

In Search of Impeccable Remineralization Technology

Harmen van der Laan, Timothy van Heeswijk, Ruud Kolpa, Willem Jan Knibbe*, Walter van der Meer

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1. The Introduction of Membrane Filtration at Oasen

Oasen drinking water company in The Netherlands uses river bank filtrate as a source for the production of drinking water at 7 production locations. Oasen is one of the ten Dutch publicly owned drinking water companies and provides 750.000 customers and over 7.000 companies with drinking water. River bank filtrate from along the river Rhine is used as source for reliable and stable raw water. It is currently treated by, consecutively, aeration and rapid sand filtration, pellet softening combined with carry-over filtration, activated carbon filtration, and UV disinfection.

The production locations can be divided in two groups, the first including 4 locations each producing less than 10 mln m³/yr, and the second including 3 locations each producing more than 10 mln m³/yr. The second (newest) group was built between 40 and 25 years ago, whereas the first (oldest) group was built at least 40 years ago. The first group is gradually being renovated. Major renovations of the second group will not start before about 15 years.

Oasen has chosen to use membrane technology, in particular reverse osmosis (RO), for the renovations. This technology, worldwide applied to desalination, provides significant benefits to the treatment of anaerobic river bank filtrate as well. In particular, the development of RO installations in combination with post treatment will enable tuning the water quality to legal requirements, customer expectations and operational demands better than currently possible with conventional treatment. Moreover, membrane treatment provides a reliable barrier to emerging contaminants, increasing salinity of source water, as well as additional protection for hygienic risks.

2. Remineralization as Part of the Introduction of Membrane Filtration

Water treated by RO has a low mineral content and is not suitable for distribution as drinking water. Usually, the permeate is remineralized by increasing the concentrations of HCO₃, Ca, and Mg ions to stabilize the pH, to make it non-aggressive (prevent the water from dissolving CaCO₃), and provide part of the daily intake of Mg.

Dutch law requires a minimal hardness of 1 mmol/l as dissolved Ca en Mg ions, and a concentration of HCO_3 ions of at least 60 mg/l.

As a first step, Oasen will comply with these requirements by blending RO permeate with conventionally treated water. Blending has the advantage of being a readily available technology, since it means continuation of (a part of) the current treatment of river bank filtrate. However, it has the disadvantage of introducing a bypass so that the benefits of membrane filtration only apply to part of the treated water. As a second step, therefore, Oasen will implement full stream treatment by membrane filtration. In order to replace blending, this requires an alternative remineralization technology.

Internationally, there has been considerable attention for the development of technology to stabilize desalinated water and raise its mineral content^{1,2,3}. Commonly, remineralization as an alternative for blending is based either on the dissolution of CaCO_3 , possibly in combination with a form of MgCO_3 , or on the direct dosage of chemicals. The choice of a suitable technology depends on local circumstances (such as water quality of the permeate, temperature), treatment process (such as additional treatment steps needed after membrane filtration), and case-specific requirements (such as operational limitations, desired water quality parameters). Since the addition of substances is a potential source of contaminants, may increase turbidity, as well as the potential of regrowth⁴, the choice of a suitable remineralization technology is essential for producing high quality drinking water.

In this paper, exploratory research of remineralization technology based on the dissolution of CaCO_3 is presented.

3. Research Approach

The aim of Oasen is to supply impeccable drinking water. This means water of the highest possible quality, free from contaminants, and positively evaluated by customers on organoleptic and esthetic properties. Therefore, the main goal of research on remineralization is to determine which technology provides the highest quality drinking water. An overview has been presented at the Amsterdam International Water Week⁵. As part

¹ Post-Treatment Stabilization of Desalinated Water, S. J. Duranceau, R. J. Pfeiffer-Wilder, S. A. Douglas, N. Peña-Holt and I. C. Watson, Water Research Foundation, 2011

² Post-Treatment of Desalinated Water, O. Lahav, N. Voutchkov and L. Birnhack, Balaban Desalination Publications, 2012

³ Fundamental chemistry and engineering aspects of post-treatment processes for desalinated water – A review, L. Birnhack, N. Voutchkov, O. Lahav, Desalination 273, 6-22, 2011

⁴ Safe Drinking-water from Desalination, WHO, WHO/HSE/WSH/11.03, 2011

⁵ Oral presentation, Harmen van der Laan, Amsterdam International Water Week, International workshop on remineralization, 3 nov 2015, Amsterdam, The Netherlands

of this research, Oasen has also investigated the influence of mineral content on the taste of drinking water⁶. Internationally, attention is given to the role of minerals in terms of economic value and additional nutrition as well^{7,8}. Part of ongoing research at Oasen is to further investigate properties relevant for customer satisfaction. This includes the following properties.

Purity: Calcium carbonate as a natural product may contain impurities. It is known to contain various elements such as aluminium, zinc, etc, in varying amounts. These elements may dissolve as well and be found in the remineralized water. Moreover, the dissolution rates may be influenced by the impurities⁹. The occurrence of such elements in various types of CaCO₃ has been investigated, as well as resulting concentration in remineralized water. No unacceptable concentrations of these elements have been found. Results are not shown in this paper. Effects on dissolution rates have not been investigated.

Turbidity: turbidity is generally used as an indication of properly functioning water treatment. Oasen, like other drinking water companies, adheres to company standards for water quality. For turbidity, it is investigated if remineralization complies with this standard. Specifically, it is investigated if the effluent of the remineralization process has a turbidity less than 0.15 NTU. Results are not shown in this paper.

Particle counts: when dissolving particles of CaCO₃, in order to obtain a desired concentration of Ca ions (and alkalinity), any additional undissolved CaCO₃ present in the water would exceed this desired concentration. Particle counts are used mainly to investigate if no undissolved CaCO₃ particles leave the remineralization process. Results are not shown in this paper.

Calcium Carbonate Precipitation: precipitation of dissolved Ca as CaCO₃ leads to scaling. Excessive scaling is generally undesired when occurring, e.g., in premise plumbing installations. It may lead to customer complaints. The desire to reduce excessive scaling has been an important driver for the implementation of centralized softening installations in The Netherlands. A limited amount of scaling during transport and distribution, however, is considered beneficial, as a precaution against corrosion. Therefore, it is essential to tune the remineralization process to obtain a suitable 'scaling potential'.

⁶ Sensory quality of drinking water produced by reverse osmosis membrane filtration followed by remineralisation, M. H. Vingerhoeds, M. A. Nijenhuis-de Vries, N. Ruepert, H. van der Laan, W. L.P. Bredie, S. Kremer, *Water Research* 94, 42-51, 2016

⁷ Designing water supplies: optimizing drinking water composition for maximum economic benefit, M. Rygaard, E. Arvin, A. Bath, P.J. Binning, *Water Research* 45, 3712-3722, 2011

⁸ An innovative drinking water nutritional quality index (DWNQI) for assessing drinking water contribution to intakes of dietary elements: A national and sub-national study in Iran, M. Abtahi, K. Yaghmaeian, M. R. Mohebbi, A. Koulivand, M. Rafiee, M. Jahangiri-rad, S. Jorfi, R. Saeedi, S. Oktaie, *Ecological Indicators* 60, 367-376, 2016

⁹ Calcium Carbonate Dissolution Rate in Limestone Contactors, R. D. Letterman, U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-95/068 (NTIS PB95-222733), 1995

The Calcium Carbonate Precipitation Potential (CCPP) provides a quantitative measure for the scaling potential, is widely used and is, e.g., referred to in German law¹⁰. It depends on parameters such as the acidity, temperature, and ion concentrations present in the water. It generally requires theoretical calculations to determine the equilibrium of various chemical precipitation reactions, and depends on the exact composition of the water^{11,12,13}.

Calcium carbonate precipitation can also be investigated experimentally. Using a Dutch protocol¹⁴, mimicking calcium scaling in water kettles, we have obtained experimental precipitation values under different circumstances. Main question for these investigations so far has been to distinguish between the effects on precipitation of different methods of remineralization. After briefly introducing the method of determination, results are shown of the experimentally determined calcium carbonate precipitation potential (CCPP_{test}), as determined for calcite dosing and calcite filtration.

4. Experimental Method: Determination of CCPP_{test} after Calcite Filtration and Calcite Dosing

The CCPP_{test} has been determined experimentally following a standard protocol. It is shown schematically in Figure 1. A two liter sample is taken and divided in 250 ml samples (with a 300 ml ±10 ml cylindrical flask) over six Erlenmeyers. Three samples are pretreated with a 0.05 µm membrane filter with an air pressure of 2.5 bar. One of the three pretreated samples is taken as filtered reference, as is one of the three non-filtered samples which serves as a blank. The remaining four samples, two of which are pretreated with the 0.05 µm filter, are used for the boiling test and serve as a duplicate measurement. The samples are heated gradually in approximately 20 minutes until the water is boiling. The water is kept boiling for 5 minutes. Then, the Erlenmeyers are removed from the heating unit and allowed to cool down in a cooling bath (15 °C). The samples are filtered over a 0.45 µm filter with air pressure at 2.5 bar. As a final step, the glass ware is cleaned with 0.1 M HCl and rinsed with demi water.

¹⁰ Verordnung über die Qualität von Wasser für den menschlichen Gebrauch, DVGW, Bonn, Germany, 2016 (German)

¹¹ Calcium Carbonate Scale Dissolution in Water Stabilized by Carbon Dioxide Treatment, P. M. Temkar, J. Harwood, R. Scholze, USACERL Technical Report N-90/01, 1990

¹² Calcium Precipitation Potential, J. A. Wojtowicz, Journal of the Swimming Pool and Spa Industry 2, 2, 23-29, 2001

¹³ Assessment of Calculation Methods for Calcium Carbonate Saturation in Drinking Water for DIN 38404-10 Compliance, P.J. de Moel, A.W.C. van der Helm, M. van Rijn, J.C. van Dijk, W.G.J. van der Meer, Drink. Water Eng. Sci. 6, 115-124, 2013

¹⁴ KWR, Validatie nieuwe kookproef kalkafzetting, 2004, Nieuwegein, The Netherlands (Dutch)

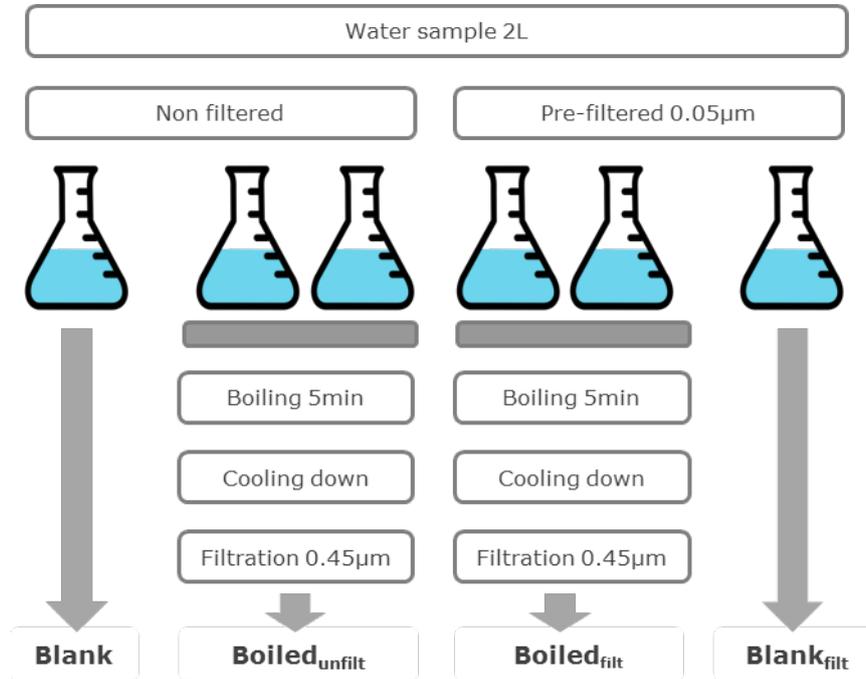


Figure 1: experimental procedure for determination of CCPP_{test}

The CCPP_{test} is calculated according to:

$$CCPP_{test} = \frac{[Blank] - [Boiled_{unfilt} \times C_e]}{M}$$

where

CCPP_{test} = calcium precipitation potential without filtration pretreatment (mmol/l)

Blank = concentration calcium in blank sample (mg/l)

Boiled_{unfilt} = concentration calcium of duplicate unfiltered boiled sample (mg/l)

C_e = correction factor for evaporation of water 0.95

M = mol mass calcium 40.1 (g/mol).

The experimental determination of the CCPP_{test} has been applied to calcite filtration and calcite dosing.

Calcite filtration has been implemented in an operational setup as shown in Figure 2. Permeate containing CO₂ is partly flowing through a bed of calcite with grain sizes between 0.5 and 4 mm. Depending on the

desired concentration of dissolved calcium, additional CO_2 can be added, and the percentage of permeate passing the calcite filter can be varied.

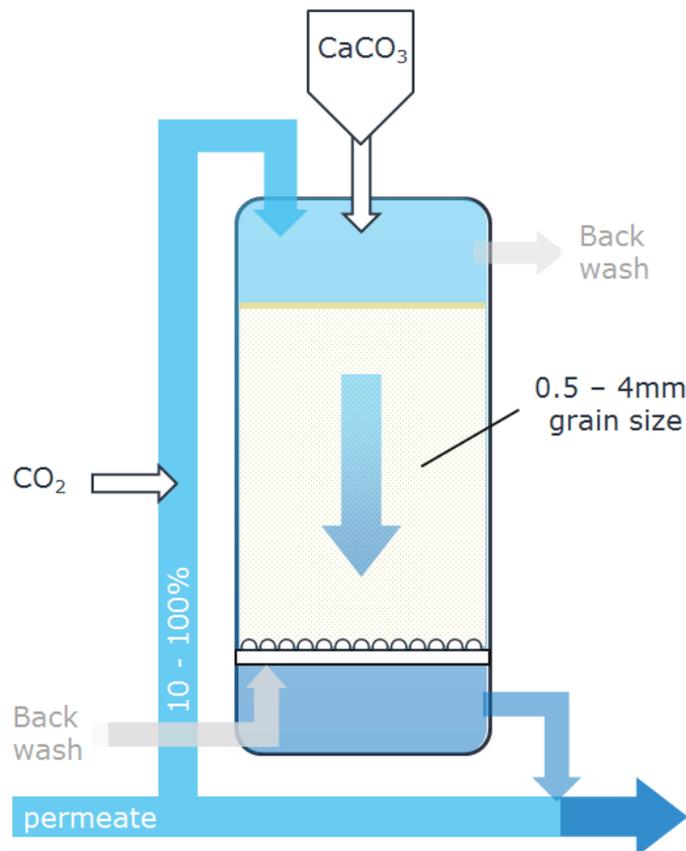


Figure 2: Schematical setup of calcite filtration

Calcite dosing is technology developed by Omya A.G. and investigated by Oasen¹⁵. The principles of the experimental setup are shown in Figure 3. Micronized calcite (grain size of $3\ \mu\text{m}$) is mixed with a small fraction of permeate containing CO_2 . The mixed / dissolved calcite is fed to a reservoir and mixed with a larger fraction of permeate with the possibility of adding additional CO_2 . The mixture passes an ultrafiltration unit.

The permeate of the ultrafiltration unit is mixed with the RO-permeate in order to obtain the desired concentration of dissolved Ca. The concentrate of the ultrafiltration unit is recirculated to the reservoir.

¹⁵ Micronized CaCO_3 slurry injection system for the remineralization of desalinated and fresh water, patent application by Omya Development Ag, WO 2012020056 A1, 2010

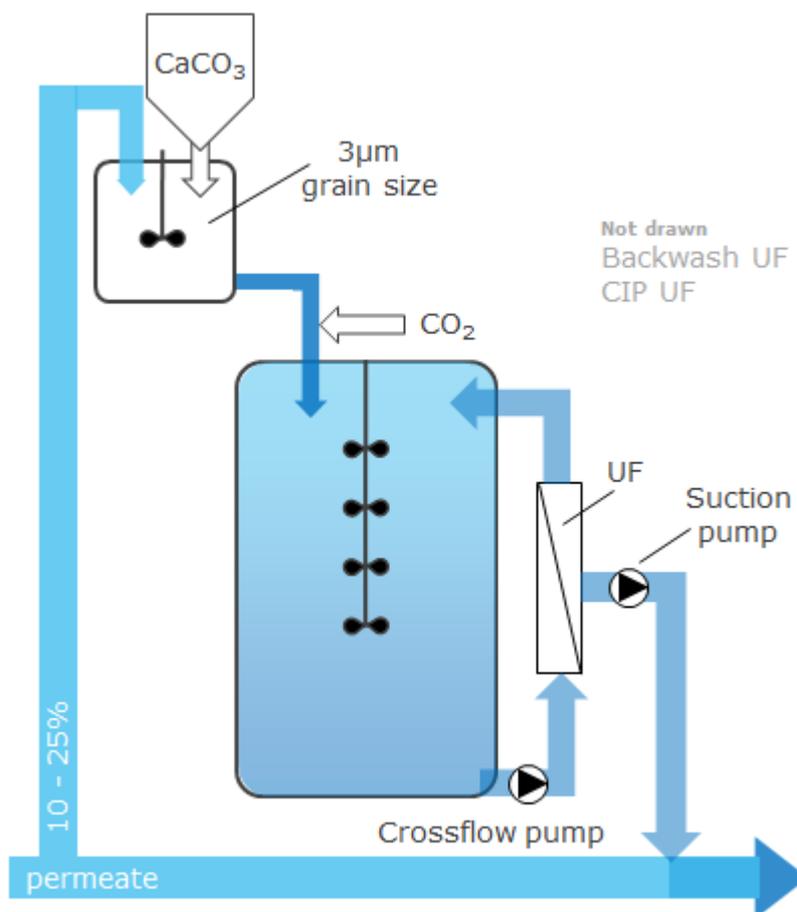


Figure 3: Schematical setup of calcite dosing

Representative operational parameters for all experiments are:

- CO_2 concentration influent: 1 mmol/l
- HCO_3^- concentration influent: 0 mg/l
- HCO_3^- concentration effluent: 2 mmol/l
- Ca concentration effluent: 40 mg/l
- Hardness in effluent: 1 mmol/l
- pH effluent: 8.0 – 8.3

Representative operational parameters differing for the experiments are shown in Table 1.

Table 1: Operational parameters for calcite dosing and calcite filtration

	<i>Calcite filtration</i>	<i>Calcite dosing</i>
Grain size [μm]	500 – 2000	3
Contact time [min]	≈ 20	< 45
Total permeate inflow [m^3/h]	1	2
Filtration velocity [m/h]	< 10	-
Calculated CO_2 efficiency	$> 85\%$	65%
Treated and untreated permeate [%]	100%	25%

5. Results: Experimentally Determined Values of $\text{CCPP}_{\text{test}}$

As a rule of thumb, the experimentally determined threshold of 0.4 mmol/l as a maximum for the calcium precipitation potential has been used¹⁶. Below this value, no excessive calcium scaling is expected. For further reference, the values that have been experimentally determined can be compared with the values of the current treatment plant, shown in Table 2, as well. These values were normalized to a calcium concentration 40 mg/l, since the remineralization has a set point of 1 mmol/l Ca, corresponding to 40 mg/l Ca. In this normalization, it is assumed that $\text{CCPP}_{\text{test}}$ linearly depends on the concentration of calcium. We note that this assumption has not been validated. The normalization was done in order to get an impression of the sensitivity of the observations for the variations in the concentration of calcium. The actual calcium concentrations in the current treatment plant are shown in Table 2 as well.

Table 2: $\text{CCPP}_{\text{test}}$ as determined for conventionally treated water

	2003	2004	2005	2013
$\text{CCPP}_{\text{test}}$ [mmol/l]	0.6	0.32	0.40	0.20
Calcium concentration [mg/l]	38	38	38	26
$\text{CCPP}_{\text{test}}$ normalized [mmol/l]	0.63	0.34	0.42	0.31

In the pilot installations in total 4 types of calcium carbonate have been used, as shown in Table 3.

¹⁶ Berekening van kalk-koolzuurevenwichten in drinkwater, KWR, Nieuwegein, The Netherlands, 2013 (Dutch)

Table 3: Calcium carbonate products used for the determination of $CCPP_{test}$

Name	Grain size	Installation
Juraperle JW [®]	1.0 – 2.0 mm	1
Jura Perle	0.5 – 1.2 mm	2
Akdolit	1.0 – 2.0 mm	2
Micronized Jura Perle	3 μ m	3

The calcium carbonate precipitation potential for four different calcite products is shown in Figure 4. In the first three cases, calcite filtration is employed, in the last case, dosage of micronized calcite is used. The light blue columns show the results. During the test, the calcium concentrations of the blank samples fluctuated a bit. In order to estimate possible effect of these fluctuations, the results have been normalized to a concentration of 1 mmol/l (40 mg/l) calcium, indicated by $CCPP_{test\ normalized}$. Normalized values are depicted with the dark blue columns. It is assumed here as well that $CCPP_{test}$ depends linearly on the concentration of calcium. The red line shows the standard of 0.4 mmol/l, and the grey line indicates the latest results from the current treatment plant. All the test were performed at 11 °C, a contact time of 20 min and a CO_2 concentration in the influent of 1 mmol/l. Only the Akdolit (1-2mm) had slightly different settings with 15 min contact time and a dosage of 1.25 mmol CO_2 .

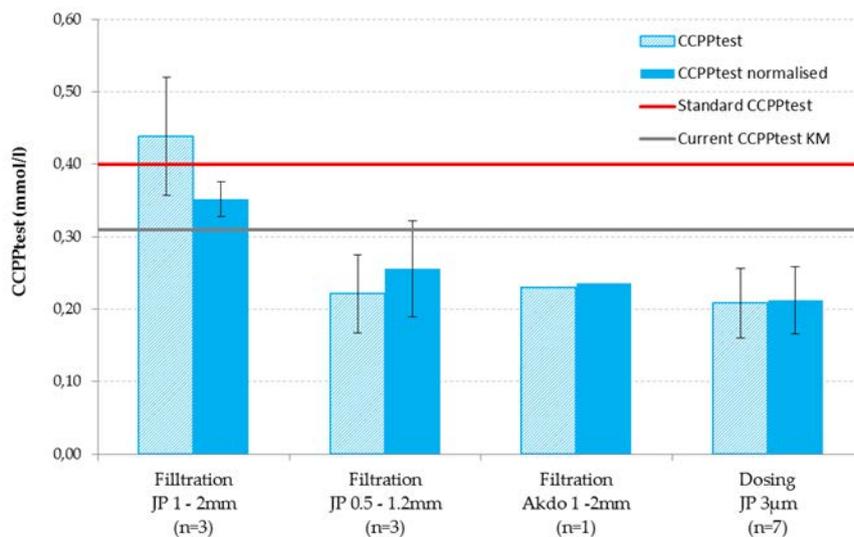


Figure 4: $CCPP_{test}$ determined for different types of calcite filtration and dosing

From these results several observations can be made. First, all values for $CCPP_{\text{test normalized}}$ are below the standard of 0.4 mmol/l. Second, the case with Juraperle 1-2 mm shows highest values (0.35 mmol/l). Third, the other three cases produce rather similar values of $CCPP_{\text{test normalized}}$, between 0.21 and 0.26 mmol/l.

Apparently, already these exploratory results, obtained without extensive experimentation and optimization of the experimental installations, show rather satisfactory results for scaling properties of the treated water.

The higher values for the first case can be explained by the fact that in this situation the backwash has been applied less frequently, and the flow rate and aeration/degasification step was operated manually. Therefore, for this case, the operational performance has been optimized less than for the other cases. The difference in the result of the first case with the other cases indicate that a better operation can improve the $CCPP$ down to approximately 0.20 mmol/l.

6. Conclusion and Further Research

The exploratory results presented in this paper indicate that both technologies investigated may provide a viable option for operational application. The results concern the experimentally determined calcium carbonate scaling potential. The technologies investigated are calcite filtration and calcite dosing.

The exploratory research will be followed by pilot installations on an almost-operational scale. In this manner, we aim to investigate the reproducibility of the results under operational circumstances, as well as the stability of the processes on a larger scale and over a longer period of time. In parallel, we will start laboratory investigations of the process of dissolution of CaCO_3 . These are aimed to be able to explain the results obtained so far as well as future results. For instance, one of the aims is to estimate dissolution rates, in order to determine contact times required to reach equilibrium.

Further research will include the role of MgCO_3 and concern other effluent properties, such as turbidity and particle counts, as well.