ALKALINITY ADDITION: THEORY AND BEST PRACTICE

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ABSTRACT

Alkalinity is an often overlooked water quality parameter in water treatment. An imbalance in the alkalinity of the water can cause problems during the treatment process and in the reticulation. Increasing alkalinity is usually achieved through the addition of alkalis such as lime and soda ash. However, these methods can cause a rapid increase in pH with no significant increase in alkalinity. Using carbon dioxide in combination with limestone allows for greater flexibility in controlling alkalinity, pH, and hardness. This article briefly discusses the theory of carbonate chemistry and how to improve water stability using the remineralisation process. It will also discuss the challenges of designing this system for the Wheatstone LNG plant to be constructed by Xylem Water Solutions (Australia).

KEYWORDS

Alkalinity, Remineralisation, Langelier Saturation Index

1 INTRODUCTION

Alkalinity is important for the coagulation process and in maintaining a stable final water quality that minimises corrosion of the supply pipework. With the focus on improving upstream treatment processes, stabilising finished water quality can be both inefficient and costly if it is ignored. Furthermore, it is important that a balance is achieved between alkalinity, hardness, pH, and Langelier Saturation Index (LSI) for the final water. For low alkalinity waters, adding either lime or soda ash will increase pH rapidly without necessarily achieving the desired increase in alkalinity of the water. The addition of carbon dioxide increases the overall carbonate concentration in the system and, when combined with a base, can provide increased control of alkalinity in the final water. A carbon dioxide system was designed for Wheatstone LNG plant remineralisation system. A system including carbon dioxide, combined with - limestone contact pressure filters and soda ash dosing was designed to provide flexibility in controlling alkalinity, pH, and LSI. This article will discuss the theory of alkalinity addition and the advantages and disadvantages of the limestone remineralisation system for the Wheatstone LNG project.

2 WHAT IS ALKALINITY?

The alkalinity of water determines its ability to neutralise acid and alkali, and is an important parameter in achieving a stabilised finished water quality. As water treatment operators will know, the higher the alkalinity of the raw water, the more acid or alkali addition is required to effect a pH change. This is due to its neutralisation effect. Alkalinity is made up of the following species:

- Carbonic acid (H_2CO_3)
- Bicarbonate (HCO_3^-)
- Carbonate (CO_3^{-2})

Of these species bicarbonate and carbonate both have the ability to neutralise acid. When acid is added to the system the carbonate and bicarbonate are converted into bicarbonate and carbonic acid respectively. The ratio of the carbonic species of the solution is determined by the final pH. This is illustrated in Figure 1.

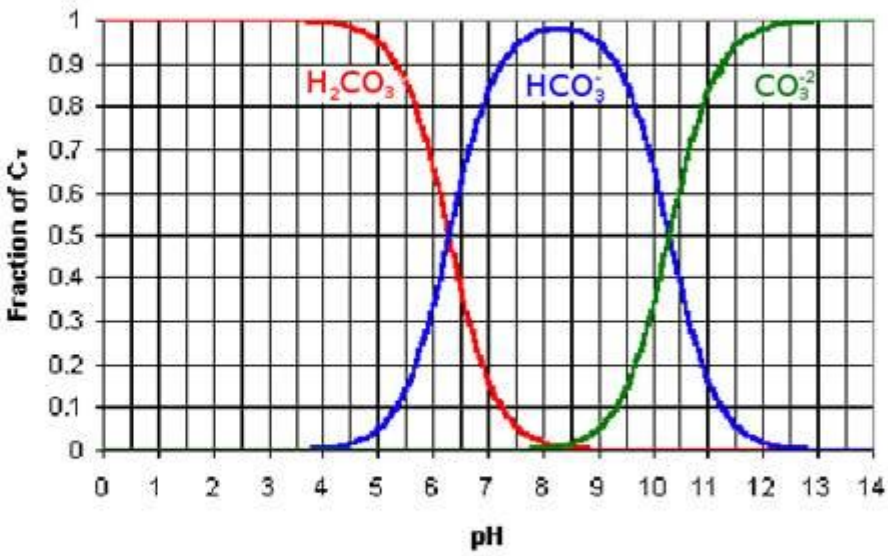

Figure 1: Carbonate equilibrium curve

When the pH is high, the carbonate species is dominant, and when the pH is low the carbonic acid species is dominant. An important point to note is that the total amount of carbonate in a system does not change unless additional carbonate is added to the system. This is important when deciding on what chemicals to dose to increase the alkalinity.

Maintaining the right balance between all carbonate species is the key to achieving stable water. If the carbonic acid species exists in higher than normal proportions, the water will be corrosive to pipework. The water treatment operator avoids this by ensuring the final water pH and alkalinity are within quality limits. However, shifting all of the carbonate species to the carbonate (CO_3^{-2}) ion increases the precipitation of calcium carbonate which can cause additional problems in the reticulation. Table 1 shows some of the problems that may occur from having high carbonic acid or carbonate species.

Table 1: Problems encountered due to imbalance of carbonate species

Carbonate	**Carbonic acid**
Precipitation of calcium carbonate	Causing red water in pipes
Reduction of pipe diameter due to the deposition of calcium carbonate	Corrosion
Alkalinity reduction due to the precipitation of carbonate	Nitrification
	Pitting and erosion of basins within the treatment process during the flocculation and clarification stage

A factor used to measure whether the right balance of carbonate species is produced for stabilisation of treated water is the Langelier Saturation Index (LSI). The Drinking Water Standards for New Zealand 2005 (Revised 2008) states that the correlation between the index and plumbosolvency is poor for some NZ waters and is therefore is not a parameter used for water quality. Furthermore, the World Health Organisation Guidelines for Drinking Water notes that there are many waters with a negative LSI that are non-corrosive and many with a positive LSI that are corrosive. It then goes on to say that there are many documented instances of the use of LSI for corrosion control based on the concept of laying down a protective “eggshell” scale of calcite in iron pipes.

In order to ascertain whether water supplied to customers will be aggressive or corrosive, the pH value and the pH at which calcium carbonate will precipitate out (pHs) must be known. The LSI is equal to the pHs subtracted from the pH. If the LSI value is negative the water is aggressive to calcium carbonate. If it is positive it will deposit calcium carbonate. The objective should be to add chemicals to produce a slightly positive LSI to form a protective scale of calcium carbonate conveying the water. i.e. The pH of the water is slightly above the pHs.

Alkalinity is also important during the coagulation process. Coagulants with a low basicity, such as aluminium sulphate (alum), have a tendency to consume more alkalinity than other coagulants and can therefore significantly reduce the pH of the water. This is a problem especially for water supplies with river sources as the coagulant demand increases during wet periods to match the increasing turbidity. Low lying surface waters typically have low to moderate alkalinity and when there is high demand for alum a large amount of alkalinity is consumed reducing the pH of the water. This then affects the performance of downstream processes and cause corrosion and pitting of basins. Some plants only dose the coagulated water with a base such as lime or caustic soda however this may not be enough to restore the alkalinity. Table 2 presents the amount of alkalinity consumed by different chemicals.

Table 2: Problems encountered due to imbalance of carbonate species

Chemical	**Alkalinity Consumed (mg/L $CaCO_3$ per mg/L of chemical)**
Ferric Chloride	0.93
Ferric Sulphate	0.53
Aluminium Sulphate	0.51
Chloride	1.41
Fluoride	2.08
Carbon Dioxide	0

It should be noted that carbon dioxide does not decrease alkalinity. It adds more carbonic acid to the system which in turn lowers the pH because the shifting carbonate species rations to carbonic acid. The addition of carbon dioxide increases the overall carbonate in the system. This increase in the overall carbonate can increase the alkalinity if there is a shift in pH to increase the presence of the carbonate ion (refer to Fig. 1). Increasing alkalinity can be achieved through the dosing of various chemicals as shown in Table 3.

Table 3: Alkalinity produced by different chemicals typically used in water treatment plants

Chemical	**Alkalinity Added (mg/L $CaCO_3$ per mg/L of chemical)**
Caustic Soda (sodium hydroxide)	1.25
Hydrated Lime (calcium hydroxide)	1.35
Limestone (calcium carbonate)	1.00
Sodium Carbonate (Soda Ash)	0.94
Sodium Bicarbonate	0.60
Sodium Hypochlorite	0.67

An important factor to note is that sodium hydroxide and lime only shift the species to the carbonate ion and do not actually increase the overall carbonate of the system. They will cause a rapid increase in pH especially for low alkalinity waters without providing a corresponding increase in alkalinity. The addition of limestone, sodium bicarbonate and soda ash will both shift the carbonate species and contribute to the overall carbonate in the system. One issue with soda ash is that it adds alkalinity in the form of carbonate (CO_3^{-2}) and the corresponding increase in pH occurs very quickly before the alkalinity increases significantly. Sodium bicarbonate provides the addition of alkalinity without a significant increase in pH, however the cost of sodium bicarbonate is higher than other alkalinity adding chemicals.

Selecting the appropriate chemical dosing system to achieve stabilised water quality is important and can have the following advantages:

- Reduced chemical consumption to achieve desired alkalinity and LSI values
- Reduced chemical costs
- Improved final stabilised water characteristics to protect pipework in the reticulation
- Reduced wear on downstream infrastructure assets
- Reduced plant maintenance issues and downtime

3 WHEATSTONE LNG PLANT

The Wheatstone project is a joint venture to develop one of Australia's largest natural gas resources. The site requires water to be supplied for its utility and potable needs. Xylem Water Solutions (Australia), are currently running a project for a desalination plant package (called Wheatstone Makeup Water), which will be the permanent water treatment plant onsite at Wheatstone LNG plant in Western Australia. Remineralisation of the desalinated water is required to provide stable water suitable for potable and utility end point use. Mott MacDonald were involved in the design of this system and used modelling tools for the estimation of chemical consumption and modelling the relationship between alkalinity, pH, and LSI. The design basis was to achieve a minimum of 50mg/Las $CaCO_3$ in the final water. Although there is no current need for desalination for municipal supplies in New Zealand, it is useful for understanding the concept of achieving the right balance of water quality parameters.

Remineralisation is the process whereby the water is stabilised with respect to the pH, hardness and alkalinity by reintroducing minerals into the desalinated water in a controlled way. In addition to not being palatable, without remineralisation the water will be corrosive to many of the materials used within the water distribution system, such as cement mortar linings of pipelines, and will be subject to significant changes in pH.

There are four main parameters of concern when considering remineralisation. These are:

- **Alkalinity**

- **pH**
- **Hardness –** This is a measure of the concentration of the hardness (metal) ions, particularly calcium and magnesium.
- **Langelier Saturation Index**

In order to satisfactorily re-mineralise the water it is normally necessary to meet targets for pH, hardness, alkalinity and LSI. Normally it is found that just the addition of an alkali (base) is insufficient to achieve compliance with all four of these parameters, as the final water pH becomes too high. It is therefore necessary to add a combination of an acid and an alkali.

The following arrangement was selected for the process at Wheatstone:

- Carbon dioxide (dosed as gas) + Calcium carbonate (in pressure filters) + Soda ash (dosed as slurry)

This method involves the filtration of product water dosed with carbon dioxide through a filter bed of limestone. The filter bed will be under 15 bar of pressure due to the requirements of the utility supply. The process is designed to produce water with a pH that is equal to the pHs. Sodium bicarbonate (soda ash) dosing is required at the filter outlet to neutralise any residual carbon dioxide and to attain the pH required to achieve the desired LSI. The reaction proceeds as follows:

$CO_2 + CaCO_3 + H_2O = Ca(HCO_3)_2$

Although this option requires three chemicals to be used, it offers the advantage of allowing the hardness, alkalinity and pH to be adjusted largely independently of each other. The use of limestone ($CaCO_3$) instead of hydrated lime $Ca(OH)_2$ also requires less CO_2 due to the CO_2 already bound in the limestone. Furthermore, the amount of calcium carbonate dissolution into the system can be controlled by varying the contact time in the vessels. This is typically 10 to 20 minutes. Despite the advantages of such a system the following challenges were encountered with the design:

- The need to design suitable pressure filters to hold the right amount of limestone to achieve optimal contact times. A balance must be achieved between filter size (cost) to achieve maximum contact times and alkalinity levels.
- High purity calcium carbonate required is >98%
- The need to design for a sand filter bed to entrain any undissolved impurities to prevent them from passing through to supply
- The difficulty in determining backwash initiation based on differential pressure due to dissolution of limestone into finer particles and build-up of impurities

4 CONCLUSIONS

Achieving stabilisation of water is important for maintaining optimum coagulation conditions, and protecting the pipework of water supplies and maintaining acceptable aesthetic qualities of the water. Some control must also be exercised to ensure excess calcium carbonate is not precipitated in the reticulation thereby reducing pipe diameters and supply capacity. Understanding the factors affecting stabilised water characteristics and their governing chemical equations is important as it can help the selection of the most suitable and cost effective alkalinity addition process for a water source. Carbon dioxide dosing, in combination with a base such as lime or limestone, can provide efficient addition of alkalinity. If added prior to the coagulation process it allows additional buffering capacity during the process and can minimise corrosion of basins while ensuring optimum enhanced coagulation pH. For the design of the Wheatstone LNG plant remineralisation process, limestone is used instead of hydrated lime $Ca(OH)_2$ as it requires less CO_2 due to the CO_2 already bound in the limestone. However, several challenges were encountered with designing the pressure filtration system as key factors must be considered including contact times, filter size, and remineralisation levels.