





National Corrosion Service

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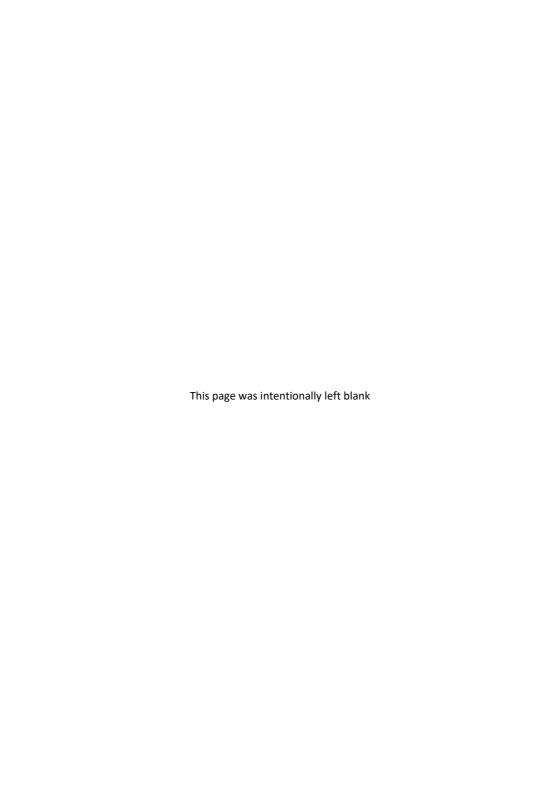
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1. Introduction

This guide has been written with the aim of advising designers and installers of copper domestic hot and cold water systems on how to avoid or minimise the risk of corrosion in these systems. It can also help in taking remedial steps to overcome any problems that may occur.

The term 'domestic water systems' means once-through systems, in particular drinking water systems, where the water in the pipes is regularly renewed. This is in contrast to recirculating heating systems, where the water is not renewed under normal circumstances. The main difference between the two in relation to corrosion is that in domestic water systems, the water is generally highly aerated whereas in closed heating systems, the dissolved oxygen level in the water is generally very low. Since the rate of corrosion is highly dependent on the dissolved oxygen level, the corrosion damage on copper that may occur in domestic water systems is much less likely in closed heating systems.

Copper has been used in plumbing for over 200 years. In the vast majority of cases, it gives a long trouble-free life. When problems of corrosion occur, this is usually down to a combination of adverse circumstances related to materials, design, installation and water quality. Problems in copper pipes manifest themselves in leakages or pinholes, due to various forms of pitting or erosion corrosion, or in so-called blue water. Although pin-holing in copper pipes is often attributed by the lay person to a faulty piece of copper pipe, defects in manufacture are very rare these days and nearly always the fault lies elsewhere. It is not the intention of this guide to go into detail on the mechanisms of the different types of corrosion of copper and copper alloys. However, there are many good reference sources for this information, some of which are given at the end of this guide.

2. Basics of Corrosion of Copper

Copper is a fairly noble metal and corrosion is relatively insignificant in water in the total absence of dissolved oxygen. In water containing dissolved oxygen, fresh copper pipe will slowly corrode liberating copper ions (Cu+ and Cu2+) into the water. However, the rate of corrosion and the release of copper ions slow rapidly in the first few weeks of operation as protective films form on the bore of the copper pipes. This limits the amount of copper that dissolves in the water to much less than the 2 mg/L limit specified in the Water Supply (Water Quality) Regulations.

The surface films (often referred to as a patina) are composed of thin brown or black coloured copper oxide (CuO or Cu2O) overlaid with a thicker green or turquoise basic copper carbonate layer. These layers, although protective, are not true passive layers (like those which form on stainless steels or aluminium and which are much thinner and invisible to the naked eye). It is

when these films on copper do not form properly in the first place or become disrupted later that problems of pitting or blue water can occur.

3. General Corrosion

This is when the whole surface of the pipe or fitting corrodes at an approximately even rate. General corrosion of copper only occurs in so-called cuprosolvent waters of low pH, when the Cu2+ ion is retained in solution rather than being precipitated as a protective layer. This should never happen in mains supply water in the UK but may happen in some private borehole waters or soft upland surface waters of pH < 6.5.

4. Pitting Corrosion

Pitting corrosion is a form of localised corrosion, which manifests itself in pin-holing of the pipe in anything from a few months to over 10 years after installation. There are several different forms of pitting corrosion with different mechanisms and influencing factors. Some of these (e.g. Types 2 and 3) are rarely, if ever, seen in the UK.

Type 1 This type of pitting has traditionally only been seen in cold water pipes with a hard borehole water supply and where a carbon film residue from the pipe extrusion process has been left on the bore of the pipe. Even then, only certain borehole waters with a pH in the range of 7-8.2 and with an unfavourable composition of inorganic constituents are prone to this form of pitting.

Since the introduction of BS EN 1057 in 1996, which laid down strict limits on the amount of carbon residues left behind after manufacturing, the problem largely went away in the UK. However, more recently similar forms of pitting have been found in copper pipes in hard water areas in the UK, which contain little or no carbon film residues. The water composition, although hard borehole water, would not normally be considered as being a 'pitting water'. Analysis of the water and deposits on the bore have shown high levels of phosphate, which seems to play a role in causing pitting.

Type 1 pits appear as hemispherical pits overlaid with a mound of blue-green malachite or basic copper carbonate (Cu2(OH)2CO3). They are usually distributed randomly along a length of pipe, although the deeper pits are nearly always found close to the bottom of horizontal pipe runs. A typical example is shown in Figure 1.



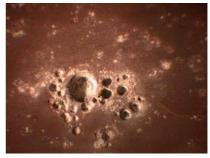
Figure 1. Type 1 Pitting.

Although it is not usually practical to change the water composition, the risk of Type 1 pitting occurring can be substantially reduced by always using pipes certified to BS EN 1057 and by avoiding long periods of stagnation between installation and bringing the system into operation. If there is a long period between filling the system and eventual hand-over, then the system should be flushed regularly (at least once a week) in order to introduce fresh aerated water into the system and build-up a stable protective film.

Microbially Influenced Pitting This type of pitting is mainly caused, as the name suggests, by the action of microbes in the water and within deposits on the bore of copper pipes. It is sometimes called MIC for microbially influenced corrosion. In particular, sulphate reducing bacteria (SRB) by their metabolism reduce sulphates in the water to sulphuric acid and hydrogen sulphide. SRB do not multiply in the bulk water but require anaerobic conditions under deposits. Other bacteria, such as pseudomonas, can form slimes or bio-films under which SRB can multiply. The aggressive localised environment produced by SRB results in a high density of tiny pits (often termed 'pepper-pot corrosion'), which can coalesce to form larger pits and eventual pinhole leaks. A good example of this pepper-pot corrosion on a copper surface after removal of the deposit is given in Figure 2. MIC usually occurs slowly, often taking several years before pin-holing results.

Although chlorinated water supplies should contain very low levels of micro-organisms, these can multiply in domestic water pipes, especially under stagnant conditions and where temperatures are between 22 $^{\circ}$ C and 45 $^{\circ}$ C. Such conditions are sometimes found in hospitals and health centres, which have been prone to this form of corrosion in domestic copper pipework systems.





(a) Before cleaning

(b) After cleaning

Figure 2. Microbially Influenced Pitting.

This form of corrosion can be avoided by taking a number of steps to remove any deposits from the system (by flushing to BS EN 806-4)¹, chlorination to HSE L8 and controlling temperatures during operation. Long periods of stagnation should be avoided by regular flushing of unused pipe runs. In addition, hot water pipes should be well-lagged, especially if they run close to cold water pipes.

Underdeposit Corrosion Like most metals, copper is susceptible to corrosion under deposits due to a process known as differential aeration. Debris and particulate matter brought into the system, either through construction or with unfiltered raw water can settle out in pipework under low flow conditions. The attack, which takes place under the deposit usually at the bottom of horizontal tubes is quite slow but perforation can eventually occur. This was a problem in Scottish hospitals in the early 1980's. Deposits in the system can also be breeding grounds for anaerobic bacteria, especially SRB. The best way to avoid this type of corrosion is to flush systems according to BS EN 806-4 and to size pipework so that flow rates are at least 0.5 m/s.

Flux Induced Pitting Copper joints are often made using soft solder, which requires the use of a soldering flux. Soldering fluxes work by removing the copper oxide from the copper surface to produce an active surface for the solder to adhere to. They often contain ammonium or zinc chlorides, which by their nature are aggressive to copper. If an excess of flux is used, then a flux run downstream of a joint is produced where corrosion can occur. In extreme cases, pinholing of the copper pipe will result, usually within a few months of installation. Analysis of the deposits surrounding such pits invariably shows high levels of chloride. Figure 3 shows a classic example of flux attack resulting in a pinhole leak several cm downstream of the soldered joint.

Flux attack is the result of poor installation practice and can easily be avoided by not using excessive amounts of flux at each joint and by using water dispersible fluxes where possible. Flushing of the system to BS EN 806-4 after installation is recommended to remove deposits and excess flux from the system.

¹BS EN 806-4 has partially superseded BS 6700



Figure 3. Pinhole caused by flux attack. 5

Type 2 This type of pitting is rare in the UK but has been reported more in Scandinavia. It occurs in hot soft water at temperatures greater than 60 °C and where the bicarbonate:sulphate ratio is < 1. It is associated with upland catchment water sources that often contain manganese.

Type 2 pits are deep with a small mouth and more irregular in shape than is the case for Type 1 pits. They are usually capped by small black or greenish black mounds of copper (I) oxide and basic copper sulphate. The rate of Type 2 pitting is much slower than that for Type I so that perforation is rare in less than 8 years.

5. Erosion Corrosion

Erosion corrosion is very rarely found in the average size house but is more likely in large buildings with recirculating hot water systems, such as those found in hotels, commercial buildings and large country houses.

Erosion corrosion occurs due to turbulent flow in copper pipes, which releases air bubbles from the water and which remove the protective patina from the copper surface. Corrosion, which then occurs in these localised regions, takes the form of grooves or horseshoes in the surface (with the 'horse' appearing to have walked upstream). In severe cases, wall perforation can develop within a matter of weeks. A typical example is shown in Figure 4.

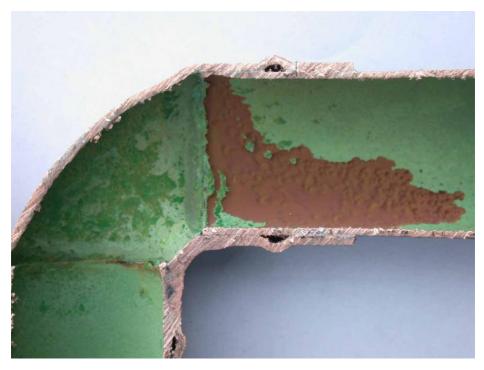


Figure 4. Erosion corrosion at elbow.

Erosion corrosion is most often found just downstream of elbows or changes in pipe section, where turbulent flow is more likely. Hot water return lines are prone to this form of corrosion. However, there is a critical flow velocity below which erosion corrosion should not occur. This is often quoted as below 3 m/s for cold water pipes and 2 m/s for hot water pipes. However, in soft water or base-exchange softened water, erosion corrosion is possible at flow velocities below these values. Other factors, such as burrs left on cut ends of copper pipes and sharp changes in sections increase the likelihood of erosion corrosion. To prevent the risk of erosion corrosion, flow rates of < 2 m/s for cold water and < 1.2 m/s for hot water systems should be met. However, in fully softened waters, flow rates should not exceed 1 m/s. Where flows are intermittent, these maximum flow velocities can be relaxed somewhat.

6. Blue Water

Blue water can occur either due to a high concentration of Cu^{2+} ions in the water or, more commonly, through the discharge of particles of copper carbonate patina, which have spalled off the bore of copper pipes. In the first case, this is induced in cuprosolvent water. In the second, it occurs due to a combination of adverse water quality and water stagnation,

particularly in the early stages after installation. In either case, it can lead to copper levels in the water exceeding the 2 mg/L limit under drinking water regulations and staining of wash hand basins and baths. Figure 5 shows an example of an irregular bluish patina that has formed on a length of copper pipe and staining of a wash hand basin.





Figure 5. (a) Irregular carbonate patina giving rise to blue water; (b) Staining in hand basin caused by blue water.

Waters that promote blue water are naturally soft with low bicarbonate hardness and relatively high sulphate levels. In the UK, blue water has hardly, if ever, been found in the South East, where hard borehole water predominates. The causes of blue water are not fully understood and several influencing factors have been suggested, including microbial activity, excessive water softening, phosphates in the water and excessive use of soldering fluxes. However, there is little supporting evidence (e.g. chemical analysis) that fluxes play a role here. Microbial activity may encourage the formation of bio-films and irregular patinas leading to blue water but patinas giving rise to blue water often show no signs of microbial activity.

In the last few years, there have been several cases of blue water in the north of England, where high levels of phosphate have been found in the copper carbonate patina. The patina itself was irregular and only loosely adherent, so that it was often removed from the top half of the bore. The phosphate derives from the supply water, which has been added by water companies in order to inhibit the corrosion of old lead pipes.

As with pitting corrosion, the likelihood of blue water can be significantly reduced by avoiding water stagnation in the pipes in the period between installation and when the system is brought into use. Chlorination to kill any microbial activity may help as could the fitting of a dolomitic limestone filter on the incoming mains in cases of very soft water. In the few cases where blue water has occurred due to excessive softening, blending the water to give a total hardness of around 60 mg/L seems to be effective. However, if a substantial irregular patina has been formed then this must be removed by a citric acid flush in order to get back to bare copper. A uniform, stable patina can then only be reformed if regular flushing with fresh water is carried out in the weeks following the citric acid flush. Even then, this treatment may not be effective in the long term, so that complete replacement of pipework may be necessary.

7. Corrosion of Brass Fittings

7.1 Dezincification

Brasses are alloys of copper and zinc and dezincification is the term given to the selective removal of zinc from brass. When this happens, a white zinc hydroxide corrosion product is formed on the surface leaving behind a porous copper mass of the same shape as the original fitting. This reduces the mechanical strength and can lead to blockage or even leakage of the fitting. There are two types of dezincification; layer (or meringue) type and plug type, which occurs in localised regions. Figure 6 shows an example of plug type dezincification of a fitting.

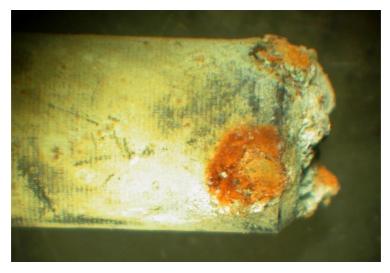


Figure 6. Dezincification of a temperature probe.



Figure 7. Stress corrosion cracking in a brass fitting.

The likelihood of dezincification depends on the alloy composition and microstructure. Alphabeta brasses may be susceptible to dezincification if zinc levels are high enough to give a continuous beta phase. However, nowadays DZR brasses (dezincification resistant brasses) are commonly used in fittings. These have been heat treated to produce a single alpha phase brass. However, brazing at high temperatures can sometimes revert the microstructure back to a two phase alloy, susceptible to dezincification. Fittings made of gunmetal (tin-zinc bronzes) are also immune to dezincification. DZR fittings should be marked with the symbol CR or DRA and should be tested in accordance with ISO 6509.

Dezincification is more likely in soft waters with high chloride and with pH > 8, although some hard waters can be very aggressive. Base exchange softening of the water, however, does not increase the likelihood of dezincification. Dezincification is also more common in hot waters and after long periods of water stagnation.

7.2 Stress-Corrosion Cracking

Stress corrosion cracking (SCC) can occur with certain alloys exposed to specific environments and under tensile stresses. The stresses may arise during manufacture (residual) or applied during service. Brasses are susceptible to SCC in the presence of ammonia. Since the concentrations of ammonia are normally very low in drinking water, SCC from the water-side is not found in drinking water installations.

However, SCC of brass fittings in drinking water installations has been found to occur under thermal lagging. For this to happen, water or condensation needs to penetrate under phenolic foam type insulation to the brass surface. In the cases where this has been found, the fitting had been over-tightened so that there was a high applied tensile stress on one component of the fitting. Figure 7 shows an example of SCC in a brass fitting.

8. Summary

CORROSION DAMAGE	CAUSE	AVOIDANCE AND POSSIBLE SOLUTIONS
Type 1 Pitting	Carbon films in tube bore resulting	Use tubes to BS EN 1057, which
	from extrusion greases act as	have been properly cleaned.
	effective cathodic surface. Occurs	European manufacturers give a
	only in cold water pipes with hard,	25 year guarantee against carbon
	organically pure (borehole) water.	film pitting.
	Stagnation in pipes, especially in first	Flushing to BS EN 806-4 and
	few weeks after installation. Failure	avoiding water stagnation in
	can occur within a few months.	early stages after installation
Microbially	Microbial activity, e.g.	Regular flushing of little used
Influenced	pseudomonads and/or sulphate	tube runs. Filtration of supply
Pitting	reducing bacteria in pipework	water. Avoid stagnant flow. Lag
	promoted by stagnant water, source	hot water pipes (to avoid 20 °C to
	of nutrients and warm water	60 °C range). Chlorinate in larger
	conditions (25 °C to 55 °C).	system such as hotels and
	Acid and H ₂ S is formed due to	hospitals.
	metabolism of microbes, which	
	causes pitting of copper (pepper-pot	
	corrosion). Time to perforate usually	
	greater than seven years.	
Under Deposit	Debris, e.g. construction material,	Avoid flow rates less than 0.5
Corrosion	particles brought in with unfiltered	m/s, which allows debris to
(differential	supply water, settling within	settle. Flush out systems
aeration)	pipework.	according to BS EN 806-4.
	Differential aeration effect causes	If supply water could contain
	copper under deposit to become	particulate matter, particularly
	anodic and corrode. Location usually	from upland source, fit filter to
	at 6 o'clock position in horizontal	incoming mains.
	tubes. Time to perforation usually	
	greater than seven years.	
Flux Induced	Soft soldering fluxes from joining are	Use minimum amount of water
Pitting	aggressive to copper (free HCI).	dispersible fluxes. Flush
	Failure, if it occurs, usually takes	thoroughly after soldering
	place in the first few months.	according to BS EN 806-4.

Hot Soft	Occurs only in soft hot water (greater	Rare in UK, if it occurs. Either
Water Pitting	,	change water composition by
J	than 60 °C) with a low bicarbonate:	fitting dolomitic limestone filter
(Type 2)	sulphate ratio. Manganese in water	
	increases likelihood. Much slower	or reduce water temperature to
	than Type 1 pitting and may take	below 60 °C.
	many years to perforate.	
Erosion	A mechano-chemical effect due to	Restrict flow rate through good
Corrosion	high water velocity – turbulent flow	design and installation practices.
	leading to formation of air bubbles in	0.5 m/s – 1.2 m/s for hot water
	water which leads to removal of	(< 1 m/s in fully softened water)
	protective patina. Corrosion then	0.5 m/s – 2.0 m/s for cold water
	occurs at exposed copper surface.	Remove burrs from cut ends and
		solder beads, which increase
		turbulence. Filter out solids, such
		as sand and silt. Avoid sharp
		bends and large changes in cross-
		section.
Blue Water	Adverse water quality and water	Avoid stagnation in pipes,
	stagnation in early stages. Naturally	especially in early stages.
	soft waters with low carbonate	Increase hardness of water by
	hardness and high sulphate and with	fitting dolomitic limestone filter
	high phosphate level in water.	to incoming mains. Shock dose
	Microbial activity may occasionally	with chlorine to kill micro-
	be involved.	organisms and remove any bio-
	Usually occurs due to formation of	films.
	irregular, non-adherent patina on	In severe cases, remove irregular
	bore of copper pipe, although	patina by citric acid flushing.
	cuprosolvent waters can also cause	Slowly build-up uniform stable
	blue water due to soluble ions in	patina on bore of pipework by
	water.	regular flushing with water over
		several weeks.
Dezincification	Specific water conditions and a	Use DZR fittings marked with CR
of brass	susceptible alloy composition and	or DRA. Do not heat fittings to
	microstructure.	high temperatures for long
		periods during brazing.
Stress	Presence of moisture and ammonia	If using phenolic foam insulation,
Corrosion	and high applied tensile stresses on	prevent condensation on pipe by
Cracking of	fitting.	taping over joints in insulation
brass		-
	<u> </u>	<u>l</u>

	with Al foil. Do not over-tighten
	fittings.

9. References

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- BS 6700:1997; Specification for design, installation, testing and maintenance of services supplying water for domestic use within buildings and their cartilages (partially superseded by BS EN 806)
- BS EN 806; Specification for installations inside buildings conveying water for human consumption; Part 4 Installation
- BS EN 1057: Copper and copper alloys. Seamless, round copper tubes for water and gas in sanitary and heating applications

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