



SPECIALITY COFFEE ASSOCIATION OF EUROPE

THE SCAE WATER CHART

MEASURE
AIM
TREAT

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SUMMARY

The new SCAE Water Chart establishes a solid framework for a unified and transparent discussion of water for coffee. The centre of this discussion revolves around the two axes alkalinity and total hardness. We have presented this booklet in order to promote a spirited exchange of ideas about the water we use for brewing within the speciality coffee community.

The SCAE Water Chart brings clarity to three fundamental questions:

- MEASURE What's the chemical composition of my water and how do I measure it?
- AIM What am I aiming to change and what are the existing recommendations with regard to sensory and technical considerations?
- TREAT Now that I've decided where I want to go, how do I choose a treatment to get me there?

When pondering these three questions, note that while "Measure" and "Treat" can be discussed on a purely rational base, the "Aim" is subjective. But also note that:

- Without the Aim, Measure and Treat become meaningless.
- Without the Measure and Treat the search for the Aim becomes obscure.

We will propose and recommend where to aim for the optimum balance in the cup. The new SCAE Water Chart is forward looking in two important ways. It presents us with:

- a framework for an ongoing discussion about the suitability of different water treatments for the proper extraction of different coffees. In other words, this booklet creates the means to best achieve our Aim.
- a space for expanding and refining our discussion of water for coffee, e.g. a more detailed and precise discussion of total hardness.

The key points of the SCAE Water Booklet can be summarized as follows:

1. Total hardness, alkalinity, and pH are the three central measures to characterize water.*
 2. Traditional hardness units (ppm CaCO₃, °d, °f) provide an easy and accurate way to assess a water's suitability for use in coffee extraction.
 3. With regard to sensory aspects, the acid buffer capacity should be referred to as alkalinity. Note that "carbonate hardness" is not necessarily the same as alkalinity.
 4. Water for coffee extraction should:
 - be odour free and hygienic. The water should be completely free of chlorine, hypochlorite and chloramines, as well as taste-influencing organic compounds, since these can impart a strongly unpleasant flavour in the resulting brew even at concentrations which are not perceivable in the water itself.
 - have a total hardness of 50–175 ppm CaCO₃ (2.9–9.8 °d).
 - have an alkalinity of 40–75 ppm CaCO₃ (2.2–4.2 °d).
 - have a pH of 6.5–8.
 - have an electrical conductivity (in µS/cm corrected to 20°C) less than three times the alkalinity (in ppm CaCO₃)
-

5. Current recommendations for optimal water composition allow for a large variation of optimum total hardness but call for a much smaller variation of alkalinity. Moreover all current recommendations share the characteristic that total hardness should exceed alkalinity.
6. The majority of waters have an alkalinity that runs slightly lower than its total hardness.
7. As most waters are severalfold too high in alkalinity and also too high in total hardness, water treatment is required.
8. For the majority of waters (dominated by calcium or magnesium carbonate) the risk of corrosion can be kept low if alkalinity is at least 40 ppm CaCO_3 at pH 6–8. For other waters containing a significant amount of gypsum (CaSO_4) the risk of corrosion can be kept low if total hardness is less than 80% higher than alkalinity. And lastly for water with a significant amount of salt (seawater intrusion or salt in the bedrock) electrical conductivity (in $\mu\text{S}/\text{cm}$ corrected to 20°C) should be no more than three times the alkalinity (in ppm CaCO_3) to reduce the risk of corrosion.
9. All water treatment techniques can be discussed and compared using the SCAE Water Chart.
10. CO_2 and other related compounds found in water (carbonic acid, hydrogen carbonate and carbonate ion, and scale) play a central role in water chemistry. These compounds have an impact on both the brewing equipment (safety and longevity) and coffee extraction.

* Except for water containing iron, lead or other unsuitable or toxic compounds in significant amounts.

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INTRODUCTION

If there's one thing that those of us in speciality coffee can agree on, it's that good quality water is essential for brewing great coffee. So the question is, how do we transform problematic water into high quality water that brings out the best our coffee has to offer while keeping our equipment in good working order?

In the recent past water treatment has focused on keeping our machines in good repair and is especially important for maintaining espresso machines. While this has the worthy goal of increasing safe operation and lowering maintenance costs, unless the correct treatment is employed, water treatment can still be ineffective. Even with treatment, many of today's espresso machines still breakdown due to scale build up leading to blockages, or in rarer cases, corrosion. Proper water treatment is a must for any economically viable operation.

Aside from equipment maintenance there is also the consideration of flavour and aroma. If the water used for extraction is unsuitable, it can mask a coffee's full flavour potential. For example, in dilute coffee preparations such as pour over, poor water can overpower a coffee's acidity, leaving the brew dull and lifeless.

Given the recent advancements in coffee processing, storage, roasting, and extraction, we need to focus on creating an individually crafted water treatment to bring out the full potential in each coffee.

The aim of this booklet is to introduce the SCAE Water Chart, consisting of a two-dimensional plot of total hardness versus alkalinity. In particular it defines and clarifies the concepts of total hardness and alkalinity and creates the base for a productive and transparent communication and application of water for coffee. While this chart effectively depicts only two out of almost a dozen relevant parameters of water composition, it encompasses the two most crucial drivers of coffee extraction. The water chart allows one to measure the water composition at a given location, aim for the chosen target composition and subsequently apply a specific method to treat the water in order to reach the target composition.

Ultimately, the SCAE Water Chart provides the speciality coffee community with a solid and useful conceptual framework (the SCAE Water Chart) together with a simple to use toolbox that will provide the answers to three questions: Where are we (our water) in terms of total hardness and alkalinity (Measure)? Where do we want to go (Aim)? How do we get there (Treat)?

The sensory impact and the "Aim" is described here only in general terms and has obviously a strong subjective element to it. We have to acknowledge that there is currently not enough data available to describe in greater detail the effects of total hardness and alkalinity of water on aroma and flavour of the coffee extract, considering different coffee origin and varieties, roasting processes and degrees, and extraction techniques. Hence the SCAE Water Chart—rather than being a definitive reference on which exact composition is most suited for coffee and coffee extraction—provides a framework for future work to be discussed and compared. While the general characteristics of water apply equally to espresso and filter coffee, the range of recommendations for total hardness and alkalinity can differ significantly. An important additional parameter to be considered here is the brew ratio, defined as coffee dose to beverage weight. We expect that the 1:2 espresso brew compared to a 1:15 ratio common for filter coffee will affect the optimal water characteristics (the "Aim") on the SCAE Water Chart. Please note that the concept of total hardness oversimplifies the relationship of calcium and magnesium ions and their impact on flavour (and potential other ions that may be introduced by specific water treatment techniques). Nevertheless, calculating the total hardness can still be quite helpful. By using this calculation we can predict the general effects of water on flavour and formulate a direction for choosing an appropriate water treatment.

Communicating about water's diverse properties presents a great challenge. That's because water has so many different interconnected phenomena happening all at once. Without a proper framework to give perspective, it's easy to spin out of control with the many counterintuitive, self-referring, and seemingly never-ending cascade of facts about water. But don't give up hope! When all the pieces of the puzzle are put together it will really make sense, so please bear with us.

To keep this booklet short, practical, and easily accessible for the vast majority of users, only the concepts of total hardness and alkalinity are covered in the main section. These users will still be able to determine their starting composition (section 1), their aimed target composition (section 2) and the treatment to choose (section 3). The last part of the practical section covers the type of quality control maintenance needed to make sure their water's total hardness and alkalinity content stays within prescribed parameters.

The second part of this booklet called fundamentals (section 6) is geared to the minority of users that have either very high alkalinity water (above 300 ppm CaCO_3) or very low alkalinity water (below 50 ppm CaCO_3), or that want to reduce alkalinity selectively (dealkalisation). The information contained in section 6 is essential for ensuring a safe and economically viable operation of your coffee equipment and of espresso machines in particular. The fundamentals section also gives the interested reader the opportunity to really understand water, namely the phenomena of pH, carbonic acid, and carbon dioxide.

1 MEASURE – COMPOSITION

There are two fundamentally different approaches for characterising a water's composition. These are:

- a. Amount Concentrations.** The concentration of ions (or other elementary entities such as molecules or atoms) is given in units proportional to the actual number of ions per volume. For example in molar units or charge equivalent units such as “ppm CaCO₃” (sometimes called American degree) or “°d” (German degree, also written as “°dH”). These concentration units are proportional to the actual ratio in which the ions enter the water by dissolution, react in an ion-exchanger or exit the water by forming scale.
- b. Mass Concentrations.** The concentration of ions is given as mass per volume, such as mg/L as it is standard for a bottled water. This method is only useful for comparison of concentrations with stated daily intake limits or toxicological thresholds (e.g. for trace metals that can occur in contaminated groundwater or old piping such as lead). Since calcium, magnesium and hydrogen carbonate all have different conversion factors from mass concentrations to number of ions they are unnecessarily troublesome for calculating total hardness or alkalinity.

The explanations and graphs in this booklet will focus on the first type of concentration units, specifically traditional hardness units such as ppm CaCO₃. The reason that traditional hardness units are used is twofold: (i) it simplifies the comparison of different water compositions with respect to their suitability for coffee extraction and (ii) it simplifies the understanding of technically relevant processes such as scale formation and water treatment. More detailed explanations on the origin and use of different concentration units are given in the Appendix (section 6.2). Before going into more detail on the composition of water we make a small assessment on how minerals get into the water in the first place.

1.1 HOW THE MINERALS GET INTO THE WATER

Water comprises a large variety of different substances as it cycles around the globe. Water vapour in the atmosphere is essentially pure H₂O, though as soon as water starts to condense and form droplets it starts to take up carbon dioxide, which in conjunction with water forms carbonic acid (see equation 1). This process makes the water slightly acidic, so rain water typically has a pH of 5.7 or below.



Equation 1:

The acidic rain water that comes into contact with carbonate rock (CaCO₃, MgCO₃ or a combination of both), dissolves part of it and thereby acquires magnesium, calcium and hydrogen carbonate ions (HCO₃⁻). In contrast to this, the acidic rain water will barely dissolve any silicate rock such as feldspar or quartz, since these minerals are much more resistant to dissolution (weathering). The amount of dissolved minerals is not only dependent on the composition of the minerals, but also on the amount of time water has been in contact with the minerals. Additionally the particle size of the minerals influences the speed of dissolution and thereby the resulting amount of dissolved minerals in water. As smaller particles of bedrock have a larger surface area, they will dissolve more readily, increasing the amount of dissolved solids. Groundwater is harder than water in rivers and lakes because it has been in contact with minerals for a longer period.

1.2 HOW TO CHARACTERISE A WATER'S COMPOSITION

As explained in the initial part of this section we will use equivalent units to explain the characteristics of water. When speaking about total hardness and alkalinity these are traditional hardness units, when referring to all the ionic components of water, these are equivalent units proportional to molar units (see section 6.2 for a detailed explanation). Figure 1 shows one of the most common graphs used by water treatment specialists or chemists investigating water compositions. It gives an overview on the complete composition of water and it is divided into three major sections. On the left side all ions are separated into the positive ions (cations) in the upper part and negative ions (anions) in the lower part. In this depiction the two bars of positive and negative ions are always of equal size, and this is because any water always has to meet charge neutrality. In other words, the amount of positive charges (from cations) has to be equal to the amount of negative charges (from anions). To be more precise this equality in size is due to the choice of unit, here namely any equivalent unit which is based on the number of ions multiplied by their charge and not based on its mass.

The middle part of the graph shows dissolved gases, in this case carbon dioxide and its aquatic twin carbonic acid. And lastly the part to the right shows uncharged components of water, namely silicates or organic compounds which in most cases make up only a very minor part of the total amount of dissolved solids in the water.

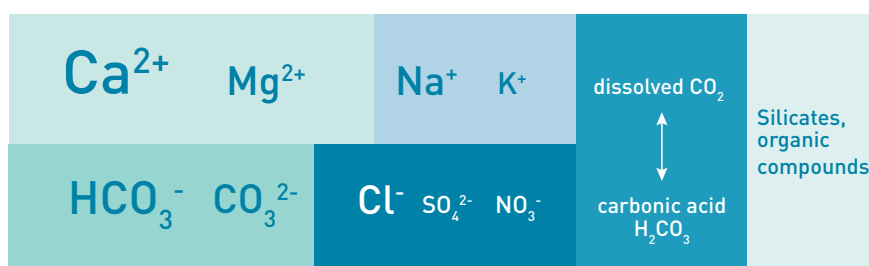


Figure 1: Overall composition of water

The pH of most tap waters is strongly influenced by excess dissolved CO₂ in the range of 5-20 mg/L (Puckorius and Brooke, 1991). In equilibrium with the atmosphere water would only contain about 0.4 mg/L dissolved CO₂ – regardless of pH and alkalinity. This means that most tap water will increase by approximately one pH unit when left standing in an open container for a day less time is needed if it is heated up (see section 6.3 on pH).

1.3 TOTAL HARDNESS AND ALKALINITY

Water analysis with regard to coffee machines has been mainly focused on the maximum amount of scale that could be formed. Fortunately the concepts developed with regard to scale formation are also helpful with regard to coffee extraction. In this work we will focus on two parameters:

- Total hardness: Defined as the sum of calcium and magnesium in equivalent concentrations (or molar concentrations). In rare cases other ions can contribute to total hardness, for example strontium (SMWW, 2012; DIN, 1986; ASTM, 2002; EPA, 1999).
- Alkalinity = Acid buffer capacity: The amount of acid that has to be added to a water sample to decrease pH to 4.3. Therefore it is attenuating the effect of adding acid to water, also called neutralising or buffering.

Figure 2 gives a representation of two different water compositions. The left panel represents the overall composition for the vast majority of tap waters. These waters have a total hardness that is higher than its alkalinity. The preponderance of this composition is also the reason why the term carbonate hardness is often misleadingly used synonymously with alkalinity. Carbonate hardness effectively corresponds to the maximum amount of scale that can form and is therefore equal to whichever of the two values of total hardness and alkalinity is lower. The right panel of figure 2 demonstrates this distinction (between alkalinity and carbonate hardness) with water having a higher alkalinity than total hardness. Here carbonate hardness does not equal alkalinity but instead equals total hardness. This is simply because total hardness is now the limiting factor for

the maximum amount of scale that can form. This type of composition can occur in regions where salt water intrudes into the ground water or when water that has been treated by a softener (exchanging calcium and magnesium ions for sodium or potassium ions see section 3).

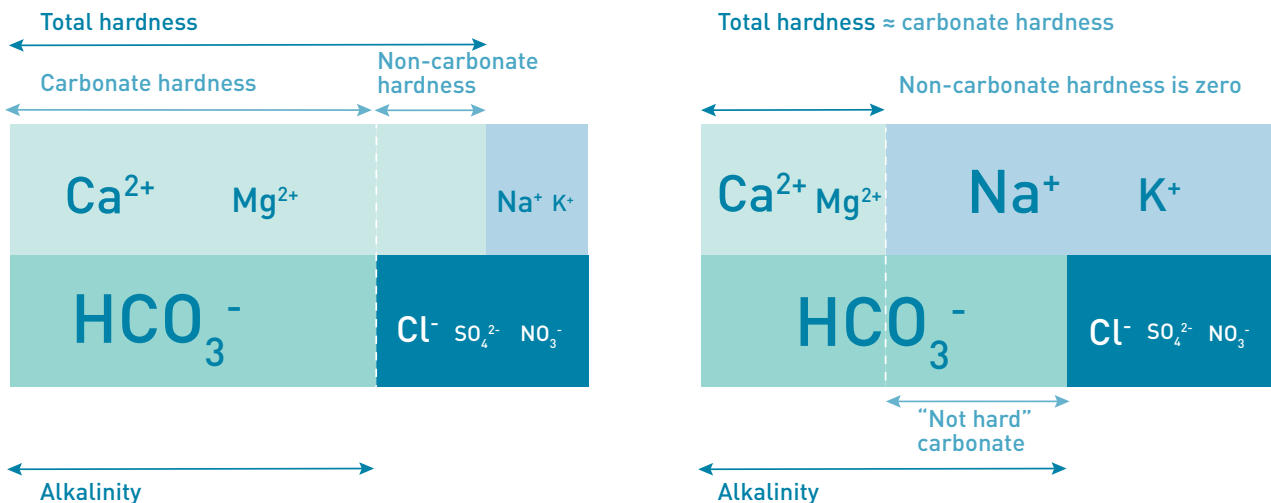


Figure 2: Total hardness, alkalinity and carbonate hardness

Beside the terms used here there are also a number of other synonyms in use:

- Total hardness = general hardness
- Carbonate hardness = temporary hardness
- Non-carbonate hardness = permanent hardness
- "Not hard" carbonate is sometimes referred to as "apparent carbonate hardness"

1.4 OTHER RELEVANT WATER CONTENT

There are other regions in the world that have significant amounts of other ions besides the ones discussed in the previous sections. These ions can negatively impact the suitability of local water for its use in coffee extraction. A couple of examples of this are iron, which causes very noticeable flavour defects in coffee extraction and lead, which is toxic. There are specialised water treatments to remove these components from the water, though this goes beyond the scope of this booklet. Of the treatments discussed here, only reverse osmosis and deionisation are capable of completely removing them from a given water supply. Some regions have a high content of gypsum in the bedrock which can cause scale formation of a different kind (to the well-known calcium carbonate). Chlorine or chloramines used for disinfection impart a strongly unpleasant flavour in the resulting brew and should be removed. Most commonly this is done by activated carbon filtration systems (see section 3).

1.5 MEASUREMENT METHODS

Given clean water free of particulates and off-flavours, a water sample can be sufficiently characterised for its use in coffee extraction by the measurement of total hardness and alkalinity. The only exception is water with a very high alkalinity (above 300 ppm CaCO_3 - see section 3.2) or extremely soft (below 50 ppm CaCO_3). In both cases a measurement of pH of the water is advised to avoid damage to the equipment. Outside of chemistry labs total hardness and alkalinity are most practically measured by titration. Total hardness is measured with a complexometric titration (with EDTA) and alkalinity with a neutralization titration (using a strong acid, e.g. HCl). In practice this means that a solution is added drop by drop to a specified amount of water until a colour change occurs (for instance from green to red). Titration kits are available from water treatment suppliers or

also in aquarium stores – minimum recommended resolution is 20 ppm CaCO_3 (or if given in German hardness degrees $^\circ\text{d}$). Although total hardness and alkalinity are measured by different reactions, both methods result in a measurement value that is proportional to the number of ions; in practical terms in hardness units rather than mass concentrations. To improve the resolution (precision) of the measurement one can simply multiply the amount of water used for the measurement. For instance, if the measurement states one drop equals 20 ppm CaCO_3 at a sample volume of 10 mL, conducting the same measurement with 20 mL of water results in one drop equaling 10 ppm CaCO_3 . If the test vial does not feature additional volume indications, the simplest way of doing this is to weigh the amount with a scale using the conversion of 1g = 1mL which introduces only a negligible error (<0.5% at temperatures below 30°C). Please note that alkalinity test kits are often incorrectly marketed as carbonate hardness test kits.

Another very common method of analysing water composition is to measure electrical conductivity and then estimating total dissolved solid (TDS) in water from this measurement. Using electrical conductivity or TDS to describe water properties is not a meaningful parameter on its own with regard to coffee extraction. This is because the conversion from electrical conductivity to TDS depends heavily on the water composition and temperature, yielding results that can vary significantly. Additionally, even if the estimated TDS value is accurate, it does not contain any information on what the TDS is actually made up of. Conductivity meters (or so-called TDS-meters) are very useful for checking for the stability of the tap water as well as the treated water described in section 4.

1.6 CONVERSION OF HARDNESS AND ALKALINITY UNITS

Table 1 provides an overview on the conversion factors for the most common concentration units in water analysis. All values have been calculated based on the IUPAC Periodic Table of the Elements (2013) and the basic definitions of the different hardness degrees. The values are in agreement with Hem (1985) and the DIN norm on water hardness (1986). The charts used in this booklet are all given in units of “ppm CaCO_3 ” but they can all be easily converted to any of the other traditional hardness units such as $^\circ\text{d}$, $^\circ\text{f}$ or $^\circ\text{e}$. Note that in contrast to mass concentration, the conversion factor for calcium, magnesium, and hydrogen carbonate are identical from one traditional hardness unit to the other.

		ppm CaCO_3	$^\circ\text{d}$	$^\circ\text{f}$	gpg US	$^\circ\text{e}$	$\text{Ca}^{2+} + \text{Mg}^{2+}$ (mmol/L)	HCO_3^- (mmol/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	HCO_3^- (mg/L)
ppm CaCO_3 [= mg CaCO_3/L]	1 ppm CaCO_3 =	1	0.05603	0.1	0.05842	0.07016	0.009991	0.01998	0.4004	0.2428	1.219
German degrees ($^\circ\text{d}$)	1 $^\circ\text{d}$ =	17.85	1	1.785	1.0423	1.252	0.1783	0.3566	7.147	4.334	21.76
French degrees ($^\circ\text{f}$)	1 $^\circ\text{f}$ =	10.00	0.5603	1	0.5842	0.7016	0.09991	0.1998	4.004	2.428	12.19
Grains per US gallon (gpg)	1 gpg =	17.12	0.9591	1.712	1	1.201	0.1710	0.3421	6.855	4.157	20.87
English degree ($^\circ\text{e}$)	1 $^\circ\text{e}$ =	14.25	0.7986	1.425	0.8327	1	0.1424	0.2848	5.708	3.461	17.38
$\text{Ca}^{2+} + \text{Mg}^{2+}$ (mmol/L)	1 mmol/L =	100.1	5.608	10.01	5.847	7.022	1	-	40.08	24.30	-
HCO_3^- (mmol/L)	1 mmol/L =	50.04	2.804	5.004	2.923	3.511	-	1	-	-	61.02
Ca^{2+} (mg/L)	1 mg/L =	2.497	0.1399	0.2497	0.1459	0.1752	0.02495	-	1	-	-
Mg^{2+} (mg/L)	1 mg/L =	4.118	0.2307	0.4118	0.2406	0.2889	0.04114	-	-	1	-
HCO_3^- (mg/L)	1 mg/L =	0.8202	0.04595	0.08202	0.04791	0.05754	-	0.01639	-	-	1

Table 1: Conversion factors for units of hardness and alkalinity rounded to four significant digits. The most common conversion factors are highlighted in grey

Note that English degrees are equivalent to degrees Clark and grains per imperial gallon.

For quick mental arithmetic the following conversion relating the two most common hardness units is quite useful and very accurate (< 2% error). To convert a value in ppm CaCO_3 to °d divide by 20 and then add ten percent to it. Analogously, to convert a value in °d to ppm CaCO_3 multiply by 20 and then subtract ten percent from it.

1.7 NATURAL WATER COMPOSITIONS

Now that we've introduced the concepts of total hardness and alkalinity, we can use the SCAE Water Chart to easily compare and depict different water compositions. And we can do this for any of the traditional hardness units using equally scaled axes starting from zero.

Examples of bottled water composition as well as the composition of 186 tap waters from a small region in Switzerland (Baselland, BL) are given in Figure 3 left panel. Most waters group along the diagonal (dotted black line) where total hardness equals alkalinity. A closer look reveals that most values are not exactly on the diagonal line but are slightly higher in total hardness than alkalinity. The diagonal line represents the dissolution of pure calcium or magnesium carbonate (CaCO_3 , MgCO_3). The small vertical offset, like most tap waters from Baselland show, is caused by small amounts of chloride or sulphate which will increase the total hardness without affecting alkalinity. In contrast a larger offset is almost exclusively due to high sulphate content (from gypsum, CaSO_4). An example of this is shown in the middle panel, depicting the composition of a number of bottled waters, with the water "Cristallo still". This water has a very high total hardness of 820 ppm CaCO_3 as compared to a medium alkalinity content of 210 ppm CaCO_3 . This large difference is due to significant content of gypsum water resulting in a high hardness and a high sulphate content of 6.24 mmol/L (or 600 mg/L as stated on the bottle label). Another example of a special case is seen in the right panel of figure 3 that shows the tap water composition of major cities in the US (Lockhart, 1955). The three waters that are located below the diagonal have a significant content of sodium that explains the difference between total hardness and alkalinity. This is caused by the intrusion of salt water that contains high concentrations of sodium and hydrogen carbonate (formerly called bicarbonate). Adding sodium and hydrogen carbonate to water increases its alkalinity but total hardness is unaffected, thereby pushing a water composition to the right, away from of the diagonal in the water chart. So even though only hardness and alkalinity are depicted in the water chart, almost all 'special' water characteristics like significant concentrations of sulphate or sodium can be recognised and even be estimated quite accurately (see the conversion table for water treatment or salt addition in section 3.4). For water that is containing significant amounts of salts other than calcium or magnesium carbonate, conductivity also has to be taken into account to reduce the risk of corrosion (see section 2).

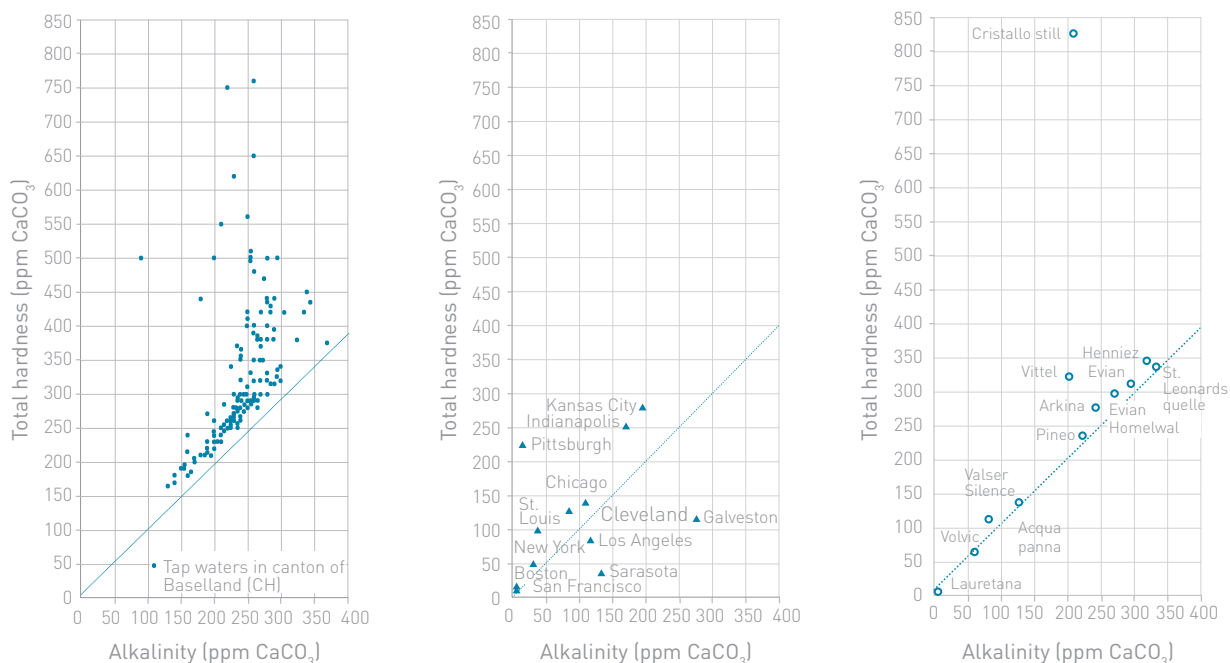


Figure 3: Sample water compositions: left panel: 184 tap water compositions from a small region in Switzerland; middle panel: composition of tap waters in the US; right panel: compositions of bottled water

Figure 4 summarises the effect of mineral dissolution on a water’s composition and thereby on its location within the water chart. The blue arrow represents the dissolution of pure carbonate rock (limestone, dolomite, etc.) moving the composition diagonally up and to the right. The red arrow represents the dissolution of minerals containing chlorides or sulphates, and magnesium or calcium (CaSO_4 , MgSO_4 , CaCl_2 , and MgCl_2), increasing total hardness only and thereby producing an offset upwards from the diagonal. And lastly the green arrow represents the introduction of sodium and hydrogen carbonate, most commonly occurring by salt water intrusion, increasing alkalinity only producing an offset to the right of the diagonal.

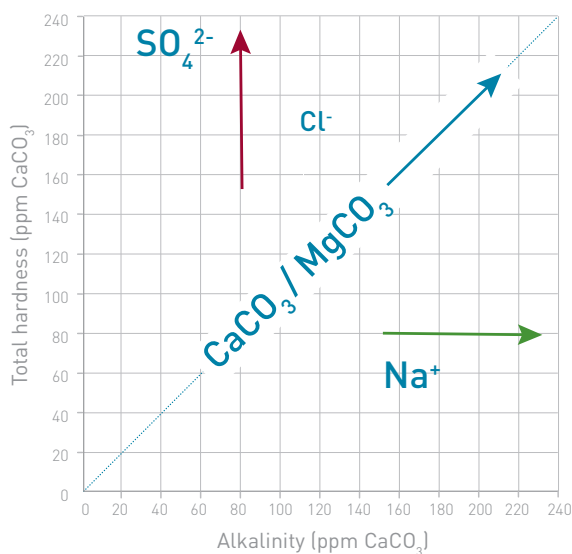


Figure 4: Interpreting a water composition based on its location on the water chart.



2 AIM –RECOMMENDATIONS

After clarifying how to characterise a water’s composition and thereby determining the initial position on the SCAE water chart for a given water, this section summarises existing recommendations for optimal water composition. We conclude with the SCAE core zone; the SCAE recommendation for the optimal water composition for coffee, that combines both technical and sensory considerations.

There are three different perspectives to define an optimal water composition: (i) technical perspective that aims to minimise maintenance and thereby reducing repair or replacement costs as well as downtime due to a defect or break-down of espresso machines or brew boilers, (ii) the sensory perspective aims to bring out the best flavour and aroma of a coffee by modifying the content of total hardness and alkalinity, and (iii) off-flavours due to iron, organic matter or dissolved chlorine (Cl₂), hypochlorite (OCl⁻) and chloramines: To avoid unpleasant odour and taste the water should be free of iron, chlorine compounds and organic matter. In case of the chlorine compounds and organic matter this can be easily addressed by active carbon filtration which efficiently reduces both. For Iron however, low levels can be removed by ion-exchanger (softeners or decarbonisers – see next section) for higher levels a more elaborate treatment involving aeration (bubbling air through the water) and subsequent removal by filtering away the iron particles that have formed through oxidation.

The most important aspects that define the optimum water composition from a technical perspective are:

1. Scale formation: Too high hardness and alkalinity lead to scaling of boilers and machines in turn leading to:
 - a. Decrease in efficiency of heat transfer.
 - b. Clogging of valves and orifices (gicleur) especially in the hot water sections.
2. Corrosion: Too low alkalinity below 40 ppm CaCO₃ (also indicated by low electrical conductivity), pH < 6 or pH > 8 and lastly high concentrations of chlorides, sulphates or nitrates (more than 80% of the alkalinity in equivalent concentrations).

Figure 5 illustrates the maximum amount of scale that can form at 95 °C and 130 °C (corresponding to 1.7 bar steam pressure). The calculations are based on a modified version of the Langelier scaling index in combination with the use of an equilibrium pH based on alkalinity and typical dissolved carbon dioxide concentrations (Puckorius and Brooke, 1991; Schulman, 2002).

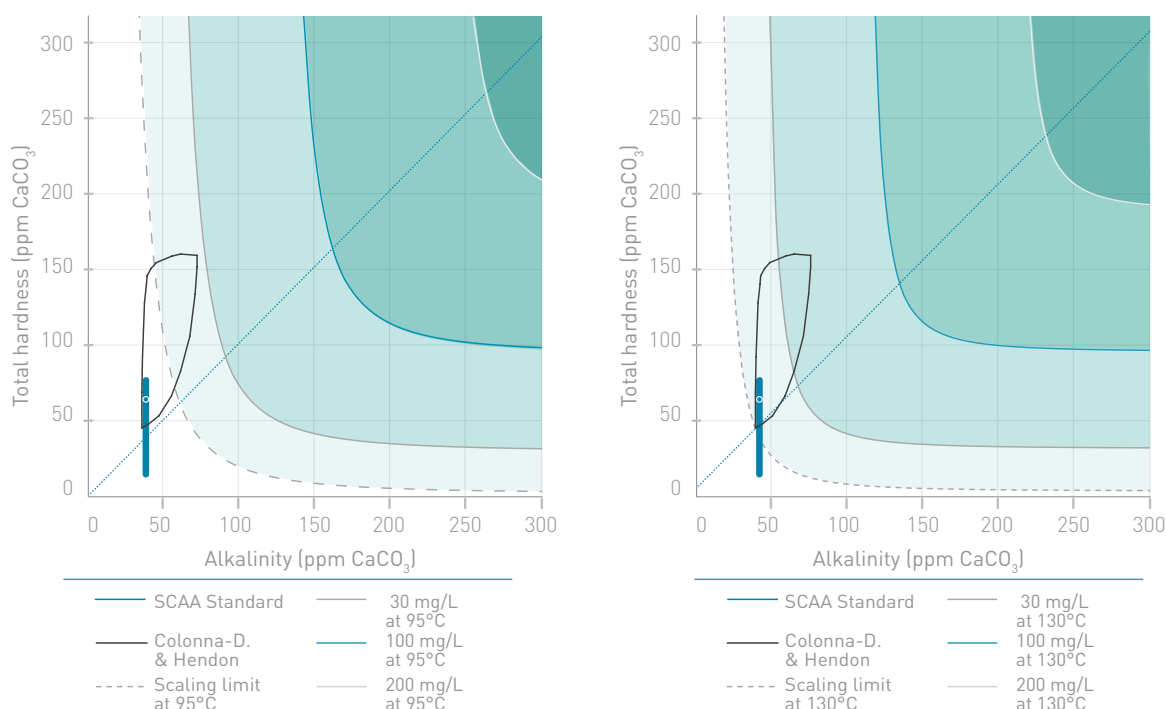


Figure 5: Maximum amount of scale formation at 95 °C and 130 °C

The lines of 30, 100 and 200 mg/L of scale can be transformed to absolute amounts by estimating the water throughput by the number of beverages. For example at 100 beverages per day and 0.1 L per beverage (including flushing) the lines correspond to 110g, 365g and 730g of scale that can form per year. In practice though especially in high-throughput situations the water is not staying heated long enough for all of the scale to form – in contrast when letting the machine stand for hours in a heated condition the indicated amounts will be quite accurate.

Figure 6 illustrates the risk zones where corrosion is likely to occur. The horizontally striped zone marks too high chloride or sulphates concentrations corresponding to a Larson-Skold-Index above 0.8. Although the index is estimated from total hardness and alkalinity alone it yields a practically useful result unless high concentrations of sodium are present (introduced with sodium hydrogen carbonate). A more general rule that also encompasses waters with a significant amount of salt (other than calcium or magnesium carbonate) has been established based on the data from Lockhart (1955) and 23 waters from the region of Barcelona (representative of salt water influenced tap waters). To keep the risk of corrosion low, the electrical conductivity (in $\mu\text{S}/\text{cm}$) at 20°C should be no more than three times the alkalinity (in ppm CaCO_3). A ratio of three to one, of electrical conductivity to alkalinity, corresponds to a value of approx. 0.8 of the S1 corrosion index (DIN 12502). The S1 corrosion index is almost identical to the Larson-Skold index but additionally also takes into account the concentration of nitrates (in addition to chloride and sulphate). The small diagonally striped zone marks a range where alkalinity is too low to act as an efficient buffer ($< 40 \text{ ppm CaCO}_3$).

The two zones in Figures 5 and 6 combined represent “risk zones”, from technical perspectives. We will come back to these when defining the SCAE core zone of optimum water for water boilers and espresso machines.

Shifting now our attention to the sensory perspective, the most important aspects to consider are:

1. Influence of total hardness on extraction efficiency: Higher total hardness is assumed to increase extraction efficiency (Hendon et al., 2014). In our own test series we could not verify this effect by means of a coffee refractometer, though a clear impact on flavour balance and aroma was detected.
2. Influence of alkalinity on perceived acidity: The higher the alkalinity the lower the perceived acidity. Moreover for high alkalinity ($> 100 \text{ ppm CaCO}_3$) the neutralization of acids extracted from coffee by hydrogen carbonate, forms large amounts of carbon dioxide. This can increase extraction time and thereby lead to overextraction (Gardner, 1958; Fond 1995; Navarini and Rivetti 2010). This effect is more pronounced if increased concentrations of sodium are present (Gardner, 1958)

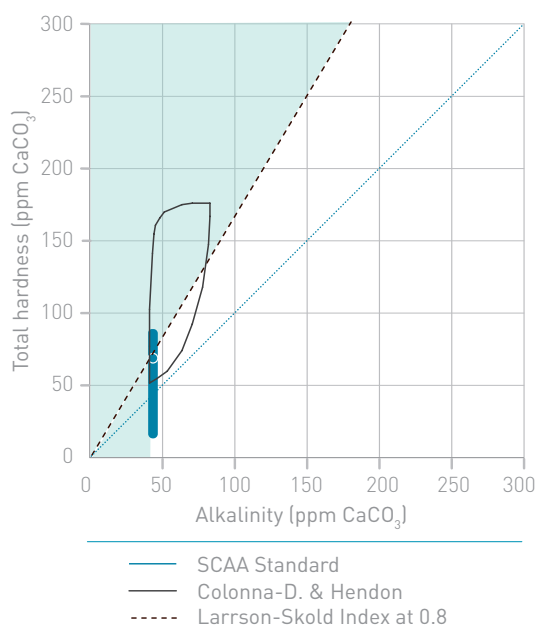


Figure 6: Corrosion risk zones

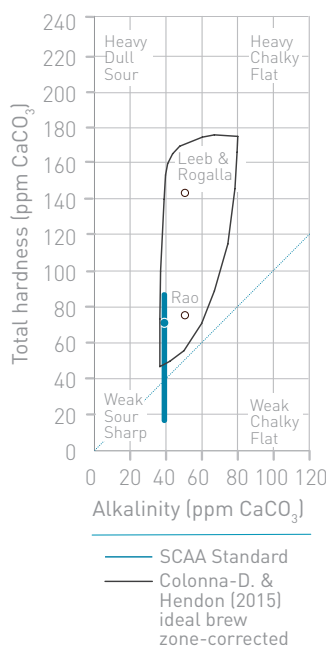


Figure 7: Existing recommendations on water compositions

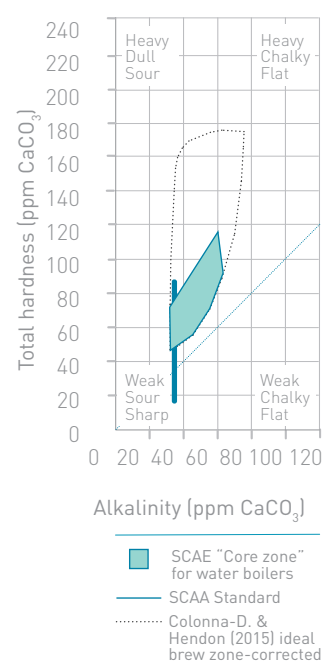


Figure 8: SCAE core zone as recommendation for espresso machines and hot water boilers

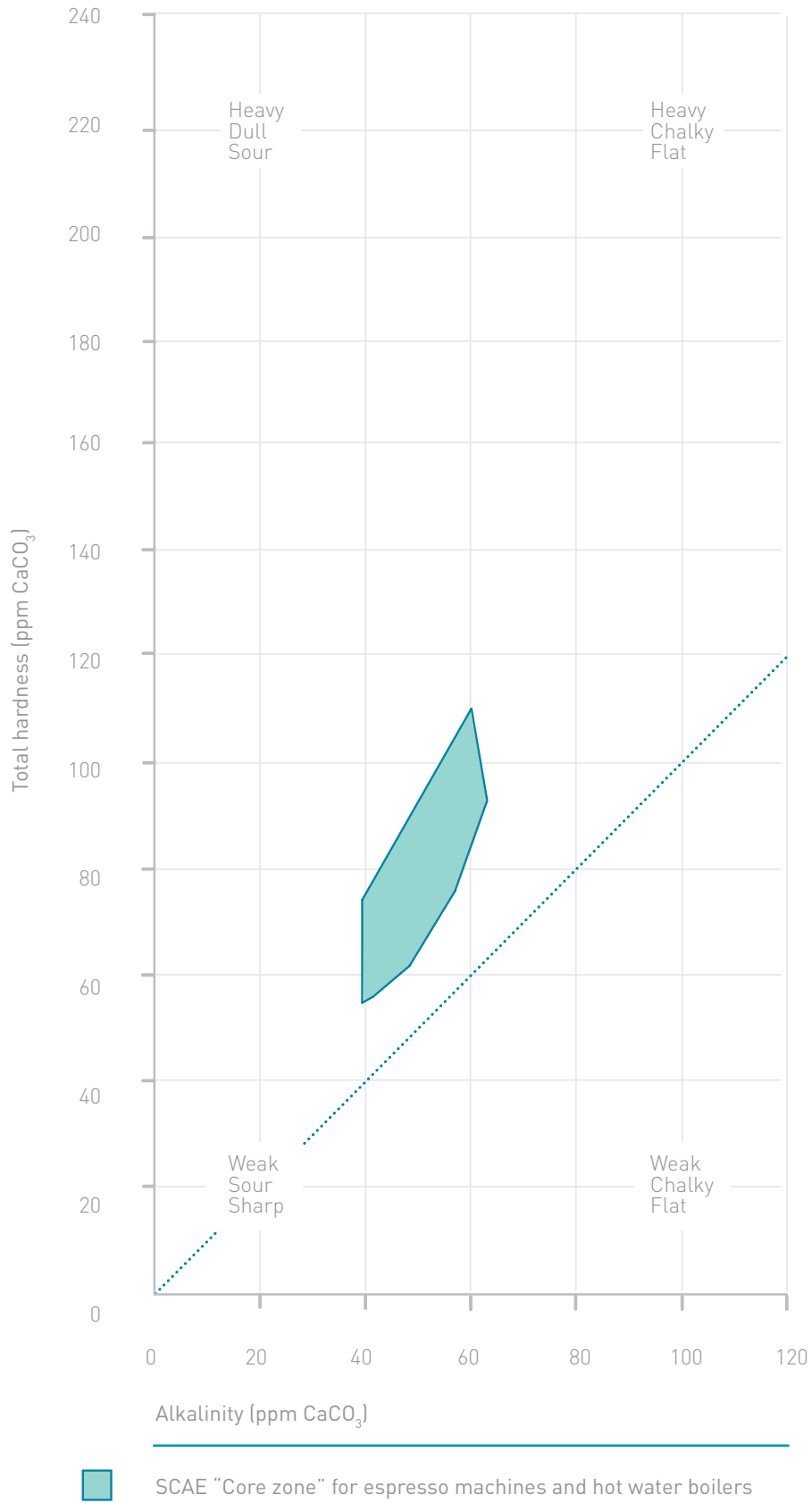


Figure 8: SCAE core zone as recommendation for espresso machines and hot water boilers

Figure 7 summarises existing recommendations (Leeb and Rogalla, 2006; Rao, 2008; Colonna-D. and Hendon 2015; SCAA, 2009) for optimal water composition for extraction from a sensory perspective. Lowest suggested optimum is from the 2016 World Brewers Cup at 51 ppm CaCO_3 . The recommended range for optimum hardness varies strongly:

- Highest suggested optimum is from “Water for Coffee” at 175 ppm CaCO_3
- Lowest suggested optimum is from the 2016 World Brewers Cup at 51 ppm CaCO_3

In contrast to this, the recommended range for alkalinity is much smaller:

- Lowest suggested optimum is at 40 ppm CaCO_3
- Highest suggested optimum is at 75 ppm CaCO_3 – applies only for total hardness values of 150-175 ppm CaCO_3

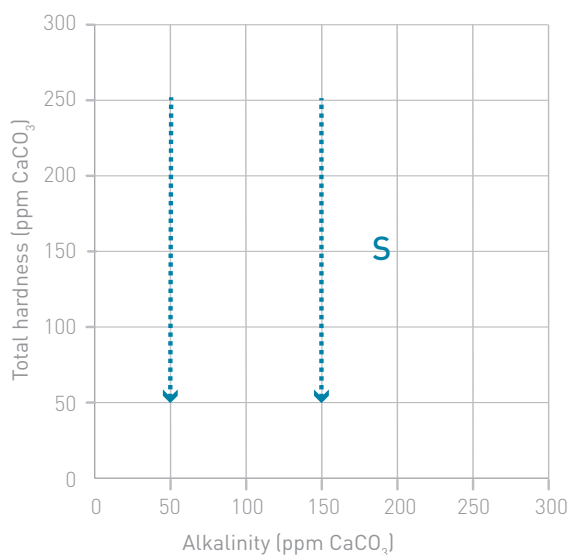
The descriptors in the corners of figure 7 illustrate off-flavours that arise from sub-optimal values for either total hardness (impact on extraction efficiency) or alkalinity (impact on degree of buffering of the coffee acids) combined from Rao (2010) and Colonna-Dashwood & Hendon (2015). While most of these recommendations are aimed at espresso extraction they can also be applied to brewed coffee. As a general tendency brewed coffee needs less alkalinity for an optimum extraction since much more water is used in the extraction in comparison to espresso, or in other terms its brew ratio is much higher. Total hardness has less of an impact than alkalinity and also water with high total hardness can yield a high quality filter brew. For cupping, some professionals prefer to use even softer water in the range of 5-10 ppm CaCO_3 of total hardness and alkalinity. While this practice reportedly did not cause corrosion in water kettles the authors strongly advise against using a water with such a low alkalinity for espresso machines since even small amounts of dissolved carbon dioxide could make this water acidic ($\text{pH} < 6$) and cause corrosion (see section 6.6).

The SCAE “core zone” recommendation for espresso machines and brew boilers, illustrated in figure 8, combines technical aspects enabling a safe operation and sensory aspects yielding a high quality brew. The core zone’s limits by the technical aspects are based on the left and upper borders by the corrosion prevention and to the right by the maximum scale formation of 30 mg/L in a steam boiler at 130 °C or 12 mg/L in a brew boiler of an espresso machine. The lower border of the core zone recommendation is based on the Colonna-Dashwood and Hendon’s line of minimal recommended total hardness and alkalinity.

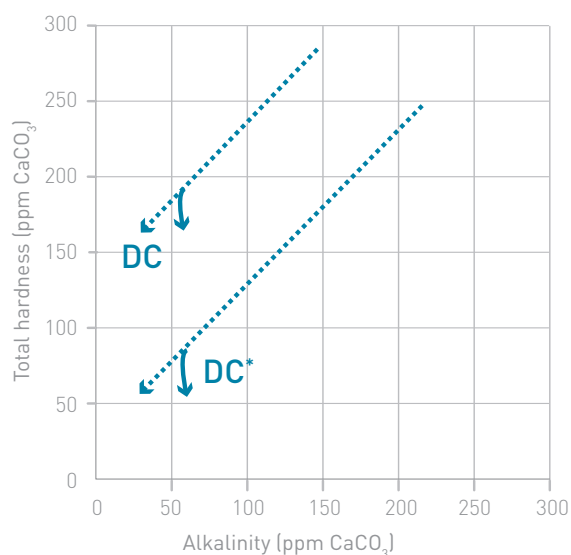
3 TREAT – METHODS

This section explains how different water treatment methods impact total hardness and alkalinity. Considerations about pH are also mentioned, though this is restricted to very hard water and the decarbonisation method. Most tap waters in central Europe and the US have total hardness and alkalinity levels that are too high. The most common treatment methods for these waters are, to either reduce the total hardness or alkalinity, or both. Figure 9-1 and 9-2 shows the impact of the four fundamental treatment methods that can be used to reduce either total hardness or alkalinity.

- The left panel in figure 9-1 shows one of the most common treatment methods, the impact of a softener (S). A softener is an ion-exchange method where calcium and magnesium ions are exchanged for either sodium or potassium ions. This treatment reduces total hardness without affecting alkalinity and is therefore directing downward on the water chart.
- The right panel in figure 9-1 shows the impact of a decarboniser (DC), probably the second most abundant treatment method for coffee applications. As the softener, the decarboniser is also an ion-exchange method, though in contrast to the former, the calcium and magnesium ions are exchanged for protons (H⁺). The released protons in turn neutralise hydrogen carbonate (by formation of carbonic acid – see section 3.1 and 6.6 for details). In this type of treatment it is essential to maintain some alkalinity because the water can get acidic and become corrosive. Decarbonisation leads to a decrease in total hardness and alkalinity by equal amounts and is therefore directed diagonally, down and to the left. Additionally also the buffered decarboniser is depicted (DC*), which is a combination of mostly decarboniser resin combined with a small fraction of softener resin. The small amount of softener resin prevents the ion exchanger from removing all of the alkalinity, and leaving behind typically a residual alkalinity of approximately 50 ppm CaCO₃.



S Softener: Ca²⁺ and Mg²⁺ for potassium (K⁺) or sodium (Na⁺)

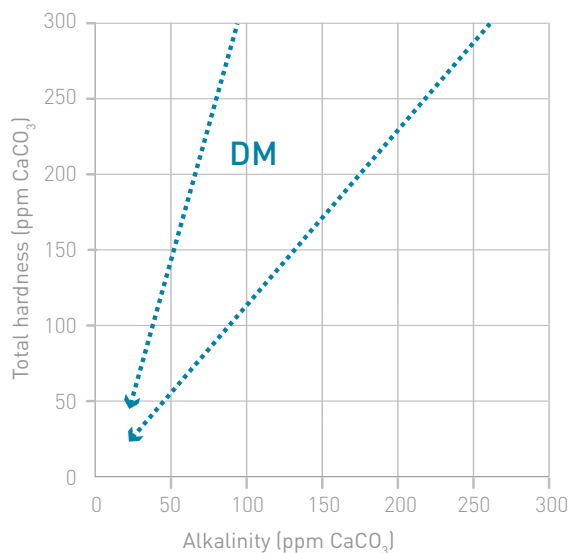


DC Decarboniser: Ca²⁺ and Mg²⁺ for H⁺ – equally reduces total hardness and alkalinity

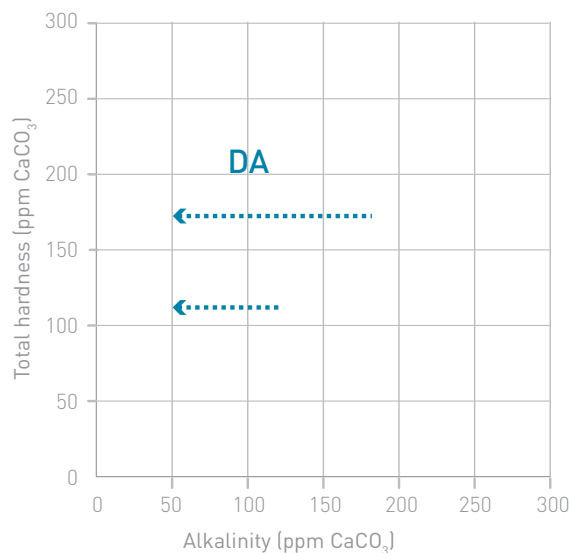
DC* Buffered decarboniser: decarboniser with a small portion of softener

Figure 9-1: Impact of treatment methods that reduce total hardness or alkalinity, or both

- The left panel in figure 9-2 shows the impact of a demineralising (DM) treatment, which can be either reverse osmosis (RO) or a deioniser. Reverse osmosis is also among the most commonly used treatment methods. In contrast to the other methods shown here, reverse osmosis is based on the use of a semipermeable membrane that allows water molecules to pass, but blocks almost all of its dissolved components resulting in water which is essentially pure. This water is often mixed-back with some tap water to increase the mineral contents to suitable levels. By mixing the pure water from the RO system with tap water any composition between the initial composition and zero total hardness and zero alkalinity (called origin) can be produced. The RO treatment method is therefore directed towards the origin and its direction varies depending on the initial composition, in contrast to the ion-exchange methods. The deioniser is another method to produce pure water. Unlike reverse osmosis, the deioniser works by exchanging all ions (with a combination of a cation exchanger and an anion exchanger) rather than employing a semipermeable membrane. Because the deioniser cartridges have a relatively low capacity (amount of water that can be processed) compared to softeners or decarbonisers, they are not suitable for large volumes.
- The right panel in figure 9-2 shows the impact of dealkalisation which can be accomplished by an ion-exchanger or by adding a strong acid. As with decarbonisation it is essential to maintain some alkalinity because the water can get acidic and become corrosive. This treatment is currently not sold as continuous systems (in form of a cartridge or dispenser).



DM Demineraliser: Reverse osmosis (RO) or deioniser



DA Dealkaliser: HCO_3^- for Cl^- - or addition of a strong acid (e.g. sulphuric acid)

Figure 9-2: Impact of treatment methods that reduce total hardness or alkalinity, or both

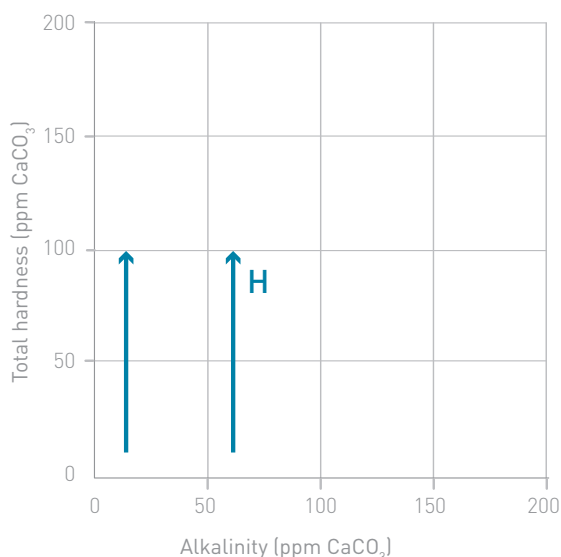
In case of low mineral content, treatment methods to increase total hardness and alkalinity can be used. Figure 10 shows the impact of four different treatment options.

- top left panel depicts the impact of a hardener that introduces calcium or magnesium as chloride or sulphate salts (CaSO_4 , MgSO_4 , CaCl_2 , and MgCl_2). Like the name suggests, it is essentially the opposite of a softener and is directed upwards. Hardening can be done by the use of mineralisation cartridges or by adding calcium or magnesium salts.
- The top right panel shows a carboniser representing the dissolution of magnesium or calcium carbonate. It is directed diagonally, up and to the right, increasing total hardness and alkalinity by equal amounts.
- Some RO systems are capable of using the leftover concentrate rather than the pure water that permeated the membrane. With such systems (shown in the lower left panel) total hardness and alkalinity of the source water can be increased. The treatment is directed away from the origin and preserves the ratio of total hardness to

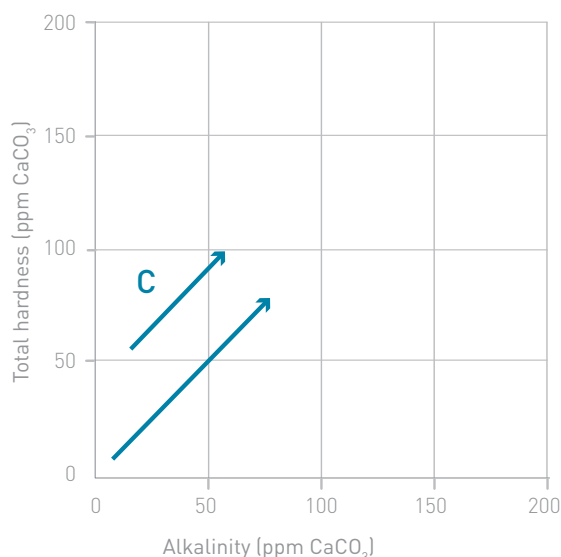


alkalinity found in the source water. The extent of increase depends on the efficiency of the RO systems but can reach an increase of more than twofold for modern systems (see section 6.8 for further details).

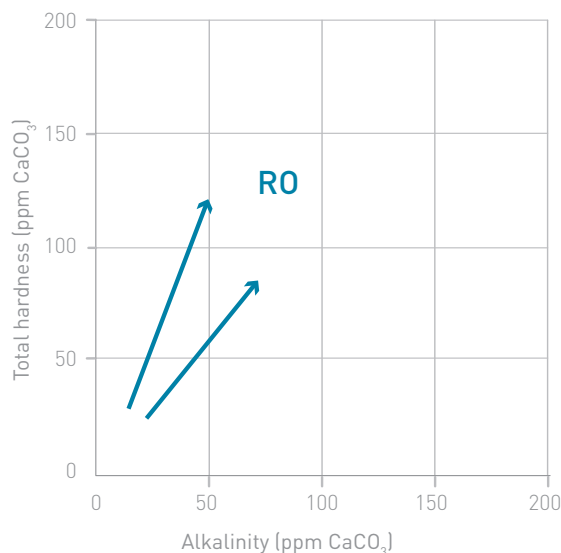
- Lastly, the lower right panel shows the effect of an alkaliser that increases alkalinity only, and therefore is directed to the right. This is accomplished by dissolution of sodium hydrogen carbonate or potassium hydrogen carbonate. This treatment is currently not sold as continuous systems (in form of a cartridge or dispenser).



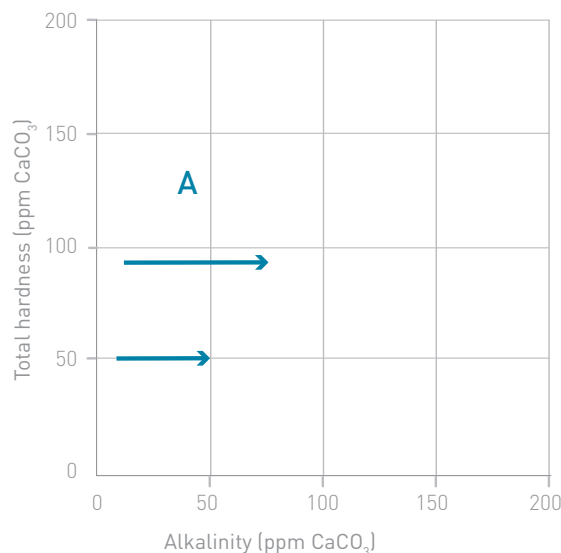
H Hardener: Dissolution of calcium or magnesium as chloride or sulphate salt



C Carboniser: Dissolution of calcium or magnesium carbonate



RO Reverse osmosis (RO) – use of water with an increased mineral content (concentrate)



A Alkaliser: Addition of sodium hydrogen carbonate

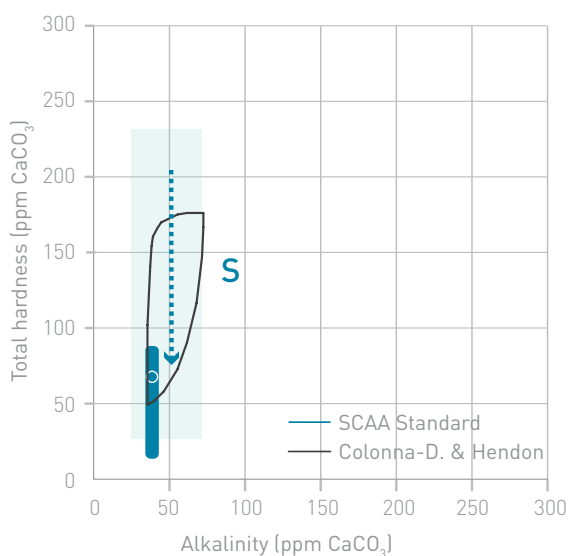
Figure 10: Impact of treatment methods that raise total hardness or alkalinity, or both

A relatively new treatment on the market is the exchange of calcium ions for magnesium ions. This form of ion exchange does not change either total hardness or alkalinity, so both values remain constant. Since calcium and magnesium can affect extraction differently, researching this has received increased attention as of late (Hendon et al., 2014).

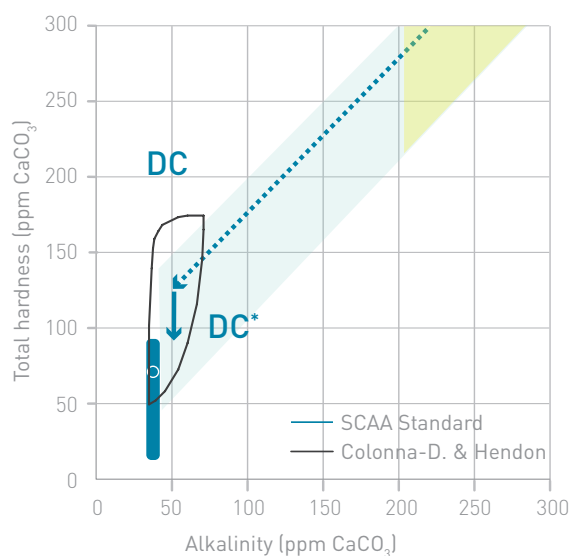
3.1 CHOICE OF WATER TREATMENT BASED ON STARTING COMPOSITION

In the following section we will illustrate the range of use for the different water treatment methods. All of the water treatment methods fall into one of the following two categories:

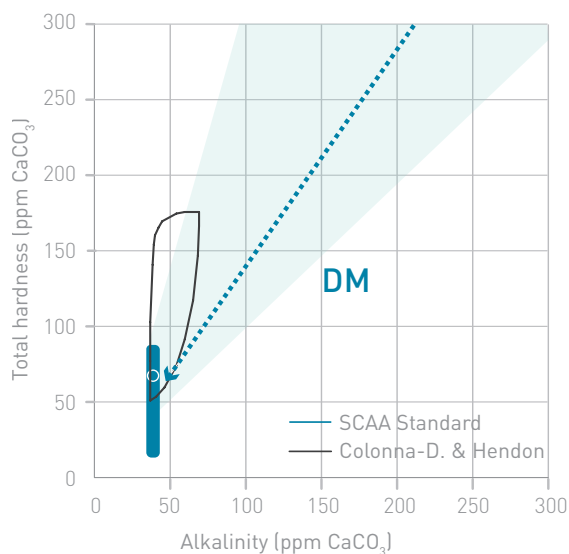
- **Continuous or inline systems:** The inlet of the water treatment system is directly connected to the tap water and its outlet to an espresso machine or brew boiler. This system allows for a continuous operation without user connected assistance. Regular control of the output water is advised for ensure a stable output.
- **Batch or off-line systems:** The water is treated batch-wise in a tank or other container. Using this system for espresso machines may require the use of an additional pump and accumulator as some pumps need positive pressure at their inlet. While all different types of ion-exchanger and RO can be operated in either of the two modes, the addition of an acid (dealkaliser) or of sodium hydrogen carbonate (alkaliser) are currently not sold as continuous systems (in form of a cartridge or dispenser).



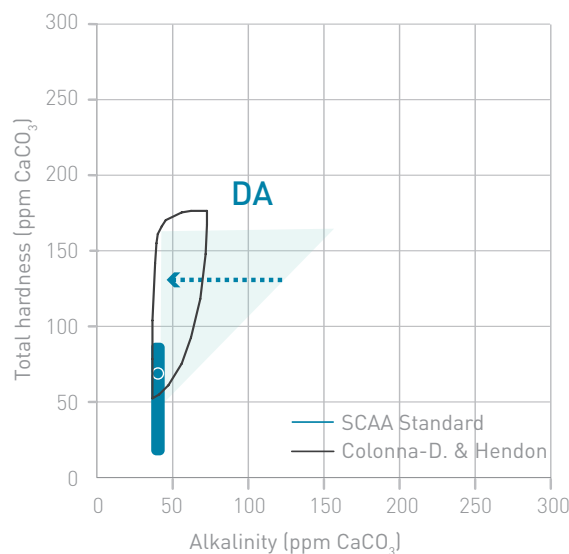
S Softener: Ca^{2+} and Mg^{2+} for potassium (K^+) or sodium (Na^+)



DC Decarboniser: Ca^{2+} and Mg^{2+} for H^+ - equally reduces total hardness and alkalinity
DC* Buffered decarboniser: decarboniser with a small portion of softener



DM Demineraliser: Reverse osmosis (RO) or deioniser



DA Dealkaliser: HCO_3^- for Cl^- - or addition of a strong acid (e.g. H_2SO_4)

Figure 11: Range of use for treatment methods that reduce total hardness or alkalinity

Figure 11 shows the potential range of use for the different treatment methods that reduce total hardness or alkalinity in order to arrive at the desired composition. As mentioned in the previous section when using decarbonisation or dealcalisation, it is essential to retain some alkalinity (the authors suggest at least 40 ppm CaCO_3) in order to avoid corrosive conditions that can breakdown boilers. Additionally, in case of the decarboniser, if it is used to treat water with high alkalinity ($> 200 \text{ ppm CaCO}_3$) the formation of carbonic acid can lead to a significant decrease in pH which also leads to corrosive conditions – marked in yellow in the upper right panel. This can be avoided if the treated water is left to degas its carbonic acid in form of carbon dioxide under ambient air conditions (see section 6.6).

Figure 12 summarises the potential range for treatment methods that can be used to increase total hardness or alkalinity. Note that the lower left panel illustrates RO systems which are capable of using the concentrated water that is usually treated as waste (for details see section 6.8).

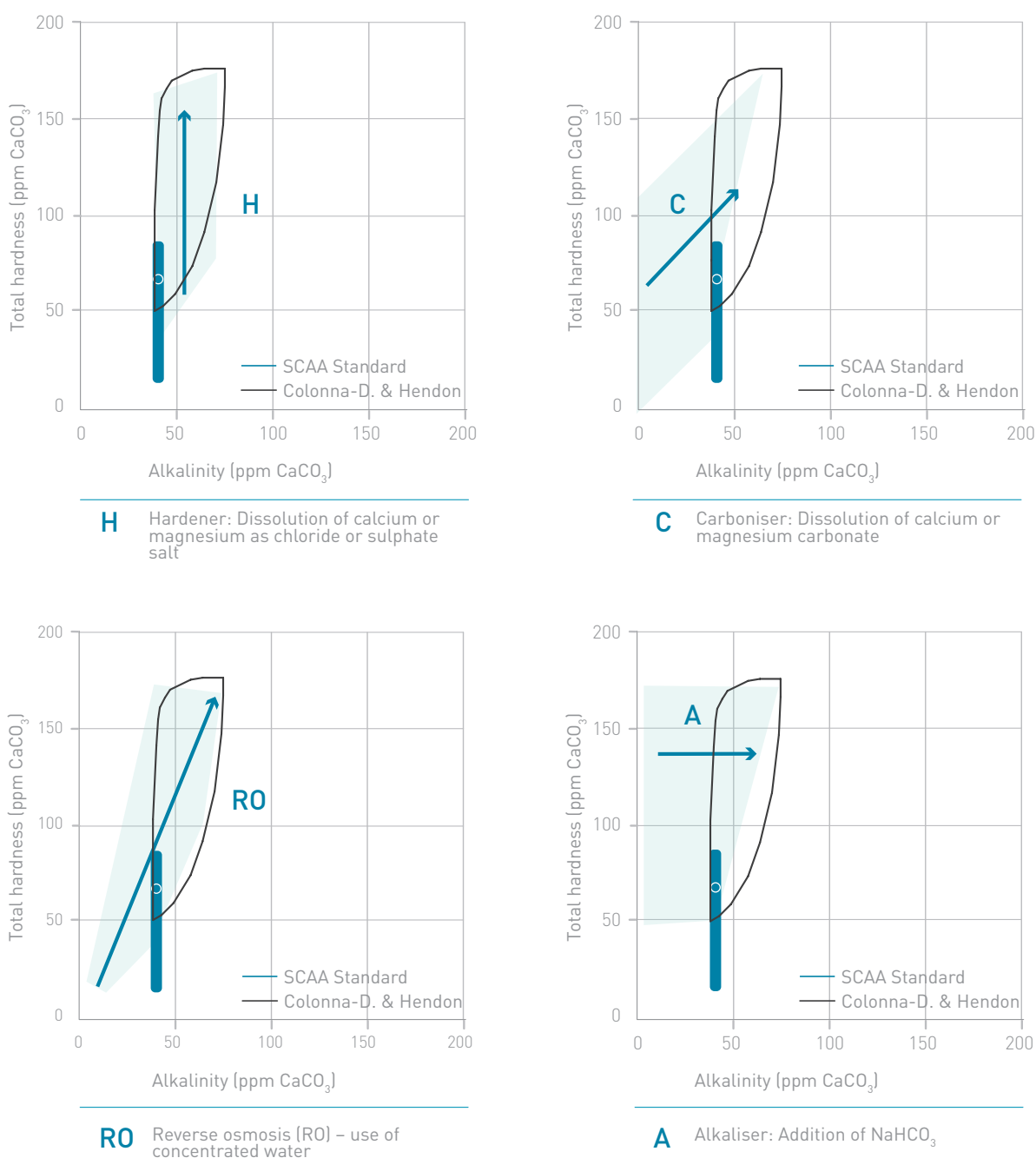


Figure 12: Range of use for treatment methods that raise total hardness or alkalinity

3.2 MIXING DIFFERENT WATERS

By mixing together water of different compositions, virtually any water composition can be produced. The mixture of two waters allows one to reach any composition on the connecting line between the two, as seen in the water charts in left and middle panel in figure 13, where the two circles represent the two initial water compositions and the line represents a mixture of the two. The three different waters shown in figure 1 represent:

1. Low concentration of both total hardness and alkalinity: demineralised water (RO or deioniser)
2. Low to medium alkalinity at high total hardness: Gypsum dominated water with a high sulphate content
3. High concentration of both total hardness and alkalinity: calcium or magnesium carbonate dominated water

The right panel in figure 13 illustrates mixing three waters, this way any composition can be achieved within the area of the triangle between the location of the three waters on the chart:

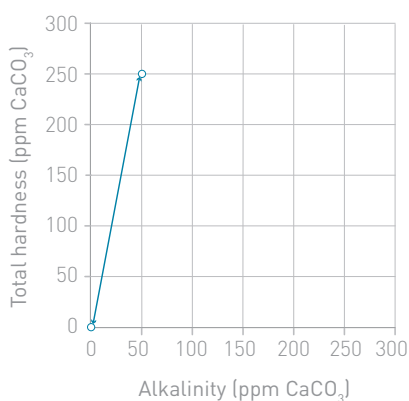


Figure 13-1

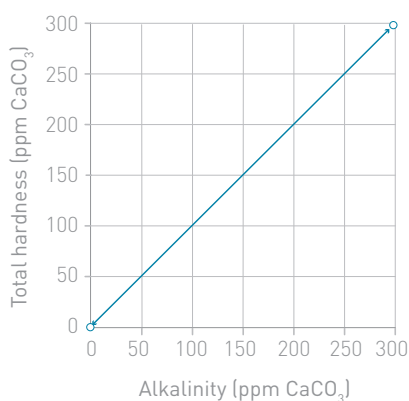


Figure 13-2

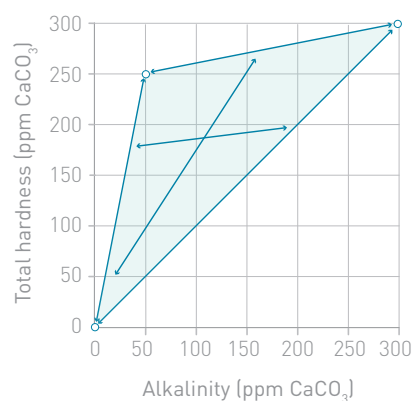


Figure 13-3

Figure 13: Examples of mixing water with different compositions

3.3 COMBINING DIFFERENT TREATMENT METHODS

In some cases no single water treatment is capable of changing the initial composition to a desired target. For instance if one desires to decrease both total hardness and alkalinity but actually increase the difference between the two (meaning alkalinity is reduced to a larger extent than total hardness), none of the described water treatments will allow you to fulfill both requirements. In these cases a combined treatment by either a decarboniser combined with a hardener, or a complete demineralisation with subsequent remineralisation can lead to the targeted composition. Also a combination of complete demineralisation and subsequent remineralisation can solve problems that arise due to the presence of additional undesirable ions such as iron (Fe^{2+}) or lead (Pb^{2+}).

3.4 CONVERSION OF HARDNESS AND ALKALINITY TO OTHER IONS

The different treatment methods listed in the previous sections exchange calcium, magnesium, or hydrogen carbonate ions for other ions. Other treatments introduce calcium, magnesium, or hydrogen carbonate ions along with other ions (for example sulphates, chlorides, or sodium ions). Table 2 lists the conversion factors used to calculate how much of these other ions is introduced into the water by a specific treatment. A special case is the production of carbonic acid that forms dissolved carbon dioxide by the decarboniser treatment (see also section 6.6).

		Na ⁺ (mg/L)	K ⁺ (mg/L)	Dissolved CO ₂ (mg/L)	SO ₄ ²⁻ (mg/L)	Cl ⁻ (mg/L)	Na ⁺ (mmol/L)	K ⁺ (mmol/L)	Dissolved CO ₂ (mmol/L)	SO ₄ ²⁻ (mmol/L)	Cl ⁻ (mmol/L)
ppm CaCO ₃ (= mg CaCO ₃ /L)	1 ppm CaCO ₃ =	0.4594	0.7813	0.4397	0.9597	0.7084	0.01998	0.01998	0.009991	0.009991	0.01998
GERMAN DEGREES (°d)	1 °dH =	8.199	13.94	7.848	17.13	12.64	0.3566	0.3566	0.1783	0.1783	0.3566
FRENCH DEGREES (°f)	1 °fH =	4.594	7.813	4.397	9.597	7.084	0.1998	0.1998	0.09991	0.09991	0.1998
GRAINS PER US GALLON (gpg)	1 gpg =	7.864	13.37	7.527	16.43	12.13	0.3421	0.3421	0.1710	0.171	0.3421
ENGLISH DEGREE (°e)	1 °e =	6.548	11.14	6.268	13.68	10.1	0.2848	0.2848	0.1424	0.1424	0.2848
Ca ²⁺ + Mg ²⁺ (mmol/L)	1 mmol/L =	45.98	78.20	44.01	96.06	70.91	2	2	1	1	2
HCO ₃ ⁻ (mmol/L)	1 mmol/L =	22.99	39.10	22.00	48.03	35.45	1	1	0.5	0.5	1
Ca ²⁺ (mg/L)	1 mg/L =	1.147	1.951	1.098	1.198	0.8846	0.0499	0.0499	0.02495	0.02495	0.0499
Mg ²⁺ (mg/L)	1 mg/L =	1.892	3.217	1.81	1.976	1.459	0.08229	0.08229	0.04114	0.04114	0.08229
HCO ₃ ⁻ (mg/L)	1 mg/L =	0.3768	0.6408	0.3606	0.7871	0.581	0.01639	0.01639	0.008195	0.008195	0.01639

Table 2: Conversion factors of total hardness and alkalinity to other ions

4 CONTROL – ENSURING STABLE WATER COMPOSITION

Depending on prior experience or locally available data on the stability of the water supply, a smaller or larger initial measurement series should be conducted. For water that is from a single groundwater source, a high stability can be expected over both the short and long term. On the other hand, if multiple sources feed the tap water network, daily and seasonal variations can occur. As a consequence, an initial measurement series should be conducted that tests both the incoming water composition throughout the day as well as measuring the changes from one day to the next as well as over the course of a whole year.

The conductivity of water can be measured with a simple instrument called conductivity meter (incorrectly also called TDS-Meter). On its own it is not a meaningful parameter (see section 6.7 for a detailed explanation), except for getting a very rough estimate of the total solids content. Yet, for a given water installation, for example tap water and a defined water treatment method, measuring the conductivity offers the opportunity to detect changes in the output water composition caused by changes in either the tap water composition or the efficiency of the water treatment method. Since conductivity can be measured with inexpensive on line sensors, this offers the opportunity of continuous real-time monitoring of water quality.

5 CONCLUSIONS AND OUTLOOK

Given a water source (tap or bottles) that provides hygienic water free of off-flavours (such as chlorine or iron or earthy and mouldy flavours), the three step approach presented in the previous sections (Measure, Aim, Treat) introduces a systematic method on handling water for coffee extraction. After measuring the initial composition of a water and deciding for a target composition the most crucial step is to choose a suitable treatment. The majority of users will find all of the necessary information to decide on for a specific water treatment or combination of multiple treatment methods, in the preceding chapters. However some users will have to delve further into the science of water in order to reach the composition of one of the recommendations. Specifically this concerns the treatment of very high alkalinity water (above 300 ppm CaCO_3), very low alkalinity water (below 50 ppm CaCO_3) or the selective reduction of alkalinity (dealkalisation). These situations are discussed in the following section on the fundamentals of water.

As explained previously the main focus of this booklet is to provide a framework to characterise water and a toolbox on how to use the various treatment methods. Though depending on the specific green beans, roasting style, storage, grinding and extraction method, the actual target composition that leads to the desired outcome will vary significantly. Therefore the next steps in research should include experiments to propose correction factors or alternate optimal zones to account for a number of variables whose influences have not yet been elucidated in detail. Namely these are:

- Influence of brew ratio on the optimal composition of water. Recent literature and simple chemical consideration suggest that low brew ratios (such as are used for espresso compared to drip coffee) shift the optimum of total hardness and alkalinity to higher values – up along the diagonal.
- Influence of temperature and pressure on the optimal values of total hardness and alkalinity. Since temperature and pressure both affect extraction efficiency this is in turn coupled to the water composition used.
- Influence of roasting style on the sensory properties of the final beverage. Anecdotal evidence suggests that the use of water with higher concentrations of total hardness and alkalinity can compensate to some extent for a roast that has not been fully developed (for example roasted too light).
- Influence of calcium versus magnesium on the extraction and the sensory properties of the final beverage. Theoretical consideration from a recent publication (Hendon et. al, 2014), as well as preliminary experiments, indicate that magnesium has a slightly higher extraction efficiency compared to calcium. The difference between calcium and magnesium with regard to their impact on the sensory properties however remains unclear and is subject to future investigations.

Beside these purely scientific considerations also regional, cultural or individual preferences can play a significant role in the choice of the optimum water composition. For example in areas where the tap water is very soft (total hardness and alkalinity below 40 ppm CaCO_3) this might have influenced the development of specific taste preferences and roasting styles.

6 FUNDAMENTALS

Water is at its foundation an unequal marriage- of one strongly electron-attracting oxygen atom and two weakly electron-attracting hydrogen atoms. Analogous to a tug-of-war between unequal partners the electrons end up being located closer to the oxygen than to the hydrogen atom. This characteristic is called polarity which refers to the uneven distribution of charge within the water molecule.

6.1 PHYSICOCHEMICAL CHARACTERISTICS OF WATER

One of the most important consequences of the polar nature of water is that water molecules have a strong tendency to align against each other in a systematic pattern where the oxygen atom of one molecule is located closest to the hydrogen atom of another water molecule. This type of weak bond is called hydrogen-bonds, which are about one twentieth the strength of the chemical bond between the hydrogen and oxygen at 25 °C (CRC, Suresh) illustrated in figure 14:

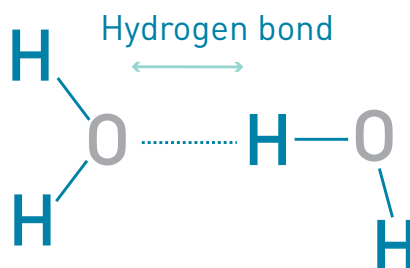


Figure 14: Hydrogen bond between two water molecules

Due to its polar nature, water is a very good solvent for polar compounds such as ionic compounds and polar molecules, e.g. during extraction. On the contrary it hardly dissolves non-polar compounds such as oils and fats, which make up approximately 10 % of the weight of roasted coffee. Yet for extraction under high pressure and temperature for espresso (approx. 9 bar and 92 °C), or moka pot (boiling temperature), or long contact times like French press (4 minutes extraction within filter), the solubility of non-polar compounds is significantly increased (Gloess, 2013).

Among the special/anomalous characteristics of water are a number of mostly well-known phenomena, namely:

- Water shows two anomalies with regard to its density:
 - Its highest density is reached at 4 °C
 - The density of water as a solid (ice) is lower than in its liquid form – i.e. water expands during freezing and shrinks when melting
- Water has a boiling point that is unusually high and a freezing point that is very low compared to substances of similar mass
- Water has a very high heat capacity – meaning it takes a lot of energy to heat or cool water
- Water is almost incompressible – at a pressure of 1000 bar (present in the deepest parts of the ocean at 10'000 m below surface) it is only 5 % more dense than at atmospheric pressure

What is of more practical relevance with respect to everyday conditions is that water has a density of almost exactly 1000 kg/m³ or 1 g/mL. The boiling point of pure water is not just determined by its temperature but in fact by the pressure of the surrounding gas phase, as it is well-known from the phenomenon of reduced boiling point temperature at high altitudes. Figure 15 shows the vapour pressure of water in absolute values, and in order to calculate overpressure with respect to the atmosphere (relative pressure), such as in a steam boiler, the absolute pressure has to be subtracted by the atmospheric pressure (e.g. of approx. 1 bar at sea level).

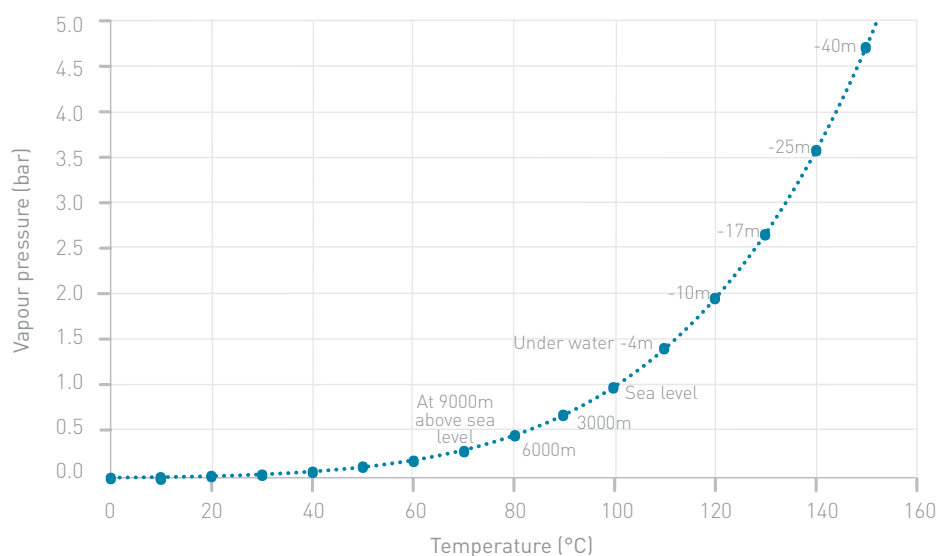


Figure 15: Vapour pressure of water as absolute pressure – equivalent values of atmospheric pressure at different altitudes is indicated on the chart ($p < 1$ bar), along with static pressure under water ($p > 1$ bar)

6.2 UNITS OF CONCENTRATION – MEASURE IN MORE DETAIL

In contrast to everyday life where mass and volume are standard units to quantify absolute (g/L) and relative substance contents (% w/w, % v/v), in chemistry substances (or more general entities) are quantified in moles which is a value proportional to the actual number of atoms, ions, or molecules. While using units of mass is common to everyone, they do not reflect the true proportions of the chemical compounds involved in terms of their number of molecules, ions, or atoms. Using units in amount concentrations instead of mass concentration is paramount to chemistry since only the proportions relative to the actual number of entities reflects the actual ratios needed to understand and explain any chemical process. Amount concentrations (also called molar concentrations) are given as mole per volume or weight, most commonly for water analysis in mmol/L. Derived directly from amount concentrations is the definition of equivalent mass units and hardness degrees which will be explained in the next section. In contrast to amount concentrations, equivalent concentrations can only be applied to (charged) ions and are calculated by multiplication of the amount concentration (mmol/L) by the charge number of the ion (z) and termed as equivalents or abbreviated “eq”, e.g. meq/L (milliequivalents per litre).

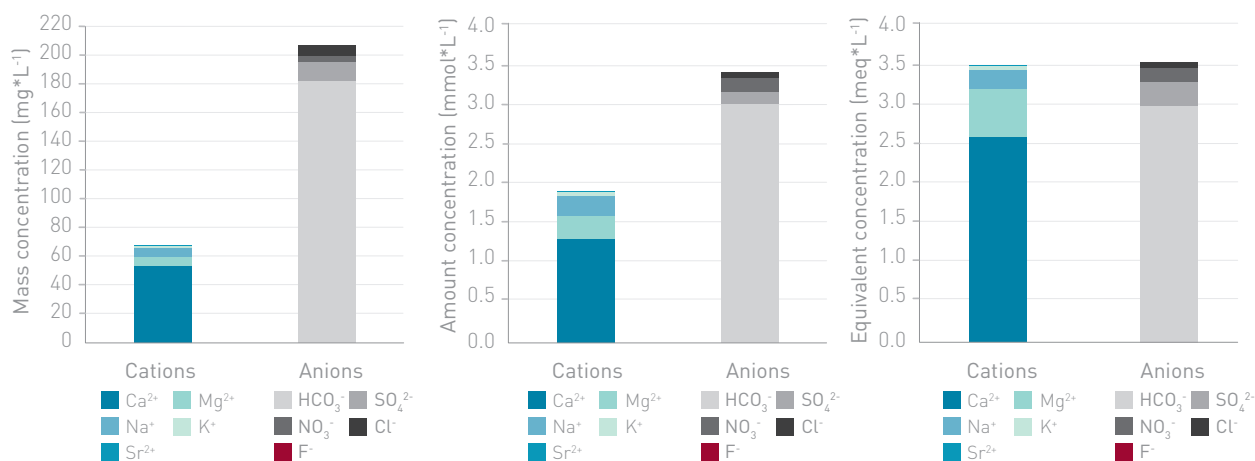


Figure 16: Water composition of Zurich tap water (average 2014), illustrating major cations and anion content in drinking water, left: mass concentrations (mg/L), centre: amount concentrations (mmol/L), right: charge equivalent concentrations (meq/L = mmol-z/L)

Since ions constitute typically over 95% of the chemical components (i.e. less than 1% of solutes are uncharged) in fresh water, this limitation is negligible for the purposes of this chapter. By multiplying the molar concentrations of all ions with their charge we can calculate the fundamental balance that has to be fulfilled for every water sample (charge neutrality). Measurements and calculations in equivalent units allow for a “double-entry bookkeeping” of water composition, since it allows for an assessment of potential gaps in the analysis. Also it is evidently the most transparent and clearest representation when assessing scale formation or water treatment methods.

For a known water composition conductivity measurements can be transformed into a value for total dissolved solids.

6.3 HARDNESS OF WATER AND SCALE FORMATION

To understand the different expressions that are used in the industry some explanations on the origins of and rationale behind the concept of hardness will be given. The term water hardness originates from the capacity of water to precipitate soaps during washing. The predominant reason for the precipitation of soaps is a high content of calcium and magnesium (SMWW, 2012; DIN, 1986; ASTM, 2002). While other polyvalent cations such as iron, barium and strontium may also precipitate soap, their presence in fresh water is seldom above trace amounts and can in most circumstances be neglected. Additionally, water used in boilers at home or in industrial equipment can become encrusted with scale residues that are being formed mainly from calcium carbonate (CaCO_3) and at high pH (>10) also by magnesium hydroxide ($\text{Mg}(\text{OH})_2$). Since the scale formation by precipitation of calcium carbonate is equally dependent on the concentration of carbonates as well as on calcium, the concept of “carbonate hardness” has been introduced and is still very common in the water industry. Most fresh water sources contain an equivalent concentration of hydrogen carbonate (HCO_3^-) that is lower than total hardness. This limits the maximum amount of total hardness that can precipitate: i.e. $c(\text{HCO}_3^-) + 2 \cdot c(\text{CO}_3^{2-}) < 2 \cdot c(\text{Ca}^{2+}) + 2 \cdot c(\text{Mg}^{2+})$. Some calcium and magnesium will remain in the water. In this case only the fraction of total hardness (calcium and magnesium) corresponding to the hydrogen carbonate content is called “carbonate hardness” or temporary hardness. The remaining calcium and magnesium content is called “non-carbonate” hardness or permanent hardness. It is the part of the total hardness that remains, after all HCO_3^- and CO_3^{2-} has been used up. Non-carbonate hardness is most commonly introduced into the water by sulphate- or chloride-minerals that do not form scale (i.e. do not precipitate). In the opposite case when the equivalent hydrogen carbonate concentration is higher than total hardness, the carbonate hardness corresponds to the total hardness as all calcium and magnesium can be precipitated and no permanent hardness remains. In this case the fraction of HCO_3^- that is higher than total hardness would have to be called, following the “hardness logic”, as “non-hard” carbonate.

6.4 UNITS OF HARDNESS

To this day it is common in the industry of all Western countries, to use equivalent units to report hardness. This means that the contents of ionic species (Mg^{2+} , Ca^{2+} , HCO_3^-) are represented by the equivalent mass of the corresponding solid they could form when precipitating. Furthermore hardness equivalent units are defined with respect to the mass of calcium carbonate (ppm CaCO_3 - USA, °fH - FR, °e - UK), except German hardness degrees (°dH) which are defined with respect to calcium oxide. This means in practice is that the lower of the two values (hardness and HCO_3^- equivalents) determine the theoretical maximum mass that can precipitate and form scale, for example in boilers.

As remarked earlier these units are not the same as the concentrations on bottled water labels that state mass concentrations in mg/L of the respective ions (or neutral molecules like silicates).

Specifically, this means that when 1 mole of calcium carbonate is removed from water (e.g. scale formation) the concentration of calcium decreases by 1 mole whereas the concentration of hydrogen carbonate decreases by 2 moles (this is due to the fundamental rule that a water always stays charge neutral for all processes of consideration in this chapter).

6.5 EXPLANATIONS AND APPLICATIONS OF pH

By definition pH is a ratio and therefore dimensionless – or more correctly has the dimension «1». For nearly pure water (> 99.9% equivalent to a TDS < 1000ppm) - such as most drinking water - the pH value can be expressed in a very tangible and precise way:

- pH 7 denotes that for every proton (H⁺) there are 560 million water molecules – and for pure water it can be stated moreover that because the proton originates from the self-dissociation of water there is also exactly one hydroxide ion (OH⁻) for the same number of water molecules.

Water molecules split off a proton to a small extent – in actuality the free proton is immediately adopted by another water molecule. This phenomenon is called autodissociation of water and is illustrated in figure 17:

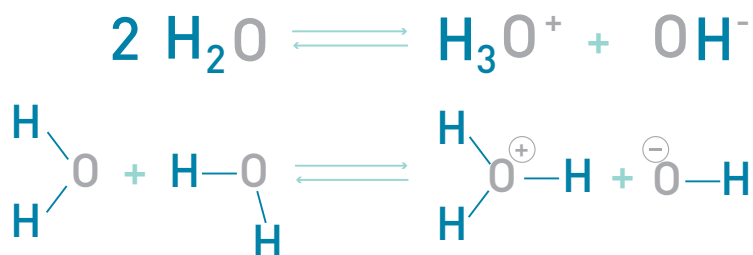


Figure 17: Autodissociation of water; top: autoprotolysis illustrated by the molecular formulas; bottom: autoprotolysis as ball-and-stick model

- For the sake of simplicity we will refer to protons (H⁺) instead of hydronium ions (H₃O⁺)
- pH is a measure for the concentration of 'free' protons (H⁺) in water
- Strictly scientifically speaking pH is a ratio and therefore is dimensionless – or more correctly has the dimension «1»

For every increase of the pH by one unit (+1) the concentration of protons decreases by a factor of 10; and for every decrease of the pH value (-1) the concentration of protons increases by a factor of 10. The opposite holds true for the hydroxide ions – specifically, the number of hydroxide ions increases by a factor of ten for every increase of the pH value by one unit and decreases by a factor of ten for every decrease by one unit in pH.

The higher the temperature, the more protons (and hydroxide ions) are present in neutral water. Only at 25 °C a neutral pH corresponds to a value of exactly 7 (see Figure 18).

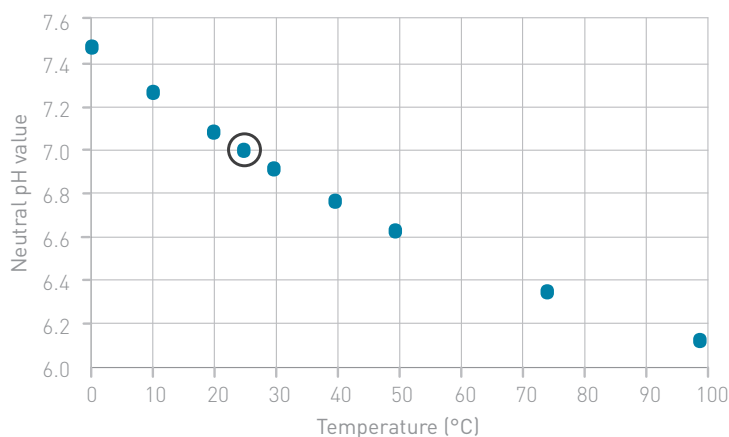


Figure 18: Dependence of neutral pH value on temperature

Figure 19 gives examples from everyday liquids across the pH range from highly acidic stomach acid to highly basic caustic soda.

Substance	Stomach acid (empty stomach)	Lemon juice	Coke	Orange and apple juice	Skin surface of humans	Human saliva	Pure water	Soap	Household ammonia (4% w/w)	Concrete	Sodium hydroxide (caustic soda)
pH Value	1.0-1.5	2.4	2.0-3.0	3.5	5.5	6.5-7.4	7.0	9.0-10.0	11.5	12.6	13.5-14
Type	Acidic					Neutral		Alkaline			

Figure 19: pH values of everyday products or chemicals

6.6 ACIDS AND BASES

The strength of an acid is measured by its power to transfer its proton to water, thereby using water as a base. Strong acids are donating virtually all of their protons to pH levels below 2 – meaning even if there are already a lot of protons present in the water (low pH) the acid will still dissociate and donate its proton to the solution.

6.7 CARBONATE CYCLE – WHY SCALE AND CARBON DIOXIDE ARE RELATIVES

When water molecules evaporate off a liquid water surface, there are only very few constituents that are transferred to the gas phase along with it, so water vapour rising from a water surface is essentially pure H₂O. The purity of water is diminishing as soon as it condensates, as this allows gases and small particulates to dissolve in the liquid. Acid rain is the most common phenomenon known in this context which is mainly caused by sulphur dioxide emissions from combustion of sulphur-containing fuels in industry and mobility. To a lesser extent acid rain is also caused by NO₂ and lastly CO₂. Thanks to elimination of sulphur in gasoline, diesel and kerosene as well as mandatory gas cleaning installation for industrial plants the emissions of both SO₂ and NO₂ have been considerably reduced over the last 10 years. Nowadays the rain water is dominated by the dissolution of CO₂ which is described in the language of chemists by the following equation:



Equation 1:

The carbonic acid (H₂CO₃), which is formed as a consequence of the dissolution of CO₂ in water is a weak acid and hence donates one of the two protons to water forming singly-charged hydrogen carbonate, according to the following equation, leading to an acidification of the water:



Equation 2:

Hydrogen carbonate is an acid as well, as it may in principle further donate its one left proton to water, forming a doubly-charged carbonate ion (CO_3^{2-}), according to the following equation:



Equation 3:

Yet under normal circumstances this is very unlikely to happen, as the proton donating power of hydrogen carbonate is small at pH values that prevail in drinking water. Only at very basic condition above pH 9 does carbonate form.

Since carbonic acid (H_2CO_3) is a much weaker acid than sulphuric or nitric acid, the average pH of rain water in Switzerland has risen from approximately pH 4.5 in 1985 to pH 5.5 in 2013, equaling a decrease of a factor 10 in proton concentration of rain water. At the current atmospheric concentration levels of CO_2 pure water in equilibrium with the atmosphere has a pH value of approx. 5.7 due to the acidification from carbonic acid (H_2CO_3).

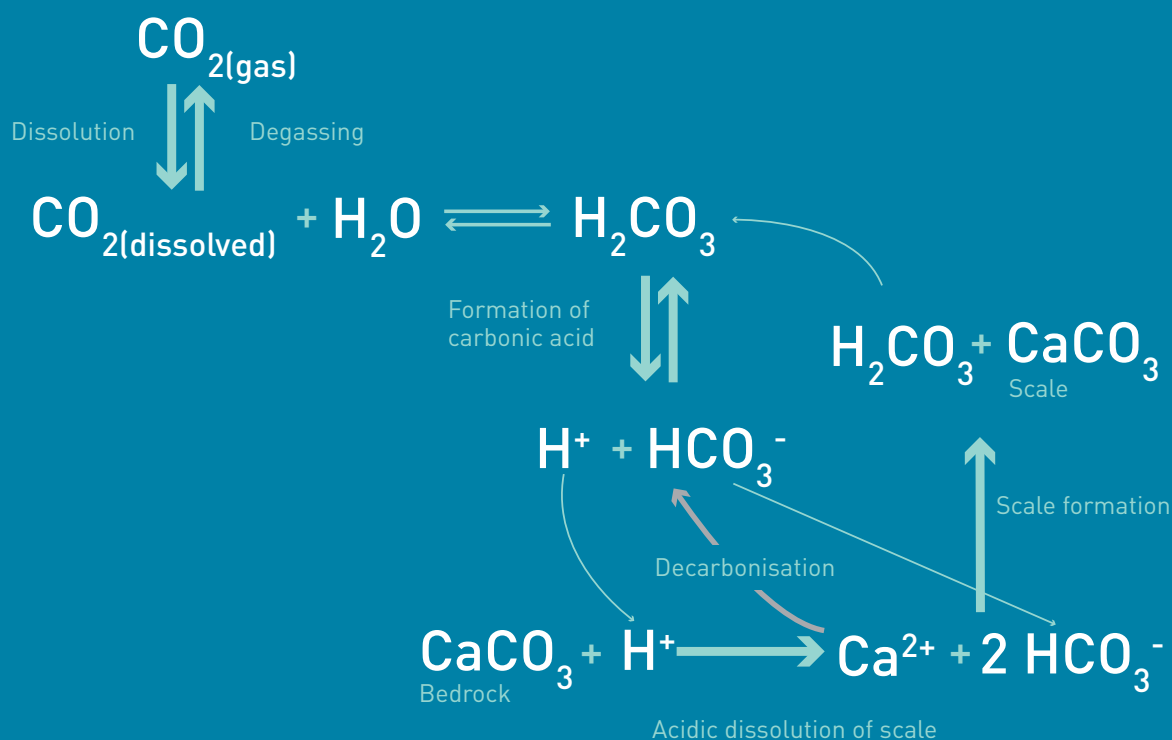


Figure 20: The carbonate cycle in coffee applications

For the purpose of this work, we treat dissolved carbon dioxide synonymously to carbonic acid, although this is not strictly true in chemical terms. This is a well-documented and researched assumption in aquatic chemistry.

Therefore we can directly link the carbon dioxide from the roasted coffee with carbonic acid in water and the hydrogen carbonate that links it to the alkalinity (acid-buffer) and scale formation.

6.8 TREATMENT OF HARD WATER BY DECARBONISATION

A special case is the treatment of hard water by decarbonisation. The working principle of the decarboniser that reduces total hardness and alkalinity is based on the exchange of magnesium or calcium ions by protons. This means that although the hydrogen carbonate is protonated and therefore not an acid buffer anymore, it is still present in the form of carbonic acid, which in turn is in a constant exchange with dissolved carbon dioxide (see section 7.4 on the carbonate cycle for a more detailed explanation). If the treatment is done by an inline system where the carbonic acid cannot escape as carbon dioxide it leads to two effects. The pH of the treated water will decrease and in the case of a water with a high starting level of total hardness (> 300 ppm CaCO_3), this can effectively make the treated water so acidic that the risk of corrosion increases drastically. Additionally the large amount of carbonic acid will also lead to excessive crema production during the extraction of espresso. As an example from a real-world application, a roaster had an issue with his espresso being very foamy (large bubbles that collapse quickly in the crema) because he used a decarboniser to treat his very hard water (above 300 ppm CaCO_3). The reduction by approx. 250 ppm CaCO_3 in alkalinity increased the dissolved carbon dioxide by 220 mg/L (in form of carbonic acid). For a standard double espresso recipe (1:2 brew ratio) this means that even for a very fresh coffee 1h after roast and 2min after grinding the water can add another 25 % to the carbon dioxide already contained in the coffee grounds. Figure 21 illustrates this decrease of pH depending on the alkalinity reduction by decarbonisation.

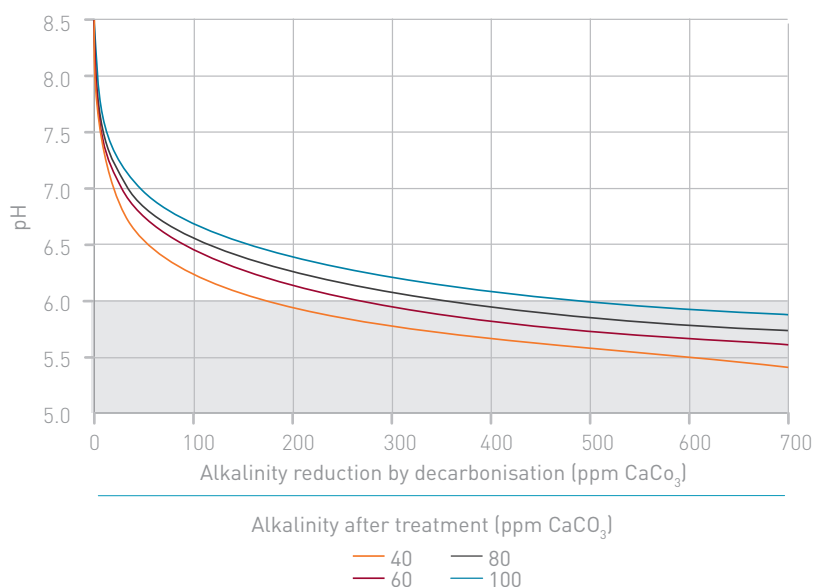


Figure 21: pH decrease due to dissolved carbon dioxide from decarbonisation

Fungi, plant roots and microorganisms in the soil release carbon dioxide which in turn is dissolved in the ground water. This effect leads to a decrease in pH by one unit or more depending on the dissolved carbon dioxide of the water out of the tap. The opposite reaction is degassing of carbon dioxide from water by letting it stand in an open container, by stirring, by putting it under vacuum or by heating. Figure 22 shows the evolution of the pH of a tap water containing 180 ppm CaCO_3 . Out of the tap the pH of the water was initially at 7.5, which corresponds to 11 mg/L of dissolved carbon dioxide. By stirring it in an open container over the course of a day in an open container, it rose by more than one pH unit. After 24h it was measured at pH 8.7 which then corresponds to 0.7 mg/L carbon dioxide which is almost down to the equilibrium level with the atmosphere which is at 0.4 mg/L – at 20°C independent of pH.

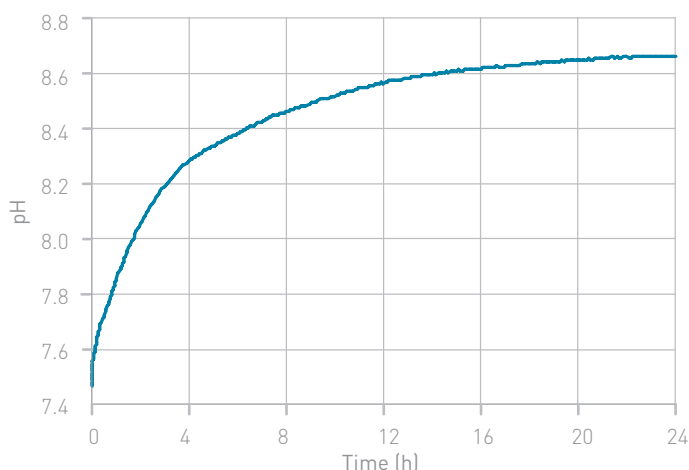


Figure 22: Evolution of pH of a tap water

6.9 CONDUCTIVITY METER AKA «TDS-METER»

As stated previously the conversion of electrical conductivity to TDS is only a very rough estimate. In more tangible terms TDS measurements have a typical error range of +/-30% (and in rare cases over 50% error) and therefore should not be used as a significant parameter to compare the water at one location to the water at another location. The reason for this uncertainty (or error) is that the actual conversion factor depends strongly on the exact composition. And moreover most of the cheaper models do not measure and correct for water temperature, which influences the conversion strongly. Figure 20 shows an overview on the error in TDS readings at two different temperatures when compared to the standard conversion factor of 0.7 (in mg/L of TDS per 1 µS/cm of electrical conductivity, used for example by the SCAA). Data on mineral composition were taken from Lockhart (1955) and Pawlowicz (2008). Figure 23 also lists the effective conversion factors from electrical conductivity (in µS/cm) to total dissolved solids (TDS, in mg/L) as labels overlaying the bars in the chart.

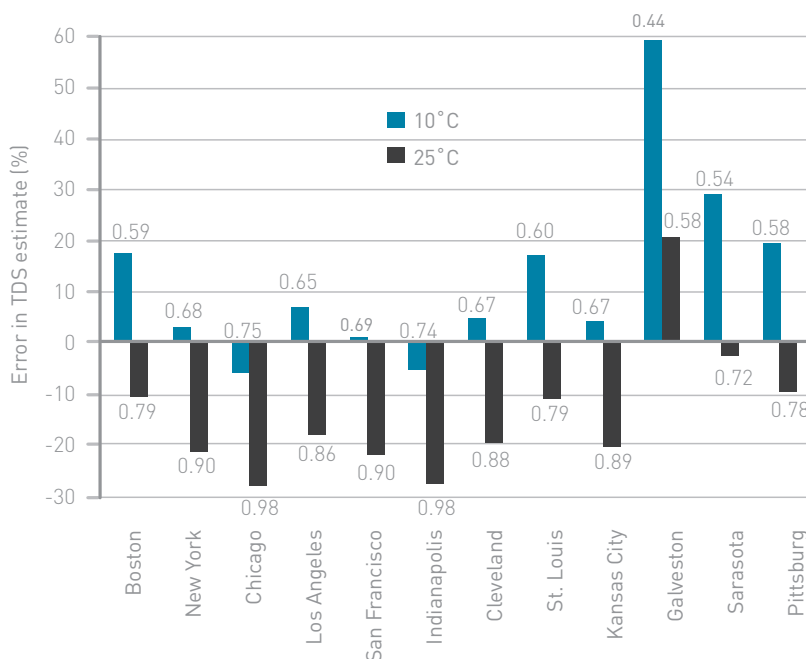


Figure 23: Examples of conductivity to TDS conversion factors at 10°C and 25°C compared to the most commonly used conversion factor of 0.7 (conductivity to TDS)

6.10 USING REVERSE OSMOSIS TO INCREASE THE MINERAL CONTENT OF WATER

In reverse osmosis the maximum degree of concentration that can be achieved is directly correlated with the efficiency (waste ratio) of the system. The less water used to produce one litre of permeate (almost pure water) the more concentrated the leftover concentrate is. Usually this leftover concentrate is treated as waste though there are also reverse osmosis systems that are capable of using this concentrate in order to increase the mineral content of water. This can be used to increase total hardness and alkalinity if the source water is of low mineral content but otherwise high quality, specifically in the absence of other undesirable or harmful compounds (for example no metals or chlorine are present). Table 2 lists conversion factors to calculate the maximum increase in mineral content of water as a function of the efficiency of a reverse osmosis system.

Waste / %	Ratio of diluted permeate to concentrated leftover	Concentration factor	Increase in mineral content / %
80	1 : 4.0	1.3	25.0
75	1 : 3.0	1.3	33.3
70	1 : 2.3	1.4	42.9
65	1 : 1.9	1.5	53.8
60	1 : 1.5	1.7	66.7
55	1 : 1.2	1.8	81.8
50	1 : 1	2.0	100
45	1.2 : 1	2.2	122
40	1.5 : 1	2.5	150
35	1.9 : 1	2.9	186
30	2.3 : 1	3.3	233
25	3.0 : 1	4.0	300
20	4.0 : 1	5.0	400

Table 3: Waste ratio and concentration factors for reverse osmosis

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