

Micronized CaCO₃: a feasible alternative to limestone filtration for conditioning and (re)mineralization of drinking water?

J. C. J. Gude, F. Schoonenberg Kegel, W. J. C. van de Ven, P. J. de Moel, J. Q. J. C. Verberk and J. C. van Dijk

ABSTRACT

Worldwide limestone filtration is used in many treatment plants for the conditioning and (re)mineralization of drinking water to increase concentrations of Ca²⁺ and HCO₃⁻, pH and saturation index, thereby improving the quality of the water regarding corrosion control, buffering and taste. Typical applications include (very) soft groundwater with (very) low alkalinity and desalinated water. In Norway, some plants use a product made of ground natural limestone, called micronized CaCO₃ slurry (MCCS), which is dosed as slurry of fine particles (1–2 µm) into the raw water. In this study the potential of MCCS as an alternative to limestone filtration was investigated. Experiments were performed to determine the dissolution kinetics of MCCS and other CaCO₃-products, including natural limestone grains and two precipitated CaCO₃ powders. As expected from theory, the dissolution kinetics are strongly influenced by the particle size of the CaCO₃ and the driving force towards the chemical equilibrium. However, all CaCO₃-products needed substantial detention times (30 min and more) to dissolve completely. It is concluded that MCCS is generally not a feasible alternative for limestone filtration as a stand-alone option for the conditioning and (re)mineralization of drinking water. Applications of MCCS are limited and should either be found in combinations with coagulation/filtration or with other conditioning and (re)mineralization methods.

Key words | conditioning, dissolution kinetics, limestone filtration, micronized CaCO₃, (re)mineralization

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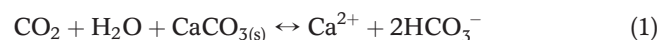
INTRODUCTION

Worldwide limestone (CaCO₃) filtration is used in many treatment plants for the conditioning and (re)mineralization of drinking water (Letterman 1995). The goals are to increase the concentrations of Ca²⁺ and HCO₃⁻, the pH and the saturation index (SI) thereby improving the quality of the water regarding corrosion control, buffering and taste (de Moel *et al.* 2006). Typical fields of application include (very) soft groundwater with (very) low alkalinity and desalinated water. It is expected that in the near future applications will increase as a result of the increasing use of desalination of seawater and brackish water and the increased attention by organizations such as the World Health Organization

(WHO) for the mineral content of drinking water (Cotruvo & Bartram 2009).

In the Dutch drinking water industry, filtration over coarse natural limestone grains (diameter 1–2 mm) is frequently used for the treatment of soft groundwater with low alkalinity.

CO₂, present in groundwater as a result of biological processes in the aquifer, is converted by the limestone to Ca²⁺ and HCO₃⁻, according to the following equation:



Limestone filters are typically operated with an empty

bed contact time (EBCT) of around 30 min. When the groundwater is anaerobic and also contains some Fe²⁺ and Mn²⁺, these compounds can be removed simultaneously in the limestone filter when pretreatment by aeration is applied (in order to provide the O₂ required for the oxidation of Fe²⁺ and Mn²⁺). A typical process scheme of a Dutch groundwater treatment plant using limestone filtration is shown in Figure 1.

In Norway, very soft and slightly acidic surface waters with very low alkalinity, low turbidity and high color due to natural organic matter, are commonly used for the drinking water supply. Some plants use an alternative CaCO₃ product to increase hardness and alkalinity (Osterhus &

Eikebrokk 1994). The product is called micronized CaCO₃ slurry (MCCS). It is also made from natural limestone, but the limestone has been ground to produce fine particles (1–2 μm) with a high specific surface area. It is dosed directly in the raw water as concentrated slurry. A typical treatment scheme is given in Figure 2. Usually, more MCCS is dosed than required according to Reaction (1); the remainder is removed through the backwash water of the (rapid sand) filter. The combination with the coagulation and filtration is essential as it traps the non-dissolved MCCS and prevents a breakthrough of turbidity. Contact times of about 20 min are provided in contact basins before the sand filtration, and/or the supernatant of the filters. Typically some 30 mg/L MCCS (as CaCO₃) is dosed of which 18 mg/L dissolves and 12 mg/L is removed through the backwash water and sludge discharge.

The present study was started to investigate the feasibility of MCCS as a general alternative for limestone filtration in conditioning and (re)mineralization applications. Potential advantages in the typical Dutch groundwater application might be either lower costs (in case MCCS could be used to replace limestone filters) or better water quality (in case MCCS could be used to convert

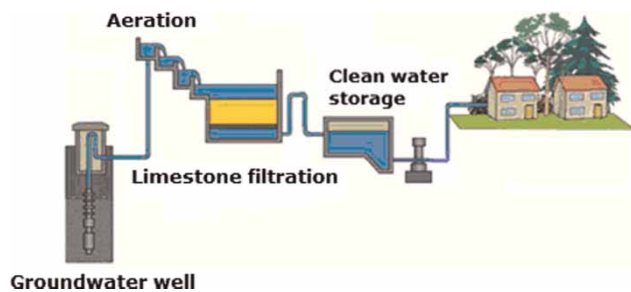


Figure 1 | Typical Dutch groundwater treatment plant for very soft water.

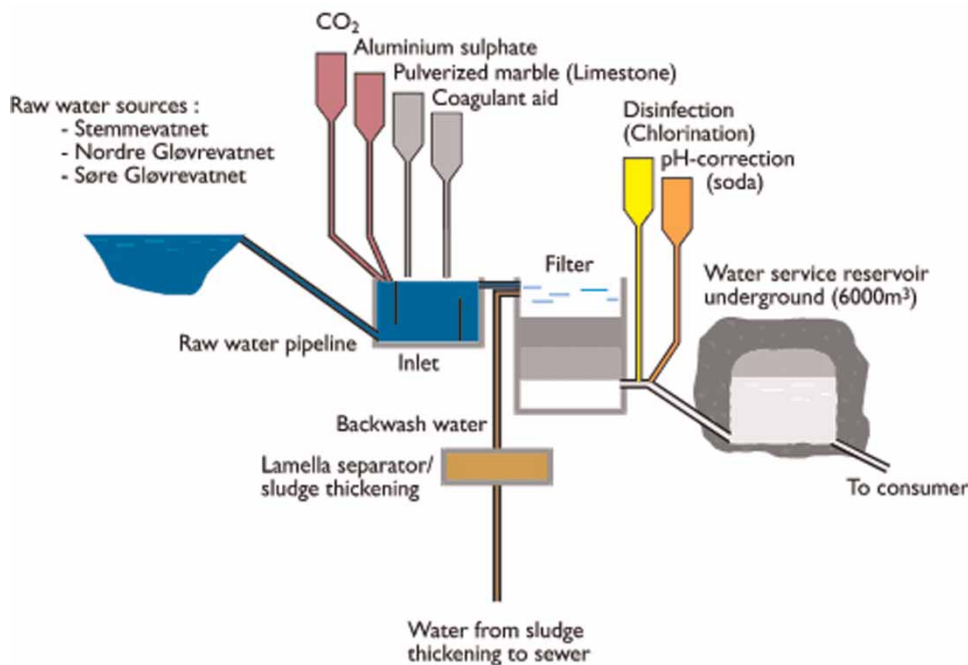


Figure 2 | Treatment scheme of a treatment plant using MCCS in Bergen city (Bergen Vann 2008).

CO₂ directly in the raw water, preventing its escape to the air during the aeration process). Also, no extensive infrastructure is needed for implementation, just a dosing pump and a storage silo. The increase in pH and HCO₃⁻ concentration in the raw water could be beneficial for the iron and manganese removal.

However, it was considered that an essential aspect for the feasibility in processes without coagulation/filtration would obviously be the detention time required to dissolve the MCCS completely. Otherwise, non-dissolved MCCS particles could end up in the clear drinking water, increasing the turbidity and sediment load on the clear water tank and distribution system. The focus in this research is therefore on completely dissolving CaCO₃ in a limited time.

Dissolution kinetics of CaCO₃

In the last 40 years most research on CaCO₃ dissolution mechanisms was carried out by geochemists and oceanologists (Plummer *et al.* 1978; Chou *et al.* 1989; Svensson & Dreybrodt 1992; Dreybrodt *et al.* 1996; Morse *et al.* 2002) as calcite dissolution plays a major part in the origin of landscapes and marine sediments.

The most commonly used model to describe the dissolution of calcite is given by Plummer *et al.* (1978). Their PWP-model is used as a standard in modeling environments such as PHREEQC (Parkhurst & Appelo 1999). Close to chemical equilibrium reaction rates can drop dramatically depending on the purity of the mineral and the presence of foreign ions and organic matter (Vosbeck 2004). For better understanding of the reaction mechanisms close to equilibrium, research has shifted from measuring bulk concentrations to direct observation of the mineral surface using techniques such as atomic force microscopy. This research showed that the actual dissolution occurs on edges on the mineral surface. Far from equilibrium new edges can be easily created but close to equilibrium the chemical driving force is too limited to create new edges. These active pits can be closed by inhibitors causing reaction rates to drop dramatically. Organic matter, phosphate and metal cations, with a carbonate solubility less than calcite (e.g. Pb, Cd, Cu, Zn, Fe and Mn), are the most effective inhibitors of calcite dissolution (Lea *et al.* 2001).

The general rate for CaCO₃ dissolution is given in Equation (2):

$$dC = R \cdot \frac{A}{V} \cdot dt \quad (2)$$

where dC = concentration change (mol/m³); A = surface area of CaCO₃ (m²); V = volume of water (m³); R = dissolution rate (mol/m²/s); dt = detention time (s).

The dissolution rate R depends on the chemical driving force. Previously mentioned researchers have developed different models for this chemical driving force. In general, the driving force can be recalculated in the form of $(1 - \Omega) = (1 - \{Ca^{2+}\} \cdot \{CO_3^{2-}\} / K_s) = (1 - 10^{SI})$ in which K_s is the solubility product of CaCO₃. The chemical driving force therefore depends on the SI. As a result of the dissolution reaction, pH, Ca²⁺ and CO₃²⁻ will increase and the chemical driving force will slowly reduce to zero (SI = 0). The dissolution rate R can now be described as $R = \text{factor} \cdot (1 - 10^{SI})$ in which the factor depends on temperature, water quality parameter(s) and researcher.

Depending on the raw water quality, a certain amount of CaCO₃ can be dissolved until chemical equilibrium is reached; this amount is called the calcite dissolution potential (CDP), referring to calcite as its most relevant crystalline form. Elsewhere this might be referred to as its opposite equivalent parameter calcium carbonate precipitation potential (CCPP).

The reaction rate consequently depends primarily on two factors, i.e. the chemical driving force and the specific surface area A/V . High A/V ratios obviously increase reaction rates.

For limestone filters the A/V ratio can be calculated using Equation (3), in which p = porosity of the filter bed [-], and d is the diameter of the limestone particles [m]:

$$\frac{A}{V} = \frac{6 \cdot (1 - p)}{d} \quad (3)$$

A/V ratios for common limestone grain sizes are shown in Table 1.

For the A/V ratios in Table 1 dissolution rates can be calculated in PHREEQC using the PWP-model. Figure 3 shows the dissolution of calcite in a limestone filter for the

Table 1 | A/V ratios for three grains sizes of limestone in a filter bed with porosity 0.4

Diameter (mm)	A/V (m ⁻¹)
2	1,800
1	3,600
0.5	7,200

three different grains sizes. The smallest grains result in a higher dissolution rate and consequently shorter contact times. The raw water quality was 0.5 mmol/L Ca(HCO₃)₂. The CDP was set at 0.6 mmol/L by calculated amounts of NaHCO₃ and HCl (pH = 6.6).

Figure 3 shows that detention times of around 600 s or 10 min are required to approach the equilibrium. As the porosity of a limestone filter is 0.4, this is equivalent to an EBCT of 10/0.4 = 25 min, which corresponds to actual design and operational experiences of limestone filters in drinking water treatment plants (bed height 2 m, filtration rate 4.8 m/h).

In cases where suspended particles are dosed such as MCCS or calcite powder, the A/V ratio depends not only on the particle size, but also on the dose and the specific gravity of the particles, in accordance with Equation (4):

$$\frac{A}{V} = \frac{6}{d} \cdot \frac{\text{dose}}{\text{specific gravity}} \quad (4)$$

As the dose is in the order of 60 g/m³ (0.6 mmol/L) and the specific gravity of calcite is 2,700 kg/m³, particles sizes

must be very small to reach A/V ratios similar to a limestone filter. Table 2 shows the required diameter of calcite particles to reach the same A/V ratios as for the limestone filters of Table 1. Moreover, it should be noted that during dissolution of calcite particles the A/V ratio drops to zero.

The dissolution rates with the A/V ratios of Table 2 are shown in Figure 4, using the same CDP as Figure 3.

Figure 4 shows that detention times of around 1,400 s or 23 min are required to approach equilibrium. As the MCCS solution is much diluted, the required EBCT for the contact tank is in this case also equal to 23 min.

So, surprisingly, theoretically about the same EBCT may result for two completely different designs, filtration through a bed of coarse grains and a dissolution reactor/contact tank with very fine particles.

The goal of this research project was therefore to develop a simple test method and to use it to determine experimentally the actual required dissolution times for different CaCO₃-products. The complete range of CaCO₃-products was tested in order to obtain a complete overview of the feasibility of the different alternatives including:

1. Coarse limestone grains (Aquatechnik, Juraperle, $d_{\text{mean}} = 1.6$ mm)
2. MCCS as used in Norway (Yara, $d_{\text{mean}} = 0.8$ μm)
3. Precipitated calcite powder (NanoPCC) (Solvay, $d_{\text{mean}} = 0.088$ μm)
4. Heyer calcite powder (Laboratory grade, diameter unspecified)

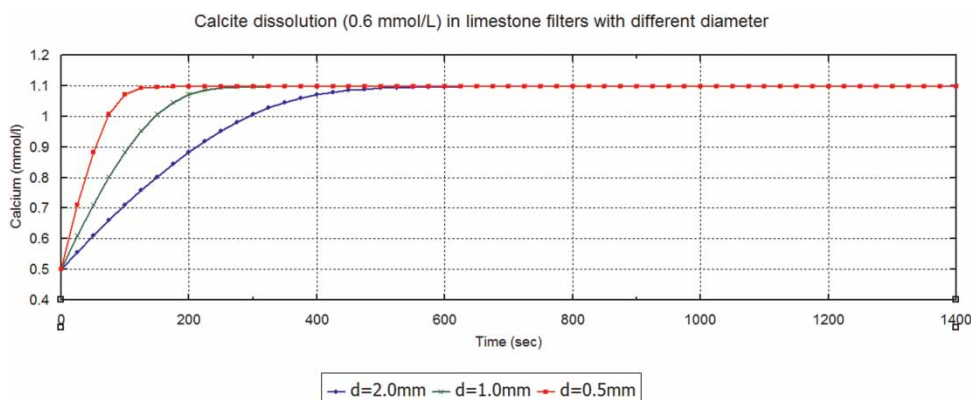
**Figure 3** | Runs with PWP-model with different A/V ratios similar to limestone filtration. A/V ratios conforming limestone diameters of 0.5, 1.0 and 2.0 mm with a filter bed porosity of 0.4.

Table 2 | A/V ratios for a dose of 0.6 mmol/L

Diameter (μm)	A/V (m ⁻¹)
0.08	1,800
0.04	3,600
0.02	7,200

MATERIALS AND METHODS

Samples and sample preparation

The limestone grains were obtained from Aquatechniek (Juraperle). They had a diameter range of 1.4 to 1.8 mm and are commonly used in limestone filters in the Netherlands.

The MCCS was obtained from Yara Norge AS, Industrial Products. The MCCS consists of 77–79 weight % CaCO₃, with negligible impurities and 21–23% water. The MCCS has a particle size distribution of <2 μm: 87–93%, <1 μm: 61–67%, with $d_{\text{mean}} = 0.8 \mu\text{m}$. This is confirmed by the SEM picture in Figure 5 where both small and large particles are seen. For accurate dosing the product was diluted 20 times by adding 19 mL pure water to 1 mL MCCS.

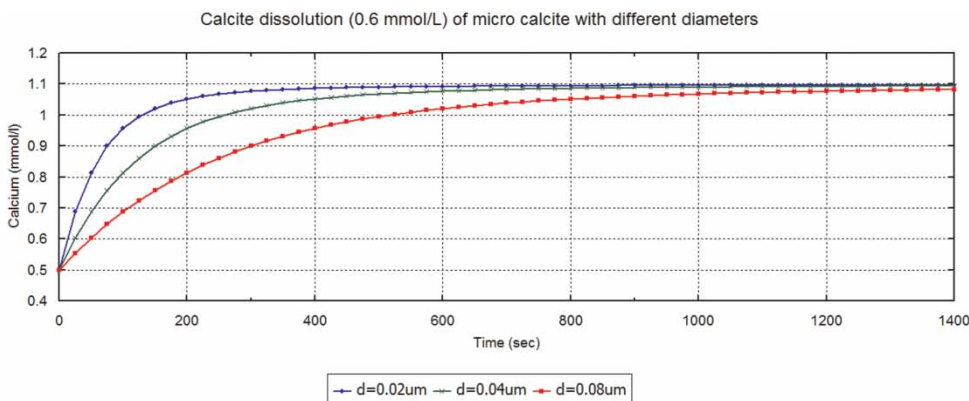
The two precipitated CaCO₃ products were obtained from two different manufacturers. The PCC was uncoated calcite, cube-like and with a mean particle size of 0.088 μm. The powder was received from Solvay GMBH. The other CaCO₃ powder (Heyer) was obtained from the laboratory and is defined as 100% pure calcium carbonate. This powder is used to determine the CDP in laboratories.

The sample water was prepared from stock solutions of CaCl₂, NaHCO₃ and HCl in batches of 10 L demineralized water. Concentrations were chosen to resemble Dutch soft ground water and to obtain the desired CDP. The actual water quality was determined in the Vitens laboratory where samples were analyzed in accordance with NEN and ISO standards for conductivity, Ca²⁺, Cl⁻, Na⁺, HCO₃⁻ and pH.

Experimental setup

The experiments were carried out in jars stirred with a propeller (500 rpm) to keep the CaCO₃ product in suspension. The solution was contained in a beaker glass with a volume of 2.0 L, such that little space was available for air. The beaker glass was sealed airtight, to simulate a closed system.

The experiment was started by filling the beaker with the prepared solution; the temperature of the solution was kept constant to a room temperature of $20 \pm 1 \text{ }^\circ\text{C}$ during all runs. After filling the beaker, a precisely measured amount of CaCO₃ was introduced and the beaker glass was then directly sealed using plastic foil and the stirrer was switched on. An increase of conductivity was always observed and measured as a function of time (WTW cond340i). The measurements were stored on a data logger (Endress + Hauser) at an interval of 3 s. As the increase in conductivity is directly related to the dissolution of CaCO₃, the conductivity can be used to describe the dissolution kinetics. The relation between Ca²⁺ and conductivity can be calculated using PHREEQC. For the

**Figure 4** | Runs with PWP-model with different grain sizes of calcite particles. A/V ratios get smaller during dissolution. Chemical equilibrium is reached at calcium 1.1 mmol/L.

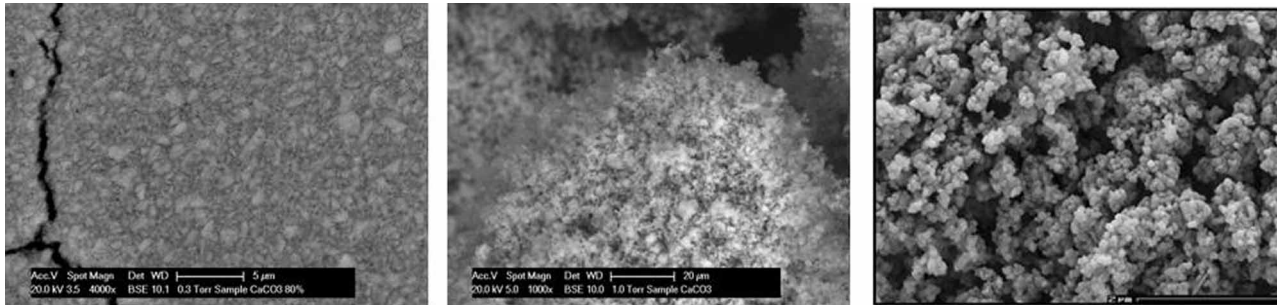


Figure 5 | SEM pictures: left: MCCS, scale 5 µm; centre: Heyer, scale 20 µm; right: PCC, scale 2 µm.

low ionic strength in the range of these experiments the relationship is linear.

RESULTS AND DISCUSSION

All compared experiments were tested with the same batch of water, thereby eliminating dosing errors. Since CO₂ levels are higher than equilibrium at atmospheric pressure a small loss of CO₂ is inevitable, but runs were maximized to 1 h to limit this effect.

Influence particle size (types of CaCO₃ products)

From theory and literature it is well known that kinetics become very slow when the chemical driving force approaches zero. To avoid this the amount of CaCO₃-products dosed was limited to 90% of the CDP of the water. The water quality for this experiment was NaHCO₃ 1.67 mmol/L, CaCl₂ 0.425 mmol/L and HCl 0.65 mmol/L. This results in a CDP of about 0.56 mmol/L CaCO₃. The CaCO₃ dosage for all samples was set at 0.5 mmol/L, see Figure 6.

Figure 6 clearly shows that the dissolution rate of Juraperle is very slow. This is in conformity with the large grain size and consequently the small *A/V*. It should be noted that in this experiment Juraperle was not used as a limestone filter reactor but, similar to the other CaCO₃ products, as a dissolution reactor/contact tank with a very low amount of particles, equivalent to a dose of 0.5 mmol/L.

Of the three other CaCO₃ products MCCS requires the longest dissolution time. It is noted that the initial dissolution rate of MCCS is the highest, but it slows down significantly. This can be explained by the large particle

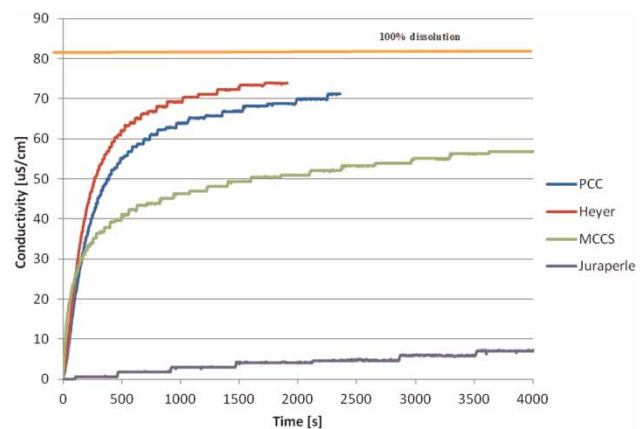


Figure 6 | Dissolution of different CaCO₃ products; lines from top to bottom: Heyer – PCC – MCCS – Juraperle

size distribution of the MCCS. It contains very fine particles which react fast, but also a significant fraction of particles in the order of 1 µm and above which react slowly.

PCC dissolves much more quickly, which is logical as the particles are even finer (order of 0.1 µm). The Heyer powder proved even more reactive than the PCC. Therefore, it appears that the particle size of the laboratory grade Heyer powder is even smaller than the commercial PCC product.

Influence dose of CaCO₃

As stated before, the reaction rate depends strongly on the chemical driving force, so the dissolution time is expected to be lower when less CaCO₃ is dosed in comparison to the CDP of the water. This was tested for the Heyer powder, which reacted the fastest. Doses of 100, 75 and 50% of the CDP were added to the samples. Water quality for this experiment was NaHCO₃ 1.67 mmol/L, CaCl₂

0.425 mmol/L and HCl 0.67 mmol/L, derived from laboratory analyses of Na, Ca, Cl, alkalinity and pH. This quality results in a CDP of 0.575 mmol/L. The CaCO₃ dosage was 0.3 mmol/L, 0.45 mmol/L and 0.6 mmol/L.

Figure 7 clearly shows that it is impossible to obtain the chemical equilibrium in acceptable contact times. At the dose of 100% of the CDP, even in 3,000 s (50 min) still less than 80% of the particles dissolved. The result is that many non-dissolved particles were still present in the sample, which had a turbidity of 28 NTU. This is a serious drawback for applications in practice.

Lower dosages seem somewhat more practical. As shown in Figure 7 when dosing 50% of the CDP capacity, some 90% of the dose is dissolved in 600 s (10 min), the dosage results in a turbidity of 1 NTU at the end of the run. When dosing 75% of the CDP, some 90% of the dose dissolved in 900 s (15 min), which led to a turbidity of around 8 NTU.

PHREEQC model results

For the Heyer dissolution experiment PWP-model calculations were performed to relate the experimental results with theoretical calculations. A uniform particle size distribution of 0.3, 0.1, 0.075, 0.05, 0.03 μm was used as the model input. The model was fitted on the Heyer 50% line with a dose of 0.3 mmol/L. For the Heyer 75% and Heyer 100% lines the calcite dosage was increased to 0.45 and 0.6 mmol/L using the same uniform particle size distribution.

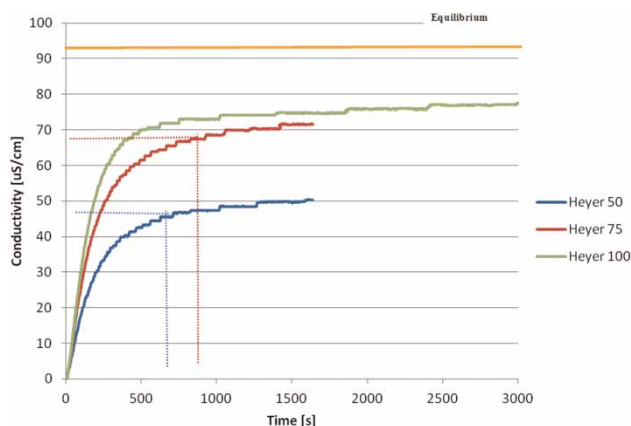


Figure 7 | Dissolution of Heyer powder in the same batch of water with different dosages; lines from bottom to top: 50% – 75% – 100% of the CDP. The horizontal line indicates the chemical equilibrium (CDP) of 0.575 mmol/L.

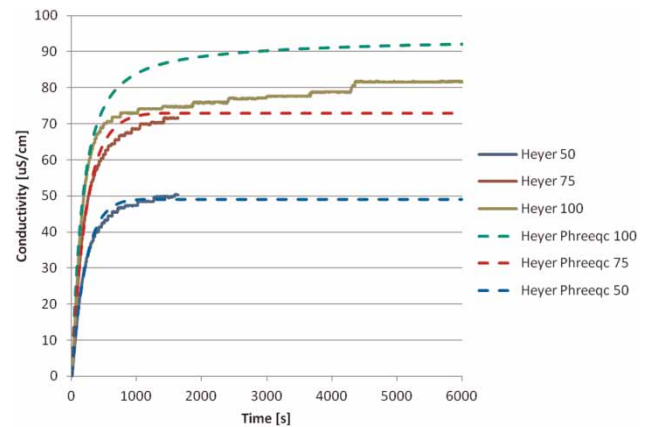


Figure 8 | PWP-model calculations compared with experimental results.

Figure 8 shows the experimental results and the PWP-modeling gives similar results for the 50% dose. For the higher doses the initial reaction rates in the experiments are also similar to the model output, but they drop to lower values after some time. This can be explained as it is known from the literature that close to the chemical equilibrium dissolution rates are difficult to model correctly using the PWP-model.

CONCLUSIONS

Experimental results

As known from theory and literature, the dissolution kinetics of CaCO₃ depend on the chemical driving force and the available specific surface area A/V . The experimental setup proved a suitable tool to test the actual required dissolution time for different products and different dosed CaCO₃. As it is known that the dissolution process can be inhibited by foreign ions and organic compounds, the experimental setup can be used to test concrete applications in practice.

The influence of specific surface area A/V was clearly shown from the experiments with different CaCO₃ products with particle size ranging from 1.6 mm down to 0.1 μm and below. The products showed different reaction rates that were clearly related to the particle size and consequently specific surface area A/V . The dissolution rate of Juraperle was very slow, which is in conformity with the large grain size ($d_{\text{mean}} = 1.6 \text{ mm}$) and consequently low A/V . Of the

three other CaCO₃ products, MCCS required the longest dissolution time. It is noted that the initial dissolution rate of MCCS is the highest, but it slows down significantly. This can be explained by the large particle size distribution of the MCCS. It contains very fine particles which react quickly, but also a significant fraction of particles in the order of 1 µm and above which react slowly.

PCC dissolved even quicker, which is logical as these particles are the even finer (order of 0.1 µm). The Heyer powder proved even more reactive than the PCC, so apparently the particle size of this laboratory grade powder was even smaller than the commercial PCC-product.

The influence of the chemical driving force was clearly shown from the experiments with different doses of CaCO₃. The dissolution time was confirmed to be depending on the dose as compared to the CDP. At a dose of 100% of the CDP, even in 3,000 s (50 min) still less than 80% of the particles dissolved. The result is that many non-dissolved particles were still present in the sample, which had a turbidity of 28 NTU. This is a serious drawback for applications in practice.

Lower dosages seem somewhat more practical. When dosing 50% of the CDP, some 90% of the dose is dissolved in 600 s (10 min), which led to a turbidity of around 1 NTU. When dosing 75% of the CDP, some 90% of the dose dissolved in 900 s (15 min), which led to a turbidity of around 8 NTU.

Practical applications

The overall conclusion for practical applications is that it is impossible to dissolve the powdered CaCO₃ products (currently on the market) completely in a contact tank within acceptable contact times (less than 30 min), when applying a dose equal to the CDP. Part of the CaCO₃ particles will always remain in suspension, which has a detrimental impact on the turbidity and sediment load to clear water tanks and the distribution system. One might speculate that in future it may be possible to develop CaCO₃ powders with significantly smaller particle sizes than 0.1 µm; at that time this conclusion might be reconsidered.

Consequently, it should also be concluded that it is not feasible to apply dosing of powdered CaCO₃ as a standalone alternative to limestone filtration. With limestone filtration

the grains do not need to dissolve completely and nearly complete removal of the CDP can be approached with an EBCT of around 30 min, as is well known from practical experience.

Are there any other applications in the drinking water field that might be more promising for the application of the powdered products? Based on the results of this research we can indicate a few as discussed below.

Doses higher than CDP

In Norway more MCCS is dosed than the CDP to enhance the reaction kinetics. The excess suspended MCCS leads to a higher A/V , enhances the kinetics and is retained by coagulation and filtration in dual media filters with sand and anthracite. The operational results are satisfactory so it can be concluded that this setup is feasible. It must be noted that in this setup the coagulation and filtration steps are essential, as was found from pilot-plant tests in a groundwater pilot installation in the Netherlands. We dosed MCCS to the raw groundwater after which the water was aerated and given contact times of 30 min in a contact pipe and the filter column. The raw water contained 1 mg/l Fe²⁺, which was nearly completely removed in the filter column. This set-up resulted in turbidity levels of >30 NTU. Therefore, apparently the sand-anthracite filter did not retain the excess MCCS without the intensive coagulation.

As the A/V in these applications is highly dependent on the dose/concentration of CaCO₃ (see Equation (4)), an alternative concept might be to further increase A/V by increasing the concentration of CaCO₃ in a system applying recirculation of sludge/CaCO₃. This could either be done in sludge contact clarifiers followed by sand or dual media filters or in a setup with ultrafiltration of microfiltration membranes and recirculation of the sludge/CaCO₃.

Doses lower than CDP

Applying doses lower than the CDP has the advantage of operating under a remaining driving force as equilibrium is never reached. As shown in this research it is possible to remove about 75% of CDP within 30 min by dosing MCCS. Therefore, it may be an option to use powdered CaCO₃ to remove the bulk of the CDP and to remove the remainder of the CDP by using other conditioning methods

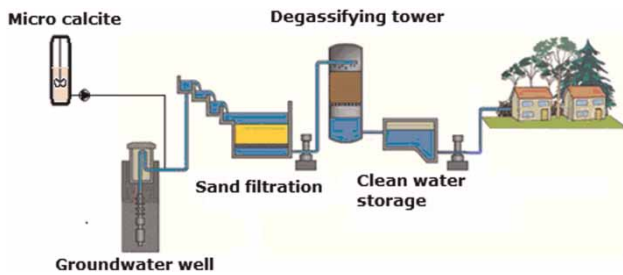


Figure 9 | Possible set-up for a groundwater treatment plant using powdered CaCO₃.

such as dosing of chemicals such as NaOH or using a degassingifying tower to remove the remainder of the CO₂. Possible options for this type of combined applications are:

- Desalinated water (permeate/distillate): Desalinated water, both from thermal and membrane processes, could be partially remineralized by powdered CaCO₃. As RO-permeate already contains excess CO₂ this will react with the CaCO₃ and the remainder could be removed in a degassingifying tower or by dosing NaOH for final pH correction.
- (Very) soft groundwater with (very) low alkalinity: Powdered CaCO₃ might be dosed to the raw water, leading to advantages of converting CO₂ into HCO₃⁻ and increasing the pH before the conventional aeration and filtration process. However, final conditioning and pH correction to chemical equilibrium should be provided by other methods, such as limestone filtration, NaOH dosing or using degassingifying towers. Figure 9 shows the possible set-up for a groundwater treatment plant with this concept.

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