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**Title: WATER STABILISATION AND CORROSION CONTROL**

**Author: Professor T J Casey**

Aquavarra Research Limited  
22A Brookfield Avenue  
Blackrock  
County Dublin  
Ireland  
[www.aquavarra.ie](http://www.aquavarra.ie)

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## DRINKING WATER STABILISATION AND CORROSION CONTROL

T J Casey  
Aquavarra Research Limited

### INTRODUCTION

Water has remarkable solvent properties as a result of which it is capable of taking into solution some quantity of the various materials with which it comes into contact between source and tap. The reactivity of water is a function of its chemical characteristics, which are typically derived from a combination of natural and applied processes. Stabilisation is the term applied to the chemical conditioning of water to reduce its solvent and corrosive capacities and to ensure that it is not scale-forming.

Water supply infrastructure comprises treatment process tanks, reservoirs and cisterns, pipelines and plumbing systems, constructed in a variety of materials. Leaching of material from conveyance conduits and storage vessels may adversely affect water potability and also, in the long term, may threaten their structural integrity. Likewise, the deposition of a scale on the internal surface of a conduit impairs performance by reducing conveyance capacity.

The primary materials used in the treatment, transport and distribution of water include cement-based materials, including concrete, asbestos cement (AC) and cement mortar-lined pipes, steel, cast iron and ductile iron pipes with bituminous and epoxy linings, plastic pipes, copper and lead pipes.

Water corrosivity is a complex issue, influenced by a various parameters including pH, alkalinity and ion content, particularly chloride and sulphate. In the drinking water field, the controlled deposition of calcium carbonate ( $\text{CaCO}_3$ ) films on the surface of water conveyance systems is the predominantly used method of corrosion control, hence an understanding of the behaviour of the carbonate system is central to the engineering of water stabilisation.

### THE CARBONATE SYSTEM

The inorganic carbon species in water, commonly called the carbonate system, comprise free gaseous carbon dioxide ( $\text{CO}_2$ ), carbonic acid ( $\text{H}_2\text{CO}_3$ ), bicarbonate ions ( $\text{HCO}_3^-$ ) and carbonate ions ( $\text{CO}_3^{2-}$ ). The sum of the concentrations of the carbonate species, expressed as molar concentration (or species equivalent) constitutes the total inorganic carbon in water, or the TIC-value.  $\text{H}_2\text{CO}_3$  is formed by the hydrolysis of free  $\text{CO}_2$  and constitutes only approximately 0.3% of the  $\text{CO}_2$  concentration. Hence, for practical computational purposes  $\text{CO}_2$  is subsequently taken to include both  $\text{H}_2\text{CO}_3$  and  $\text{CO}_2$  ( $\text{H}_2\text{CO}_3^*$  is commonly used in the literature to designate the sum of these two species).

The distribution of the carbonate species is a function of water pH, as illustrated in Fig 1. The equilibrium expressions, on which the graphical plots in Fig 1 are based, are given in the Appendix.

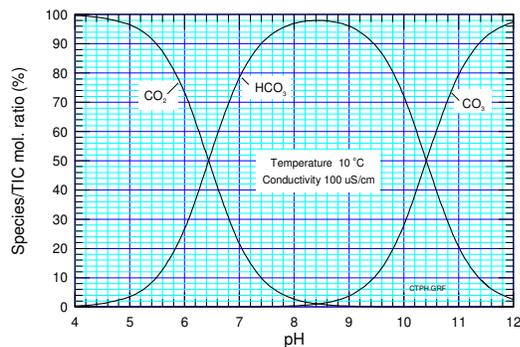
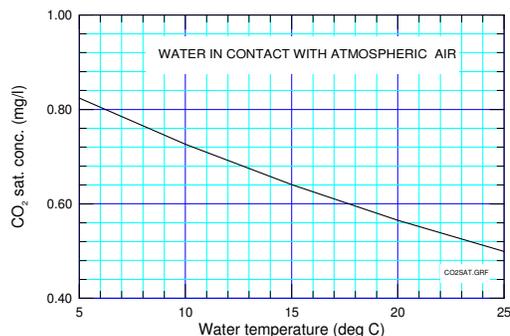


Fig 1 Distribution of carbonate species as function of pH

It will be noted that as the water pH increases, CO<sub>2</sub> is converted to HCO<sub>3</sub><sup>-</sup>, which in turn is converted to CO<sub>3</sub><sup>=</sup> as the pH increases above about 8.5.

Water and air are both reservoirs of CO<sub>2</sub>. The solubility of CO<sub>2</sub> in water is proportional to its partial pressure in air. Atmospheric air contains 0.0314% CO<sub>2</sub> by volume, exerting a partial pressure of 3.14 x10<sup>-4</sup> atm at an air pressure of 1 atm. The computed saturation concentration of CO<sub>2</sub> in water in contact with air is plotted in Fig 2, as a function of water temperature.



**Fig 2 Solubility of Carbon dioxide in water**

As indicated in Fig 2, the equilibrium concentration of CO<sub>2</sub> in water is in the range 0.5 to 0.8 mg/l in the normal natural surface water temperature range. However, many natural surface waters and groundwaters are found to have CO<sub>2</sub> levels greatly in excess of this value range.

The TIC-value and the carbonate species distribution in water are effectively defined by two parameters, namely pH and total alkalinity, both of which are easily measured in the laboratory. Total alkalinity (T<sub>alk</sub>) is defined as follows:

$$T_{alk} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \text{ eq / l}$$

where [ ] indicates molar concentration.

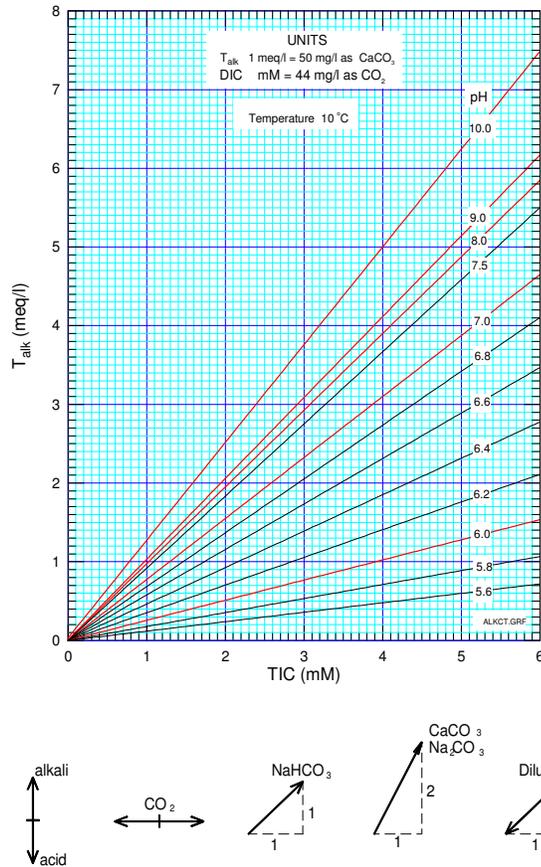
As indicated in Fig 1, the CO<sub>3</sub><sup>=</sup> concentration in water is very low below pH 8.5, hence HCO<sub>3</sub><sup>-</sup> is the primary source of alkalinity in natural waters. Free CO<sub>2</sub> is the priming species for the generation of HCO<sub>3</sub><sup>-</sup> in natural waters, through its enabling of the dissolution of carbonates according to the reaction:



Fig 3, which shows pH as a function of alkalinity and TIC, illustrates the inter-relationship of these 3 parameters. Knowledge of any two allows computation of the third. In practice; pH and T<sub>alk</sub> are routinely measured in the laboratory.

The chemicals used in water treatment include primary coagulants such as the trivalent aluminium (Al<sup>3+</sup>) and iron (Fe<sup>3+</sup>) salts, strong acids such sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), strong alkalis such as lime (Ca(OH)<sub>2</sub>), and a range of alkalinity-boosting chemicals such as sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>). The addition of these chemicals to water alters the water pH and hence the distribution of the carbonate species. Fig 3 provides a convenient means of graphically checking the influence of such chemical additions on pH. Strong acids and alkalis and trivalent coagulants alter the alkalinity but do not change the TIC value, resulting in a vertical movement of the equilibrium point. Alkalinity-boosting chemicals alter both alkalinity and TIC value, resulting in a diagonal shift in the equilibrium point. Dilution also results in a diagonal shift of the equilibrium point, affecting both alkalinity and TIC in the same degree. Stripping or addition of CO<sub>2</sub> does not change alkalinity, but alters the TIC value, resulting on a horizontal shift in pH in Fig 3.

The changes in  $T_{alk}$  and TIC values, due to the addition of 1 mg/l of a range of chemicals used in water treatment, are given in Table 1. These values can be used in conjunction with Fig 3 to estimate the influence of such chemicals on pH.



**Fig 3** Dependence of pH on alkalinity and TIC

**Table 1**  
**Water treatment chemicals**  
 Effect of 1 mg/l addition on alkalinity and TIC

Chemical	Alkalinity (meq/l)	TIC(mM)
$Al^{3+}$	-0.111	0
$Fe^{3+}$	-0.054	0
$H_2SO_4$	-0.020	0
HCl	-0.028	0
$CO_2$	0	+0.023
$NaHCO_3$	+0.011	+0.011
$CaCO_3$	+0.020	+0.010
$Na_2CO_3$	+0.019	+0.009

As noted earlier, many surface and groundwaters are found to have  $CO_2$  concentrations considerably in excess of the atmospheric equilibrium value (Fig 2), potentially making water corrosive as discussed later. The  $CO_2$  concentration is a function of pH and alkalinity and can be determined by combined use of Fig 3 and Fig 1 or alternatively from the approximate relationship:

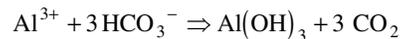
$$\text{CO}_2 \text{ (mg / l)} = \frac{T_{\text{alk}}}{10^{(\text{pH}-6.34)}}$$

where the units of measurement are:  $T_{\text{alk}}$  as mg/l  $\text{CaCO}_3$  and  $\text{CO}_2$  as mg/l  $\text{CO}_2$ .

It has become the standard practice in water engineering and water analysis to express  $T_{\text{alk}}$  as mg/l  $\text{CaCO}_3$ , where 1 meq/l = 50 mg/l  $\text{CaCO}_3$ .

### WATER STABILITY - THE LANGELIER INDEX

As noted in the introductory paragraphs, water is considered to be stable if it is slightly supersaturated with  $\text{CaCO}_3$  such that its tendency is to form a  $\text{CaCO}_3$  scale on contact surfaces. However, in the treatment of surface waters for colour and turbidity removal, added chemicals, such as the trivalent salts of aluminium and iron, reduce pH and alkalinity and increase  $\text{CO}_2$  concentration, hence also  $\text{CaCO}_3$  solubility. In the case of high alkalinity waters, a strong acid such as sulphuric acid, may be also used to reduce the coagulation pH for improved process performance. The precipitation reactions reduce the water alkalinity and produce  $\text{CO}_2$ , thereby reducing the alkalinity/ $\text{CO}_2$  ratio and also reducing pH, as illustrated in Fig 3.



Thus, inevitably, most chemically coagulated waters are supersaturated with  $\text{CO}_2$  and are capable of dissolving calcium carbonate. Such waters can be made chemically stable by the addition of an alkali and/or by the stripping out of excess  $\text{CO}_2$ . Lime ( $\text{Ca}(\text{OH})_2$ ) is the most commonly used alkali for this purpose. It is doubly effective insofar as it raises both the calcium and the carbonate concentrations, thus moving their product closer to the  $\text{CaCO}_3$  solubility product  $K_{\text{sp}}$ , expressed as follows:

$$\text{At } \text{CaCO}_3 \text{ saturation} \Rightarrow [\text{Ca}^{2+}][\text{CO}_3^{2-}] = K_{\text{sp}}$$

The pH at which a water sample would be at  $\text{CaCO}_3$  saturation, without changing its Ca or  $T_{\text{alk}}$  values, is generally referred as the saturation pH or  $\text{pH}_s$ . The Saturation Index (SI), also known as the Langelier Index, is defined as follows:

$$\text{SI} = \log \left[ \frac{[\text{Ca}][\text{CO}_3]}{K_{\text{sp}}} \right] = \text{pH} - \text{pH}_s$$

A positive SI-value for a water sample indicates that it is supersaturated with respect to  $\text{CaCO}_3$ , whereas a negative SI-value indicates under-saturation. Hence, water that has a negative SI is aggressive towards  $\text{CaCO}_3$  and is considered chemically unstable. The degree of over or under-saturation of a water sample can be calculated from its pH, alkalinity and  $\text{Ca}^{2+}$  concentrations and is known as the calcium carbonate precipitation potential or CCPP.

Estimated SI and CCPP values for a range of Irish surface waters are presented in Table 2 (negative values indicate a  $\text{CaCO}_3$  saturation deficit). Two features of the data are noteworthy (a) as may be expected, only the hard alkaline waters have positive SI and CCPP values, and (b) the SI value is not a good index of the magnitude of the  $\text{CaCO}_3$  saturation excess or deficit. For example, the data indicate that Lough Gill water has a much greater  $\text{CaCO}_3$  deficit than Pollaphuca Reservoir water but it has a lesser negative SI value.

**Table 2**  
 Computed chemical stability characteristics of some Irish surface waters  
 (Reference temperature 10 °C)

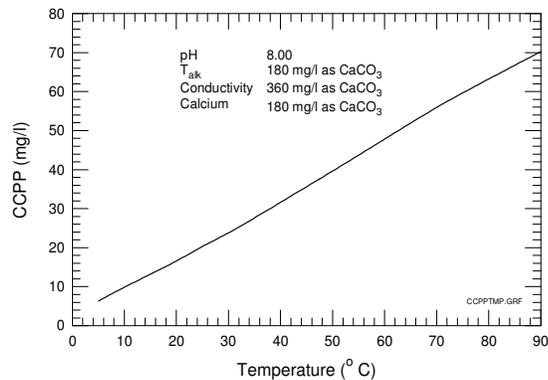
Surface water	Measured values <sup>(1)</sup>			Calculated values <sup>(2)</sup>		
	pH	Alkalinity (mg/l CaCO <sub>3</sub> )	Calcium (mg/l CaCO <sub>3</sub> )	TIC mg/l CO <sub>2</sub>	SI	CCPP (mg/l)
R. Boyne, Roughgrange	7.80	272	322	248.4	0.59	35.7
R. Shannon, Clareville	7.98	180	180	162.0	0.35	9.5
R. Corrib, Galway	7.87	124	124	112.6	-0.07	-1.0
Lough Mask	7.45	104	104	100.1	-0.64	-13.8
R. Liffey, Leixlip	7.91	95	104	86.0	-0.22	-2.4
R. Liffey, Pollaphuca	7.35	35	35	34.5	-1.66	-10.4
Lough Gill, Sligo	7.15	85	85	88.9	-1.11	-27.2
Lough Owel, Mullingar	8.20	86	91	76.4	-0.04	-0.2
Dundalk	7.66	71	82	66.0	-0.69	-7.1
R. Lee, Inniscarra	7.42	54	65	52.3	-1.14	-11.1
R. Suir ?, East Waterford	7.48	43	49	41.2	-1.30	-8.9
R. Lee, Cork WTW	7.21	34	43	34.9	-1.72	-12.8
R. Vartry, Roundwood	7.91	20	20	18.1	-1.58	-5.4
R. Feale, Listowel	6.39	20	24	37.9	-3.02	-46.0
R. Owennasop, Inishowen	6.40	10	10	18.5	-3.68	-25.4

Footnotes

1. The indicated values are characteristic of the value range for each source
2. The basis of calculation is outlined in the Appendix

**Influence of temperature**

It is a common observation that hard waters give rise to scaling problems, particularly in hot water systems. Unlike most solids, the solubility of calcium carbonate decreases with increase in temperature. This reflects the temperature dependence of the equilibrium constants that govern the carbonate system, as outlined in the Appendix. The influence of temperature on calcium carbonate solubility is illustrated by the data plotted in Fig 4. The plotted data indicate an almost linear increase in CCPP with temperature rise.



**Fig 4** Influence of temperature on CCPP

**WATERMANS**

The pipe materials used in water supply networks include ferrous metals (cast iron, ductile iron and steel) plastics (uPVC and polyethylene), asbestos cement, concrete. Invariably, ferrous metal pipes are protected from both internal and external corrosion by appropriate protective coatings.

Metal pipe lining materials include bituminous compounds, epoxy resin materials and cement mortar. It is obviously important that any matter leached from such linings should not pose a danger to human health. The use of materials in contact with drinking water is regulated in the UK by DWI Regulation 31 (2000) and in the USA by ANSI/NSF Standard 61: Drinking Water System Components – Health Effects (NSF International, 2001).

### **Plastic Water mains**

uPVC and polyethylene pipes are widely used for water distribution, particularly in the size range up to 300mm diameter. They are effectively immune to corrosion and therefore to the leaching of corrosion products into the conveyed water. However, they may leach small amounts of organic materials used in their manufacture. For example, it is noted in a paper prepared for the USEPA (AWWA, 2002) that uPVC pipes manufactured prior to 1977 contain elevated levels of vinyl chloride monomer, which are prone to leaching. It is not known if this also applies to pipes manufactured in Europe at that time. Vinyl chloride is a toxic chemical with known carcinogenic effects. The permissible level of vinyl chloride in Irish drinking water is 0.5 µg/l (SI278, 2007).

### **Concrete, asbestos cement (AC) pipes and cement mortar-lined pipes**

The extent of leaching from cement-based materials is dependent on the aggressivity of the conveyed water to the hydrated cement. Hydrated cement consists of calcium silicates and calcium aluminates in various proportions depending on the type of cement. The cement hydration process creates a highly alkaline environment within the matrix of the hardened material.

Cement mortar linings are widely used to protect ductile iron pipes from metal corrosion. They provide excellent protection where the conveyed water is chemically stable. Where the water is unstable i.e. where it contains aggressive free CO<sub>2</sub>, the pore water in the cement matrix reacts with calcium hydroxide to form calcium carbonate, which then further combines with CO<sub>2</sub> to form calcium bicarbonate. If the water has a high alkalinity this will have little impact on the water pH. However, if the water is a soft low alkalinity water, the rise in pH may be significant, possibly exceeding the drinking water upper limit value of 9.5 (SI 278, 2007). There is also the consequent risk that a high water pH may cause enhanced leaching of aluminium from cement mortar linings (Berend & Trouwborst, 1999). The availability of aluminium in cement mortar linings varies with the cement type used. Expressed as Al<sub>2</sub>O<sub>3</sub>, it can vary from about 5% in Portland cement to about 36% in high-alumina cement

The leaching extent is likely to be greater in smaller diameter pipes, as the lining contact area per unit water volume is inversely proportional to the pipe diameter. It is also likely to be significantly influenced by the contact time between the water and the lining.

In the case of soft low alkalinity waters, where leaching from a cement mortar lining would cause an excessive pH rise in the conveyed water, the lining may be sealed with a coating of either an epoxy resin or asphalt.

To avoid scaling and corrosion problems, the SI value should be close to zero. The preferred range for SI values is  $-0.2 < SI < +0.3$  (Mons et al., 2006). This band width is illustrated in Fig 5, as a function of water hardness. The acceptable pH range in Fig 5 should be taken as indicative only, as the SI value is dependent on alkalinity as well as hardness. The empirical alkalinity/hardness correlation for Irish river waters, given in the Appendix, was used in calculating the correlations plotted in Fig 5.

The chemical coagulation process, commonly applied in the production of drinking water from surface water sources, exerts an alkalinity demand, thereby reducing pH and alkalinity and generally resulting in an aggressive water.

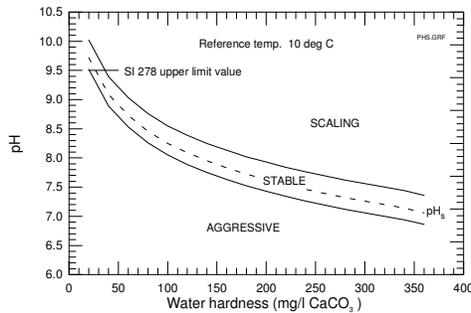


Fig 5 Acceptable SI range for stable water

### Ductile iron and steel

A positive SI value is obviously of benefit in the protection of iron and steel pipes from corrosion as it results in the formation of a calcium carbonate scale. It has also been found that chloride and sulphate ions promote corrosion of these metals. The German guidelines for materials applied in drinking water supply (DIN EN 12502: 2004/2005) indicate a negligible risk of iron and steel corrosion where the alkalinity is sufficient to satisfy the criterion:

$$([\text{Cl}^-] + [\text{NO}_3^-] + 2[\text{SO}_4^{2-}]) / [\text{HCO}_3^-] < 1$$

### PLUMBING PIPES

Plumbing pipes are manufactured from a variety of materials including plastics (uPVC and polyethylene), copper and lead.

Plastic plumbing is effectively corrosion free and hence does not transfer corrosion byproducts to drinking water.

While lead plumbing systems are no longer installed, there is still a significant amount of lead plumbing in old urban dwellings. Copper tubing is extensively used for cold and hot water systems in current building construction practice.

Copper and lead plumbing piping is subject to corrosion by water, the extent of which varies, depending on the chemical characteristics of the water. As lead and copper are damaging to human health, permissible limit values in drinking water are specified in drinking water standards. The Irish Drinking Water Regulations (SI 278, 2007) specify a limit value of 25 µg/l for lead in drinking water up to 24/12/2013 and a limit value of 10 µg/l thereafter. The SI 278 limit value for copper is 2 mg/l. The USEPA, in its Lead & Copper Rule (LCR) of 1991 sets an 'action level' for lead at 15 µg/l and an action level for copper at 1.3 mg/l, at the consumer's tap.

Although the chemistry of lead dissolution or plumbosolvency has been widely studied and has an extensive published literature, accurate predictive modeling has not been established. Empirical evidence (Edwards et al., 1999) indicates that alkalinity, pH and the mass ratio of chloride to sulphate all influence lead corrosion by-product release. Waters with a low pH (< 7.0) and low alkalinity (< 20 mg/l as CaCO<sub>3</sub>) are known to be aggressive to lead plumbing. The solubility of lead in such waters, which invariably have a negative SI value, has been observed to be lowest in the alkalinity range 20-40 mg/l as CaCO<sub>3</sub> at pH > 8.5.

A high chloride/sulphate ratio has been found to favour lead dissolution, other water quality parameters being equal. Thus, where chemical coagulation is required for soft low alkalinity waters, it would be preferable to use a sulphate-based coagulant, such as alum, rather than a chloride-based coagulant, such as ferric chloride, from a lead corrosion control viewpoint.

The pH and alkalinity values of soft low alkalinity waters can be increased by the addition of  $\text{Ca}(\text{OH})_2$  or  $\text{NaOH}$ , where there is sufficient free  $\text{CO}_2$  present to generate alkalinity. Where such is not the case, the alkalinity must be boosted by the addition of bicarbonate, possibly in combination with small amounts of either  $\text{Ca}(\text{OH})_2$  or  $\text{NaOH}$ .

Copper pipes, cylinders and copper alloy fittings are extensively used in plumbing systems. While they are highly corrosion-resistant, some unstable waters may cause corrosion (Oliphant, 2003). The basic water quality parameters affecting dissolution of copper are pH, alkalinity and chloride to sulphate ratio. Utility experience in the United States (Dodrell et al., 1995) indicates that for low and medium alkalinity waters ( $T_{\text{alk}} < 90 \text{ mg/l as CaCO}_3$ ), problems with exceedence of the copper permissible limit (1.3 mg/l) were not encountered unless the pH was  $< 7.0$ . In the case of high alkalinity waters no copper exceedences were found if the pH was  $> 7.8$ . The latter pH value is likely to exceed the  $\text{pH}_s$  value for many high alkalinity waters that have been through a chemical coagulation process and subsequently stabilised by the addition of  $\text{CaCO}_3$ . Presumably, chemically stable waters, which have a  $\text{pH} < 7.8$ , are unlikely to cause copper corrosion.

Localised corrosion or pitting of copper plumbing pipes and cisterns, leading to pinhole leaks, while an uncommon phenomenon, is an acknowledged long-standing problem, the fundamental chemistry of which is complex and apparently not fully understood. As a result, there is sometimes a divergence between theoretical models of the process and practical experience.

A classification of copper corrosion problems, presented by Edwards et al. (1994) is set out in Table 3. This classification divides copper corrosion problems into four categories comprising uniform corrosion and three types of pitting corrosion.

Table 3  
**Summary of copper corrosion problems**

Characteristic	Uniform corrosion	Type I Pitting (cold water)	Type II Pitting (hot water)	Type III Pitting (soft water)
Pit shape	No pits	Deep and narrow	Narrower than Type I	Wide and shallow
Problem	Blue or green water, high by-product release	Pipe failure	Pipe failure	Blue water, high by-product release, pipe blockage
Water quality	Soft waters of low pH ( $< 7.2$ )	Hard cold waters pH between 7 and 7.8, high sulphate relative to chloride and bicarbonate, high $\text{CO}_2$	Hot waters, pH $< 7.2$ , high sulphate relative to bicarbonate.	Soft waters, pH $> 8$
Remedial measures	Increase pH or bicarbonate	Increase pH and bicarbonate	Increase pH and bicarbonate, reduce temperature	Increase hardness and alkalinity, raise $\text{Cl}_2$ residual to $> 0.5 \text{ mg/l}$

Of the two anions, chloride and sulphate, the latter has been found to be more aggressive towards copper than the former. Thus, where chemical coagulation is required for raw waters with copper corrosion potential, it would be preferable to use a chloride-based coagulant, such as polyaluminium chloride or ferric chloride, rather than a sulphate-based coagulant, such as aluminium sulphate.

In order to avoid copper corrosion by drinking water, the following recommendation was developed in the Netherlands (Mons et al., 2006):

$$\text{pH} > 0.38 \text{ TIC} + 1.5[\text{SO}_4^{2-}] + 5.3$$

where TIC and  $[\text{SO}_4^{2-}]$  are expressed as mM/l.

Where the necessary modification of the water pH and/or alkalinity required for the control of plumbosolvency and/or cuprosolvency is not feasible, phosphate-based inhibitors may be considered (AwwaRF, 2005). The dosing of orthophosphate at a rate of 3 to 5 mg/l as  $\text{PO}_4^{3-}$  has been found to have

beneficial effects in reducing the release of corrosion by-products in both copper and lead plumbing systems.

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## Appendix Carbonate System Constants

### Aqueous reactions



### Carbon dioxide solubility

The concentration of free  $\text{CO}_2$  in water is proportional to its partial pressure in air in accordance with Henry's law.

$$[\text{CO}_2] = K_H P_{\text{CO}_2} \text{ mol/l} \quad (\text{A4})$$

where  $K_H$  is the Henry's law constant and  $P_{\text{CO}_2}$  is the partial pressure (atm) of  $\text{CO}_2$  in air.

At equilibrium, the ratio of  $[\text{CO}_2]/[\text{H}_2\text{CO}_3]$  is about 631:1 (Snoeyink & Jenkins, 1980), hence it is convenient for computational purposes represent the sum of these two species by the hypothetical species  $\text{H}_2\text{CO}_3^*$ . Thus, equation (A4) becomes:

$$[\text{H}_2\text{CO}_3^*] \cong K_H P_{\text{CO}_2} \quad (\text{A5})$$

### Dissociation constants for carbonate species

$$\frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]} = K_1 \quad (\text{A6})$$

$$\frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = K_2 \quad (\text{A7})$$

**Dissociation constant for water** 
$$[\text{H}^+][\text{OH}^-] = K_w \quad (\text{A8})$$

### Calcium carbonate solubility

Calcium carbonate is poorly soluble in water, its solubility being defined by the equilibrium condition:

$$[\text{Ca}^{2+}][\text{CO}_3^{2-}] = K_{\text{SO}} \quad (\text{A9})$$

Equations (A5) to (A9), inclusive, are used to calculate the distribution of the carbonate species in water. Two related composite parameters, namely total alkalinity (Talk) and total inorganic carbon (TIC) are commonly used in such computations. They are defined as follows:

$$T_{\text{alk}} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \text{ eq/l} \quad (\text{A10})$$

$$TIC = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \text{ mol/l} \quad (\text{A11})$$

The magnitudes of the dissociation and other constants are influenced both by the water temperature and ionic strength. Empirical expressions quantifying the temperature dependence of the carbonate system constants are given in Table A1.

Table A1  
**Temperature dependence of carbonate system constants**  
(Loewenthal and Marais, 1976)

Parameters:  $pK = -\log(K)$ ;  $t = ^\circ\text{C}$ ;  $T = \text{absolute temp. (K)} = 273 + t$

$$pK_1 = \frac{17052}{T} + 215.21 * \log(T) - 0.12675 * T - 545.56$$

$$pK_2 = \frac{2902.39}{T} + 0.02379 * T - 6.498$$

$$pK_w = \frac{4787.3}{T} + 7.1321 * \log(T) + 0.010365 * T - 22.801$$

$$pK_H = 0.0138 * t + 1.12 \quad \text{for } t = 0 \text{ to } 35 \text{ } ^\circ\text{C}$$

$$pK_H = 0.0069 * t + 1.36 \quad \text{for } t = 35 \text{ to } 80 \text{ } ^\circ$$

$$pK_s = 0.01183 * t + 8.03$$

### Ionic strength correction

The adjustment of the values of the constants to allow for ionic strength is conveniently made on the basis of conductivity, which is a readily measurable parameter. The following empirical relation between ionic strength ( $\mu$ ) and conductivity is taken from Snoeyink & Jenkins (1980):

$$\mu = 1.6 \times 10^{-5} \times \text{conductivity } (\mu\text{S} / \text{cm}) \quad (\text{A12})$$

The following ionic strength corrections for the foregoing equilibrium constants are taken from Fair, Geyer & Okun (1968).

$$pK_{1\mu} = pK_1 - (\mu)^{0.5} / [1 + 1.4(\mu)^{0.5}] \quad (\text{A13})$$

$$pK_{2\mu} = pK_2 - 2(\mu)^{0.5} / [1 + 1.4(\mu)^{0.5}] \quad (\text{A14})$$

$$pK_{SO\mu} = pK_{SO} - 4(\mu)^{0.5} / [1 + 3.9(\mu)^{0.5}] \quad (\text{A15})$$

$$pK_{w\mu} = pK_w - (\mu)^{0.5} / [1 + 1.4(\mu)^{0.5}] \quad (\text{A16})$$

### Reaction kinetics

The foregoing relationships define the carbonate system in its equilibrium state. When this state is disturbed by the addition of a strong acid or a strong alkali, the resultant reactions proceed rapidly to completion with the exception of reaction (A1), involving free  $\text{CO}_2$  and  $\text{H}_2\text{CO}_3$  (Snoeyink & Jenkins, 1980), which proceeds at a slower rate than the others. As a consequence there may be an initial overshoot in pH change, while the  $\text{CO}_2$ : $\text{H}_2\text{CO}_3$  equilibrium is being established. This is because the  $\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^-$  interchange is more rapid than the  $\text{CO}_2 \rightleftharpoons \text{H}_2\text{CO}_3$  interchange. For example, in the

alum-based chemical coagulation process, used to remove colour and turbidity in the production of drinking water,  $\text{Al}^{3+}$  reacts with  $\text{HCO}_3^-$  to form  $\text{H}_2\text{CO}_3$ , thereby reducing the pH. Following the addition of alum, the pH is likely to temporarily drop below the equilibrium value, to which it then gradually returns as the  $\text{H}_2\text{CO}_3:\text{CO}_2$  equilibrium ratio is re-established.

### **Empirical Correlations**

The following empirical correlation of alkalinity (Alk), hardness (H) and conductivity (C) for Irish river waters (Casey, 2009) has been used in carbonate system calculations:

$$\text{Alk} = 0.37 \text{H}^{1.5} = 0.014 \text{C}^{1.53}$$

### **Appendix References**

Casey, T J (2009) The carbon flux in Irish rivers, [www.aquavarra.ie/publications](http://www.aquavarra.ie/publications)

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Fair, G M, Geyer, J C and Okun, D A (1968) Water Purification and Wastewater Treatment and Disposal, Vol. 2, John Wiley & Sons Inc., New York.