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Remineralization and Stabilization of Desalinated Water

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Abstract

Permeate or distillate from desalination processes is typically void of minerals and alkalinity, inherently acidic and therefore corrosive to water distribution infrastructure. The reintroduction of both minerals and alkalinity is essential for the stabilization of the water before it is sent to consumers making this the last step of the treatment process. Classical water stability is evaluated with respect to its calco-carbonic equilibrium which looks at the balance of calcium hardness, alkalinity and pH to determine whether the water has a tendency to dissolve or precipitate calcium carbonate. The purpose of remineralization processes is replenish the levels of calcium hardness and alkalinity in the water and then adjust the pH to deliver a stable water quality that is safe for human consumption and non-aggressive to water distribution infrastructure.

Keywords: remineralization, stabilization, potabilization, post-treatment, hardness, calcium, magnesium, alkalinity, bicarbonate, pH, corrosion, calcium carbonate, calcite contactors, lime, saturator, carbon dioxide, chemicals, indices

1. Introduction

As the name suggests, desalination processes are responsible for the removal of dissolved salts or ions from sea-, brackish- or tertiary-treated wastewater. These processes however, are not selective, and desirable minerals are just as readily removed along with the unwanted salts. The resultant desalination permeate or distillate is therefore void of essential minerals and alkalinity, rendering it unstable and corrosive. If left untreated, desalinated water will corrode the distribution infrastructure and will deteriorate the linings used as a protective barrier between the conduit and the drinking water. This creates a huge financial burden on asset owners. Recent estimates by the American Water Works Association suggested a program in excess of $300 billion over a 20-year period would need to be spent in the US alone to replace pipe damaged as a result of corrosion [1]. The financial impact of corrosion does not stop with the cost of pipework replacement either: a recent study by the Chicago-based Center for Neighborhood Technology in conjunction with the Chicago Metropolitan Agency for Planning found that up to 22 billion gallons of potable water is lost on a yearly basis due to leaks within the distribution network [2].

More important than the cost of pipework replacement however, is the health risk posed to consumers of non-stabilized water. Corrosion of pipework by aggressive water can lead to the release of heavy metal ions such as lead, copper and iron

to levels that are considered unsafe for human consumption, inducing "red water" incidents [3] and posing health risks to its consumers. Lead, for example, is considered one of the most toxic heavy metals and has been shown to impede both the physical and mental developments in children [4]. Ingestion of copper on the other hand, can result in liver and kidney damage. Cadmium, found in galvanized piping, is also highly toxic, considered a carcinogenic and even short-term exposure can lead to problems of the liver, heart and kidney [5]. Finally trace metals such as cadmium, barium, chromium and aluminum have been found to leach from the mortar linings of concrete lined pipes [6]. Therefore it is critical that following desalination processes, minerals and alkalinity are added to the water to achieve a buffered and stabilized water quality that is non-corrosive and safe for use.

2. Targets for remineralization

When designing remineralization systems and determining the appropriate water quality targets, a handful of key parameters are taken into consideration: alkalinity, calcium hardness and pH. The importance of these parameters are discussed further in detail in the following sections.

2.1 Importance of alkalinity

Alkalinity is one of the most important water quality parameter due to its ability to maintain a stable and buffered system, as well as its effectiveness in protecting against various mechanisms of corrosion. In general terms, alkalinity is defined as the capacity of an aqueous solution to accept a proton, or rather to neutralize an acid. Although other systems can contribute to alkalinity, for drinking water processes, it is only the carbonate system that is taken into account to define alkalinity. This is due to its predominance over other buffering systems in the pH ranges usually associated with water chemistry. Alkalinity for drinking water is therefore expressed as the following:

$$\text{Alkalinity} = 2\left[CO_3{}^{2-}\right] + [HCO_3{}^-] + [OH^-] - [H^+] \tag{1}$$

As seen in Eq. (1), alkalinity is determined primarily by the concentration of carbonate and bicarbonate ions, and to a lesser extent by the concentration of hydroxide and hydrogen ions, which also define the pH. Bicarbonate ions are particularly important, due to their ability to consume both hydrogen and hydroxide ions, and therefore provide a buffer to pH shifts in both directions.

In addition to providing a buffer to protect against shifts in pH, alkalinity is one of the most important parameters in corrosion control. The World Health Organization recommends high alkalinity levels as a suitable technique for preventing many mechanisms of corrosion in their Guidelines to Drinking Water Quality [7]. This is backed up by a multitude of studies into corrosion control and experts responsible for setting water quality targets.

More particularly, alkalinity is essential in controlling the corrosion of many metal materials of construction. One of the best methods of controlling iron, copper, zinc or galvanized iron corrosion, is the precipitation of the respective carbonates, such as siderite ($FeCO_3$), basic copper carbonate and basic zinc carbonate, for the formation of a passivation layer on the surface of the material [8]. A higher alkalinity content is therefore imperative to ensure sufficient carbonate species are available for the formation of these compounds. These protective layers are also an effective strategy against microbiologically induced pitting [9]. Lead on the other

hand, is released into the water either directly from the pipe, or from lead-containing corrosion products that are formed on the pipe surface. In terms of lead corrosion products, the most common of these is lead carbonate whose propensity of lead (II) carbonates to dissolve into the water stream is directly related to the concentration of carbonate species already within the water. Finally, alkalinity is essential to prevent the degradation of concrete and cement-based systems that in many cases are used as a lining to protect large bore conduits constructed from mild steel or ductile iron.

2.2 Importance of calcium

Next to alkalinity, calcium hardness is the most important parameter for post-treatment process for a number of reasons. Firstly, it is the most suitable counter-ion to the anionic alkalinity species. Other potential alternatives can result in water that is toxic to plant life (e.g. sodium ions), or are not so readily available (e.g. potassium). Calcium carbonate on the other hand, is one of the most readily sourced minerals in the world, making up 4% of the earth's crust [10]. Secondly, it is the concentration of calcium ions in addition to alkalinity and pH that defines the calco-carbonic equilibrium of the water. The calco-carbonic equilibrium defines a water's propensity to dissolve or precipitate calcium carbonate and is the primary indication of water stability for a number of reasons. Water that is aggressive to calcium carbonate, will be aggressive to concrete or cement-lined pipe, along with asbestos cement pipe. Because of the amount of water distribution infrastructure that is either made from concrete (storage tanks) or cement-lined (mild-steel concrete-lined or ductile iron concrete-lined pipe), this represents one of the largest investment costs for utility owners and highlights the importance of protecting these from corrosion. Whilst on the other hand, the precipitation of a thin layer of calcium carbonate on the surfaces of water treatment infrastructure is considered a suitable strategy against corrosion for a wide range of materials.

Finally, calcium has a number of health benefits to the consumer, with increased calcium levels within drinking water being linked to decreased incidences of cardiovascular disease. This has been acknowledged and accepted by the World Health Organization, who have clearly stated in their background document for the development of Guidelines for Drinking Water Quality, that insufficient calcium intake is associated with increased risks of osteoporosis, kidney stones, hypertension, stroke, coronary artery disease, some cancers and even obesity [11]. Calcium in drinking water is not just important for the body, but also for the teeth. Demineralization and remineralization processes are constantly taking place on the surface of tooth enamel based largely on the surrounding fluid. Saturation of the surrounding fluid with respect to calcium is critical to promote the remineralization or repair of dental tissue [12].

2.3 Importance of pH

pH is the final parameter that is considered for determining quality as part of post treatment processes. The desired target pH is often determined as a by-product of the previously mentioned parameters: alkalinity and calcium content. This is due to the fact that 1) the dissolution or precipitation potential of the water with respect to calcium carbonate is often used as the key indicator to the stability of water; and 2) the alkalinity, calcium content and pH are the three major contributing factors in determining dissolution or precipitation potential of the water. As noted earlier, this calco-carbonic balance is extremely important for cement-lined or concrete infrastructure. In such circumstances, system designers often opt for a slightly

precipitative water (pH > pH$_{sat}$) so that a protective scale is built up on the surface of the cement lined pipes or tanks. For other materials of construction, pH also appears to play an important role in controlling corrosion. The World Health Organization for example recommends a pH range of 6.8–7.3 to deal with iron corrosion, 8.0–8.5 to deal with lead and copper corrosion and a pH of less than 8.3 to deal with brass corrosion [13].

3. Methods for measuring and characterizing stabilized water

Individual parameters are not sufficient enough to predict the corrosivity of water and a number of indices have therefore been developed that look at the relationship of these parameters in an attempt to quantify the corrosivity or aggressivity of the water. The majority of these are based on the observation that if the water is aggressive to calcium carbonate, it will also be aggressive to other materials of construction. Furthermore, if conditions are such to encourage the precipitation of calcium carbonate, then this can be used to form a protective calcium carbonate film on the surface of the infrastructure, then this could be considered an effective strategy to mitigate corrosion. As a result most indices use the dissolution or precipitation of calcium carbonate as the basis to determine the stability of the water. This does not however tell the whole picture as water can still be considered corrosive despite having a positive Calcium Carbonate Precipitation Potential (CCPP). The Larson-Skold Index (LI) stands out as the only index that look at other factors such as concentrations of chloride and sulfate ions and their impact on the corrosivity of water to iron and steel pipe, and therefore should always be considered on top of a calcium-carbonate based indices. The most common indices are described below.

3.1 Calcium carbonate precipitation potential (CCPP)

The Calcium Carbonate Dissolution Potential (CCDP) or Calcium Carbonate Precipitation Potential (CCPP) is a most reliable water stability index that is often used in the context of guidelines or regulations without leading to misunderstanding. It provides a quantitative measure of the total amount of calcium carbonate that the water will either dissolve or precipitate giving an accurate guide not only to the nature of the water, but the extent to which it is under saturated with respective to calcium carbonate or over-saturated. The CCPP is an iterative function whose complexity requires the application of computer software for its calculation, but results in the most accurate representation of the water.

When CCPP is calculated, positive values represent a propensity to precipitate calcium carbonate and negative values a propensity to dissolve calcium carbonate. When CCDP is calculated the opposite relationship is formed.

Water is then classified based on the CCPP value (expressed in mg/l CaCO$_3$) as:

- Scale formation for CCPP >10 mg/l

- Protective layer formation for 3 < CCPP <10 mg/l

- Neutral for −3 < CCPP <3 mg/l

- Mildly corrosive for −10 < CCPP < −3 mg/l

- Aggressively corrosive for CCPP < −10 mg/l

3.2 Langelier saturation index (LSI)

The most commonly used index that provides a measure of the stability of a water with respect to its degree of calcium carbonate saturation is the Langelier Saturation Index (LSI). This is due to the fact that it provides both qualitative representation of the corrosivity of water, and is relatively easy to calculate. First proposed by Prof. WF Langelier in 1936 [14], the Langelier Saturation Index can be calculated as follows:

$$LSI = pH - pH_s$$

where pH_s represents the saturation pH of the water, in which condition the water is in the equilibrium state and neither dissolves, nor precipitates calcium carbonate.

The saturation pH is a complex iterative calculation, similar to the calculation for CCPP, requiring a program to accurately determine it. A simplification of this can be performed by using the ABCD method, which is calculated as follows:

$$pH_s = (9.3 + A + B) - (C + D)$$

and the parameters defined as:
A = (log [TDS] − 1)/10.
B = −13.12 × log (°C + 273) + 34.55.
C = log [Ca^{+2}].
D = log [Alk].
with TDS expressed in mg/l, Ca^{2+} expressed as mg/l as $CaCO_3$, and Alk expressed as equivalent $CaCO_3$ in mg/l. The plots of **Figure 1** show the slight discrepancy between these two calculation methods.

Waters with positive LSI are oversaturated and tend to form a protective layer of calcium carbonate (scaling effect) on the pipe walls. Highly positive LSI are
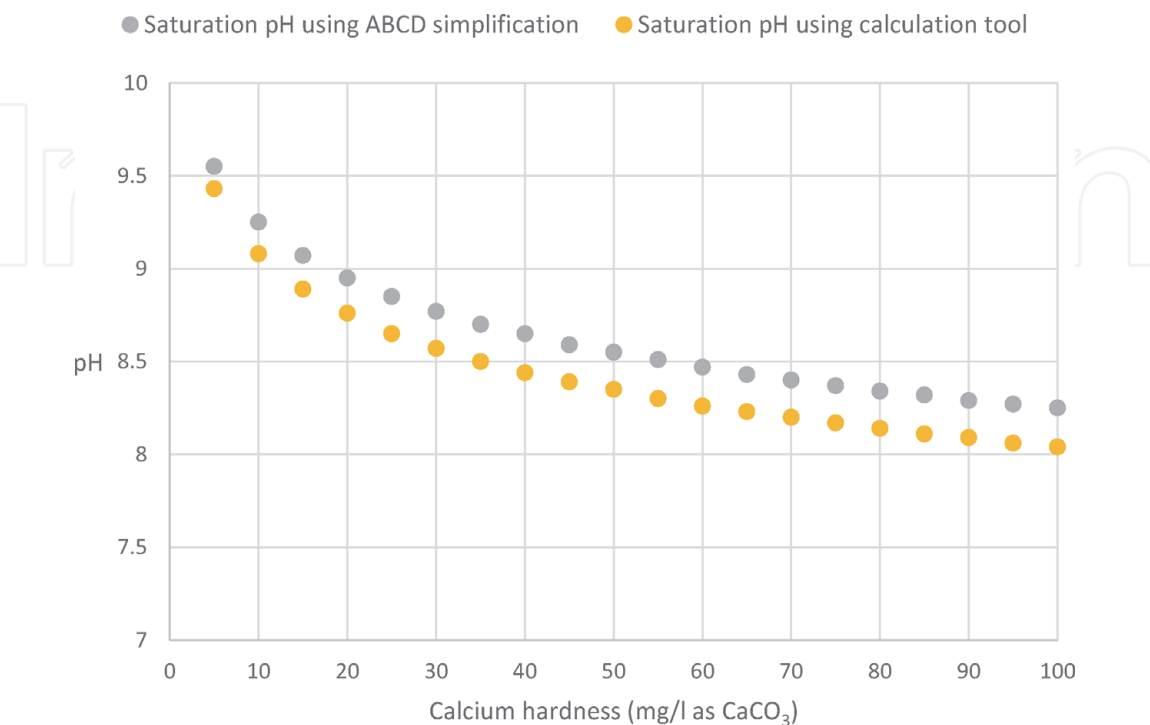

Figure 1.
Relationship between calcium hardness and saturation pH for water with 80 ppm of alkalinity (as CaCO₃).

corresponding to high precipitation effect resulting in incrustation. On the other hand, a water with negative LSI value is typically under-saturated with respect to calcium carbonate and so it will potentially dissolve the protective calcium carbonate scale and so be potentially corrosive. LSI alone however, cannot provide an indication of the true indication of the corrosivity of water, as the pH also needs to be considered. A water with LSI of −0.5 at pH 6.0 is much more corrosive than a water with LSI -0.5 at pH 8.0 for example.

LSI is not a reliable indicator of the corrosive tendencies of potable water and that the use of this index together with other models such as empirical determination of chloride, sulfate, alkalinity, dissolved oxygen, buffer capacity, calcium and length of time of exposure would provide information that is more reliable [15].

3.3 Ryznar stability index (RI)

Another parameter similar to the LSI is the Ryznar Stability Index [16], which is looks at the relationship between the saturation pH of the water (with respect to calcium carbonate) and the actual pH of the water. It is given by:

$$RSI = 2pH_s - pH$$

Based on the value assumed by the RSI index, waters are classified as:

- Strongly encrusting, when RSI ranges between 4.0 and 5.0

- Slightly encrusting, when RSI ranges between 5.0 and 6.0

- Slightly corrosive, when RSI ranges between 6.0 and 7.0

- Significantly corrosive, when RSI ranges between 7.0 and 7.5

- Strongly corrosive, when RSI ranges between 7.5 and 9.0

- Unbearably corrosive, when RSI ≥ 9.0

This index provides a reasonably good estimate of expected scale formation even in the presence of phosphate-based inhibitors.

3.4 Puckorius scaling index (PSI)

Similar to both the Langelier Saturation Index and the Ryznar Stability Index, also the Puckorius Scaling Index (PSI) also considers the corrosion potential of the water based on the calcium carbonate saturation of the water [17]. Instead of considering the actual pH of the water however, it defines a new parameter – the equilibrium pH and is defined as:

$$PSI = 2\left(pH_{EQ}\right) - pH_s$$

where, pH_s is the saturation pH as calculated for the previous indices, and pH_{EQ} is the equilibrium pH as calculated by:

$$pH_{EQ} = 1.465 \times \log\left[Alk\right] + 4.54$$

Thus the water will be:

- Scaling for PSI < 4.5

- Stable for 4.5 ≤ PSI ≤ 6.5,

- Corrosive for PSI > 6.5

3.5 Larson-Skold index (LI)

In contrast to the previously descried indices, the Larson–Skold Index (LI) describes the corrosivity of water towards iron or mild steel due to the presence of chloride and sulfate ions [18]. No consideration is given to calcium concentration or pH. This index looks at the relative ratio of chloride and sulfate ions to alkalinity in the water. The reactive anions on one-hand have a strong acidic effect in the anodic pits generated in the exposed corroding metal. The alkalinity due to combined bicarbonate and carbonate ions counter this effect by creating a stabilized and buffered environment that reduces the acidic tendency of the water. The Larson-Skold Index is calculated as follows:

$$LI = \frac{[Cl^-] + [SO_4^{2-}]}{[HCO_3^-] + [CO_3^{2-}]}$$

where the concentrations of each of the species involved is expressed in milliequivalents per liter (meq/L).
The water is then classifies as:

- Non-corrosive for LI < 0.8

- Corrosive for 0.8 ≤ LI ≤ 1.2

- Highly corrosive for LI > 1.2

4. Processes used for remineralization of desalinated water

The most common techniques that are currently employed worldwide for water remineralization and stabilization of desalinated or naturally soft water can be divided into three categories: (1) direct dosing of two or more chemical solutions, (2) lime dosing systems, and (3) calcite contactors. Each technique comes with its own benefits and disadvantages, from both a water quality perspective as well as process considerations. Of these three processes, lime dosing systems and calcite contactors see the most widespread application, especially for large desalination plants. This is due to the major drawbacks and costs associated with chemical dosing, as demonstrated below.

4.1 Direct dosing of two or more chemical solutions

One of the simplest and most effective ways of controlling the quality of the final water leaving a treatment facility is through the direct dosing of chemical solutions, either prepared offsite, or involving a simple slurry make down on site when supplied as a solid material. Whilst any combination of chemicals is possible,

the most common combination is calcium chloride ($CaCl_2$) for hardness addition in conjunction with sodium bi-carbonate ($NaHCO_3$) to increase the alkalinity of the final water. Expensive sodium hydroxide may in some cases also be needed to reach the required pH. Direct dosing of two or more chemicals has the advantage over other techniques of being able to precisely regulate the quantities of ions added, by controlling the volumes dosed of known solutions. In addition, full dissociation of these highly pure compounds in water avoids any complications of the generation of waste by-products or residual turbidity resulting from low solubility of products.

Despite being a very simple process the greatest drawback of this process is the cost of the chemicals. For this reason, this approach sees very limited application, used at best on small plants where relatively speaking CAPEX has a much greater impact than OPEX.

As an example, in order to achieve 80 mg/l of hardness and alkalinity within the final water (measured as $CaCO_3$), then the required dosage of $CaCl_2$ and $NaHCO_3$ is equivalent to:

$$CaCl_2\left(\frac{mg}{l}\right) = 80\left(\frac{mg}{l}\right) \div 100.08\left(\frac{g}{mol}\right) \times 110.98\left(\frac{g}{mol}\right) = 89\left(\frac{mg}{l}\right)$$

$$NaHCO_3\left(\frac{mg}{l}\right) = 80\left(\frac{mg}{l}\right) \div 100.08\left(\frac{g}{mol}\right) \times 84.006\left(\frac{g}{mol}\right) \times 2 = 134\left(\frac{mg}{l}\right)$$

As two molecular equivalents of $NaHCO_3$ are required to generate one molecular equivalent of alkalinity (measured as $CaCO_3$).

Using the modest values of chemical costs of 300 €/tonne for calcium chloride and 400 €/tonne for sodium bicarbonate (in some locations sodium bicarbonate can be as expensive as 900–950 US$/tonne), then the cost of consumables of this process alone exceeds the total treatment cost of the other treatment processes when energy costs and amortization of investment costs are taken into account (refer **Table 1** below).

Another major drawback of this process and something that is often overlooked, is the increase of the undesired chloride ions that are introduced to the process, as for every mol of calcium that is added, two mol of chloride is also added. This increases the tendency of the water to be corrosive to iron and steel pipe and equipment, as measured and indicated by the previously mentioned Larson-Skold Index.

4.2 Lime dosing systems

Lime dosing systems involve the on-site preparation of a saturated lime solution from either a hydrated lime powder (calcium hydroxide) or quicklime (calcium oxide) which is slaked on-site to produce hydrated lime. The saturated solution is produced by feeding a calcium hydroxide slurry into a lime saturator along with make-up water and a flocculant. The saturator allows for the separation of a clear

	Unit price (EUR/dmt)	Dosage (mg/l)	Cost (EUR/m³)
Calcium chloride	300	89	0.027
Sodium carbonate	400	134	0.054
TOTAL COST			**0.081**

Table 1.
Chemical costs of calcium chloride and sodium bicarbonate dosing to achieve 80 mg/l of hardness and alkalinity.
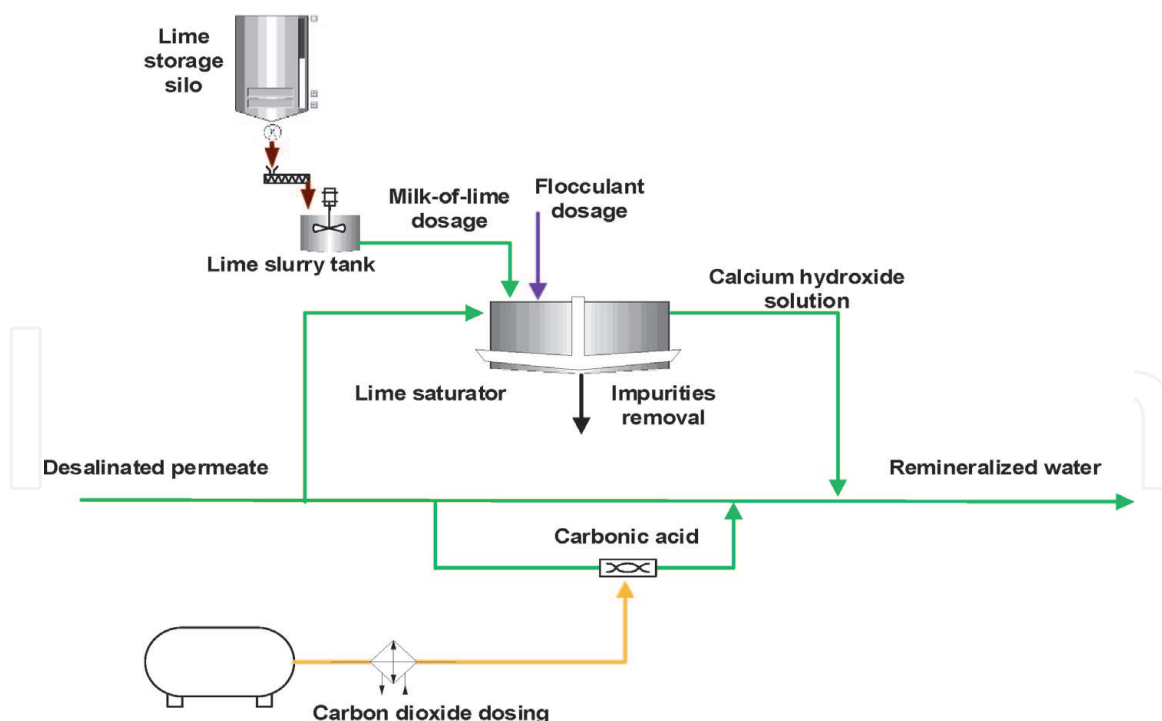
Figure 2.
Schematic of a typical lime dosing system.

solution of calcium hydroxide from the insoluble contents which are settled to the bottom with the aid of the flocculant (**Figure 2**).

The saturated lime solution is then dosed into the final water stream along with carbon dioxide to form bicarbonate alkalinity in the following reaction:

$$Ca(OH)_{2\ (aq)} + 2\ CO_{2\ (g)} \rightarrow Ca(HCO_3)_{2\ (aq)} \tag{2}$$
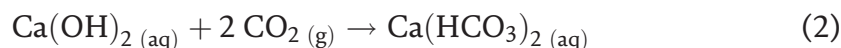
One of the advantages of lime and reasons that it has been a popular choice for system designers is its worldwide availability as a commercial product and relatively low cost in comparison to other chemicals. It's solubility up to 1700 mg/l at 20°C makes ideal for its preparation within a side stream lending to its smaller footprint relative to calcite contactors.

Lime dosing systems do however have a number of drawbacks and are often the bane of many operators assigned the task to clean and maintain the lime slurry pipework or lime saturators. In comparison to calcium carbonate, lime is more expensive per kilogram of available $CaCO_3$. This can be attributed to the fact that lime is produced by the calcination (burning) and further slaking (hydration) of calcium carbonate which is then dried to produce a powdered hydrated lime. As a result, lime is not only more expensive to produce, but has a much higher carbon footprint. For every kilogram of quicklime that is produced, approximately 700 kcal is required for dissociation and 0.785 kg of carbon dioxide is released [19]. This difference in carbon footprint is not only a concern for plants which strive for environmentally sustainable solutions, but will no doubt further increase the price of lime production as carbon emission taxes are set to play a bigger role in the future.

The operational costs of lime systems are also increased in comparison to calcium carbonate due to the fact that for the same desired quantity of calcium hardness and alkalinity within the final water, twice as much carbon dioxide is required. As can be seen from the chemical reaction equations, remineralization using calcium hydroxide requires two molecular equivalents of carbon dioxide for each mole of calcium hydroxide (refer Eq. (2)). Remineralization using calcium carbonate however, requires only one molecular equivalent of carbon dioxide for

each mole of calcium carbonate (refer Eq. (3)). Carbon dioxide is in most cases the largest operating cost for post treatment systems, so this has an important impact on the overall cost per cubic meter of treated water.

As mentioned previously, hydrated lime contains an insoluble content. This insoluble content is for the most part is unburnt calcium carbonate but can also include silicates and other impurities. These impurities are usually in the order of 5–15% and must be removed and dealt with as a waste product. Needless to say the lower the insoluble content, the purer the product and the higher the price of the product. If the impurities are not effectively removed, they will add to the turbidity in the final water. To improve the efficacy of the clarification process, a flocculant is often dosed to aid in the settling. This waste then needs to be thickened on site and sent away for proper disposal. These factors further add to the operational cost and complexity of lime dosing systems. The operation of a lime clarifier is very sensitive to factors such as temperature, flocculent dosing, and throughput flow rate, meaning they do not handle fluctuations in plant flow very well. Even a perfectly functioning lime clarifier can still be susceptible to turbidity problems. Absorption of carbon dioxide from the atmosphere can lead to the increase in dissolved inorganic carbon within the lime solution resulting in precipitation of calcium carbonate and producing a cloudy solution.

Extending the example for chemical dosing, in order to achieve 80 mg/l of hardness and alkalinity within the final water (measured as $CaCO_3$), then the required dosage of $Ca(OH)_2$ and CO_2 is equivalent to:

$$Ca(OH)_2\left(\frac{mg}{l}\right) = 80\left(\frac{mg}{l}\right) \div 100.08\left(\frac{g}{mol}\right) \times 74.1\left(\frac{g}{mol}\right) \div 90\% = 65\left(\frac{mg}{l}\right)$$

(assuming a $Ca(OH)_2$ purity of 90%)

$$CO_2\left(\frac{mg}{l}\right) = 80\left(\frac{mg}{l}\right) \div 100.08\left(\frac{g}{mol}\right) \times 44.01\left(\frac{g}{mol}\right) \times 2 = 70\left(\frac{mg}{l}\right)$$

As two molecular equivalents of CO_2 are required to generate one molecular equivalent of alkalinity (measured as $CaCO_3$). Considering also 10% of product is removed as waste from the lime saturator, and then dewatered to a maximum of 30% solids:

$$Waste\ generated\left(\frac{mg}{l}\right) = 65\left(\frac{mg}{l}\right) \times 10\% \div 30\% = 22\left(\frac{mg}{l}\right)$$

This generates treatment costs that are a fraction of that required for chemical dosing as presented below in **Table 2** below.

4.3 Calcite contactors

Remineralization of demineralized water using calcite contactors is achieved by passing a stream of acidified water through a bed of calcite chips. These chips are

	Unit price (EUR/dmt)	Dosage (mg/l)	Cost (EUR/m^3)
Calcium hydroxide	250	65	0.016
Carbon dioxide	200	70	0.014
Waste disposal	50	22	0.001
TOTAL COST			**0.031**

Table 2.
Approximate operational costs for lime dosing systems to achieve 80 mg/l of hardness and alkalinity.

usually limestone or marble, but in some cases dolomite, chalk, precipitated calcium carbonate or even muscle shells is used. The acidified water dissolves the calcium carbonate, increasing the calcium hardness of the water, the carbonate alkalinity and the pH through the following reaction (when carbon dioxide is used as the acidifying agent) (**Figure 3**):

$$CaCO_{3 \ (s)} + CO_{2 \ (g)} + H_2O \rightarrow Ca(HCO_3)_{2 \ (aq)} \tag{3}$$

As noted earlier, calcium carbonate is one of the most common minerals available, taking up almost 4% of the earth's crust [10]. As a result it is a readily sourced product and processing requirements are minimal as the chemical composition does not need to be altered before use. Consequently, and as alluded to previously, calcium carbonate can be supplied at a lower cost than lime. In addition, it requires half as much carbon dioxide for the same quantity of calcium bi-carbonate (refer Eqs. (2) and (3)). Added to this, calcium carbonate used for water remineralization can be very pure, with an insoluble content as little as 0.1%. This further reduces operating costs, with more available product for use and less produced waste which requires further handling and disposal. Calcium carbonate is also chemically stable and non-corrosive making it easy for manual handling. In comparison, calcium hydroxide is classified as hazardous, and exposure can cause burning and irritation.

The main disadvantage of calcium carbonate is its chemical solubility which is only 13 mg/l in pure water, and requires the addition of an acid to dissolve quantities above this. As the water gets closer to the saturation point, the rate of reaction slows down dramatically. As a result, thermodynamic equilibrium is almost impossible to reach in such a dissolution reactor [20], and requires excessive contact time between the water and the calcite bed. This increases the overall size of the plant required to treat a certain volume of water and the resultant capital investment.
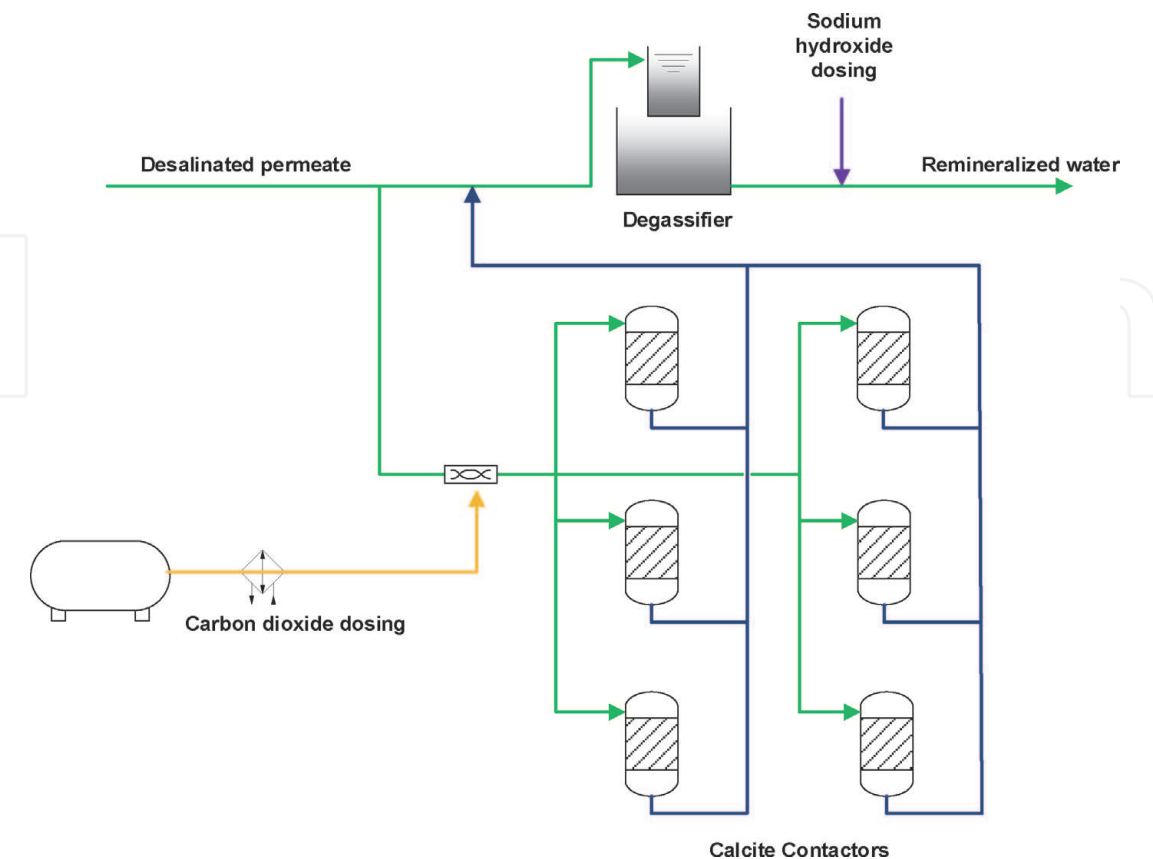

Figure 3.
Schematic of typical calcite contactor process.

In order to increase the rate of reaction and circumvent this problem, the pH of the feed water is often decreased before the calcite contactor, in excess of what would normally be required. This results in a faster dissolution rate so that the required hardness and alkalinity increase occurs in a shorter time period. The water however, does not achieve saturation levels with respect to calcium carbonate, as the pH of the effluent leaving the reactor is much lower than the saturation pH for its calcium carbonate content. This also decreases the efficiency of the process described by Eq. (3), as it requires excess carbon dioxide to be dosed for the increased acidity. This not only increases the chemical costs for the process, but produces effluent leaving the reactor with a quantity of unreacted CO_2. The pH of the water must then be adjusted either by the dosage of a strong base (e.g. sodium hydroxide) or the liberation of carbon dioxide to achieve a zero or slight positive LSI (Langelier Saturation Value) value, as required by most treatment facilities.

This pH adjustment step adds to both the investment costs: due to the requirement of additional infrastructure for stripping equipment or an additional chemical dosing system, and the operational costs: due either to additional chemical consumption when a strong base is used, or additional power consumption when the excess CO_2 is stripped. In some instances both are required. Sodium hydroxide is a relatively expensive chemical, and even a small dosage can add significantly to the overall cost of the remineralization process. In many cases, it is most cost effective to waste the excess CO_2 through stripping rather than convert it to additional alkalinity through the dosage of a strong base. For plants that require a low level of remineralization though, (e.g. 50 mg/l) the quantity of free of CO_2 that remains in the water at saturation level is so low that this cannot be achieved through stripping alone and requires some dosage of a strong base for partial or total pH adjustment.

Other issues facing operators of calcite contactors are turbidity spikes in the treated water leaving the contactor. These are generally a result of the introduction of new material to the calcite reactor and the accompanying "fines" supplied with the raw material. To deal with this calcite contactors require frequent backwashes, in particular following the loading of new material. This adds an additional need for a backwash treatment and handling system at plant to deal with this waste stream. The change in bed heights between fills also result in a change in water quality leaving the calcite contactor due to variances in the quantity of product available for reaction. In most cases calcite contactors are loaded manually, increasing the operational costs due to additional operator utilization. Lime systems on the other hand are fed automatically from a lime storage silo, requiring operator input only to receive new deliveries. Calcite contactors also require regular backwash with both air and water. This serves to remove excess fines and insoluble waste material caught on the calcite chips as well as resettling the calcite bed to prevent preferential flow paths of the water through the bed.

Completing the cost comparison example to achieve 80 mg/l of hardness and alkalinity within the final water (measured as $CaCO_3$), then the required dosage of $CaCO_3$ and CO_2 is equivalent to:

$$CaCO_3\left(\frac{mg}{l}\right) = 80\left(\frac{mg}{l}\right) \div 99\% = 65\left(\frac{mg}{l}\right)$$

Assuming a $CaCO_3$ purity of 99%,

$$CO_2\left(\frac{mg}{l}\right) = 80\left(\frac{mg}{l}\right) \div 100.08\left(\frac{g}{mol}\right) \times 44.01\left(\frac{g}{mol}\right) \times 130\% = 46\left(\frac{mg}{l}\right)$$

Assuming 30% extra carbon dioxide is required to increase the rate of reaction, and finally an addition of 2.5 ppm of sodium hydroxide is required after degassing to bring the pH to saturation conditions.

	Unit price (EUR/dmt)	Dosage (mg/l)	Cost (EUR/m^3)
Calcite chips	100	81	0.008
Carbon dioxide	200	46	0.009
Sodium hydroxide	800	2.5	0.002
TOTAL COST			0.019

Table 3.
Approximate operational costs for calcite contactors to achieve 80 mg/l of hardness and alkalinity.

The approximate treatment costs for calcite contactors are shown below in **Table 3** demonstrating that they are not only less expensive to operate than lime dosing systems, but they offer a more environmentally friendly solution. The big drawback for calcite contactors, which is not demonstrated here are the large physical footprint and investment required. These elements alone can often drive a designers decision towards lime dosing system, particularly in locations such as Singapore, where space is a premium.

5. Latest developments and trends

Historically, the main focus for developments within the field of desalination has been the improvement and optimization of the reverse osmosis and pre-treatment processes. This is due to the fact that these areas comprise the largest fractions of capital investment and are responsible for the largest portion of operating costs. In comparison, only minor inroads have been made to improve and optimize post treatment processes. In spite of this, the value and importance of post treatment processes should not be underestimated, as it is these processes that are ultimately responsible for the final water quality sent to the consumer.

Whilst calcite contactors have many advantages over lime dosing systems, their major drawbacks are centered around their slow reactivity which result in large physical footprint and investment for the dissolution reactors. In order to address the issue of slow dissolution kinetics of calcite chips, new and innovative processes have been developed over the last few years that utilize micronized calcium carbonate. These processes take advantage of the increased surface area and reaction kinetics available from the micronized products to achieve decreased contact times, higher concentrations, improved carbon dioxide efficiency, or a combination of these factors. Micronized calcium carbonate is dissolved in a Membrane Calcite Reactor (MCR) which combines a submerged ultrafiltration membrane immersed in a suspension of micronized calcium carbonate. Carbon dioxide is added to the calcium carbonate suspension, which in turns reacts to form a calcium bi-carbonate solution. The membrane acts as a barrier between the dissolved and undissolved calcium carbonate enabling a perfectly clear solution to be extracted from the reactor that can be dosed into the desalination permeate. The use of micronized calcium carbonate results in fast reaction times, and hence decrease footprint and investment offering an improvement over current processes (**Figure 4**).

Although remineralization processes primarily concern themselves with the replenishment of calcium hardness and alkalinity, more recently attention has been given to the need to replenish magnesium ions, with some countries considering the implementation of legislation for these purposes. Magnesium is arguably the most important mineral for the body, being utilized by every organ, in particular the heart, muscles and kidney. It is the fourth most abundant cation in the body, and the second most in intracellular fluid [21]. Magnesium deficiency has also been
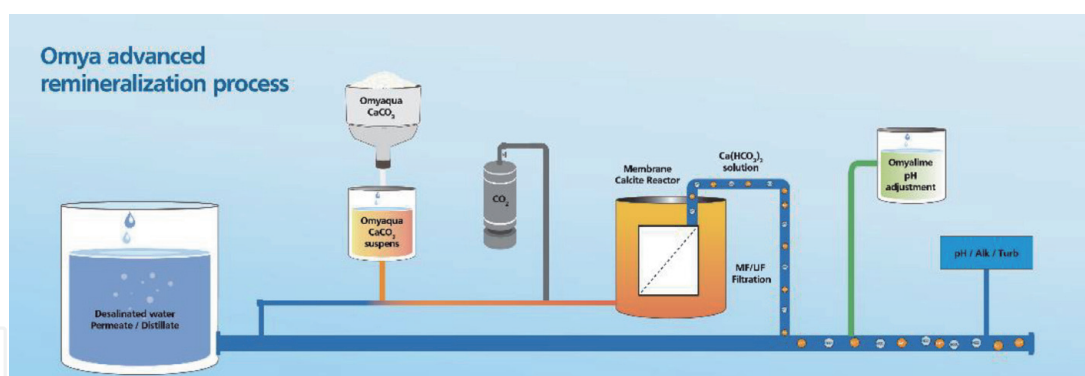
Figure 4.
Schematic of the Omya advanced remineralization process (OARP) based on micronized calcium carbonate.

scientifically proven to either trigger or cause the following health problems: heart disease, diabetes, migraines, anxiety, hypertension, depression, fatigue, blood clots, liver disease, kidney disease, osteoporosis, insomnia, fatigue, cystitis, nerve problems and hypoglycemia [22]. Despite these facts and the relative importance of magnesium, up to 75 percent of people do not receive the recommended daily intake of magnesium (based on studies performed in the US – global intakes vary greatly based on local diets) [23].

Magnesium deficiency has also been specifically linked to higher rates of mortality in terms of cardiovascular deaths as well as general mortality. A recent German study sampling over 4000 people showed a strong correlation between low serum magnesium levels (< 0.73 mmol/l) and cardio-vascular deaths at a rate of 3.44 deaths per 1000 person years, in comparison to 1.53 deaths per 1000 person years for those with higher magnesium concentrations. More importantly though, an even stronger correlation was found between serum magnesium levels and all-cause deaths. For those with low serum magnesium levels, the mortality rate was 10.95 deaths per 1000 person years compared to 1.45 deaths per 1000 person years at higher serum magnesium concentrations [24]. Researchers from the Bar Ilan University together with the Tel HaShomer Hospital gave more weight to this argument based on their review of death rates in Israel in areas serviced by desalinated water in comparison to those supplied by natural water. In their study they noted a marked difference in the number of deaths from heart disease in the areas that were supplied water from desalination in comparison to those supplied by natural water which had not been previously recognized when comparisons were made before desalination was introduced [25]. The conclusion was drawn by the researcher that this was as a result of decreased magnesium intake in these areas after the introduction of desalination. Only causal links however were established with direct links still to be proven.

Furthermore when reviewing the total number of epidemiological studies from the 1950's until present that had been performed on the link between magnesium in drinking water and cardiovascular mortality, it was determined that there is enough evidence to support a link, especially for concentrations above 5 mg/l [26]. The World Health Organization (WHO) also recommends maintaining a minimum Mg^{2+} concentration of 10 mg/l in all drinking waters [27]. Despite these recommendations, the replenishment of magnesium salts is rarely performed, if at all. One of the main obstacles is the relative cost of current methods, which significantly increases the total cost to desalinate and stabilize the water. The addition of magnesium to drinking water is commonly achieved through the dosing of chemical solutions such as magnesium chloride or magnesium sulphate. The high solubility of both salts allows for the supply of highly concentrated solutions, or simple solution make-down systems on site using crystalline salts, and the accurate dosing of these

solutions to produce the magnesium concentration in the final water as desired. Whilst this process is very effective, it is also extremely expensive. This tends to position this subject as a question of luxury rather than necessity. The use of these chemicals in fact renders an additional cost to treat the drinking water by as much as 10 US cents/m^3 [28]. For this reason, more cost-effective replenishment methods are becoming of high interest in order to be prepared to face the coming soon changes in drinking water regulation.

The use of natural minerals for the replenishment of magnesium offers both a low cost and sustainable alternative to chemical dosing. Like natural calcium carbonate, magnesium minerals are found within the earth's crust as a range of sparingly soluble compounds, that naturally replenish themselves through dissolution and precipitation cycles. The fact that these minerals are sparingly soluble, increases their prevalence and concentrations in nature, as they are more likely to precipitate from solution than their highly soluble counterparts such as magnesium chloride and magnesium sulphate, which are only found in limited locations such as the dead sea, and in these cases require further refining. The limited solubility of the minerals means that they alone, struggle to provide the required levels of dissolved magnesium without the addition of an acid, to increase both their rate of dissolution and total concentration. Additionally, because the low solubility and slow reaction kinetics of these minerals, large contact tanks and an expensive installation are often required to achieve the required levels of dissolution. These issues can be effectively countered through the dissolution of powdered products within Membrane Calcite Reactors, similar to that for calcium carbonate.

Alternatively, some companies and research institutions are investigating the "mining" of natural resources from the brines rejected by desalination processes. These are often rich in a number of metals and minerals that are essential for industry and otherwise not scarce in availability [29]. These include magnesium, scandium, vanadium, gallium, boron lithium, indium, molybdenum and rubidium. These processes could offer a cheap source of magnesium at desalination sites where they could be immediately reinjected into the final water to replenish some of what has been extracted.

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