and these, too, should be avoided.

Once a stable film has formed, the rate of corrosion depends on the cathodic reaction. The oxygen-reduction reaction can be prevented by keeping the oxygen content of the water as low as possible. Pumps should be placed so they do not pump water through an open expansion tank or draw air into the system. The water in an open expansion tank should be kept cold to minimize evaporation. It is preferable to use a sealed air cushion expansion tank instead of an open expansion tank. Obviously, the system should not be drained if this can be avoided. The hydrogen-reduction reaction can be minimized by keeping the pH high, and the temperature low.

Because many systems depart from these ideals, it is common to add inhibitors. But these must be used and specified correctly. They are generally recommended for systems which contain aluminium because its oxide film breaks down under mildly alkaline conditions. To get the best results, the internal surfaces should first be cleaned by circulating a chemical descaling agent through the system. The system is then rinsed, and the inhibitor is added immediately afterwards. The inhibitor will react strongly with the bright metal surfaces, and will penetrate well into the crevices formed at the welds.

Inhibitors are often supplied as a multicomponent "package". Sodium nitrite can attack the lead–tin solder in soldered joints; nitrite-based inhibitors often contain sodium *nitrate* to prevent this. Sodium benzoate is often added because it resists pitting better than sodium nitrite. When the water contains more than one inhibitor, the overall effect is usually better than the sum of the effects of the individual inhibitors (there is usually a *synergistic* effect). The pH of the water is controlled by adding a buffer such as sodium borate. Many packages contain specific copper inhibitors such as benzotriazole; this is especially important when the system contains aluminium. In hard-water areas, a scale inhibitor is also added to stop hardness deposits building up in the boiler. Finally, a biocide is needed to stop bacterial corrosion. The design of inhibitors is a complex business which draws on long experience of laboratory tests and field performance.

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APPENDIX A: POURBAIX DIAGRAMS

Pourbaix diagrams for the metals commonly used in central heating systems are shown in Figs A1–A4 [1]. The vertical axis of the diagram is the electrochemical potential of the metal in volts measured relative to the standard hydrogen electrode. The horizontal axis is the pH of the water-based solution in which the metal is immersed. The diagram is divided into a number of fields as follows. A field of *immunity* shows the range of potential and pH where corrosion of the metal is thermodynamically impossible. A field of *corrosion* shows the range of conditions where there is a thermodynamic driving force trying to make the metal dissolve as ions in the solution. A field of *passivation* shows where there is a thermodynamic driving force trying to make a stable film (such as an oxide or hydroxide) form on the surface of the metal. It is important to note that the film may or may not be an effective barrier to corrosion. If it is, then the passivation field is also a field of no corrosion. If it is not, the passivation field will be a field in which corrosion takes place.

The edges of the corrosion fields are defined by a concentration of metal ion in solution of $10^{-6} \, \mathrm{mol \, l^{-1}}$. This is an arbitrary value which is taken to represent such a low tendency of the solid to dissolve that the rate of attack is essentially zero.

It should be noted that diagrams for alloys will be different from those of the parent metals mainly because of the effect of the alloying elements on the nature of the surface film. The stability of the film will also be affected by the presence in the solution of ions which have a chemical interaction with the film.

Fig. A1.

Fig. A2.

Fig. A3.

Fig. A4.
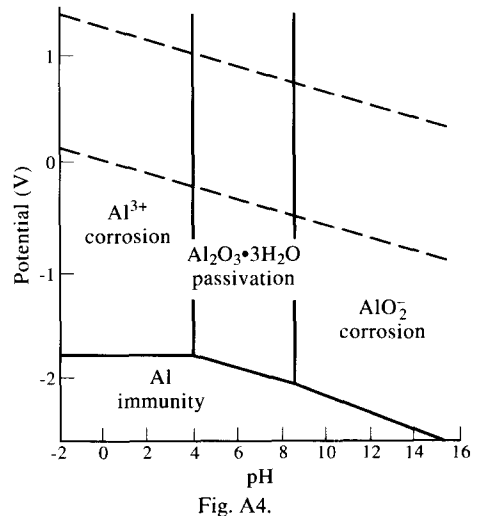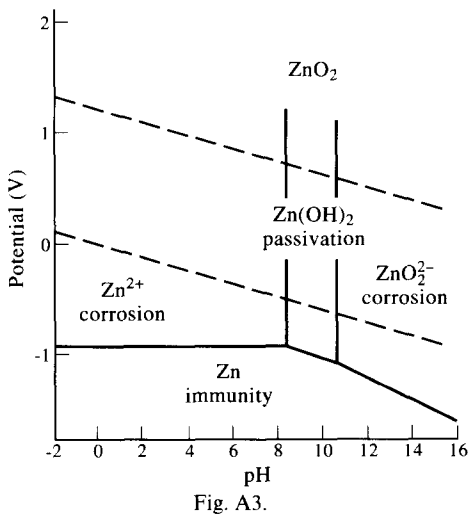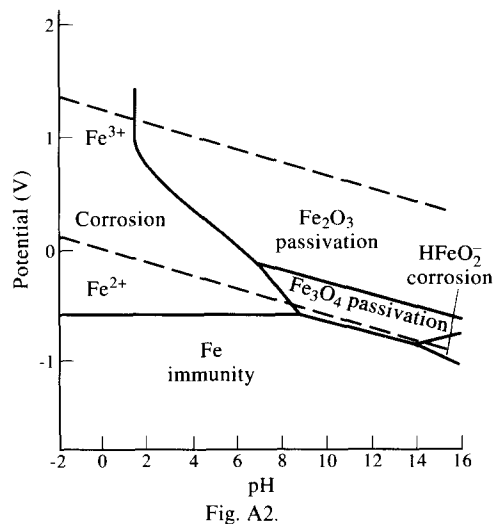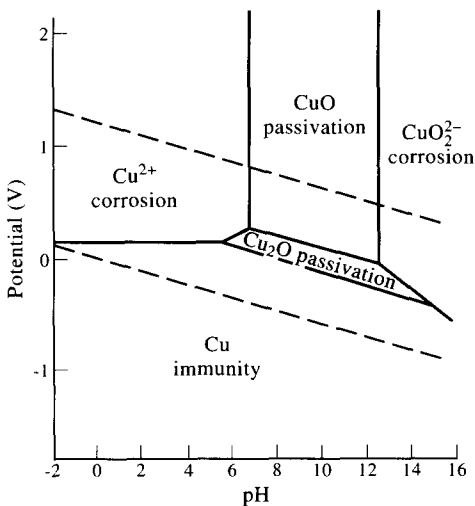
The diagrams give no indication of the rates of corrosion: these can only be found by doing suitable experiments. The diagrams show: (a) where corrosion cannot occur, and (b) where a surface film should form which might prevent or slow down corrosion.

Corrosion cannot occur in practice unless an electron-accepting (cathodic) reaction also takes place. The two most important cathodic reactions (which involve hydrogen and oxygen, respectively) are marked on the diagrams as dashed lines. They are detailed in Fig. A5 [1].
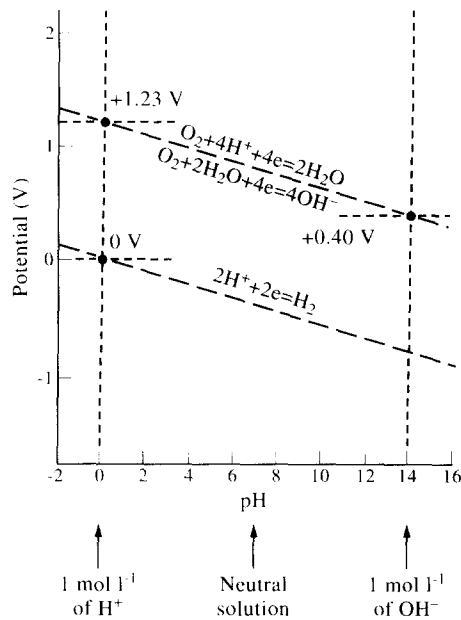

Fig. A5.