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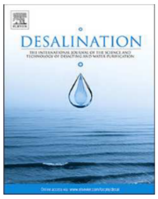

Remineralization of desalinated water: Methods and environmental impact

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ABSTRACT

Desalinated water is not suitable for direct use as it is prone to corrosion and has adverse effects on human health and the environment. Desalinated water is slightly acidic, lacks minerals and cannot be used un-buffered, thus making remineralization an important component downstream of desalination. We systematically review re-mineralization requirements and regulations with respect to corrosion control, human health and agriculture needs. This includes not only concentrations of specific ions, but also relative ratios. We compare and contrast existing remineralization methods with emerging, energy-efficient methods that require less chemicals. The impact of the lack of certain minerals such as magnesium, calcium and sulfate, on health and environment are evaluated in order to guide regulatory bodies towards maintaining safe standards. Emerging methods include harvesting minerals from seawater or brine through the combination of nanofiltration membranes with others (CIX, UF, Diananofiltration) and using them to re-mineralize the product stream. This reduces the need for chemicals from an external source and thus lowers the environmental impact. This review is to be used as a tool for guiding readers in proper remineralization choices depending on their application.

1. Introduction

Rapid population growth and increasing urbanization since the beginning of the industrial era in the 19th century have led to an ever-growing demand for freshwater for drinking, irrigation and industrial uses. Fresh water overconsumption has led to the lowering of the groundwater table and in some areas increase in salinity and sea water intrusion. However, there are enormous quantities of seawater with Total Dissolved Solids (TDS) of 35,000 up to 50,000 ppm and brackish water with TDS of 500 to 35,000 ppm that cannot be consumed without desalination treatment because of their high salinity. The United States Environmental Protection Agency defines an upper TDS limit of 500 ppm for drinking water [1]. Desalination processes are employed to remove salts and minerals from water sources to comply with this 500 ppm limit [2,3].

In the last 50 years, advances in desalination technologies have led to the widespread installation of large-scale facilities worldwide. Desalination processes can be divided into two categories: thermal desalination processes and membrane desalination processes. Thermal desalination processes such as multi-stage flash and multi-effect distillation are phase change processes that rely on evaporation and condensation. These processes are associated with high energy consumption compared to membrane processes, such as reverse osmosis (RO), which do not typically involve phase change. Pressure-driven membrane processes such as RO and nanofiltration (NF) rely on semi-permeable membranes through which selective passage of water occurs under an applied transmembrane pressure greater than the osmotic pressure of the solution being separated [4–6]. The lower energy cost of RO processes has allowed it to surpass other desalination technologies in terms of global installation capacity. However, thermal desalination techniques are still widely used especially in the Middle East. Improvements in materials and configurations for both types of processes have lowered the cost of desalinated water over the years. Additionally, advances on the renewable energy front are also driving desalination systems towards sustainable solutions.

Regardless of the type of process employed, all desalination plants involve the following key components (Fig. 1): feed intake, pretreatment, desalination and post-treatment. While there is emphasis on pretreatment and desalination technologies, the various aspects of post-treatment are sometimes neglected. Post-treatment involves preparing the water from the desalination process for its end use. It may include disinfection, corrosion control as well as degasification, depending on the gases present in the desalination product [7]. Re-mineralizing desalinated water to control its pH, alkalinity and hardness is considered an important step in post-treatment.

Although the composition of desalinated water varies depending on plant design and technique used, removal of salts in desalinated water results in a product that is very low, often too low, in minerals, has a

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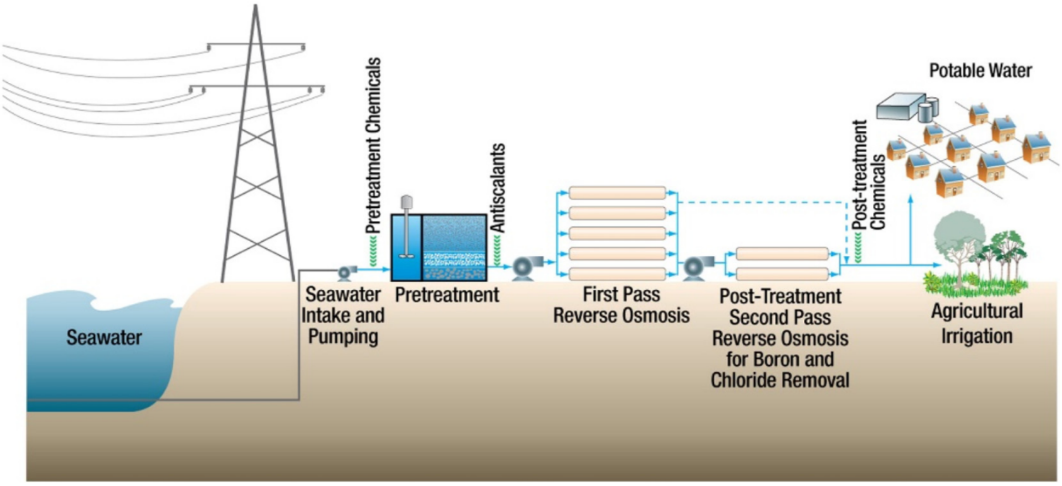

Fig. 1. Seawater desalination using Reverse Osmosis for both potable water and agriculture irrigation. Reproduced with permission [8].

slightly acidic pH, and very low buffering capacity. Before delivery to the water network, the water needs to go through a series of post-treatment steps to prevent and/or control various problems such as:

- Corrosion, which has been known since the development of water networks [9]. Various empirical parameters have been defined to characterize corrosion potential, for example Chloride to Sulfate Mass Ratio (CSMR) or Langelier Saturation Index (LSI).
- Negative effects on human health potentially leading to diseases. The main minerals considered are calcium and magnesium; however fluoride, iodide and trace elements also impact human health.
- Irrigation with lack of essential nutrients for crops or soil compatibility such as sodium, potassium, calcium, magnesium and sulfate, or presence of toxic trace elements such as boron.

Birnhack and Lahav [10] reviewed remineralization post-treatment methods already industrially used, such as calcite and direct chemical dosage addition. They also introduced two membrane processes for post-treatment. Wang et al. [11] reviewed parameters for seawater reverse osmosis product water where they also addressed remineralization; however they focused solely on corrosion control of the water distribution network. There remains a need to assess and review appropriate parameters and mineral targets for the remineralization of desalinated water. In this review, we analyze quantities and relative ratios for minerals to be added during post-treatment considering three main aspects: corrosion control, human health and agricultural needs. We also evaluate traditional and emerging techniques for remineralization of desalinated water in line with national and international regulations.

2. Post-treatment re-mineralization for corrosion and scale control

The composition of desalinated water is similar to that of soft groundwater or rainwater. Soft water is water containing low concentrations of ions, specifically calcium and magnesium. Rainwater, when abundant and going through rocks from which minerals do not leach like granite or sandstone, remains very soft and can lead to corrosion, as was the case in Sweden [12]. In 2016, USGS tested 27,000 groundwater private well sites in the USA. One third of the sites were evaluated as potentially corrosive [13]. This means that the corrosion problem has existed for a long time. Solutions proposed to limit corrosivity of such water may be extended to desalinated water.

From desalination plant to household tap, desalinated water is exposed to various materials. In their review, Barton et al. [14] assess the types of materials and approximate installation periods for water distribution pipe materials in the UK. Materials reported are: cast iron, spun iron, asbestos cement, ductile iron, steel, polyvinyl chloride and most recently introduced is polyethylene. In 2006, the World Health Organization reported on health aspects of plumbing that included an exhaustive list of materials considered safe to use [15]. There are two main categories: metallic, such as iron, galvanized steel, copper, lead or lead containing materials (typically in older systems), non-metallic, such as polymeric materials (PE, PVC…), and concrete. Metallic materials are susceptible to corrosion which releases heavy metals into the water [16–25] such as copper, lead, iron, zinc; concrete or asbestos-reinforced concrete are susceptible to leaching of minerals when in contact with very soft water such as desalinated water.

In Kuwait, Al-Mudhaf et al. [22] studied the corrosion of metallic materials in a desalinated.

seawater water network. They gathered outdoor and indoor samples from 99 locations representing > 95% of Kuwait's residential areas. The outdoor samples integrate the heavy metals produced from corrosion of metallic materials from its production and transportation in the drinking water network. Indoor private household samples integrate the corrosion effects on the housing plumbing materials. This study provides extensive analysis of the presence of heavy metals in the distribution network and the increase in those metals in household plumbing clearly indicating that some corrosion is occurring all along the drinking water path. However, information on crucial aspects such as composition of the desalinated seawater at the production plant and the use or lack of a post-treatment step to reach corrosion indicators targets is missing. Mahmoud et al. [26] in UAE studied desalinated seawater from 30 households in an Abu Dhabi district. For each house, they sampled water from the main water pipe and indoor location: kitchen faucet, bathroom faucet and household water tank. Their data showed that the water main contained more heavy metals than the in-house samples, but that the concentration of lead was above the regulation of 10 μg/L in all the locations, lying within a range of 11 to 81.8 μg/L.

In order to gain a deeper understanding of this issue, we consider the parameters used to measure and control water corrosivity. The two most commonly used parameters are the LSI and the CSMR which we describe in the two following sections. An example of different water qualities from feed water to post-treated requirements is reported by Bajahlan et al. and Khawaji et al. [27,28] in Table 1 from the reverse osmosis desalination plant developed in Yanbu (Saudi Arabia) by the Red Sea.

Data indicates that the permeate is acidic and low in minerals apart from sodium and chloride. Out of the parameters considered, LSI is the

Table 1
Comparison between Seawater, Desalinated Water and Post-treatment water provided by Bajahlan et al. and Khawaji et al. [27,28].

	Seawater	Permeate	Post-treated	Saudi Arabian regulation	
Parameter				Min	Max
TDS (mg/l)	41,300-46,400	< 500	30	100	500
pH	8.1–8.3	5	8–8.5	6.5	8.5
Cl^-(mg/l)	21,600–23,500	< 250	1		250
$SO_4{}^{2-}$(mg/l)	3000	15			250
$HCO_3{}^-$(mg/l)		3			
Na^+(mg/l)	11,700–12,500	135			20–30
K^+(mg/l)	425–650	6			10
Ca^{2+}(mg/l)	490–560	3		30	
Mg^{2+}(mg/l)	1500–1600	6		5	
Total alkalinity as $CaCO_3$, ppm	120–130			40	
Bicarbonate alkalinity as $CaCO_3$, ppm	85–95		38		
Langelier saturation index			+0.1 to +0.3		

most widely used at the industrial level for post-treated desalinated water.

2.1. Corrosivity to steel

Corrosivity of water depends on many parameters of the constituent water stream including pH, alkalinity, hardness, dissolved inorganic carbon, sulfate, chloride and TDS [29]. To lower water corrosivity, pH is adjusted to values above 7 and generally between 8 and 8.5 [10,30] as the final step of post-treatment, most commonly through addition of sodium hydroxide [10]. Alkalinity is defined as the capacity of water to accept protons [31]. It is the parameter that is adjusted to give buffering to water and is measured using the Eq. (1).It uses the carbonate system with two pH at 6.35 and 10.33 [32]. Therefore, it is not only CO_2 that adjusts alkalinity; but adding base helps brings the pH to the appropriate range.

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

As early as 1958, Larson et al. [33] reported that bicarbonate is a mild corrosion inhibitor whereas chloride and sulfate accelerate steel corrosion. They defined the Larson Ratio (LR) presented in Eq. (2):

$$\mathrm{LR} = \frac{([\mathrm{SO}_4^{2-}] + [\mathrm{Cl}^-]}{[\mathrm{HCO}_3^-]} \tag{2}$$

Then depending on the LR values, a corrosion index can be evaluated.

- If LR $<$ 0.2 no probability of corrosion
- between 0.2 and 0.4 low probability of corrosion
- Between 0.4 and 0.5 slight probability of corrosion
- Between 0.5 and 1 moderate probability of corrosion
- LR $\geq$ 1 Clear risk of corrosion.

Shi et al. [34] studied the effect of both chloride and sulfate and demonstrated that for the same LR, corrosion increased with chloride content. Sun et al. [35] demonstrated that after sulfate concentration increases, corrosion scales are destabilized and heavy metals are released in water. This leads to a sharp increase in heavy metal release followed by decrease over time. This necessitates an integrated approach that allows simultaneous control of the constituents of desalinated water so as to minimize the effects of corrosion.

The most commonly used parameter is still the LSI. This parameter was one of the first to be used since it was defined in 1936 by Langelier [36]. The concept is that a steel surface will be corroded if it is not protected by a calcium carbonate scale. LSI formula is reported in Eq. (3).

$$\mathrm{LSI} = \mathrm{pH} - \mathrm{pH}_{\mathrm{sat}} \tag{3}$$

pH_{sat} is the saturation pH defined as A + B – log [Ca^{2+}] – log total alkalinitywith A and B being calculating from TDS and Temperature respectively [37].

If TDS concentration $<$ 500 mg/l, Gebbie [38] proposed a simplified Eq. (4)

$$pH_{sat} = 11.5 - log\,[Ca^{2+}] - \log total\ alkalinity \tag{4}$$

- Water with LSI $>$ 0 is supersaturated and tends to precipitate a scale layer of $CaC0_3$
- Water with LSI = 0 is saturated (in equilibrium) with $CaC0_3$; a scale layer of $CaC0_3$ is neither precipitated nor dissolved.
- Water with LSI $<$ 0 is under saturated, tends to dissolve solid $CaC0_3$

Desalination plants aim to achieve a positive LSI but close to 0 as in the case of Yanbu [27]. If LSI is too high, there will be abundant calcium carbonate scaling which will ultimately plug the pipes.

In 1976, Merrill and Sanks [39] introduced a new parameter called CCPP for Calcium Carbonate Precipitation Potential. Compared to LSI, which is a more qualitative measure, CCPP is recognized as being a more quantitative estimate of how much calcium carbonate can precipitate from an oversaturated solution [10,30,40]. Rossum and Merill [41] proposed in 1983 a calculation method for this index. Recently, Mehl and Johannsen [42] developed software methods to calculate the CCPP index using OpenModelica. De Moel et al. [43] also assessed different calculation methods for calcium carbonate saturation in drinking water for norms. Subsequently, Trussel et al. [44] defined temperature correction that can be used for both LSI and CCPP.

2.2. Corrosion of lead and copper containing networks

In 2008, Rabin [45] published a comprehensive study on the lead sources in drinking water, their evolution with time and their impact on health. Most water sources do not contain lead. Lead in drinking water usually comes from plumbing materials. Historically, lead has been used as a plumbing material and was only banned progressively as its toxic effect was demonstrated. As an example, in the United States, the Environmental Protection Agency [46] report the different dates at which regulatory actions were taken to reduce the lead content of drinking water. The first, in 1986, banned lead pipes and required the use of lead-free materials. However, “lead-free” pipes and pipe fittings could still contain up to 8.0% lead in copper or brass alloys. This limit was reduced to 0.25% by the Reduction of Lead in Drinking Water Act of 2011 [46]. This new limit was only implemented in USA in 2014. Lei et al. [47] studied the composition of 21 new premise plumbing materials including stainless steel, copper, polyvinyl chloride and brass by different methods such as leach test, surface characterization using Scanning Electron Microscopy/Energy Dispersive X-Ray Analysis EDX and Inductively Coupled Plasma/Optical Emission Spectroscopy on fully digested samples. They found that brass-based plumbing materials released between 2.5% and 6.8% lead as weight percentage of the plumbing material body.

Corrosion of pipes containing lead and copper occurs when a water distribution network contains different metals that allow galvanic corrosion, such as in old housing that still contains lead pipes or with copper pipes that have been soldered with tin containing lead but also with low-lead concentration galvanized steel [25]. A major concern of galvanic corrosion is that it can release heavy metals (lead, copper, zinc) causing health issues. In 1985, Gregory [48] and Gregory and Gardiner identified that the water composition and particularly the ratio of the concentration of chloride ions to sulfate ions or CSMR was correlated to higher corrosion of lead and copper. The CSMR formula is presented in Eq. (5):

$$\frac{[\mathrm{Cl}^-]}{[\mathrm{SO}_4^{2-}]} \tag{5}$$

The rationale for this is that at 20 °C $PbCl_2$ has a solubility in water > 200 times greater than that of lead sulfate [49] which means that lead sulfate can form a deposit at the surface of the metal and protect it from further corrosion, whereas lead chloride will be solubilized in the water stream. Nguyen at al [50]. added the influence of alkalinity in the galvanic lead corrosion and they defined a corrosion tree, correlating CSMR range to warranted level of concern:

- CSMR > 0.2: no concern,
- 0.2 < CMSR < 0.5 or CMSR > 0.5 and alkalinity > 50 mg/l as calcium carbonate: slightly elevated concern,
- CMSR > 0.5 and alkalinity < 50 mg/l as calcium carbonate: serious concern.

2.3. Desalinated water network corrosion examples

We found that literature provides only a few examples of actual industrial water network corrosion examples and even less involving desalinated water. This does not mean there are no incidents similar to the one in Flint, USA [51] but they are usually not reported. Marangou et al. [52] described the effects of desalinated product water aggressivity on the water distribution network from the water produced by the first desalination plant in Cyprus. Water in the far end of the network was yellowish brown from high Iron content. To fix the issue, pH was adjusted by carbon dioxide and lime dosage. With pH above 8.5 the LSI increased to 0–0.5 range and iron content of water decreased.

Apart from industrial reports, few studies address the blending of desalinated water in a water distribution network are reported. Blute et al. [53] realized a six-month pilot study on desalinated water on distribution system materials including brass meters and lead solder on copper pipes. After defining desalinated water conditioning to obtain positive LSI and CCPP, they conclude that municipality water was more corrosive than conditioned desalinated water. Their conditioning consisted of an alkalinity of 45 mg/l as calcium carbonate, a hardness of 40 mg/l as calcium carbonate and a pH of 8.5. Although they studied the possibility of lead corrosion in a lead copper system and the concentrations of sulfate and chloride for conditioned water was 3 mg/l and 145 mg/l respectively. This led to the worst-case scenario for CSMR and the concentration of lead in their system was 2.0 μg/l which is below the regulated level.

This could be attributed to the fact that their system was under permanent flow and that no galvanic cell could be established. However, it doesn't represent what happens in houses.

2.4. Re-mineralization needed for corrosion control

To prevent future corrosion-related incidents in water distribution networks, measures need to be taken to adjust the water chemical composition through post-treatment. These should consider the following elements in the case of desalinated water:

- carbon dioxide for buffering,
- [Calcium for steel, lead, copper and zinc corrosion control,
- Low sulfate concentration and chloride concentration for steel corrosion control,
- Sulfate concentration at least twice as high as that of chloride for lead and copper corrosion control.

The last two points are somewhat contradictory and an appropriate solution requires a trade-off between low chloride and some sulfate.

3. Desalinated water for drinking

More countries are relying on desalination for obtaining their drinking water. However, demineralized water obtained from desalination is very low in minerals and can affect not only health but taste also. In this section, we focus on water mineral concentration and its effect on parameters such as taste, contribution to daily intake such as calcium, magnesium, iodide, fluoride.

3.1. Desalinated water sensory quality

The first study related to the sensory quality of re-mineralized desalinated water was carried out in 1983 by Gabrielli and Gerofi [54]. More recently, Vingerhoeds et al. [55] compared the sensory quality of different drinking water as perceived by a panel of 119 people. They tested natural tap water with different TDS, permeate from RO and permeate remineralized with added calcium and/or magnesium. The result of their study indicates that the freshness score was the lowest with TDS < 100(mg/l) with optimal score between 200 and 400 mg/l. Devesa and Dietrich [56] found similar results in a later study. They indicate that a variation of TDS of > 150 mg/l is needed for people to differentiate between different types of water.

Several studies focusing on the taste aspect of water have been published in the past [57–59]. Marcussen et al. [60] reviewed the composition and flavor preferences of bottled water. They linked water composition to organoleptic properties. Calcium carbonate is sweet whereas depending on the concentration, calcium chloride can be described as sour, irritating or astringent. The taste of water mostly comes from cations (sodium, calcium, magnesium) with anions serving to modify its intensity (chloride, nitrate, sulfate). These studies indicate that personal preference also plays a significant role in the choice of drinking water and hence post-treatment can be carried out to alter the taste of product water from desalination plants. Hence taste also needs to be considered when choosing the appropriate method and extent of remineralization for desalinated water.

3.2. Effect of desalinated water on health

World Health Organization(WHO) has regularly published International Standards for Drinking Water and Guidelines for Drinking Water Quality since 1958 [61–63]. However, since desalinated water is increasingly being used because of freshwater scarcity in many parts of the world, WHO started consultations as early as 1985 [64] to define guidelines for desalinated water [65]. WHO reports highlight that some essential minerals removed during desalination should be added before distribution. However, most of those reports do not give minimum values for essential minerals like magnesium, only maximum threshold.

For calcium and magnesium, a 2009 WHO report [66] considered health aspects of the calcium and magnesium content in drinking water. Even the latest WHO 2017 Guidelines for Drinking Water Quality [62] does not contain minimum threshold for calcium and magnesium concentrations.

Many studies raise concerns about drinking desalinated water [67–76] without remineralization. As indicated in Section 2, calcium is always added in the post-treatment of desalinated water as is sodium hydroxide for pH adjustment. We will focus in this section on minerals that are usually not included such as magnesium, iodide and fluoride.

3.2.1. Effect of low magnesium intake on health

Magnesium is a co-factor of > 300 enzyme systems. As a result, magnesium deficiency has numerous adverse health effects. The estimated average requirement for magnesium in adults is 260 mg for female and 340 mg for men [66]. Sources of magnesium are both food and drinking water. However, if drinking water is low in magnesium and is used for cooking, it will also remove minerals from cooked food and lower the daily magnesium intake [68,74]. It has been observed that mineral content of foods has decreased by 5–40% over the past 50 to 70 years [77,78]. WHO estimates that > 40% of the US population does not reach the targets for adequate Intake values for calcium and magnesium [66].

Rosanoff et al. [79,80] not only reported a suboptimal magnesium status in the United States but also pointed out a correlation of the evolution of calcium to magnesium ratio to the prevalence of diabetes, from 1977 to 2008. This high calcium to magnesium ratio is also reported in Israel tap water [72] that contains desalinated water. Rosanoff et al. observed that increasing magnesium concentration in drinking water from 3.2 mg/l to 17 mg/l decreases the odd ratio of death by heart infarction by 37%.

The difficulty with magnesium is that serum magnesium does not always reflect total stored magnesium, Razzaque [81] underlined that for magnesium deficiency evaluation, magnesium loading test is more accurate. Nevertheless, Koren et al. [82] used the evolution of serum magnesium concentrations to demonstrate the effect of introducing desalinated water in the drinking network. The test was conducted on a population of 66,000 people and a 24% increase in the proportion of people suffering from hypomagnesemia was observed. In 2016, Rosen et al. [72] realized a thorough study on drinking water quality in Israel by measuring various minerals in 26 locations and compared their data to a 2008 campaign before the introduction of desalinated water in the network. About half of the 2016 locations presented magnesium deficiencies whereas none were found in 2008.

Shlezinger et al. [75,83,84] published several articles related to health and consumption of desalinated water. In one article [83], magnesium content was reported to be 5.1 ± 2.2 mg/l in desalinated water and 25.1 ± 3.4 mg/l in non-desalinated water. Serum magnesium levels of 1.94 ± 0.24 mg/dl and 2.08 ± 0.27 mg/dl have been reported in desalinated and non-desalinated water regions respectively [84]. Reduced magnesium intake is linked to increase ischemic heart disease hazard ratio. Spungen et al. [85] reported that both consumption of calcium and magnesium were lower in Israeli communities supplied with desalinated water.

Independently of the drinking water source, magnesium deficiency is getting more attention. Since magnesium is used in 80% of human body metabolic functions, it is linked to several health pathologies as Al Alawi et al. [86] have summarized. Veronese et al. [87] also published in 2020 evaluated past literature concerning magnesium and health outcomes. In 2018, Dinicolantonio et al. [88] published a comprehensive study on magnesium deficiency.

Magnesium deficiency can affect several organs indicated as shown in Table 2.

Additionally, magnesium deficiency has also been linked to certain types of cancer [69,80].

3.2.2. Desalinated water and low iodine intake

Seawater is rich in iodide and bromide, however these elements are removed during desalination. Deficiencies in iodine leads to ‘severe adverse effects on neurological development’ [103].

Table 2

Effect of magnesium deficiency on various organs of the human body.

Organ	Effect	Reference
Heart	• Increased risk of mortality in patient with heart failure • Increased risk of coronary artery disease	[75,89–94]
Vascular system	• Increased risk of hypertension • Increased risk of atherosclerosis	[89,95–98]
Pancreas	• Lower high density lipoprotein (‘good cholesterol’) • Increased triglycerides and total cholesterol • Increased risk of diabetes mellitus	[87,89,94,99]
Brain	• Neurological disorders	[100,101]
Bones	• Increased risk of osteoporosis • Decrease in vitamin D levels	[99,102]

Several articles raise the question of iodine deficiency due to the use of desalinated water for drinking [70]. Iodide deficiency has been observed in Israel after introduction of desalinated water [104]. However, the addition of iodide as post-treatment of desalinated water is not advisable as it can, similar to bromide, lead to toxic disinfection by-products [105–107]. It is rather suggested that iodized table salt be used for cooking [96,108] but this information has to be appropriately conveyed to the public [109].

3.2.3. Desalinated water and low fluorine intake

Although fluoride is present in groundwater, brackish and seawater, its concentration is usually too low in desalinated water to be detected [110,111]. Lack of fluoride has incidence on both teeth decay and bones. When low levels of fluoride are found in drinking water, authorities either request to add fluoride in the drinking water or provide fluoride tablets to children [110]. WHO [65] in its 2011 ‘Safe Drinking-water from Desalination’ gave a recommendation for a minimum fluoride concentration of 0.2 mg/l.

3.3. Re-mineralization needed for Human Health

Minerals required for human health are lacking in desalinated water and there is a clear need for the addition of calcium and magnesium in the post-treatment process. The ratio between calcium and magnesium should be in the two to three range [78–80]. For iodide, addition to desalinated water could lead to the formation of toxic disinfection by-products and it is preferable to get it from iodized table salt. Addition of fluoride to desalinated water is recommended but it is still a cause for debate in the scientific community. Today, some districts incorporate it while others do not because of the possibility of overexposure leading to dental fluorosis.

4. Desalinated water for agriculture

With increasing global population adding stress to the water-energy-food nexus, rising irrigation needs for agriculture translates into greater demand for water, as water is required to produce more food to both improve water agricultural efficiency [113] and to utilize all possible sources of water.

The Food and Agriculture Organization [114] proposed seawater [8,115–127], brackish water [119,124,128–133], wastewater [119,127,134–137] and oilfield/gasfield-produced brine [138–140] as potential sources of water for desalination for agricultural applications.

These different sources of water have varying characteristics and each of these requires different treatments, which is not included in the scope of this review. However, they are all exploited to produce water which is compatible with agricultural use. Monterrey-Viña et al. [116] summarized in Fig. 2 the elements needed for defining the requirements for irrigation. Although they considered mainly seawater reverse osmosis, the same principles are present in any desalination process. Desalination removes minerals from feed water and produce a permeate that can be used for irrigation. Depending on the techniques used and the composition of the feed, the composition of the irrigation water can vary greatly. Table 3 present some desalinated seawater water compositions coming from different articles [116,125,141]. In the case of irrigation, water quality not only affects the crops' yield but also soil structure quality. In the following sections, we explore the parameters that can affect water quality from an irrigation water composition point of view. Some of the parameters we consider are:

- Sodium adsorption ratio (SAR),
- Essential nutrients such as calcium, magnesium and sulfate
- Calcium to magnesium Ratio,
- Chloride and sodium phytotoxicity,
- Boron phytotoxicity.

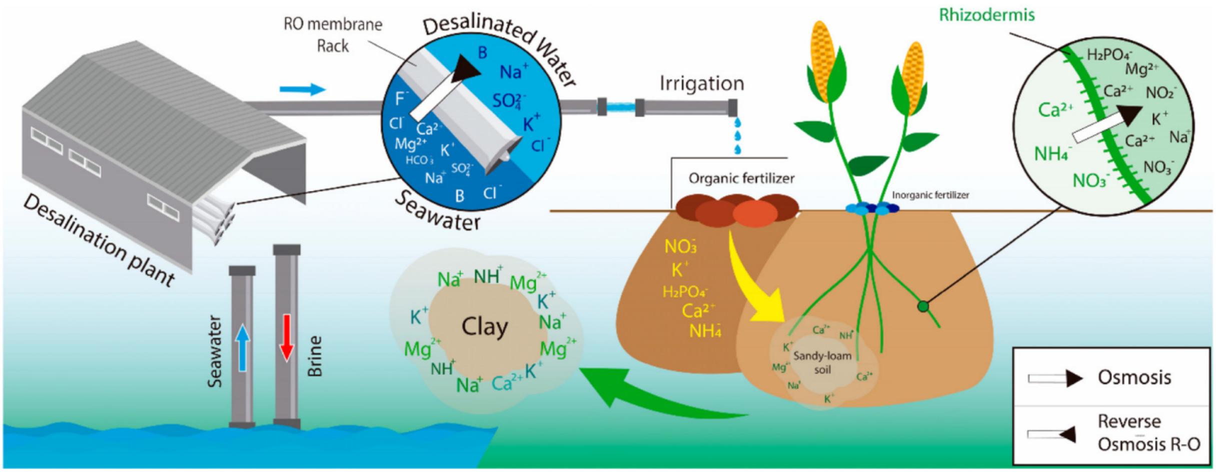

Fig. 2. Graphical description of the key elements' absorption supplied for a desalinated seawater. Reproduced from open access reference [116].

4.1. Sodium adsorption ratio (SAR)

The two traditionally used parameters for evaluating soil structural stability irrigated with water were first defined in 1955 by Quirk and Schofield [142]. These parameters are sodium absorption ratio (SAR), defined in Eq. (6), and the exchangeable sodium percentage (ESP), defined in Eq. (7).

$$\mathrm{SAR} = \frac{[\mathrm{Na}^{+}]}{\sqrt{\frac{[\mathrm{Mg}^{2+}]+[\mathrm{Ca}^{2+}]}{2}}} \tag{6}$$

$$\mathrm{ESP} = \frac{[\mathrm{Na}^{+}]}{\mathrm{CEC}} \times 100\% \tag{7}$$

where CEC is the cation exchange capacity representing the sum of the cations sodium, potassium, calcium and magnesium and can be measured directly. The combined effect of both parameters allows to define a risk factor that indicates potential degradation of both soil and crop yields.

In their 1985 report on Water Quality for Agriculture [143], Ayers and Wescot thoroughly studied the phenomenon modeled by these parameters. When water salinity increases, it affects both soil and crops. For crops, water enters the roots by osmosis whose strength depends on the salinity difference between sap and water in the soil; the higher the salinity in soil or water, the less plants will thrive. On the soil, the effect of water salinity depends on ions charge. Monovalent ions have the tendency of dispersing clays whereas divalent ions flocculate them. High monovalent ions concentration affects the water infiltration rate and progressively replace divalent ions on the clays degrading the soil quality.

As sodium water concentration is generally much higher than potassium, the effect of the latter is generally not considered as can be seen in the SAR formula. However, in some cases, SAR does not accurately predict the effect of water. Then, Marchuk and Rengasamy [144] extensively studied the clay cation bonds for lithium, sodium, potassium, magnesium, calcium, strontium and barium and defined new parameters.

The cation ratio of soil structural stability CROSS [145–147] as defined in Eq. (8) replaces SAR and is more accurate at low sodium concentrations, as was observed in some Australian waters [147].

$$\mathrm{CROSS} = \frac{[\mathrm{Na}^{+}] + 0.556[\mathrm{K}^{+}]}{\sqrt{\frac{0.6[\mathrm{Mg}^{2+}]+[\mathrm{Ca}^{2+}]}{2}}} \tag{8}$$

The exchangeable dispersive percentage (EDP) as defined in Eq. (9) replaces ESP and considers the effects of potassium and magnesium for the possibility to exchange with calcium on clays. The importance of this new definition can be seen in cases where magnesium is actually more concentrated than calcium as reported by Qadir et al. [148] and Abdollahpour et al. [149] but also where potassium is more concentrated than sodium [150].

$$\mathrm{EDP} = \frac{[\mathrm{Na}^{+}] + 0.556[\mathrm{K}^{+}] + 0.037[\mathrm{Mg}^{2+}]}{\mathrm{CEC}} \mathrm{x100} \tag{9}$$

To prevent these soil impairments and effects in crop productivity, when irrigation water salt concentration is too high, additional water is used to leach the salts and drain them. So the use of desalinated water with low salt concentration in that context allows water savings [115] as leaching is not required. However, if the salt concentration in irrigation water is too low, a lack of nutrients for the plants could result, as discussed below.

4.2. Essential nutrients such as calcium, magnesium and sulfate

Food and Agriculture Organization [114] recognizes that some mineral elements could be missing for plants to grow and give the optimal yield. These deficiencies are compensated by fertilization (nitrogen, phosphorus and potassium). However, in the case of untreated desalinated water, some other nutrients are also missing. Table 3 shows that in the case of Ashkelon desalination plant in Israel, no magnesium was added in post-treatment. For Torrevieja, Escombreras and Vadelentisco in Spain, no sulfate was added. Table 3 shows that at a global level most desalination plants do not provide at least one of the regulated mineral requirement values of the Israel Authorities concerning calcium, magnesium or sulfate.

Although calcium, magnesium and sulfate are secondary nutrients, their deficiency will not only affect yields but it can also degrade the quality of the crops for food. Raveh and Ben Gal [151] reported the magnesium content of different crops related to Food and Drugs Administration standards after the use of desalinated Seawater with very low salinity. This content is low and is in line with trends observed in USA.

Guo et al. [152] underlined in 2016 that magnesium deficiency in plants is becoming an increasing problem. Nayar and Lienhard [153] indicated that in the case of greenhouse, since minerals are not brought by the soil, the requirements are different from field irrigation water and the desired nutrient water composition are 23–115 mg/l for sodium, 120–200 mg/l for calcium and 40–80 mg/l for magnesium^{+}. Martinez-Alvarez et al. [115] report that the horticultural crops requirements are 80–120 mg/l for calcium and 24–36 mg/l for magnesium and 100–150 mg/l for sulfate.

Bar-Tal et al. [154] defined optimum concentration values for high fruit yield for Tomato irrigated with desalinated water as

Table 3
Examples of desalinated seawater irrigation water composition from different location, with recommendations for comparison from Israel.

		Spain					Israel
Parameter	(1)	Torrevieja(2)	Aguilas(2)	Escombreras(2)	Vadelentisco(2)	Gran Canaria(3)	Ashkelon(4)
EC (dS/m)	< 0.3	0.46	0.48 ± 0.08	0.54	0.54 ± 0.15	0.7 ± 0.2	0.2–0.3
$[Cl^-]$ (mg/l)	< 20	147	140 ± 30	140	182 ± 47	209 ± 69	15–20
$[Na^+]$ (mg/l)	< 20	86	76 ± 14	88	115 ± 18	126 ± 39	9–10
$[Ca^{2+}]$ (mg/l)	32–48	29	14.9 ± 2.4	20	15.6 ± 1.8	4.0 ± 2.7	40–46
$[Mg^{2+}]$ (mg/l)	12–18	4.3	1.4 ± 0.5	2.4	2.1 ± 1.1	6.0 ± 4.1	0
$[SO_4{}^{2-}]$ (mg/l)	> 30	6.6	–	4	–	4.1 ± 2.9	20–25
[B] (mg/l)	0.2–0.3	0.56	0.85 ± 0.16	0.9	0.92 ± 0.14	1.2 ± 0.3	0.2–0.3
Alkalinity (mg/l as $CaCO_3$)	> 80	–	–	52	–	13.5 ± 3.1	48–52
LSI		–	−0.06 ± 0.17	−0.10	−0.18 ± 0.18	−4.1 ± 0.6	
CCPP (mg/l as $CaCO_3$)	3–10						0.7–1.0
SAR		4	5.3 ± 1.2	5	5.6 ± 1.5	10.5 ± 2.0	
pH	< 8.5	8.3	8.6 ± 0.2	8.2	8.7 ± 0.2	5.8 ± 0.2	8.0–8.2

(1) Recommendation from Israel Authority for domestic and agricultural usage [141].
(2) Data from [125].
(3) Data from [116].
(4) Data from [141].

1.5–2.5 mmol/l for calcium combined with 0.25 mmol/l for magnesium.

4.3. *Calcium to magnesium ratio*

Calcium to magnesium ratio in water for irrigation purposes is not as important as it is for health, but Qadir et Al. [148] reported in their review that “a ratio of magnesium-to-calcium > 1 in irrigation waters and an exchangeable magnesium percentage N 25% in soils are considered high enough to result in soil degradation and impact crop yields negatively”. Therefore, irrigation water should contain more calcium than magnesium.

4.4. *Cl^- and Na^+ phytotoxicity*

Sodium and chloride are the most concentrated ions as reported in Table 3 , after desalination, depending on the process used, they can still present at concentrations considered too high for agriculture. Martinez-Alvarez et al. [122] report parameters for water quality in agriculture and the toxicity risk level for both sodium and chloride is low when the sodium concentration is lower than 70 mg/l and the chloride concentration is lower than140 mg/l and high when the sodium concentration is higher than 210 mg/l and the chloride concentration is higher than 350 mg/lBoron and phytotoxicity.

Sensitivity of crops to boron varies greatly as reported in Table 4 [122]. Most crops are sensitive to boron concentrations > 1.0 mg/l [155]. Pandey [156] presented in 2018 a thorough description of the roles of boron in plants where it is needed in small quantities. Its deficiency leads to ‘impairment in membrane function’. For example, boron is involved in carbohydrates metabolism, nodule development and plant reproduction. So, it is needed in small quantities but toxic at higher concentration. Both values depend on the crop. If boron concentration is too high, an additional desalination step is required as post-treatment as shown in Fig. 1. The process for boron removal as post-treatment has been reviewed elsewhere [155,157]

4.5. *Re-mineralization needed for Irrigation*

From an irrigation point of view, there are minerals that are needed for irrigation and others need to be removed. Calcium and magnesium are both needed for soil quality with a ratio of calcium to magnesium higher than one and for plant growth. Sulfate is also needed for plant growth. Those three ions need to be added in post-treatment of desalinated water. Bar-Tal et al. [154] studied the concentration of calcium and magnesium that are needed for the fertigation of tomato. They concluded that the optimal calcium concentration was in the 1.5–2.5 mmol/l range with a magnesium concentration of 0.25 mmol/l with the ratio calcium to magnesium not being a driving factor. If sodium, chloride and boron are still too concentrated after the desalination process, an additional post-treatment step to lower their concentration is required. Other elements such as potassium are usually added separately through fertilizers.

5. Remineralization of desalinated water

In this section, we explore present state-of-the-art as well as emerging remineralization techniques.

5.1. *State-of-the-art techniques for remineralization of desalinated water*

The most common post-treatment sequence is to use carbon dioxide to acidify the seawater desalination permeate and use lime or limestone

Table 4
Boron maximum permissible concentration in groundwater without yield or vegetative growth reduction. Reproduced with permissions from [122].

Tolerance	Boron (mg l^{-1})	Crops
Extremely sensitive	< 0.5	Blackberry, lemon
Very sensitive	0.5–0.75	Avocado, grapefruit, orange, apricot, peach, cherry, plum, persimmon, Kadota fig, grape, walnut, pecan, onion, apple, plum
Sensitive	0.75–1.0	Garlic, sweet potato, wheat, sunflower, mung bean, sesame, lupine, strawberry, Jerusalem artichoke, kidney bean, snap bean, peanut
Moderately sensitive	1.0–2.0	Broccoli, red pepper, pea, carrot, radish, potato, cucumber, lettuce, pumpkin, spinach, tobacco, olive, roses
Moderately tolerant	2.0–4.0	Cabbage, turnip, Kentucky bluegrass, barley, cowpea, oats, corn, artichoke, mustard, sweet clover, squash, muskmelon, cauliflower
Tolerant	4.0–6.0	Alfalfa, purple vetch, parsley, red beet, sugar beet, tomato, cranberry, cotton, gladiolus, sesame, tulip, peppermint, rye.
Very tolerant	6.0–10.0	Sorghum, cotton, celery
Extremely tolerant	10.0–10.5	Asparagus

dissolution [10,158–163].

As early as 1981, Gabrielli [164] introduced the possibility of using carbon dioxide and natural carbonate rocks to reach basic desalinated water stability parameters. It is interesting to see that they suggest that dolomite and sulfuric acid as candidates for remineralization so early on. They also report the composition of post-treated water, as follows: 107 mg/l for chloride, 14 mg/l for sulfate, 183.8 mg/l for bicarbonate, 0.5 mg/l for bromide, 34.5 mg/l for calcium, 24.5 mg/l for magnesium, 2 mg/l for potassium, 60.5 mg/l for sodium 60.5 and 0.8 mg/l for fluoride. This composition is quite close to the regulations specified today by Israel. Their post-treatment process represented < 10% of the desalinated water cost. Subsequently, in 1987, Yamauchi et al. [165] published an article on "Remineralization of desalinated water by limestone dissolution filter". They indicate that limestone process is widely used as post-treatment in both MSF and RO plants. The additional step proposed in their study is aeration to remove excess carbonate before alkali addition to adjust pH. They indicate that this aeration decreases the annual cost of remineralization by 20%. Hasson and Bendrihem [163] modeled desalinated water re-mineralization by limestone dissolution with carbon dioxide acidification. This acidification can be done by carbon dioxide addition or, as recently shown [166], using a mixture of carbon dioxide and sulfuric acid. The latter method allows not only to use less carbon dioxide but also to bring SO_4^{2-}. When the calcium concentration content is reached for reaching the target values for corrosion control, pH is then adjusted by NaOH addition [158] or partial carbon dioxide stripping [167]. Most of the world's desalination plants do not currently add magnesium [10] nor sulfate.

To visualize this process, Fig. 3 presents a schematic of the desalination process, followed by re-mineralization as well as pH adjustment.

Desalinated water can be mixed with groundwater [11,21,168,169] to achieve target water quality. Rygaard et al. [73] evaluated all the costs associated to the comparative use of desalinated water alone or mixed with groundwater. They considered costs associated to health and corrosion or post-treatment. They concluded that remineralization can reduce negative impacts to the point that all costs considered, money is saved Euros 0.14 ± 0.08 Avni et al. [169] emphasized the importance of magnesium in drinking and irrigation water and to meet magnesium regulation requirements in Israel. They proposed the blending of different water sources such as partially re-mineralized desalinated seawater and natural water. Their target was to reach a magnesium concentration of 10 mg/l. Cai et al. [170] indicated that desalinated seawater containing bromide could led to brominated disinfection by-products when blended with drinking water and chlorinated.

In 2012, Duranceau et al. [29,171] surveyed desalination post-treatment in twenty-five water utilities, twenty-one from USA, three in Europe and one in the Caribbean. Four sources of water were used as feed: seawater (3), brackish water (14), groundwater (6) and wastewater (2) [171]. A variety of methods was used, including blending with groundwater but re-mineralization with targets for calcium, magnesium and sulfates was not included. Post-treatment was for pH and corrosion control. However, twenty-four of the twenty-five plants were producing water for irrigation. From this survey, they published an article for suggesting post-treatments [29]. However, re-mineralization for reaching mineral content targets was not included.

In 2007, Lahav and Birnhack [172] published an article on quality criteria for desalinated water following post-treatment. They reported data from fourteen articles indicating four parameters with target suggestions (all concentrations in mg/l as calcium carbonate):

- Alkalinity > 80,
- $80 < [Ca^{2+}] < 120$,
- $3 < \text{CCPP} < 10$,
- $\text{pH} < 8.5$

However, as previously mentioned, magnesium or sulfate target concentrations were not reported.

5.2. Conventional remineralization techniques

Magnesium remineralization is gaining more significance in research. In this section, we present different methods proposed for magnesium addition during post-treatment of desalinated water.

Lehmann et al. [173] evaluated various methods for magnesium addition with respect to cost estimation and carbon footprint. From these data direct addition by dosage of magnesium chloride, magnesium sulfate or magnesite are the highest methods in cost. They proposed a combined nanofiltration-precipitation method. The nanofiltration step is for enriching in doubly charged ions together with relatively low boron, chloride and sodium. They then precipitate brucite ($Mg(OH)_2$) on micro-magnetite particles that are separated magnetically. In the last step, magnesium is resolubilized in demineralized water. To add 10 mg/l of magnesium, the cost is \$0.00076/m^3 of desalinated water, and the added concentrations of sodium, chloride, calcium and boron are (in mg/l) 0.04, 0.18, 0.05 and 0.0094, respectively. Other methods have been reported in literature for magnesium re-mineralization of desalinated water as described below.

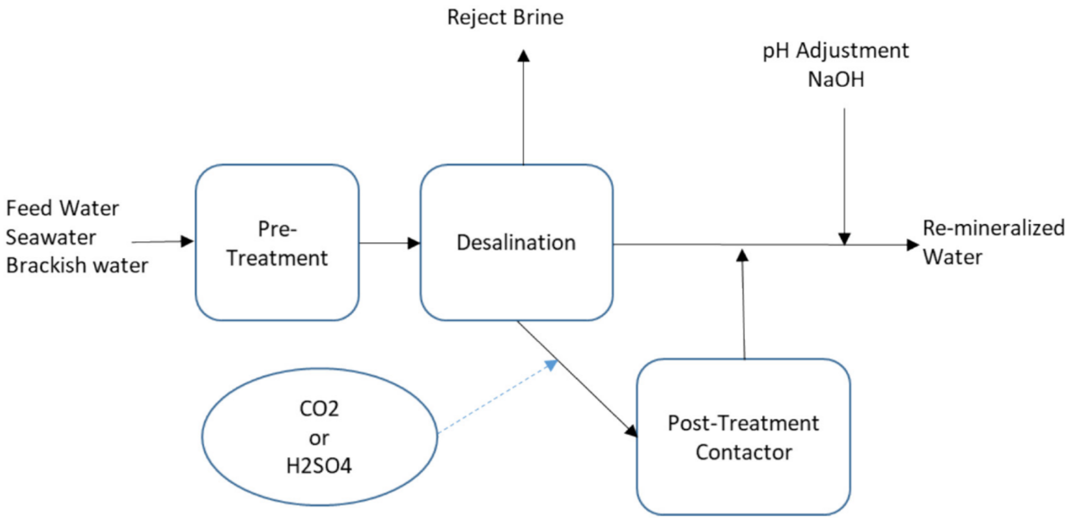

Fig. 3. Schematics for desalination and re-mineralization of desalinated water.

Lehmann et al. [173] first use nanofiltration to increase magnesium concentration and then precipitate brucite by increasing pH, preferably with CaO addition, and adsorbing it on magnetite particles. Particles are then magnetically separated and brucite is used for increasing magnesium concentration in the desalinated water post-treatment. Deng et al. [18] studied that magnesium addition limits the scaling of calcium carbonate in pipes and also provides protection for cement lined pipes.

Penn et al. [174] as well as Birnhack et al. [175] proposed to solubilize and excess of calcium ions and then use an ion exchange column to replace the excess by magnesium ions. The regeneration of the ion exchange column is made by using the seawater desalination brine which is rich in magnesium.

Since dolomite ($MgCa(CO_3)_2$) is a double carbonate of magnesium and calcium, it has been actively studied as a potential source of magnesium for post-treatment [176–181]. Since 2007, Lahav, O. has been co-author of several studies and reports on dolomite dissolution [10,30,128,141,176,178]. Recently, he highlighted [176]the technical challenges of dolomite dissolution for magnesium addition to desalinated water. In his work, the use of carbon dioxide to acidify water leads to slow dissolution of dolomite and the use of sulfuric acid necessitates very high sodium hydroxide dosage to reach final water quality targets.

Greiserman et al. [177] also presented data on dolomite dissolution realized dolomite dissolution experiments in a fixed bed using dilute acid solution using sulfuric acid and carbonic acid. The main breakthrough they obtained was through the use of micronized dolomite which allow much faster dissolution. Using mass transfer control, they established a kinetic model for dolomite dissolution. They however do not provide an economical assessment of the overall process including the basification need in the post treatment step.

Schwartz et al. [180,182] studied the dissolution of magnesia pellets for re-mineralization of desalinated water. Using a packed bed, they compared the concentration of magnesium obtained by dissolution in 5 mM acid with acid being either sulfuric acid or carbonic acid. Acidification with sulfuric acid allows a much faster dissolution of magnesia than carbon dioxide and led to a maximum magnesium concentration of 120 mg/l. A kinetic model based on mass transfer control provided a good agreement between calculation and experimental data. However, the article does not indicate re-mineralized water analysis with magnesium and sulfate content.

Mohammed et al. [183] proposed to precipitate magnesium from the rejection brine as brucite $Mg(OH)_2$ by addition of ammonia. They optimized parameters such as temperature, pH and magnesium to ammonia ratio. They conclude that the obtained brucite could be used for post-treatment but do not define in their studies economical parameters not show post-treatment experimental data.

Since seawater has a high concentration of magnesium, mixing the desalinated water with 0.5% seawater brings the magnesium concentration to 20 mg/l. However, this technique presents several drawbacks as it increases sodium concentration and adds non-desired elements such as boron and bromide. Bromide is then potentially involved in reactions leading to the formation of toxic brominated trihalomethanes as disinfection by-products [184] when disinfection is used.

Most of the processes mentioned in this section require the use of chemicals and external products to be added in the post-treatment step, whereas seawater already contains minerals which could potentially be used. Developing cost-effective solutions to separate specific minerals from seawater and then using these in the post-treatment of desalinated water could potentially lower costs.

5.3. The role of membrane processes in desalinated water remineralization

To alleviate the need to acquire and add additional materials, several teams [131,153,185–193] propose the isolation of divalent ions from seawater itself. Table 5 compiles recently developed methods for remineralization of desalinated water. The common factor among these methods is that they use seawater or brine enrichment in doubly charged ions. This not only allows the addition of magnesium, but also calcium, sulfate and potentially other minerals that could be useful for both human health and industrial uses. Recently, membranes have been applied to isolate seawater or brine streams rich in specific minerals for the purpose of remineralization of desalinated water, as is highlighted in this section.

Tang et al. [185] developed a membrane based process consisting of the combination of NF-NF-DiaNF. First, nanofiltration is used to obtain a total hardness to sulfate ratio close to 1 and the successive cycles of DiaNF to remove monovalent ions. For an addition of 20 mg/l of magnesium, the authors indicate the addition of 1 mg/l of sodium and a negligible amount of boron species. For the beneficial species such as calcium, potassium and sulfate, the respective additions are 2.7, 0.07 and 70.4 mg/l. The final cost depends on the final chloride concentration required and was $0.0017/m^3 in counter-current mode. Birnhack et al. [186] uses a succession of different process such as ultrafilration whose target is to reject sulfate thus obtaining a total hardness to sulfate ratio close to 1. $(([Ca^{2+}] + [Mg^{2+}])/[SO_4{}^{2-}] \rightarrow 1)$ followed by cycles of combined nanofiltration-dianafiltration to separates monovalent ions from divalent ions. It thus generates a $Mg^{2+}/Ca^{2+}/SO_4{}^{2-}$ solution that can be used for the post treatment at a cost of $0.014/m^3 for adding 20 mg/l of magnesium, this target corresponding to the Israeli regulation. The article does not indicate how much calcium and sulfate would be also added in that case.

Tang et al. [187] developed a new process using Cation Exchange Resin with diananofiltration. In the cation exchange step is to bring the total hardness to sulfate ratio close to unity whereas the diananofiltration step is to decrease the content of singly charge ions such as chloride, sodium and potassium. The concentrated magnesium sulfate solution can be used for re-mineralization of the permeate from the seawater desalination. In this article, they evaluate the price of enriching desalinated water with 20 mg/l of magnesium is around $0.032/m^3. This price is higher than other methods described in this review, however the authors claim that contrary to other methods, this one does not add anti-scalants and the concentrations of sodium and chloride at 5 and 6 mg/l respectively is lower than other methods. The concentrations of calcium and sulfate brought by the method are not indicated.

Nativ et al. [188] applied a hybrid nanofiltration-electrodialysis process for separation of $MgSO_4$ from seawater and used this magnesium-rich solution to replenish magnesium ions into desalinated water. Fig. 4 shows a schematic of electrodialysis membrane for selective removal of monovalent ions from Mg^{2+} rich brines. desalinated water.

They first use nanofiltration for generation of a magnesium-rich retentate, then diananofiltration step for removing components such a boron, sodium and chloride. This was followed by a selective electrodialysis process aimed at producing a high purity magnesium sulfate solution with a chloride to magnesium mass ratio lower than 0.2. They also indicate a cost of $0.014/m^3 for adding 20 mg/l of magnesium together with 4 mg/l of chloride. However, they do not provide the concentration of other ions that added in the process, such as calcium, sulfate and sodium.

Most membrane processes use antiscalant in differing quantities depending on the process requirement. However, since systems that require less antiscalant quantities would use the same source as the main desalination plant, the quantity of antiscalant will be the one needed for the desalination process. Such systems should define their parameters in the context of a fully integrated system and consider the costs in such a case. For example, membrane processes for remineralization do not require acidification as calcite or dolomite dissolution does.

Table 5
Membrane methods for desalinated water remineralization.

Source	Method	Mg^{2+} mg/l	Ca^{2+} mg/l	SO_4^{2-} mg/l	K^+ mg/l	Na^+ mg/l	Cl^- mg/l	Cost $/m^3	Ref
Seawater	CIX/NF/DiaNF	20	3.57	95	0.28				[187]
Seawater and brine	NF/NF/DiaNF	20	2.7	70.4	0.07	1	32	0.006	[185]
							12	0.017	
Seawater	UF/NF-DiaNF	20				3.8	5.4	0.0168	[186]
Brines	NF/DiaNF/ED	20					4.0	0.014	[188]
	NF/DiaNF	10						0.01	[192]

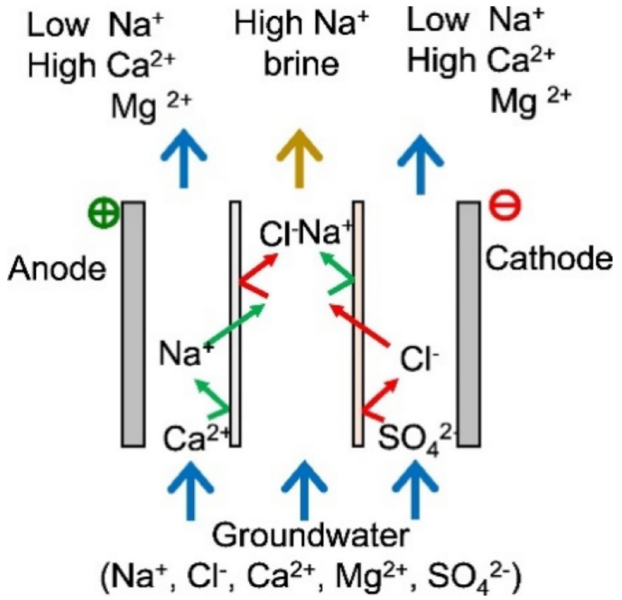

Fig. 4. Diagram showing monovalent selective electrodialysis reversal (MS-EDR) membranes selectively separating monovalent ions. Reproduced with permission [153]

5.4. Desalinated water remineralization for irrigation

For irrigation, different water sources are often available and their quantities varies depending on climate and undergrounds reserves. Thus, Martinez-Alvarez et al. [115,118,122,125] indicates that post-treatment for re-mineralization can be replaced by blending with brackish water. Avni et al. [169] studied the optimization of blending desalinated seawater with other sources. Their optimization parameter was magnesium concentration to meet the requirements of drinking and irrigation water.

Table 6
Guidelines values for the major drinking water major cations and anions as well as the number of countries having set values [194].

Element	WHO Guideline value	Number of countries or territories	Min (mg/l)	Max (mg/l)	Median (mg/l)
Calcium	None	31/104	30	500	150
Magnesium	None	34/104	10	1000	100
Sodium	None	81	100	400	200
Potassium	None	12	1.5	50	10
Chloride	250 mg/l	100	20	1200	250
Sulfate	None	97	50	800	250
Fluoride	1.5 mg/l	102	0.6	4.0	1.5

6. Water regulations and standards

In 2018, WHO compiled the water regulations and standards collected for 104 countries and territories up to 2015 [194] covering 89% of the world population. From the elements we studied in this review, Table 6 report the guideline range as well as the number of countries and territories having a regulatory/guideline value. However, from this report the list of countries having set values is not specified.

Table 7 report the minimum concentrations and the recommended range for calcium, magnesium and TDS in some European Union(EU) member states [195].

The existence of these regulations with minimum values for calcium and magnesium indicates the start of the expanding recognition of the

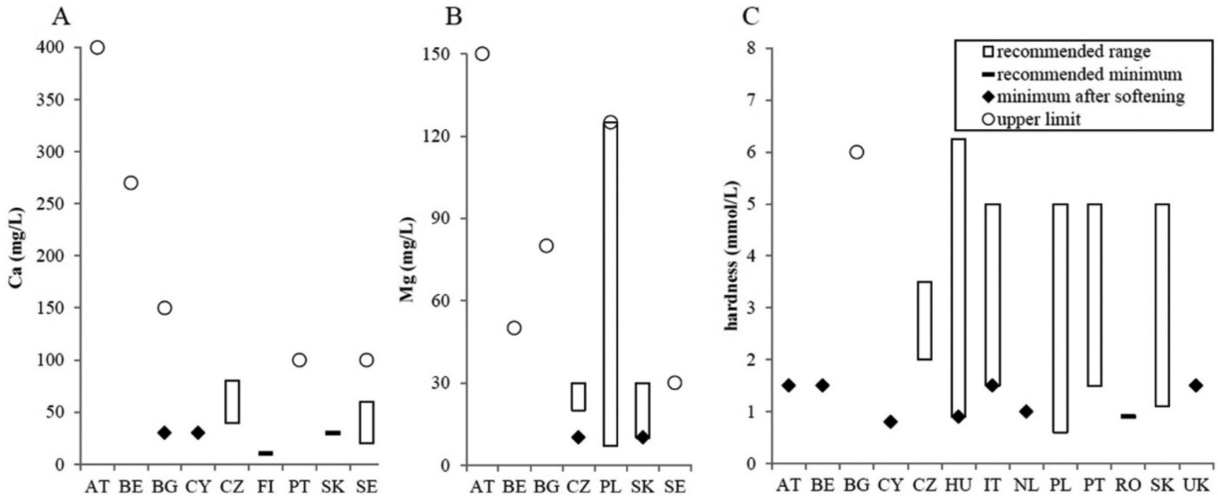

Fig. 5. Comparisons of limit values or recommended ranges for drinking water calcium (A), magnesium (B) and hardness (C) in different EU member states. Data include both legal regulations and technical guidelines [195]. reproduced with permission.

Table 7

Minimum required and recommended concentrations of minerals in softened or demineralized (desalinated) water as proposed by several member states for the recast of the EU Drinking Water Directive. Reproduced with permission [195]

Parameter	Unit	Minimum concentration required in softened or demineralized (desalinated) water	Recommended optimum concentration from health point of view
Calcium	mg/l	30	40–80
Magnesium	mg/l	10	20–40
Total Dissolved Solids	mg/l	100	200–500

Table 8

Water quality parameters defined by the Israeli Authority for desalinated water.

Desalinated water parameter	Values from Israeli authority recommendation
EC	< 0.3 (dS/m)
$[Cl^-]$	< 20 (mg/l)
$[Na^+]$	< 20 (mg/l)
$[Ca^{2+}]$	32–48 (mg/l)
$[Mg^{2+}]$	12–18 (mg/l)
$[SO4^{2-}]$	> 30 (mg/l)
[B]	0.2–0.3 (mg/l)
Alkalinity	> 80 (mg/l as $CaCO_3$)
CCPP	3–10 (mg/l as $CaCO_3$)
pH	< 8.5

importance of those minerals in drinking water. Fig. 5 compiles graphically the minimum values and the recommended ranges for calcium, magnesium and TDS for EU member states that have regulations. It shows that from the 28 EU members, only three are defining minimum concentration for magnesium and 6 for calcium. Hardness concerns more members as 12 of them are defining minimum threshold.

To date, only two countries have defined regulations that apply specifically to desalinated water: Israel and Cyprus as discussed by Birnhack and Lahav in 2018 [10]. Yermiyahu et al. [141] reported in 2007 the Israeli Authority recommendations of the water quality parameters after post-treatment for domestic and agricultural usage [141]. Those parameters are consigned in Table 8.

In Tables 7 and 8, in addition to the recommended individual ranges for calcium and magnesium concentrations ranges, a 2–3 ratio of calcium to magnesium concentration should be added as a parameter for human health, as established in Section 3. From the data collected in this review, Table 8 is not only the only one indicating a minimum value for sulfate concentration at 30 mg/l but this threshold is also above the maximum concentration value of chloride. Such a combination will provide a value for CSMR at which lead and copper corrosion will be prevented.

7. Conclusion

Although desalination has existed on an industrial scale for decades, the main focus of post-treatment around the world remains corrosion control in which carbonates are added for buffering, calcium is added for steel protection and pH is adjusted. However, other essential minerals such magnesium and sulfate which are required at different levels and ratios are often neglected. Sulfate is needed to prevent corrosion of copper and lead that are still present in housing pipes and is also an important nutrient for agriculture. Magnesium is also used against corrosion but is much more important for human health and agriculture. Since those minerals are present in seawater, the membrane methods presented in this review not only allow to limit the use of external chemicals but allow to lessen the brine discharge. We surveyed remineralization of desalinated water from the parameters used, limits and regulations set as well as conventional and non-conventional techniques applied. The following parameters could be used as guidance.

Apart from the already applied parameters to control iron corrosion through calcium carbonate deposition and pH buffering, the parameters to control lead and copper corrosion should be added.

- Sulfate concentration at least twice as high as that of chloride for lead and copper corrosion control or CSMR < 0.5,
- When sulfate is added, low sulfate and chloride concentrations for steel corrosion control or LR < 0.4,

For human health, apart from calcium which is always added for corrosion control:

- Magnesium concentration should be higher than 10 mg/l and preferably higher than 20 mg/l,
- The calcium to magnesium ratio should be in the 2 to 3 range, preferably close to 3,
- If fluoride and iodide are not added, information should be given to populations to use iodized table salt and provide fluoride tablets to kids.

For irrigation, apart from calcium which is always added together with carbonates for corrosion control: magnesium should also be added at a concentration lower than calcium. Sodium, chloride and boron concentrations should be low, the values depending on the crops.

- The following gaps in literature were identified and could be targeted for future work in this area: full water compositions with macro but also micro elements for human health and for irrigation remain to be scientifically defined.
- Not many countries have set lower limits for crucial minerals such as magnesium and calcium with respect to human health and agriculture. This means that drinking water produced by desalination often has very low levels of Mg, which does not significantly contribute to daily intake, as was outlined in this review.
- Remineralization methods using salts coming from the feed source would limit the use of external chemicals, decrease the liquid discharge and thus would be more environmentally friendly. Such integrated remineralization methods as well as economic considerations for simultaneous addition of appropriate amounts of different minerals are still lacking, as many studies focus on a specific mineral.
- Studies on other sources of obtaining minerals such as brackish water and/or ground water are limited.

Declaration of competing interest

The authors of this manuscript declare that there is no conflict of interest.

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