

A Review of Current Knowledge

**CAUSES OF COPPER
CORROSION IN
PLUMBING SYSTEMS**

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Review of Current Knowledge

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Review of Current Knowledge

CAUSES OF COPPER CORROSION IN PLUMBING SYSTEMS



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Review of Current Knowledge

CONTENTS

Introduction	3
1 History of copper pipes and products used today	4
2 Problems and solutions	6
2.1 Copper pipes and cylinders	6
Cuprosolvency	7
Blue water problems	7
Leaks	9
Type I pitting	10
Type II pitting	11
Type III pitting	12
Rosette corrosion of cylinders	13
Microbiologically induced pitting	14
Erosion corrosion	16
Flux induced pitting	17
Concentration cell corrosion	18
Stress corrosion cracking	18
Blockage	19
2.2 Copper alloy fittings	19
Copper alloys	19
Dezincification of brasses	19
Corrosion of gunmetals	21
Lead leaching from copper alloys	21
Problems with solders	21
2.3 Concluding Remarks	22
3 Copper Chemistry	22
Introduction to copper chemistry	22
Forming protective layers	23
Cuprosolvency	25
Blue water problems	25
Type I pitting	27
Type II pitting	27
Rosette corrosion of cylinders	28
Copper alloys	29
Dezincification of brasses	29
Glossary of chemical terms	31
References	32

Review of Current Knowledge

Introduction

Leaking water pipes inside buildings can cause serious damage before the leak is detected. Therefore corrosion of copper pipes and fittings incur significant costs. Fortunately, problems with copper corrosion are relatively rare and the cause is usually well understood.

Problems include coloured (blue) water, pinholes in the pipe or fitting, and failure of copper hot water cylinders. Cuprosolvency is usually readily addressed by raising the pH of the supply. The understanding of blue water problems has progressed to the identification of risk factors and to a listing of remedies that have been found to be effective in some cases.

The localised breakdown of the protective films that form on copper makes it vulnerable to various forms of pitting corrosion, see Table 1. It should be noted that the differences between the different types are not clear-cut.

The original main 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 problems of lead contamination from leaded solders are no longer relevant as the use of lead solders in contact with drinking water has been banned for some time.

This publication describes:

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

It is intended for anyone with an interest in the design or the installation of a water supply system using copper pipes or hot water cylinders. It is relevant to plumbers, water industry staff, architects and property owners who operate such a system. It covers hot and cold water supplies inside buildings, but not central heating systems.

The guide starts with an introduction to the history of copper pipes and the products that are most commonly used today. This will help you identify what products are used in your property.

Review of Current Knowledge

Section 2 helps identify the causes of problems and how these can be rectified.

Section 3 provides a more detailed account of the science behind copper and copper corrosion.

1 History of copper pipes and products

Copper pipes have been used for domestic water services for nearly 200 years. The introduction of copper pipes offered a stronger, lighter and cheaper alternative to lead. 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 gauge) 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 light 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 or soldered joints (<i>see below</i>) and compression fittings (<i>see below</i>) for joining pipe introduced.
1939	British Standard revised to include capillary (soldered) and compression fittings.
1996	First publication of European Standard BS EN 1057 for Copper and copper alloys. Seamless, round copper tubes for water and gas in sanitary and heating applications introduced.

Review of Current Knowledge

Copper pipes have been used in the majority of domestic and commercial plumbing systems, although they are increasingly being replaced by plastic pipes in new-build properties.

Capillary (soldered) fittings are formed from copper tubes or copper alloys by pressing or stamping, see Photograph 1. Once the pipe is inserted into the fitting, the whole joint is heated and solder runs into the narrow space between the pipe and the fitting. The solder can either be end-fed into the joint using solder wire or included in the fitting during manufacture.



Photograph 1. A selection of capillary (soldered) fittings

Compression fittings are stamped or sand-cast from copper alloys, see Photograph 2. Once the pipe is inserted into the body of the fitting, the nut is tightened onto the body. Compression fittings normally incorporate metal sealing rings (called olives) that grip onto the outside wall of the pipe when the retaining nut is tightened. Two different olives can be seen on the right hand side in Photograph 2 where one is copper coloured and one is brass coloured.

Review of Current Knowledge



Photograph 2. A selection of compression fittings

Press fittings are made of copper or copper alloy. The pipe is inserted into the fitting and passes through an 'O' ring. Using a special tool the fitting is pressed onto the pipe. The interference between the fitting and pipe made by the pressing tool provides the mechanical attachment and the 'O' the watertight seal.

Push fittings are made of copper or copper alloy. The pipe is inserted into the fitting and passes through an 'O' ring and a grab ring. The grab ring provides the mechanical attachment and the 'O' the watertight seal.

2 Problems and solutions

2.1 Copper pipes and cylinders

Under most circumstances the use of copper pipes causes no problems to the homeowner.

In contact with most drinking water supplies, copper develops a virtually protective layer of copper oxides and copper carbonates on the inside of the pipe. This limits the amount of copper that can dissolve into the water to values well below the maximum of 2 milligrams per litre (mg/l) specified in the Drinking Water Directive (Reference 1), which defines the quality of the drinking water to be supplied at the consumer's tap.

Review of Current Knowledge

However, problems can occur if the layer that forms on the inside of the pipe is non-protective. This can arise if during formation of the layer there was a long period of stagnation, Other causes include poor plumbing practice or the presence of certain water types. The latter is especially true for private water supplies, which rarely receive any treatment that would reduce the corrosivity of the supply.

Problems with coloured water, leaks and blockages can occur under special circumstances and these are reviewed below. It should be noted that new pipes release considerably more copper than old pipes, which can potentially lead to a slight metallic taste to, or discolouration of, the water. The release will generally decrease with time as the protective corrosion layer develops, typically within six months. No action needs to be taken during this time.

Cuprosolvency

What to look for: This condition typically manifests itself through blue-green staining of sinks and taps

Cause: Under some water conditions, the Cu^{2+} ion is retained in solution rather than being precipitated. These kinds of waters are referred to as being *cuprosolvent* (copper dissolving). Examples of cuprosolvent waters include borehole (often private) supplies containing high concentrations of carbon dioxide. This has the effect of lowering the pH of the water, often below pH 6.5, which increases the solubility of copper. Very soft, low pH upland waters can have the same effect. As the same conditions also cause *plumbosolvency* (leading to the presence of elevated lead concentrations in drinking water), *cuprosolvency* is now rare in water supplied by water utilities as treatments are in place to avoid problems with lead. See Section 3 for further information.

What to do about it: High levels of copper are often associated with prolonged stagnation of the drinking water in the plumbing system. Stagnation can be avoided by careful design of the system or by replacing the affected pipework by smaller diameter pipes.

Blue water problems

What to look for: Water has a characteristic transparent or opaque blue colour

Cause: This occurs due to high levels of dissolved copper in the drinking water. It has been suggested (Reference 3) that copper(II) hydroxide ($\text{Cu}(\text{OH})_2$) is the initial corrosion product that is formed in all waters. Normally, the soluble copper(II)

Review of Current Knowledge

species precipitate in a relatively short period of time into the much less soluble copper oxides or carbonates depending on water composition and the levels of contamination in the water decrease significantly.

Blue water problems occur in those waters where the conversion of the copper(II) species is for some reason prevented or delayed. The relatively high solubility of copper(II) ions accounts for the high levels of copper found in the water and the 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:

- Low concentration of bicarbonate (HCO_3^-)
- High pH
- Microbiological growths
- Sulphate-reducing bacteria or sulphides
- Stagnation of water early in pipe life
- Silica films on clean copper

A more in-depth explanation of these factors is given in Section 3.

What to do about it: There are a number of actions that could be taken to limit the problem. The choice will depend upon which of the factors above are identified as being contributory.

For immediate effect (as a temporary measure):

- Heat shock using hot water in excess of 60°C , conversion of the surface to the more protective black copper(II) oxide
- Super-chlorination (e.g. 5 mg/l of free chlorine), conversion of the surface to the more protective black copper(II) oxide
- Replace afflicted sections of pipe (not effective in presence of sulphate-reducing bacteria)

For long-term effect (no immediate benefit):

- Maintain long-term chlorine residual (to reduce microbiological growths)
- Periodic super-chlorination (e.g. 5 mg/l of free chlorine) plus initiating factor removed
- Addition of bicarbonates
- Addition of polyphosphates (reduces blue water problems but not copper concentrations)
- Lower pH to 7.5, although this would not be acceptable where there was a danger of creating plumbosolvency problems.
- Check the design of the affected system to ensure minimum water residence times.

Review of Current Knowledge

Leaks

Copper pipes are normally relatively well protected against corrosion due to the semi-protective film that forms on the surface. However, if there is a breakdown of the protective film, particularly in a small area, copper corrosion can be concentrated at that point causing perforation of the tube wall and leaks. This is referred to as pitting corrosion and can occur in cold and hot water pipes, as well as hot water cylinders.

What to look for: A small pinhole in the pipe, fitting or cylinder which leads to a water leak.

Cause: There are various reasons for pitting corrosion. The different types of corrosion are reviewed below. However, it must be borne in mind that in many situations there may not be an absolute and clearly identified distinction between the different types of copper pitting (Reference 4).

Table 1. Types and causes of pitting corrosion

Type of pitting	Initiation conditions	Propagation conditions
Type I	Presence of a carbon film on the bore of the tube and cold (less than 40°C) hard, organically pure water	Unfavourable combination of six inorganic parameters (see Section 3)
Type II	Hot, soft water with low pH	Unfavourable $\text{HCO}_3^-/\text{SO}_4^{2-}$ ratio
Type III	Stagnation early in pipe's life; pH >8; aluminium sulphate (alum) coagulation	Soft waters with pH above 8
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 carbon
Erosion corrosion	High velocity water	Soft water
Flux induced corrosion	Presence of a flux run	
Concentration cell corrosion	Debris and deposits in pipe	

Review of Current Knowledge

Type I pitting

Type I pitting (or cold water pitting) occurs in those parts of the plumbing system which never exceed 40°C (i.e. in cold water pipes and the base of hot water cylinders of traditional design). Typical Type I pitting waters are borehole supplies, which are largely free of organic matter and have pH values in the range 7 – 8.2.

What to look for: Typically the pipe or cylinder fails after three to four years of service but sometimes within a few months. When a failed section of pipe is removed and sectioned longitudinally, corrosion deposits can be seen that are deep-green usually well-spaced mounds above the pits or pinholes in the pipe wall, see Photographs 3 and 4. Smaller inactive pits may be seen between the active pits.

Cause: The type of corrosion requires a continuous carbon film in the bore of the pipes and a specific water quality. In pipes, the presence of a carbon film produced in the manufacturing of pipes (References 5 and 6) can provide the driving force for the propagation of a pit. The water has to be hard, organically pure and is typically from a borehole. Type I pitting does not normally occur in surface sources as this water contains natural organic material that inhibits corrosion (Reference 7). For further information, see Section 3.



Photograph 3. Typical distribution of Type I pits in copper pipe

Review of Current Knowledge

What to do about it: The conditions which lead to Type 1 can be avoided by using products which meet BS EN 1057. It is normal practice for manufacturers to take measures to remove, or prevent the development of, deleterious carbon films. Tubes conforming to BS EN 1057 should not be susceptible carbon film cold water pitting as the standard specifies a carbon content and carbon film test.



Photograph 4. Detail of a Type I pit with a central mound of malachite above the initiating site surrounded by secondary mounds above daughter pits

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. $>60^{\circ}\text{C}$) and is associated with soft moorland waters that often contain manganese.

What to look for: Typically the pipe or cylinder fails after a reasonable length of time in service, rarely producing a perforation in less than eight years. When the section of pipe is removed and sectioned longitudinally, deep pits can be seen of small cross-section containing very hard crystalline copper(I) oxide (Cu_2O) capped by small black or greenish-black mounds of copper(I) oxide and basic copper sulphate.

Review of Current Knowledge

Cause: 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 manganese. Such waters are normally soft, moorland supplies that have been treated to raise their pH to above 7.4. Deposits of iron and aluminium have also caused problems. See Section 3 for further information.

Ratio of bicarbonate to sulphate: In Scandinavia, where Type II is the most common form of copper pitting, manganese is not considered an important factor. Work by Mattsson (Reference 8) suggested that a $\text{pH} < 7$ and a low ratio of bicarbonate to sulphate ($\text{HCO}_3^-/\text{SO}_4^{2-}$), were the critical factors.

What to do about it: Advice on prevention has centred on creating conditions that discourage the corrosion. These include:

- Reducing the system operating temperatures to less than 60°C
- Increasing the bicarbonate level of the water to greater than the sulphate level (measured as mg/l)
- Keeping the pH below 8.5 to prevent precipitation of manganese salts if present in the water

Type III pitting

Type III copper pitting was first identified in Germany and is quite rare in the UK. It is associated with soft, cold alum (aluminium sulphate) coagulated waters of low conductivity, low alkalinity and high pH.

What to look for: Type III pitting is usually not associated with pinhole leaks, but rather blue water problems and blockages. When the section of pipe is removed and sectioned longitudinally, voluminous corrosion products can be seen consisting of mainly copper sulphates, often taking the form of semi-continuous 'fences' that run along the invert of horizontal tubes.

It should be noted that the phenomenon of voluminous corrosion products developing in pipes after prolonged contact with soft waters is seen with some UK water supplies, see Photograph 5. However, these structures are not usually associated with pitting.

Review of Current Knowledge



Photograph 5. Voluminous corrosion deposits produced by soft water

Rosette corrosion of cylinders

‘Rosette corrosion’ is a phenomenon causing premature failures in copper hot water cylinders containing an aluminium protector rod. Due to a redesign of hot water cylinders, this type of failure should now be rare.

What to look for: Typically the cylinder will fail due to thinning of the cylinder wall, leading to perforation, after prolonged use. When the cylinder is opened up, heavy sediments can be seen of an aluminium corrosion product that varies from white with a bluish tinge to light green in colour (Photograph 6). Underneath these deposits, the copper is a vivid brick red magenta colour consisting of large platelets of copper(I) 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.

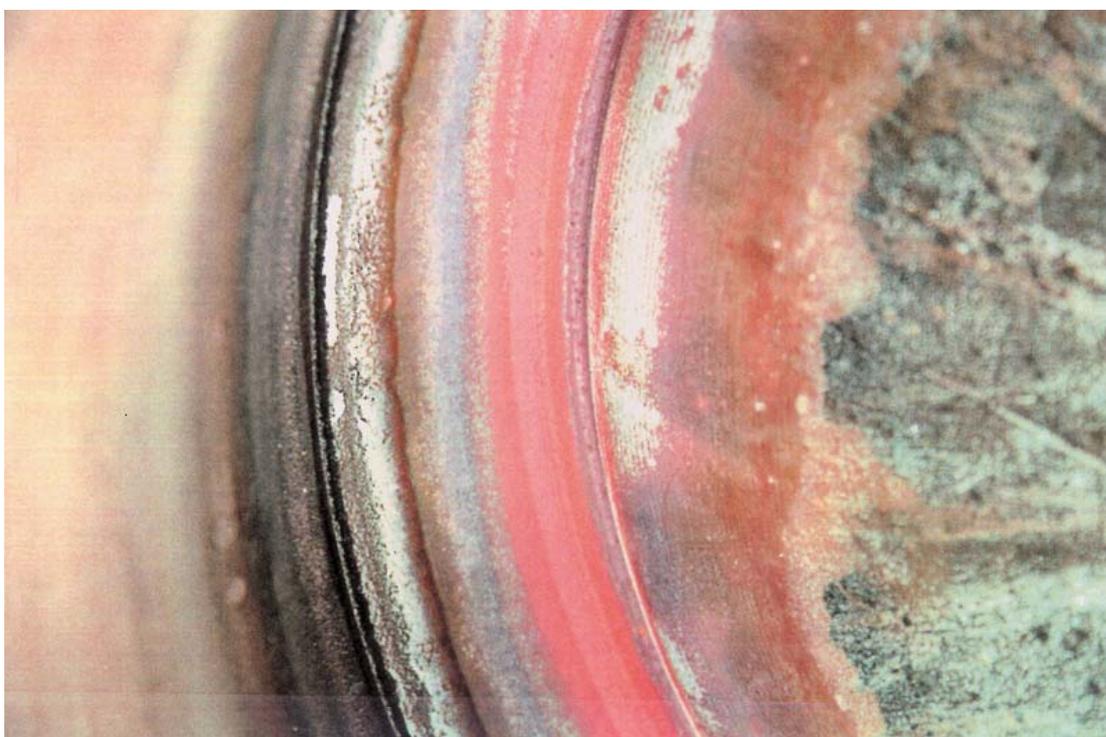
Cause: Research (Reference 9) into the causes of this problem established that the aluminium/copper galvanic couple was so energetic that it reduced the nitrate in the water to ammonia and some of the sulphate to sulphide. Both of these ions are highly corrosive to copper. It was clear from the composition of the waters in which Rosette corrosion was occurring that there was not an absolute level of

Review of Current Knowledge

nitrate and sulphate at which problems arose, rather it was the ratio of the compounds that was important. More information on Rosette corrosion can be found in Section 3.

Since the discovery of the cause of Rosette corrosion, the aluminium protector rod was removed from the Hot Water Association's specifications for hot water cylinders in 2002 and it is today not possible to buy this type of hot water cylinder.

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. The re-design has involved lowering the position of the heating coil so that the base of the cylinder operates above 40° C where a semi-protective corrosion layer is formed.



Photograph 6. 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

Microbiologically induced pitting

The presence of biofilms has been detected in pipes that have been in service. In some instances they can lead to severe copper pitting in large installations e.g.

Review of Current Knowledge

institutional buildings, particularly hospitals (Reference 10). The biofilms are thin, continuous layers of bacteria containing polysaccharides or thick, copious slimes. Pitting can occur in both hot and cold water systems.

What to look for: (i) Leakage in the pipework occurs as a result of the thinning of the wall leading to pitting/ pinholes. When the section of pipe is removed and sectioned longitudinally, copper tubercles can be seen, often above multiple initiation sites, overlaid with a black precipitate ('pepper pot corrosion', Photograph 7). (ii) General corrosion also leads to the sporadic release of copper into the water, which could lead to a slight metallic taste to, or discolouration of, the water.

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

Pipe temperatures in the range 20-40°C: In large installations cold pipework can attain relatively high temperatures, 30°C, e.g. in false ceiling voids. Equally, in large hot water systems with insufficient heat input pipework can run at 30-40°C. In both instances bacterial growth can be extensive.

Soft, low-alkalinity water: Low levels of bicarbonate in the transported water will prevent the production of the protective basic copper carbonate layer.

High levels of 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 problem in Section 3).

Stagnation of water early in pipe life: (see blue water problem in Section 3).

What to do about it: There are a number of actions that could be taken but these have been found to be only partially effective. The choice will depend upon the factors contributing to the problem.

- Address system problems: ensure hot water is maintained hot and cold water kept cool.
- Clean out the corrosion deposits with a citric acid solution containing surfactants.
- Flush with hot water (>60°C) where a cold water system is affected.
- Add carbonate hardness using carbon dioxide and a filter of marble chips.

Review of Current Knowledge



Photograph 7. An acid cleaned copper pipe surface showing ‘pepper pot corrosion’ produced by microbiological action

Erosion corrosion

High water velocities and/or turbulence can lead to damage by *erosion corrosion* as the protective corrosion layer is prevented from thickening.

What to look for: Leakage in the pipework occurs as a result of the thinning of the wall leading to pitting/ pinholes. When the section of pipe is removed and sectioned longitudinally, broad, shiny horseshoe shaped pits which are free of any deposits can be seen. The orientation of the pits indicates the direction of the flow of water – ‘horses walk upstream’.

Cause: Restrictions and changes to flow direction will cause the water velocity to increase locally, leading to mechanical damage usually of the copper pipe and sometimes of a fitting. As the flow pattern of water through a pipe system is fairly consistent, the damage will always occur at approximately the same point. Gas bubbles can also temporarily form due to the increase in velocity. When the gas bubbles eventually collapse, this will cause a local water hammer effect.

Review of Current Knowledge

Besides too high water flow velocity, poor workmanship can cause erosion corrosion. Examples include poorly planned pipework with too many bends, unreamed cut tube ends, globules of solder, tube ends not fully inserted into fittings before soldering, tube ends not cut square, dented tubes and tubes crimped during bending (Reference 11). The presence of abrasive solids, e.g. sand, in the pipework has also been associated with erosion corrosion. Cuprosolvent waters (see Page 7) and waters softened to near-zero hardness are known to further facilitate this effect.

What to do about it: The conditions which lead to erosion corrosion can be avoided by good plumbing design. To avoid erosion corrosion it is suggested that the water flow velocities should not exceed 2 m/s in cold water and 0.5 m/s in hot water systems. The installation defects mentioned above should also be avoided.

Flux induced pitting

Pitting of copper can be associated with the presence of flux runs inside the pipe. 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 12).

What to look for: Typically multiple pinhole failures around the edge of the flux run in the bore of the tube.

Cause: If residues of flux are left in the tube after the joint has been made, these may continue to corrode the copper. If excess flux is used to make a solder joint, when heat is applied to melt the solder, the excess flux may flow along the tube producing a 'run'. If this is not washed out, pitting may subsequently occur.

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

- Following the WRAS (Water Regulations Advisory Scheme) approved installation method on solders and fluxes (Reference 12).
- Using the minimum amount of flux.
- Using water-soluble fluxes and washing the tubes internally after jointing.
- Using one of the less aggressive fluxes listed in Reference 13.

Review of Current Knowledge

Concentration cell corrosion

The presence of deposits will cause the water to have varying levels of oxygen around the deposit. This will lead to concentration gradients and corrosion can develop under the deposit.

What to look for: Non-corrosion deposits in the pipework.

Cause: Debris and deposits in the pipe can cause an oxygen gradient to build up with low oxygen concentrations under the debris and higher in the main flow. This gradient can accelerate corrosion. Examples of deposits include silica, iron oxides (rust) and building debris.

What to do about it: Problems may be avoided by thorough flushing after installation and not letting debris enter the pipework in the first place. Affected pipes can be flushed or replaced.

Stress corrosion cracking

During the manufacturing of copper pipes, the tube is partially worked cold which results in residual stress in the pipe. This is required for the pipe to conform to the requirements of standards such as BS EN 1057 and is normally not of any concern. Under certain conditions this can, however, lead to a crack developing in the pipe.

What to look for: Usually a crack along the longitudinal axis of the tube.

Cause: Four simultaneously occurring factors are needed for stress corrosion cracking to occur:

- Residual stress in copper pipe
- Stress cracking agent (ammonia or mercury)
- Moisture
- Alkaline environment

The stress cracking agent most likely to be encountered is ammonia, although mercury could potentially be found in dental surgeries. Alkaline conditions can be created by plaster and concrete.

Review of Current Knowledge

What to do about it: Good installation practice will normally prevent cracking from occurring. Remove one of the four factors and stress corrosion cracking will not occur. If pipes are likely to encounter the above combination of conditions, the bare metal should be protected. Copper pipes with factory-applied plastic covering are available or appropriate tape can be spiral wrapped around the copper pipe. Alternatively other suitable pipe should be used.

Blockage

If voluminous corrosion products are formed, this could eventually lead to blockage of pipes. This would however most likely be associated with conditions causing leaks, problems with colour or conditions causing problems with copper alloys.

2.2 Copper alloy fittings

Copper alloys

There are two families of copper alloys commonly used for jointing 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 30 – 40% but can be down to 15%.

Gunmetals are alloys of copper, tin and zinc and may also contain lead. They can only be used for manufacturing cast items. 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 generally more vulnerable than gunmetals. For further information on alloys, see Section 3.

Dezincification of brasses

Under certain conditions brasses may suffer dezincification, which is 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.

Review of Current Knowledge

What to look for: 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 (Photograph 6). The timescale involved is anything from 6 months to 15 years.

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

- To initiate corrosion, the pH has to be ≥ 7.6
- To propagate the corrosion the ratio of chloride to calcium carbonate (Cl/CaCO_3) in the water has to be > 0.33

If the pH of the water is in the range 7.6 - 8.2, no build-up of deposit occurs and it takes in the region of 15 years for the walls of the fittings to become penetrated. 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 > 8.2 , the corroded zinc precipitates in the bore of the fitting, greatly reducing the flow of water. This form of attack is known as ‘meringue dezincification’ (Photograph 8) and is the form that leads to most frequent complaints from the consumer because it happens in a relatively short period, typically from 0.5 – 5 years.

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

For further information on dezincification, see Section 3.



Photograph 8. Brass fitting affected by meringue dezincification

Review of Current Knowledge

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 not high enough; $\geq 15\%$ is necessary for dezincification to occur.

Lead leaching from copper alloys

A more 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 reduction in the level of lead allowed in drinking water. In the current EC Directive (Reference 1) the allowable level of lead is 25 micrograms per litre ($\mu\text{g/l}$) and reducing to 10 $\mu\text{g/l}$ in 2013, a reduction from the previous level of 50 $\mu\text{g/l}$.

Work (Reference 15) on the development of a British Standard to demonstrate the acceptability of metals for use with drinking water (BS 7766:1994) used copper alloys as the trial material. It indicated there was no simple relationship between the lead content of an alloy and the level of contamination it produced. BS 7766:1994 and later standards have now been superseded by the European standards EN 15664-1 (Reference 16) and EN 15664-2 (Reference 17). In addition, the European Commission is developing a voluntary acceptance procedure for copper alloys utilising the European standards.

Problems with solders

Lead contamination from leaded solders is of historic interest only, such materials having been banned in the UK for use with drinking waters for two decades. However, cases of continued use have come to light, most likely due to the fact that leaded solders are still available for other applications, such as electrical purposes.

A few problems have been experienced with the replacement non-leaded solder, a tin silver alloy with a typical composition of 97% tin, 3% silver and a maximum of 0.1% lead (Reference 18). When solders melt in the presence of flux there is turbulence and spitting of the molten solder. This results in small balls and tails of solder being expelled from the joint. In the case of high tin solder the ability of the stray solder to 'tin' the cooler surfaces is low due to its higher melting temperature, narrow pasty range and surface tension effects. Consequently, small balls and tails of solder are sometimes seen embedded in flux residues in close proximity to the joint. These can become dislodged and flushed out at a later time. Although this is

Review of Current Knowledge

a problem that necessarily diminishes with time, especial care is needed, as with all solders, to use the minimum amount of solder to complete the joint.

2.3 Concluding remarks

Although the potential modes of failure of copper in drinking water are numerous, the actual number of failures, compared to the total length of copper pipe successfully in use, is very low. For example, the number of failures by Type I pitting for pipe manufactured to the European standard is now less than 1 per 1,000,000 metres of pipe sold. Of course, a significant number of the failures that do occur arise from the actions of the end-user. It is hoped that this publication will help reduce such occurrences thereby further enhancing the excellent performance of copper-based products in drinking waters.

3 Copper Chemistry

Introduction to copper chemistry

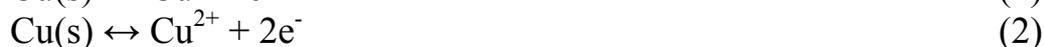
Copper is a metal that has been used for some 10 000 years, either pure or as an alloy, e.g. bronze (copper and tin) and brass (copper and zinc). Copper acquired its name from being mined on Cyprus during the Roman era, Cyprium or Cuprum meaning “metal from Cyprus”. Copper is usually mined as copper sulphide minerals, e.g. chalcocite (Cu_2S) and covellite (CuS). Copper metal is an exceptionally good electrical conductor.

Copper is an element essential for all higher organisms, the human body requiring a daily intake of 2-4 mg (Reference 19). The normal sources of the element are from the diet rather than the drinking water. However, although copper is an essential element, at high concentrations it is toxic and so is limited under the Drinking Water Directive (Reference 1) to a maximum of 2 mg/l.

Although copper is a relatively noble metal and is more stable in the atmosphere than e.g. iron and zinc, it can form ions in water. Copper forms two cations (positively charged ions) by losing one or two electrons (e^-), see Equations 1 and 2. The process of losing electrons is referred to as oxidation by chemists as oxygen often picks up the electrons, see Equation 3. The process of picking up electrons is called reduction. Copper can thus react with oxygen in water as outlined in Equations 4 and 5. This field of chemistry is called electrochemistry and beyond the scope of this publication. The interested reader is referred to text books on the subject, although internet encyclopaedias, such as Wikipedia, contain a reasonably

Review of Current Knowledge

good introduction. The National Physical Laboratory also has some good literature on their website, www.npl.co.uk.



Cu^+ ions (Cu(I)) form colourless solution in water whereas Cu^{2+} ions (Cu(II)) can form the blue colour often associated with the presence of copper. Cu^+ ions predominate under conditions where little or no oxygen is present (anaerobic conditions) and Cu^{2+} ions predominate when air is present (aerobic conditions).

The Cu^+ and Cu^{2+} ions can exist on their own in solution but they can also form soluble or solid complexes with a variety of anions (negatively charged ions), e.g. hydroxide (OH^-), chloride (Cl^-), carbonate (CO_3^{2-}), and sulphate (SO_4^{2-}) ions. Together with oxygen, these are all part of the major corrosion products found in copper pipes and on copper roofs, see the section below. Copper ions also form complexes with organic compounds. Soluble complexes can also considerably increase the copper concentration in water, and thereby the corrosion rate. In most instances there is a balance between the soluble products remaining in solution and precipitation out onto the surface. Which complexes form is dependent on their thermodynamics and kinetics.

Forming protective layers

Copper's resistance to corrosion relies upon a small amount of corrosion 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. For cold water these can be categorised into four general conditions that are summarised in Figure 1 and described below.

1. In waters with a low oxygen content (anaerobic conditions, e.g. a stagnant water) the metal itself is stable, that is, it will not corrode readily.
2. In acidic waters ($\text{pH} < 6$) with oxygen present (aerobic conditions, e.g. in a moving water), the metal will dissolve to form the Cu^{2+} ion that is the most stable form in these conditions. Such waters are termed *cuprosolvent* and the condition is discussed in the main text.

Review of Current Knowledge

3. In neutral to alkaline waters (pH 6-8) with a reasonably high oxygen content (>2 mg O_2/l , aerobic conditions e.g. in a moving water), the metal will initially produce an insoluble layer of copper(I) oxide or cuprite (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. In alkaline waters (pH >8) with a high oxygen content, copper will form a layer of copper(II) oxide, or tenorite (CuO). This jet black to brown corrosion product will be the most stable species in these conditions and will form a protective scale against further corrosion.

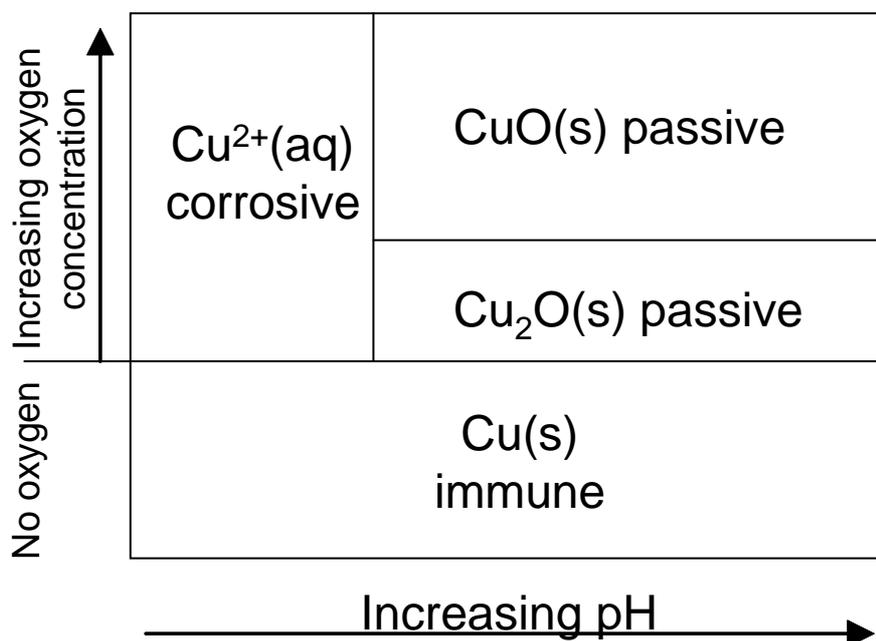


Figure 1. Copper corrosion products as a function of pH and oxygen concentration. (aq) = dissolved, (s) = solid.

For hot water the protective black copper(II) oxide is nearly always formed.

Layering of the solid corrosion products, much like the solids in Figure 1, can be seen inside pipes where Cu_2O forms closest to the copper metal surface (where the oxygen concentration is lower) and CuO forms a layer on top of the Cu_2O and in contact with the water (where the oxygen concentration is highest).

Of these four species in Figure 1, only the Cu^{2+} ion is significantly soluble. The films that form on copper are only semi-protective and corrosion continues, albeit at a much reduced rate to that of the initial bare metal rate. The semi-protective scales that initially form in case 3 and 4 often develop further insoluble layers, e.g.

Review of Current Knowledge

the mineral malachite which is a basic copper carbonate ($\text{Cu}_2(\text{OH})_2\text{CO}_3$). This deposit has a characteristic turquoise/green colour, see Photograph 2. For malachite to be produced, the water needs to contain carbonate combined with a sufficiently high pH. The formation of this copper mineral will limit the level of copper dissolved in the water and is therefore beneficial in both the long-term performance of the pipe and the levels of copper present in drinking water. These composite deposits can however experience localised breakdown leading to different types of pitting corrosion.

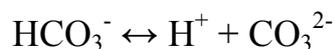
For the layer to be protective, periods of prolonged static water conditions have to be avoided. Systems that have been initially filled, to establish their hydraulic soundness, but then left standing full of water until the building becomes occupied, often give unsatisfactory long-term results. It is for this reason and to maintain cleanliness of the system that flushing regimes have been introduced for installations that have been completed but not brought into use.

Cuprosolvency

Cuprosolvent waters include borehole supplies containing high concentrations of carbon dioxide. This has the effect of lowering the pH of the water, which increases the solubility of copper. The reason for the decrease in pH is that when carbon dioxide (CO_2) dissolves in water it forms carbonic acid, H_2CO_3 :



Carbonic acid can dissociate to form bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions and H^+ :



As the concentration of H^+ (acid) increases, the pH decreases.

Reservoir waters derived from upland peaty areas on granitic rocks (e.g. places in Scotland and the West Country) are very soft and acidic (containing humic and fulvic acids). If untreated, these waters will also be cupro- and plumbo-solvent.

Blue Water Problems

Characteristic features: Water has a characteristic transparent or opaque blue colour

Review of Current Knowledge

In Section 2, it has been suggested that copper(II) hydroxide ($\text{Cu}(\text{OH})_2$) is the initial corrosion product formed in all waters. The copper(II) species is then normally transformed into the much less soluble copper oxides (Cu_2O and CuO) or other species such as the basic carbonate (e.g. malachite, $\text{Cu}_2(\text{OH})_2\text{CO}_3$) and the levels of copper in the water decrease significantly. Blue water problems occur in those waters where the conversion of the copper(II) species is for some reason prevented or delayed. Organic compounds are known to form soluble complexes with the copper ions and to block precipitation sites on the surface scales. In some very rare cases, microbial activity can cause the water to be an opaque blue colour due to high levels of copper combining with organic material. Other workers attribute the blue colour to mineral forms of copper such as brochantite ($\text{Cu}_4\text{SO}_4(\text{OH})_2$) and posnjakite ($\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}$) (Reference 20). 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:

Low bicarbonate: Low levels of bicarbonate in the transported water will prevent the production of the basic copper carbonate layer (malachite), leaving the initial oxide layer less protected. This alone need not lead to blue water problems if the insoluble copper(I) oxide could still be formed. Softened water can create blue water problems where the Ca^{2+} has been replaced by Na^+ and precipitation of the basic carbonate cannot take place. It is for this reason that water should not be fully softened and should be blended back with the original water to give a bicarbonate level of about 50 mg/l. However, if the carbonate concentration is low enough and the sulphate concentration high enough, brochantite and posnjakite could form.

High water pH: In high pH water (greater than pH 9), the highly soluble copper(II) hydroxide can be formed in preference and it converts only slowly to the less soluble copper oxides due to kinetic effects, even though formation of CuO is thermodynamically more favourable. High pH can therefore initiate blue water problems.

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

Sulphate-reducing bacteria : 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.

Review of Current Knowledge

Stagnation of water early in pipe life: Anaerobic conditions can develop as the dissolved oxygen in the water is consumed by corrosion reactions. This stifles the production of protective scales. Prolonged stagnation in the early life of the system (e.g. after hydraulic testing and before going into service), dead-legs and long residence times (e.g. factory shutdown periods) should be avoided. The British Standard BSEN806-4 requires regular flushing at no more than seven day intervals to avoid this problem.

Silica: Silica films on copper surfaces can facilitate reactions that would not happen if the metal were in immediate contact with oxygenated water. Silica deposits have been implicated in pitting of copper in specific waters in Scandinavia. Dissolved silica contents of 10-20 mg/l seem to be critical for the formation of porous silica films leading to pitting.

Type I pitting

Type I pitting (or cold water pitting) occurs in those parts of the plumbing system which never exceed 40°C. 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 5 and 6). For Type 1 pitting to occur, the electrochemical potential of copper has to be above a critical value. Occasionally high electrochemical potentials can be achieved because of high dissolved copper levels in pipes where a 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 for further details). Thus a carbon film is not enough for pitting to occur, the water itself needs to be of a composition favourable to initiation of corrosion.

The propagation of pitting has previously been thought to be a function of water quality; specifically the water has to have a critical composition of six inorganic parameters (dissolved oxygen, sulphate, chloride, nitrate, sodium and pH). The British Non-ferrous Metals Technology Centre developed a nomogram using these six factors to calculate a water's Pitting Propensity Rating (PPR, Reference 21). A positive value for the PPR indicates the water will propagate the attack, a negative value that it is non-pitting. Empirical observation has however shown that PPR is not always an accurate guide to the tendency of a water to cause pitting.

Type II pitting

Type II pitting also known as 'hot-soft water pitting' occurs in hot water systems only (i.e. >60°C) and in the UK is associated with soft moorland waters that often contain manganese. One view of the problem presumes that the soluble manganous

Review of Current Knowledge

ion (Mn^{2+}) oxidises to the insoluble manganese(IV) 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. Type II pitting has been observed in water with as little as 30 $\mu\text{g/l}$ of manganese.

The ratio of bicarbonate to sulphate is the most common factor for Type II pitting and work by Mattsson (Reference 8) suggested that a $\text{pH} < 7$ and a low ratio of bicarbonate to sulphate ($\text{HCO}_3^-/\text{SO}_4^{2-}$), were the critical factors.

Rosette corrosion of cylinders

Rosette corrosion is a phenomenon causing premature failures in copper hot water cylinders containing an aluminium protector rod.

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 30 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 that 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.

Research (Reference 9) into the causes of this problem established that the aluminium/copper galvanic couple was so energetic that it did not just suppress the electrochemical potential of the copper but also reduced the nitrate in the water to ammonia and some of the sulphate to sulphide. Both of these ions are highly corrosive to copper. It was clear from the composition of the waters in which Rosette corrosion was occurring that there was not an absolute level of nitrate and sulphate at which problems arose, rather it was the ratio of the anions that was important. This could be understood as a competitive process where the anions concentrate around the aluminium rod (the anode of the couple) and the extent to which the nitrate and sulphate are reduced depends on the extent to which they are 'crowded out' by the chloride and bicarbonate ions.

The critical nature of the nitrate ion would explain why it took 30 years for the problem to occur. During that period the design of cylinders with protector rods

Review of Current Knowledge

did not change but the general concentration of nitrate in drinking waters gradually rose because of the increased use of agricultural fertilisers. This idea is further supported by the preponderance of Rosette corrosion failures being in the south-eastern part of England, i.e. in the most intensive arable agricultural area of the country.

Copper alloys

There are two families of copper alloys commonly used for jointing 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 typically in the range 30-40% but can be down to 15%. For fittings in water systems, a single-phase α -brass (up to 30% zinc) is generally used for sand-cast fittings and a two-phase (duplex) α - β brass (30-40% 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.

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 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. 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

Review of Current Knowledge

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.

Review of Current Knowledge

Glossary of chemical terms

Alum	$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, used in water treatment
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.
Brochantite/Basic copper sulphate	$\text{Cu}_4(\text{OH})_6\text{SO}_4$ (deep blue colour)
Cation	Positively charged atom created by loss of electrons e.g. copper cation (Cu^{2+}). This is the process that occurs when a metal corrodes
Cupric hydroxide	$\text{Cu}(\text{OH})_2$ (sky blue colour)
Cupric ion	Cu(II) ion, Cu^{2+} (blue aqueous solution)
Cuprite/ cuprous oxide/ Cu(I) oxide	Cu_2O (magenta red to brown colour)
Cuprous ion	Cu(I) ion, Cu^+ (colourless solution disproportionating to Cu^{2+} even at low concentrations in water)
Malachite/ Basic copper carbonate	$\text{Cu}_2(\text{OH})_2\text{CO}_3$ (turquoise to green colour)
Microgram (μg)	$1 \mu\text{g} = 0.001 \text{ mg} = 0.000001 \text{ g}$
Milligram (mg)	$1 \text{ mg} = 0.001 \text{ g}$
Oxidation	The loss of electrons
Posnjakite	$\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ (from sky-blue to dark blue colour, might be slightly greenish-blue)
Reduction	The gain of electrons
Tenorite/ cupric oxide/ Cu(II) oxide	CuO (from jet black to brown colour)

Review of Current Knowledge

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