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Article

Dolomite for Supplementation of Desalinated Drinking Water in Saudi Arabia with Magnesium, Calcium, and Hydrogen Carbonate Ions Part 2

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Highlights

What are the main findings?

- Partial replacement of limestone with dolomite in post-treatment contactors at a 1,000,000 m^3 per day seawater desalination plant increased Mg levels by 1 to 2 ppm
- No additional costs were incurred
- Supersaturation of dolomite limits further addition of Mg without capital work

What are the implications of the main findings?

- Increasing the concentration of magnesium in desalinated water has been mandated
- Replacement of limestone with dolomite is a cost-effective way to approach mandated targets.

Abstract

Maintaining the concentration of magnesium in potable water above minimum levels has been suggested to have public health benefits. A twelve-month trial of attempting this goal by partial replacement of limestone with dolomite in eight out of twenty-six post-treatment contactors at the Ras al Khair seawater desalination plant, the largest such plant in Saudi Arabia with a daily production of over 1,000,000 m^3 of desalinated water. Over the course of the trial increases in Mg concentration in the range 1 to 2 ppm were achieved without necessitating increases in carbon dioxide utilization or any reduction in production volume. Alkalinity, calcium, and total dissolved solids remained within acceptable parameters. Calculated supersaturation values suggest strongly that it will not be possible to increase concentrations significantly further at the pH and temperature conditions of the study. Thus, while use of dolomite to this extent is a very low-cost strategy for magnesium supplementation, its scope of application without additional carbon dioxide consumption and capital investment is limited. The ratio of magnesium to chloride in SWRO product water was estimated in the course of the study and was found to be approximately half of the ratio in Standard Seawater, suggesting that under operational conditions (giving 1500 mg/L from first pass reverse osmosis) rejection of magnesium was significantly greater than rejection of sodium.

Keywords: seawater desalination; post-treatment; magnesium

1. Introduction

Low concentrations of magnesium (Mg) in drinking water have been reported to correlate with poor cardiovascular health outcomes [1–4]. As Mg is abundant in most ground and surface waters, concerns about low levels of Mg have focussed on localities where desalination is the main source of drinking water. Commercial desalination processes, such as seawater reverse osmosis (SWRO) and

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Multi-Stage Flash (MSF) [5] remove almost all dissolved matter from water to give a very low value of total dissolved solids (TDS). To this are added in post-treatment only small quantities of calcium carbonate and sodium hydroxide, to reduce the corrosivity of this water to transmission and distribution systems, [6] and disinfectant species such as sodium hypochlorite or chlorine dioxide to inhibit bacterial growth [7]. A large epidemiological study that observed populations before and after connection to desalinated water supplies suggested a negative impact on cardiovascular health [8] potentially linked to magnesium deficiency [9].

Most water used for domestic and industrial purposes in KSA is produced from desalinated seawater, with approximately half coming from SWRO and half coming from thermal desalination processes, predominantly MSF. Based on the reported health issues regarding Mg in drinking water and suggestions that the World Health Organization (WHO) would soon announce guidelines for minimum Mg content of drinking water, the Saudi Water Authority (SWA) announced specifications in October 2020 setting Mg targets in product water for new seawater desalination projects in KSA without mandating a particular method for sourcing Mg [10,11]. It is most likely that the WHO guidelines will target 5-10 ppm, rather than the higher and more costly levels which have been demonstrated to achieve positive health outcomes [12].

One method for potentially reaching a target of 5-10 ppm dolomite in a typical desalination system employing limestone contactors in post-treatment is to replace a part of the $CaCO_3$ with dolomite ($Ca.Mg.(CO_3)_2$) [13–15]. However, dolomite dissolves significantly more slowly than calcium carbonate under equivalent conditions, by a factor of approximately two to four times slower at temperatures between 20 and 40 °C [16–18]. This slow rate has been addressed in experimental trials by using an excess of acid, leading to a reduced pH in the treated water which then needs to be adjusted with base to give a reasonable pH and LSI [13]. The additional costs and solids loading required for such a treatment led Lahav et al. to discount dolomite addition as a credible strategy for increasing the magnesium content of desalinated water [19]. More recent work with pre-treated micronized dolomite has demonstrated dissolution rates that are consistent with desalination plant operations [20,21]. However, micronized dolomite is significantly more costly than the current food-grade limestone used in desalination post-treatment.

The most attractive aspect of dolomite for increasing magnesium content from an operational point of view is the potential capacity to use existing infrastructure without extensive capital investment. If the goal of supplementation is 5 to10 ppm Mg in treated water, then partial replacement of calcium carbonate with dolomite in existing limestone contactor infrastructure may be sufficient to meet targets without incurring significant increase in post-treatment cost. An additional benefit of dolomite in comparison to alternative options where Mg is added with a chloride or sulfate counter-ion is that the carbonate should have a positive rather than a negative impact on the corrosion resistance of transmission and distribution systems [7,10].

Initial studies at two desalination plants in KSA, one using RO and one MSF, showed that partial replacement of limestone with dolomite in existing limestone contactors could raise the Mg content of the product water by 2 to 3 ppm, meeting an overall target of 5 ppm Mg [15]. In this study, dolomite was applied for remineralization of a mixed product water at the SWCC desalination plant at Ras al Khair on the Arabian Gulf Coast. Completed in 2018, this plant is the largest in Saudi Arabia produces approximately 700,000 m^3 of water by MSF and 300,000 m^3 of water by RO daily. These waters are mixed before post-treatment and approximately 300,000 m^3 is diverted for remineralization.

2. Materials and Methods

The remineralization system employed at the Ras al Khair seawater desalination plant is shown schematically below (Figure 1). Each of the contactors has a capacity of 165 tons of limestone. In this study, limestone in eight of the 26 contactors, four in line A and four in line B, was replaced with food grade dolomite (Saudi Lime Industries, Jeddah, Saudi Arabia). Analysis provided by the supplier indicated that 0.5% of the mass was retained on a 4 mm sieve and 95% on a 1 mm sieve, bulk density

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was 1380 kg/m³, and the composition of the dolomite was 57% $CaCO_3$, 42% $MgCO_3$, 1.4% SiO_2, 0.13% Fe_2O_3 and 0.11% Al_2O_3.

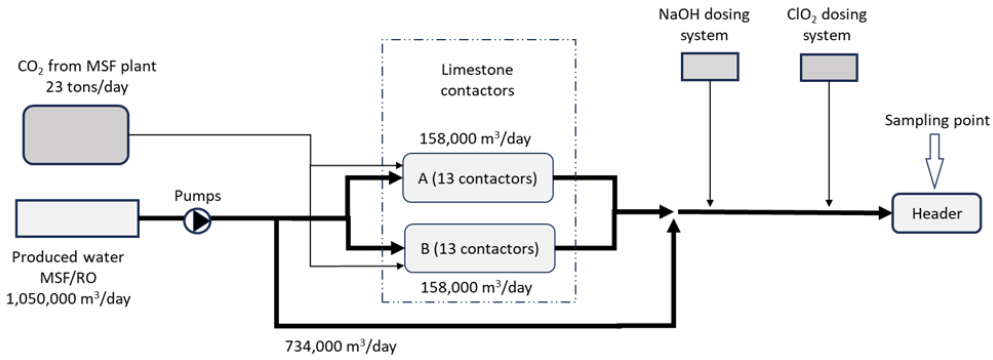

Figure 1. Schematic of post-treatment system at Ras al Khair seawater desalination plant.

For each of the two lines, the system was operated initially at a carbon dioxide dosing rate of 624 kg/hr (winter) to 792 kg/hr (summer) at 4.2 atm pressure and 50 °C into a liquid flow of 7,000 m³/hr out of a total product water flow of 21,400 m³/hr, giving a pH of 4.5 and approximately 90 ppm CO_2 in product water on entering the contactors. For pH readjustment 500 L/hr of 30% NaOH was typically added to water exiting each line. The pH of the final product water was maintained within a narrow range of 8.32 ± 0.06 over the course of the study.

Samples were taken between four and six times daily from the potable water and analysed by the Ras al Khair laboratory (Accreditation ISO 17025) for temperature, pH (AWWA Standard Method #4500-H+ B / ASTM D1293, potentiometry using a standard hydrogen electrode)), conductivity, total hardness AWWA Standard Method #2340 / ASTM D1126, EDTA titration)), calcium hardness (AWWA standard method #2500-Ca D, EDTA titration), total alkalinity (ASTM D 1067, acid titration), and calcium and magnesium ion concentration (AWWA Standard Method #3120B, inductively coupled plasma optical emission spectroscopy, ICP-OES)). Daily measurements of potable water quality also measured bromate (AWWA Standard Method #4110 B / ASTM D6581, ion chromatography with chemical suppression of eluent conductivity), sulfate (AWWA Standard Method #4110A, ion chromatography), copper, boron iron and sodium concentrations (AWWA Standard Method #3120B). Conductivity, pH, and temperature were also reported between four and six times daily for the product water from each reverse osmosis unit and the conductivity and temperature of the seawater intake from two to four times daily.

Analysis of the data showed that TDS and chloride concentration reported were frequently obtained at the plant by applying a multiplying factor to the obtained conductivity value, and that hardness values reported and calculated from reported calcium and magnesium values were identical prior to September 2024. Accordingly comparable TDS values were calculated from all conductivity measurements made using the coefficient reported by Rusyni (0.65 ppm.cm/µS) was applied and these estimated TDS values used in subsequent calculations [22].

Baseline data was recorded over eight months (January-August 2024) followed by thirteen months of data with dolomite application (September 2024-September 2025).

After September 2025, no additional dolomite was added to the system, but the dolomite already present was retained.

Up until 12th December 2024 the RO production system was operated with only partial use of the 2nd pass unit (7 out of 8 units in each line). This gave a TDS of product water entering the contactors of 168 ± 37 ppm, as estimated from the chloride concentration of the final product water; 166± 37 ppm was the TDS estimated from the reported TDS of the product of the RO units. The proportion of the RO product fed through the 2nd pass was then increased so that all production was treated with 2nd pass RO, giving a TDS of product water entering the contactors of only 108 ± 29 (87 ± 22 ppm) from the 13th of December 2024 onwards.

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The Langelier Saturation Index (LSI) [23] was calculated according to the following expression, used in the SWA laboratories, which has simplified approximation terms for the temperature (B) and ionic strength (A) dependence of calcium carbonate solubility [24]:

$$\mathrm{LSI} = \mathrm{pH} - \mathrm{pH_S} \tag{1}$$

where

$$\mathrm{pH_S} = 9.3 + A + B - C - D \tag{2}$$

$$A = (\log(\mathrm{TDS\ (ppm)}) - 1)/10 \tag{3a}$$

$$B = 34.55 - 13.12(\log(T(K)) \tag{4b}$$

$$C = \log(\mathrm{Ca\ (ppm\ Ca^{2+})}) \tag{5c}$$

$$D = \log(\mathrm{Alkalinity\ (ppm\ CaCO_3)}) \tag{6d}$$

Note that as defined here the LSI does not take into account the potential contribution of $MgCO_3$ and $Mg(OH)_2$ deposition, and thus will systematically underestimate the scaling potential of magnesium-containing waters.

The Larson-Skold (L-S) index is another measure for assessing corrosivity of waters, proposed to assess the impact of water on mild steel [25]:

$$\mathrm{L-S} = \frac{[Cl^-] + 2[SO_4^{2-}]}{[HCO_3^-] + 2[CO_3^{2-}]} \tag{3}$$

3. Results

3.1. Magnesium Concentration

The concentration of magnesium in the product water was reported to be 3.1 ± 1.3 ppm over the eight month period that was monitored before replacement of dolomite with limestone in the contactors (Figure 2). During the same period the measured chloride concentration was 95 ± 24 ppm, corresponding to a TDS before post-treatment of 172 ± 43 ppm. Reported magnesium concentrations in this period were proportional to chloride concentrations, as expected since both species were derived from seawater (Figure 3). A factor of 0.0326 was determined for the mass ratio of magnesium to chloride in the product water, which is close to half the expected value (0.0665 for standard seawater) [25]. This may imply that the relatively old SWRO membranes, producing an average of 1500 mg/L permeate in the first pass, were acting to some extent as nanofiltration membranes over the course of the study, giving greater rejection of divalent than monovalent ions.

Upon addition of dolomite, the average magnesium concentration gradually increased over a month until it reached a level of 5.6 ± 0.6 ppm, over which period the chloride concentration remained similar, at 89 ±16 ppm. This extent of additional magnesium in the final product water is similar to what was observed in the previous smaller scale study [15].

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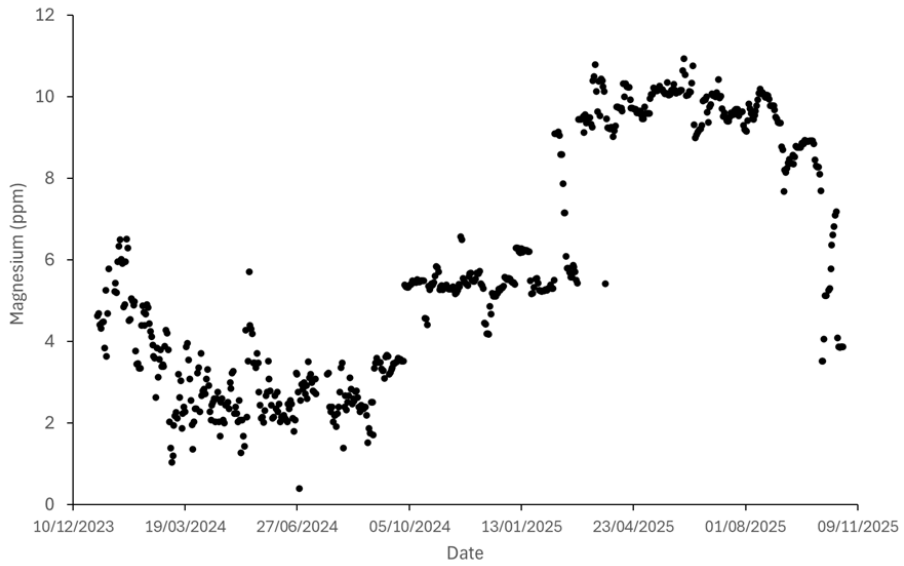

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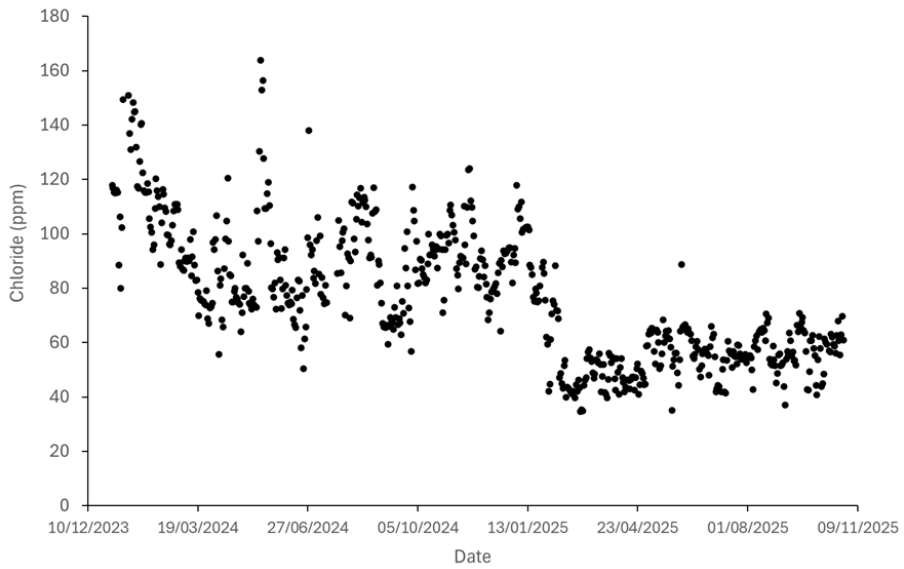

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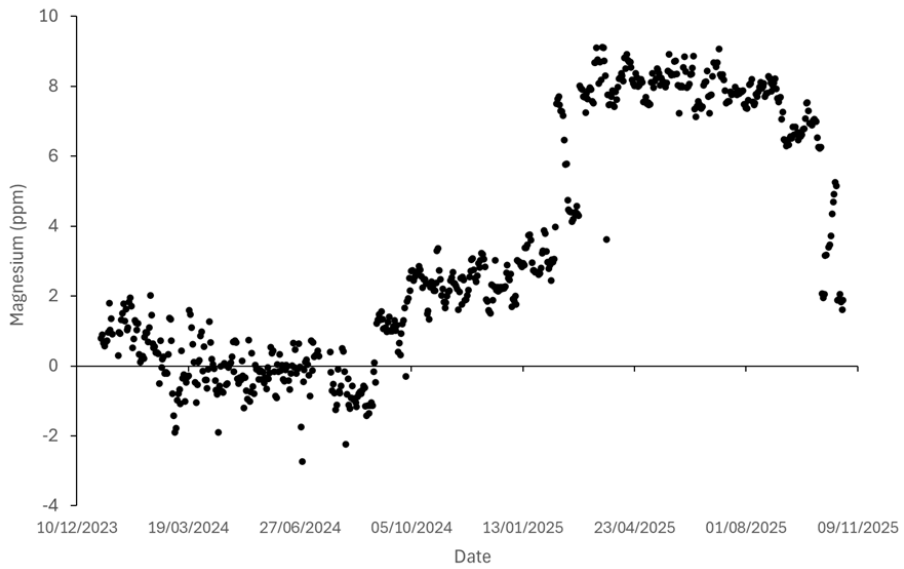

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Figure 2. (**a**) Magnesium, (**b**) Chloride, and (**c**) Calculated Excess Magnesium in product water from reported values at Ras al Khair, 1st January 2024 to 27th October 2025.

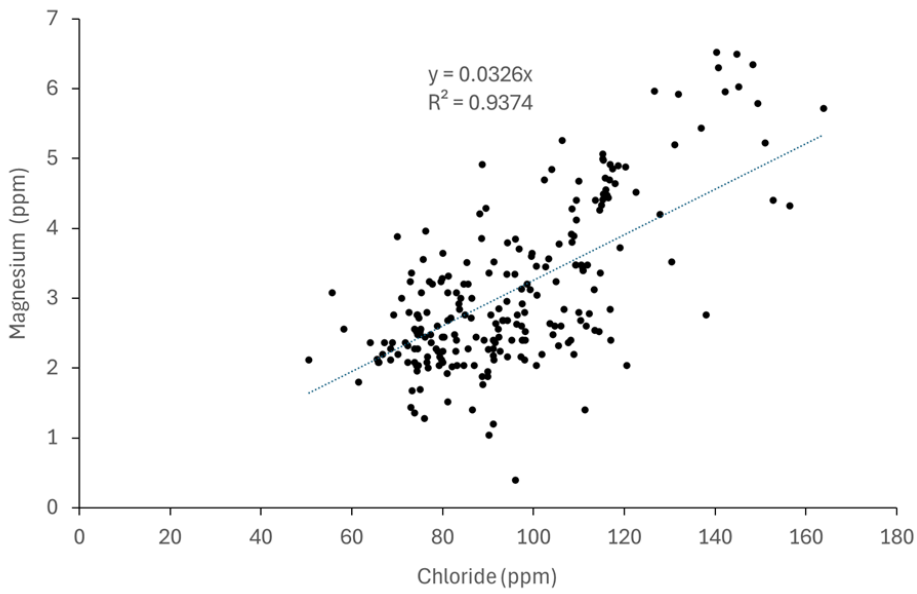

Figure 3. Relationship between reported magnesium concentration and reported chloride concentration during the control period (1st January to 31st August 2024).

From 12th December to 17th January 2025 the TDS of the incoming water was gradually reduced by increasing the proportion of the RO product being passed through the second stage RO system, with the calculated excess Mg rising from approximately 2 to approximately 3.5 over this period. After this a further rise in magnesium concentration was reported (Figure 2a), but this was judged to be artefactual. While TDS was not measured directly before remineralization, the average chloride concentration fell to 55 ± 11 ppm over the later phase of the trial (Figure 2b).

From 3rd March 2025 onwards there was a dramatic rise in the amount of dissolved magnesium and the data before and after that date were very clearly clustered separately. Clear trends with system parameters could be observed for data from the first three months of operation with dolomite but these were not evident in the latter part of the trial (Supplementary Figure 1).

As dolomite contributes the hydrogen carbonate ion as well as magnesium and calcium to the product water, it is not surprising that a weak positive correlation is observed between alkalinity and excess magnesium concentration (Figure 5a).

A dependence of the contribution of dolomite to the magnesium content of the product water with temperature was observed, with a linear fit to the data suggesting dolomite dissolution under the test conditions could potentially provide 5 ppm at 29 °C but only 1 ppm at 40 °C and most likely a negligible contribution above 42 °C (Figure 5b).

There is also a marked inverse correlation between dolomite dissolution and the estimated TDS of the water entering the contactors, with TDS less then 100 ppm giving greater than 4 ppm excess Mg in most cases and TDS greater than 200 ppm giving less than 2 ppm excess Mg (Figure 4c). This may be related to the dependence of dissolution rate on relative saturation, which is dependent on the total concentration of Mg present—the higher TDS solutions contributing more Mg—or to changes in the pH of the incoming water, with low TDS potentially being at a lower pH.

As a cross-check, the values of total hardness and calcium concentration measured in the study were used to back-calculate magnesium concentrations (Figure 4). Note that in the early part of the study it is clear that these were not independent measurements. Examination of the reports from the plant indicated that magnesium and calcium concentration values reported over this period were in fact calculated from total hardness and calcium hardness measurements. The estimates track well

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with the reported magnesium concentrations up until March 2025, after which the two data sets diverge markedly. This is strong evidence that the high magnesium concentration reported in the later part of the study (Figure 1a) are artefactual. The average increase in magnesium concentration from replacement of limestone by dolomite from January 17th 2025 until the end of the study can thus be estimated as 0.9 ±1.3 ppm.

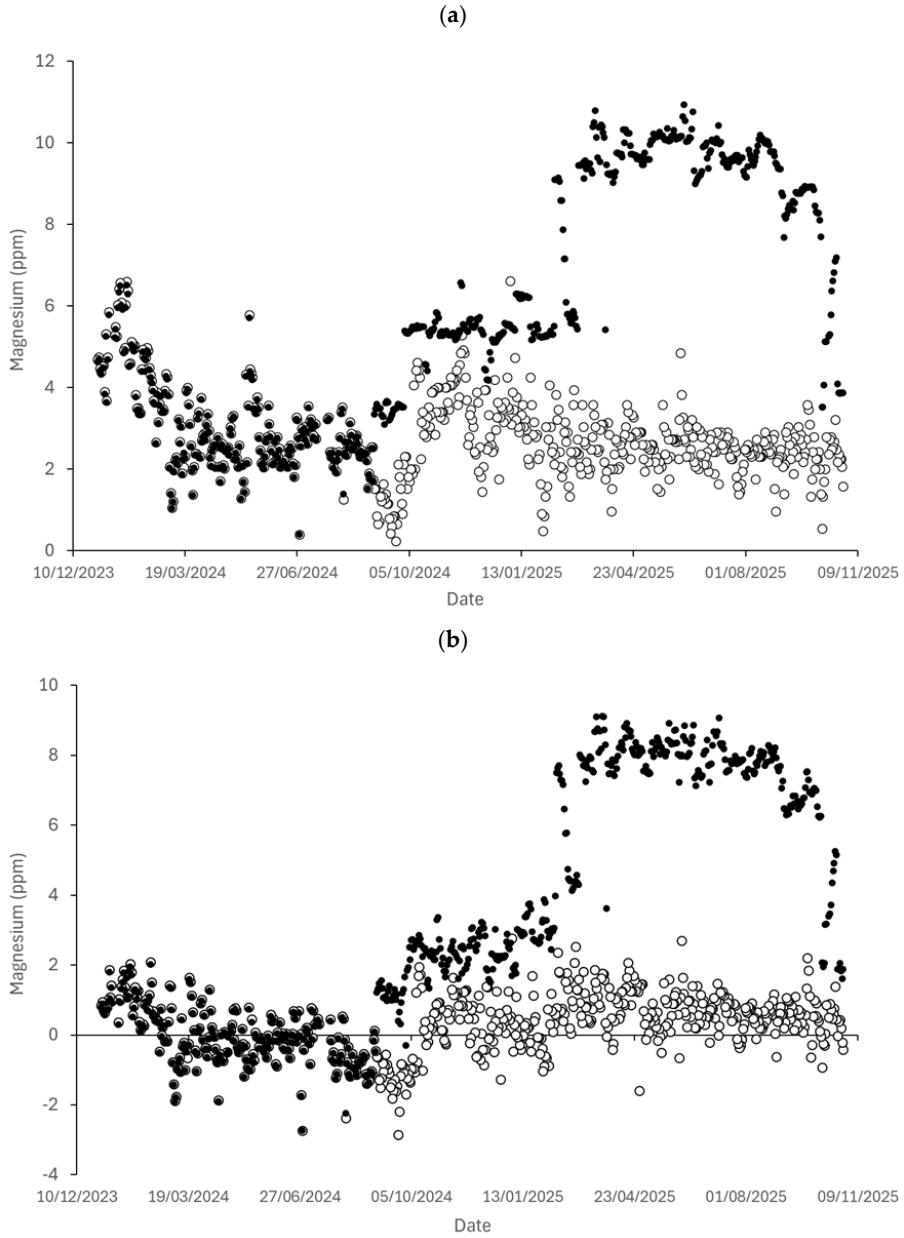

Figure 4. (**a**) Magnesium concentration and (**b**) excess magnesium concentration in product water as reported (solid circles) and estimated from total hardness and calcium concentration data (open circles).

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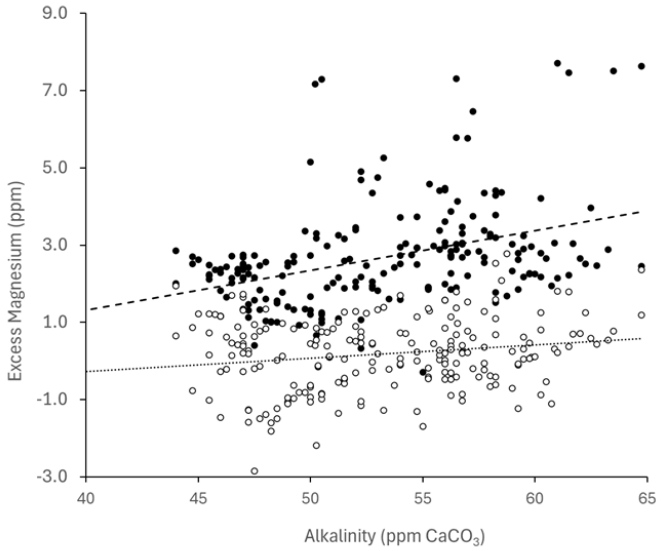
(**a**)



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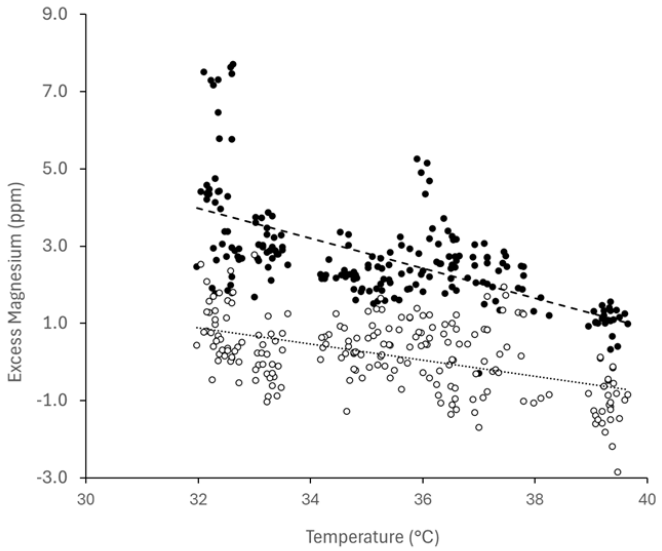

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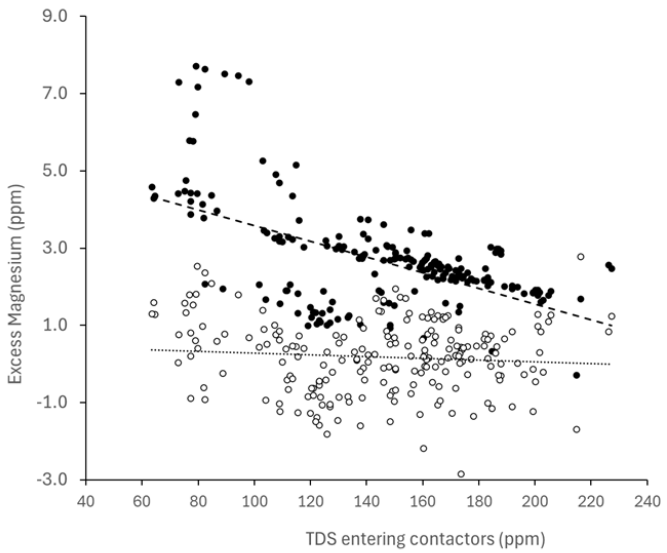

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Figure 5. Dependence of excess magnesium concentration as reported (solid circles) and estimated from total hardness and calcium concentration data (open circles) as a function of (**a**) total alkalinity, (**b**) intake temperature, (**c**) total dissolved solids.

The solubility product for dolomite, $Q_{sp} = [CO_3^{2-}]^2[Mg^{2+}][Ca^{2+}]$ was calculated using pK_a values for HCO_3^- interpolated between the values 10.29 (30 °C), 10.25 (35 °C) and 10.22 (40 °C) to determine carbonate concentration from total alkalinity and pH [26]. Q_{sp} was compared to the empirical K_{sp} for dolomite as a function of temperature reported by Robertson et al. ($pK_{sp} = 14.7545 - 0.0624959T - (3993.5/T)$) [27].

It can be seen that the post-treatment water is almost always supersaturated with regard to dolomite ($Q_{sp}/K_{sp} > 1$), whether the reported magnesium concentration or calculated magnesium concentration are used (Figure 6). Thus the observed levels of magnesium are likely to be at the limit of what is thermodynamically feasible in the system.

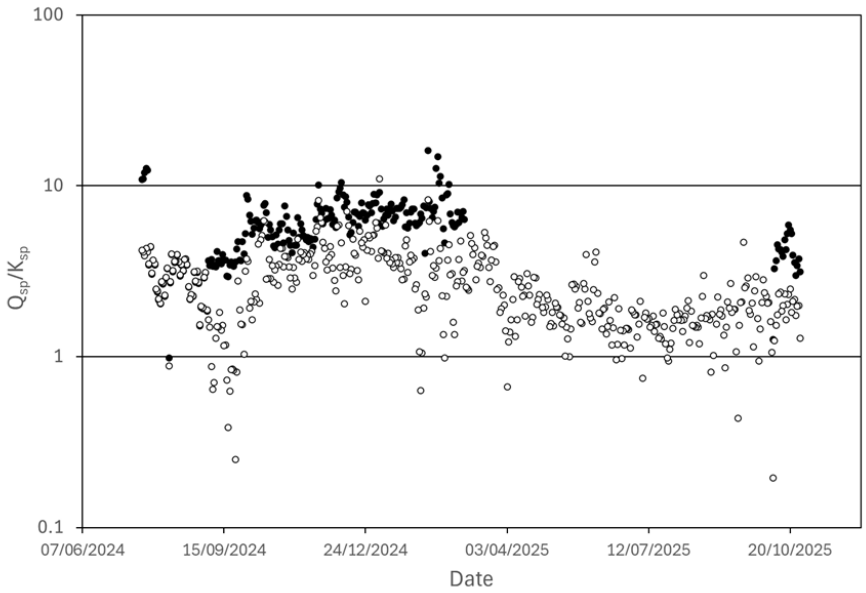

Figure 6. Calculated saturation of product water with respect to dolomite, calculated from reported magnesium concentrations (solid circles) and magnesium concentrations calculated from reported hardness and calcium hardness (open circles).

3.2. Alkalinity

One concern with replacement of limestone with dolomite is a potential reduction in alkalinity due to reduced dissolution rates, leading to a reduced scaling potential of the product water and hence the resistance to corrosion of transmission lines and distribution systems (see Langelier Saturation Index, below). Overall alkalinity of the product water was maintained after transition to use of dolomite, with an average alkalinity of 58 ± 7 in the initial control period and 52 ± 7 over the 12 months from October 2024 to September 2025 (Figure 7). Over the period of the study, there is a seasonal correlation of lower alkalinity in warmer months, consistent with the expected dissolution behaviour of limestone and dolomite with temperature. There are no marked inflection points in the data corresponding with changes in post-treatment practice over the course of the study.

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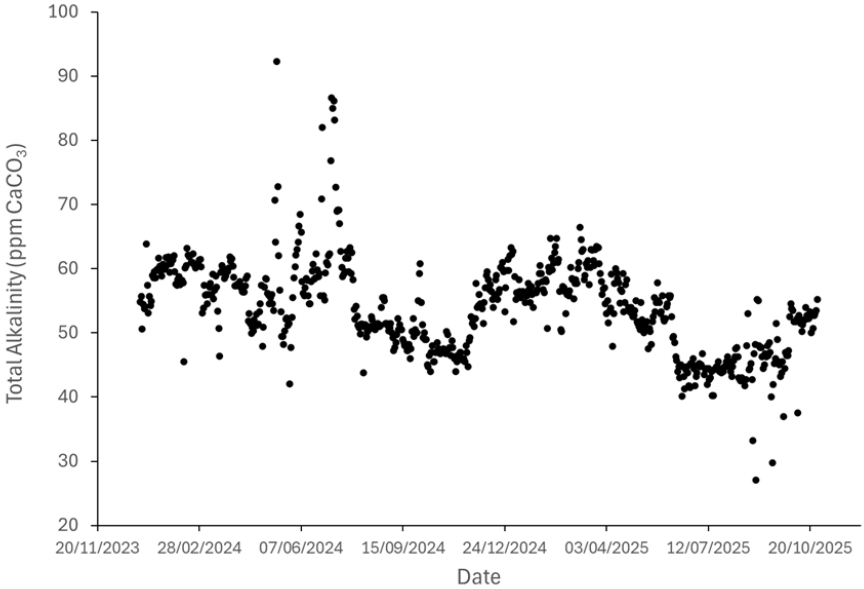

Figure 7. Reported total alkalinity in equivalent ppm of $CaCO_3$ over the course of the study.

3.3. Calcium Hardness

Potential reduction in the concentration of calcium has also been raised as a concern with replacement of limestone by dolomite. In the course of this study, calcium concentration was found to fall to about the same extent as alkalinity, with average values of 22 ± 4 ppm in the control period and 19 ± 3 under dolomite addition (Figure 8). As with alkalinity, a seasonal dependence in concentration could be seen over the course of the study, with lower concentrations measured in the summer months.

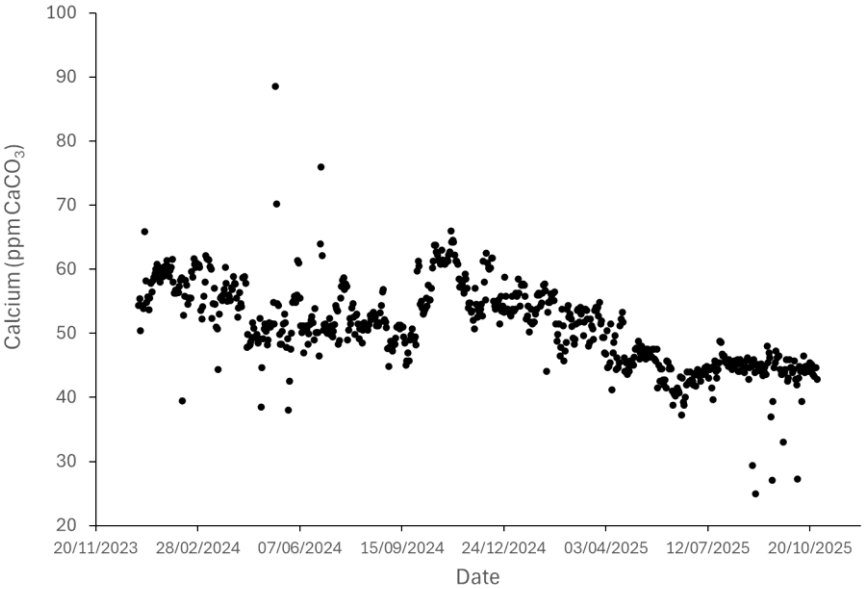

Figure 8. Calcium concentration over the course of the study.

3.4. Langelier Saturation Index

Another reported concern with the process of replacement of limestone with dolomite involving additional carbon dioxide dosing is a potentially lower scale-forming propensity in the product

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water, giving less effective protection of the transmission system against corrosion. This scale-forming propensity is conventionally quantified in terms of the Langelier Saturation Index, LSI. The target range is 0.0-0.3 to prevent corrosion in the transmission lines.

LSI values calculated from parameters measured over the course of the study are shown in Figure 9. During the initial control period, an average value of 0.10 ± 0.12 was obtained, while the average LSI while all eight dolomite contactors were in operation was 0.00 ± 0.11. As found in previous observations of LSI in product water, values were lower during the warmer months of the year. The drop in LSI did not correspond with the initiation of dolomite replacement nor with the reported dates of reduction of TDS in the feed water.

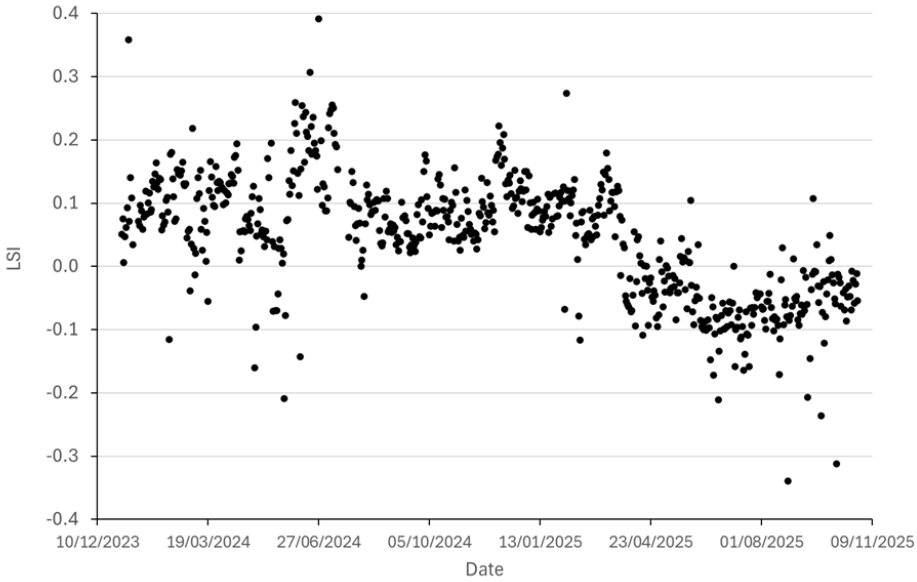

Figure 9. Calculated Langelier Saturation Index over the course of the study.

3.5. Larson-Skold Index

Above a Larson-Skold index value of 1.2, waters can present a potential corrosion hazard to both exposed metal and cement surfaces, while below this level they should be innocuous. Current guidelines for safeguarding transmission pipelines in the Kingdom of Saudi Arabia mandate an upper bound of 1.2 for the Larson-Skold value. Sourcing magnesium from dolomite rather than from seawater in this study reduced the amount of chloride and sulfate in the transmitted water, bringing the Larson-Skold Index into an acceptable range while keeping the TDS above mandated limits (Figure 10).

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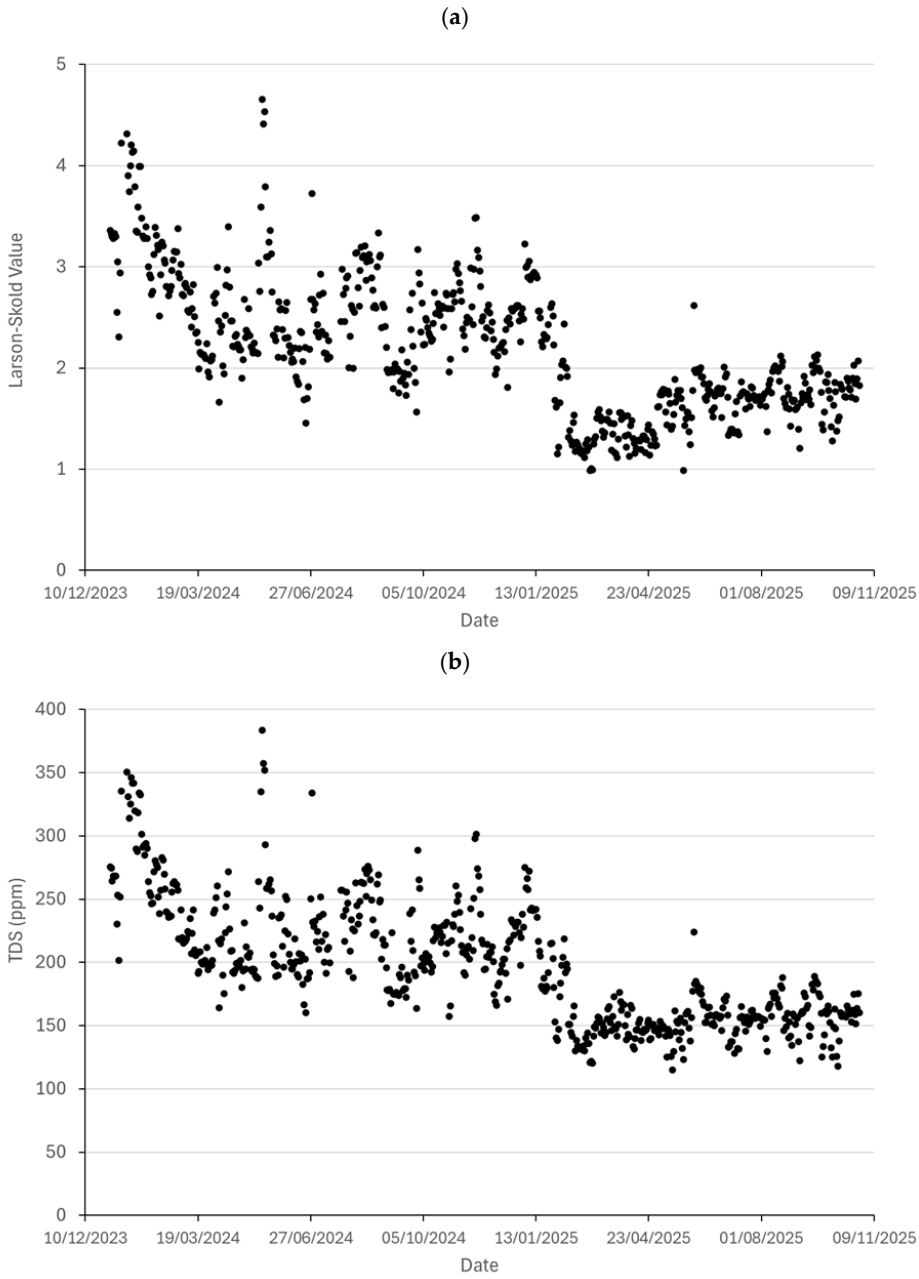

Figure 10. (**a**) Calculated Larson-Skold Index and (**b**) measured total dissolved solids over the course of the study.

4. Discussion

Dolomite, as a carbonate mineral, has an intrinsic advantage over use of magnesium sulfate or magnesium chloride in fortification of desalinated water as it will make a positive rather than negative contribution to the corrosion resistance of the transmission and distribution systems. Replacement of limestone with dolomite in 31% of the existing limestone contactors (eight out of 26) at a remineralization plant treating desalinated water which was a mixture of MSF (70%) and RO (30%) product, without adjusting the carbonation protocol, resulted in an increase in Mg concentration of 1-2 ppm, with an additional benefit of a significantly improved Larson-Skold index meeting water transmission specifications. This was at a cost of slightly lower calcium concentrations and lower alkalinity which led in turn to a lower Langelier Saturation Index, no longer meeting specifications; it must however be recalled that the LSI does not take into account the potential protective effect of $Mg(OH)_2$ scaling. Calculations of supersaturation suggested that the concentrations of carbonate and calcium in the systems were such as to make dolomite dissolution

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unfavourable beyond the relatively low levels obtained. However, the results were correlated inversely both with temperature and with pre-mineralization TDS.

A large difference was found between reported magnesium levels derived from magnesium hardness and reported magnesium levels derived from ion chromatography, with magnesium hardness measurements suggesting a marginally significant degree of magnesium supplementation from the use of dolomite (0.45 ± 0.82 ppm), while ion chromatography measurements suggested a more substantial increase (2.7 ± 1.4 ppm). It is not yet clear which is the more accurate value, though the larger one is consistent with earlier studies carried out on a smaller scale at other desalination plants [15].

Reported excess magnesium concentrations of order 5 ppm were found consistently by ion chromatography when the water temperature was 32 °C (the lower limit of the range of temperatures observed in the study) and when the TDS was of order 50 ppm (the lower limit of the range of TDS observed in this study). Thus, dolomite replacement in contactors to this level without operational change may be an effective strategy for increasing magnesium concentrations by up to 5 ppm for high-quality, low-temperature waters. The low TDS is most readily achieved by thermal desalination processes, while low temperature is readily achieved only by SWRO. Authors should discuss the results and how they can be interpreted from the perspective of previous studies and of the working hypotheses. The findings and their implications should be discussed in the broadest context possible. Future research directions may also be highlighted.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org, Figure S1: Variation of magnesium concentration with product water values of (a) alkalinity, (b) pH, (c) temperature, and (d) calculated TDS before post-treatment.

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