Method for an accelerated reproducible calcite-layering of potable water systems to validate decalcification procedures

Aylin Höckendorf, Klaus Johannsen, Thorsten Dorsch, Matthias Reiß, Sebastian Flashaar, Ole Becker and Bernd Bendinger

ABSTRACT

This article describes a method for an accelerated, controlled and reproducible build-up of limescale in potable water systems. The concept of this method is to systematically generate water with a high calcium carbonate precipitation potential (CCPP) by CO_2-enrichment, hardening with $CaCO_3$ followed by CO_2-desorption. Water with a CCPP of about 100 mg/L $CaCO_3$ led to the intended calcification on inner steel tube surfaces in a simplified test plant. The limescale built-up was performed at ambient temperature. The procedure is an enabler for validation, verification and comparison of both the efficiency of decalcification methods, as well as scale-preventing methods under comparable and defined conditions. An economical and time efficient calcification method has been developed that provides solid calcite deposits of reproducible thickness and characteristics. The method can be used for studies with all water-carrying systems in household, public transportation or industrial applications.

Key words | calcification, calcium carbonate precipitation potential, decalcification, drinking water, limescale, scaling

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INTRODUCTION

Limescale of potable water installations in both household and industrial applications presents an omnipresent burden worldwide. According to published estimates, the economic impact of limescale on the total industrialized world, including domestic, commercial and industrial processes, adds up to about US$ 27 billion. For the UK such an impact was estimated to reach US$ 700–930 million, for the USA US$ 8,000–10,000 million and for Japan US$ 3,062 million, respectively (MacAdam & Parsons 2004a). This significant economic impact of limescale derives from increased energy costs for warm water production due to an inefficient heat transfer to water. Other consequences of limescale can be reduced flow rates in pipes for drinking water distribution, fouling in membrane filtration for water treatment, inevitable descaling measures and reduced life time of machines and electrical devices in contact with water. Limescale build-up is also a cost driver for the aviation industry. In particular, water-carrying electrical consumers connected to the potable water system of an aircraft are affected. As a result of limescale build-up, time consuming and extensive maintenance procedures with a significant cost impact are necessary to overcome this issue.

Water hardness is a key factor in limescale formation. The water hardness depends on the geographic region of the origin of the water as well as any potential treatment of the water prior to its use. Classification of hardness is arbitrary. Water with calcium carbonate ($CaCO_3$) content of up to 100 mg/L (2.5 mmol/L) can be considered as soft to moderately soft, water with 100–250 mg/L (2.5–6.25 mmol/L) $CaCO_3$ as slightly to moderately hard, and

water with $CaCO_3$ concentration above 250 mg/L as hard to very hard (Gray 1994). An option for the reduction of water hardness is softening. A cost-benefit analysis of central softening in a region with hard water (4.7 mmol/L Ca^{2+} or 47 French degrees of water hardness, °F) in Flanders, Belgium revealed benefits for customers which were higher than the costs for the water utility. When the water is softened from 4.7 to 1.5 mmol/L Ca^{2+} (equals 47 to 15°F) estimated savings were in the order of 82 € per year for an average family (2.8 persons per family and an average water consumption of 115 L per person per day). A conclusion of this case study was that softening is beneficial if water hardness is decreased by at least 0.5 mmol/L Ca^{2+} (equals 5°F) (Van der Bruggen *et al.* 2009). The results from a life cycle assessment of the environmental impacts of central softening of drinking water in an area with very hard drinking water (Copenhagen, Denmark) indicated a softening depth of only 22 mg/L $CaCO_3$ (equals 0.22 mmol/L $CaCO_3$ or 2.2°F) as the environmental break-even point where central softening became overall beneficial from an environmental point of view (Godskesen *et al.* 2012). According to Hesse *et al.* (2004), central softening (reduction by 0.53 to 0.71 mmol/L Ca^{2+} (equals 5.3–7.1°F or 3–4 German degrees of water hardness, °dH) down to 0.36 mmol/L Ca^{2+} (equals 3.6°F or 2°dH) can save costs for a household with a consumption of 110 m^3/year of around 0.5–0.6 €/m^3. The total savings of 55–66 € per year are in the same range as the estimate by Van der Bruggen *et al.* (2009). These cost savings are expected to be even higher in the aviation industry due to high maintenance/down-time costs for civil airplanes. However, in contrast with the process water, hardness is sometimes considered to be an essential in drinking water as a source of minerals (WHO 2009). Furthermore, water with low alkalinity (which is generally related with low hardness) can have negative effects on metal corrosion (DIN EN 12502-1 2005).

The theoretical parameter that determines the potential of water to form limescale is the calcium carbonate precipitation potential (CCPP). This is a calculation of the calcium and carbonic acid equilibrium point considering water hardness, content of inorganic carbon, pH value and temperature. The CCPP is defined to be zero when the ion activity product (IAP) of calcium and carbonate is equal to the solubility product of calcite ($CaCO_3$). When the IAP is smaller than the solubility product the water is considered calcite solubilising. When the IAP is greater than the solubility product, the water is considered calcite precipitating (supersaturated). Since the solubility of calcite in water decreases with increasing temperature, the CCPP increases. Müller-Steinhagen (2000) noted that at temperatures above 60°C the CCPP increases significantly.

However, the actual limescale built-up does not depend on the CCPP alone but is influenced by many other parameters such as hydrodynamic conditions and surface material type and its roughness (MacAdam & Parsons 2004a). In addition, the precipitation rate of calcite increases with increasing particle concentration (available sites for nucleation) and natural organic matter may act as an inhibiting agent (Van der Bruggen *et al.* 2009).

The level of calcification by a provided test water is difficult to predict. Little information about precipitation potentials resulting in scale formation can be found in the literature and are mostly associated with heating of the water. In Germany a testing procedure for the evaluation of the effectiveness of water conditioning devices for the diminution of scaling has been developed (DVGW code of practice W 512 1996). This procedure recommends a CCPP of at least 30 mg/L $CaCO_3$ (calculated for 15°C) in order to achieve calcite scales in experiments. Van der Bruggen *et al.* (2009) stated that a calcite scaling can be expected to occur at 90°C if the CCPP (theoretical calcium carbonate scaling potential at 90°C; in Dutch: 'Theoretische Afzetbaar Calciumcarbonaat bij 90°C, $TACC_{90}$') is higher than 60 mg/L $CaCO_3$ or 6°F. In contrast to theoretical calculations of the precipitation potential, a method developed in the Netherlands determines the practical concentration of $CaCO_3$ that precipitates after boiling of the water (in Dutch: 'Praktjk Afgezette Calciumcabonaat, PACC'). If the PACC is above 100 mg/L $CaCO_3$ or 10°F the calcite scaling during water use for domestic purposes is so pronounced that water softening is recommended (Van der Bruggen *et al.* 2009).

Currently, no appropriate method is available that can be applied to simulate limescale build-up in a close-to-practice water system at ambient temperature in order to validate the design of equipment or maintenance procedures such as decalcification with acid solutions. Hence, it remains difficult to evaluate and compare different decalcification procedures. Common procedures include the definition of

dedicated test waters to induce precipitation of calcite (Stuyven *et al.* 2009). However, due to the difference in water qualities at different locations, it is barely possible to create a reproducible effect in calcite precipitation, especially if only limited numbers of chemical parameters are controlled during the test. Furthermore, this approach postulates the use of initially hard water, i.e. water containing large amounts of alkaline minerals and carbonate. If this is not available on-site, this water needs to be imported to the test facility, which increases the cost of such a test setup.

Several studies about prevention of calcite scaling used artificial hard water. This was produced by mixing equimolar amounts of calcium (e.g. $CaCl_2$) and carbonate (e.g. $NaHCO_3$ or $NaCO_3$) in the form of solutions (Chibowski *et al.* 2003; MacAdam & Parsons 2004b; Cheong *et al.* 2013) or powders (Tijing *et al.* 2011) shortly before the experiment. A disadvantage of this procedure for large scale application is the handling of concentrated solutions or powders of chemicals and accuracy with their appropriate dosage. Furthermore, only limited volumes of test water can be produced for batch tests. A major drawback of the resulting test water is the fact that it reflects no natural water-chemical conditions, which in turn affects the characteristics of the limescale. Most natural waters contain two hydrogencarbonate ions per calcium ion. When mixing a calcium solution (e.g. as calcium chloride) and a bicarbonate solution (e.g. as sodium bicarbonate), the respective counter ions are solved in unnatural concentrations in the test water, whereby the ionic strength is increased to unnaturally high values. In order to avoid any side effect of foreign ions, Fathi *et al.* (2006) produced hard water by dissolving $CaCO_3$ in water by inducing CO_2 gas bubbles for one day. Different water qualities with defined degrees of supersaturation were obtained by pH shifts to defined levels after desorption of CO_2 by strong stirring of the water. The precipitation of calcite from the water with high CCPP was mostly induced by an increase of the temperature (up to 85 °C) (Chibowski *et al.* 2003; MacAdam & Parsons 2004b; Tijing *et al.* 2011; Cheong *et al.* 2013) or by stripping of CO_2 with nitrogen gas bubbles distributed through a diffuser (Fathi *et al.* 2006).

The objective of this study was to develop a method for a defined and close-to-natural calcite-layering, which can be applied by any manufacturer worldwide under similar boundary conditions, independently from the local water supply parameters. This method shall be reliable and reproducible in order to compare the results across different locations, manufacturers and systems. Moreover, it is crucial that the test can be performed in a time-efficient and economical manner to reduce test effort and thereby ensuring acceptance throughout the industry.

In addition, a standardized reproducible degree of calcification should be achieved in order to be able to compare further descaling or preventive measures avoiding limestone formation, or to achieve a controlled calcification to investigate the effects of calcification on, for example, electrical appliances.

METHODS

Generation of hard water

One possibility to solve larger amounts of calcium with bicarbonate as a counter ion is the reaction of carbonated water with calcium carbonate (Equation (1)) along the lines of nature. In nature, the essential source for hardness is dissolving carbonate rocks (e.g. limestone, marble or dolomite) in carbonated groundwater to form bicarbonate ions (HCO_3^-). Here, calcium and bicarbonate are dissolved in a stoichiometric ratio:

$$CO_2 + H_2O + CaCO_3(s) \leftrightarrows Ca^{2+} + 2HCO_3^- \qquad (1)$$
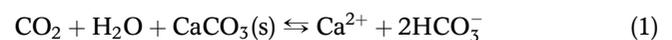
In this work a calcification facility was constructed inspired by the above-mentioned natural reaction. Figure 1 shows a scheme of the calcification plant for the generation of supersaturated water and production of solid calcite deposits in stainless steel pipes. Figure 2 (left) shows a photograph of the plant. In a first step, water was enriched with CO_2 for subsequent dissolving of $CaCO_3$. Therefore, a gassing column (height 3.5 m, diameter 10 cm) was flowed through from top to bottom with potable water taken from local premise plumbing of Hamburg University of Technology (TUHH) at a rate of 40 L/h. At the bottom of the column CO_2 streamed in via a porous stone (microporous filter cartridge, 13×22 mm, porosity 2) and dissolved in
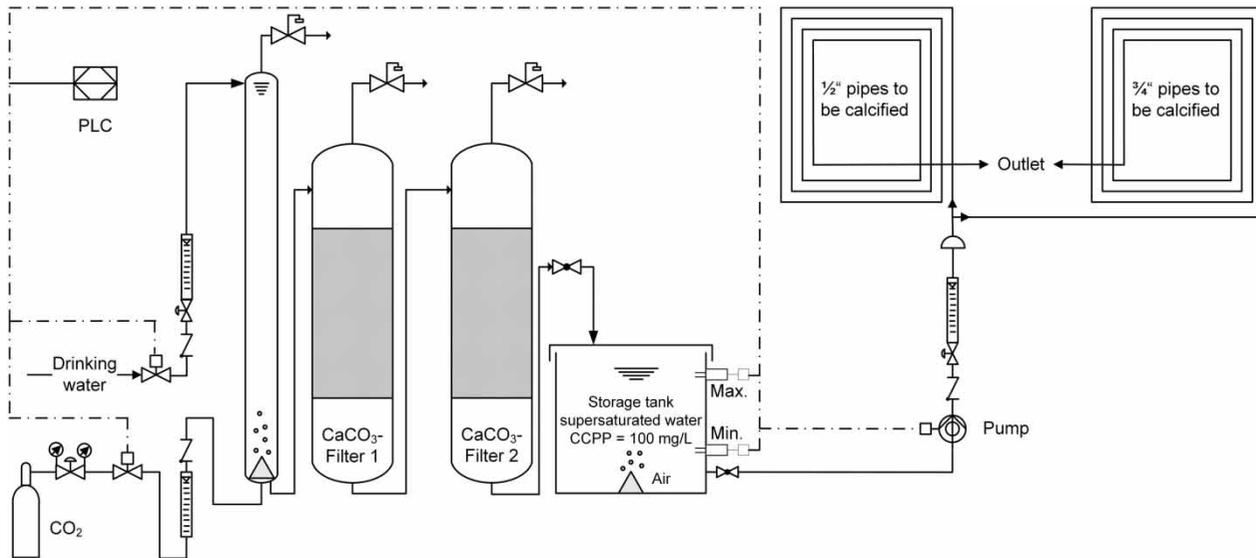
Figure 1 │ Schematic of the calcification plant for the generation of supersaturated water and formation of solid calcite deposits in stainless steel pipes. The plant is controlled via the programmable logic controller, PLC. ½″ and ¾″ pipes have an inner diameter of 10.0 and 15.7 mm, respectively.

the water during ascent in the water column (height 2.5 m). The amount of CO_2 was adjusted to emerge gas bubbles with a diameter of about 1 mm in the lower third of the column which rose up as finer bubbles in the upper part of the column. The acidified, strongly calcite dissolving water was routed through two cascaded filter columns (height 2.0 m, diameter 24 cm) which were filled to a height of 1.5 m with juraperl (EVERZIT® Carbonate with a particle size of 1.0–2.0 mm, EVERS GmbH & Co. KG, Hopsten, Germany according to DIN EN 1018 (2012)). The $CaCO_3$-enriched hard water was collected in a storage tank. The level of water hardness can be controlled by the amount of carbon dioxide and/or the residence time of water in the filter column. During filtration the reaction of carbonated water with calcium carbonate cannot reach equilibrium since the contact time is limited in the filter. As a result, not all the excess carbon dioxide was buffered by calcium carbonate.

Generation of water with high CCPP

The parameter CCPP describes the ability of water to precipitate calcium carbonate. This is dependent on the concentration of calcium and carbon dioxide/bicarbonate/carbonate, which is dependent on the pH value. By stripping of carbon dioxide in an intensive degassing unit with air

bubbles, the pH was raised and a CCPP of about 100 mg/L $CaCO_3$ (supersaturated water) was achieved immediately before the water was entering the pipe section to be calcified. As shown in Equation (2), carbonate ions are necessary for the calcite precipitation. By stripping of carbon dioxide the concentrations of carbonate ions and protons decrease with concomitant increase of the pH value (Equation (3)). However, with increasing pH value the fraction of carbonate ions among the inorganic carbon increases, which results in a net increase of the carbonate ion concentration and water supersaturated with calcite:

$$Ca^{2+} + CO_3^{2-} \leftrightarrows CaCO_3(s) \tag{2}$$

$$CO_2 + H_2O \leftrightarrows CO_3^{2-} + 2H^+ \tag{3}$$

Calcification of pipes

The supersaturated water was transferred from the storage tank via a peristaltic hose pump at a rate of 12 L/h through pipes with either 10.0 or 15.7 mm inner diameter and 24 m length each (24 pieces with a length of 1 m). Two 20 cm long pipe sections at the beginning and at the end of the precipitation lines were used to determine the amount of calcium

Figure 2 │ Calcification plant for the generation of supersaturated water (left) and formation of solid calcite deposits in stainless steel pipes (right). CO_2 gassing column (a); filter columns with $CaCO_3$ (b); programmable logic controller PLC (c); storage tank with degassing unit (d); air inlet (e); inlet of supersaturated water into 10.0 mm stainless steel pipes (f); outlet of 10 mm stainless steel pipes with flow meter (g); inlet of supersaturated water into 15.7 mm stainless steel pipes (h); and outlet of 15.7 mm stainless steel pipes with flow meter (i).

carbonate that had been precipitated inside the pipelines. Figure 2 (right) illustrates the setup for the generation of calcified pipes.

CCPP was calculated based on DIN 38404-10 (2012) from acid neutralizing capacity (ANC) to pH 4.3 and the pH of the sample ($ANC_{4.3}/pH$ (T)) with the software package CAS4.1 (Johannsen 2012). The underlying parameters for pH value, temperature at pH measurement, electrical conductivity at 25°C, $ANC_{4.3}$, $BNC_{8.2}$, titration temperature, temperature and calcium concentration of the sample were taken from the sample analysis data. The following data were taken from water analysis of drinking water from TUHH plumbing: 38.0 mg/L calcium, 9.32 mg/L sodium, 0.89 mg/L potassium, 2.58 mg/L magnesium,

10.8 mg/L chloride, <0.5 mg/L nitrate, and 9.4 mg/L sulfate. The groundwater waterworks Nordheide supplies the TUHH with potable water. Acid solubility was determined according to DIN EN 12902 (2005). pH value was determined according to DIN 19261 (2005). Electrical conductivity was determined according to DIN EN 27888 (1993).

Ions

The concentrations of sodium, potassium, calcium and magnesium were determined according to DIN EN ISO 11885 (2009). The concentrations of chloride, sulfate, and nitrate were determined according to DIN EN ISO 10304-1 (2009).

ANC and base neutralizing capacity

ANC was determined by titration with HCl to pH 4.3 ($ANC_{4.3}$) and base neutralizing capacity (BNC) was determined by titration with NaOH to pH 8.2 ($BNC_{8.2}$) according to DIN 38409-7 (2005).

RESULTS AND DISCUSSION

Generation of water with a high CCPP

A soft potable water was turned into a water with high CCPP by a three step procedure including (1) CO_2-enrichment, (2) hardening with $CaCO_3$ and (3) desorption of CO_2 with air bubbles.

After dosing of CO_2, the pH of the water dropped from 7.8 down to, for example, 5.08 (Table 1). The increased CO_2 concentration of 32.5 mmol/L led to a solution of 8.05 mmol/L of Ca^{2+}, which turned the water hard. The hardness of the water could be adjusted by the amount of dosed CO_2 and by its volume flow rate controlling the residence time in the $CaCO_3$ filter. A flow rate of 40 L/h and dimensions of the $CaCO_3$ filter of 300 cm height and 24 cm diameter resulted in a residence time of the water in the filter of 202 min. The result was very hard water with 9.0 mmol/L Ca^{2+} which is equivalent to a hardness of 90°F or 50°dH. The subsequent stripping of carbon dioxide (comparable to a mechanical de-acidification) resulted in a water with a relatively high

pH of 7.95 and a considerably high CCPP of 429 mg/L $CaCO_3$. This water led to a fast lime precipitation. However, this turned out to be impractical for the intended formation of lime precipitates in the stainless steel pipes, since the plastic (Polyethylene, PE) inlet pipes tend to clog quickly. By throttling of the CO_2 influx while keeping the volume flow rate constant at 40 L/h, the calcite precipitation potential was lowered to 90 mg/L $CaCO_3$.

Table 1 shows an example of measured and calculated values for the individual stages in the production of highly calcite precipitating water, as well as for a final CCPP of approximately 100 mg/L $CaCO_3$.

Correlation between pH-value after CO_2-stripping and CCPP

Table 2 shows the theoretical CCPP that will be reached after hardening of water and subsequent stripping of CO_2. The CCPP was calculated for different combinations of pH values between 6.5 and 8.0 (adjustable by stripping of CO_2) and calcium concentrations between 5 and 10 mmol/L (adjustable by contact time in $CaCO_3$ filter). By this procedure it is possible to obtain CCPP between 0 and 500 mg $CaCO_3$/L.

Figure 3 illustrates the correlation between CCPP and pH-value at constant calcium concentrations. From this, it can be inferred which combination of pH value and calcium concentration is needed in order to obtain a desired CCPP. Vice versa, the CCPP can be estimated for a given pH value

Table 1 | Stages in the production of highly calcite precipitating water

Parameter	Inlet water	After CO_2 dosage	After $CaCO_3$ filtration	After CO_2 stripping	After CO_2 stripping
pH (T)[a]	7.80	5.08	6.46	7.95	8.20
Temperature, °C	10.0	14.0	21.7	22.8	21.4
Electrical conductivity, μS/cm (25°C)	245	245	1,521	1,443	593
$ANC_{4.3}$, mmol/L	2.0	1.61	17.3	17.0	6.95
$BNC_{8.2}$, mmol/L	0.06	30.00	11.50	0.60	0.04
Ca^{2+}, mmol/L	0.95	0.95	9.00	8.84	2.90
Total hardness, mmol/L	1.05	1.05	9.11	8.95	3.01
CO_2 calculated, mmol/L	0.00	32.45	11.16	–0.097	–0.080
HCO_3^- calculated, mmol/L	1.90	1.51	17.19	16.89	6.84
CCPP calculated, mg/L $CaCO_3$	–3	–818	201	429	90

The numbers in grey represent the settings for obtaining a CCPP of 90 mg/L $CaCO_3$. The volume flow rate was 40 L/h. Experiments were performed with drinking water taken from the TUHH water premise plumbing.
[a]pH at the measured temperature.

Table 2 | Calculated CCPP after hardening and subsequent stripping of CO_2 for various calcium and CO_2 concentrations (calculations were performed for pure water at a temperature of $10°C$)

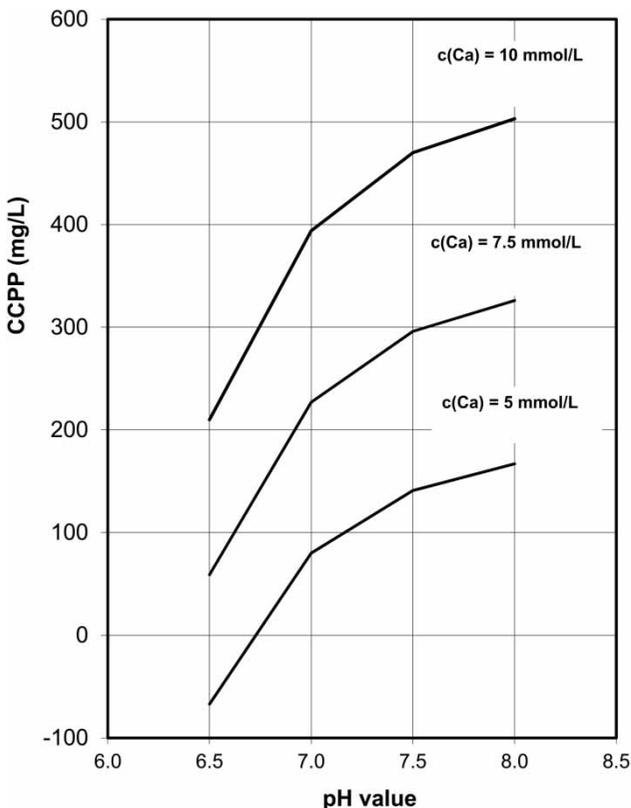| Hardness	$c(CO_2)$ (mmol/L)	pH	CCPP (mg/L $CaCO_3$)
$c(Ca) = 5$ mmol/L	7.84	6.5	−67
	2.46	7.0	80
	0.733	7.5	141
	0.103	8.0	167
$c(Ca) = 7.5$ mmol/L	11.33	6.5	59
	3.55	7.0	227
	1.04	7.5	296
	0.095	8.0	326
$c(Ca) = 10$ mmol/L	14.65	6.5	210
	4.57	7.0	394
	1.32	7.5	470
	0.06	8.0	503

Figure 3 | Correlation between the calculated CCPP and various combinations of calcium concentrations and pH values in water (calculations were performed for pure water at a temperature of $10°C$).

and a given calcium concentration. It also becomes obvious that several combinations of pH values and calcium concentrations lead to the same CCPP.

The described method for the production of strongly calcite precipitating water can also be applied for the testing of procedures for the prevention of calcification. For this purpose, a CCPP between 30 and 100 mg/L $CaCO_3$ should be suitable.

Calcification of pipes

It was possible to build a uniform layer of calcite along the 24 m long precipitation lines in a continuous process by using water with a CCPP of about 100 mg/L $CaCO_3$ at a mean temperature between 18 and $21°C$. Figure 4 illustrates the uniform and solid calcite layers in 10.0 and 15.7 mm pipes.

The electrical conductivity of the water decreased from 841 µS/cm at the inlet to the storage tank down to 608 µS/cm at the outlet of the precipitation line. Since calcium and bicarbonate ions contribute to the electrical conductivity of water, their precipitation in the form of $CaCO_3$ decreases the electrical conductivity. The formation of calcite layers could be seen in the storage tank and, thus, the precipitation of $CaCO_3$ inside the pipes of the precipitation lines can be assumed (Table 3).

The average duration of calcification in three series of calcification runs was 69 days. An overview of the test periods and prevailing water temperatures is given in Table 4.

Figure 4 | Uniform and solid calcite layers inside stainless steel pipes with original 10 and 15.7 mm inner diameter (½″ and ¾″, respectively) after precipitation process for about 69 days.

Table 3 | Decrease of electrical conductivity of the water on its way from the storage tank through the precipitation line

Sampling site	Electr. conductivity (μS/cm)	pH	Temperature (°C)
Inlet storage tank	841	6.5	27
Storage tank	666	8.1	25
Inlet precipitation line	640	7.8	25
Outlet precipitation line	608	7.6	26

Table 4 | Duration of the individual calcification series with prevailing average temperatures

Test run	Test period	Days	Mean temperature with standard deviation (°C)
1. Calcification run	09.08.2013– 14.10.2013	62	21.0 ± 3.1
2. Calcification run	24.10.2013– 20.01.2014	72	18.2 ± 1.4
3. Calcification run	03.02.2014– 17.04.2014	74	19.5 ± 1.7

Over the entire length of the precipitation line with 24 pipes of 1 m length, a continuous solid layer of scale had been built up (Figure 4). The pattern of thickness of the calcite layer in the last pipe of the line was comparable with the first pipe. A uniformly thin calcite layer (about 0.1–0.5 mm) was formed within every 1 m pipe section except for the end of each tube in flow direction (outlet) where a thicker calcite layer of up to 2 mm was built up (Figure 5). This may have been caused by the fact that the pipes were installed in the form of a square and each pipe was connected by a 90° angle manifold with the adjacent pipe. One possible
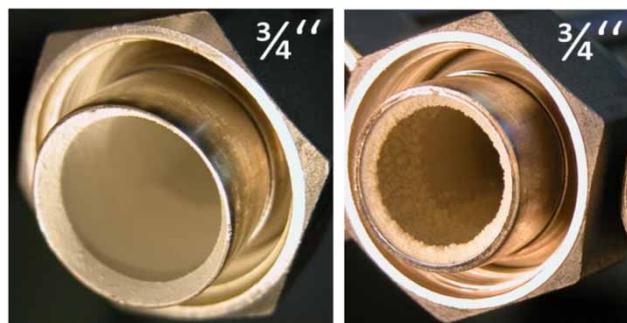
Figure 5 | Different thicknesses of the calcite layer at inlet (left) and outlet (right) of a single 1 m pipe with original 12.7 mm inner diameter (¾).

explanation for the increased deposition at the end of each pipe section could be calcite particles which are caught at the junction between the pipe and connector where they serve as nuclei for further precipitation. A junction also creates turbulence in the water flow leading to an altered precipitation. Altered friction and/or pressure loss in angled pipes are other possible impact factors.

For an estimate of the total amount of calcite deposited on the surface it has been assumed that about 1/8 of a 1 m pipe (12.5 cm) has a $CaCO_3$ mass surface loading rate comparable to the 0.2 m pipe sitting before the 90° angle manifold at the inlet of the precipitation line. For the rest of the pipe a $CaCO_3$ mass surface loading rate as in the 0.2 m pipe sitting after the 90° angle manifold at the outlet of the precipitation line has been assumed. The calculated mean precipitate of a 1 m pipe was 60, 50, and 53 mg $CaCO_3$/cm^2, respectively, for the three test runs. The average mass surface loading rate was 54 mg $CaCO_3$/cm^2 with a maximum deviation of 6 mg $CaCO_3$/cm^2, which corresponds to an error of 11%. The individual values are given in Table 5.

Lessons learned from calcification experiments

(1) A peristaltic hose pump was utilized in order to prevent calcification inside the pump. When using centrifugal pumps, heat generation caused enhanced calcite precipitation in the pump. This in turn resulted in overheating of the pump due to reduced water flow.

Table 5 | $CaCO_3$ mass surface loading rate in pipe pieces of 0.2 m length at the inlet and at the outlet of the precipitation line

Test run	Total precipitate in 0.2 m pipe before right angle manifold at inlet (mg $CaCO_3$/cm^2)	Total precipitate in 0.2 m pipe after right angle manifold at outlet (mg $CaCO_3$/cm^2)	Calculated mean precipitate in 1 m pipe[a] (mg $CaCO_3$/cm^2)
1. Calcification run	108	53	60
2. Calcification run	93	43	50
3. Calcification run	108	45	53

[a]Assumption: 1/8 of the pipe length with thick calcite layer (mass surface loading of 0.2 m pipe sitting before right angle manifold) and 7/8 of the pipe length covered with thin layer (mass surface loading of 0.2 m pipe sitting after right angle manifold).

(2) All inlet pipes as well as angled manifolds and pipe junctions needed to be checked regularly and were decalcified if thick calcite layers reduced the volume flow rate substantially.

(3) For the measurement of the volume flow rate, the feed rate and the discharge rate of water were determined. Installed impeller flow meters had the disadvantage that they were calcified rapidly which reduced the volume flow rate at the inlet of the precipitation line. Thus, they were removed.

(4) The original idea to circulate water with high CCPP through the pipes in order to produce calcite layers was abandoned because the warming of the water during circulation led to enhanced precipitations and repeated blockage of the supply lines.

(5) The variant of calcification by using highly alkaline lime water with $Ca(OH)_2$ instead of stripping the CO_2 for an increase of the pH was discarded because the $CaCO_3$ precipitated directly at the dosing point and formed slimy deposits which did not adhere to the tube wall. These loose deposits clogged the lines and interrupted the water flow. The result was an uneven distribution of lime precipitation with higher amounts of precipitates close to the dosing point and less precipitates at the end of the precipitation line. Furthermore, this method had the disadvantage of high lime water consumption.

CONCLUSIONS

A method for an accelerated and defined calcification of potable water systems and equipment has been developed. A pilot plant was built that systematically generated water with a high CCPP and enabled the controlled and reproducible built-up of calcite-layering in stainless steel pipes with an inner diameter of 10.0 and 15.7 mm. This procedure emulates natural limescale formation and comprises the enrichment of soft water with CO_2, hardening with $CaCO_3$ and subsequent desorption of CO_2. Water with a CCPP of about 100 mg/L $CaCO_3$ and a mean temperature between 18 and 21°C led to the build-up of solid and firmly adhering calcite-layers of reproducible thickness and characteristics in 24 pipes of 1 m length each and connected by angled manifolds. The calculated average mass surface loading rate was about 54 mg $CaCO_3$/cm^2 after 69 days of flow-through operation of the calcification plant. Calcite layers reached a thickness of up to 2 mm. Even though the thickness of calcite layers cannot be predicted and might depend on local water qualities, the potential of scale forming can be well estimated.

Based on water chemical calculations, the combination of calcium concentration and pH after CO_2-stripping necessary for obtaining a desired CCPP had been determined. Theoretically, a CCPP between 0 and 500 mg/L $CaCO_3$ can be adjusted.

Compared to other methods that use solutions of calcium ions or carbonate ions for production of artificial hard water (Chibowski *et al.* 2003; MacAdam & Parsons 2004b; Tijing *et al.* 2011; Cheong *et al.* 2013), the method described here introduces no foreign ions such as Cl$^-$ or Na$^+$. The presence of these ions would increase the ionic strength of the test water and thus would change the characteristics of the natural limescale. Like the method described by Fathi *et al.* (2006), only $CaCO_3$ and CO_2 are used to produce hard water and calcite precipitates. However, instead of a batch production, the use of a flow-through system with a gassing column for adjustable CO_2-enrichment and a filter column with $CaCO_3$ grains for defined hardening of the water and subsequent CO_2-desorption enabled a continuous production of calcite precipitating water. Thus, test water with defined CCPP can be provided for the build-up of calcite layers in water-carrying systems from semi-technical to full scale plants.

While Fathi *et al.* (2006) performed calcite precipitation experiments with water with a CCPP of 300–500 mg/L $CaCO_3$, in the present study a CCPP of 100 mg/L $CaCO_3$ proved to be sufficient for solid limescale formation without additional heating. This enabled comfortable handling of the test water and avoided clogging of pipes and built-in parts.

The new method allows standardized comparison of the limescale prevention as well as removal performance independent from local boundary conditions and can be applied worldwide. The method is a prerequisite for validation and verification of test procedures. As aging aspects and failure limits are important results in system and equipment development, the calcite-layering can be used as an accelerated life time testing in order to predict a possible

time until failure due to limescale may occur. This test may achieve similar industrial acceptance for testing other environmental factors such as vibration or temperature.

The method is economically important because it allows the evaluation of a break-even analysis for different procedures and technologies for limescale prevention or removal. Compared to state of the art testing, it reduces test effort and costs significantly. From an environmental point of view the method can contribute to saving energy and chemicals since the most efficient procedures can be selected and applied.

Whilst the motivation was specifically driven by the aviation industry, the method can be used for all applications dealing with water-carrying systems or equipment; household or large scale industrial processes are possible examples as well as mobile water systems with water-connected heating equipment.

ACKNOWLEDGEMENTS

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