

WATER STABILITY - WHAT DOES IT MEAN AND HOW DO YOU MEASURE IT ?



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ABSTRACT

Currently there is no requirement under the Australian Drinking Water Guidelines to produce a stable water that is not potentially corrosive to water treatment plant equipment and reticulation systems. This paper discusses the concept of water stability, describes various indices available to gauge the corrosivity of a water and their methods of calculation. An approach is also outlined whereby the stability of water can be determined following a particular treatment regime and how it can then be conditioned to make it less aggressive. Using a worked example, these concepts are illustrated by examining treatment and conditioning of a typical water; the Waranga Channel supply at Rochester, Victoria.

KEY WORDS

Corrosivity, Water Stability, Calcium Carbonate, Langelier Index, CCPP

1.0 INTRODUCTION

Many surface waters require a coagulant such as alum for effective treatment. After treatment and disinfection with chlorine, the water can become aggressive. At present there is no requirement to produce a water that is stable (neither scale forming or corrosive) other than having a pH in the range 6.5 to 8.5 (Australian Drinking Water Guidelines, 1996).

This paper describes water stability and shows how several indices may be calculated to assess the likely corrosivity of a water. An approach is also outlined whereby the stability of a water can be determined following a particular treatment regime and how the water can then be conditioned to make it less aggressive, using a worked example.

2.0 WATER CHEMISTRY

The following are the most important water quality parameters affecting corrosivity, alkalinity, pH and calcium.

The concentration of various constituents in a water can be expressed in one of two ways: as the ion or “as is” or as calcium carbonate. To convert from one form to the other, the conversion factors listed in Table 1 are used. The chemical formula and formula weights of these constituents are also listed. It is usual practice to report the concentration of alkalinity as mg/L CaCO₃ rather than “as is”.

Positively charged ions are called “cations” (e.g. calcium ion or Ca⁺⁺) and negatively charged ions, “anions” (e.g. bicarbonate or HCO₃⁻). When we sum the concentration of cations expressed as mg/L CaCO₃, the total should be the same as the sum of the anions, thus giving a *balanced water analysis*. Table 2 is a list of chemicals commonly used in water treatment processes, giving their chemical formula, formula weight and factor to convert to equivalent weight as CaCO₃.

Table 1: *Chemical Formula, Formula Weight and Factors to Convert Concentration from “AS IS” to “CaCO₃” for Common Cations and Anions*

ION	CHEMICAL FORMULA	FORMULA WEIGHT	FOR EQUALVALENT AS CaCO ₃ MULTIPLY BY
Aluminium	Al ⁺⁺⁺	27.0	5.56
Ammonium	NH ₄ ⁺	18.0	2.78
Calcium	Ca ⁺⁺	40.1	2.50
Ferric (Iron)	Fe ⁺⁺⁺	55.9	2.69
Ferrous (Iron)	Fe ⁺⁺	55.9	1.79
Magnesium	Mg ⁺⁺	24.3	4.12
Sodium	Na ⁺	23.0	2.18
Potassium	K ⁺	39.1	1.28
Bicarbonate	HCO ₃ ⁻	61.0	0.82
Carbonate	CO ₃ ⁻⁻	60.0	1.67
Chloride	Cl ⁻	35.5	1.41
Hydroxide	OH ⁻	17.0	2.94
Sulphate	SO ₄ ⁻	96.1	1.04

Table 2: *Chemical Formula, Formula Weights and Factors to Convert Concentration from “AS IS” to “CaCO₃” for Common Chemicals Used in Water Treatment*

CHEMICAL	CHEMICAL FORMULA	FORMULA WEIGHT	FOR EQUALVALENT AS CaCO ₃ MULTIPLY BY
Alum (Aluminium Sulphate)	Al ₂ (SO ₄) ₃ .18H ₂ O	666.1	0.45
Ammonia	NH ₃	17.0	2.94
Calcium Carbonate	CaCO ₃	100.1	1.00
Lime (Calcium Hydroxide)	Ca(OH) ₂	74.1	1.35
Quicklime (Calcium Oxide)	CaO	56.1	1.78
Carbon Dioxide	CO ₂	44.0	1.14
Ferric Chloride	FeCl ₃ .6H ₂ O	270.3	0.56
Ferric Sulphate	Fe ₂ (SO ₄) ₃	399.9	0.75
Ferrous Sulphate	FeSO ₄ .7H ₂ O	278.0	0.36
Hydrochloric Acid	HCl	36.5	1.37
Soda Ash (Sodium Carbonate)	Na ₂ CO ₃	106.0	0.94
Caustic Soda (Sodium Hydroxide)	NaOH	40.0	1.25
Sodium Bicarbonate	NaHCO ₃	84.0	0.60
Sulphuric Acid	H ₂ SO ₄	98.1	1.02

Table 3: *Water Analysis Waranga Channel at Rochester*

	AS ION	AS CaCO ₃		AS ION	AS CaCO ₃
Calcium	7.9	19.7	EC 180 pH 7.6	Alkalinity	18.3
Magnesium	4.0	16.5		Chloride	45.0
Sodium	22.0	47.9		Sulphate	4.0
Potassium	2.3	2.9			
		87.0			82.7

As an example of how to apply these ideas, let’s look at a typical water supply: the Waranga Channel at Rochester, Victoria (Table 3).

From this analysis we can conclude:

- ◆ The sum of the cations and the sum of the anions are not the same: 87.0 v 82.7 mg/L as CaCO₃. However, in practice we generally label a water analysis *balanced* if the (sum of cations / sum of anions) is within + or - 5%. In this case it is + 5%, so it is acceptable.
- ◆ Alkalinity of the water is 15.0 mg/L, which is relatively low, suggesting this water will require supplemental alkali addition for effective treatment when using alum.
- ◆ Total hardness of the water ([Ca]+[Mg]) is equal to 36.2 mg/L as CaCO₃; a *soft* water.
- ◆ The total dissolved solids (TDS) level is approximately 125 mg/L “as is” derived from the conductivity (EC) of the water.

3.0 SOME BASIC CONCEPTS

To determine what happens when we add various chemicals to a water and to determine if it is corrosive or stable, we first need to understand several important “rules”:

- ◆ **Alkalinity is consumed when an acid is added to a water.** In this instance, an “acid” can be one in the usual sense, such as sulphuric acid, or more often than not, a metal cation. Hence, when we add a cation to a water, say aluminium from alum, we consume alkalinity. The same is also true when we add chlorine gas.
- ◆ **Alkalinity increases when an alkali is added to a water.**
- ◆ **Carbon dioxide is produced in a water when alkalinity is consumed.**
- ◆ **Carbon dioxide is destroyed when an alkali is added to a water.**
- ◆ **The pH of a water will decrease when carbon dioxide is formed and will increase when CO₂ is destroyed.**

Knowing the changes that various chemicals make to alkalinity and carbon dioxide levels allows prediction of the pH of the water as a result of different treatment regimes. Table 4 gives the changes in alkalinity and carbon dioxide that occur when various chemicals are added to a water.

Table 4: *Alkalinity Consumed and Carbon Dioxide Produced per mg Chemical Dose*

CHEMICAL	mg ALKALINITY, CaCO ₃ per mg CHEMICAL	mg CO ₂ , per mg CHEMICAL
Alum	-0.45	0.40
H ₂ SO ₄	-1.02	0.90
HCl	-1.37	1.20
Ca(OH) ₂	1.35	-1.19
Na ₂ CO ₃	0.94	-0.41
NaOH	1.25	-1.10
NaOCl	0.67	-0.59
Chlorine (gas)	-1.41	1.24

We can then calculate the pH of the water using Equation (1) which applies for waters with a pH of between 4.5 to 8.5, at 25°C.

$$\text{pH} = \log(2.2 \times 10^6 \cdot [\text{ALK}] / [\text{CO}_2]) \quad - (1)$$

4.0 WATER STABILITY INDICES

Although a number of indices have been developed, none has demonstrated the ability to *accurately* quantify and predict the corrosivity or aggressiveness of a water. They can only give a probable *indication* of the *potential corrosivity* of a water. Experience has shown that if conditions encourage the formation of a protective calcium carbonate film, then corrosion will generally be minimized. Several models and indices are available that use calcium carbonate chemistry to evaluate water stability (Rossum and Merrill, 1983). Three calcium carbonate-based indices are described and values for each are calculated with reference to the Rochester water.

A commonly used index is the **Langelier Saturation Index (LSI)**. This index provides a measure of the stability of a water with respect to its degree of CaCO₃ saturation. If a water has a *negative LSI* value, it is under-saturated with respect to calcium carbonate and is potentially *corrosive*. Conversely, for waters with a *positive LSI*, a protective layer of calcium carbonate can form as the water is over-saturated with CaCO₃ and the water is *scaling*. *Saturated* water has a LSI of *zero*.

The pH at which a water is saturated with CaCO₃ is known as the *pH of saturation* or pH_s.

At 25°C and TDS less than 500 mg/L (the case for most Victorian surface waters), the LSI can be calculated from Equations (2) and (3):

$$\text{LSI} = \text{pH} - \text{pH}_s \quad - (2)$$

$$\text{pH}_s = 11.5 - \log[\text{Ca}_i] - \log[\text{ALK}] \quad - (3)$$

In practice, a water is considered to be potentially aggressive if it has a LSI of less than -1.5.

The Rochester water has a pH of 7.6, Ca of 7.9 mg/L “as is” and an alkalinity of 15 mg/L as CaCO₃. By substitution, we can calculate the LSI to be -1.8. We can therefore say that this water is potentially *mildly corrosive*.

Another related parameter is the **Ryznar Stability Index**, which is given by:

$$\text{RSI} = 2\text{pH}_s - \text{pH} \quad - (4)$$

The RSI value of a water should be less than 10 for it to be considered to be stable and non-corrosive. For the Rochester water, the RSI value is 11.2; again suggesting this water is *mildly corrosive*.

The **Calcium Carbonate Precipitation Potential (CCPP)** is a more reliable water stability index to use since this index provides a *quantitative* measure of the calcium carbonate deficit or excess of the water, giving a more accurate guide as to the likely extent of CaCO₃ precipitation. Previously, CCPP has been less frequently applied because the longhand calculation procedure is time-consuming and quite tedious. The AWWA (1996) released a PC-based spreadsheet program based on the Rothberg, Tamburini and Winsor Model, which allows speedy calculation of a number of corrosivity indices, including CCPP. The program also allows calculation of the effects of various chemical additions to a water.

A measure of the corrosivity of a water for different values of CCPP is presented in Table 5.

Table 5: Corrosivity State of Water for Different CCPP Values

CORROSION STATE OF WATER	CCPP VALUE, mg/L CaCO ₃
Scaling (protective)	> 0
Passive	0 to -5
Mildly Corrosive	-5 to -10
Corrosive (aggressive)	< -10

Another method of determining the CCPP value is a graphical procedure involving the use of water conditioning diagrams originally developed by Caldwell and Lawrence (1953). These diagrams can also be used to solve a wide range of water treatment and conditioning problems (including lime and lime-soda softening).

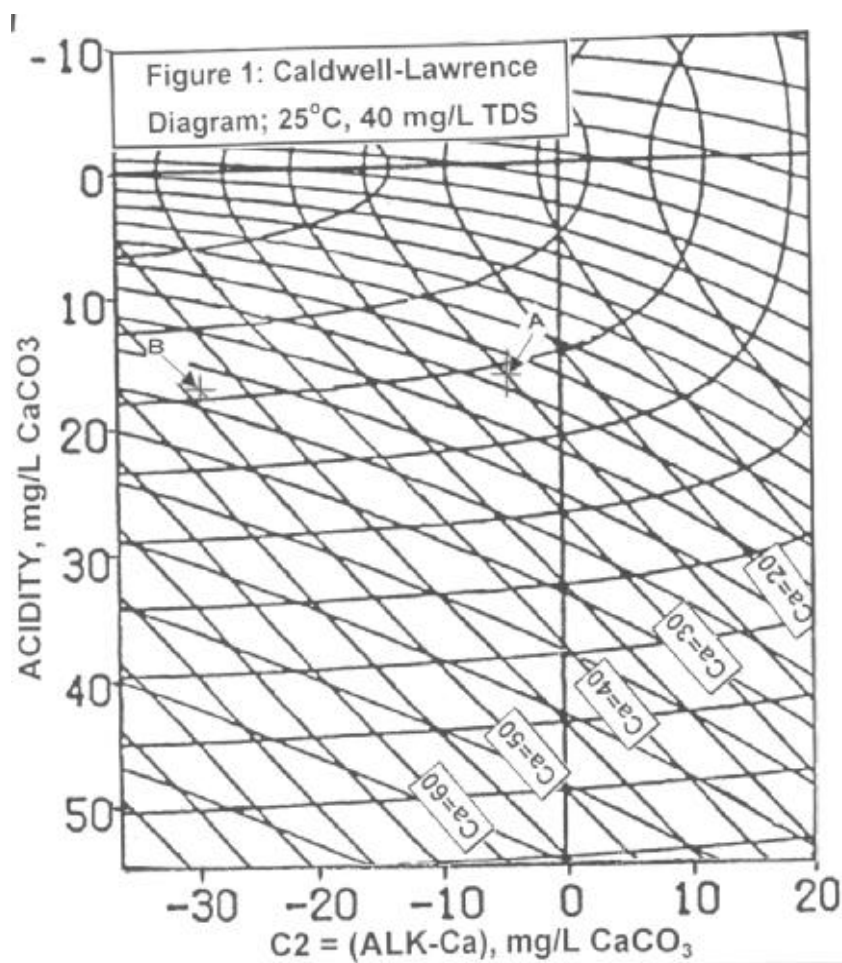
Figure 1 is part of a C-L Diagram drawn for water at 25°C with a TDS of 40 mg/L. Although a unique C-L Diagram should be used for the temperature and TDS of the water in question, in practice Figure 1 can be used over a range of conditions without serious error.

To determine the CCPP of a water, two parameters are calculated:

- ◆ $C2 = (ALK - Ca)$, and
- ◆ ACIDITY. The approximate acidity of a water may be found using Equation (5).

$$ACIDITY = [ALK](1 + 4.245 \times 10^{-6} \cdot 10^{-pH}) \quad - (5)$$

Figure 1: Caldwell-Lawrence Diagram : 25°C , 40 mg/L TDS.



Equation (5) is valid for a water at 25°C, with a TDS of up to 200 mg/L. C2 and ACIDITY are expressed as calcium carbonate.

(ALK-Ca) and ACIDITY are plotted on the C-L Diagram and at the point of intersection, we can then read off the Ca concentration at saturation. The CCPP value is then found from Equation 6:

$$\text{CCPP} = ([\text{Ca}] - [\text{Ca}_{\text{sat}}]) \quad \text{---(6)}$$

For the Waranga Channel water: (ALK-Ca) = 15.0 - 19.7 = - 4.7 mg/L CaCO₃, and ACIDITY = 16.6 mg/L CaCO₃ from Equation (6).

From Figure 1 (Point A), we can read off the calcium value at saturation as 25.0 mg/L and hence:

$$\text{CCPP} = (19.7 - 25.0) = - 5.3 \text{ mg/L CaCO}_3.$$

The precise value of CCPP is - 4.7 mg/L. The CCPP value suggests the water is “passive” and acceptable. Note that agreement between the two techniques is approximate only.

Table 6 summarizes the various water corrosivity indices considered for the Rochester water, compared with accepted values for a stable, non-corrosive water.

Table 6: *Stability Indices for Rochester Water Compared with Typical Values for Stable Water*

STABILITY INDEX	ROCHESTER WATER	ACCEPTABLE VALUE
Langelier Saturation Index	-1.8	> -1.5
Ryznar Stability Index	11.2	< 10
Calcium Carbonate Precipitation Potential	- 4.7	> -5
Aggressiveness Index	10.3	> 10

Comparing the calculated indices for the Rochester against acceptable values, we can conclude this water is probably non-corrosive to iron and steel.

5.0 WATER CONDITIONING

The water at Rochester has a true colour and turbidity of 60 Pt/Co units and 40 NTU respectively. We would anticipate that an alum dose of 50-60 mg/L is required for effective treatment in a conventional WTP. If we add 50 mg/L of alum to the water, the pH will be too low for effective coagulation. We must raise the pH to typically 6.5 by adding an alkali in the form of hydrated lime (calcium hydroxide), soda ash (sodium carbonate) or caustic soda (sodium hydroxide).

Starting with the raw water analysis, we can compute what will happen as a consequence of dosing 50 mg/L alum with supplemental alkali addition. Aluminium hydroxide is formed when alum is added so there is no addition of cations to the water. The alum consumes alkalinity and to maintain a balanced water analysis, sulphate will increase by an equivalent amount.

Assume we add 12.2 mg/L lime. As a result of this addition, we will increase both the calcium and alkalinity of the water. The new water analysis will be:

- ◆ cations: Ca= 19.7+2.5X12.2X40.1/74.1 = 36.2 mg/L CaCO₃. (The factor (40.1/74.1) gives the mg of calcium added per mg Ca(OH)₂ added as CaCO₃, from Tables 1 and 2).
- ◆ anions: alkalinity=15.0-0.45X50+12.2X1.35=9.0 mg/L, sulphate=4.2+0.45X50=26.7 mg/L CaCO₃

Next, we calculate the change to the CO₂ level.

- ◆ Initial CO₂: from Equation (1). $7.6 = \log(2.2 \times 10^6 \times 15 / \text{CO}_2)$, CO₂ = 0.8 mg/L as is
- ◆ CO₂ added from destruction of alkalinity by alum addition = $50 \times 0.4 = 20.0$ mg/L
- ◆ CO₂ destroyed by lime addition = $-12.2 \times 1.19 = -14.5$ mg/L
- ◆ Final CO₂ concentration = 6.3 mg/L

Now, we calculate the pH of the water following chemical addition: $\text{pH} = \log(2.2 \times 10^6 \times 9.0 / 6.3) = 6.5$.

This pH is satisfactory for alum coagulation and so the assumed lime dose is adequate. If the calculated pH was higher or lower than 6.5, then adjustments to the lime dose assumed would be required until this value was obtained.

We can also check the LSI of this water:

$$\text{pH}_s = 11.5 - \log[14.5] - \log[9.0] = 9.4, \text{LSI} = 6.5 - 9.4 = -2.9$$

This water is now aggressive and if chlorinated will be corrosive to the reticulation system. The solution to this potential corrosivity problem is conditioning using post-treatment alkali addition.

Assume the water is disinfected by adding 1.5 mg/L chlorine and that we will add 5.8 mg/L of lime to condition the water. The same procedure as above is again followed. The new water analysis will be:

- ◆ cations: $\text{Ca} = 36.2 + 2.5 \times 5.8 \times 40.1 / 74.1 = 44.0$ mg/L CaCO₃
- ◆ anions: $\text{alkalinity} = 9.0 + 5.8 \times 1.35 - 1.5 \times 1.41 = 14.7$ mg/L
- ◆ chloride: there will be an increase in the chloride level equivalent to the decrease in alkalinity due to chlorine addition, i.e. 2.1 mg/L.

Next, we calculate the change to the CO₂ level.

- ◆ Initial CO₂: 6.3 mg/L as is
- ◆ CO₂ added from destruction of alkalinity by chlorine addition = $1.5 \times 1.24 = 1.9$ mg/L
- ◆ CO₂ destroyed by lime addition = $-5.8 \times 1.19 = -6.9$ mg/L
- ◆ Final CO₂ concentration = 1.3 mg/L

The final pH of the conditioned water will be: $\text{pH} = \log(2.2 \times 10^6 \times 14.7 / 1.3) = 7.4$.

The LSI of this water will be: $\text{pH}_s = 11.5 - \log[17.6] - \log[14.7] = 9.1, \text{LSI} = 7.4 - 9.1 = -1.7$.

The conditioned water now has a pH of 7.4 and a LSI of -1.7, which is probably satisfactory from a corrosivity standpoint. We can also check the CCPP value using the graphical method outlined earlier. In this case:

- ◆ $(\text{ALK} - \text{Ca}) = 14.7 - 44.0 = -29.3$ mg/L CaCO₃.
- ◆ $\text{ACIDITY} = 17.2$ mg/L CaCO₃ from Equation (6).

From Figure 1 (Point B), we can read off the calcium saturation value as 48.0 mg/L, and hence CCPP = $(44.0 - 48.0) = -4.0$ mg/L CaCO₃. The precise value of CCPP is -3.6 mg/L, suggesting the water is "passive" and has been conditioned to a satisfactory level. The assumed lime dose used in our calculations is therefore sufficient. We can also calculate the final sum of the cations and anions and from this determine the TDS of our conditioned water.

The new water analysis is shown in Table 7 and the TDS of the conditioned water will be 164 mg/L as is. Note that Mg, Na and K levels in the raw water all remain unchanged as a consequence of water conditioning with lime. The difference between the sum of the cations and the sum of the anions is +4.3 mg/L, which is the same as our original water analysis and hence our calculations are correct.

We could also repeat this procedure using caustic soda and soda ash for post-treatment pH adjustment.

Table 7: *Water Analysis Waranga Channel at Rochester Following Chemical Conditioning*

	AS ION	AS CaCO ₃
Calcium	17.6	44.0
Magnesium	4.0	16.5
Sodium	22.0	47.9
Potassium	2.3	2.9
		111.3

pH
7.4

	AS ION	AS CaCO ₃
Alkalinity	17.9	14.7
Chloride	46.5	65.6
Sulphate	25.7	26.7
		107.0

6.0 CONCLUSIONS

Three calcium carbonated-based water stability indices have been reviewed with a focus on the Langelier Saturation Index and the Calcium Carbonate Precipitation Potential. Methods of calculating these parameters have been outlined as well as an approach to determining the impact different treatment regimes can have on treated water quality. The techniques outlined are straightforward and can be readily adapted to a PC-spreadsheet, providing the WTP Operator with a powerful tool.

Operators should anticipate that water stability indices will be used more frequently in the future as the general trend to improve treated water quality and reduce plant operating costs continues. The methods presented in this paper will hopefully contribute towards this goal.

7.0 REFERENCES

Australian Drinking Water Guidelines (1996), National Water Quality Management Strategy, NHMRC and ARMCANZ, Canberra

American Water Works Association (1996), The Rothberg, Tamburini and Winsor Model for Corrosion Control and Process Chemistry, Denver, Colorado, USA.

Caldwell, D.H. and Lawrence, W.B. (1953) "Water Softening and Conditioning Problems: Solution by Chemical Equilibrium Methods", *Industrial and Engineering Chemistry*, **45**, 3, 535-548.

Rossum, J.R. and Merrill, D.T. (1983) "An Evaluation of the Calcium Carbonate Saturation Indexes", *Journal AWWA*, February, 95-100.

8.0 NOMENCLATURE

pH = measured pH

pH_s = pH at saturation

[ALK] = alkalinity, mg/L CaCO₃

[CO₂] = carbon dioxide, mg/L as CO₂ ("as is")

[Ca] = calcium concentration, mg/L CaCO₃

[Ca_i] = calcium concentration, mg/L ("as is")

[Ca_{sat}] = calcium concentration at saturation, mg/L CaCO₃

[TH] = total hardness, mg/L CaCO₃