

CAUSES OF COPPER CORROSION IN PLUMBING SYSTEMS

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A Review of Current Knowledge

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Review of Current Knowledge

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Causes of Copper Corrosion in Plumbing Systems

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Causes of Copper Corrosion in Plumbing Systems

Author: R. J Oliphant

Foreword

It is a well-attested phenomenon of medical students that, having read a textbook on human diseases, they become convinced they have at least half the conditions described and that being alive is a very hazardous undertaking. Similarly, a book on the problems that have been experienced with copper in plumbing systems may convince the reader that it is a very hazardous material that should be avoided as far as possible. As with the medical student and his text book, a sense of proportion is required and the reader should appreciate that the conditions described in this booklet are rare when compared with the total length of copper that has successfully been used in plumbing systems world-wide. Furthermore, a significant number of the problems that do occur arise from the actions of the end-user and can be avoided by the application of current knowledge. This last fact is the reason this review has been prepared.

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General Introduction

This review is intended for anyone with an interest in the design or the installation of water supply systems using copper pipes or hot water cylinders. It is relevant to plumbers, water industry staff, architects and property owners.

It covers both hot and cold water supplies inside buildings, but **not central heating systems**.

The review describes:

- Problems that can occur **inside** the pipework and fittings of water supply systems made of copper and copper alloys (such as brass);
- How to identify the cause of problems when they do arise; and
- How problems might be avoided.

In contact with oxygenated drinking-waters copper develops a semi-protective corrosion product layer. This usually ensures an economic life for the pipework and limits the concentration of copper in the water to values well below the maximum of 2 milligrams per litre (mg/l) allowed under the UK Drinking Water Regulations (Reference 1). These same regulations control the general composition of UK public water supplies. In such waters copper pipe is normally resistant to corrosion. However, problems can occur if a non-protective layer is formed through prolonged stagnation during a system's early life and in the presence of certain water characteristics.

The localised breakdown of the protective films that form on copper may lead to **pitting corrosion**. The earliest known and most common forms of this mode of attack are carbon film cold water pitting (also known as Type I), hot, soft water pitting (also known as Type II) and erosion corrosion. All these forms are reasonably well understood and effective ways of avoiding them have been identified. The more recently identified Rosette corrosion, which affects copper

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hot water cylinders with an aluminium protector rod, is now understood and can be completely avoided by using an improved design of cylinder where the heating coil is positioned closer to the base (Reference 23).

Microbiologically induced pitting is a more intractable problem because of its intrinsically complex nature and the practical difficulty of treating a system once it has become infected. Current understanding only allows the identification of risk factors and remedies that have been useful in some instances.

In some circumstances copper surfaces may suffer general corrosion because the water is cuprosolvent or because the local conditions and water composition create a 'blue water' problem. **Cuprosolvency** is fairly well understood and in UK waters is usually readily solved by raising the pH of the supply. The understanding of **blue water problems** has only progressed to the identification of risk factors and to a list of remedies that have been found to be effective in some cases.

The historical problem with copper alloy fittings, the **dezincification of brass**, is now well characterised and alloys that are resistant or immune to this form of attack have been developed. The future problem with these alloys may be the leaching of lead that may become significant as the permitted concentration of lead in drinking-water is reduced over the next decade (Reference 17).

The problems of **lead contamination from leaded solders** should have already been confined to history because leaded solders have been banned in the UK for use with drinking-waters for more than 15 years. Current regulations ban the use of lead based solders for domestic hot and cold water systems and other installations where the water is required to be wholesome (see later section entitled 'Problems with solders').

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History of copper products in water supply applications

Copper pipes have been used for domestic water services for nearly 200 years. Before that, water supply pipework was most commonly made from lead. The introduction of copper pipes offered a stronger, lighter and cheaper alternative. The first pipes, used in 1810 (Reference 2) were made from sheet metal. Since then, there have been a number of developments in the manufacture and joining of copper pipes.

1850 onwards	Thick (known as heavy gauged) pipes made from sheet metal and joined by screw threads were being used in hospitals and similar institutions.
1894	The introduction of the process of extrusion of copper allowed thinner pipes to be made.
1910	Thinner (known as lighter gauge) pipes first used – joined by fine screw thread or push-fit joint (incorporating a rubber ring).
1921	The Liverpool Corporation started to use light gauge pipes for both internal and external water supply.
1936	The first British Standard for copper pipes was published. Capillary (soldered) joints and compression fittings for joining pipe introduced (see below).
1939	British Standard revised to include capillary (soldered) and compression fittings.
1996	European Standard BS EN 1057: Copper and copper alloys. Seamless, round copper tubes for water and gas in sanitary and heating applications.

Copper pipes are now used in most domestic and commercial plumbing systems.

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Capillary (soldered) fittings are formed from copper tube or copper alloy by pressing or stamping. Copper pipe is inserted into the fitting and the assembled joint is heated to allow solder (which is either end-fed into the joint using solder wire or included in the fitting during manufacture) to run into the narrow space between the pipe and the fitting.

Compression fittings are stamped or sand-cast from copper alloys. Once the pipe is inserted into the body of the fitting, a nut is tightened onto the body thereby compressing a metal sealing ring (called an olive) that grips onto the outside wall of the pipe.

A **copper alloy** is the combination of copper with one or more other metals to form a material that can improve upon the performance of pure copper. The most commonly encountered copper alloys are brasses and gunmetals.

- Brasses are alloys made primarily from copper and zinc. Brasses can be used for producing sand-cast fittings and for hot stamped or forged fittings.
- Gunmetals are alloys of copper, tin and zinc, which may also contain lead. They can only be used for manufacturing cast items. Products made from gunmetal exhibit very few problems in drinking-water but tend to be more expensive than those made of stamped brass due to the number of rejects during production.

An introduction to copper corrosion processes

Copper's resistance to corrosion relies upon a small amount of corrosion occurring at the pipe surface to form a protective (semi-passive) layer that stifles further corrosion. Whether a significant amount of corrosion occurs, and the type of corrosion product that is formed, will depend upon the conditions to which the pipe is subjected.

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1. In water with low oxygen content (less than 2 mg/l of oxygen) the metal itself is stable and it will not corrode readily.
2. In acidic water (pH less than about 6) with high oxygen content (greater than 2 mg/l of oxygen), the metal may dissolve to form the copper ion (Cu^{2+} , also called cupric ion), which is the most stable form in these conditions. Such waters are **cuprosolvent** and this condition is discussed later.
3. In around neutral to slightly alkaline water (pH 6 to 8) with high oxygen content the metal may initially produce an insoluble layer of cuprous oxide (Cu_2O). This magenta red to brown corrosion product will be the most stable species in these conditions and will form a semi-protective scale against further corrosion.
4. Similarly in water with high oxygen content, which is strongly alkaline (pH greater than 8), the copper may form a layer of cupric oxide (CuO). This jet-black to brown corrosion product will be the most stable species in these conditions and will form a semi-protective scale against further corrosion.

Of these four sets of conditions, only the second leads to uninhibited corrosion. Where the initial semi-protective scales form (3 & 4 above), corrosion continues, but at a much-reduced rate. A deposit can form on top of the oxide layer which typically consists of basic copper carbonate or malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$). This deposit has a characteristic turquoise green colour. For malachite to be produced, the water needs to contain carbonate combined with a sufficiently high pH. The formation of this copper salt will limit the level of copper dissolved in the water. The composite deposits are also beneficial for the long-term structural performance of the pipe, but can experience localised breakdown leading to different types of **pitting corrosion**, which are described later.

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For the layers to be protective, periods of prolonged static water conditions have to be avoided. It is for this reason that systems that have been initially filled, to establish their hydraulic soundness, but then left standing full of water until the building becomes occupied, often give unsatisfactory long-term performance. Consequently, it is recommended that newly completed copper pipework be drained after testing if it is not to be used within a few days (Reference 19). If this is not feasible, or if existing pipework is temporarily unused, flushing is recommended at least weekly to avoid loss of the protective layer (Reference 19).

Dissolved and particulate copper in drinking-water

Potential problems

Copper is an essential nutritional element. According to the World Health Organization (Reference 3), the human body requires a daily copper intake of 2 to 4 milligrams. The normal sources are food rather than drinking-water. However, although copper is an essential element, at very high concentrations it is potentially toxic and so is limited under the UK Drinking Water Regulations (Reference 1) to a maximum permitted concentration of 2 mg/l.

Consequently, the concentration of copper in the conveyed water is as important as the effect of the water on the mechanical integrity of the pipework. High concentrations of copper will occur under conditions where the Cu^{2+} ion (cupric ion) is the stable species (i.e. **cuprosolvent** water) or where an insoluble copper corrosion product forms but does not adhere to the pipe wall, creating a **blue-water** problem. These problems can be avoided and are described below.

Cuprosolvency

A cuprosolvent water is one in which either the Cu^{2+} ion (cupric ion) is the stable species or in which the copper salts that form on the metal's surface are highly

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soluble. The latter situation leads to a thinner and consequently less protective layer; the result is a corrosion rate nearer to that of the bare metal and high copper levels in the water. Cuprosolvent waters are normally borehole supplies (often private) containing an excess of free carbon dioxide, which lowers the pH of the water and increases the solubility of all the copper corrosion species that might form. These are the same conditions that cause a water to be plumbosolvent to lead pipework, leading to the presence of lead in drinking-water. Most plumbosolvent public water supplies have been identified and are now treated to prevent plumbosolvency. Those supplies containing excessive free carbon dioxide are treated to remove this (usually by pH elevation), and as a consequence cuprosolvency is now rarely encountered. However private supplies may not be so treated.

Another cause of high copper concentrations is prolonged stagnation of drinking-water in a plumbing system. In such cases the solution is to reduce stagnation by redesigning the layout of pipework or by replacing with smaller diameter pipes.

Blue-Water problems

In some situations, water that has been conveyed or stored in a copper system may exhibit a characteristic opaque blue colour.

It has been suggested (Reference 4) that cupric hydroxide ($\text{Cu}(\text{OH})_2$) is the initial corrosion product that is formed in all aerated waters. Normally, the cupric hydroxide converts in a relatively short period of time into the more familiar and much less soluble cuprous oxide (the magenta red to brown layer, Cu_2O) and the levels of contamination in the water decrease significantly. Blue-water problems occur in those waters where the conversion of the cupric hydroxide is for some reason delayed. The relatively high solubility of this compound accounts for the high levels of copper found in the water and the

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characteristic blue colour. Unfortunately, the current understanding of this problem does not allow reliable predictions of where it will occur, only the identification of risk factors. These include the following, which are listed with possible scientific explanations.

Low bicarbonate. Low levels (less than 20 mg/l as calcium carbonate) of bicarbonate (HCO_3^- ion) in the transported water will prevent the production of the basic copper carbonate layer, leaving the initial oxide layer less protected. This alone need not lead to blue water problems if the insoluble cuprous oxide could still be formed.

High pH water. In high pH water (greater than pH 9), the highly soluble cupric hydroxide is either the most stable compound and is formed in preference or it converts only slowly to the more usual and less soluble copper oxides. High pH will therefore tend to initiate blue water problems.

Microbiological growths. The presence of microbiological growths inhibits the supply of oxygen to the metal's surface and hence the production of the protective cuprous oxide layer. Low chlorine residuals, temperatures of 25 - 55°C, and high assimilable organic carbon content in the water (i.e. material that bacteria can use as a food source) all encourage microbiological growths.

Sulphate-reducing bacteria or sulphides. These anaerobic bacteria reduce sulphates to hydrogen sulphide (H_2S), the presence of which has been proven to be deleterious to copper even at high pH values.

Stagnation of water early in pipe life. Anaerobic conditions can develop as the dissolved oxygen in the water becomes consumed as part of the corrosion reaction. This stifles the production of the protective cuprous oxide layer. Prolonged stagnation in the early life of the system (e.g. after hydraulic testing and before going into service), dead-ends and long residence times (e.g. factory

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shutdown periods) should be avoided. See Reference 19 where it is recommended that newly completed copper pipework be drained after testing if it is not to be used within a few days, or that the pipework be flushed at least weekly if not drained.

Solving a severe blue-water problem will depend upon which of the above factors are identified as contributing to the problem. In some situations an immediate improvement has been obtained by: -

- heat shock using hot water in excess of 60°C;
- super-chlorination (e.g. 5 mg/l of free chlorine);
- replacing afflicted sections of pipe (not effective in presence of sulphate-reducing bacteria).

Improvements in the long-term may be obtained by: -

- maintaining a chlorine residual (to reduce microbiological growths);
- adding bicarbonates;
- adding polyphosphates (reduces blue water appearance but not copper concentrations);
- lowering the pH to 7.5, although this would not be acceptable where there was a danger of creating plumbosolvency problems;
- redesigning the affected system to ensure minimum water residence times.

However, these solutions are often speculative and best identified by a corrosion specialist. In most cases the associated costs will confine investigational work to problems encountered in large buildings and institutions.

Pitting corrosion of copper pipes, fittings and cylinders

Introduction

Copper pipes, fittings and cylinders can exhibit localised breakdown of the semi-protective scale leading to pitting, which may result in leakage by pinhole

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failures in the pipe wall. For a failure to occur by pitting, certain conditions need to be present which start the breakdown of the semi-protective scale (initiation conditions) and furthermore, specific conditions are needed to continue the process (propagation conditions) in most cases.

Several different types of pitting have been identified which are differentiated by the conditions required for their occurrence (Table 1).

Type of Pitting	Initiation conditions	Propagation conditions
Type I	Presence of a harmful film (usually carbon) in the tube and cold water (less than 40°C)	Unfavourable combination of six inorganic parameters
Type II	Hot, soft water with low pH	Unfavourable bicarbonate/sulphate ratio
Rosette corrosion	Copper hot-water cylinder with aluminium protector rod	Unfavourable ratio of inorganic anions
Microbiologically induced corrosion	Development of a biological film in the pipe	Soft water with high level of assimilable organic carbon
Erosion corrosion	High velocity water	Cuprosolvent water
Flux induced corrosion	Presence of a flux run	

Table 1. The different types of pitting corrosion found in UK waters.

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Each of the types of pitting in the Table above is discussed in more detail below. However, it must be borne in mind that in many situations there may not be absolute and clearly identified distinctions between the different types of copper pitting (Reference 5).

Type I pitting

Type I pitting (or cold water pitting) is confined to those parts of the plumbing system that never exceed 40°C (i.e. in cold water pipes and the bottom of traditional hot water cylinders where the heating elements were positioned high above the base).

Characteristic features. Corrosion deposits are deep green, semi-isolated mounds above pits or pinholes in the pipe wall (see Photographs 1 and 2). Typically the pipe or cylinder fails in a short period of time, usually between three and four years but sometimes within a few months. Two or more factors need to be present for Type I pitting damage to occur.

Initiation of pitting is generally related to the condition of the metal before it is exposed to water. In pipes, initiation usually occurs due to the presence of a carbon film produced in manufacture from the pyrolysis of the drawing oils during the inert gas annealing process (References 6 & 7). The presence of a continuous carbon film, rather than the quantity of carbon present, seems to be the key factor in creating this condition.

Technical notes: For Type I pitting to initiate, the electrochemical potential of copper has to be above a critical value (greater than +100 mV against a standard calomel electrode). Occasionally high electrochemical potentials can be achieved because of high dissolved copper levels in pipes where cuprosolvent water has been static for a prolonged period. However, this is usually more of a problem with copper hot water cylinders; see 'Rosette corrosion' later for further details.

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The propagation of the pit is normally a function of water quality. The water has to have a critical composition that is determined by a combination of six inorganic parameters (dissolved oxygen, sulphate, chloride, nitrate, sodium and pH).

The British Non-ferrous Metals Technology Centre has developed a nomogram (Reference 8), which uses these six factors to calculate the Pitting Propensity Rating (PPR) of a water supply. A positive value for the PPR indicates the water will propagate the attack, a negative value that it is non-pitting.

Type I pitting does not normally occur under the following conditions:

- Water pH less than 7 where more rapid, generalised corrosion will occur;
- In surface-derived supplies which normally contain a natural organic material that inhibits corrosion (Reference 9);
- Water with high chloride content (i.e. greater than 60 mg/l) where more rapid, generalised corrosion will occur.

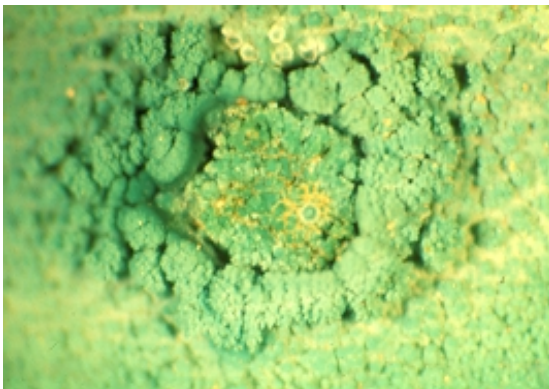
Typical Type I pitting waters are borehole supplies, which are largely free of organic matter and have pH values in the range 7 to 8.2.

What to do about it. It is normal practice for manufacturers to take measures to remove, or prevent the development of, deleterious films. Tubes conforming to the European Standard BS EN 1057 (Reference 22) should not initiate carbon film cold water pitting because this standard specifies a carbon content or carbon film test.

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Photograph 1. Typical distribution of Type I pits in copper pipe



Photograph 2. Detail of a Type I pit with a central mound of malachite above the initiating site surrounded by secondary mounds above daughter pits.

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Type II pitting

The potential for Type II pitting (or hot soft water pitting) in the UK is much less than Type I and consequently Type II has not been studied in such depth. It occurs in hot water systems only (i.e. greater than 60°C) and is associated with very soft waters (usually derived from upland catchments) that often contain manganese. Type II pitting is much slower than Type I, rarely producing a perforation in less than eight years.

Characteristic features. Deep pits of small cross-section containing very hard crystalline cuprous oxide (Cu_2O) capped by small black or greenish-black mounds of cuprous oxide and basic copper sulphate.

The occurrence of Type II pitting appears to be primarily related to water quality, but the mechanism is still in question.

Deposition of manganese. Problems have arisen with waters containing as little as 30 micrograms per litre ($\mu\text{g/l}$) of manganese. Such waters are normally soft, upland supplies that have been treated to raise their pH to above 7.4.

Technical notes. The problem is believed to occur when the soluble manganous ion (Mn^{2+}) oxidises to the insoluble manganic ion (Mn^{4+}) to form manganese dioxide (MnO_2). The latter acts as a powerful cathodic depolariser (it is used as such in dry cell batteries) and thus stimulates the corrosion reaction.

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Ratio of bicarbonate to sulphate. In Scandinavia, where Type II is the most common form of copper pitting, manganese dioxide is not considered an important factor. Work by Mattsson (Reference 10) suggested that the ratio of bicarbonate to sulphate ($\text{HCO}_3^-/\text{SO}_4^{2-}$), was the critical factor. This work is at variance with the advice of British workers.

What to do about it. Advice on prevention has centred on creating conditions that discourage the deposition of manganese dioxide. These include:

- Not running the system at temperatures above 60°C.
- Avoiding oxidising conditions such as over chlorination or entrainment of air in the system.
- Keeping the pH below 7.5, although this would not be acceptable where there was a danger of creating plumbosolvency problems.

Rosette corrosion of cylinders

‘Rosette corrosion’ is a recently recognised phenomenon causing premature failures in copper hot water cylinders containing an aluminium protector rod (see technical notes below).

Characteristic features. Heavy sediments of an aluminium corrosion product that vary from white with a bluish tinge to light green in colour. Underneath these deposits, the copper is a vivid brick red magenta colour (see Photograph 3) consisting of large platelets of cuprous oxide separated by deep trenches; hence the original name ‘Rosette pitting’. However, it is probably more accurately described as a general attack due to the development of highly corrosive conditions beneath the aluminium corrosion deposits. Failure occurs due to the thinning of the cylinder wall eventually leading to perforation.

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Photograph 3. View of the internal surface of the base of a hot water cylinder (after the removal of all loose deposits) showing the broad intensely red corrosion product layer in the peripheral crevice where Rosette corrosion has become initiated.

Technical notes. *A high electrochemical potential, sufficient to initiate Type I pitting, can be generated by the presence of high levels of dissolved copper in the water. Such conditions typically arise at the base of new hot water cylinders due to initial high corrosion rates of the clean metal walls.*

Aluminium protector rods have been successfully used for over thirty years to prevent Type I pitting in copper hot water cylinders. A rod of pure aluminium is mechanically attached to the base of the cylinder to form a galvanic couple with the copper. Preferential corrosion of the more electronegative aluminium produces a flow of electrons onto the copper, which suppresses the latter's electrochemical potential to below its pitting initiation potential even in the presence of copper ions. After a few months in service a semi-protective film forms over upper parts of the cylinder wall, thereby reducing the flow of copper ions into the water, and the protection of the aluminium rod is no longer needed.

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Research (Reference 11) into the causes of rosette corrosion has established that the aluminium/copper galvanic couple is so energetic that it does not just suppress the electrochemical potential of the copper but also reduces any nitrate (NO_3^-) in the water to ammonia and some of the sulphate (SO_4^{2-}) to sulphide (S^{2-}). Both of these chemical species are highly corrosive to copper. There appears to be no minimum concentration of either nitrate or sulphate for the occurrence of Rosette corrosion; however, the relative concentrations of all the negatively charged ions (called anions) are important. It is thought that all the anions concentrate around the aluminium rod (the anode of the aluminium/copper couple) and the extent to which the nitrate and sulphate are reduced depends on the extent to which they are 'crowded out' by other anions such as chloride (Cl^-) and bicarbonate (HCO_3^-).

In some areas of the UK there has been a general increase in the nitrate concentration of the water supply. This increase and the critical nature of the nitrate ion may explain why it has taken thirty years for the problem to be noticed.

What to do about it. The problem of Rosette corrosion has been solved by a re-design of the hot water cylinder so that an aluminium protector rod is no longer required (Reference 23). The re-design has involved lowering the position of the heating coil so that the base of the cylinder operates above 40° C. Above this temperature cupric oxide (CuO), rather than cuprous oxide (Cu_2O), is the stable species and, not being a semi-conductor, it does not support Type I pitting.

Unfortunately, although Rosette corrosion should now be of historical interest only, contractors are still specifying cylinders with aluminium protector rods and manufacturers are still making them to meet this demand. Part of the problem is

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the perception that cylinders with aluminium rods are generally protected against corrosion, rather than just the specific problem of Type I pitting. As a consequence such cylinders have been used in a wider range of waters than necessary, i.e. even in waters where Type I pitting did not occur. Whereas in the past, apart from the unnecessary extra cost, this was of little consequence, now a contractor runs the risk of experiencing Rosette corrosion with a water that does not support Type I pitting and so did not require an aluminium protector rod in the first place.

Microbiologically induced pitting

The presence of biofilms in pipes has led to severe copper pitting in large institutional buildings, particularly hospitals (Reference 12). The biofilms are thin, continuous layers of bacteria containing polysaccharides or thick, copious slimes. They create alternating aerobic/anaerobic environments and promote the growth of sulphate-reducing bacteria.

Characteristic features. Pitting consists of copper tubercles, often above multiple initiation sites ('pepper pot corrosion'), overlaid with a black precipitate (see Photograph 4). General corrosion also leads to the sporadic release of copper into the water. Leakage in the pipework occurs as a result of the thinning of the wall. Pitting can occur in both hot and cold water systems.

A range of factors can promote microbiologically induced pitting. These are discussed below.

Soft, low-alkalinity water. Low levels of bicarbonate (less than 20 mg/l as calcium carbonate) in the transported water will prevent the production of the basic copper carbonate layer, leaving the oxide layer unprotected. Treatment to reduce this problem includes the addition of carbonate hardness, e.g. by adding carbon dioxide to the water and passing it through a filter of marble chips.

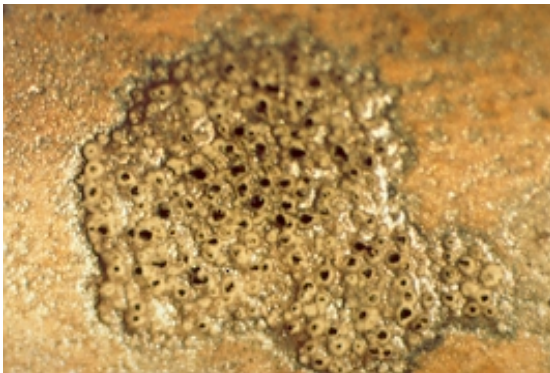
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High levels of assimilable organic carbon. Organic carbon acts as a food source for bacteria. Other factors that encourage the growth of bacteria will also increase the likelihood of microbiologically induced pitting (see blue water problems).

Stagnation of water early in pipe life (see blue water problems).

What to do about it. The following actions may be taken: these have been found to be only partially effective. The choice will depend upon the factors contributing to the problem.

- Clean out the corrosion deposits with a citric acid solution containing surfactants.
- Flush with hot water (greater than 60°C) where a cold water system is affected.
- Add carbonate hardness using carbon dioxide and a filter of marble chips.



Photograph 4. An acid cleaned copper pipe surface showing 'pepper pot corrosion' produced by microbiological action.

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Erosion corrosion

Cuprosolvent waters (see section on cuprosolvency) combined with high water velocities can lead to damage by erosion corrosion. High water velocity in the pipe leads to mechanical damage of the already thin corrosion product layer and exposes the bright metal underneath. The bare metal corrodes at a higher rate than the protected pipe wall.

Characteristic features. Broad horseshoe shaped pits clean of any deposits. The orientation of the pits indicates the direction of the flow of water – ‘horses walk upstream’.

As discussed in the section on cuprosolvency, the water will dissolve the copper salts that form on the surface of the pipes leading to a thinner and hence less protective layer.

Technical notes. *At restrictions in the copper pipework, or changes in the direction of flow of the water (e.g. fittings and bends), the water speed increases and the local pressure drops (the Venturi effect). The drop in pressure causes the dissolved carbon dioxide to form gas bubbles. Downstream of the restriction or bend, the water speed and pressure resume their original values. The gas bubbles collapse as the carbon dioxide dissolves, creating a local water hammer effect and actual mechanical damage (impingement) of the corrosion layer.*

The flow pattern of water through a pipe system is fairly consistent. Therefore the damage will always occur at approximately the same point and will be very localised. The exposed bare metal will corrode at a high rate and the water flow will prevent the formation of any protective layer. The ongoing corrosion of the bare metal will lead, in time, to perforation of the pipe wall.

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What to do about it. A system should be designed for flows between 0.5 and 1.0 m/sec for hot water and 0.5 and 2 m/sec for cold water to avoid erosion corrosion at the higher velocities and to prevent debris settlement at the lower velocities. These maximum velocities are lower than the maximum design flow rates recommended to reduce noise from pipework (Reference 13). Installation defects (burrs, solder beads etc.) can also change the flow patterns and should be avoided.

Flux induced pitting

Pitting of copper can be associated with the presence of flux runs in the bore of the tube. The purpose of flux is to create and maintain oxide free surfaces on the two pieces of copper during jointing. Such surfaces are necessary if a sound bond is to be achieved with the solder that is to make the joint. In order to create the oxide free surfaces, many types of fluxes contain chemicals that are aggressive to copper (Reference 13). If residues of flux are left in the tube after the joint has been made, these may continue to corrode the copper. Residual flux may also affect the quality of the conveyed water including unwholesome levels of copper through leaching. Therefore, fluxes must meet the requirements of the Water Regulations Advisory Scheme (WRAS) concerning contamination of drinking-water (Reference 18).

When heat is applied to melt the solder, any excess flux may flow down the tube producing a 'run'. If this is not washed out, pitting may subsequently occur.

Characteristic features. Typically multiple pinhole failures around the edge of the flux run.

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What to do about it. Problems may be avoided by :-

- using the minimum amount of flux;
- using water soluble fluxes and washing the tubes internally after jointing;
- following practical advice provided by WRAS (Reference 19) and the UK Copper Board (Reference 20).

Problems experienced with copper alloys in water supply

Copper alloys

There are two families of copper alloys commonly used in copper pipework systems: brass and gunmetal.

Brass is the generic name for alloys made primarily from copper and zinc. The proportion of zinc is in the range 10 – 45%. For fittings in water systems, a single-phase α -brass (up to 30% zinc) is generally used for sand-cast fittings and two-phase (duplex) α - β brass (~ 40% zinc) for hot stamped or forged fittings. Hot stamping produces a smooth surface finish to the final product and, as the problem of rejects due to casting porosity does not arise, they are cheaper.

Gunmetals are alloys of copper, tin and zinc and may also contain lead. They can only be used for manufacturing cast items. As with the cast brasses, the problem of rejects, due to through-wall porosity, adds to the unit cost of these fittings. One of the functions of the lead in these alloys is to reduce casting porosity; the lead is the last component to solidify and becomes drawn into any pores in the solid copper alloy matrix.

Both alloys can be affected by erosion corrosion (see section above) although brasses are more vulnerable than gunmetals.

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Dezincification of brasses

Under certain conditions brasses may suffer dezincification, i.e. the selective dissolution of zinc leaving a porous and low strength copper structure behind. Dezincification can occur in both hot and cold water systems, but is markedly quicker in hot water systems.

Characteristic features: the normally yellow brass takes on a black/maroon colour and/or mechanical failures of spindles occur, or deposition of a voluminous 'meringue-like' corrosion product.

For a water to support dezincification, certain conditions have to be present (Reference 14):

- To initiate corrosion, the pH has to be 7.6 or above.
- To propagate the corrosion the chloride concentration in the water has to be a third or more of the carbonate hardness (the latter expressed as mg CaCO₃/l).

If the pH of the water is in the range 7.6 to 8.2, no build-up of deposit occurs and it takes about fifteen years for the walls of the fittings to become penetrated. Consumers do not complain about this form of the problem if only for the fact that few of them occupy the same house for fifteen years. The snapping of tap and valve spindles, weakened because of the soft nature of the copper left behind after removal of the zinc, is another manifestation of the problem.

When the pH of the water is greater than 8.2, the corroded zinc precipitates in the bore of the fitting, usually as hydrozincite (a basic zinc carbonate) greatly reducing the flow of water. This form of attack is known as 'meringue dezincification' and is the form that leads to most frequent complaints from the consumer because it happens in a relatively short period, typically from six months to five years (see Photograph 5).

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Photograph 5. A Brass fitting partially blocked by meringue dezincification

Technical notes. Dezincification can be prevented entirely in a single-phase α -brass by the addition of a very small amount of arsenic (0.02 – 0.06%). Alloys treated in this way are described as dezincification immune. The arsenic is only effective for α -phase structures so that a two-phase, duplex (α - β) alloy cannot be made immune. When duplex brasses dezincify, it is primarily the zinc-rich β phase that is at risk of attack.

There is another category of alloys described as dezincification resistant, e.g. CW602N (formerly designated CZ 132). In these alloys the concentration of zinc (~ 36%) means the alloy is duplex at elevated temperatures, so that it can be hot stamped, and single phase at room temperature, so it can be protected from dezincification by the addition of arsenic.

In order for the arsenic present in the CW602N to be effective against dezincification, the brass has to be held after forming at a temperature below that used for the hot stamping, but above ambient, to give time for the structure to convert from the duplex α - β to a single α phase. In service, a superficial layer of dezincification may occur until the β phase material at the surface has become exhausted. After this, the corrosion cannot penetrate the continuous wall of α phase material immunised by the arsenic.

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What to do about it. Use only *Dezincification immune* or *Dezincification resistant* brasses in waters that both initiate and propagate this form of corrosion.

Corrosion of gunmetals

Gunmetals have good corrosion resistance in drinking-waters. The intrinsically high corrosion resistance of copper is enhanced by the tin, which produces a tough surface layer that increases the alloy's resistance to erosion corrosion. Gunmetals do not suffer dezincification because the zinc levels are never high enough; 15% or more zinc is necessary for dezincification to occur.

Lead leaching from copper alloys

A recent area of research has been the leaching of the lead from copper alloys in contact with drinking-water. This has arisen because of the planned reduction in the level of lead allowed in drinking-water. In the new EC Directive (published in 1998), the current allowable level of lead is 50 $\mu\text{g/l}$ (the UK standard since 1989). At the end of 2003 this value will halve and finally move to 10 $\mu\text{g/l}$ at the end of 2013. This last value is being interpreted as a weekly average figure and the method of taking the water sample to show compliance (not yet agreed) will have to be chosen accordingly.

The development of a British Standard to demonstrate the acceptability of metals for use with drinking-water (originally BS 7766:1994 now replaced by DD 256:2002) used copper alloys as the trial material. The test showed that, whereas all the current alloys commonly used comply with the current 50 $\mu\text{g/l}$ standard, it was not clear if they would all comply with a standard of a weekly average of 10 $\mu\text{g/l}$. The work also established there was no simple relationship between the lead content of an alloy and the level of contamination it produced (Reference 15).

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Problems with solders

Lead contamination from leaded solders is a problem that should now only be of interest to the historian, such materials having been banned in the UK for use with drinking-waters for more than 15 years. Current regulations ban the use of lead based solders for domestic hot and cold water systems and other installations where the water is required to be wholesome (i.e. water to be used for drinking, cooking or food production purposes). A leaflet explaining this (entitled 'Using lead-free solder for drinking-water fittings') is available from the Drinking Water Inspectorate (Reference 21). Related practical advice is available from the Water Regulations Advisory Scheme (Reference 19) and from the UK Copper Board (Reference 20).

Some problems have been experienced with the replacement non-lead solder, a tin silver alloy with a typical composition of 97% tin, 3% silver and a maximum of 0.1% lead (Reference 16). This has arisen because of the low mechanical stability of the solder runs that are flushed out and appear as bits in the water. Although this is a problem that necessarily diminishes with time, especial care is needed with these alloys to use the minimum amount of solder and limit the scale of the initial problem.

Concluding comments

Copper pipework, copper cylinders and copper alloy fittings have evolved to become the most widely used materials for plumbing systems. This is due to their properties of ease of use, corrosion resistance, mechanical strength and resistance to external penetration by liquids and gases, and ability to convey water without tainting it. However, internal corrosion by the conveyed water can occur in certain circumstances. This review has identified those circumstances and where possible, how to avoid or remedy them.

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Glossary of chemical terms

Common Name	Chemical formula
Cuprous ion	Cu(I) ion, Cu^+ (colourless solution disproportionating to Cu^{2+} even at low concentrations in water)
Cupric ion	Cu(II) ion, Cu^{2+} (blue aqueous solution)
Cuprite/cuprous oxide/Cu(I) oxide	Cu_2O (magenta red to brown colour)
Tenorite/cupric oxide/Cu(II) oxide	CuO (from jet black to brown colour)
Cupric hydroxide	$\text{Cu}(\text{OH})_2$ (sky blue colour)
Malachite/Basic copper carbonate	$\text{Cu}_2(\text{OH})_2\text{CO}_3$ (turquoise to green colour)
Brochantite/Basic copper sulphate	$\text{Cu}_4(\text{OH})_6\text{SO}_4$ (deep blue colour)
Hydrozincite/Basic zinc carbonate	$\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ (white colour)
Anion	Negatively charged atom or molecule created by addition of an electron e.g. chloride (Cl^-), sulphate (SO_4^{2-}) etc. This process is the counter balancing reaction to an ongoing corrosion attack.
Cation	Positively charged atom or molecule created by loss of an electron e.g. zinc cation (Zn^{2+}) etc. This is the process that occurs when a metal corrodes

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