

# Up the Pipe: A literature review of the leaching of copper and zinc from household plumbing systems



Source: Copper Development Association ([www.copper.org](http://www.copper.org))

Prepared for The Cawthron Institute

By

Robina Ang, BEng, MSc  
Senior Technician  
Environmental Health – Water Group, ESR

October 2012

# **Up the Pipe: A literature review of the leaching of copper and zinc from household plumbing systems**

Project Leader: Dr Louis Tremblay (Cawthron Institute)

Peer Reviewers: Dr Chris Nokes, Dr Alma Siggins and Dr Jacqui Horswell

**DISCLAIMER**

This report or document ("the Report") is given by the Institute of Environmental Science and Research Limited ("ESR") solely for the benefit of The Cawthron Institute and other Third Party Beneficiaries as defined in the Contract between ESR and The Cawthron Institute and is strictly subject to the conditions laid out in that Contract.

Neither ESR nor any of its employees makes any warranty, express or implied, or assumes any legal liability or responsibility for use of the Report or its contents by any other person or organisation.

## **ACKNOWLEDGEMENTS**

This work was funded by a Ministry for the Environment (MfE) Waste Minimisation Fund grant, ESR Capability Funding and supported by the New Zealand Ministry for Business, Innovation and Employment (MBIE) funding. The author would like to thank the researchers Dr Emily Sarver, Dr David Kimbrough, Dr Marc Edwards, and Antonius Armanious for personally providing her their papers, Dr Alma Siggins and Dr Jacqui Horswell for their comments, and Dr Chris Nokes for his assistance in matters of chemistry.

## **Executive summary**

Some materials in New Zealand buildings' plumbing systems have the potential to leach significant amounts of copper and zinc into our wastewater systems. These materials are copper, copper alloys, and galvanised steel. The effects of leached copper and zinc on our soil, water and wider ecosystems are not yet fully understood, thus it is in our common interest to take precautionary actions to minimise this leaching.

Factors governing the leaching of copper and zinc from plumbing materials into water can be described as metallurgical, water chemistry-related, or physical/physiochemical. Metallurgical factors are well understood, and standards exist for the production of corrosion-resistant materials. However, the New Zealand Building Code does not require all plumbing components in new buildings to adhere to these standards. Water chemistry-related factors include many variables such as pH, alkalinity and concentrations of other ions. While concentrations of these species can be controlled, it is challenging to ensure the supply of ideal, non-corrosive water: currently, no standards or standardised tests for the corrosivity of water to plumbing materials exist. The third group of corrosion factors, physical/physiochemical factors such as differential flow, or the order of components within a system, are among the least well-understood of the corrosion factors, and can be unique to particular plumbing installations.

Recommendations for minimising the leaching of copper and zinc from household plumbing systems include:

- Using the Building Code to require corrosion-resistant materials to be used for all components in contact with water in household plumbing systems, including tapware and home water filtration units;
- Sharing information with suppliers, homeowners and plumbers about the importance of the use of corrosion-resistant materials in household plumbing systems via pamphlets in plumbing shops, information on websites, meetings with industry stakeholders etc.;
- Development and application of standard tests for the corrosivity of waters to the relevant materials;
- Development of protocols to prevent deleterious environments for young pipes and fittings, e.g. avoiding extended stagnation in newly installed systems; and
- Elucidating the effects of physical/physiochemical factors on copper and zinc leaching, especially in the increasingly popular 'all plastic' systems.

## Contents

Introduction.....	8
Aim .....	9
Structure of the literature review .....	9
Sources of environmental copper and zinc contamination .....	10
Plumbing materials in New Zealand.....	11
Allowable limits of copper and zinc in drinking water in NZ .....	12
Section 1: Types of corrosion .....	13
1.1 Modes of corrosion affecting copper .....	13
1.1.1 General corrosion.....	13
1.1.2 Pitting.....	13
1.1.3 Erosion corrosion .....	13
1.1.4 Oxygen differential-type concentration cell corrosion .....	14
1.1.5 Stress corrosion cracking .....	14
1.2 Modes of corrosion affecting brass.....	14
1.3 Modes of corrosion affecting galvanised steel.....	15
Section 2: Metallurgical factors .....	16
2.1 Copper.....	16
2.1.1 Standards for copper .....	16
2.2 Brass.....	16
2.2.1 Alpha/Beta brasses.....	17
2.2.2 Alpha brasses .....	17
2.2.3 Dezincification resistant brasses .....	18
2.2.4 Standards for brass .....	19
2.3 Hot-dip galvanised steel.....	23
Section 3: Water Chemistry .....	25
3.1 Concentration of dissolved oxygen.....	25
3.1.1 Effect on copper.....	26
3.1.2 Effect on brass.....	27
3.1.3 Effect on galvanised steel .....	28
3.2 pH.....	28
3.2.1 Effect on copper.....	28
3.2.2 Effect on brass.....	29
3.2.3 Effect on galvanised steel .....	29
3.3 Alkalinity .....	30
3.3.1 Effect on copper.....	30
3.3.2 Effect on brass.....	30
3.3.3 Effect on galvanised steel .....	31
3.4 Chlorine.....	31
3.4.1 Effect on copper.....	32
3.4.2 Effect on brass.....	33
3.4.3 Effect on galvanised steel .....	33
3.5 Hardness.....	34
3.5.1 Effect on copper.....	34
3.5.2 Effect on brass.....	35
3.5.3 Effect on galvanised steel .....	35
3.6 Sulphate ions.....	36
3.6.1 Effect on copper.....	36
3.6.2 Effect on brass.....	36
3.6.3 Effect on galvanised steel .....	37

4.1 Galvanic connections .....	38
4.2 Metal fittings in combination with plastic pipes.....	39
4.3 Manufacturing residues inside drawn copper pipes.....	40
4.4 Differential flow.....	40
4.5 Velocity of water.....	41
4.5.1 Effect on copper.....	41
4.5.2 Effect on brass.....	41
4.5.3 Effect on galvanised steel .....	41
4.6 Temperature .....	42
4.6.1 Effect on copper.....	42
4.6.2 Effect on brass.....	42
4.6.3 Effect on galvanised steel .....	43
Conclusions.....	47
References.....	49
Appendix A: Aggregate terms describing chlorine in water .....	54

## Introduction

Copper (Cu) and zinc (Zn), while essential micronutrients in plants and animals (including humans), are nonetheless known to be toxic to those same organisms at excessive concentrations (Gaetke and Chow 2003; Irwin et al. 1997; McClaren and Cameron 1996). Therefore, to safeguard human health, the Ministry of Health (MoH) has a maximum acceptable value for the concentrations of copper in drinking water supplied to New Zealand homes (MoH 2008). The drinking water standards also include a guideline value for concentrations of zinc, which MoH considers an aesthetic determinand (MoH 2008). There are also guidelines for concentrations of these heavy metals in freshwater and soil, although knowledge about the effects of these metals on soil micro-organisms is not yet complete and remains the subject of scientific research (Perrie and Cockeram 2010; NZWWA 2003).

Some monitoring of concentrations of copper and zinc in fresh water is performed in New Zealand. MoH publishes an annual review of drinking water quality, which includes information on copper concentrations in drinking water from suppliers who service more than 500 people and whose water contains copper at potentially health-significant concentrations (MoH 2008). Regional councils publish annual reports on the state of their freshwater bodies, albeit with differing quality variables and monitoring methods (Provost 2011). The 2009/10 annual freshwater quality monitoring report for the Wellington region by Perrie and Cockeram (2010) showed that some freshwater bodies are exceeding chronic toxicity guideline values for copper and zinc, as determined by toxicity studies on aquatic species (ANZECC 2000).

Despite this, the Ministry for the Environment does not hold any comprehensive reports on the *sources* of zinc and copper in the environment (M Carrington, personal communication, September 11, 2012). Recent studies suggest that ‘consumption emissions’ of metals leaching from consumer/household activities are beginning to outweigh ‘production emissions’ of metals contaminating water from industrial sites and activities (Sörme and Lagerkvist 2002). The annual review of drinking water supplies records copper concentrations in water supplies that service more than 500 people and that are known to contain copper at potentially problematic concentrations, but this information is collected at the level of distribution i.e. before the water passes through consumers’ household plumbing systems (MoH 2011). Studies have long shown that plumbing components leach significant zinc and copper (Turner 1961; Kimbrough 2008), and taps and associated fittings have been singled out as significant sources of these metals (MoH 2011). Although MoH acknowledges that heavy metals do leach from the pipes and fittings that comprise household plumbing systems, they do not monitor these, instead recommending that the public ‘flush’ a small amount of water out of their taps before drawing water for consumption (MfE 2012, MoH 2011).

While this approach protects human consumers in the short term, any heavy metals leaching from household plumbing systems are still going down the pipe to greywater and wastewater treatment plant outputs. Re-using domestic greywater for irrigation can save vast amounts of water, and applying treated sewage sludge (biosolids) to land can improve soil fertility and quality, but contamination of these resources with heavy metals complicates their re-use (NZWWA 2003). Therefore, in order to be able to use these resources to greatest effect, it is important to minimise copper and zinc leaching at every stage in the water supply and wastewater disposal system, including household plumbing systems. Regulatory bodies, homeowners, manufacturers and suppliers of plumbing materials, builders and plumbers all have important roles to play in maintaining the health of our shared environment by taking responsibility for what goes on Up the Pipe.

## **Aim**

The aim of this report is to provide a comprehensive literature review on the contribution of household plumbing systems to copper and zinc contamination in wastewater.

## **Structure of the literature review**

This review begins by investigating the sources of copper and zinc in our wastewater systems. It is followed by a list of the materials which are approved for use in new New Zealand buildings as of August 2012. The potential of these materials to leach copper and zinc is reviewed in subsequent sections. Section 1 describes the types of corrosion each of these materials are susceptible to. The following sections are each dedicated to one of the three groups of corrosion factors as described by Sarver and Edwards (2011), namely:

- **Metallurgical factors**  
These factors relate to the composition and structure of the metal components themselves e.g. the zinc content of brass.
- **Water chemistry**  
These include diverse variables such as pH, alkalinity, chloride concentration, dissolved oxygen concentration etc.
- **Physical or physiochemical factors associated with specific installations**  
These factors are related to whole plumbing system set ups – they are not concerned with a single component in itself. Examples include flow conditions, location of components within a system, combinations of materials, and water temperature.

Subsequently, the section entitled “Recommendations” lists some especially useful reviews and texts, and discusses possible avenues of action to reduce contamination of our wastewater with copper and zinc.

The “Conclusions” section gives an overview of the key findings of this literature review.

Boxes summarising key points can be found at the end of relevant sections.

## Sources of environmental copper and zinc contamination

Around the world, contamination of soils with heavy metals has increased in parallel with industrialisation (McClaren and Cameron 1996). The Ministry for the Environment (2004) lists as likely sources for the contamination of land with zinc and copper sites where:

- Agrichemicals have been manufactured, stored or persistently used;
- Metals have been worked or used (e.g. defence works, foundries, electronics manufacturing plants, motor vehicle workshops);
- Hazardous substances have been used or produced (e.g. tanneries, paint manufacturers, battery manufacturers/recyclers, mines, timber preserving sites); and
- Contaminated biosolids have been applied.

Urban freshwater systems in New Zealand also show significant contamination with zinc and copper. This is a serious concern, as in some locations, concentrations of dissolved copper and zinc are exceeding chronic toxicity guidelines (GWRC 2010).

It is difficult to precisely pinpoint sources of zinc and copper solely by analysing freshwater bodies (Scholes 1997). Scholes (1997) found that concentrations of zinc were high near industrial sites and stormwater outlets. A more recent study found that stormwater produced during rainfall events contained elevated levels of dissolved copper and zinc as compared to base flow conditions, particularly that from suburban residential areas, suggesting that urban houses/roofs and activities such as vehicle use are also significant contributors of heavy metal contaminants (Alsager 2012).

Roofs, vehicles and contaminated industrial sites release zinc and copper into stormwater and streams, or directly onto land. But where do the copper and zinc in our wastewater system originate from? As regulations and technology for industrial waste management improve, diffuse 'consumption emissions' of heavy metals are beginning to outweigh 'production emissions' (Sörme and Lagerkvist 2002). A case study of a wastewater treatment plant in Stockholm, Sweden, showed that leaching from household pipes and taps was the single biggest contributor of copper to wastewater, and also contributed around 5% of zinc (Sörme and Lagerkvist 2002). Studies have shown that plumbing fittings and taps are important sources of zinc and copper in wastewater systems (MoH 2011; Sarver and Edwards 2011; Oliphant 2003; Sörme and Lagerkvist 2002; Lytle and Schock 1996; Viraraghavan et al. 1996). Interestingly, this is also the case even in 'all plastic' plumbing systems where the only possible source of copper and zinc is brass taps (Kimbrough 2009). This finding is of special interest for New Zealanders, as systems with plastic pipes have been becoming more popular in new buildings here since the 1970s (BRANZ 2012).

Another potential source of copper and zinc in wastewater is largely unregulated home water filtration systems such as 'kinetic degradation fluxion' (KDF) filters, which contain small uninhibited brass granules that are purported to remove heavy metals such as lead and mercury from water but release zinc or copper ions in the process (KDF Fluid Treatment, Inc. 2012). Some of the filtration systems available in New Zealand are accredited by NSF International, but a number are not (P Coleman, personal communication, December 17, 2012).

These studies suggest that to reduce heavy metal contamination of wastewater, it is important to also consider non-industrial sources and examine choices of plumbing materials and fittings at the individual household level.

## Plumbing materials in New Zealand

All new building work in New Zealand must comply with the New Zealand Building Code (NZBC) (MBIE 2012 a). The part of the Building Code which is relevant to this review is Clause G12 – Water Supplies. A design method for water supply systems may be verified as satisfying the performance requirements of NZBC G12 if it complies with:

- a) AS/NZS 3500.1.2 [1998] Section 3 and Appendix B; and
- b) AS/NZS 3500.4.2 [1997] (MBIE 2012 b).

*Table 1: List of materials that comply with the New Zealand Building Code when installed correctly. Adapted from Appendix B of AS/NZS 3500.1:2003.*

Material	Relevant standard(s)	Contains Cu or Zn
Acrylonitrile butylene styrene (ABS)	AS 3518.1 AS 3518.2	No
Cast iron fittings (grey cast iron)	AS/NZS 2544	No
Copper pipes and fittings	AS 3795 NZS 3501 (pipes)	Yes
Copper and copper alloy fittings	AS 3688	Yes
Ductile iron pipes and fittings	AS/NZS 2280	No
Galvanized steel pipes and fittings	AS 1074 or NZS/BS 1387 or AS 4728 and AS/NZS 4792 HDG300	Yes
Polybutylene (PB) pipes	AS/NZS 2542: Parts 1-3 AS/NZS 2642.3	No
Polyethylene (PE) pipes and fittings (cold water only)	NZS 7601 (up to 0.9 MPa) NZS 7602 (up to 1.2 MPa) NZS 7610 (up to 1.2 MPa) AS/NZS 4130 AS/NZS 4129	No
Cross-linked polyethylene (PE-X) pipes and fittings	AS 2492 AS 2537	No
Macro-composite (PE-Al-PE or PEX-Al-PEX)	AS 4176	No
Unplasticised polyvinyl chloride (PVC-U) pipes and fittings (cold water only)	AS/NZS 1477	No
Modified polyvinyl chloride (PVC-M) pipes and fittings	AS/NZS 4765(Int).	No
Oriented polyvinyl chloride (PVC-O) pipes and fittings	AS 4441(Int).	No
Chlorinated polyvinyl chloride (PVC-C) pipes and fittings	ASTM D2846	No
Stainless steel (SS) pipes and fittings	ATS 5200.053 ATS 5400.461	No
Polypropylene (PP) pipes and fittings	Pr-EN 12202	No

Table 1 shows that of the pipes and fittings that are acceptable according to the NZBC, those that have the potential to leach copper or zinc are pure copper, copper alloys such as brass, and galvanised steel. Copper and polybutylene are the most common pipe materials (Palmer

2007), and in fact galvanised pipes are only to be used for non-drinking water systems that are installed above ground.

A standard for tapware, AS/NZS 3718, also exists but this was not included in the Building Code at the time this report was written. This tapware standard requires that copper alloy parts in contact with water be made of dezincification resistant brass which is certified to AS 2345 (Standards Australia 2006). Two reputable tapware suppliers in New Zealand, Methven and Greens Tapware, confirmed that their tapware products conform to AS/NZS 3718 (Methven staff member, personal communication, December 17, 2012; B Leggett, personal communication, December 17, 2012). However, there are dozens of taps available on sites such as TradeMe that are not known to be certified to any particular standard. In addition, the composition of components in widely available home water filtration systems is not covered in the New Zealand Building Code, and some are known to contain brass granules and leach copper and zinc (KDF Fluid Treatment, Inc. 2012).

### **Allowable limits of copper and zinc in drinking water in NZ**

For health reasons, the Drinking Water Standards for New Zealand (DWSNZ) require drinking water to contain copper at concentrations no greater than 2mg/L.

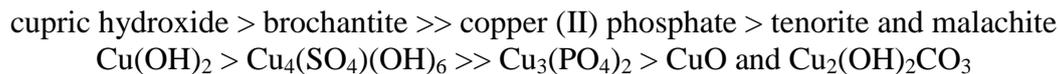
Zinc is considered an aesthetic determinand, and as such, is not subject to a maximum acceptable value (MAV). The suggested upper limit ('guideline value') for zinc in drinking water is 1.5 mg/L.

## Section 1: Types of corrosion

This section describes the basis for the corrosion resistance of copper, copper alloys, and galvanised steel, and the different modes of failure of this corrosion resistance for each material.

### 1.1 Modes of corrosion affecting copper

The corrosion resistance of copper comes from a protective layer of copper oxides or carbonates (Oliphant 2003). Over time and depending on a range of factors, the following compounds can coat a copper surface (Edwards et al. 2001). In order of decreasing solubility:



Young copper pipes are thought to be coated in scale in which cupric hydroxide dominates (Edwards et al. 2001). As the pipe ages, the cupric hydroxide is converted to other less soluble compounds, ideally to CuO and Cu(OH)<sub>2</sub>CO<sub>3</sub> (Edwards et al. 2001).

While this layer does protect the metallic copper, each of these compounds still contributes to free copper concentrations, with the most insoluble compounds (CuO and Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>) producing the lowest concentrations. When this protective layer is compromised or does not form correctly, copper can be subject to several kinds of corrosion. Some important modes of copper corrosion are described below.

#### 1.1.1 General corrosion

General corrosion is also known as cuprosolvency or blue water problems (Oliphant 2003). Copper is lost fairly evenly from the whole surface, resulting in blue-green water and stains on plumbing fixtures (Cohen 1993). The Australian Water Association (2010) states that staining of fittings and tiles usually occurs at copper concentrations greater than 1 mg/L.

#### 1.1.2 Pitting

Pitting is a mode of corrosion whereby metal is lost from small, clearly defined zones, resulting in a surface marked by small holes. It is caused by these small zones losing their passivity and becoming anodic to the surrounding metal. Pitting can occur under a range of conditions, thus there are sub-categories of pitting, including:

- Type I pitting, also known as cold water pitting, or hard water pitting
- Type II pitting, also known as hot water pitting, or soft water pitting
- Type III pitting, associated more often with blue water problems and blockages. It causes voluminous copper sulphate corrosion products
- Microbiologically induced pitting, whereby biofilms of bacteria cause a characteristic 'pepper pot' pitting corrosion site.
- Flux induced pitting, caused by excess flux (a substance used to ensure a strong bond during soldering of fittings/pipes to each other) running into the pipe or fitting  
(Oliphant 2003, DeBerry et al. 1982)

#### 1.1.3 Erosion corrosion

Erosion corrosion, also known as impingement attack, is recognised by areas which are bright, shiny and free of passivating corrosion products (Cohen 1993). These areas are frequently horse-shoe shaped (DeBerry et al. 1982). As the name implies, corrosion in this

case is facilitated by the abrasion of the passivating layer by excessive turbulence, high water velocity, bubbles, particulate matter etc.

#### **1.1.4 Oxygen differential-type concentration cell corrosion**

This mode of corrosion can arise wherever oxygen concentration gradients occur, e.g. under non-corrosion particulate matter such as building debris or rust, or in the crevices of a threaded pipe or fitting (Oliphant 2003). These concentration gradients can lead to corrosion as the occluded sites become anodic to the surrounding metal and attract negatively charged chloride ions – effectively accumulating hydrochloric acid at the site.

#### **1.1.5 Stress corrosion cracking**

Under certain conditions, residual stress in the pipe from the manufacturing or installation process can, in the presence of moisture and a stress cracking agent, facilitate corrosion (Oliphant 2003).

### ***1.2 Modes of corrosion affecting brass***

Of the various alloys of copper, copper-zinc alloys known as brasses are most common for plumbing applications (Copper Development Association 2005). Brasses are commonly used for fittings and are frequently found in taps (MoH 2011). The corrosion resistance of brass relies upon the formation of a compact oxide layer on the metal, comprised of copper and zinc oxides (Yohai et al. 2011).

Brass can undergo pitting under certain circumstances, but this is generally similar to that experienced by copper (DeBerry et al. 1982). Stress corrosion cracking and erosion corrosion can also affect some brasses in a similar way to copper (Andersen et al. 2011).

The most important kind of corrosion for brass in household plumbing systems is dezincification. Dezincification is a ‘de-alloying’ process, the net result of which is that the zinc is selectively dissolved away from the brass, causing zinc contamination of wastewater and leaving a reddish, porous, and weak copper solid (Sarver and Edwards 2011). The most widely accepted mechanism for dezincification is that copper and zinc are dissolved simultaneously at the anode site, but that the copper is re-deposited while the zinc is lost to the water (Lytle and Schock 1995).

The process of dezincification has been observed to have two phases: during the first phase, lead, nickel and zinc are preferentially lost; in the second phase, copper leaching dominates (Kimbrough 2009). Dezincification can also be subdivided into several kinds:

- Plug-type dezincification, where zinc is lost from a very localised pit (Cohen 1993);  
and
- Layer-type dezincification, where zinc is lost over the whole brass surface to an approximately equal depth (Cohen 1993; Sarver and Edwards 2011).

‘Meringue’ formation is the most commonly cited complication of dezincification (Turner 1961). This kind of dezincification leads to the formation of large, voluminous, white ‘meringue-like’ deposits inside pipes and fittings which can block the flow of water, and can occur with either plug or layer type dezincification (Sarver et al. 2010).

### **1.3 Modes of corrosion affecting galvanised steel**

The corrosion resistance of galvanised (zinc coated) steel arises from the deposition of a protective scale of a combination of  $ZnCO_3$ ,  $ZnO$  and  $CaCO_3$  (Cohen 1993, Standards Australia/Standards New Zealand 2006), as well as galvanic protection by which the zinc coating corrodes preferentially to the steel (see page 22 for details) (Marder 2000).

Galvanized steel can suffer pitting and oxygen differential-type concentration cell corrosion, and in some cases galvanised pipes can also form flow-restricting tubercles, similar to those in type III pitting in copper (Cohen 1993). The distinct metallic layers present in galvanised steel mean that galvanic corrosion between two exposed layers is also possible (DeBerry et al. 1982).

#### **Key points for Section 1: Types of corrosion**

- **Copper** is corrosion resistant when covered by a layer of insoluble copper oxides or carbonates.
- Copper can nonetheless experience various forms of corrosion depending on the chemistry of the water, the manufacturing of the parts, and the physical stresses in the plumbing system.
- **Brass**, a copper-zinc alloy, relies on a protective coating of oxides and carbonates for corrosion resistance.
- **Dezincification** is the most important kind of corrosion for brass parts in plumbing systems.
- **Galvanized steel** relies on a layer of calcium carbonate for corrosion resistance.
- Galvanized steel suffers similar types of corrosion to copper.
- **Good workmanship** (ensuring no debris in pipes, proper installation, no rough edges on cut pipes etc.) **is very important** in preventing oxygen differential-type concentration cell corrosion, stress corrosion cracking, and erosion corrosion.

## Section 2: Metallurgical factors

This section discusses the impact of composition and manufacturing processes on the corrosion resistance of copper, copper alloys, and galvanised steel. It also describes the relevant standards applicable to each material, in order to qualify as an acceptable solution according to the compliance document of the New Zealand Building Code (NZBC).

### 2.1 Copper

Using copper for pipes and fittings in household and commercial plumbing systems has long been popular (Oliphant 2003). This is because as it comes in contact with water, it usually forms a semi-passive layer of copper oxides or carbonates – depending on the water composition and other conditions (Oliphant 2003). This layer greatly slows the rate at which copper can dissolve into water. Indeed, copper plumbing installed in New Zealand art deco houses built in the 1930s may have retained this passive layer and still be in good working condition today (BRANZ 2012). However, plastic piping is now a common substitute in new buildings in New Zealand due to the comparatively high price of copper (BRANZ 2012).

The corrosion behaviour of copper pipes and fittings in New Zealand household plumbing systems is largely dependent on external factors such as water chemistry and physical/physiochemical factors, not the metallurgy of the copper itself.

#### 2.1.1 Standards for copper

The standard NZS3501 given in Table 1 as an acceptable solution under the NZBC requires copper tubing for water, gas and sanitation to be at least 99.85% copper (including silver), and sets limits for other allowable impurities (SANZ 1976).

#### ***Key points for Section 2.1: Metallurgical factors – copper***

- *Copper pipes and fittings should adhere to **NZS3501** and be at least **99.85% copper** to be acceptable under the NZBC.*
- *For such pure copper, **chemistry and physical/physiochemical factors are more important** in determining corrosion behaviour than metallurgical factors.*

### 2.2 Brass

Brasses are in general quite resistant to corrosion, but under certain conditions, some brasses still corrode and leach copper and zinc into plumbing systems (SANZ 1976). The composition and treatment of brasses are important factors in their corrosion behaviour. By definition, brasses are alloys of copper with zinc as the main alloying constituent. However, brasses may also contain traces of lead, iron, nickel, aluminium and other elements that can affect corrosion behaviour (Kimbrough 2007). Iron (Fe) and manganese (Mn) have been shown to accelerate dezincification, while low concentrations of arsenic, antimony, phosphorus, bismuth and tin have been observed to reduce the rate of dezincification (DeBerry et al. 1982).

There are two main kinds of brasses: alpha/beta and beta brasses, which are differentiated by their zinc content.

### 2.2.1 Alpha/Beta brasses

Alpha/Beta brasses generally contain less than 65% copper and greater than 35% zinc. Because these brasses exist as a mixture of distinct alpha (relatively low zinc) and beta (relatively high zinc) phases, they are also known as duplex brasses (Copper Development Association 2005). The beta phase crystals are extremely ductile at high temperatures – a quality which makes alpha/beta brasses with suitable for hot working (a manufacturing technique whereby metals are shaped at temperatures close to their molten state) (Copper Development Association 2005).

Although alpha/beta brasses are cheap and convenient to work, they are particularly susceptible to dezincification (Hendrix group 2011). Moreover, they cannot be made ‘dezincification resistant’ by the addition of inhibitors (Turner 1961). This is because such inhibitors do not protect the beta phases (Joseph and Kundig 1999). However, special heat treatments and compositions can be employed to ‘shelter’ the vulnerable beta phase crystals with more dezincification resistant alpha phase crystals (see Section 2.2.3 DZR brasses) (Joseph and Kundig 1999).

### 2.2.2 Alpha brasses

Alpha brasses generally contain at least 65% copper and less than 35% zinc. These brasses exist as a single phase: the zinc atoms are distributed throughout the copper as a solid solution. The properties of alpha brasses make them excellent materials for cold working (Copper Development Association 2005). They are also more resistant to dezincification than alpha/beta brasses – the lower the zinc content, the more dezincification-resistant the alloy (Oliphant 2003).

Alpha brasses can be further subdivided into different classes, including ‘yellow’ and ‘red’ or ‘leaded red’ brasses.

#### 2.2.2.1 Yellow brasses

Yellow brasses are the alpha brasses with the lowest content of copper, typically 61-70% (Kopeliovich 2012; Alu-bra 2010; Olin Corporation 1966). Welding of yellow brasses can cause crystals of beta phase to form, which reduces corrosion resistance (Austral Wright Metals 2008). Yellow brasses have been reported to be susceptible to dezincification and associated plumbing failure (Anchor Bronze and Metals Inc. 2012a), and this has led to a number of lawsuits in the USA (Yellow Brass Claims 2012).

An example of the composition of a commercially available yellow brass, C268 is given in Table 2 below (Metal Suppliers Online 2012).

Table 2: Composition of copper alloy C268, a yellow brass

Element	Minimum (%)	Maximum (%)
Copper	64	68.5
Iron	-	0.05
Lead	-	0.15
Zinc	Remainder	

### 2.2.2.2 Red brasses

Red brasses, also known as gunmetals or leaded red brasses, contain over 85% copper, have a higher proportion of lead as compared to yellow brasses, and are generally resistant to dezincification (Oliphant 2003; DeBerry et al. 1982). Cohen (1993) recommends that only red brasses be used for plumbing applications. Unfortunately, red brasses are more expensive than yellow brasses: as of the 8<sup>th</sup> of October 2012, scrap yellow brass was selling for NZ\$4.04/kg, while scrap red brass was selling for NZ\$4.60/kg (Scrapmonster.com 2012).

An example of the composition of a commercially available red brass, leaded red brass (C83600) is given below in Table 3 (Anchor Bronze and Metals Inc. 2012b).

Table 3: Composition of copper alloy C836000, a leaded red brass

Element	Minimum (%)	Maximum (%)
Copper	84	86
Zinc	4	6
Aluminium	-	.005
Antimony	-	.25
Iron	-	.30
Lead	4	6
Nickel	-	1
Phosphorus	-	.05
Silicon	-	.005
Sulphur	-	.08
Tin	4	6

### 2.2.3 Dezincification resistant brasses

Dezincification resistant (DZR) brasses are a particular kind of brass with around 63% copper, and a small amount of arsenic (0.02-0.15%), the remainder being zinc (Andersen et al. 2011). Developed in the early 1970s by the brass industry and the British Non-Ferrous Metals Research Association, these brasses contain enough beta phase to perform well under hot working conditions, but subsequently undergo a carefully controlled heat treatment to convert the metal to a more corrosion-resistant all-alpha structure (Hendrix Group 2012). As the name implies, DZR brasses are especially resistant to the selective leaching of zinc in aggressive aquatic environments (Callcut 2000).

An example of the composition of a commercially available dezincification resistant brass, alloy 352 is given below in Table 4 (Tata Steel 2010).

Table 4: Composition of alloy 352, a DZR brass

Element	Minimum (%)	Maximum (%)
Copper	61	63
Lead	1.7	2.8
Arsenic	0.02	0.15
Zinc	Remainder	

## 2.2.4 Standards for brass

The NZBC compliance document outlines standards for acceptable brass pipes and fittings as given in Table 1.

A small but significant gap in the NZBC is the ambiguity around tapware. According to Clause G12 of the compliance document of the NZBC, a design method for water supply systems may be verified as satisfying the NZBC without specifying what materials are to be used in the taps (DBH 2011a). This oversight could contribute significantly to heavy metal contamination of wastewater, as taps with cheap yellow brass components (e.g. C36000, a high-zinc, uninhibited brass) have been shown to be significant contributors of copper, zinc and lead to household plumbing systems (Sarver and Edwards 2011). A standard for tapware, AS/NZS3718:2005, does exist. It specifies that tap components in contact with water must be corrosion resistant and conform to other standards. This ambiguity around tapware has been recognised by the Ministry of Business, Innovation and Employment, and AS/NZS3718:2005 will be included in the next revision of the Building Code compliance documents (MBIE staff, personal communication, October 26, 2012).

Since tapware is important for both functional and aesthetic reasons, choosing tapware for a new or renovated home is sometimes undertaken by homeowners instead of plumbing professionals. These buyers should understand the importance of choosing tapware with components certified to standards that ensure that copper and zinc leaching is minimised. Possible conduits for this information include printed material for plumbers and prospective customers at plumbing supply shops, the Building Research Association of New Zealand (BRANZ), the Consumer Institute, and a website dedicated to information about plumbing best practices.

Another gap in the NZBC is the lack of standards regulating materials in home water filtration systems. For example, 'kinetic degradation fluxion' (KDF) filters – a kind of filter readily available from New Zealand suppliers – contain small uninhibited brass granules that are purported to remove heavy metals such as lead and mercury from water but release zinc or copper ions in the process (KDF Fluid Treatment, Inc. 2012). Some of the filtration systems available in New Zealand are accredited by NSF International, but a number are not (P Coleman, personal communication, December 17, 2012)

### 2.2.4.1 Tubes

The NZBC states that correctly and appropriately installed brass tubes that conform to the standard AS3795:1996 are acceptable solutions (MBIE 2012a). AS3795:1996 specifies that for brass tubes to be used in plumbing and drainage applications, they must have the chemical composition outlined in Table 5 below:

*Table 5: Composition for brass tubes required by standard AS3795:1996 (Standards Australia 1996)*

Element	Minimum (%)	Maximum (%)
Copper	69.0	71.0
Lead	-	0.05
Iron	-	0.05
Arsenic	0.02	0.06
Zinc	Remainder	

This is an alpha brass with increased resistance to dezincification due to the addition of arsenic (Hendrix Group 2012).

As an additional safeguard against the leaching of heavy metals from copper alloy tubes into household water, clause eight of the standard AS3795:1996 states that copper alloy tubes shall comply with AS3855 – *Suitability of plumbing and water distribution systems products for contact with potable water* (Standards Australia 1996). This standard specifies basic requirements for plumbing and water distribution system products in contact with hot or cold potable water to ensure the quality of potable water e.g. not greater than 4.5% lead in all metallic materials (Standards Australia 1994). However this standard was withdrawn on the 29<sup>th</sup> of October 2002 and this has not yet been reflected in AS3795:1996.

#### **2.2.4.2 Fittings**

Acceptable solutions for copper and copper alloy fittings are governed by a different standard, AS3688:2005 – *Water supply: metallic fittings and end connectors*. This standard specifies requirements for:

*...metallic body pipe fittings and connectors for use with copper tube and stainless steel pipes, and tubes and adaptor fittings for connection to other pipe materials in water supply and gas systems...*

(Standards Australia 2005)

This standard states that if these components are made of copper alloys and are in contact with water in water supply systems, they must comply with AS2345:2006 – *Dezincification resistance of copper alloys*. A copper alloy can be said to comply with standard AS2345:2006 under one of two categories:

- **Category I:** those copper alloys that are accepted as dezincification resistant based on their chemical composition alone. Category I alloys must contain no more than 15% zinc.
- **Category II:** those copper alloys that do not meet the compositional requirements but pass the dezincification resistance test described in Appendix C of AS2345:2006.

Some examples of Category I alloys as given by the standard AS2345:2006 are given in Table 6 below.

The standard AS3688:2005 also specifies that materials in contact with drinking water shall comply with AS/NZS4020:2005, which limits copper levels in drinking water to no more than 2mg/L at the point of use (e.g. kitchen or bathroom tap), in line with the drinking water guidelines of New Zealand and Australia (Standards Australia/Standards New Zealand 2005; MoH 2008). AS/NZS5020:2005 does not include limits on the leaching of zinc from components in contact with drinking water.

### **Key points for Section 2.2: Metallurgical factors – copper alloys**

- There are **many different brasses**, which differ based on composition and heat treatment. These different brasses have different corrosion behaviour.
- The **less zinc a brass contains, the more dezincification resistant it is**. Brasses with **≤15% zinc** are generally considered dezincification resistant, and are therefore preferred for plumbing applications.
- Brasses can be made **dezincification resistant (DZR)** by carefully controlling their composition and heat treatment before use.
  
- The NZBC specifies standards for acceptable solutions for some brass plumbing components. **Components should be certified to these standards to minimise corrosion and copper/zinc leaching.**
  - For pipes - AS3795:1996. This standard references AS3855, a standard specifying requirements for plumbing components in contact with potable water, but has been withdrawn. AS3795 should reflect this.
  - For fittings - AS3688:2005. This standard specifies that:
    - Materials in contact with water must comply with AS2345:2006.
    - Materials in contact with drinking water must comply with AS/NZS4020:2005.
  
- **Standards for tapware and home water filtration units are not yet specified under the NZBC**, despite the fact that these are important sources of copper and zinc contamination of wastewater.

Table 6: Examples of Category I alloys determined to be DZR brasses based on chemical composition (Standards Australia 2006).

Alloy designation	Alloy name	Chemical composition, percent																	
		Copper		Lead		Iron		Tin		Zinc		Aluminium		Phosphorous		Nickel	Bismuth	Silicon	Antimony
		Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Max.	Max.	Max.	Max.
<i>Wrought alloys</i>																			
C220000	90/10 gilding metal	89.0	91.0	—	0.05	—	0.05	—	—	REM	—	—	—	—	—	—	—	—	—
<i>Cast alloys</i>																			
C83600*	85/5/5/5 leaded gunmetal	84.0	86.0	4.0	6.0	—	0.30	4.0	6.0	4.0	6.0	—	0.005	—	0.05	1.0	—	—	0.25
C83810	83/3/9/5 leaded gunmetal	REM	—	4.0	6.0	—	0.3	2.0	3.5	7.5	9.5	—	0.005	—	—	2.0	0.10	0.01	—
C92410†	87/7/3/3 leaded gunmetal	REM	—	2.5	3.5	—	0.20	6.0	8.0	1.5	3.0	—	0.005	—	—	2.0	0.05	0.005	0.25
C92610†	88/10/2 gunmetal	REM	—	—	1.5	—	0.15	9.5	10.5	1.7	2.8	—	0.005	—	—	1.0	0.03	0.005	—
CW602N‡		61.0	63.0	1.7	2.8	—	0.1	—	REM	REM	—	—	0.05	—	—	0.3	—	—	—

\* S 0.08%

† Mn 0.03%

‡ As 0.02% min–0.15% max

NOTE: REM indicates that the remainder of the alloy is comprised of the particular element.

### 2.3 Hot-dip galvanised steel

Hot-dip galvanising is the process of submersing materials in a bath of almost 100% molten zinc - small amounts of other elements can occasionally be present in the molten zinc. In the case of steel, an alloy of iron with carbon and other elements, hot-dip galvanising provides a metallic coating to the steel. The coating consists of three distinct iron-zinc alloy layers (Figure 1), with those closest to the steel exhibiting the highest iron and lowest zinc content (Roberge 2012; Marder 2000).

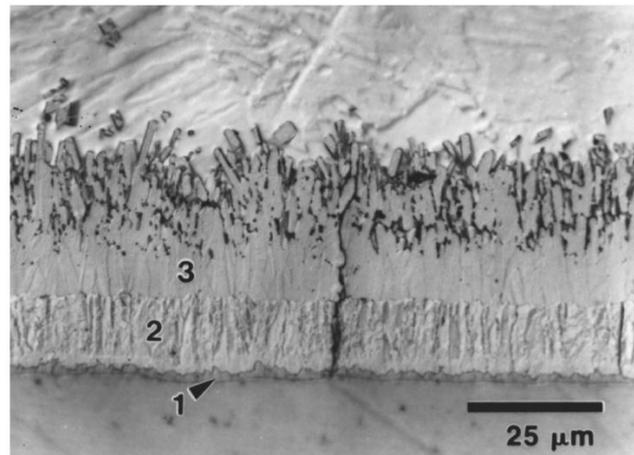


Figure 1: Microstructure of the typical morphology for pure Zn hot-dipped galvanised steel showing distinct alloy layers: 1= gamma phase (23.5-28.0 wt% iron); 2=delta phase (7.0-11.5 wt% iron); 3=zeta phase (5-6 wt% iron). Image from Marder (2000).

Galvanised steel pipes were used for household plumbing systems up to around the 1930s, after which they were largely replaced by copper and, eventually in the 1960s, polybutylene (BRANZ 2012). Plastics such as polybutylene are cheaper than galvanised steel, and copper has a longer potential service life (BRANZ 2012). It is nowadays uncommon for hot-dip galvanised steel to be employed for household plumbing systems, although they remain an acceptable solution according to the NZBC (BRANZ 2012; DBH 2011a).

The corrosion-resistance benefits of galvanising steel are twofold.

- (1) A *protective layer* consisting of insoluble  $ZnO$  and  $ZnCO_3$  is formed by zinc in the presence of oxygen and carbon dioxide (Standards Australia/Standards New Zealand 2006).
- (2) The zinc layer provides *galvanic protection* to the steel in an aqueous environment such as a plumbing pipe by sacrificially corroding, even if the steel surface is exposed to the environment (Marder 2000). This is because zinc occupies a lower position on the galvanic scale relative to steel i.e. zinc loses electrons more readily than the iron in steel (Roberge 2006).

The service life (time to 5% of rusting of the steel surface) of a galvanised material is directly proportional to the coating thickness (Marder 2000).

#### 2.3.1 Standards for hot-dip galvanised steel

Clause G12 of the compliance document of the NZBC describes several standards through which galvanised steel can be considered an acceptable solution for pipes and fittings (DBH 2011b). One of these standards, AS/NZS4792:2006, describes the HDG300 ( $300g/m^2$  zinc) coating requirement. Such a coating would have a service life of around 15 years in a

suburban setting (Marder 2000). This aligns with Clause 2 of the NZBC which states that the durability of an important but non-structural and moderately difficult to access building element must be 15 years (DBH 2011a). However, this is still a relatively short time frame compared to the potential service life for copper pipes, which may still be in working condition in art deco houses from the 1930s (BRANZ 2012).

***Key points for Section 2.3: Metallurgical factors – hot-dip galvanised steel***

- ***Galvanised steel pipes and fittings are uncommon in modern buildings because of the development of alternatives which are:***
  - *Cheaper (plastic); or*
  - *Longer lasting (copper).*
- ***Thicker zinc layers provide longer lasting corrosion protection.***
- ***Hot-dip galvanised steel components should adhere to AS/NZS4792:2006 (300g/m<sup>2</sup> zinc coating) to be acceptable according to the NZBC.***

## **Section 3: Water Chemistry**

This section on water chemistry discusses the impact of variables commonly studied in the literature on corrosion of copper, brass, and galvanised steel in plumbing systems. It is sometimes difficult to elucidate the effect of a single water chemistry variable due to the interaction of chemical species. As far as possible, the section has been structured so as to focus on the effect of one variable on one material at a time.

The chemistry of water entering household plumbing systems in New Zealand varies widely according to the source of the water, the materials used to conduct the water to the house etc. The Ministry of Health releases an annual review of drinking water quality in New Zealand that contains detailed information on compliance with the Drinking Water Standards of New Zealand (DWSNZ). The DWSNZ include water chemistry requirements (e.g. pH limits) which would help to control the leaching of heavy metals from plumbing components (MoH 2008).

These reviews cover around 91% of the population of New Zealand, as some water suppliers do not provide the necessary information, and some small and rural communities receive water from an unregistered supply such as private rainwater tanks (MoH 2011). For the purposes of this review, it is worth considering unregistered supplies of roof-collected rainwater for two reasons. Firstly, roof-collected rainwater is frequently the only available domestic water source in rural households in New Zealand, and as such affects a significant number of household plumbing systems (Simmons et al. 2001). Although these households are unlikely to be connected to reticulated wastewater systems and may thus not be included in municipal-level biosolid re-use, metals leaching from them may still get into soils from septic tank discharges or greywater diversion. Secondly, roof-collected rainwater can also be used for non-drinking purposes such as toilet flushing or laundry, even in urban areas with reticulated water supply. While water used for these purposes does not have a direct impact on human health through consumption, it still passes through household plumbing systems and therefore has the potential to contribute to copper and zinc contamination of wastewater and our environment. Thus, even if all water from registered water suppliers complied fully with the DWSNZ, unregistered roof-collected rainwater could still be exceeding guideline values in the DWSNZ and cause significant copper and zinc contamination in waterways and soils.

### ***3.1 Concentration of dissolved oxygen***

The Ministry of Health gives no maximum acceptable value (MAV) or guideline value for concentration of dissolved oxygen in drinking water, although dissolved oxygen content can affect consumers' perception of drinking water quality (Hoko 2005). Some dissolved oxygen is likely to be present in household water, unless the water is from groundwater which has not been exposed to the atmosphere for an appreciable length of time, is very hot, or has been stagnant for a very long time e.g. when a plumbing system in a new house is filled with water to check for leaks, but does not become inhabited for some months (Atlas et al. 1982). As there is no MAV for dissolved oxygen in drinking water, it is not typically measured by water suppliers in New Zealand (N Ulrich, personal communication, December 17, 2012). In the literature, typical ranges of dissolved oxygen concentrations in water from water treatment plants are in the order of 1-4 mg/L (Champaign, Illinois, United States of America) and 4.8-9 mg/L (Karlsruhe, Germany) (Sarin et al. 2004; Merkel et al. 2002).

### 3.1.1 Effect on copper

Dissolved oxygen concentration, together with pH, impacts the corrosion behaviour of copper in cold water<sup>1</sup> as shown in the simplified schematic (Figure 2) below:

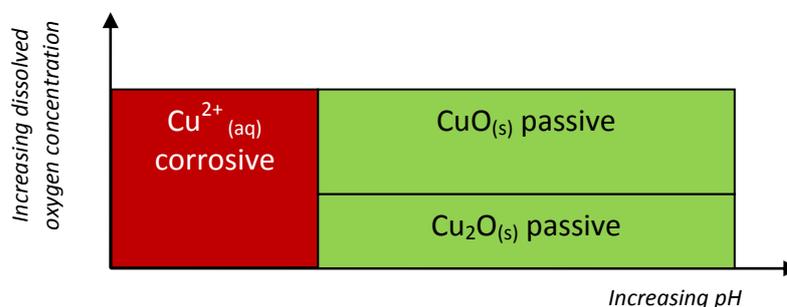


Figure 2: Adapted from Oliphant (2003). Schematic of stable species of copper as a function of pH and dissolved oxygen concentration in cold water. (s) = solid, (aq) = dissolved.

These combinations of dissolved oxygen concentration and pH affect copper corrosion in the following ways:

- Dissolved oxygen present, pH <6  
Copper will dissolve into soluble Cu<sup>2+</sup>, which will then be present in tap water and consequently in wastewater (Oliphant 2003).
- ≤2mg dissolved oxygen/L, pH between 6 and 8  
Copper will form a protective layer of Cu<sub>2</sub>O which will retard further corrosion (Oliphant 2003).
- ≥2mg dissolved oxygen/L, pH >8  
A highly protective scale of insoluble CuO will form (Oliphant 2003).

Ministry of Health guidelines (2008) state that the pH of drinking water should be between 7.0 and 8.5, and preferably between 7.0 and 8.0 if chlorine is being used for disinfection. Under these conditions, a protective layer that greatly limits the further dissolution of copper should form (Oliphant 2003). Roof-collected rainwater in New Zealand has been found to have pH in the range from pH 5.2 to pH 11.4, thus ranging from corrosive (pH <6) to promoting the formation of insoluble protective scales (pH >8) (Simmons et al. 2001).

Despite several studies stating that the total absence of oxygen in potable water theoretically proscribes copper corrosion (DeBerry et al. 1982), empirical research shows that significant and measurable copper corrosion can still occur in stagnant water with very little or no dissolved oxygen, albeit at a lower level than in the presence of oxygen (Hultquist et al. 2011; Szakálos et al. 2007; Merkel et al. 2002; Atlas et al. 1982). After all dissolved oxygen has been consumed, corrosion of copper can continue by consuming oxygen from the water molecules themselves, generating hydrogen gas in the process (Hultquist et al. 2011; Szakálos et al. 2007; Merkel et al. 2002; Atlas et al. 1982). Long term stagnation studies by Merkel et al. (2002) showed that copper pipes leach copper, even at pH 7.3 and with little dissolved oxygen. Concentrations of leached Cu<sup>2+</sup> in water in stagnation tests increased initially then decreased to a steady state when most dissolved oxygen is consumed (Merkel et

<sup>1</sup> In hot water, CuO (which is insoluble in water and therefore corrosion-resistant) is the primary corrosion product (Oliphant 2003).

al. 2002). This steady concentration was around 0.25mg/L, which is below the DWSNZ maximum acceptable value of 2mg/L (MoH 2008).

The same study showed that as the pipes aged, the copper leaching peaked at lower concentrations, as shown in Figure 3 (Merkel et al. 2002). It is therefore recommended that prolonged periods of stagnation and low dissolved oxygen concentrations are avoided in young pipes e.g. when newly installed plumbing systems are filled to check that there are no leaks, but are then left standing until the building becomes occupied (Oliphant 2003). Alternative dry testing methods, such as that using air pressure to identify leaks, are recommended instead (DBH 2010).

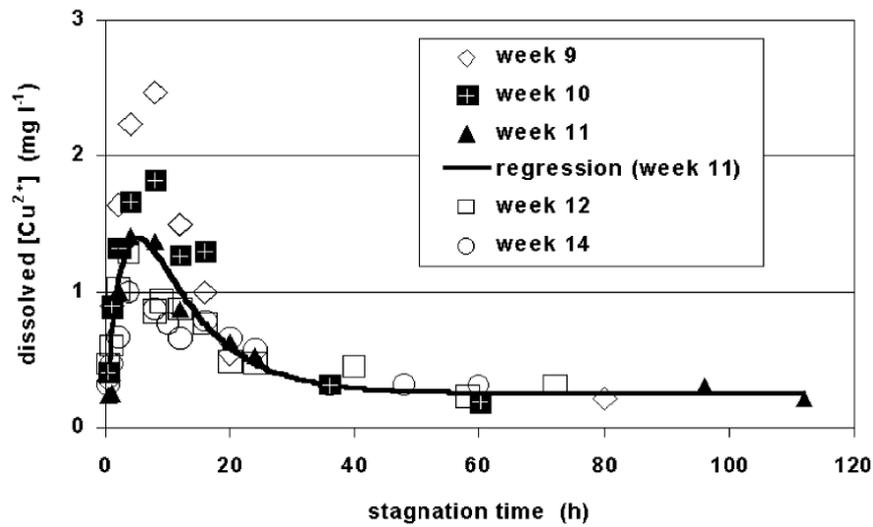


Figure 3: Stagnation curves for copper release from copper pipes after 9, 10, 11, 12 and 14 weeks of alternating flow and stagnation periods. Image from Merkel et al. (2002). The decrease in these typical ‘Werner curves’ is observed after all dissolved oxygen is consumed (Merkel et al. 2002).

It should be noted that if free chlorine (hypochlorous acid, HOCl, or the hypochlorite ion, OCl<sup>-</sup>) is present in the water, the free chlorine plays a much more important role in regulating copper corrosion than dissolved oxygen because of its greater oxidising strength (Atlas et al. 1982). See Section 3.4 for more information on the effects of chlorine on copper corrosion.

### 3.1.2 Effect on brass

A search for literature on the effect of dissolved oxygen on brass corrosion yields few results. This is probably for several reasons, including the following:

- High concentrations of dissolved oxygen will increase the corrosion rate of brasses, as for copper and most other metals, since dissolved oxygen is a direct participant in metal corrosion (MRWA 2002);
- As for copper, the effect of dissolved oxygen concentrations typical of drinking water on brass corrosion rates is likely to be minor compared to other variables e.g. pH or free chlorine concentration (Atlas et al. 1982); and
- Dissolved oxygen concentrations in the water that supplies household plumbing systems are not commonly modified and are therefore difficult to change, as opposed to adjustment of pH, chlorine concentrations etc.

### 3.1.3 Effect on galvanised steel

The effect of dissolved oxygen on galvanised steel is similar to that for brass and copper. The American Galvanizers Association (2012) describes dissolved oxygen as more aggressive to galvanised steel than carbonic acid. However, it is likely that other factors are more important in controlling the corrosion of galvanised steel in households plumbing systems, such as alkalinity and pH (DeBerry et al. 1982).

#### **Key points for Section 3.1: Water chemistry – effect of dissolved oxygen**

- **Dissolved oxygen** is consumed in the formation of corrosion products on copper, brass and galvanised steel.
- Dissolved oxygen **concentrations decrease over time** in stagnant pipe water.
- The **effect of dissolved oxygen on corrosion is relatively minor** compared to that of other water chemistry factors such as pH and free chlorine concentrations etc.

## 3.2 pH

MoH guidelines (2008) state that the pH of drinking water should be between 7.0 and 8.5, and preferably between 7.0 and 8.0 if chlorine is being used for disinfection. According to Oliphant (2003), a copper pipe under these conditions should form a protective layer which greatly limits the further dissolution of copper.

Non-registered supplies of roof-collected rainwater in New Zealand have been found to have pH levels with a much greater range - between pH 5.2 and pH 11.4 (Simmons et al. 2001).

### 3.2.1 Effect on copper

It is widely agreed that a pH between 7 and 8 is ideal for domestic water supplies (MoH 2008; Cantor et al. 2000; Atlas et al. 1982). As previously described in Section 3.1.1, a low pH (<6) increases the rate of corrosion of copper (Rahman et al. 2007; Boulay and Edwards 2000; DeBerry et al. 1982). Low pH has also been shown to exacerbate corrosion in the presence of disinfectants such as free chlorine, monochloroamines, and chlorine dioxide (Rahman et al. 2007)

However, pH also interacts in a complex manner with other chemical species involved in corrosion. An excessively high pH (>8.0) greatly diminishes the effectiveness of chlorine as a disinfectant (Cantor et al. 2000), and the DWSNZ reflect this (MoH 2008). In addition, high pH, in combination with soft, cold alum coagulated waters of low alkalinity and conductivity, is associated with type III pitting (Oliphant 2003), but this is a rare type of copper corrosion, which has only been recorded in Germany and Scandinavia (Joseph 1999).

The effects of pH on cuprosolvency are complicated by the very complex relationship of pH and dissolved inorganic carbon (DIC)<sup>2</sup>, which is present in virtually all drinking waters (Schock et al. 1995). Cu<sup>2+</sup> forms several very strong and some weaker aqueous complexes with the carbonate species HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>. Schock et al. (1995) report that at high pH or in new plumbing, where cupric solubility is controlled either by Cu(OH)<sub>2</sub> or CuO, DIC complexes dominate copper speciation above approximately pH 6.5, resulting in increased

<sup>2</sup> Dissolved inorganic carbon is the sum of the following species, expressed here as equilibria:  
$$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \rightleftharpoons 2\text{H}^+ + \text{CO}_3^{2-}$$

solubility of copper. However, they also note that, logically, moderate DIC levels would accelerate the formation of a passivating  $\text{Cu}_2(\text{OH})_2\text{CO}_3$  film in the pH/DIC region where this compound is thermodynamically stable, so conditions favouring the formation of  $\text{Cu}_2(\text{OH})_2\text{CO}_3$  or  $\text{CuO}$  relative to  $\text{Cu}(\text{OH})_2$  would result in a net lower copper(II) solubility (Schock et al. 1995).

### 3.2.2 Effect on brass

Overall, brass also behaves as a typical metal with respect to pH. In stagnant tests, leaching levels of both copper and zinc were significantly higher at lower pH (Schock et al. 1995). Zhang and Edwards (2011) showed that the leaching of zinc from stagnant C36000 brass<sup>3</sup> is significantly lower at higher pH.

However, brasses leach their component metals at different rates, depending on pH. For C36000, the ratio of leached zinc to zinc in the original alloy increases from pH 6.0 to a peak at pH 8.0, before decreasing until pH 10 where virtually no zinc was leached (Zhang and Edwards 2011). The same study also determined that the critical pH range for meringue dezincification of C36000 is relatively high (pH 8-9) (Zhang and Edwards 2011). This finding corroborates the observations of Turner (1961), and Oliphant (2003).

Another alloying constituent whose leaching is affected by pH is lead. Red brasses have been shown to leach greater amounts of lead at low pH levels, whereas in yellow brasses, pH has little effect on lead leaching (Schock et al. 1995).

### 3.2.3 Effect on galvanised steel

Schock et al. (1995) reported that stagnant coupon tests of pure zinc in water showed the highest corrosion rate at the lowest pH. Corresponding results were obtained by Zhang and Edwards (2011) who found that zinc solubility in stagnant tests decreased markedly at pH levels above pH 8.0. This parallels the decrease in selective leaching of zinc from brass at higher pH levels (Zhang and Edwards 2011). The overall corrosion rate of zinc in short-term tests is lowest between pH 7 and pH 12, although there is a significant increase in zinc corrosion even as pH decreases from 8 to 7, apparently regardless of other parameters such as alkalinity and hardness, although the composition of the corrosion deposits is altered by changes in these parameters (DeBerry et al. 1982).

The corrosion behaviour of galvanised steel is different to that of copper and brass because of its structure of distinct layers as described by Marder (2000). As the outermost, pure zinc layer corrodes, corrosion products are deposited which protect the surface somewhat, thus slowing the corrosion to a steady, pH dependent rate. When the underlying zinc/iron alloy phase is reached, the rate drops again to a new, steady, pH dependent rate (DeBerry et al. 1982).

---

<sup>3</sup> Composition of C36000: 61.5% Cu,  $\geq 2.5\%$  Pb,  $\leq 0.35\%$  Fe, 35.4% Zn (Anchor Bronze and Metals Inc. 2012). This alpha/beta brass is commonly used in plumbing fittings in the USA (Zhang and Edwards 2011).

### **Key points for Section 3.2: Water chemistry – effect of pH**

- *pH should ideally be maintained between pH 7-8 to minimise copper corrosion, meringue dezincification, and galvanised steel corrosion while not compromising chlorine disinfection*
- *pH <7 leads to increased general corrosion of copper, brass and galvanised steel.*
- *pH >8 can lead to type III copper pitting and meringue dezincification of brass.*
- *Water samples from un-registered roof-collected rainwater tanks in New Zealand frequently have pH levels outside this ideal range.*

### **3.3 Alkalinity**

Alkalinity is a measure of buffering capacity, usually from carbonate ( $\text{CO}_3^{2-}$ ) or bicarbonate ( $\text{HCO}_3^-$ ) ions. Reported as mg/L  $\text{CaCO}_3$ , it is measured as the amount of acid needed to bring the water sample to a pH of ~4.2 (US EPA 2012). It is an important variable in determining the corrosivity of water to metals. Alkalinity protects plumbing systems from sudden severe drops in pH, and the presence of carbonate ions is necessary for the formation of corrosion-resistant carbonate layers.

In water, bicarbonate concentrations, and therefore alkalinity, are increased when acidic rain water dissolves naturally occurring carbonates such as  $\text{CaCO}_3$  (limestone) in soils and riverbeds (Weiner and Matthews 2003). Therefore, rainwater collected directly in tanks has very low alkalinity (Weiner and Matthews 2003).

There are no regulations for levels of alkalinity in New Zealand drinking water (MoH 2008). It is known that many of New Zealand's waters are soft and have moderate to low levels of alkalinity (MoH 2008).

#### **3.3.1 Effect on copper**

Soft waters with very low levels of bicarbonate can prevent the production of the basic protective copper carbonate layer in copper pipes (Oliphant 2003). Edwards et al. (2001) found that bicarbonate has a positive influence on the transition of the cupric hydroxide scale present on young pipes to less soluble compounds over the short and long term. Copper subjected to low alkalinity waters are also at risk of type III pitting if other factors such as cold alum coagulation, low conductivity, high pH and free chlorine are also present (Lytle and Nadagouda 2010; Oliphant 2003, Sarver et al. 2010).

High alkalinity is not necessarily less corrosive to copper in all cases. Grace et al. (2012) note that research and field experience have shown that high-alkalinity waters can be associated with elevated copper levels in drinking water. Broo et al. (1997) reported that high alkalinity in combination with low pH favours uniform copper corrosion. Also, Oliphant (2003) reported that an alkaline environment can facilitate corrosion of copper if there is also residual stress in the pipe from manufacturing, a stress cracking agent such as ammonia or mercury, and moisture present.

#### **3.3.2 Effect on brass**

A recent comprehensive review of brass dezincification corrosion in potable water systems concluded that high chloride, low hardness and low alkalinity waters are especially prone to

dezincification (Sarver et al. 2010). More specifically, Zhang and Edwards (2011) investigated the solubility of zinc in waters of varying alkalinity using jar tests, in order to better understand how zinc might leach from brass. Zinc sulphate was added to other chemicals in nanopure water, and the jars left to stagnate before filtering the water and quantifying the soluble zinc using ICP-MS. Results confirmed that higher alkalinity reduced zinc solubility (Zhang and Edwards 2011). Additional work by the same authors showed that high alkalinity made it more likely for passive scale layers to form on solid brass, reduced rates of galvanic corrosion between brass and copper, and protected the brass surface from marked drops in pH (Zhang and Edwards 2011).

### 3.3.3 Effect on galvanised steel

As for brass, high alkalinity is reported to assist in the deposition of passivating films and decrease the corrosion rate of galvanised steel (AGA 2012).

Under hot water conditions however, galvanised steel behaves quite differently to copper and brass. In aerated, high alkalinity waters above 60°C, the polarity between zinc and iron is reversed: instead of zinc corroding sacrificially to protect the underlying steel structures, the steel corrodes preferentially (DeBerry et al. 1982). The New Zealand Building Code dictates that hot water storage bodies and heaters must be set at 60°C to prevent outbreaks of Legionella bacteria (DBH 2010). It is therefore important that temperatures in hot water storage bodies and heaters with galvanised steel components are very tightly controlled to prevent both Legionella outbreaks without causing corrosion of galvanised steel.

#### ***Key points for Section 3.3: Water chemistry – effect of alkalinity***

- *Bicarbonate helps create corrosion resistant layers on copper, brass, and galvanised steel.*
- *High alkalinity reduces zinc solubility, and therefore dezincification of brass.*
- *High alkalinity reduces rates of galvanic corrosion of brass/copper couples, and protects brass surfaces from drops in pH.*
- *Excessive alkalinity with low pH or mechanically stressed components can facilitate copper corrosion.*
- *Galvanised steel should not be used in high alkalinity water above 60°C (the steel will corrode preferentially to the zinc coating).*

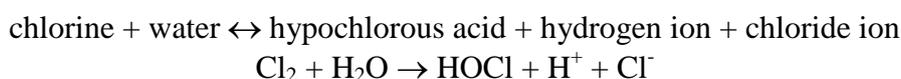
### 3.4 Chlorine

Chlorine compounds tend to be strong oxidisers that effectively kill bacteria and viruses, and as such are used as a disinfectant by most water treatment plants in New Zealand (MoH 2008). The Ministry of Health also recommends the use of chlorine to treat bacterial and viral contamination in private, un-registered supplies, but this is not monitored and controlled by all councils (MoH 2007).

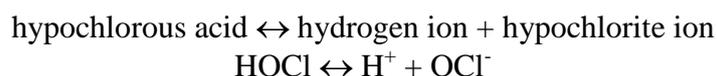
Chlorine for disinfection purposes is usually added to water in one of three chemical forms: chlorine gas, sodium hypochlorite solution, or calcium hypochlorite (NZWWA 1997). Below is a brief discussion of their chemistry in water.

### Chlorine, gas or liquid (Cl<sub>2</sub>)

The maximum acceptable value (MAV) for chlorine in drinking water is 5mg/L (MoH 2008). Chlorine in water hydrolyses to hypochlorous acid (this weak acid is a strong oxidising agent and the primary disinfection agent) and hydrochloric acid:



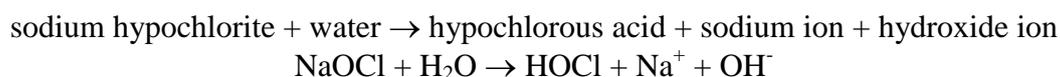
Hypochlorous acid dissociates further to hydrogen ions and hypochlorite ions:



The degree of this dissociation depends on pH. To maintain relatively high concentrations of hypochlorous acid, le Chatelier's principle dictates that it is important that the concentration of hydrogen ions does not drop too low i.e. pH does not become too high (Morganti 2002). This is the reason for the DWSNZ guideline's recommendation that the pH of drinking water be limited to 7.0 – 8.0 if chlorine is used as the disinfection agent.

### Sodium hypochlorite (NaClO) solution – also known as bleach

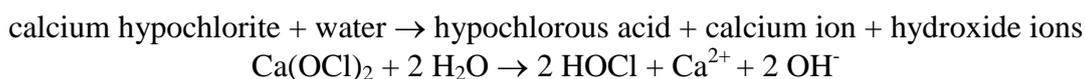
Sodium hypochlorite hydrolyses in water to form the disinfection agent hypochlorous acid and sodium hydroxide:



The same dissociation equilibrium then applies for hypochlorous acid (Morganti 2002).

### Calcium hypochlorite (Ca(OCl)<sub>2</sub>) powder or tablets

Calcium hypochlorite is hydrolysed to hypochlorous acid and calcium hydroxide:



The same dissociation equilibrium then applies for hypochlorous acid (Morganti 2002).

Free chlorine will also react with ammonia or nitrogenous organic compounds to form chloramines: chlorine compounds that can interconvert amongst themselves, depending on pH and chlorine concentration (C Nokes, personal communication, December 17, 2012). Chloramines degrade over time (Morganti 2002).

Because of the multiple equilibria that are involved when chlorine reacts in water, there are some commonly used aggregate terms to express amounts of chlorine species present. See Appendix A for a list of these.

#### **3.4.1 Effect on copper**

Boulay and Edwards (2001) performed a literature review to investigate the effect of chlorine on copper corrosion, and found mixed results; they observed that chlorine has been found to both increase and decrease the corrosion of copper in drinking water pipes. Atlas et al. (1982) reported increased copper corrosion with higher free chlorine concentrations, especially at

low pH. In this work, pH 5 waters with 5 mg/L of free chlorine resulted in levels of dissolved copper exceeding the MAV after 23 hours of stagnation, whereas dissolved copper levels under the same conditions but with pH 8 were well within the limits (Atlas et al. 1982). Boulay and Edwards (2001) found that in six month pipe tests with pH 9.5 water, copper by-product concentrations were significantly higher in waters with 0.7mg/L of Cl<sub>2</sub> than without chlorine, at both 20°C and 60°C. However, their results also showed that copper corrosion did not increase with chlorination at pH 7.0 (Boulay and Edwards 2001), which seems to contradict the findings of Atlas et al. (1982).

In contrast, a study by Broo et al. (1997) showed that a chlorine residual of 2 mg/L Cl<sub>2</sub> decreased the copper corrosion rate in pH 9.3 water, leading to the conclusion that a chlorine residual might prevent the unusual 'blue water' or soft-water pitting problems. Another study using stagnant coupon tests demonstrated that the presence of chloride ions (produced when both Cl<sub>2</sub> and HOCl are reduced) up to rather high concentrations (~6mM) at pH 8.0 actually *decreases* the copper corrosion rate relative to no chloride (Broo et al. 1997).

Chloride has also been reported to indirectly influence the corrosion rate of copper by modifying the crystal structure, morphology and compactness of the corrosion deposits formed on the pipe or fitting's surface (Schock et al. 1995).

On the basis of this mixed collection of findings, the disinfection value of chlorine cannot be ignored, but it is recommended that the pH be maintained between 7.0 and 8.0 (Morganti 2002). Within this range, any increase in copper corrosion attributable to chlorine or chlorine species should be minimal.

### **3.4.2 Effect on brass**

The seminal work of Turner (1961) identified the ratio of chloride to temporary hardness<sup>4</sup> as being the critical determinant for meringue dezincification. It has since been suggested that this effect is in fact due to alkalinity, not temporary hardness (Zhang and Edwards 2011), but nevertheless, chlorine and other chlorine species have been shown to be very important determinants of brass corrosion rates. Consistently, studies have shown that higher levels of chlorine, chloride, and chloramines cause more severe weight loss and dezincification in brass (Zhang and Edwards 2011; Cohen 1993; Sarver et al. 2010).

### **3.4.3 Effect on galvanised steel**

DeBerry et al. (1982) report that waters with 'appreciable' quantities of chlorides make zinc vulnerable to pitting attack. As with copper, chloride also affects the composition, morphology and compactness of corrosion products formed on zinc and galvanised steel. Relatively porous and bulky deposits form on zinc in NaCl solution as compared to NaOH solution for example, and this can lead to a less robust passivating layer (Mouanga et al. 2010).

An additional effect of chloride on galvanised steel corrosion can be observed at high temperatures. At temperatures above 60°C, steel can corrode preferentially to the zinc layers which are supposed to be protecting it, but waters high in chloride decrease this tendency (DeBerry et al. 1982).

---

<sup>4</sup> Temporary hardness is that due to calcium and magnesium bicarbonates. For more information, see Section 3.5.

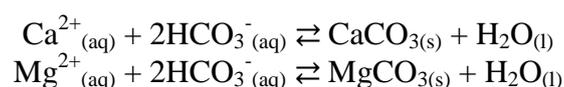
### **Key points for Section 3.4: Water chemistry – effect of chlorine**

- Chlorine compounds are **important disinfectants** of drinking water.
- Chlorine species have been found to **both increase and decrease copper corrosion** under various conditions.
- Chlorine, chloride and chloramines **promote dezincification** of brass.
- **Chloride affects the morphology of corrosion products** on galvanised steel and copper, making them bulky and porous and reducing their corrosion resistance properties.
- Between **pH 7.0 and pH 8.0**, negative effects of chlorine species on copper corrosion should be **minimal**.

### **3.5 Hardness**

Hardness is caused by the presence of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , and is expressed as the equivalent quantity of  $\text{CaCO}_3$  (Singley et al. 1984). In general, hardness makes water less corrosive, as it allows the formation of protective  $\text{CaCO}_3$  layers on the walls of pipes and fittings, if alkalinity is sufficiently high (Singley et al. 1984). According to the New Zealand Ministry of Health (2012), the relative softness of New Zealand's water sources results in a general tendency for our drinking waters to dissolve metals from plumbing fittings. Rainwater collected directly into tanks will also be relatively soft, as it will not contain dissolved, naturally occurring carbonates from soils and rocks.

A subcategory of hardness is temporary hardness. This is an archaic measure of water chemistry, which is not widely used today (Sarver et al. 2010). Temporary hardness is caused by calcium and magnesium bicarbonates, which can be removed from water by heating. This is because an increase in temperature drives the equations below in the forward direction, causing calcium (or magnesium) ions to precipitate out of solution as calcium (or magnesium) carbonates, also known as lime scale.



Permanent hardness, that caused by salts other than bicarbonate salts (e.g.  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^{2-}$ ), cannot be eliminated in this way.

#### **3.5.1 Effect on copper**

Hardness has been shown to decrease the corrosion rate for copper (Broo et al. 1997). Hardness impacts on several specific kinds of copper corrosion. Cohen (1993) reported that near-zero hardness waters with appreciable amounts of dissolved oxygen and carbon dioxide made copper particularly susceptible to erosion corrosion. Type II pitting is most common in soft, manganese-containing water in the hottest parts of hot water systems, thus giving this kind of corrosion the alternative names of hot water or soft water pitting (DeBerry et al. 1982; Oliphant 2003). Soft water is also one of the conditions which promote type III pitting of copper (Oliphant 2003.).

### **3.5.2 Effect on brass**

A range of studies have shown that low hardness or temporary hardness is correlated with increased dezincification of brass and meringue formation (Andersen et al. 2011; Cohen 1993; Turner 1961). Turner (1961) investigated meringue dezincification, which was poorly understood at the time, in a range of waters all above pH 8.3. This study determined that there was a certain ratio of chloride to temporary hardness above which meringue dezincification could be expected to occur (Turner 1961). However, Turner (1961) observed only the correlation between this ratio and dezincification, and provided neither data nor explanations as to the relative accuracy of using temporary hardness as a variable (Zhang and Edwards 2011).

The recent work of Zhang and Edwards (2011) has shown that the impact of hardness on dezincification propensity is weak and inconsistent, and that the key variable is in fact alkalinity, which is often strongly correlated to temporary hardness, as in Turner's work (1961). This elucidation of the effects of hardness and alkalinity on dezincification is important for practical reasons, since some water treatments can affect these variables independently. For example, home softening of water removes hardness and temporary hardness but leaves alkalinity unchanged (Zhang and Edwards 2011). Where one might have expected this to lead to an increase in dezincification problems based on the DWSNZ, the work of Zhang and Edwards (2011) shows that this should not greatly increase the propensity of the water for dezincification. It should be noted that changes in hardness may still impact other metals.

High hardness can also be detrimental. Andersen et al. (2011) found that hard water with high conductivity caused intergranular corrosion and stress-cracking corrosion in a dezincification resistant brass, CuZn36Pb2As, after just one year in service in Copenhagen.

### **3.5.3 Effect on galvanised steel**

The American Galvanizer's Association (2012) states that increased hardness results in reduced corrosion of galvanised steel. This is because in combination with the carbonate and bicarbonate ions that are responsible for alkalinity, hardness allows the formation of a layer of protective scale inside galvanised steel pipes. However, excessive scale can clog pipes and fittings. In the special case of low alkalinity waters at 65°C, hard water has been reported to cause more severe corrosion than soft water (DeBerry et al. 1982).

Interestingly, DeBerry et al. (1982) noted that the type of hardness (permanent or temporary) affected the morphology of scale deposits, similar to the effect of chloride ions. Carbonates of calcium and magnesium deposit an uneven and only somewhat adherent scale. In contrast, bicarbonates of calcium and magnesium produce a thin, dense scale of basic carbonates of zinc, which adheres much more tightly to the metal surface and provides increased corrosion resistance (DeBerry et al. 1982).

### **Key points for Section 3.5: Water chemistry – effect of hardness**

- **Hardness decreases corrosion of copper**, particularly type II and type III pitting in copper.
- Hardness allows the formation of a **protective scale on galvanised steel**.
- **For brass, alkalinity is much more important than hardness**, which has little effect on corrosion.
- High hardness can promote **intergranular and stress-cracking corrosion in dezincification resistant brass**.
- At **high temperatures in low alkalinity water**, hardness causes **increased corrosion of galvanised steel**.

## **3.6 Sulphate ions**

### **3.6.1 Effect on copper**

It is accepted that under some circumstances, copper concentrations in water are controlled by the solubility of the compounds comprising the scale on the walls of a pipe/fitting (Edwards et al. 2001). While the scale in copper pipes usually begins as cupric hydroxide and converts to less soluble compounds such as CuO over time, sulphate affects this transition (Edwards et al. 2001). Low levels of sulphate (<0.25 mM) have been found to hasten the transition of cupric hydroxide to less soluble compounds over a period of 24 hours, but higher levels retard this process relative to sulphate-free waters (Edwards et al. 2001). Furthermore, longer term experiments showed that when added to cupric hydroxide in water, sulphate caused an initial drop in soluble copper concentrations, but caused copper solubility to reach a long term steady state at a level higher than in waters without sulphate (Edwards et al. 2001). The hypothesised reason for this phenomenon is that sulphate promotes the transformation of cupric hydroxide to cupric sulphate and phosphate, but ultimately prevents the formation of even less soluble  $\text{Cu}_2(\text{OH})_2\text{CO}_3$  and CuO scale (Edwards et al. 2001).

Oliphant (2003) also suggests that excessive sulphate makes water aggressive to copper – he reports that a low ratio of bicarbonate to sulphate can cause type II pitting.

### **3.6.2 Effect on brass**

The influence of sulphate on dezincification is complex, and has not been investigated to the same extent as chloride (Sarver et al. 2010). Turner (1961) found a complementary relationship between chloride and sulphate concentrations: if chloride is present to at least 90% of the concentration required to cause meringue dezincification, the presence of sulphate at three times the concentrations of the ‘missing’ chloride will cause meringue dezincification.

In their comprehensive review of brass dezincification, Sarver et al. (2010) report a synergistic effect between sulphate and chloride. At low levels of sulphate (<60 mg/L), high levels of chloride (up to 250 mg/L) could be tolerated without resulting in dezincification. However, when sulphate concentrations exceeded 60 mg/L, even chloride at 60 mg/L was deemed problematic (Sarver et al. 2010.).

### 3.6.3 Effect on galvanised steel

There is relatively little information available on the effect of sulphate on galvanised steel in domestic water systems. Perez and Alfantazi (2012) immersed high-purity zinc in solutions of 3.5% (w/v) NaCl and added Na<sub>2</sub>SO<sub>4</sub> to obtain concentrations between 1% and 4% (w/v). Their results suggest that in the presence of chloride, increasing concentrations of sulphate lead to increased corrosion rates. DeBerry et al. (1982) also reported that sulphates in soft water caused pitting attacks on zinc.

#### ***Key points for Section 3.6: Water chemistry – effect of sulphate ions***

- *In the long term, waters with sulphate ions result in **greater copper solubility** than waters without sulphate ions.*
- *Sulphate and chloride ions have a **negative, synergistic effect, promoting dezincification** of brass.*
- *Relatively little is known about the effects of sulphate on galvanised steel in domestic water systems, but findings suggest sulphate ions **increase corrosion rates of zinc**.*

## Section 4: Physical/Physiochemical factors

### 4.1 Galvanic connections

It is widely known that if two dissimilar metals are in electrical contact and are also in contact with a common fluid electrolyte, corrosion will occur due to the metals' different positions relative to each other on the galvanic scale (Roberge 2006). There are a number of scenarios in which this mode of corrosion could be relevant in household plumbing systems. The first is if parts from dissimilar metals are actually attached to one another e.g. galvanised steel couplings joining copper pipes, steel nipples closing brass valves (Cohen 1993, DeBerry et al. 1982), or brass fittings joining galvanised steel pipes (Andersen et al. 2011). It is inevitable that these assemblies will protect the cathodic metal part, but will eventually result in corrosion of the anodic metal. Galvanic connections between dissimilar metals can also arise when metallic components and inappropriate solders are used e.g. copper pipes and lead-tin solder (Gregory 1990).

A more insidious problem involves dissimilar metal parts which are not in direct contact. If copper dissolves into the water from a pipe or fitting upstream of a galvanised steel component, tiny amounts of copper can be deposited on the galvanised surface, thus setting up microgalvanic corrosion cells (Andersen et al. 2011). This assembly – copper parts upstream of galvanised steel – should be avoided. If two separated, dissimilar metal parts come into electrical contact, this has been shown to accelerate corrosion of the anodic metal part (Sarver and Edwards 2011).

Stray currents – currents from electrical systems that follow paths other than their intended circuit because of poor electrical connections or poor insulation – can also cause general or localised corrosion of buried pipes (Ghali et al. 2007). Points where current enters the pipe will become cathodic, while the area where the current leaves the metal will become anodic and therefore corrode (Ghali et al. 2007). This kind of corrosion can be reduced through the use of sacrificial anodes, but ideally, the current leakage itself should be eliminated through good electrical connections and insulation (Ghali et al. 2007).

#### **Key points for Section 4.1: Physical/Physiochemical factors – galvanic connections**

- **Dissimilar metals in a plumbing system should never come into electrical contact** e.g. do not use galvanised steel couplings to connect copper pipes; or brass fittings to connect galvanised steel pipes.
- **Conversely, identical metals in contact will not suffer galvanic corrosion** e.g. copper fittings connecting copper pipes, or brass fittings connecting brass pipes with identical chemical compositions.
- **Appropriate solder materials that do not cause galvanic corrosion must be used.**
- **Copper components should not be installed upstream of galvanised steel components.**
- **Ensure any buried metallic pipes are not exposed to stray currents in soil.**

## ***4.2 Metal fittings in combination with plastic pipes***

As the relative price of copper increases, plastic pipes are becoming increasingly popular for household plumbing applications. Anecdotal information from professional plumbers indicates that plastic pipes (often polybutylene) with brass fittings have become increasingly common in the new houses in New Zealand. Innovative new fittings have been devised (e.g. Buteline™ plumbing systems) which are intended to allow the installation of ‘all plastic’ household plumbing systems. Unfortunately, even if all pipes and joining fixtures are of plastic, the vast majority of household taps will still have metal parts in contact with water, thus reducing but not completely eliminating the number of zinc- and copper-containing components in household plumbing systems. The Australian and New Zealand standard for tapware specifies copper and certain copper alloys, as well as certain stainless steels as acceptable for use (Standards Australia/Standards New Zealand 2005). It is highly unlikely that galvanised steel fittings would be used in combination with plastic pipe systems.

Polymer pipes do not affect the corrosion of metallic fittings directly as in the case of galvanic connections between metal components described in Section 4.1. Instead, corrosion of a metal fitting in plastic pipe systems is governed by the properties of the part itself and the water (Andersen et al. 2011). A key study on the leaching of copper and zinc from new all plastic piping systems in houses was performed by Kimbrough (2007). An interesting opportunity for a natural experiment arose in Southern California where a new public water system was created to supply a tract of new houses which had all plastic piping systems. These homes had brass taps, but there were no other sources of copper or zinc in their interior plumbing systems – no copper pipes, no solder of any kind, no brass connectors. Concentrations of zinc and copper in water from taps in these homes were compared to houses with traditional copper and galvanised steel piping in a nearby area (though it should be noted that these traditionally plumbed houses were supplied with water from another source). Kimbrough (2007) showed that concentrations of copper and zinc (as well as lead and nickel) were in fact higher in the all plastic plumbing houses than the traditionally plumbed houses. It was also shown that the ratio of elements and correlation coefficients were very similar in the two populations, suggesting that brass corrosion was a main contributor of copper and lead in the samples. Thus, while corrosion failures of pipes may be dramatic and costly, the gradual leaching of heavy metals from tapware must also be addressed if the concentrations of these contaminants in wastewater are to be reduced.

Several mechanisms have been proposed for the somewhat unexpected phenomenon of greater copper and zinc leaching from all plastic plumbed houses. Sarver and Edwards (2011) noted that copper tubing can consume oxidants in water, while plastic pipes are inert. This allows higher concentrations of chemical species such as chlorine to persist in the water for longer in plastic pipes, which increases the likelihood of a high dose and long duration exposure of tapware to corrosive water. Another possible interaction suggested by the same authors is that soluble copper from copper piping might limit copper leaching from brass fittings downstream via equilibrium and mass transport phenomena, thus increasing selective zinc leaching from brass (Sarver and Edwards 2011).

**Key points for Section 4.2: Physical/Physiochemical factors – metal fittings in combination with plastic pipes**

- **'All plastic'** plumbing systems with poor quality brass taps **can still leach copper and zinc.**
- Plastic piping systems in conjunction with high quality brass taps, which comply with AS/NZS3718:2005 and AS/NZS4020:2005 should leach **minimal amounts of copper and zinc.**

### **4.3 Manufacturing residues inside drawn copper pipes**

During the manufacture of copper pipes, abnormal conditions can result in the formation of a certain 'glassy' copper oxide layer inside the pipe (DeBerry 1982). This layer is cathodic to the copper surface, which makes the copper corrode preferentially and can cause pitting. A similar effect has been attributed to carbonaceous thin films by Schafer (1964). The deposition of any kind of particulate matter inside a pipe provides an opportunity for oxygen concentration cell corrosion to occur, and this has been seen to be the case if graphite residues are present after manufacturing (Atlas et al. 1982). This highlights the importance of a clean copper surface inside new pipes and fittings to ensure long-lasting service.

**Key points for Section 4.3: Physical/Physiochemical factors – manufacturing residues inside drawn copper pipes**

- Copper pipes must comply with **NZS3501:1976**, which require that there are no deleterious films in the bore.

### **4.4 Differential flow**

Although practical experience has shown that identical brass fittings at different locations in a given building's plumbing system often corrode at different rates (Sarver et al. 2010), relatively little research has been undertaken to investigate the reasons for this. The bulk of research efforts have instead focussed on the metallurgy of the part, or the chemistry of the water, with flow being treated as a binary on/off variable, which does not accurately model the complex range of differential flow conditions present within a plumbing system (Sarver et al. 2010).

The phenomenon of identical brass fittings corroding at different rates inside the same plumbing system can be explained by considering the separation of anodic and cathodic sites (Sarver et al. 2010). If these sites are, or become separated, they may experience different flow conditions and chemical micro-environments, which can result in accelerated dezincification (Sarver et al. 2010). Specifically, a reduced flow rate at the anode surface (for example, a brass surface below a meringue-like scale, the crevices between threaded brass parts, or a brass T fitting connecting a pipe filled with stagnant water to an in-line pipe with flowing water) will cause the site to accumulate chloride and lower pH locally, thus accelerating increasing dezincification (Sarver et al. 2010). Conversely, increased flow at a cathodic site will increase the supply of oxidant, accelerating the corrosion at the distant anode (Sarver et al. 2010).

Most work on the effects of differential flow has been focussed on brass dezincification, but theoretically, the same principles would apply for galvanically connected dissimilar metals of any kind, where the cathodic and anodic metal sites were exposed to differential flow.

**Key points for Section 4.4: Physical/Physiochemical factors – differential flow**

- **Identical brass fittings** in different local flow conditions can **corrode at different rates**.
- Using **plastic fittings** would eliminate leaching from this kind of corrosion. Corrosion from tapware and home water filters would still need to be considered and prevented to minimise leaching from the system as a whole.

## **4.5 Velocity of water**

### **4.5.1 Effect on copper**

DeBerry et al. (1982) state that erosion corrosion attack is promoted by flow velocities greater than 5 ft/s (1.52 m/s). Cohen (1993) supports this finding, giving a range for the critical velocity above which erosion corrosion can occur (>1.2 to 1.5 m/s) and adding that turbulence further exacerbates the effect of fast flowing water on the rate of erosion corrosion.

It has also been shown that flow conditions early in the life of a copper pipe have important effects on long term corrosion resistance (DeBerry et al. 1982). Excessive flow velocities in a young pipe can prevent the formation of a copper oxide layer with optimal morphology (small grained, compact and therefore protective), while at the other extreme, Oliphant (2003) notes that stagnation in a young pipe can later result in type III pitting.

### **4.5.2 Effect on brass**

Cohen (1993) and DeBerry et al. (1982) both report that stagnant water promotes both plug and layer type dezincification. In contrast, Sarver et al. (2010) in their review of dezincification note that practical observations of brass corrosion and dezincification are often accelerated by increased water velocity. They further note that this seeming contradiction is consistent given considerations of separate anodic and cathodic areas in the different experimental set-ups as described in Section 4.4 above.

Other types of corrosion have a simpler relationship to flow velocity. Brass fittings and valves can be vulnerable to stress corrosion cracking because of the bends, angles and convoluted internal structure of such parts, and the work of Andersen et al. (2011) showed that small dimension brass fittings and valves were overrepresented for this particular type of corrosion. This could be due to smaller parts being subject to greater tensile stress during manufacturing or installation, but could also be partially due to the greater flow velocity through a smaller diameter part than a larger diameter part for a given flow rate.

### **4.5.3 Effect on galvanised steel**

The American Galvanizers Association (2012) states that fluid agitation can disrupt the protective film of carbonates from the zinc surface and accelerate the corrosion of zinc coatings. This is similar to the erosion corrosion suffered by copper fittings and pipes.

However, stagnation in new galvanised pipes may also be problematic, and can result in concentrations of zinc in oxidic colloid form at concentrations of 5 to 10 ppm after 8 – 40 hour exposure times (DeBerry et al. 1982).

**Key points for Section 4.5: Physical/Physiochemical factors – velocity of water**

- **Extended stagnation periods should be avoided** where practical e.g. avoiding filling plumbing systems in new buildings months before they come into use.
- Plumbing systems should be designed so **flow rates do not exceed 1.2m/s**.
- Fittings and pipes should be **smooth and free of defects** that could cause turbulence and subsequently erosion corrosion. This is a requirement in the standards for plumbing components given as acceptable solutions under the NZBC.

## **4.6 Temperature**

In New Zealand, the Building Code dictates that hot water storage bodies and heaters must be set at 60°C to prevent outbreaks of Legionella bacteria. Water delivered to sanitary fixtures must not exceed 45°C for buildings where people vulnerable to scalding are likely to use the fixtures (elderly, young children etc.), and 55°C for all other buildings (DBH 2010).

### **4.6.1 Effect on copper**

Work by Boulay and Edwards (2001) in static pipe tests showed that holding the water at 60°C exacerbated copper release as compared to identical pipes containing water at 4°C, 20°C and 24°C, but this effect was not always significant at 95% confidence. The temperature also affected the form of copper released; the pipes with 60°C water released a higher percentage of particulate (as opposed to soluble) copper (Boulay and Edwards 2001). Tronstad and Veimo (1940) corrected for the change in solubility of carbon dioxide with temperature, and found that initial copper dissolution rates increased when temperature was increased from 46°C to 70°C, but that maximum concentrations of dissolved copper were not greatly affected by changes in temperature in this range.

There is general agreement on other aspects of the effects of temperature on copper corrosion. Water between 20°C and 40°C can support bacterial activity and cause microbiologically-induced pitting, so cold water should be kept cold, and hot waters maintained hot (Oliphant 2003). Type III soft water pitting or blue water problems are known to improve with hotter waters, possibly because of a reduction in microbiological activity (Boulay and Edwards 2001). In fact, Oliphant (2003) suggests heat shock above 60°C as a treatment for these forms of corrosion, as this will reduce microbiological activity and encourage the conversion of the protective scale layer to less soluble cupric oxide.

### **4.6.2 Effect on brass**

In their review of brass dezincification, Sarver et al. (2010) state that many studies have shown that dezincification is more common in hot water systems, although it can also occur in cold water. They cite work that suggests that heating enhances dezincification by precipitating out temporary hardness and thus exacerbating meringue formation, and by increasing pH (Sarver et al. 2010).

Other kinds of brass corrosion may also be temperature dependent. Cohen (1993) recommends maintaining 54°C as a safe and energy-efficient temperature for hot water systems to avoid hot water pitting, but this does not meet the requirements of the New Zealand Building Code, which requires hot water to be stored at 60°C.

#### **4.6.3 Effect on galvanised steel**

The effect of high temperature water on galvanised steel is different to those on copper and brass because of the combination of two metals in one pipe material. In certain waters above 60°C, the polarity between the galvanised coatings and the steel beneath reverses, because ZnO (a compound able to perform as a noble cathode) forms instead of Zn(OH)<sub>2</sub> (Carbucicchio et al. 2008; Cohen 1993; DeBerry et al. 1982). This polarity reversal causes the steel to corrode preferentially to the coating, so it is recommended that galvanised steel not be used at temperatures above about 60°C (Cohen 1993).

#### ***Key points for Section 4.6: Physical/Physiochemical factors – temperature***

- *Hot water must be stored at 60°C to avoid Legionella outbreaks.*
- *To avoid bacteria-related health and corrosion problems, **water should not be maintained between 20°C and 40°C.***
- ***Galvanised steel should not be used in contact with water >60°C.***

## Recommendations

A great many studies have made recommendations on ways to reduce the corrosion of copper, brass and galvanised steel, and a significant number of these relate directly to the application of these materials in plumbing systems. It would be inappropriate to list all their findings here, but some particularly helpful reviews and reference texts can be identified:

- **Oliphant (2003, revised 2010). *A Review of Current Knowledge: Causes of copper corrosion in plumbing systems*. Bucks: Foundation for Water Research.**  
This practical and accessible text details ways to recognise and reduce many modes of copper corrosion.
- **Sarver E, YF Zhang and M Edwards (2010). Review of brass dezincification corrosion in potable water systems. *Corrosion Reviews*, Vol. 28, No. 3-4, pp. 155-196.**  
This text is a comprehensive review of current knowledge of the effects of all three groups of corrosion factors (metallurgical, water chemistry-related, and physical/physiochemical) on brass dezincification.
- **Zhang XG (1996). *Corrosion and Electrochemistry of Zinc*. New York: Plenum Press**  
Described by reviewers as “the final word’ on zinc for some considerable time to come,” this monograph covers in detail the modes of corrosion affecting zinc and galvanised steel, as well as the effects of metallurgy, water chemistry and some physical/physiochemical factors on corrosion.

A review of the recommendations shows that they can be grouped into categories which correspond to the three groups of corrosion factors as described by Sarver et al. (2011). A fourth group of recommendations,

### Group 1: Metallurgical recommendations

By far the most common recommendation is a metallurgical one: to promote the use of appropriate metals which are not susceptible to corrosion (Sarver et al. 2010). This reflects the large body of widely accepted knowledge about the effects of metallurgical factors on corrosion. Buying fittings and pipes of a particular kind of brass or galvanised steel is also a relatively simple action to undertake – it is a matter of suppliers, plumbers and home owners being aware that plumbing components must comply with the existing relevant standards. Many New Zealand plumbing component suppliers use only high quality materials and adhere to the relevant standards, but home owners and non-professionals are still able to purchase inferior components online, for example. Home water filtration systems are of particular concern as these do not appear to be regulated, and certain models that are known to leach copper and zinc are readily available from New Zealand suppliers (KDF Fluid Treatment, Inc. 2012). Information resources such as pamphlets for customers in the plumbing sections of hardware shops, or websites for tradespeople, should be developed and disseminated.

The Building Code of New Zealand provides an excellent framework for ensuring only quality materials are used in new buildings, and describes relevant standards for household plumbing system components, but there are some gaps. The Code does not specify a standard for materials in tapware, despite the fact that taps have been shown to be an important source of copper and zinc leaching, especially in the increasingly popular all plastic systems (Kimbrough 2007). This omission has been recognised by plumbing inspectors and staff at the Ministry for Business, Innovation and Employment (I Culver, personal communication, October 26, 2012; MBIE staff, personal communication, October 26, 2012), and the standard

*AS/NZS 3718:2005 – Water supply – tapware* will apparently be included in the next update to the Code compliance documents (MBIE staff, personal communication, October 26, 2012). All home water filtration systems should also be required to comply with relevant materials standards.

While regulation, support for manufacturers/suppliers, and public education are necessary and costly components of this approach, choosing appropriate materials at the individual household level is likely to be a cost-effective course in the long term. Retrofitting existing buildings with corrosion resistant metallic materials could be prohibitively expensive, but for a new building, insisting on such materials would minimise the likelihood of costly plumbing failures later, as well as helping to minimise the presence of these heavy metals in our wastewater.

#### Group 2: Water chemistry recommendations

Water chemistry can be adjusted to minimise its tendency to cause zinc and copper leaching (MoH 2011). Much research has been conducted into the adjustment of the corrosivity of waters by adding chemicals (for example Cantor 2000; Yohai et al. 2010). Guidelines for some water chemistry parameters that affect corrosion (e.g. pH, hardness) are given in the Drinking Water Standards of New Zealand, but water suppliers are not required to adhere to these guidelines, as they are not considered to be of health significance (MoH 2008). In addition, some parameters that are important determinants of corrosivity are not mentioned in the DWSNZ – alkalinity is a notable example. While some water suppliers may be independently monitoring such water chemistry parameters, this information is not widely available. This lack of baseline data makes it impossible to determine how to optimise water chemistry to minimise health risks and heavy metal leaching.

It is therefore recommended that standard tests to determine the propensity of specific water compositions for causing potentially harmful corrosion of plumbing systems be developed in collaboration with the water industry. These tests would include the measurement of important variables not controlled for in the DWSNZ, such as alkalinity, which have significant effects on the corrosivity of water. They would also include guideline values for key determinands, much like those in the DWSNZ. With this standard baseline data, water suppliers could adjust the chemistry of the reticulated water they supply, and thereby play an important role in decreasing the leaching of zinc and copper from household plumbing systems. For technical details regarding the adjustment of water chemistry, readers are referred to specialist handbooks and guides such as the National Health and Medical Research Council and Natural Resource Management Ministerial Council of Australia (2011).

This approach – adjustment of the chemistry of reticulated water from suppliers – is technically challenging because of the complex multiple interactions between different chemical species present, the differing chemical requirements at various stages of the water treatment process, and the present lack of standard tests for some specific types of corrosion, such as brass dezincification (Sarver et al. 2010). A further complication is that since different materials are susceptible to different waters, a centralized adjustment could not suit all houses optimally: and only general adjustments could be made. Moreover, modification of reticulated water chemistry would most likely be an on-going public expense as opposed to the one-off choice of corrosion-resistant materials described in the section on metallurgical recommendations above.

The challenge of a devising centralised solution for a problem with many unique manifestations would not apply in the case of households with private, un-registered supplies of water from bores or rainwater collection. With appropriate testing kits and technical support, these households could benefit greatly from adjusting water chemistry, since they could optimise parameters for their unique plumbing systems. This could make a significant difference, as it is not uncommon that roof-collected rainwater exceeds guideline values for pH (Simmons et al. 2001), which is relatively simple to adjust. Adjustment of water chemistry for these households would be less disruptive than retrofitting their entire plumbing system to use the best available materials, and involve small but regular costs for monitoring and continued adjustment of water chemistry.

### Group 3: Physical/Physiochemical recommendations

Some of these factors (galvanic connections between metal components, residues inside drawn copper pipes) have clear solutions; they require high standards of workmanship, compliance with existing standards, and knowledge on the part of plumbers regarding appropriate combinations of metallic materials.

Other factors are very difficult to adjust, both in existing and proposed future plumbing systems. Changes in temperature are not an option since the range of possible working temperatures is limited by important health and safety considerations, which are primary concerns for domestic water supplies. Negative effects of temperatures can be mitigated by appropriate material choices, once again demonstrating that in the long term, selection of suitable materials at the beginning of a plumbing system's life is the most time- and cost-efficient way to reduce harmful copper and zinc leaching.

Differential flow is another physical/physiochemical factor which cannot be completely avoided in any network of connected pipes. Leaching of copper and zinc from metal components exposed to different local flow conditions can be eliminated by using new plastic fittings, but it is important to note that the presence of a single copper- or zinc-containing component in the system (e.g. a poor quality yellow brass tap) can still result in leaching of these heavy metals into wastewater at levels equal to or even greater than those typical of traditional plumbing systems. This must not be interpreted as a wholesale endorsement of plastic systems: it is important to recognise that resistance to copper and zinc leaching is only one of several important characteristics of a plumbing component, others being service life, proclivity for failure, cost, propensity for leaching other harmful substances etc., which are not covered in this review.

Given the potential for differential flow effects and the characteristics of individual plumbing set-ups to fill significant gaps in our current understanding of corrosion in plumbing systems, these factors should be a focus of future research. Priority should be given to elucidating the mechanisms of copper and zinc leaching in the increasingly common systems comprising plastic piping and a small number of metal parts.

## **Key Recommendations**

- **Standards for tapware and home water filters** should be included in the Building Code compliance documents.
- All **new buildings** should be required to have **only corrosion resistant plumbing components**, including dezincification resistant **taps**.
- The importance of choosing corrosion-resistant materials that comply with relevant standards should be **communicated widely to suppliers, plumbers, and homeowners**.
- Older buildings should **replace corrosion-prone plumbing components with corrosion resistant alternatives** where possible/feasible.
  
- **Compulsory limits for key water chemistry parameters** should be set, monitored for, and adhered to.
- **Monitoring** and subsequent **adjustment** of the chemistry of reticulated water by suppliers **should be promoted and supported**.
- **Standard tests** to determine the corrosivity of water to plumbing systems should be **developed with the water industry**.
- **Information resources** on water chemistry guidelines and adjustment for people with **un-registered water supplies should be developed and disseminated**
  
- The **contribution of skilled and knowledgeable plumbers** to the protection of our health, wastewater and the receiving environment should be **recognised and appreciated**.
- **Long-term studies on innovative plumbing materials in realistic differential flow set-ups** should be conducted to evaluate their impact on copper and zinc leaching, and their suitability for plumbing systems as a whole.

## **Conclusions**

In order to be able to reuse our biosolids and greywater in a safe, efficient, and environmentally friendly way, it is important to minimise contamination of wastewater by zinc and copper. Corrosion of components in household plumbing systems causes significant amounts of copper and zinc to leach into wastewater.

Using the Building Code to ensure that all metallic materials in new plumbing systems are of high quality material and are used only under conditions to which they are suited is an effective way to reduce this corrosion. Adjustment of water chemistry to minimise corrosion is a complementary approach: limits for key water chemistry parameters that influence corrosion of plumbing systems should be set and adhered to by suppliers, whether through the Drinking Water Standards of New Zealand or another mechanism.

At the individual household level, plumbers need expert knowledge of installation techniques and appropriate material combinations to avoid problematic corrosion. New Zealand companies are also developing innovative plumbing materials and systems, and long-term research on these in realistic experimental set-ups should be done to improve our understanding of heavy metal leaching from plumbing systems in modern New Zealand homes. Results of such work will help us develop a blueprint for great household plumbing systems that are long-lived, cost-efficient, and safe for us and our environment.

These recommendations require improved awareness about the role of plumbing systems in contamination of wastewater on the part of many actors. Current knowledge and future findings must be effectively communicated to water suppliers, plumbing component manufacturers and suppliers, plumbers, homeowners and renovators, all of whom have active roles to play in ensuring that what goes on Up the Pipe leaves our environment healthy and safe.

## References

- Alsager OA (2012). *Copper, zinc and iron contamination in Wellington streams after rainfall events*. (Master's thesis). Retrieved 9<sup>th</sup> October from <http://researcharchive.vuw.ac.nz/bitstream/handle/10063/2035/thesis.pdf?sequence=1>
- Alu-bra (2010). *Standard properties of typical brass, bronze, and aluminium alloys*. Retrieved 23<sup>rd</sup> October 2012 from [www.alubra.com/pdf/catalog.pdf](http://www.alubra.com/pdf/catalog.pdf)
- American Galvanizers Association [AGA] (2012). *How long does hot dip galvanised steel last in water?* Retrieved 17<sup>th</sup> September from <https://www.galvanizeit.org/about-hot-dip-galvanising/how-long-does-hdg-last/in-water>
- Anchor Bronze and Metals Inc. (2012a). *Copper Alloy No. C36000*. Retrieved 25<sup>th</sup> September 2012 from <http://www.anchorbronze.com/c36000.htm>
- Anchor Bronze and Metals Inc. (2012b). *Copper Alloy No. C83600*. Retrieved 23<sup>rd</sup> October 2012 from <http://www.anchorbronze.com/c83600.htm>
- Andersen A, F Fontenay, LR Hilbert (2011). Corrosion of brass in drinking water with high alkalinity. Paper no. 4809 at the EUROCORR 2011 Conference.
- Australian and New Zealand Environment and Conservation Council [ANZECC] (2000). *Australian and New Zealand Guidelines for Fresh and Marine Water Quality: Volume 1 – the Guidelines, Chapters 1-7*. Retrieved 17<sup>th</sup> December 2012 from <http://environment.gov.au/water/publications/quality/nwqms-guidelines-4-vol1.html>
- Austral Wright Metals (2008). *Metal alloys – properties and applications of brass and brass alloys by Austral Wright Metals*. Retrieved 26<sup>th</sup> September 2012 from <http://www.azom.com/article.aspx?ArticleID=4387#10>
- Australian Water Association (2010). *Copper (blue water) facts*. Retrieved 17<sup>th</sup> October 2012 from <http://www.awa.asn.au/AdvocacyTwo.aspx?pageid=4294969989>
- Atlas D, J Coombs and OT Zajicek (1982). The corrosion of copper by chlorinated drinking waters. *Water Research*, Vol. 16, pp. 693-698
- Boulay and Edwards (2001). Role of temperature, chlorine, and organic matter in copper corrosion by-product release in soft water. *Water Research*, Vol. 35, No. 3, pp. 683-390
- BRANZ (2012). *Renovate: the technical resource for industry*. Retrieved 7<sup>th</sup> September 2012 from <http://www.renovate.org.nz>
- Broo AE, B Berghult and T Hedberg (1997). Copper corrosion in drinking water distribution systems – the influence of water quality. *Corrosion Science*, Vol. 39, No. 6, pp. 1119-1132
- Callcut (2000). *Copper Applications in Metallurgy of Copper & Copper Alloys* Retrieved 9<sup>th</sup> October 2012 from <http://www.copper.org/publications/newsletters/innovations/2000/01/brasses02.html>
- Cantor AF, JK Park, P Vaiyavatjamai (2000). *The effect of chlorine on corrosion in drinking water systems*. Illinois: Midwest Technology Assistance Centre
- Carbucicchio M, R Ciprian, F Ospitali, G Palombarini (2008). Morphology and phase composition of corrosion products formed at the zinc-iron interface of a galvanised steel. *Corrosion Science*, Vol. 50, pp. 2605-2613
- Cohen A (1993). Corrosion by potable waters in building systems. *Materials Performance*. Houston: NACE International
- Copper Development Association (2005). *Pub 117 – The Brasses – properties and applications*. Retrieved 29<sup>th</sup> August 2012 from <http://www.copperinfo.co.uk/alloys/brass/brasses-properties-and-applications.shtml>
- DeBerry DW, JR Kidwell, DA Malish (1982). *Corrosion in potable water systems*. Washington DC: United States Environmental Protection Agency

Department of Building and Housing [DBH] (2011a). *Compliance Document for New Zealand Building Code – Clause B2: Durability*. Department of Building and Housing: Wellington.

Department of Building and Housing [DBH] (2011b). *Compliance Document for New Zealand Building Code – Clause G12: Water Supplies – Third Edition*. Department of Building and Housing: Wellington.

Edwards M, K Powers, L Hidmi and MR Schock (2001). Chapter II: The role of pipe aging in copper corrosion by-product release. *Water Science and Technology: Water Supply*, Vol. 1, Issue 3.

Gaetke LM, CK Chow (2003). Copper toxicity, oxidative stress, and antioxidant nutrients. *Toxicology* Vol. 189, pp. 147-163

Ghali E, VS Sastri, M Elboudjaini (2007). Corrosion prevention and protection: Practical solutions. *John Wiley and Sons Ltd.*: Chichester, England, 574 pages

Grace S, DA Lytle, MN Goltz (2012). Control of new copper corrosion in high-alkalinity drinking water. *Journal of the American Water Works Association*. Vol. 103, No. 1, pp. 39-40

Gregory R (1990). Galvanic corrosion of lead solder in copper pipework. *Water and Environment Journal*, Vol. 4, No. 2, pp. 112-118

The Hendrix Group (2012). *Dezincification*. Retrieved 30<sup>th</sup> July 2012 from <http://hghouston.com/resources/material-property-data/copper-and-copper-alloys/brasses/dezincification.aspx>

Hoko Z (2005). An assessment of the water quality of drinking water in rural districts in Zimbabwe. The case of Gokwe South, Nkayi, Lupane, and Mwenezi districts. *Physics and Chemistry of the Earth*, Vol. 30, pp. 859-866

Hultquist G, MJ Graham, P Szakálos, GI Sproule, A Rosengren, L Gråsjö (2011). Hydrogen gas production during corrosion of copper by water. *Corrosion Science*, Vol. 53, pp. 310-319

Irwin RJ, M VanMouwerik, L Stevens, MD Seese, and W Basham (1997). *Environmental contaminants encyclopaedia: Zinc entry*. Colorado: National Park Service of the USA

KDF Fluid Treatment, Inc. (2012). *KDF 55 and 88 provide non-chemical water treatment media for the removal of lead and other heavy metals*. Retrieved 17<sup>th</sup> December 2012 from [http://www.kdff.com/success\\_metal.htm](http://www.kdff.com/success_metal.htm)

Kimbrough DE (2007). Brass corrosion as a source of lead and copper in traditional and all plastic distribution systems. *Journal of the American Water Works Association*, Vol. 99, No. 8, pp. 70-76

Kimbrough DE (2009). Source identification of copper, lead, nickel, and zinc loading in wastewater reclamation plant influents from corrosion of brass in plumbing fixtures. *Environmental Pollution*, Vol. 157, pp. 1310-1316

Kopeliovich (2012). *Cast copper alloy C85500 (Yellow Brass)*. Retrieved 23<sup>rd</sup> October 2012 from [http://www.substech.com/dokuwiki/doku.php?id=cast\\_copper\\_alloy\\_c85500\\_yellow\\_brass](http://www.substech.com/dokuwiki/doku.php?id=cast_copper_alloy_c85500_yellow_brass)

Joseph G, JAK Kundig (1999). *Copper: Its trade, manufacture, use and environmental status*. Novelty, Ohio: ASM International

Lytle DA and MR Schock (1996). *Stagnation time, composition, pH and orthophosphate effects on metal leaching from brass*. Washington DC: United States Environmental Protection Agency

Lytle DA and MN Nadagouda (2010). A comprehensive investigation of copper pitting corrosion in a drinking water distribution system. *Corrosion Science*, Vol. 52, pp. 1927-1938

Marder AR (2000). The metallurgy of zinc-coated steel. *Progress in Materials Science*, Vol. 45, pp. 191-271

McClaren RG and KC Cameron (1996). *Soil Science: Sustainable production and environmental protection* (2<sup>nd</sup> ed.). *Oxford University Press*: Auckland, 304 pages

Merkel TH, HJ Groß, W Werner, T Dahlke, S Reicherter, G Beuchle, SH Eberle (2002). Copper corrosion by-product release in long-term stagnation experiments. *Water Research*, Vol. 36, pp. 1547-1555

Metal Suppliers Online (2012). *Copper alloys yellow brass, C268*. Retrieved 23<sup>rd</sup> October 2012 from <http://www.suppliersonline.com/Research/Property/result.asp?FamilyID=6&MetalID=1274&Chemical=1&Physical=1&Mechanical=1>

Ministry for Business, Innovation and Employment [MBIE] (2012 a). *Building and Housing: Building code*. Retrieved 9<sup>th</sup> October 2012 from <http://www.dbh.govt.nz/blc-building-code-and-review>

Ministry for Business, Innovation and Employment [MBIE] (2012 b). *Building and Housing: Evaluation of pipe suitability*. Retrieved 9<sup>th</sup> October 2012 from <http://www.dbh.govt.nz/codewords-10-article-4>

Ministry for the Environment (2004). *Contaminated land management guidelines – Schedule B. Hazardous activities and industries list (HAIL) with hazardous substances*. Retrieved 9<sup>th</sup> October 2012 from <http://www.mfe.govt.nz/issues/hazardous/contaminated/hazardous-activities-industries-list-scheduleb.pdf>

Ministry for the Environment (2012). *A Guideline to the Ministry of Health Drinking Water Standards for New Zealand: Assessing compliance with the DWSNZ*. Retrieved 24<sup>th</sup> September 2012 from <http://www.mfe.govt.nz/publications/water/guide-moh-drinking-water-standards-nz-jun08/html/page4.html>

Ministry of Health (2007). *Household water supplies*. Retrieved 29<sup>th</sup> October 2012 from <https://www.health.govt.nz/resource/household-water-supplies#s6>

Ministry of Health (2008). *Drinking-water Standards for New Zealand 2005 (Revised 2008)*. Wellington: Ministry of Health

Ministry of Health (2011). *Plumbosolvency: Technical fact sheet*. Retrieved 8<sup>th</sup> October 2012 from <http://www.health.govt.nz/our-work/environmental-health/drinking-water/plumbosolvency>

Ministry of Health (2012). *Annual Report on Drinking-water Quality 2010-2011*. Wellington: Ministry of Health

Minnesota Rural Water Association (2002). *Corrosion*. Retrieved 31<sup>st</sup> July 2012 from <http://www.mrwa.com/OP-Corrosion.pdf>

Morganti L (2002). *Sodium hypochlorite generation for household water disinfection: A case study in Nepal* (Master's thesis). Retrieved 3<sup>rd</sup> October 2012 from <http://web.mit.edu/watsan/Docs/Student%20Theses/Nepal/Morganti2002.pdf>

Mouanga M, P Berçot, JY Rauch (2010). Comparison of corrosion behaviour of zinc in NaCl and in NaOH solutions: Part 1 – Corrosion layer characterization. *Corrosion Science*, Vol. 52, pp. 3984-3992

Mountain Empire Community College (2012). *Water/Wastewater Distance Learning Website: Chlorination chemistry*. Retrieved 3<sup>rd</sup> October 2012 from <http://water.me.vccs.edu/concepts/chlorchemistry.html>

National Health and Medical Research Council and Natural Resource Management Ministerial Council of Australia (2011). *Australian Drinking Water Guidelines Paper 6 National water Quality Management Strategy*. Canberra: Commonwealth of Australia

New Zealand Water and Wastes Association (NZWWA) (2003). *Guidelines for the safe application of biosolids to land in New Zealand*. Wellington: New Zealand Water and Wastes Association

New Zealand Water and Wastes Association (NZWWA) (1997). *Standard for the supply of chlorine for use in drinking water treatment*. Auckland: New Zealand Water and Wastes Association

Olin Corporation (1966). *The useful characteristics and applications of Olin Alloy 268*. Retrieved 23<sup>rd</sup> October 2012 from <http://www.olinbrass.com/companies/fineweld/Literature/Documents/Alloy%20C268%20Data%20Sheet.pdf>

Oliphant (2003, revised 2010). *A Review of Current Knowledge: Causes of copper corrosion in plumbing systems*. Bucks: Foundation for Water Research

Palmer E (2007). *Build magazine of BRANZ: When pipes fail...* Retrieved 8<sup>th</sup> October 2012 from [http://www.branz.co.nz/cms\\_show\\_download.php?id=69a52e796d5e9bb3f32d47cd1c4dacf3c8cd772a](http://www.branz.co.nz/cms_show_download.php?id=69a52e796d5e9bb3f32d47cd1c4dacf3c8cd772a)

Perez VEP and A Alfantazi (2012). Effects of oxygen and sulphate concentrations on the corrosion behaviour of zinc in NaCl solutions. *Corrosion*, Vol. 68, No. 3

Perrie A and B Cockeram (2010). *Annual freshwater quality monitoring report for the Wellington region, 2009/10*. Wellington: Greater Wellington Regional Council

Provost L (2011). *Performance audit report: Managing freshwater quality: Challenges for regional councils*. Wellington: Office of the Auditor-General

Rahman S, BC McDonald, GA Gagnon (2007). Impact of secondary disinfectants on copper corrosion under stagnation conditions. *Journal of Environmental Engineering*, Vol. 133, No. 2, pp. 180-185

Roberge PR (2006). *Corrosion Basics – An Introduction (2<sup>nd</sup> ed.)*. Houston: NACE International

Roberge PR (2012). *Corrosion doctors: Galvanizing*. Retrieved 6<sup>th</sup> September from <http://www.corrosion-doctors.org/Definitions/Galvanizing.htm>

Sarin P, VL Snoeyink, J Bebee, KK Jim, MA Beckett, WM Kriven, JA Clement (2004). Iron release from corroded iron pipes in drinking water distribution systems: effect of dissolved oxygen. *Water Research*, Vol. 38, No. 5, pp. 1259-1269

Sarver E and M Edwards (2011). Effects of flow, brass location, tube materials and temperature on corrosion of brass plumbing devices. *Corrosion Science*, Vol. 53, pp. 1813-1824

Sarver E, YF Zhang and M Edwards (2010). Review of brass dezincification corrosion in potable water systems. *Corrosion Reviews*, Vol. 28, No. 3-4, pp. 155-196

Sarver E, K Dodson, RP Scardina, S Lattyak-Slabaugh, M Edwards, C Nguyen (2011). Copper pitting in chlorinated, high-pH potable water. *Journal of the American Water Works Association*. Vol. 103, No. 3

Schafer GJ (1964). Why copper pipes sometimes corrode. *Technical bulletin of the Ministry of Works, Architectural Division, New Zealand*, No. 60

Schock MR, DA Lytle and JA Clement (1995). *Effect of pH, DIC, orthophosphate and sulphate on drinking water cuprosolvency*. Cincinnati: United States Environmental Protection Agency

Scholes P (1997). *Assessing urban nonpoint source water pollution in Christchurch*. (Master's thesis). Retrieved 9<sup>th</sup> October from <http://researcharchive.lincoln.ac.nz/dspace/handle/10182/2329>

Scrapmonster.com (2012). *Global scrap prices*. Retrieved 23<sup>rd</sup> October 2012 from <http://www.scrapmonster.com/>

Simmons G, V Hope, G Lewis, J Whitmore and W Gao (2001). Contamination of potable roof-collected rainwater in Auckland, New Zealand. *Water Research*, Vol. 35, No. 6, pp. 1518-1524

Singley JE, BA Beaudet and PH Markey (1984). *Corrosion manual for internal corrosion of water distribution systems*. Washington DC: United States Environmental Protection Agency

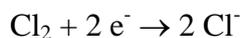
Standards Association of New Zealand (1976). *Specification for copper tubes for water, gas, and sanitation*. Wellington: Standards Association of New Zealand

Standards Australia (1996). AS3795:1996 – *Copper alloy tubes for plumbing and drainage applications*. Sydney: Standards Australia

- Standards Australia (2005). *AS3688:2005 – Water supply – metallic fittings and end connectors*. Sydney: Standards Australia
- Standards Australia (2006). *AS 2345:2006 – Dezincification resistance of copper alloys*. Sydney: Standards Australia
- Standards Australia/Standards New Zealand (2005). *AS/NZS 3718:2005 – Water supply – tapware*. Sydney: Standards Australia and Wellington: Standards New Zealand
- Standards Australia/Standards New Zealand (2006). *AS/NZS 4792-2006 – Hot-dip galvanised (zinc) coatings on ferrous hollow sections, applied by a continuous or a specialized process*. Sydney: Standards Australia and Wellington: Standards New Zealand
- Szakálos P, G Hultquist and G Wikmark (2007). Corrosion of copper by water. *Electrochemical and solid-state letters*, Vol. 10, No. 11, pp. C63-C67
- Sörme L and R Lagerkvist (2002). Sources of heavy metals in urban wastewater in Stockholm. *The Science of the Total Environment*, Vol. 298, pp. 131-145
- Tata Steel (2010). *Non-ferrous metals: Dezincification resistant brass – Alloy 352*. Retrieved 24<sup>th</sup> October 2012 from [http://www.tatasteelnz.com/downloads/Brass\\_Alloy352.pdf](http://www.tatasteelnz.com/downloads/Brass_Alloy352.pdf)
- Tronstad L and R Veimo (1940). The action of water on copper pipes. *Water and Water Engineering*, Vol. 42, pp. 189-191
- Turner ME (1961). Influence of water composition on the dezincification of duplex brass fittings. *Proceedings of the Society for Water Treatment and Examination*, Vol. 10, No. 162
- US EPA (2012). *5.10 Total Alkalinity*. Retrieved 28<sup>th</sup> September 2012 from <http://water.epa.gov/type/rsl/monitoring/vms510.cfm>
- Viraraghavan T, KS Subramanian, BV Rao (1996). Drinking water at the tap: Impact of plumbing materials on water quality. *Journal of Environmental Science and Health: Part A-Environmental Science and Engineering & Toxic and Hazardous Substance Control*, Vol. 31, Issue 8, pp. 2005-2016
- Weiner RF and R Matthews (2003). *Environmental Engineering (4<sup>th</sup> ed.)*. Burlington, MA: Butterworth Heinemann
- Yellow Brass Claims (2012). *Yellow brass claims: Information*. Retrieved 23<sup>rd</sup> October 2012 from <http://www.yellowbrasslawsuit.com/index.php>
- Yohai L, WH Schreiner, M Vazquez, MB Valcarce (2011). Surface characterization of copper, zinc and brass in contact with tap water inhibited with phosphate ions. *Applied Surface Science*, Vol. 257
- Yohai L, M Vazquez, MB Valcarce (2010). Brass corrosion in tap water distribution systems inhibited by phosphate ions. *Corrosion Science*, Vol. 53
- Zhang Y and M Edwards (2011). Effects of pH, chloride, bicarbonate, and phosphate on brass dezincification. *Journal of the American Water Works Association*, Vol. 103, No. 4, pp. 90-102.
- Zhang XG (1996). *Corrosion and Electrochemistry of Zinc*. New York: Plenum Press

## Appendix A: Aggregate terms describing chlorine in water

“**Available chlorine** is a measure of the oxidizing capacity of a solution in terms of equivalent molecular chlorine. One mole of molecular chlorine can accept two moles of electrons, as shown in Reaction 2.8, and this is assumed as the reference point (100% of available chlorine).



*Reaction 2.8 – Molecular chlorine reduction*

A mole of hypochlorite can also accept two moles of electrons, as shown in Reaction 2.9; therefore, the oxidizing capacity of hypochlorite is considered the same as molecular chlorine.



*Reaction 2.9 - Hypochlorite ion reduction:*

**Applied Chlorine** is the concentration of available chlorine in the treated water after a given dosage of a pure chlorine disinfectant, calculated according to the dilution.

**Chlorine Demand** is defined as the quantity of available chlorine consumed by water impurities.

**Free (Residual) Chlorine** is an aggregate measure of the quantity of chlorine compounds that, after the dosage, has not reacted with ammonia or organic matter, i.e. molecular chlorine, hypochlorous acid, and hypochlorite ion, each of them expressed as available chlorine.

**Combined (Residual) Chlorine**, complementarily, measures the amount of chlorine that has reacted with ammonia forming chloramines. Combined chlorine is important since chloramines are not detectable as free chlorine, but still provide disinfecting action.

**Total (Residual) Chlorine** is the total amount of chlorine compounds detectable by titration. If no organic matter, phenols or organic nitrogen are present in the water, no stable chlorine compounds are formed and total residual chlorine equals the sum of the free and combined chlorine.”

Adapted from Morganti (2002).