



Re-mineralization of Desalinated Water

by

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1. Introduction

Product water from desalination plants is characteristically low in mineral content, hardness, alkalinity, and pH. Therefore, desalinated water must be conditioned (re-mineralized) prior to final distribution and use. Typically, re-mineralization aims to: (1) provide protection of the water distribution system against corrosion; (2) add essential minerals needed to meet human dietary needs and to facilitate other potential uses of the desalinated water such as irrigation.

Chemicals containing calcium (i.e., lime, calcite, calcium hypochlorite) or calcium and magnesium (i.e., dolomite) are typically added to the desalinated water in a dosage of 60 to 120 mg/L (as CaCO_3) for water distribution system corrosion control and public health protection. These chemicals produce calcium carbonate or a combination of calcium and magnesium carbonate in the desalinated water which, when in adequate quantity precipitate on the inner distribution pipe surface to form protective film that serves as a physical barrier preventing corrosion. Supplementation of desalinated water with protective film-forming chemicals also increases its hardness and therefore, it is often referred to as addition of hardness.

2. Alternative Re-Mineralization Technologies

Re-mineralization of desalinated water is typically completed by three main groups of technologies: (1) processes that are based on direct addition of chemicals containing calcium (i.e., calcium hydroxide/lime) and magnesium (i.e., magnesium chloride and sulfate); (2) processes where re-mineralization is accomplished by mixing of desalinated water with a portion of the source water used for desalination, or with other fresh water sources with high calcium and magnesium content; (3) processes where magnesium and/or calcium are added by dissolving naturally occurring minerals such as limestone (calcium carbonate/calcite) and dolomite (calcium and magnesium carbonate). This desalination course focuses on the practical use of these technologies.

Re-mineralization by Chemical Addition

Calcium Addition. Most seawater and brackish water desalination plants today typically add only calcium to the desalinated water in the form of lime, because this chemical is usually readily available as a commercial product, and is less expensive to use for achieving the same target level of total water hardness as compared to using magnesium salts. Calcium re-mineralization is needed because magnesium alone cannot provide adequate corrosion protection.

Over 90 % of the existing seawater desalination plants worldwide use a sequential feed of calcium hydroxide (hydrated lime) and carbon dioxide to supply hardness and alkalinity to the



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product water needed to protect distribution system and household plumbing from corrosion. The re-mineralization using lime and carbon dioxide follows the chemical reaction presented below:



Based on the equation above, 0.74 mg/L of hydrated lime (0.56 mg/L of quicklime) and of 0.88 mg/L of carbon dioxide would need to be added in order to increase desalinated water hardness and alkalinity by 1.0 mg/L (as CaCO_3) each. Therefore, for a target recommended dosage of alkalinity and hardness in the product water of 100 mg/L the water produced by the desalination system will need to be treated with 74 mg/L of lime and 88 mg/L of carbon dioxide.

The lime product used for re-mineralization is usually delivered and stored at the desalination plant site in silos as either powdered hydrated lime or as pebble-lime (CaO) which is then slaked to generate hydrated lime ($\text{Ca}(\text{OH})_2$). In smaller desalination plants, powdered lime is often stored in 25 kg bags. Hydrated lime is fed into lime saturators in the form of lime slurry (milk of lime). This lime slurry is blended with the fresh water produced by the desalination process and is thoroughly mixed in lime saturator tanks to create saturated limewater which is then injected into the unconditioned desalinated water (see Figure 1).

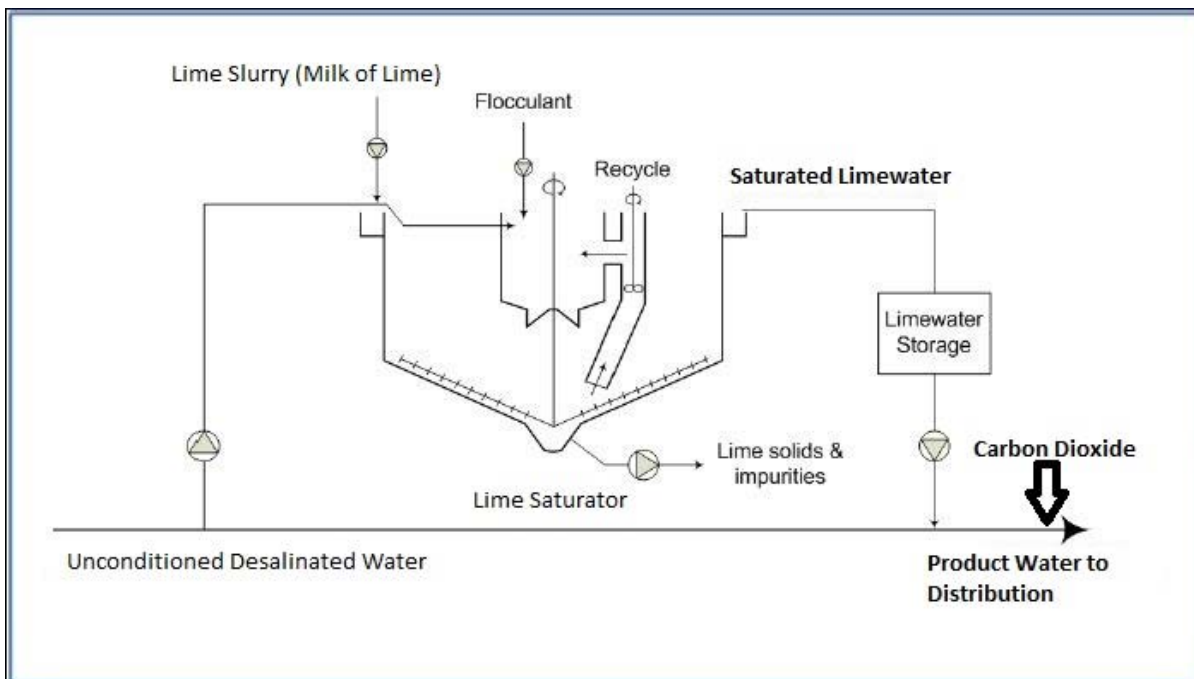


Figure 1
Schematic of Typical Lime/Carbon Dioxide Addition System



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Figure 2 depicts the lime storage silos and saturator of the 72 MGD (272,000 m³/day) groundwater replenishment plant located in Orange County, California. The lime saturator is shown on the left while the lime silos can be seen on the right.



Figure 2
Lime Storage Silos and Saturator

Carbon dioxide is typically delivered to the desalination plant site in a liquefied form and is stored under pressure in metal storage tanks (see Figure 3). In thermal desalination plants however, carbon dioxide released from the source water can be recycled and reused for the re-mineralization process described above instead of adding commercial carbon dioxide product. A solution of carbon dioxide and water (carbonic acid) is injected into the desalinated water downstream of the point of introduction of the saturated lime water.



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Figure 3
Carbon Dioxide Storage Tanks

Majority of desalination plants are designed to produce finished water of total (calcium and magnesium) hardness of 80 to 120 mg/L as CaCO₃. Since desalinated water usually contains less than 2 mg/L of magnesium, over 90 % of the total hardness of drinking water conditioned with lime is calcium hardness.

When adding lime to desalinated water, it is important to keep in mind that the solubility of calcium carbonate is dependent upon pH, temperature and ionic strength. Lime may not dissolve easily, and may add residual turbidity of 0.05 to 0.5 NTU (or higher) to the finished water, which is a disadvantage of this type of re-mineralization process.



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Lime-based re-mineralization typically requires the addition of acid (e.g., carbonic or sulfuric acid) to enhance lime solubility and to produce finished water with desired hardness and calcium carbonate precipitation potential (CCPP) adequate to provide corrosion protection. If the desalinated water is too warm (i.e., its temperature is 25⁰C or higher), the rate of lime solubility slows down and therefore, acid addition for pH reduction to enhance lime solubility would be beneficial.

There are a few methods to enhance solubility of slaked lime in water with temperatures higher than 25°C. One method is to introduce multiple points for carbonic acid and/or sulfuric acid injection into the desalinated water and a separate lime contact chamber that creates highly turbulent conditions and provides contact times of 5 to 10 minutes or more. Another approach used to enhance the solubility of lime in relatively warm plant desalinated water is turbulent mixing of the lime suspension with the plant desalinated water in the product water storage tank using large recirculation pumps. This approach however, is cost-effective only if the unit power cost is relatively low (i.e., US\$0.03–0.05/kWh).

Magnesium Addition. While it is acceptable for total hardness to be added only as calcium hardness for the purpose of protecting the water distribution system against corrosion, such water provides somewhat limited human health protection and is of lesser agricultural value. Therefore, some countries, such as Cyprus and Israel, are currently practicing or planning for addition of magnesium to desalinated water. At present, in desalination plants magnesium is added as a commercially available food grade product of magnesium sulfate or magnesium chloride.

Re-mineralization by Mixing of Desalinated water with Saline Source Water

Minerals, including calcium and magnesium, could be added to desalinated water by blending it with seawater or brackish source water. This practice is frequently used for both brackish water reverse osmosis (RO) plants and thermal desalination plants, and is acceptable only when the source water is of high quality, and is pretreated appropriately for both microbial and chemical concerns, and when the blend meets all applicable water quality standards.

When desalinated water and seawater are blended, the amount of source seawater is typically limited to 1% or less due to taste and other water quality considerations. For example, blending ratio of 1-to-99 of Pacific Ocean water of salinity of 33,500 mg/L and desalinated water produced by a single pass seawater reverse osmosis (SWRO) system of salinity of 220 to 350 mg/L would yield finished water with calcium content of 4 to 5 mg/L and magnesium of 19 to 20 mg/L. However, this water will have relatively high TDS content (550 to 680 mg/L) as well as



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high sodium (180 to 230 mg/L) and chloride (310 to 370 mg/L) levels. High level of bromide in seawater (typically in a range of 60 to 90 mg/L), may also lead to excessive formation of disinfection byproducts (DBPs) in the finished water, which are considered carcinogenic and are therefore regulated by the US Environmental Protection Agency (US EPA). Because of these implications, blending of permeate produced by SWRO plants with source seawater is typically not practiced. However, blending of low-salinity brackish water and desalinated water is a common practice in many parts of the world – including in the US, the Middle East and Europe.

The saline source water used for blending must be treated prior to its mixing with the desalinated water. The type and complexity of source water treatment depend on its quality. As a minimum, the saline source water used for desalinated water re-mineralization has to be filtered through cartridge filters. Enhanced source water treatment such as granular activated carbon filtration is recommended for source water exposed to potential contamination from excessive algal growth, surface runoff or other human-made sources of elevated organics or turbidity in the water. Pretreatment chemicals (such as acid) may need to be added, depending on where the blending source water is split from the feed water piping.

Re-mineralization by Dissolving Natural Minerals in Desalinated Water

Calcium Addition – Limestone (Calcite) Contactors. Limestone is a natural mineral made of calcite (calcium carbonate). Processing water through calcite media allows to dissolve this calcium source and in reaction with carbon dioxide to add both calcium hardness and bicarbonate alkalinity to the desalinated water. Re-mineralization using calcite and carbon dioxide follows the following chemical reaction:



Based on the equation 2 above, 1.00 mg/L of calcite and of 0.44 mg/L of carbon dioxide would need to be added in order to increase desalinated water hardness and alkalinity by 1.0 mg/L (as CaCO_3) each. Therefore, for a target recommended dosage of alkalinity and hardness in the product water of 100 mg/L the water produced by the desalination system will need to be treated with 100 mg/L of calcite and 44 mg/L of carbon dioxide.

Comparison of equations 1 and 2 indicates that re-mineralization using calcite requires two times less carbon dioxide. While only 0.74 mg/L of lime vs. 1.0 mg/L of calcite is required to add 1.0 mg/L of alkalinity and hardness, the cost of lime usually is over two times higher than that of calcite. In addition, since lime is typically produced from high temperature treatment of calcite, the carbon footprint of producing 1 kg of lime is several times higher than that associated with the production of calcite suitable for drinking water applications. Therefore, the use of calcite is



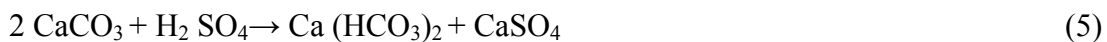
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usually more cost effective and environmentally palatable than the application of lime for re-mineralization.

Alternative to direct use of carbon dioxide is the addition of sulfuric acid which indirectly creates the carbon dioxide needed for the formation of bicarbonate alkalinity following the chemical reactions described below:



In summary:



As seen from the comparison of the process Equations (5) and (2), the use of sulfuric acid instead of carbon dioxide would require the addition of two times more calcite to provide the same amount of alkalinity to the finished water, because a one-half of the added calcite is used in the formation of calcium sulfate. However, sulfuric acid is often preferred because it allows to easily reduce desalinated water pH to practically any level needed for desalinated water enrichment with calcium, and because the rate of solubility of calcite with sulfuric acid is much higher than that associated with using carbon dioxide. This allows to treat only a fraction of the desalinated water flow through the calcite filters and to reduce the size of these filters. However, if the unit chemical costs for sulfuric acid are significantly higher than that of carbon dioxide, than the trade-off between higher capital costs for larger calcite contactors and lower operation and maintenance (O&M) expenditures may warrant the use of carbon dioxide instead of sulfuric acid.

Another advantage of using sulfuric acid for enhanced calcite solubility is that this process yields dissolved calcium to alkalinity concentration ratio of 2:1 (or higher) measured in equivalent units, while the use of carbon dioxide would yield to only 1:1 calcium to alkalinity ratio.

Using sulfuric acid for calcite solubility increases the sulfate (SO_4^{2-}) concentration of this water. This may be advantageous if the water intended for agricultural irrigation use, because typically desalinated water has significantly lower sulfate content than most surface water sources.

A schematic of typical calcite contactor system for re-mineralization is presented on Figure 4. Most existing desalination plants with low pH target for finished water (i.e., pH of 7.5 or less)



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are usually designed to process 100 % of the RO desalinated water through the calcite filters, especially when the cost of sulfuric acid or carbon dioxide used for desalinated water acidification before the calcite contactors is relatively high. However, for desalination plants with higher target pH range of the finished water (8.0 to 8.5) it usually is more cost effective to treat a portion (20 to 50 %) of the entire desalination flow through the calcite contactors and to blend this highly saturated stream with the remaining desalinated water in order to achieve target hardness, alkalinity and pH in the finished product water.

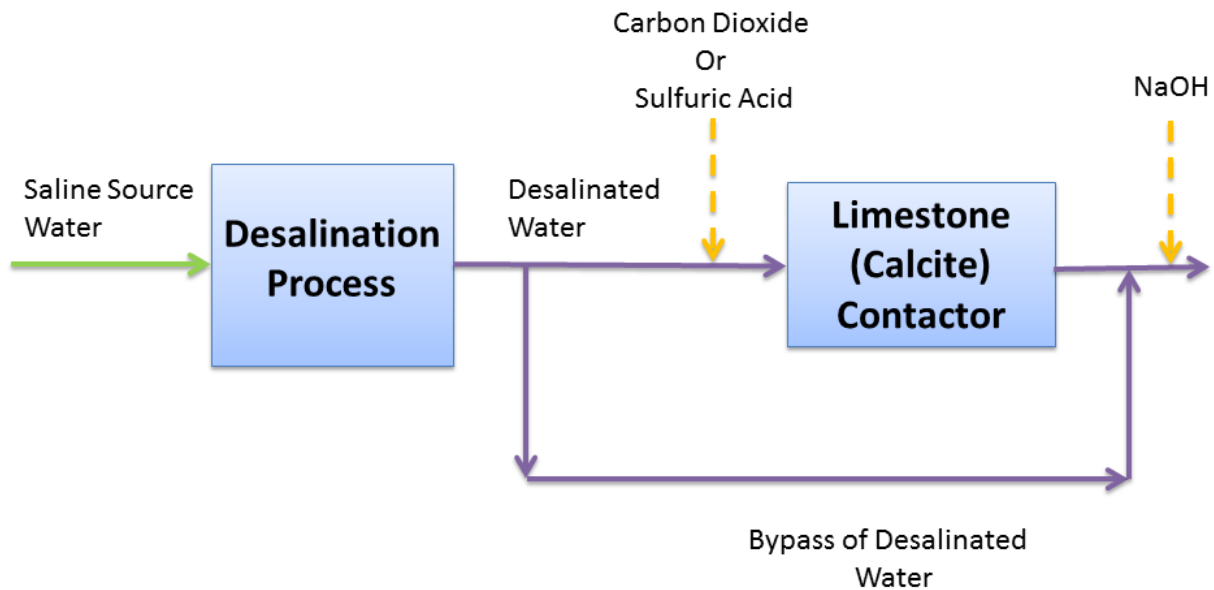


Figure 4
Schematic of Typical Limestone (Calcite) Contactor Re-mineralization System

In a typical calcite contactor re-mineralization system the pH of the desalinated water is first reduced down to 4.5 or less by addition of carbon dioxide or sulfuric acid, and this water is then conveyed through a filter bed composed of calcite granules (referred to also as beads, grains or pebbles) at a contact time of 10 to 30 minutes, thereby achieving target hardness and alkalinity levels in the finished water. The calcium concentration of the re-mineralized water can be controlled very reliably by adjusting the acid dosage of the desalinated water fed to the calcite contactor.

Calcite contactors are proven technology and have found implementation at the 87 MGD (330,000 m³/day) SWRO desalination plant in Ashkelon, Israel (see Figure 5), which at present is the largest operational membrane desalination facility in the world.



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Figure 5
Calcite Contactors of Ashkelon Desalination Plant, Israel

Such contactors are also used at the 16 MGD (60,000 m³/day) Larnaka SWRO plant in Cyprus and the 53 MGD (200,000 m³/day) Barcelona SWRO plant. Calcite for water re-mineralization has been successfully applied at a number of other desalination plants worldwide.

The largest thermal desalination plant using calcite contactors for re-mineralization of desalinated water is located in Bahrain [the 90 MGD (340,000 m³/day) Hidd Phase 1 and -3 plant]. This plant employs pressure-driven calcite contactors divided in three parallel treatment trains with 14 contactors per train (42 contactors in total). This plant uses CO₂ to lower the pH of the distillate prior to filtration through the calcite vessels. Sodium hydroxide is added as a final step of the re-mineralization process to adjust the pH of the finished water to the target level. An interesting challenge associated with the operation of this re-mineralization system was the relatively high content of organic and particulate residues in the natural limestone used for re-



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mineralization, which resulted in intermittent episodes of increased TOC and turbidity levels of the finished water. Such performance challenges were resolved by using higher quality limestone and modifying the flushing procedures for the calcite contactors.

As compared to the lime-based re-mineralization systems, calcite contactor systems are usually less costly in terms of both capital and chemical expenditures; require less carbon dioxide; and typically produce lower turbidity finished water. However, in many locations worldwide, high-quality food grade calcite is not as readily available as lime, which is one of the main reasons why this technology has not been used as frequently as lime/carbon dioxide conditioning to date. Therefore, most of the existing large seawater desalination plants in Australia, the USA, the Middle East, Spain, and North Africa have adopted conditioning of desalinated water using a combination of lime and carbon dioxide.

Calcium and Magnesium Addition – Dolomite Contactors: Dolomite is a natural mineral which contains calcium and magnesium carbonate and passing desalinated water through a dolomite contactor, similar in configuration and design to calcite contactors, would allow to add both minerals to the finished product water. In nature, the dolomite rock mineral is often non-homogenous and is inter-bedded with limestone. Therefore, the exact quality of the product water is more difficult to predict than when using pure limestone (grains, pebbles or granules).

Solubility of dolomite to enrich desalinated water with adequate amount of both calcium and magnesium requires pH reduction of this water to less than 4.5 via sulfuric acid or carbon dioxide addition. Because magnesium does not dissolve well in water with pH higher than 5.5, the pH adjustment to target level of 8 to 8.5 needed for corrosion protection often results in relatively low level of carbonate alkalinity and of magnesium in the water as compared to calcium hardness. For example, in order to achieve a target magnesium level of 10 mg/L, the calcium hardness of this water has to be several times higher than necessary. Therefore, if the water quality regulations have a maximum limit for total hardness in the water, as it is in Israel for example, the use of dolomite contactor may not be viable.

Water re-mineralization with dolomite is less feasible than using limestone for several reasons: (1) usually dolomite is more costly and less readily available than limestone; (2) solubility of dolomite occurs at over three-times slower rate than limestone, which necessitates the dolomite contactors to be significantly larger in size and therefore, more costly to construct and install; (3) dolomite is naturally more non-homogenous than limestone, which requires dolomite-based re-mineralization systems to be designed with higher contingency, a factor that additionally increases the application costs of this technology.



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Because of the process constraints listed above and the limited availability of food-grade dolomite, this mineral has not found full-scale application for re-mineralization of desalinated water to date. It should be pointed out however, that dolomite has found full-scale applications for treatment of soft fresh surface water.

Another reason for the limited application of dolomite re-mineralization contactor system is that using this technology for combined calcium and magnesium addition will be more costly than traditional lime/carbon dioxide/magnesium sulfate process described previously.

3. Design Considerations for Lime Feed Systems

Key Design Criteria

Lime Silo and Slurry System. As indicated previously, lime is typically delivered to the desalination plant site as bulk powdered hydrated lime which is stored on site in cylindrical metal silos with 60-degree cone bottom (lime bins). These silos are often the tallest structures on the desalination plant site and typically have diameter between 6.6 ft. and 20 ft. (2 and 6 m) and height of 16 ft. to 50 ft. (5 to 15 m).

The silos are designed to store lime for 15 to 60 days and are reloaded by delivery trucks suited with pneumatic conveyance equipment. They are equipped with vent filters for the conveying air and with bin vibrators, to promote flow of lime from the silo into a transition bin hopper. The feed of lime is controlled by a rotary discharge (airlock) valve which is motorized and closed or opened automatically based on the level of lime in the hopper.

A volumetric feeder draws from the transition bin hopper and delivers lime proportionally to the pH/flow into a slurry (milk of lime) mixing tank where the dry powdered lime is mixed with desalinated water or process water to generate lime slurry.

This lime slurry is then conveyed to the feed line of the lime saturators using slurry pumps/eductors. In order to prevent the scaling and accumulation of the slurry in the conveyance pipelines, this slurry is transferred to the lime saturator at very high velocity.

Lime silos are typically welded/bolted stainless steel structures equipped with level sensors, fill line with long-radius elbows and truck hose loading fitting with dust cap. The minimum lime silo capacity is 13,000 gallons (50 m³). The maximum lime silo capacity is often determined by the height of the maximum size of the silos.

Key design criteria for a typical lime silo and slurry system are presented in Table 1.



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Table 1
Lime Silo and Slurry System

Component/Parameter	Specifications/Design Criteria
Lime Dosage (as 100 % pure product)	0.74 mg/L per 1.0 mg/L of Target Alkalinity and Hardness Concentrations (as CaCO ₃)
Lime Consumption (kg/day as 100 % pure product) per 1000 m ³ /day of Desalinated Water For Addition of Alkalinity & Harness in a Range of 80 to 120 m/L (as CaCO ₃)	59.2 – 88.8
Lime Purity	85 – 94 %
Silo Vessel <ul style="list-style-type: none"> • Diameter, m • Height, m • Storage Time, days • Structure – Material Type 	2 to 6 5 – 15 15 to 60 Coated Carbon or Stainless Steel
Silo Vent Filter <ul style="list-style-type: none"> • Material Type • Type 	Stainless Steel Cartridge Type with Polyester Felt Cartridges
Lime Flow Facilitating Equipment	Bin Vibrator Fluidized Air Pads
Lime Slurry <ul style="list-style-type: none"> • Concentration, % • Slurry Tank Retention Time, hrs. • Pumps 	10 3 to 5 Progressing Cavity – Equipped with Flushing System

Note: 1 m = 3.3 ft.

Lime Saturator System. Lime slurry is pumped from the slurry tank to the lime saturation system by a progressive cavity type of pump. The lime saturation system is also fed with permeate which is used for dissolve and dilute the lime slurry from 10 % down to 0.1 %. In addition, polymer is frequently added at a dosage of 0.5 to 1.0 mg/L to the feed water in order to reduce the turbidity of the limewater. The lime saturator system consists of saturator tanks, recirculation pumps or mixers, saturated limewater tanks, and limewater dosing pumps. Lime saturators are thickener-clarifier tanks which main purpose is to produce homogenous and fully dissolved lime solution (saturated limewater) and to remove the solid lime impurities inherently contained in the commercial lime product. Typically, these facilities are constructed as circular



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metal tanks which consist of central feed well (reaction zone) to dissolve and mix the lime slurry with the desalinated water and a settling zone where the un-dissolved lime material and impurities are separated from the saturated lime water and removed by a bottom scraper and hopper (see Figure 1). Lime saturators are equipped with mechanical propeller-operated (turbine) mixers or pumps with variable speed drives which recirculate lime slurry from the tank bottom to the reaction zone in order to accelerate the lime solubility process. Lime slurry is fed continuously into the reaction zone and mixed to enhance and accelerate the solubility process. Key design criteria of a typical lime saturator system are summarized in Table 2.

Table 2
Lime Saturator System

Component/Parameter	Specifications/Design Criteria
Lime Slurry Feed Concentration, %	10
Lime Slurry Feed Volume	Estimated for the Target Lime Dosage at 10 % Concentration
Saturator Solids Loading Rate, kg lime/m ² .hr	1.5 to 4.0
Saturator Hydraulic Loading Rate, m ³ /m ² .hr	0.7 to 1.0
Saturator Retention Time, min	100 to 120
Saturator Diameter, m	2 to 20
Saturator Depth: <ul style="list-style-type: none"> • Depth of Water, m • Total Depth, m 	3.0 to 4.5 3.5 to 5.0
Retention Time in Reaction Zone, min	8 to 15 min
Reaction Zone Diameter, % of Total Lime Saturator Diameter	25 to 35
Reaction Zone Height, % of Depth of Water	75 to 85
Limewater Storage Tank <ul style="list-style-type: none"> • Total Retention Time, hrs. • Limewater Concentration, mg/L 	18 to 24 900 – 1,400

Note: 1 m = 3.3 ft.

The maximum lime solubility in water is approximately 1,500 mg/L and saturated limewater is designed to be at concentration of 900 to 1,400 mg/L (typically 1,000 mg/L). The saturated



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limewater is collected in overflow launders at the top of the saturator tanks from where it flows by gravity to a limewater tank or tanks. The volume of the lime water tank should be selected such that it provides storage for 18 to 24 hours of the limewater needed to condition the entire daily volume of desalinated water. This volume allows ample time to take out the lime saturator for cleaning periodically. Limewater is pumped to the dosing point/s along the length of the product water pipeline using centrifugal pumps equipped with variable frequency drives.

Lime solids are collected at the bottom of the settling zone. Portion of these solids is recycled to the feed well to enhance solubility and particle flocculation and settling. Polymer is often added to accelerate the flocculation process and minimize the carryover of fine solids into the saturated limewater because these solids contribute turbidity to the final product water. Polymer addition also assists in increasing of the solids concentration of the lime bed, which in turn reduces the volume of the sludge generated by the lime saturator system.

Design and Operational Issues

Lime Purity. Depending on its quality and origin, commercially available lime products usually have purity of 85 to 94 %. The actual lime purity is a very important factor to consider when assessing the finished desalination plant product water quality.

For example, if lime product of 90 % purity is used, the addition of 74 mg/L of 100 % pure lime needed to produce water of 100 mg/L of alkalinity and hardness (as CaCO₃) would also result in the introduction of 8.2 mg/L of impurities, typically in the form of suspended solids. Unless these impurities are completely removed by the lime saturator tanks, they will find their way into the plant finished product water and increase its turbidity/suspended solid content.

Use of lime of highest commercially available purity (typically 94 %) is recommended despite of its elevated costs because of the numerous negative implications associated with removing and disposing of the solids associated with the lime impurities. These solids tend to accumulate in the lime feed system pipelines and equipment, and must be removed periodically because they could result in equipment malfunction over time. In addition, the costs of treatment and disposal of solids generated by lime impurities could be significant.

For example, a 18 MGD (70,000 m³/day) desalination plant which is using lime of commercial grade purity of 85 % and is adding 74 mg/L of lime as a pure product (87.1 mg/L of 85 % purity commercial product) will be generate 335 dry tons/year of impurities which would need to be separated and disposed of. The use of high (94 %) purity lime instead will reduce this solids content to only 121 tons/yr.



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Maintenance. Dosing lines for saturated lime water are exposed to potential blockages from lime solids buildup and therefore, are recommended to be equipped with flushing system and to be flushed every one to two weeks with carbon dioxide saturated water. Dosing valves are recommended to be exercised weekly in order to prevent buildup.

Saturators have to be monitored routinely and de-sludged as needed. The turbidity of the limewater from well-operated saturators typically does not exceed 30 to 35 NTU. The sludge solids concentration is usually between 10 and 15 %.

Elevated turbidity of the limewater is an indication for potential buildup of sludge in the tanks and/or lime bed turnover which may be triggered by colder temperatures. Such turbidity increase may also be caused by buildup of lime in the mixer lift piping over time. Therefore, the mixer system would need to be cleaned once every 6 to 12 months.

Saturator launders also accumulate lime over time and need periodic cleaning. In order to accommodate their routine maintenance, lime saturators have to be designed with access platform for launder cleaning.

Design Considerations for Carbon Dioxide Feed Systems

Carbon dioxide is used for addition of alkalinity to desalinated water in combination with both lime and limestone and for pH adjustment to enhance the limestone solubility process. As indicated previously, 0.88 mg/L of carbon dioxide would need to be added to the desalinated water to increase its alkalinity by 1 mg/L (as CaCO_3).

Key Design Criteria. Carbon dioxide is delivered to and stored at the desalination plant in compressed liquid form (20 bars of pressure at $-20\text{ }^{\circ}\text{C}$). The liquid chemical is converted into gaseous form in evaporators at 3 bars at $12\text{ }^{\circ}\text{C}$, dissolved in carrier water of 55 to 70 psi (4 to 5 bars) and the carbonic acid solution is injected into the desalinated water.

A typical carbon dioxide feed system consists of liquid carbon dioxide storage tanks equipped with refrigeration units; vaporizers; vapor heaters; carbon dioxide dosing system with pressurized gas solubility panel and an in-line gas feed diffuser. Table 3 summarizes key design criteria for a typical carbon dioxide feed system.

Design and Operational Issues. For operational flexibility, carbon dioxide system is recommended to be designed with two points of delivery – one upstream of the lime feed system for pH adjustment and one after the point of addition of lime. For limestone or dolomite contactors, carbon dioxide is often added to reduce the pH of the desalinated water and thereby to accelerate their solubility.



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The dosage of carbon dioxide fed to the desalinated water is adjusted proportionally to the desalinated water flow rate by flow control valves installed on the gas feed lines from the vaporizer to the point of chlorine dioxide gas injection in the desalinated water conveyance pipe.

Table 3
Carbon Dioxide Storage and Feed System

Component/Parameter	Specifications/Design Criteria
Carbon Dioxide Dosage (as 100 % pure product)	0.88 mg/L per 1.0 mg/L of Target Alkalinity and Hardness Concentrations (as CaCO ₃)
CO ₂ Consumption (kg/day as 100 % pure product) per 1000 m ³ /day of Desalinated Water For Addition of Alkalinity & Harness in a Range of 80 to 120 m/L (as CaCO ₃)	70.4 – 105.6
CO ₂ Purity, %	100
Liquid CO ₂ Storage Tank (Refrigerated) <ul style="list-style-type: none"> • Storage Pressure/Temperature, bars/⁰C • Diameter, m • Length/Height, m • Storage Time, days • Structure Material Type 	20 bars/ -20 ⁰ C 0.8 to 3.0 5 – 15 15 to 60 days Carbon Steel
Vaporizer <ul style="list-style-type: none"> • Type • Capacity, Horsepower/kg CO₂.day • Delivery Pressure/Temperature, bars/⁰C 	Electric 0.03 – 0.05 3 bars/ 12 ⁰ C
Vapor Heater <ul style="list-style-type: none"> • Type • Capacity, Horsepower/kg CO₂.day 	Electric 0.01 – 0.02

Note: 1 m = 3.3 ft.; 1 bar = 14.225 psi; 1 kg = 2.2 lbs.

Design Considerations for Limestone (Calcite) Contactors

Limestone (calcite) contactors are well suited for re-mineralization of desalinated water produced by all types of desalination processes (thermal, RO and EDR desalination). Typically they are contactors designed to operate in an upflow mode and are configured similar to gravity or pressure-driven granular media filters. Because of the low solubility of calcite at the near-neutral pH of the desalinated water, the addition of adequate calcium concentration requires pH



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reduction of permeate to usually less than 4.5 (corresponding to CCDP of at least 200 mg/L as CaCO₃) before the water enters the contact tanks.

Calcite Contactor Configuration. Typical calcite contactor system consists of calcite bed with supporting layer and feed water distribution system; feed (inlet) line; backwash system; feed (inlet), outlet and overflow lines (see Figure 6). The desalinated water is introduced through the distribution system located at the bottom of the contactor and saturated with calcium carbonate as it flows upwards through the calcite bed.

In order to enhance the solubility process, the pH of the feed water is reduced typically below 4.5 and as the water travels upwards its pH, alkalinity and hardness increase. The pH, alkalinity and hardness of the conditioned water depend on a number of factors, including the initial pH, CO₂ content, alkalinity, TDS, water temperature, upflow velocity and the contact time the reactor.

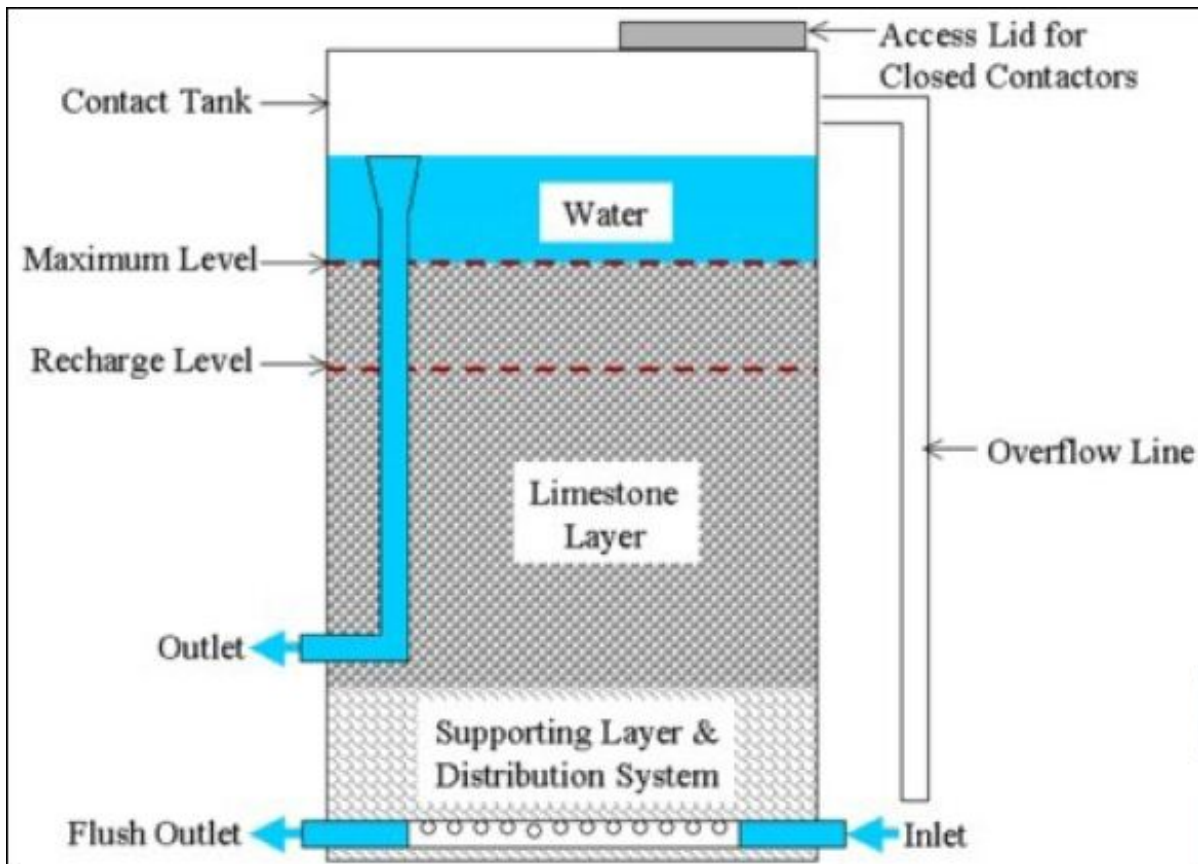


Figure 6
Calcite Contactor Schematic



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Distribution System. The feed water distribution system is located at the bottom of the tank and has the same configuration and design as these of an upflow granular media filter. Some designs have infiltration platforms with nozzles distributed uniformly on its surface for even flow distribution.

Supporting Layer. The supporting layer is usually 0.5 to 2.0 ft. (0.15 to 0.35 meter) deep and consists of gravel, granite aggregate or other inert materials. The size of the support media should be larger than the size of the limestone.

Limestone (Calcite) Bed. The calcite bed consists of either crushed limestone pebbles or limestone granules (grains) with diameter of 0.06 to 0.1 in (1.5 to 2.5 mm). Table 4 provides recommendations for the quality of limestone to be used in calcite contactors.

Table 4
Recommended Calcite Grain Specifications

Parameter	Value
Grain Size, mm	1.5 – 2.5
Purity, %	99 % or more
Iron Oxide Content, %	Less than 0.1 %
SiO ₂ , %	0.3 %
Al ₂ O ₃ , %	0.1 %
MgO, %	0.2 %
Hardness, Mohs	3
Specific Weight, tons/m ³	1.5

The depth of the contact zone of the calcite bed is usually between 5 to 10 ft. (1.5 and 3.0 m) and is a function the source water temperature, pH, the target mineral content of the conditioned water and the calcite grain size. The contact zone portion of the limestone bed is the volume of calcite between the recharge level and the surface of the support layer (see Figure 6).

Since limestone is consumed during the re-mineralization process, an additional working volume of calcite has to be added on the top of the contact zone. This calcite bed working (reload) zone



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is denoted on Figure 6 as the zone between the maximum and recharge levels of calcite. The volume of this zone is determined based on the daily consumption of calcite and the time between two calcite bed-reloads (typically two to eight weeks).

Calcite Media Consumption and Working (Reload) Volume. As indicated previously, 1 mg/L of calcite (as CaCO_3) is needed to add 1 mg/L of hardness to the desalinated water. If the amount of the desalinated water contains a measurable amount of calcite, the additional calcite which has to be added could be reduced. For example, permeate produced by a single pass RO system from Pacific Ocean seawater usually contains a minimum of 0.6 mg/L of calcium ion. Taking into consideration that 1 mg/L of calcium ion equates to 2.493 mg CaCO_3/Ca , the actual available content of CaCO_3 in the desalinated water would be only $0.6 \text{ mg/L} \times 2.943 = 1.8 \text{ mg/L}$ as CaCO_3 .

If the target hardness of the desalinated water is 100 mg/L (as CaCO_3), than the actual maximum amount that would be consumed daily is $100 \text{ mg/L} - 1.8 \text{ mg/L} = 98.2 \text{ mg/L}$ of calcite as 100 % pure product. At calcite purity of 99 %, the quantity of the commercially available chemical used will be: $98.2/0.99 = 99.2 \text{ mg/L}$ (g/m^3). The volume of the calcite media which has to be re-loaded is calculated based on the quantity of daily calcite consumption; the specific weight of the product (see Table 4); and time between two media reloads.

Conditioned Water Zone. This is the zone of conditioned water between the limestone layer and the outlet overflow of the filter. Usually this zone is 2 to 3 ft. (0.6 to 1.0 m) high.

Limestone Feed Zone. The limestone bed has to be replenished periodically because it is dissolved during the re-mineralization process. Limestone media is typically refilled from the top of the filters (Figure 7). Refilling is competed manually if limestone is delivered in 55 lbs. (25 kg) packages (typical for small plants) or the bed is reloaded using gentry crane installed above the filter cells if the limestone is packaged in 1.1-ton bags (common for large plants).

Empty Bed Contact Time (EBCT). The hydraulic residence time of the desalinated water in the limestone bed is a key design parameter for this system. EBCT is calculated by dividing the volume of the limestone layer (bed) by the feed flow rate. EBCT is typically in a range of 10 to 30 minutes depending on the temperature, CO_2 and HCO_3^- content of the desalinated water.

The needed EBCT increases with decrease in desalinated water temperature. In order to provide adequate product water quality at all times, this contact time should be sized for the daily minimum temperature of the desalinated water and for daily maximum product water flow.

Surface Loading Rate. The typical average design surface loading rate is in a range of 4 to 8 $\text{m}^3/\text{m}^2 \cdot \text{hr}$ and the maximum rate is 4 gallons per minute per square foot ($\text{gpm}/\text{sq ft.}$), or $10 \text{ m}^3/\text{m}^2$.



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hour. Higher surface loading rates typically result in elevated turbidity of the re-mineralized product water.



Figure 7

Refilling of Calcite Media

Calcite Bed Backwash System. It is recommended to backwash the limestone contactors weekly in order to maintain consistent product water quality. Backwash is completed through the distribution system and is recommended to include the following sequence: (1) air purge for 3 to 5 minutes at a rate of 24 gpm/sq ft. ($60 \text{ m}^3/\text{m}^2 \cdot \text{hr.}$); (2) air and water backwash for 5 to 10 minutes at air rate of 24 gpm/sq ft. ($60 \text{ m}^3/\text{m}^2 \cdot \text{hr.}$); and water rate of 4 to 5 gpm/sq ft. ($10 \text{ to } 12 \text{ m}^3/\text{m}^2 \cdot \text{hr.}$); (3) water backwash only for 10 to 15 minutes at rate of 6 to 10 gpm/sq ft. ($15 \text{ to } 25 \text{ m}^3/\text{m}^2 \cdot \text{hr.}$).



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In addition, it is recommended to down-flush the filter bed at least once per month to remove fine dust and waste material introduced during filter cell loading. Calcite filter cells should be provided with flush outlet for this purpose (see Figure 6).

Design and Operational Issues

Calcite Grain Size Impact on Calcite Bed Depth. It is important to note that calcite grain size has an impact on the needed depth of the contact zone of the calcite bed, especially if limestone grains are larger than 0.08 in (2 mm). The required depth of the contact zone increases proportionally with the increase of the calcite grain size. For example, if calcite grains of 0.12 in (3 mm) are used instead of 0.1 in (2.5 mm), the depth of the contact zone of the calcite bed would need to be increased with approximately 30 %. Similarly, the required height of the contact zone of the bed could be reduced by approximately 25 % if calcite grain size is reduced from 0.1 down to 0.8 in (2.5 mm down to 2.0 mm). Further grain reduction to 0.06 in (1.5 mm) or less however, has lesser impact on the needed depth of the calcite bed. Therefore, the optimum size of the calcite grains is between 0.06 and 0.08 in (1.5 and 2.0 mm).

Calcite Quality Impact on Performance. Practical experience indicates that calcite contactor turbidity is closely related to the type of calcite used and the surface loading rate of the calcite filters. If well washed calcite is used (i.e., calcite that contains less than 1 % fines), the product water turbidity is not affected until the surface loading rate of the filters exceeds 6 gpm/sq ft. (14 m³/m²·h). For calcite with higher content of fine particles (2 % or more) the maximum surface loading rate of the calcite contactor cells under which the finished water quality is not affected is 4.5 to 5.0 gpm/sq ft. (11 to 12 m³/m²·h).

Refilling of Calcite Cells. Contactor cells should be filled with calcite only when water is present in the cells because otherwise the calcite grains may be compacted and form clusters which will hinder the solubility process.

Calcite Media Replacement. Over time calcite media in the contact bed deteriorates and accumulates surface scale and therefore, it would have to be replaced completely once every 5 to 10 years.

Operations Monitoring. As a minimum it is recommended to monitor the pH of the re-mineralized water frequently in order to make sure that the design equilibrium pH is maintained at all times. A steady decrease of pH usually is an indication for the need to re-load calcite. Another important monitoring parameter is the calcite bed media headloss. Over the course of the re-mineralization process the filter headloss increases steadily and once it reaches its maximum design level, the calcite bed would need to be backwashed.

4. Innovative Re-Mineralization Systems

Calcite Beds with Continuous Feed (DrinTec Calcite Contactors)

Description. An innovative upflow calcite reactor with continuous feed of limestone into the calcite bed has been developed by DrinTec Solutions (Spain) and recently implemented for re-mineralization of permeate produced of the SWRO system of the 53 MGD (200,000 m³/day) Barcelona desalination plant in Spain. A cross-section of such a calcite bed cell is shown on Figure 8.

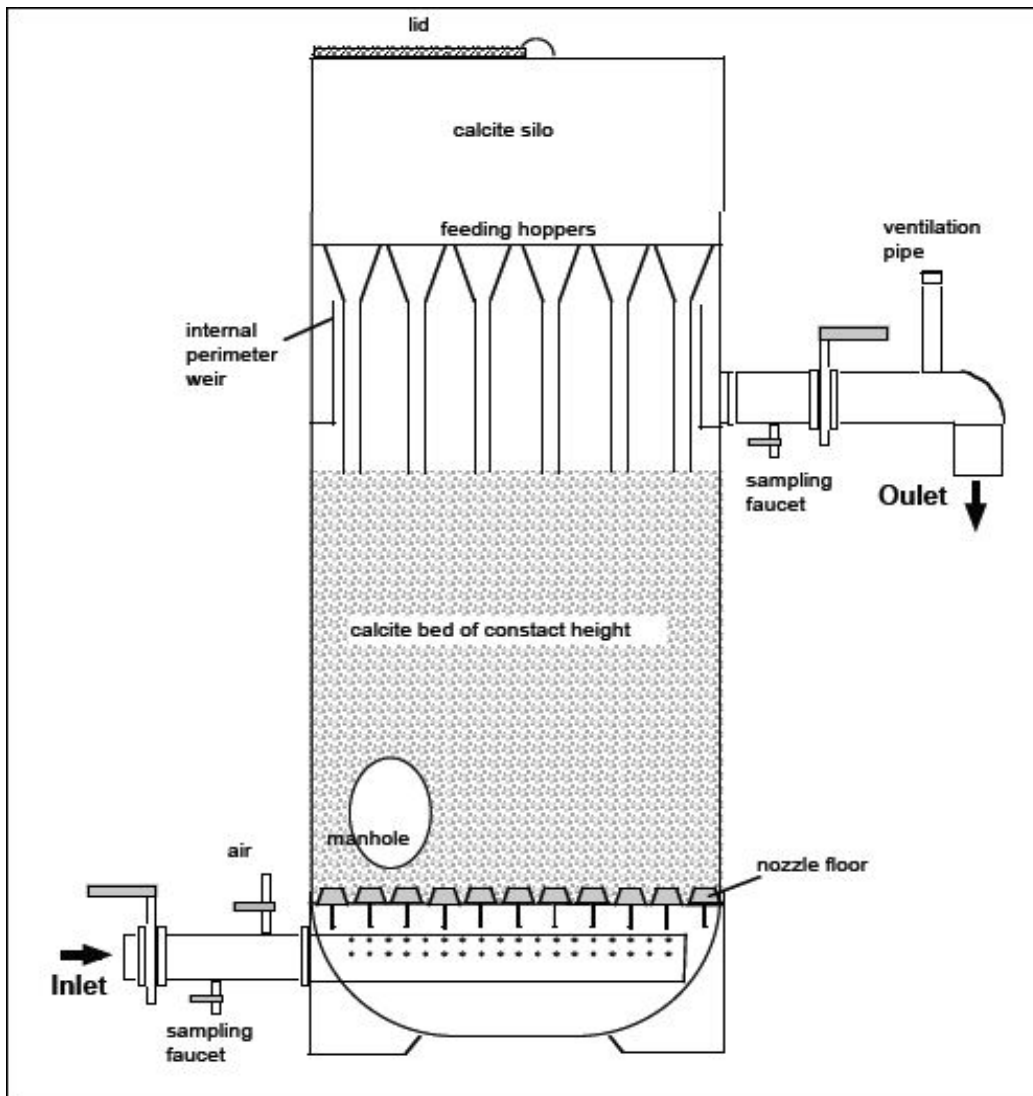


Figure 8
Cross-section of DrinTec Calcite Contactor Cell



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The general configuration of the calcite bed in Figure 8 is similar to that of typical calcite contactors (Figure 6). The desalinated water is fed at the bottom of the calcite bed. However, as compared to conventional calcite contactors which are reloaded intermittently, the DrinTec calcite bed is reloaded continuously under water by series of small guiding funnels which are installed on the bottom of the feeding hoppers and located above the bed (see Figure 9).



Figure 9
Calcite Hopper and Feed Funnels

Calcite grains are fed to the bed through the funnels from calcite storage silos which are integral part of the filter cell structure. The silos typically contain several weeks of calcite supply. The calcite cells for large plants such as the Barcelona desalination facility are concrete structures. Enclosed fiberglass reinforced plastic (FRP) cells are used for smaller facilities. This novel technology can operate both for gravity and pressurized calcite contactors. The calcite grains introduced through the funnels are delivered to the bed at a very low velocity (one 2-mm calcite grain per minute) which eliminates the turbulence and turbidity spike of the re-mineralized water which are typically created during the reloading of conventional calcite beds. This feature allows increasing the design hydraulic surface loading rate (upflow velocity) of the calcite bed without the penalty of elevated turbidity which is a key limitation in conventional limestone



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systems. Desalinated water saturated with carbon dioxide enters the calcite cells through perforated floor equipped with FRP flow distribution nozzles. As the desalination water moves upwards through the calcite bed, the carbon dioxide contained in this water dissolves the calcite forming calcium bicarbonate. As a result the bicarbonate alkalinity of the desalinated water increases until it reaches equilibrium. After the water passes through the calcite bed it enters a quiescent zone from where it is conveyed out of the cells. The alkalinity content of the finished water quality is controlled by the dosage of carbon dioxide (feed water pH). Similar to most conventional calcite contactors, the DrinTec units are also backwashed periodically with air and water (once every two to three weeks). However, the DrinTech system has a provision for turbid water recirculation to the entrance of the calcite facility in order to prevent significant turbidity increase of the finished water during backwash events. Table 5 shows the key design criteria of the DrinTec calcite contactors for the Alicante II and Barcelona seawater desalination plants in Spain.

Table 5

Design Criteria for DrinTec Calcite Contactors of the Alicante II and Barcelona Plants

Parameter	Value	
	Alicante II Plant	Barcelona Plant
Plant Production Capacity, MGD/m ³ /day	18/67,200	53/200,000
Calcite Consumption/Alkalinity Addition, mg/L as CaCO ₃	59	56
Carbon Dioxide Dosage, mg/L	26	25
pH of Re-mineralized Water	8.0 – 8.2	8.0 – 8.2
Total Surface of Calcite Contactors, m ²	320	648.4
Number of Cells	32	32
Cell Dimensions (Width x Length), m	2.0 x 5.0	3.02 x 7.02
Design Flow rate per Cell, m ³ /day	2,100	6,250
Surface Loading Rate, m ³ /m ² . hr.	8.75	9.64
Bed Height, m	1.6	2.5
EBCT, minutes	11.0	12.2



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Comparison of DrinTec to Traditional Calcite Contactor Technologies

The low and uniform calcite loading rate of the cells allows to increase the surface loading rate of the filters from a typical range for conventional designs of 1.6 to 3.3 gpm/sq ft. (4 to 8 m³/m².hr) to as high as 7.4 gpm/sq ft. (18 m³/m².hr) while still maintaining the turbidity of the finished water below 1 NTU.

The typical design loading rate of these units is 3 to 5 gpm/sq ft. (8 to 12 m³/m².hr). Filter bed headloss at surface loading rate of 5 gpm/sq ft. (12 m³/m².hr) is 2.8 in/foot (23.4 cm per meter) of calcite bed depth. This headloss is proportional to the loading rate and drops to 2.4 in/foot (20.0 cm/per one meter) of bed depth at surface loading rate of 4 gpm/sq ft. (10 m³/m².hr). The higher design surface loading rate the DrinTec Calcite Contactors allows reducing their size and associated capital costs.

The continuous loading of the calcite reactors also allows achieving more uniform and predictable product water quality with minimal operator attention. This feature also results in reduced filter backwash and flushing frequencies, and in simplified and fully automated filter maintenance.

Calcium-Magnesium Ion Exchange System (RWM)

Description. Renewed Water Minerals, Ltd (RWM) has recently developed an advanced re-mineralization technology for cost-effective addition of calcium and magnesium as well as carbonate alkalinity to desalinated water from seawater and brackish water desalination plants. The RWM system re-mineralizes desalinated water by first raising its calcium content through a limestone (calcite) contactor, and then by adding magnesium to the water using ion exchange reactor which contains magnesium-saturated resin (see Figure 10).

Sulfuric acid or carbon dioxide is used to reduce desalinated water pH to less than 4.5 and thereby to enrich the desalinated water with calcium. The ion exchange resin is periodically replenished with magnesium ions originating from the pretreated source water used for desalination.

In order to minimize the capital costs for the calcite reactors and ion exchangers, only 16 to 30 % (on average 25 %) of the entire desalinated water volume is treated through the re-mineralization facilities. This portion of the desalinated water is enriched with calcium and magnesium at levels three to six times (on average four times) higher than the target concentration of these minerals in the finished product water, and then it is blended with the remaining water.

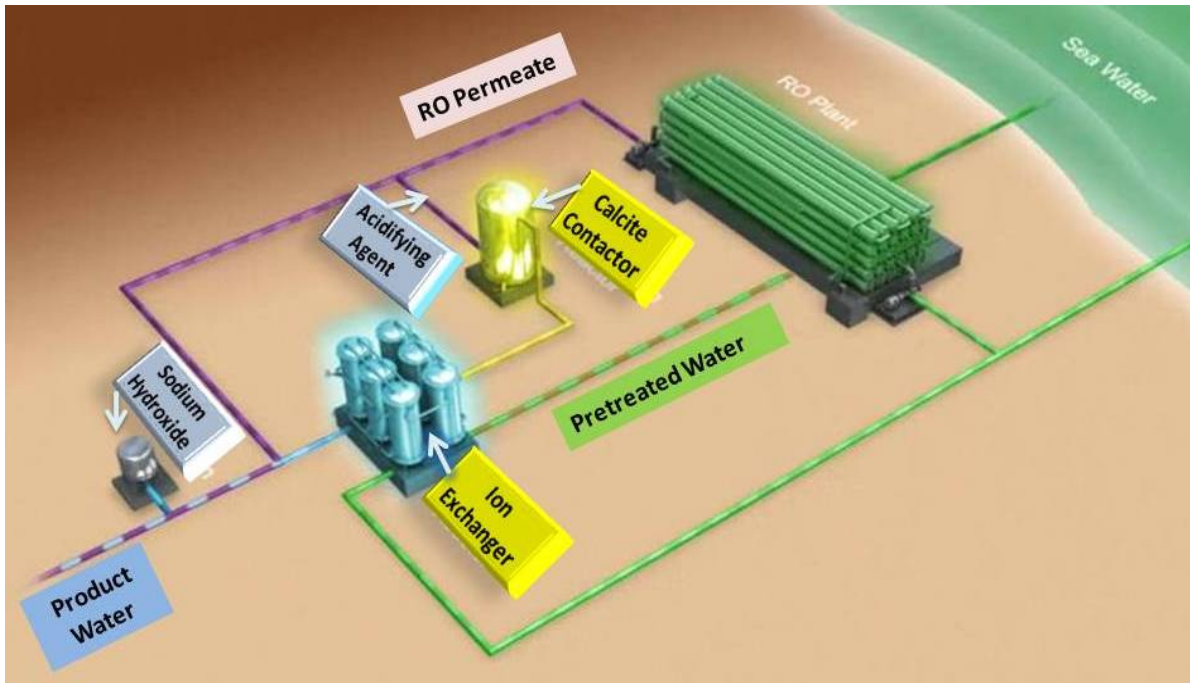


Figure 10
Process Schematic of RWM Re-mineralization System

The desalinated water blend after re-mineralization has a pH level close to 5 to 7. Therefore, as a final treatment step, the pH of the blended desalinated water is adjusted to a target level (usually 7.5 to 8.5) by addition of sodium hydroxide or by carbon dioxide stripping. This step is also aimed at achieving a low positive level of CCPP and a slightly positive LSI. This chemical stabilization is important for preventing corrosion of the water distribution system. The key RWM system components include:

- Acidifying Agent Feed System;
- Calcite Contactors;
- Innovative Ion Exchange Resin System;
- Post-mineralization pH Adjustment System.

Acidifying Agent Feed System. Approximately 16 to 30 % (an average of 25 %) of the desalinated water (desalinated water) is treated with sulfuric acid or carbon dioxide in order to facilitate the enrichment of this water with calcium. Taking under consideration that all of the calcium would need to be delivered to only one-quarter of the total plant desalinated water flow, the desalinated water treated through the calcite contactors and ion exchange resin has to be



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raised to a calcium level that is approximately four times higher than the total hardness of the finished product water. Usually, the pH of desalinated water produced by a SWRO system is between 8 and 7. Because of natural limitations associated with calcite solubility kinetics, at this pH only a small portion (10 to 15 %) of the needed calcium can be dissolved into the RO system desalinated water. However, desalinated water pH reduction down to 2.2 to 2.5 using sulfuric acid, or down to 4.3 using carbon dioxide allows enriching the desalinated water with calcium up to the needed levels.

Calcite Contactors. The main purpose of this RWM system component is to enrich the desalinated water (i.e., SWRO desalinated water) with calcium. As indicated previously, calcite contactors are enclosed and sealed cylindrical vessels periodically filled with calcite (limestone) grains which are designed and operated similar to pressure filters (see Figure 11).



Figure 11
RWM System Calcite Contactors



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The calcite grains are dissolved by the low-pH desalinated water fed to the calcite contactors. The flow regime in the calcite contactors resembles plug flow, where the passing desalinated water is enriched with both calcium (Ca^{2+}) and carbonate (CO_3^{2-}) ions. Because of the low pH of the water, a portion of the carbonate ions are transformed into bicarbonate (HCO_3^-) ions and carbonic acid (H_2CO_3), and therefore, the pH of the desalinated water at the end of the re-mineralization process increases to close to 7. The calcium concentration of the desalinated water exiting the calcite contactor is typically in a range of 500 mg/L to 1,000 mg/L as CaCO_3 .

Ion Exchange Resin System. The purpose of the ion-exchange system is to add magnesium ions to the desalinated water. In this system, a portion (approximately 25 to 50 %) of the calcium added to the desalinated water in the calcite reactors is exchanged with equivalent amount of magnesium originating from the source seawater. As a result, the calcium concentration of the desalinated water decreases while the magnesium concentration increases. The ion exchange reactors are cylindrical plastic (usually high-density polyethylene – HDPE) or steel pressure vessels (see Figure 12).



Figure 12
RWM System Ion Exchange Reactors



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These ion exchange reactors are filled with cation resin which has a high affinity to divalent ions, such as magnesium and calcium and very low affinity to mono-valent ions such as sodium, potassium and boron.

Long-term testing completed by RWM indicates that resins commercially available from Rohm & Haas, Inc. and from RWM can be used for reliable and steady-state operation of this ion exchange process. The minimum reaction contact time for these resins is 1.5 minutes, which translates to maximum flow rate of 40 bed volumes (BV) per hour (i.e., 40 BV/h).

The ion exchange system is operated in a batch (cyclical) mode which has two key steps: (1) “load step”, during which magnesium is loaded on the resin; (2) “exchange step”, which is the period when a portion of the calcium in the water introduced through the calcite contactor is exchanged with magnesium from the resin. Usually, the ion exchange system is designed such that at any given time one of the ion exchange reactors is in load step while the others are in exchange step. A full cycle of one ion exchange reactor continues for approximately 0 to 5 hours.

Load Step: During the load step, the ion exchange resin is enriched with magnesium originating from pretreated seawater. The volume of seawater needed for regeneration is less than 2 % of the total source water intake of the desalination plant and therefore, would not create significant changes to its operation or design.

After passing through the ion exchangers, the pretreated source water used for resin regeneration is either discharged with the concentrate, returned to the head of the pretreatment filters or used for backwashing of the desalination plant pretreatment filters. Since the volume of this water is relatively small and the stream is intermittent, despite the fact that it contains a high load of calcium (and low load of magnesium), this water is not expected to have a significant material impact on the overall scaling potential of the water fed to the desalination process. Experience shows that when seawater is used, the load step can be practically stopped after 25 BV.

Exchange Step: During this step a portion (25 to 50 %) of the calcium delivered to the desalinated water by the calcite contactors is exchanged with the magnesium contained on the ion exchange resin. The batch volume of desalinated water that can be processed during the exchange step is a function of two parameters: the specific $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio targeted in the product water and the total hardness concentration of the ion exchange columns influent. An exchange step of 120 to 250 BV (an average of approximately 220 BV) is needed for water with a high total hardness concentration (achieved when sulfuric acid is used in the calcite solubility



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process). Much longer exchange steps 350 BV to 650 BV are necessary when carbon dioxide is used in the calcite solubility process, resulting in lower total hardness concentrations in the treated water.

System for Post-mineralization pH Adjustment. This system is used to adjust pH of the product water exiting the ion exchange system from a near-neutral level (pH of under 7) to a target level between 7.5 and 8.5, depending on the site specific needs of a given project. Sodium hydroxide is usually added at a dosage of 10 to 25 mg/L. It should be noted however, that in many cases carbon dioxide stripping may be a cost effective alternative to sodium hydroxide dosage; particularly when calcite is dissolved using carbon dioxide as the acidifying agent.

All key RWM system components described above can be configured as prefabricated, pre-tested modules which are integrated on site. This modular configuration facilitates accelerated and simplified system assembly and equipment deployment, and allows expedited plant installation and commissioning.

Comparison of RWM to Traditional Re-mineralization Technologies

The RWM technology addresses the limitations and disadvantages of currently available traditional technologies for re-mineralization (i.e., lime/carbon dioxide) of desalinated water in a cost effective manner. A common basis for technology comparison is system performance and costs for production of drinking water of quality meeting the minimum WHO health protection guidelines for calcium and magnesium of 50 mg/L as CaCO₃ and 10 mg/L, respectively; and providing adequate corrosion protection in terms of total hardness (i.e., hardness > 80 mg/L as CaCO₃); total alkalinity (i.e., alkalinity > 80 mg/L as CaCO₃); calcium carbonate precipitation potential, CCPP (range of 3 to 10 as CaCO₃) and pH (i.e., pH of 7.5 to 8.5).

As compared to the conventional re-mineralization technology for adding lime and carbon dioxide, the RWM system has three key advantages:

- **Both Calcium and Magnesium Are Added to the Product Water**, making it more valuable in terms of human health protection and agricultural use, and closer in mineral content to other natural fresh water resources. The main reason for the difference is that the RWM system includes a sequence of calcite contactor for calcium addition, and ion-exchange system for magnesium addition, while the conventional lime/carbon dioxide system adds only calcium originating from lime.
- **Calcium and Magnesium are Supplemented at Lower Total Capital and O&M Costs** than the costs for lime addition for the same level of corrosion protection. If



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magnesium addition is practiced as well, the cost gap between the RWM system and the lime/carbon dioxide/magnesium salt exceeds 80 %. In addition, when a magnesium salt is dosed chloride and sulfate are also added to the finished product water. The cost savings come from several distinctive features of the RWM system:

- **Improved Stability of the Product Water** - because the reaction is slow, the attained water quality is stable. Unlike calcite solubility, lime solubility may result in problems in maintaining constant pH and consequently Langlier Saturation Index (LSI) or CCPP.

Design Considerations

Use of Sulfuric Acid for Calcite Solubility. While sulfuric acid provides much more rapid solubility of calcite than carbon dioxide, it releases sulfates in the product water that could cause precipitation of calcium sulfate (gypsum) in the calcite reactors and downstream facilities and piping. This challenge can be addressed by a proper design aimed to avoid reaching the threshold concentrations of calcium and sulfate, above which calcium sulfate precipitation would occur.

The sulfates introduced with the sulfuric acid will cause a slight increase in the finished water salinity concentration. However, their level will not result in a finished water of total sulfate concentration over the US EPA national secondary drinking water limit of 250 mg/L and in most cases will be lower than the sulfate level in other fresh water sources.

Calcite Contactors. Critical issues to consider associated with the use of the calcite contactors are:

- Availability of high-purity limestone;
- Head loss characteristics of the available calcite grains.

High-purity limestone, which is suitable and certified for production of drinking water, is often not as readily commercially available as high-purity lime, which is one of the key reasons why lime has found a wider application for re-mineralization of desalinated water to date. Despite of this potential constraint, high-purity limestone is commercially available in most countries worldwide and the costs and carbon footprint for its production are significantly lower than that of lime.

The headloss characteristics of the calcite grains are important, because if the headloss they create are not too high, the calcite contactors can be operated without re-pumping of the RO desalinated water, and the pressure of this desalinated water (which usually is in a range of 11 to 17 pounds per square inch (psi) (0.8 to 1.2 bars) would be adequate to operate the contactors.



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Using calcite grains of effective size smaller than 0.03 in (0.8 mm) however, may create headloss large-enough to require pumping of desalinated water through the calcite contactors.

Calcium-Magnesium Ion Exchange System. Besides exchanging magnesium with calcium the ion exchange resin will also add small amounts of total dissolved solids and boron to the water. Based on long-term testing, as a result of the ion exchange process the TDS concentration of the finished product water will increase with approximately 0.1 to 0.2 mg/L, which is insignificant as compared to the typical TDS concentration of the desalinated water (100 to 500 mg/L). In addition, the boron content of the product water will increase with 0.0005 to 0.01 mg/L, which increase is negligible.

The amount of calcium and magnesium in the desalinated water exiting the ion exchange system changes over the length of the exchange step of the process. A single ion exchange column will produce water with high content of magnesium and low content of calcium at the beginning of the exchange step and water of low magnesium content and high calcium content at the end of this step. Therefore, the system has to be designed to minimize the magnesium and calcium content fluctuations.

Uniform concentrations of calcium and magnesium could be achieved by either downstream equalization in a downstream product water storage tank or by increasing the number of ion exchange columns and staggering their operations cycles. The optimum number of required ion exchange columns is established according to multiple factors such as the treated water capacity and the water quality range required in the product in terms of calcium and magnesium concentrations.

5. Re-Mineralization System Costs

The capital costs of lime/carbon dioxide systems vary between US\$0.3 million (MM)/million gallons per day (MGD) to US\$0.6 MM/MGD (US\$50 to US\$100 per m³/day) of finished desalinated water. For comparison, the capital cost of calcite re-mineralization systems producing the same finished water quality is between US\$0.1 and US\$0.3 MM/MGD (US\$30 and US\$70 per m³/day) of produced finished water. The capital costs of most other re-mineralization systems are typically in a range of US\$0.3 MM to US\$0.6 MM/MGD (US\$80 to US\$160 per m³/day).

Cost breakdown of Typical Lime/Carbon Dioxide Re-mineralization System

Breakdown of the capital and O&M costs of a typical lime/carbon dioxide re-mineralization system for a hypothetical SWRO desalination plant of fresh water production capacity of 26 MGD (100,000 m³/day) is presented in Table 6.



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Table 6
Capital and O&M Costs of Lime/Carbon Dioxide Re-mineralization System
for 53 MGD (100,000 m³/day) SWRO Plant

Capital Costs	Lime/CO₂ System (1,000 US\$)
Lime Silos & Slurry Preparation System	1,100
Lime Slurry Tanks	400
Lime Saturators	1,500
Limewater Storage Tank	150
Lime Feed System	130
Carbon Dioxide Storage System	940
Carbon Dioxide Evaporators	130
Carbon Dioxide Feed System	120
Lime Clarifier Sludge Handling System	100
Other Auxiliary and Service Facilities	470
Land Costs	230
Engineering and Construction Management	850
Start Up and Commissioning	180
Other Costs	790
Total Capital Costs	7,090
<i>Amortized Capital Costs, US\$/1,000 gallons/ US\$/m³</i>	<i>0.06/0.016</i>

Operation and Maintenance Costs	Lime/CO₂ System (1,000 US\$/yr.)
Labor	90
Lime	500
Carbon Dioxide	195
Polymer for Lime Clarification	105
Polymer for Lime Sludge Dewatering	45
Lime Sludge Disposal	80
Maintenance & Spare Parts	210
Power Use	115
Other O&M Costs	180
Total Annual O&M Costs, 1,000 US\$/yr.	1,520
<i>Annual O&M Costs, US\$/1,000 gallons/ US\$/m³</i>	<i>0.16/0.042</i>



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Total Cost of Water Re-mineralization, US\$/1,000 gallons/ US\$/m³	0.22/0.058
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The lime/carbon dioxide system is designed to achieve alkalinity and hardness of the re-mineralized water of 70 mg/L (as CaCO₃) and pH of 8.0 – 8.3. The capital costs included in this table are amortized using capital recovery factor (CRF) estimated for amortization rate of 5% over a period of 20 years (CRF = 12.462).

The lime/carbon re-mineralization system for this example uses hydrated lime which is delivered periodically to the plant as powdered lime and stored in two (2) 40-ton lime silos. The lime feed system also includes slurry mixing and dosing systems and limewater saturators. The limewater from the saturators is conveyed to a saturated limewater feed tank and from there it is dosed into the desalinated water for re-mineralization.

Sludge from the limewater clarifiers is removed and processed along with the sludge generated by the spent filter water from the pretreatment filters of the desalination plant. Polymer is added to enhance limewater clarification. Carbon dioxide is delivered by 25-ton tankers in liquid form and stored on site in two 50-ton steel storage tanks. This chemical is passed through evaporator and introduced into the lime-conditioned desalinated water to add alkalinity.

The capital costs presented in Table 6 include the expenditures for all key components of the lime/carbon dioxide re-mineralization system along with associated interconnecting piping, fittings, monitoring, instrumentation and control systems and equipment, electrical system, and other service and auxiliary facilities needed for the normal operation of the systems. The dosages and unit costs of the chemicals used for the development of the cost estimate in Table 6 are summarized in Table 7.

Table 7
Chemical Doses and Unit Costs Used in Cost Estimate for
53 MGD (100,000 m³/day) Desalination Plant

Chemical	Dose (as 100 % concentration)	Unit Chemical Costs (US\$/ton)
Lime	52 mg/L	263
Carbon Dioxide	63 mg/L	85
Polymer for Lime Clarifiers	0.6 mg/L	4800/ton
Polymer for Sludge	2 kg/ton of sludge	1000/ton



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Dewatering		
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The total cost of drinking water production associated with re-mineralization (re-mineralization) for protecting human health and the integrity of the distribution system for a hypothetical 53 MGD (100,000 m³/d plant) is estimated at US\$0.22/1,000 gallons (US\$0.058/m³) - see Table 6. This cost is approximately 3% to 6% of the total water production cost for a seawater reverse osmosis desalination plant of this size (US\$3.8 to US\$7.6/1,000 gallons - US\$1.0 m³ to US\$2.0/m³).

Taking under consideration that a conventional facility for feeding magnesium sulfate or magnesium chloride is added to the re-mineralization stage, the additional capital cost for such facility would be approximately US\$500,000 for a 53 MGD (100,000 m³/day) desalination plant. This expenditure will correspond of additional amortized capital cost of US\$0.004/1,000 gallons (US\$0.001/m³).

The additional annual O&M cost for chemical of feed of 10 mg/L Mg²⁺ (by dosing either magnesium sulfate or magnesium chloride) is estimated at US\$630,000/year (US\$0.064/1,000 gallons - US\$0.017/m³). As a result, the total additional cost for supplementing post-treated RO desalinated water with 10 mg/L of magnesium is calculated at US\$0.068/1,000 gallons (US\$0.018/m³). This cost would vary depending on the unit cost of magnesium sulfate or chloride used for supplementing magnesium. Similarly, the expenditures for implementing the conventional lime/carbon dioxide system would vary as a function of the costs of conditioning chemicals – lime and carbon dioxide.

Cost breakdown of Calcite/Ion Exchange Re-mineralization System. This section provides a cost estimate for a hypothetical 53 MGD (100,000 m³/day) RWM system for addition of both calcium and magnesium to the desalinated water. This system was selected to illustrate the low-end cost of commercially available re-mineralization technologies. As indicated in the previous section, the RWM re-mineralization system includes the following key components: acidifying agent feed system; calcite (limestone) contactors; ion exchange reactors; post-mineralization pH adjustment system. In this example, the first three systems are designed to treat 25 % of the desalinated water (desalinated water) produced by the desalination plant and to reduce pH of the desalinated seawater from ~7.5 to 2.2 units in order to be able to increase the calcium concentration of the desalinated water to approximately 170 mg/L as CaCO₃.

Calcite contactors are constructed as enclosed cylindrical steel vessels internally lined with protective coating and have construction and configuration similar to that of vertical pressure filters. The contactors are loaded with food-grade calcite grains of effective particle size of 0.03



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in to 0.05 in (0.8 mm to 1.2 mm) and the reactor vessels have an empty-bed contact time of 10 to 15 minutes. The calcium feed system consists of a total of 4 calcite contactor units, and each system has a calcite bed volume of 10,570 gallons (40 m³), each.

The desalinated water usually has adequate pressure (10 to 17 psi - 0.7 to 1.2 bars) to operate the re-mineralization facilities and it does not need to be re-pumped for processing through the calcite contactors. A separate set of feed pumps is used to transfer the water leaving the calcite filters to the downstream ion exchange reactors.

The ion exchange reactors are high-density polyethylene (HDPE) vessels loaded with magnesium-rich Amberlite IRC747 (Rohm & Haas) resin, which is designed for relatively short contact time of 1.5 minutes (i.e., a maximum flow rate of 40 bed volumes (BV) per hour – BV/hr.) and a total resin volume of 7,930 gallons (30 m³). This design assumes the use of ten (10) ion exchange columns each with 793 gallons (3 m³) of resin each.

A full cycle of each ion exchange column is approximately 3 hrs. The ion exchange columns are recharged with pretreated source water supplied for the desalination plant operations. The desalinated water exiting the ion exchange system contains high concentrations of calcium and magnesium and is blended with the remaining 75 % of the total plant desalinated water flow. Following blending, the pH of this desalinated water will be adjusted from approximately 7.0 to 7.5 up to 8.0 to 8.3 by addition of sodium hydroxide.

Capital and O&M Costs of the RWM System. The capital costs presented in Table 8 includes the expenditures for all key components of the RWM re-mineralization system along with associated interconnecting piping, fittings, monitoring, instrumentation and control systems and equipment, electrical system, and other service and auxiliary facilities needed for the normal operation of the systems. This table also provides a breakdown of the system annual O&M costs.

6. Comparison of Alternative Re-Mineralization Systems

Costs

The lowest cost re-mineralization alternative for permeate produced by brackish water desalination plants is blending it with pre-treated source water. This alternative however, is not viable for SWRO permeate re-mineralization. Usually, calcite contactor based systems have the lowest capital costs and often (depending on the cost of the conditioning chemicals) they also have lower O&M costs.

Table 8



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**Capital and O&M Costs of RWM Re-mineralization System
For 53 MGD (100,000 m³/day) SWRO Plant**

Capital Costs	RWM System (in 1,000 US\$)
Sulfuric Acid Feed System	260
Calcite Contactors	1,200
Interim Transfer Pumps	230
Ion Exchange Reactors	980
Sodium Hydroxide Feed System	120
Pretreated Seawater Feed System for Magnesium Recharge	110
Other Auxiliary and Service Facilities	100
Land Costs	120
Engineering and Construction Management	420
Start Up and Commissioning	100
Licensing Fees and Other Costs	1,400
Total Capital Costs	5,040
<i>Amortized Capital Costs, US\$/1,000 gallons/ US\$/m³</i>	<i>0.04/0.011</i>

Operation and Maintenance Costs	RWM System (in 1,000 US\$/yr.)
Labor	65
Sulfuric Acid	210
Limestone (Calcite)	175
Ion Exchange Resin	25
Sodium Hydroxide	275
Maintenance & Spare Parts	110
Power Use	60
Other O&M Costs	100
Total Annual O&M Costs, 1,000 US\$/yr.	1,020
<i>Annual O&M, US\$/1,000 gallons/ US\$/m³</i>	<i>0.11/0.028</i>
Total Cost of Water Re-mineralization, US\$/1,000 gallons/ US\$/m³	0.15/0.039

Usually, lime/carbon dioxide conditioning is the most costly technology for re-mineralization of desalinated water. Analysis of the cost-breakdowns presented in Tables 6 and 8, for 53 MGD (100,000 m³/day) lime/carbon dioxide and RWM re-mineralization systems, clearly indicates that the capital costs for the RWM system (which is representative of low-cost calcite re-



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mineralization system) are approximately 1.4 times lower than these for construction of conventional lime/carbon dioxide system (US\$5.04 MM vs. US\$7.09 MM).

The key capital cost differences come from the different level of complexity and the different size of the two systems – the lime feed system is a complex multi-structural facility which, includes large lime storage silos, lime saturators, and carbon dioxide storage vessels, and typically it is designed to treat the entire volume of the desalinated water produced by the desalination system.

For comparison, the limestone contactors in general, and the RWM facility in particular are very compact, and consist of relatively small, low-profile tanks which are of standard design and construction. Since calcite filters typically processes only 25 to 50 % of the total flow through the size and footprint of these facilities are significantly smaller.

If a conventional facility for feeding magnesium sulfate or chloride needs to be added to lime/carbon dioxide system in order to produce exactly the same content of calcium and magnesium of the product water processed by the RWM re-mineralization system, the additional capital cost for such facility would be approximately US\$500,000 for a 26 MGD (100,000 m³/day) desalination plant. This expenditure will correspond of additional amortized capital cost of US\$0.004/1,000 gallons (US\$0.001/m³).

The annual O&M costs included in Tables 6 and 8 incorporate all components of these costs – chemicals, equipment, maintenance, labor, etc. As indicated in these tables, the annual O&M costs for the RWM system are approximately 50 % lower than these for the traditional lime/carbon dioxide system - US\$0.11/1,000 gallons vs. US\$0.16/1,000 gallons (US\$0.028/m³ vs. US\$0.042/m³), even though the desalinated water conditioned with the lime/carbon dioxide system does not contain the same amount of magnesium.

If magnesium sulfate is added to meet a target concentration of 10 mg/L, the annual O&M costs of the traditional lime/carbon dioxide system will increase to US\$0.22/1,000 gallons (US\$0.059/m³), which is approximately two (2) times higher than the O&M costs for producing the same water quality with the RWM re-mineralization system (US\$0.11/1,000 gallons/ US\$0.028/m³). The main difference comes from the fact that the RWM system supplements magnesium at very little extra costs associated with the operation of the ion exchange system, which costs are approximately three times lower than the costs for purchasing food grade magnesium sulfate or chloride from a commercial supplier and maintaining the magnesium salt feed system.



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As seen from Tables 6 and 8, the RWM system can re-mineralize desalinated water at approximately 50 % lower cost than the traditional lime/carbon dioxide system – US\$0.15/1,000 gallons vs. US\$0.22/1,000 gallons (US\$0.039/m³ vs. US\$0.058/m³), if the only goal of the re-mineralization process is corrosion protection. However, if the product water is to be supplemented with magnesium in order to enhance its human health protection and agricultural irrigation value, the RWM system can re-mineralize desalinated water at two (2) times lower production cost (i.e., US\$0.15/1,000 gallons vs. US\$0.29/1,000 gallons - US\$0.039/m³ vs. US\$0.076/m³).

The total costs for re-mineralization of desalinated water for re-mineralization systems described herein are a range of US\$0.15/1,000 gallons to 0.30/1,000 gallons (US\$0.04/m³ to US\$0.08/m³) for this size plant and depending on the unit cost of some of the chemicals it could be outside this range. Re-mineralization costs are very sensitive to the unit costs of chemicals added for conditioning of the desalinated water, which in turn can vary widely from one location to another. Therefore, the cost information provided herein will need to be considered as a guideline rather than as a design or budgeting tool.

As indicated previously, cost of chemicals is one of the key expenditures for re-mineralization of desalinated water. Typically, most desalination projects target addition of 60 to 120 mg/L of total alkalinity to the desalinated water. Desalinated water alkalinity can be increased using a number of different commercially available chemicals. However, these chemicals add different amounts of alkalinity for the same amount of delivered chemical and their unit costs differ as well. Table 9 presents a summary of the key chemicals used for alkalinity addition and their typical unit prices.

Analysis of Table 9 indicates that calcite is the most cost-effective compound for adding alkalinity to desalinated water because it has the lowest costs per 1 mg/L of CaCO₃ added. Use of calcite has the advantage of adding both alkalinity and total hardness to the finished water. The combination of hydrated lime and carbon dioxide is the most widely used re-mineralization method today, although the total costs for this combination of conditioning chemicals is typically one-and-a-half to two times higher than that for calcite and sulfuric acid.

Use of hydrated lime instead of quick lime is usually two to three times more costly for the same amount of alkalinity and total hardness increase of the desalinated water. Soda ash and sodium bicarbonate are the most costly chemicals for delivery of target alkalinity to the desalinated water. Because in general the unit costs of soda ash and sodium hydroxide are comparable, and because sodium hydroxide is easier to handle, it is more commonly used than soda ash for final pH adjustment of the finished desalinated water.



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Table 9
Cost of Common Chemicals Used for Increase of Water Alkalinity

Chemical	Alkalinity addition (as CaCO₃) per mg/L of chemical	Unit chemical costs (US\$/ton)	Unit costs in US\$/ton per 1 mg/L of added alkalinity as CaCO₃
Calcite	1.00	30 to 40	30 to 40
Carbon Dioxide	1.14	70 to 90	61 to 78
Sulfuric Acid	1.02	50 to 80	49 to 78
Quicklime	1.78	120-150	67 to 84
Hydrated Lime	1.35	260 to 280	193 to 207
Soda Ash	0.94	540 to 580	574 to 617
Sodium Hydroxide	1.25	700 to 750	560 to 600
Sodium Bicarbonate	0.60	900-950	1,500 to 1,583

Carbon Footprint

A site-by-site comparison of the greenhouse gas (GHG) emissions, also known as carbon footprint, associated with the operation of traditional lime/carbon dioxide generation system (considered the highest carbon footprint system) and calcite contactor system (considered lowest carbon footprint system) for a hypothetical 26 MGD (100,000 m³/day) plant is presented in Table 10. The RWM system was chosen as an example calcite system which also adds magnesium to the water thereby providing a wholesome re-mineralization.

Table 10 includes operational emissions associated with power purchased for plant operations; embodied emissions of chemicals; chemical deliveries; and transportation of waste offsite. In the case of the calcite (RWM) system, the waste that will be generated is the pretreated saline source water after it passes through the ion exchange reactors. However, since this water is further processed in the desalination plant, it does not contribute to the GHG emissions while in the case of the lime/carbon dioxide system the main amount of waste originates from the sludge generated in the lime clarifiers. Analysis of the information presented in Table 10 clearly indicates that the carbon footprint of the calcite systems is 2.6 times smaller than that of a traditional lime/carbon dioxide feed system. This difference is expected even further if the GHG emissions associated with the use of magnesium salts in the lime/carbon dioxide system are taken under consideration.

Table 10
**Carbon Footprints of Alternative Re-mineralization Systems
for 53 MGD (100,000 m³/day) Seawater Desalination Plant**



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Parameter	Unit GHG Emissions	RWM Re-mineralization System		Lime/CO ₂ Re-mineralization System	
		Annual Amount	Annual GHG Emissions (tons CO ₂ /yr.)	Annual Amount	Annual GHG Emissions (tons CO ₂ /yr.)
Sulfuric Acid	0.08 tons CO ₂ /ton	3,650 tons	292	0	0
Calcite (Limestone)	0.10 tons CO ₂ /ton	5,750 tons	575	0	0
Sodium Hydroxide	0.87 tons CO ₂ /ton	622 tons	541	0	0
Power Use	0.4 tons/MWh	584 MWh/yr.	234	1,131 MWh/yr.	453
Transportation of Work Force	0.5 ton/worker	2 workers	1	4 workers	2
Chemical Deliveries	0.01 tons CO ₂ /ton Chem.	9,960	100	4,207	42
Lime	0.90 tons CO ₂ /ton	0	0	1,900	1,710
Carbon Dioxide	1.0 tons CO ₂ /ton	0	0	2,300	2,300
Polymer for Lime Clarifiers	0.30 tons CO ₂ /ton	0	0	2	1
Polymer for Lime Sludge Dewatering	0.10 tons CO ₂ /ton	0	0	1	1
Disposal of Lime Sludge	0.01 tons CO ₂ /ton	0	0	4	1
Total Carbon Footprint (tons CO₂/yr.)	-	-	1,743	-	4,510

Operational Flexibility

Because of its relatively simple configuration and fully automated process control, state-of-the-art calcite contactor systems such as the DrinTec and RWM technologies have high reliability



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and performance consistency in terms of both quality and quantity of the produced finished water as well as production costs. The mineralized water quality can be controlled by either: (1) changing the portion of the desalinated water processed through the calcite contactors; or (2) by adjusting the pH of the feed water to the calcite contactors. Increase in feed flow or decrease of feed water pH will increase the content of calcium (and magnesium for the RWM and dolomite systems) in the finished water. For comparison, traditional lime/carbon dioxide re-mineralization systems are somewhat more cumbersome to operate and control because of their higher complexity.