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Assessment of calculation methods for calcium carbonate saturation in drinking water for DIN 38404-10 compliance

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Abstract

The new German standard for calcium carbonate saturation in drinking water, DIN 38404-10, 2012 (DIN), marks a change in drinking water standardization from using simplified equations applicable for nomographs and simple calculators to using extensive chemical modeling requiring computer programs. The standard specifies the chemical outlines for the modeling and presents a dataset with 10 water samples for validating used computer programs. The DIN standard, as well as the Standard Methods 2330 (SM) and NEN 6533 (NEN) for calculation of calcium carbonate saturation in drinking water were translated into chemical databases for use in PHREEQC (USGS, 2013). This novel approach gave the possibility to compare the calculations as defined in the standards and internationally accepted chemical databases provided with PHREEQC. From the research it is concluded that the computer program PHREEQC with the developed chemical database din38404-10_2012.dat complies with the DIN standard for calculating Saturation Index (SI) and Calcite Dissolution Capacity (Calcitlösekapazität) or Calcium Carbonate Precipitation Potential (CCPP). This compliance is achieved by assuming equal values for molarity as used in DIN (obsolete) and molality as used in PHREEQC. From comparison with internationally accepted chemical databases it is concluded that the use of molarity limits the use of DIN to a maximum temperature of 45 °C. For current practical applications in water treatment and drinking water applications, the PHREEQC database stimela.dat was developed within the Stimela platform of Delft University of Technology. This database is an extension of the internationally accepted chemical database phreeqc.dat and thus in compliance with Standard Methods 2330. The database stimela.dat is also applicable for hot and boiling water, which is important in drinking water supply with regard to scaling of calcium carbonate in in-house drinking water practices. The SM and NEN proved to be not accurate enough to comply with DIN, because of their simplifications. The differences in calculation results for DIN, SM and NEN illustrate the need for international unification of the standard for calcium carbonate saturation in drinking water.

1 Introduction

In general, calculation of calcium carbonate saturation in drinking water is performed with a simplification of the processes as shown in Table 1, in which ion pairs are neglected and calcite is assumed to be the determining crystalline phase. The equations for equilibrium constants in Table 1 do not apply to the concentrations of diluted species, but to their (relative) activities which are smaller than the concentrations because of their interference with each other and with the surrounding water molecules (dipoles).

Further simplification of calcium carbonate saturation calculation is based on the fact that the pH of drinking water is usually between 5.5 and 8.5. In this pH range the concentrations of H^+ and OH^- are small ($<0.004\,\mathrm{mmol\,kgw^{-1}}$) and therefore neglected. The concentration of CO_3^{2-} is also small ($<2\,\%$ of the total inorganic carbon), and therefore it is assumed that carbonate is only present as bicarbonate. With these simplifications the saturation index (SI), which is a measure for the thermodynamic driving force to the equilibrium state for a precipitation/dissolution reaction, for calcium carbonate can be determined with:

$$\mathrm{SI} = \lg\left(\frac{\left\{\mathrm{Ca}^{2+}\right\}\left\{\mathrm{CO}_3^{2-}\right\}}{K_S}\right) = \lg\left\{\mathrm{Ca}^{2+}\right\} + \lg\left\{\mathrm{HCO}_3^-\right\} + \lg K_2 - \lg K_S + \mathrm{pH} \tag{1}$$

Langelier combined the first four terms in the last part of Eq. (1) into the parameter $-\mathrm{pH_s}$ (Langelier, 1936). Therefore SI for calcium carbonate is often called Langelier Index (LI) or Langelier Saturation Index (LSI). The parameter SI is dimensionless, because the activities in Eq. (1) are relative dimensionless values compared to standard conditions (standard molality, $1\,\mathrm{mol\,kgw^{-1}}$). This is also the case for pH and the K values in Table 1 (Buck et al., 2002; Gamsjäger et al., 2008).

A practical parameter that is associated with the calcium carbonate saturation and generally used is the Calcium Carbonate Precipitation Potential (CCPP) (Standard

Methods 2330, 2010), which is a measure for the amount of calcium carbonate which theoretically can precipitate until equilibrium.

SI and CCPP are positive for oversaturated water, zero for saturated water, and negative for undersaturated water. Negative CCPP values are also reported as Calcium Carbonate Dissolution Potential, Calcite Dissolution Capacity or Aggressive Carbon dioxide. Positive CCPP values are also reported as Theoretical Amount of Calcium Carbonate precipitate (TACC) (van Dijk and de Moel, 1983). Calcium carbonate equilibrium or saturation according to Eq. (1) is shown in Fig. 1, assuming $\{HCO_3^-\} = 2\{Ca^{2+}\}$. The pH at equilibrium is higher for water with lower calcium content, i.e. for softer water.

In December 2012, a new German standard for the calculation of calcium carbonate saturation in drinking water was released (DIN 38404-10, 2012, hereinafter referred to as DIN). According to the DIN, it is no longer allowed to calculate the SI and CCPP with the simplifications as described above. The DIN requires these parameters to be calculated with all given species, including complex compounds with sulphate and phosphate. In order to do so, the DIN standard describes the calculation method with the chemical principles and a data set containing 10 water samples for validation of the calculation method or computer program used.

The objective of this research is to determine the best calculation method for SI and CCPP in drinking water by testing the calculation methods described in the recent German standard (DIN 38404-10, 2012), the equivalent US standard (Standard Methods 2330, 2010, hereafter referred to as SM), the Dutch standard (NEN 6533, 1990, hereafter referred to as NEN) and a number of internationally accepted databases for calculating chemical equilibria in water, with a validation set given in the DIN standard.

2 Materials and methods

2.1 Calculation method DIN 38404-10

Table 2 gives an overview of all elements, phases and dissolved species in DIN. For both calcium and magnesium this standard distinguishes eight different dissolved species. The standard covers only calcite as less soluble crystalline form of $CaCO_3$, and applies only to "water for distribution as drinking water". The standard requires that the concentrations of all the elements mentioned are known, as well as pH and temperature. Because of its complexity DIN requires an extensive iterative computer calculation for both SI and CCPP determination, the latter reported in DIN as Calcitlösekapazität (Calcite Dissolution Capacity).

Chemistry in DIN is based on molarity ($mol\,L^{-1}$ solution) instead of molality ($mol\,kg^{-1}$ solvent i.e. water) as used in chemical thermodynamics (Gamsjäger et al., 2008). The values expressed as molarity and molality are equal for a solution with a density of $1\,kg\,L^{-1}$ while assuming that the mass of the solution equals the mass of water.

2.2 Calculation method Standard Methods 2330

SM gives a set of equations for calculating the value for SI. For CCPP no analytical equation is available and the value can only be obtained by iterative computer calculations. SM distinguishes three crystalline forms of $CaCO_3$ (calcite, vaterite and aragonite) and further only Ca^{2+} and HCO_3^-, with the assumption that either all other species can be neglected or the reduction to these two species can be estimated. The influence of other ions is discounted for through the ionic strength and successively in the activity coefficients of Ca^{2+} and HCO_3^-. The standards DIN, SM and NEN have slightly different defined parameters for alkalinity. Therefore Total Inorganic Carbon (C_T, or TIC) or Dissolved Inorganic Carbon (DIC) is used, which requires calculation of the concentrations of CO_2 and CO_3^{2-} (via K_1 and K_2). Standard Methods gives K_2 as published by Plummer and Busenberg (1982). This study uses K_1 from the same publication. In Table 3 the chemical elements used in SM are shown.

2.3 Calculation method NEN 6533

Just as SM, NEN gives a set of equations for calculating the value for SI. For CCPP no analytical equation is available and the value can only be obtained by iterative computer calculations. NEN considers only Ca^{2+}, HCO_3^- and H^+ and uses only one crystalline form of $CaCO_3$ (calcite), but adjusts the solubility product of $CaCO_3$, in order to take into account the soluble species of $CaCO_3^0$ and $CaHCO_3^+$, by decreasing the pK_S value with 0.037 (at 0 °C) to 0.057 (at 30 °C) based on a combination of K_s values from Plummer and Busenberg (1982) and Jacobson and Langmuir (1974). Recent literature assesses the approach for K_s used by Jacobson and Langmuir (1974) as incorrect (de Visscher et al., 2012). NEN uses the term aggressiveness for calcium carbonate expressed as aggressive carbon dioxide.

2.4 Calculation software PHREEQC

The computer program PHREEQC, developed by the United States Geological Survey (USGS, 2013) is the de facto international standard for calculating chemical equilibria in groundwater. This program (PHREEQC.exe) solves the mathematical equations which are generated from a chemical database (.dat) and an input file (.pqi), both adjustable by the user (Parkhurst and Appelo, 2013). PHREEQC version 3.0.3 was used to assess the different calculation methods for SI and CCPP according to DIN, SM, NEN and the chemical databases from Table 4. All databases in the upper part of Table 4 are distributed with PHREEQC version 3.0.3 in which "phreeqc.dat" is the default database.

2.5 Calculation method with internationally accepted chemical databases

Several internationally accepted computer programs for calculating chemical equilibria in water have been developed by different institutions for different purposes. These programs include their own chemical database, all in their own specific data format. The most prominent databases are also available in the data format for the computer program PHREEQC. The upper part in Table 4 shows a number of databases available in the PHREEQC data format that are able to calculate SI and CCPP, with their institution of origin and the computer program for which they were originally developed.

The computer program PHREEQC and its related database phreeqc.dat is widely used and also listed in Standard Methods for use of calculation of calcium carbonate saturation indices. The phreeqc.dat database was developed for the calculation of chemical equilibria in groundwater. The calcium carbonate chemistry in the database phreeqc.dat is based on Nordstrom et al. (1990), which is the most recent update of the much-cited publications of Jacobson and Langmuir (1974), Truesdell and Jones (1974) and Plummer and Busenberg (1982). Nordstrom et al. (1990) give equilibrium constants for natural water for a temperature range from 0 to 100 °C, at a pressure of 1 bar. Their dataset is also adopted by Stumm and Morgan (1996). In phreeqc.dat more ion pairs are included than in DIN, such as ion pairs of sodium with sulphate, phosphate, bicarbonate, carbonate and hydroxide.

The database wateq4f.dat is also based on Nordstrom et al. (1990) and therefore almost identical to phreeqc.dat for SI and CCPP calculation. The minteq.v4.dat database has been developed by US EPA, for version 4 of MINTEQA2. The llnl.dat database, compiled by the Lawrence Livermore National Laboratory (Daveler and Wolery, 1992), is by far the most extended database with respect to thermodynamic equilibrium constants. The databases sit.dat and pitzer.dat are in accordance with the specific ion interaction theory (SIT) of Grenthe et al. (1997) respectively the specific ion interaction model of Pitzer (1973). They were designed to extend the calculation methods for natural water with a high content of dissolved salts (ionic strength $> 500\,\mathrm{mmol\,kgw^{-1}}$) and they were calibrated on for instance seawater and brine. In pitzer.dat, oxygen (dissolved and as gas phase) and all compounds with N and P are not included.

2.6 Calculation method with specific chemical databases

The specifically developed chemical databases are summarized in the lower part of Table 4. The stimela.dat database is developed specifically for water treatment by Omnisys and Delft University of Technology as part of the Stimela modelling environment (van der Helm and Rietveld, 2002). The database is based on phreeqc.dat with extra species and phases to comply to Standard Methods 2330 and DIN 38404-10 and with additional redox-uncoupled elements (de Moel et al., 2013). The stimela.dat database will be used in further calculations instead of phreeqc.dat.

The chemical specifications of DIN were converted into a newly developed database for PHREEQC (referred to as "din38404-10_2012.dat"). Starting with phreeqc.dat as a basis, all elements, species and phases were removed which are not mentioned in DIN. An exception was made for the parts of the database that PHREEQC needs in order to run, such as the elements H and O, the gases O_2 and CO_2, and H_2O, alkalinity and the oxidation state (E). Subsequently the numerical values for the equilibrium constants of the reactions (log_k in PHREEQC and $\lg(K_0)$ in DIN), the change in enthalpy of the reactions (delta_h in PHREEQC and ΔH in DIN) and the activity coefficients (gamma in PHREEQC and the $f(i)$ with the ion size parameter $g(i)$ in DIN) were adjusted to the values given in DIN. The last step for building din38404-10_2012.dat was the determination of A_1 to A_6 in the analytical expressions for the equilibrium constants (k) in PHREEQC for the reactions with a heat capacity (C_p in DIN):

$$A_1 = \lg(K_0) + \frac{\dfrac{\Delta H}{T_0} - C_P\,(1 + \ln(T_0))}{R\ln(10)} \tag{2}$$

$$A_2 = A_5 = A_6 = 0 \tag{3}$$

$$A_3 = \frac{C_P T_0 - \Delta \mathrm{H}}{R \ln(10)} \tag{4}$$

$$A_4 = \frac{C_P}{R} \tag{5}$$

The DIN parameters *A*, *B*, and *DK* in the calculation of the activity coefficients are included in PHREEQC in an equivalent way. DIN assumes no effect of uncharged ions, therefore *b* in the Debye-Hückel equation as used in WATEQ (Truesdell and Jones, 1974) is set to 0 in din38404-10_2012.dat (the default value used in PHREEQC is 0.1).

Similar to the development of the DIN database for PHREEQC, also databases were newly developed for Standard Methods 2330 (sm2330_2010.dat) and NEN 6533 (nen6533_1990.dat) and therefore a number of issues was resolved. In order for PHREEQC to run, log_k values for ion pairs need to be defined. However, in SM and NEN ion pairs are not included, see Table 3, therefore the log_k values of all reaction equations of these species was set to −100 in "sm2330_2010.dat" and "nen6533_1990.dat". SM uses the Davies equation for the influence of the ionic strength for charged ions according to the default method in PHREEQC, therefore, the gamma option in sm2330_2010.dat has been omitted. NEN uses the WATEQ Debye-Hückel equation for charged ions, thus the gamma option is used in nen6533_1990.dat. For species without charge (including H_2O and CO_2) an activity coefficient of 1.0 has been assumed in both sm2330_2010.dat and nen6533_1990.dat ($b = 0$ in gamma). For all calculations with PHREEQC it is assumed that the oxygen content is always 100 % saturated at 1.0 atm in dry air with an oxygen content of 20.8 %.

2.7 Drinking water validation data set

For validation of the calculation methods, the data set of 10 water quality validation samples given in DIN was used. The validation data set in DIN contains the measured water quality parameters of the 10 samples, part of the data is summarized in Table 5, and the through DIN calculated SI and CCPP values, see Table 5. Actually, in the DIN the Calcitlösekapazität (D_C) in mg L^{-1} is given from which the CCPP in Table 5 in mmol L^{-1} is calculated with:

$$\text{CCPP} = \frac{-D_C}{MW_{\text{CaCO}_3}} \tag{6}$$

The water quality dataset in Table 5 ranges from very soft water (sample 4) to hard water with high sulphate content (sample 3). The water temperature of the samples is between 10 °C and 15 °C, and 61 °C (sample 10). According to DIN most water samples in the validation set are slightly calcium carbonate dissolving ($-0.2 < \text{CCPP} < 0.0\,\text{mmol L}^{-1}$), except for sample 4, which is highly calcium carbonate dissolving, and for sample 9, which has a very small calcium carbonate precipitation potential. The parameter alkalinity is not included in Table 5, because for proper comparison of the DIN, SM and NEN standard the sum of inorganic carbon species in a solution is used. The density of the different samples is not given in DIN, as it is based on molarity. This is converted into the molality system of PHREEQC by assuming a density of $1.0\,\text{kg L}^{-1}$ for all samples, regardless of water temperature. The assumption of a density of $1.0\,\text{kg L}^{-1}$ is only used for the calculations with DIN, SM and NEN. For the calculations with the other databases from Table 4 the solution density for proper conversion from concentrations in mmol L^{-1} into mmol kgw^{-1} is calculated by PHREEQC itself.

3 Results

3.1 SI for calcium carbonate

In Fig. 2 the deviations are shown between the SIs calculated in PHREEQC according to the DIN, SM and NEN standards and the SIs according to the DIN validation data set, see Table 5. Also the tolerance for calculated SI values of 0.01 given in the DIN standard is shown in Fig. 2.

From the data shown in Fig. 2, it is observed that the SI values calculated with din38404-10_2012.dat in PHREEQC have a maximal deviation of 0.0011. The calculation method with din38404-10_2012.dat complies with the DIN standard in which a tolerance of ±0.01 SI is specified for the calculation results.

SI values calculated with the SM database are on average 0.030 higher than the SIs according to DIN. This is mainly caused by the neglection of ion pairs in SM; more specifically, the ion pair $CaSO_4^0$, which leads to an overestimation of the Ca^{2+} concentration. The overestimation is smaller for sample 4 because of the low concentration of ions in the sample and the overestimation is larger for the samples 3, 7 and 9 with high sulphate concentrations. Almost all calculated SI values are out of the DIN tolerance range.

For most samples, the NEN database provides SI values which are more than 0.01 lower than the DIN database because of the higher K_s value used in NEN, except for the samples 3, 7 and 10. The NEN database gives better results for the samples 3 and 7 with higher sulfate concentrations than the SM database. This is remarkable since the reason for decreasing pK_s value in NEN is to take into account the effect of ion pairs $CaCO_3^0$ and $CaHCO_3^+$, and not $CaSO_4^0$ ion pair. Even though the calculation methods of SM and NEN are similar, the lower pK_s value leads to an almost equal difference of around 0.045. It should be noted that pK_w in NEN is only validated for a temperature range of 0 to 30 °C, therefore the calculated SI value for sample 10 with a temperature of 61 °C is only illustrative.

In Fig. 3 the deviations are shown between the SIs calculated in PHREEQC according to the internationally accepted chemical equilibrium databases and the SIs according to the DIN validation data set, see Table 5. Also the tolerance for calculated SI values of 0.01 given in the DIN standard is shown in Fig. 3.

Differences between the calculated SI values with stimela.dat and the values according to the DIN validation data are on average 0.012. The differences are caused by small differences in the values of equilibrium constants and activity coefficients, and not by ion pairs which are present in stimela.dat but are not present in the DIN standard. For 5 of the 10 samples stimela.dat calculates SI within the tolerance of 0.01 as specified in the DIN standard. The larger error observed for sample 10 is caused partly by the fact that DIN neglects the change in density due to the higher temperature.

The SI values calculated with stimela.dat and wateq4f.dat are almost the same for all samples. The SI values with minteq.v4.dat and llnl.dat are, with sample 10 left out, on average 0.022 higher than the SI values according to DIN. This is mainly due to a slight difference in the values of $\lg K_2$-$\lg K_s$ for both databases at a temperature between 10 °C and 15 °C. At 61 °C (sample 10), the difference in SI for these databases is very large due to the large differences in K_s. The large difference in sample 4 for minteq.v4.dat is the overall effect of many small differences that reinforce each other, from which half is caused by a difference in $\lg\{HCO_3^-\}$.

The database sit.dat gives for most samples a difference of less than 0.01. The differences are mainly caused by small differences in K_s and K_2. The database pitzer.dat gives large differences up to 0.065. The differences between stimela.dat and pitzer.dat are entirely due to the difference in the activity of Ca^{2+} and HCO_3^-, since K_2 and K_s are the same. It can be observed that the pitzer model is less suitable for the “low salt” samples given in the DIN standard.

The bandwidth of the calculation results with the comprehensive databases in Fig. 3 is smaller than the bandwidth for the results with the simple calculations according to SM and NEN shown in Fig. 2.

3.2 Calcium carbonate precipitation potential

In Fig. 4 the deviations are shown between the CCPPs calculated in PHREEQC according to the DIN, SM and NEN standards and the CCPPs according to the DIN validation data set, see Table 5. Also the tolerance for calculated CCPP values of 0.001 mmol L^{-1} given in the DIN standard is shown in Fig. 4.

From the data shown in Fig. 4, it is observed that the CCPPs calculated with the DIN database comply with the validation values. The maximum deviation observed is +0.0011 mmol L^{-1} (sample 3), which is not significant out-of-tolerance.

CCPPs calculated with the SM database gives values which are on average 0.018 mmol L^{-1} higher than CCPPs according to DIN, with a peak of 0.062 mmol L^{-1} for sample 3. This is due to neglection of ion pairs in SM. The CCPP calculated with the NEN database always gives lower values than calculated with SM due to difference in pK_s as described for SI. The fixed difference in the pK_s gives variable differences for the CCPP, because of the differences in calcium, carbonate and bicarbonate concentrations in the ten samples. It should be noted that pK_w in NEN is only validated for a temperature range of 0 to 30 °C, therefore the calculated CCPP for sample 10 with a temperature of 61 °C is only illustrative.

In Fig. 5 the deviations are shown between the CCPPs calculated in PHREEQC according to the internationally accepted chemical equilibrium databases and the CCPPs according to the DIN validation data set, see Table 5. Also the tolerance for calculated CCPPs of 0.001 mmol L^{-1} given in the DIN standard is shown in Fig. 5.

From the data in Fig. 5 it is observed that for most samples the CCPPs calculated with stimela.dat are 0.000 to 0.005 mmol L^{-1} (0.0 to 0.5 mg $CaCO_3$ L^{-1}) larger than the values in the DIN validation data set. This means that for calcium dissolving water, according to stimela.dat, less $CaCO_3$ might be dissolved than according to the DIN standard. The differences are slightly larger for samples 9 and 10, and for sample 3 the difference is 0.021 mmol L^{-1} (2.1 mg $CaCO_3$ L^{-1}). This difference is caused by accumulation of several small differences, and not by ion pairs which are in stimela.dat but not in din38404-10_2012.dat. For only 2 of the 10 samples stimela.dat calculates SI within the tolerance of 0.001 mmol L^{-1} as specified in the DIN standard.

From the calculation with stimela.dat it is observed that the free ion Ca^{2+} forms 90–99 % of the total calcium content in all ten samples, the remainder is present as $CaSO_4^0$, $CaHCO_3^+$, $CaCO_3^0$ and $CaHPO_4^0$ (in order of importance). These ion pairs cause the large deviation as mentioned for sample 3 calculated with sm2330_2010.dat. Other ion pairs for Ca are negligible. From the calculation with stimela.dat it can also be observed that the carbon ion pairs are of less importance since all carbon in the 10 samples is for 98–100 % present as CO_2, HCO_3^- or CO_3^{2-}. The CCPP values calculated with wateq4f.dat are almost the same as for stimela.dat for all 10 samples.

It can be observed that the differences between the CCPPs from the DIN validation data and the CCPPs calculated with minteq.v4.dat, llnl.dat, sit.dat and pitzer.dat are generally larger than the differences calculated with stimela.dat and watq4f.dat, and that all values are generally in the range of ±0.01 mmol L^{-1}. The causes for the differences of minteq.v4.dat, llnl.dat, sit.dat and pitzer.dat are the same as for the differences observed in SI values. The largest differences occur for samples 3 and 9 due to a large influence of the ion pair $CaSO_4^0$. In addition, a large difference occurs for sample 10, which is mainly caused by the differences in K_s and K_2.

4 Discussion

4.1 SI versus CCPP

SI stands for thermo dynamical driving force, i.e. initial speed of the reaction, while CCPP stands for total mass $CaCO_3$ converted to equilibrium. Both parameters are not quantitatively related, as shown in Fig. 6, only qualitatively; SI and CCPP are positive for oversaturated water, zero for saturated water, and negative for undersaturated water. In 2003 the German drinking water regulations were changed from SI as guideline parameter to CCPP (“Calcitlösekapazität”). This approach focuses better on the water quality issue, which is precipitation and dissolution of calcium.

4.2 Tolerance and accuracy

For natural water the DIN tolerance range for SI (0.01) and for CCPP (0.001 mmol L^{-1}) are not equivalent. An error of 0.01 in the log-concentration parameter SI corresponds to errors of 2.3 % (= $10^{0.01}$) in concentration of monovalent ions and 1.2 % (= $10^{0.01/2}$) for bivalent ions, at equal equilibrium constant. Natural soft water with a calcium concentration of 1.0 mmol L^{-1} would allow for a deviation of (1.0 × 1.2 % =) 0.012 mmol L^{-1}, which is 12 times larger than the tolerance range for CCPP. The tolerances for SI and CCPP are equivalent at a calcium concentration of (0.001/1.2 % =) 0.083 mmol L^{-1} (3.3 mg L^{-1}). The DIN dataset has an average calcium concentration of 1.38 mmol L^{-1} and a lowest concentration of 0.15 mmol L^{-1}. This shows that in DIN the restrictions for CCPP are by far more stringent than for SI (or pH).

The allowable tolerance for SI and CCPP as defined in DIN is smaller than the deviations caused by the inaccuracy of the measurements of the chemical parameters, which form the input of the calculations. The DIN specifies for pH a tolerance of 0.05 based on determination of *p* value (acidity), *m* value (alkalinity), measured pH and calculated pH. Consequently, 0.05 is also the minimal accuracy for SI, which is 5 times larger than the tolerance of the SI calculation of 0.01 defined in DIN. The DIN specifies a minimal accuracy for the ionic balance of 5 % (ionic strength > 4 mmol L^{-1}) to 10 % (ionic strength < 4 mmol L^{-1}) which can be adopted as minimal accurary levels for calcium and alkalinity. Depending on the ionic strength, natural soft water with a calcium concentration of 1.0 mmol L^{-1} would allow for a deviation of (1.0 × 5 % =) 0.05 mmol L^{-1} to (1.0 × 10 % =) 0.1 mmol L^{-1}, which is 50 to 100 times larger than the DIN tolerance range for calculation of CCPP. Figures 2 to 5 show that almost all presented models for the calculation of SI and CCPP comply with a tolerance range of 0.05 for SI and 0.05 to 0.1 mmol L^{-1} for CCPP. It would be preferable to introduce tolerances for SI and CCPP which are consistent with eachother and based on the accuracy of the measurements of at least pH and calcium.

4.3 Molarity versus molality

The equations for equilibrium in DIN are based on the obsolete molarity system (mol L^{-1}). Modern chemistry uses molality (mol kgw^{-1}). For drinking water with its low salt content and its temperature between 0 °C and 25 °C the difference is very small. However at higher temperatures, the difference in density is no longer negligible. Above 45 °C the density is below 0.99 $\mathrm{kg\,L^{-1}}$ giving differences in concentration above 1 %. The density of sample 10 in the DIN validation set is 0.983 $\mathrm{kg\,L^{-1}}$, as calculated by PHREEQC with stimela.dat. The differences in SI and CCPP calculated according to DIN due to neglecting changes in density are respectively 0.013 and 0.004 $\mathrm{mmol\,L^{-1}}$. This makes the applicability of DIN for water with a temperature higher than 45 °C unjustified and sample 10 should therefore be omitted from the DIN validation database.

4.4 Warm, hot and boiling water

DIN and NEN are only applicable in cold water. NEN gives as temperature range 0 to 30 °C, while DIN does not give temperature limits but from the calculations performed in this research it is found that it is valid up to a range of 40 to 50 °C. Standard Methods gives a temperature range for K_s and K_2 of 0 to 90 °C, according to Plummer and Busenberg (1982). For drinking water practice the temperature range should be extended up to 100 °C since customers heat up and boil water and scaling of calcium carbonate is a critical factor for in-house drinking water practices. This requires that equilibrium constants and activity coefficients used for calculation of SI and CCPP should be valid in the temperature range of 0 to 100 °C.

In addition, the vapor pressure of water is important, in combination with the concentrations of dissolved gases. At a higher vapor pressure the gas partial pressure of N_2, O_2, CO_2 might result in degassing and therefore in a reduction of CO_2 content. This process occurs during gas bubble formation when heating water, which already occurs below the boiling point of water. The partial pressure of oxygen in contact with wet air is around 0.20 atm for water samples 1 to 9 from the DIN validation set with water temperatures from 10 to 15 °C, and 0.16 atm for sample 10 with a temperature of 61 °C.

The current standards do not fulfil the need from drinking water practice to include calculation of calcium carbonate scaling at high temperatures. In future research, the effect of higher temperatures up to 100 °C on calcium carbonate saturation in drinking water will be assessed. In this research stimela.dat, which is based on phreeqc.dat, will be used since values for equilibrium constants and activity coefficients are valid up to 100 °C and effects of degasifying can be taken into account.

4.5 Scientific justification

The chemical databases and standards appear to have significant differences in the values of the equilibrium constants. The influence of the difference in activity coefficients is less significant, with the exception of the unsuitable models (SIT and Pitzer) which have not been calibrated for potable water with a low ionic strength. An international standardization of this basic chemistry is performed within the "IUPAC-NIST Solubility Data Series" of the International Union for Pure and Applied Chemistry (IUPAC) and the National Institute of Standards and Technology (NIST). A volume on alkaline earth carbonates has been published recently and an additional part is in preparation (de Visscher et al., 2012). The values of K_1, K_2 and K_w in phreeqc.dat and thus in stimela.dat appear to be well in accordance with the presented analytical equations (equations for K_s have not yet been published).

It is expected that the results will be included by USGS in a future version of phreeqc.dat and will be adopted in stimela.dat. Pending this scientific justification, the K values in stimela.dat will be used in further research, according to Nordstrom et al. (1990), mainly because of the wide temperature range. This approach is in compliance with Standard Methods 2330 D.

5 Conclusions

The computer program PHREEQC (USGS, 2013) with the developed chemical database din38404-10_2012.dat complies with the new German standard DIN 38404-10 (2012) for calculating SI and CCPP. This standard covers water that is intended for distribution as drinking water with its specific limitations on concentrations and temperature. This compliance is achieved by assuming equal values for molarity as used in DIN (obsolete) and molality as used in PHREEQC. From comparison with internationally accepted chemical databases it is concluded that the use of molarity limits the use of DIN to a maximum temperature of 45 °C. Alternative international standards (Standard Methods and NEN) are not accurate enough to comply with DIN, because of their simplifications. It should be noted that the DIN tolerance range is more stringent than the accuracy of the chemical analyses which serve as input for the computer calculations. On the other hand, the differences in calculation results for DIN, SM and NEN illustrate the need for international unification of these standards. Running extensive chemical models i.e. databases on the DIN validation data set results in deviations outside the DIN tolerance range. None of these widely accepted models fully complies with the DIN standard. However, it must be noted that all models, including DIN, lack proper scientific justification and/or scientific acceptance. This might be achieved in the near future within the framework of the "IUPAC-NIST Solubility Data Series" of the International Union for Pure and Applied Chemistry (IUPAC) and the National Institute of Standards and Technology (NIST). For application of drinking water supply it is concluded that the standards should also be applicable for hot and boiling water, since scaling of calcium carbonate is a critical factor for in-house drinking water practices. For current practical applications the PHREEQC database stimela.dat was developed within the Stimela platform of Delft University of Technology. This database is an extension of phreeqc.dat focused on water treatment and drinking water applications. This approach is in compliance with Standard Methods 2330 D.

6 Supplementary material

For use of the supplementary material the free software phreeqc-3.0.6-7757.msi and IPhreeqcCOM-3.06-7757-win32.msi or a higher version should be installed. List of files:

1. CalciumCarbonateSaturation_v20130617.xlsm containing din38404-10_2012.dat and the din validation data set.
2. din38404-10_2012.dat
3. sm2330_2010.dat
4. nen6533_1990.dat
5. stimela.dat
6. DIN38404-10_compliance.pqi

Supplementary material related to this article is available online at: http://www.drink-water-eng-sci-discuss.net/6/167/2013/ dwesd-6-167-2013-supplement.zip.

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Table 1. Processes generally used for description of calcium carbonate ($CaCO_3$) saturation in drinking water.

Part	Reaction equations	Equilibrium constants
Dissolution/precipitation of $CaCO_3$	$CaCO_3 (s) <-> Ca^{2+} + CO_3^{2-}$	$K_s = \{Ca^{2+}\} \times \{CO_3^{2-}\}$
Dissociation of carbon dioxide $CO_2 + H_2O = H_2CO_3$	$CO_2 + H_2O <-> HCO_3^{2-} + H^+$ $HCO_3^- <-> CO_3^{2-} + H^+$	$K_1 = \{HCO_3^-\} \times \{H^+\}/\{CO_2\}$ $K_2 = \{CO_3^{2-}\} \times \{H^+\}/\{HCO_3^-\}$
Ionisation of water	$H_2O (l) <-> OH^- + H^+$	$K_w = \{H^+\} \times \{OH^-\}$ $\lg \{H^+\} = -pH$

{X} = relative activity of dissolved species/ion X.

Table 2. Chemical elements, phases and dissolved species in DIN 38404-10 (2012).

Element	Phase	Dissolved species
Ca	$CaCO_3$ (s)	Ca^{2+}, $CaCO_3^0$, $CaHCO_3^+$, $CaOH^+$, $CaSO_4^0$, $CaH_2PO_4^+$, $CaHPO_4^0$, $CaPO_4^-$
Mg		Mg^{2+}, $MgCO_3^0$, $MgHCO_3^+$, $MgOH^+$, $MgSO_4^0$, $MgH_2PO_4^+$, $MgHPO_4^0$, $MgPO_4^-$
Na		Na^+
K		K^+
C*	$CaCO_3$ (s)	H_2CO_3 (= CO_2.aq), HCO_3^-, CO_3^{2-}
Cl		Cl^-
N		NO_3^-
S*		HSO_4^-, SO_4^{2-}
P*		H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}
H	H_2O (l)	H^+, OH^-

[*] The dissolved species already specified for the cations Ca en Mg are not repeated for the anions.

Table 3. Chemical elements, phases and dissolved species in Standard Methods 2330 (2010).

Element	Phase	Dissolved species
Ca	$CaCO_3$ (s)*	Ca^{2+}
C	$CaCO_3$(s)*	HCO_3^-, CO_3^{2-}
H	H_2O (l)	H^+, OH^-

[*] 3 crystalline forms of $CaCO_3$: calcite, aragonite and vaterite.

Table 4. Databases in the PHREEQC data format for calculating chemical equilibria in water.

Database	Institution	Program
phreeqc.dat	US-USGS	PHREEQC
wateq4f.dat	US-USGS	WATEQ4F
minteq.v4.dat	US-EPA	MINTEQA2, VISUAL MINTEQ and MINEQL+
llnl.dat	US-LLNL	Q3/6 and Geochemist's Workbench (GWB)
sit.dat	FR-ANDRA	PHREEQC
pitzer.dat	US-USGS	PHRQPITZ
stimela.dat	NL-Omnisys/Delft UT	PHREEQC/Stimela
din38404-10_2012.dat	NL-Omnisys/Delft UT	PHREEQC/Stimela
sm2330_2010.dat	NL-Omnisys/Delft UT	PHREEQC/Stimela
nen6533_1990.dat	NL-Omnisys/Delft UT	PHREEQC/Stimela

Table 5. Water quality validation data set from DIN consisting of 10 different drinking water samples.

Parameter		Unit	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Temperature		°C	10.0	15.0	10.0	10.0	10.0	15.0	12.0	10.0	15.0	61.0
pH		–	7.34	7.80	7.00	5.60	7.37	7.86	7.59	7.47	7.30	7.30
Calcium	Ca	$\text{mmol}\,\text{L}^{-1}$	1.40	0.75	3.50	0.15	1.40	0.78	1.30	1.00	2.65	1.00
Magnesium	Mg	$\text{mmol}\,\text{L}^{-1}$	0.23	0.10	0.70	0.05	0.25	0.10	0.25	0.25	0.20	0.18
Sodium	Na	$\text{mmol}\,\text{L}^{-1}$	0.30	0.40	2.30	0.30	0.40	0.45	1.60	0.20	0.30	0.20
Potassium	K	$\text{mmol}\,\text{L}^{-1}$	0.05	0.10	0.30	0.10	0.07	0.05	0.15	0.06	0.06	0.05
Total Inorganic Carbon	C	$\text{mmol}\,\text{L}^{-1}$	2.737	1.630	6.724	1.375	2.662	1.584	1.159	2.094	4.672	2.057
Chloride	Cl	$\text{mmol}\,\text{L}^{-1}$	0.25	0.30	2.70	0.34	0.55	0.28	0.85	0.35	0.75	0.10
Nitrate	N	$\text{mmol}\,\text{L}^{-1}$	0.15	0.03	0.50	0.18	0.20	0.00	0.10	0.05	0.05	0.05
Sulfate	S	$\text{mmol}\,\text{L}^{-1}$	0.38	0.15	1.20	0.05	0.25	0.15	1.40	0.20	0.55	0.25
Phosphate	P	$\text{mmol}\,\text{L}^{-1}$	0.00	0.00	0.00	0.00	0.07	0.07	0.00	0.03	0.00	0.03
By DIN calculated validation results												
SI		–	−0.402	−0.279	−0.121	−4.155	−0.381	−0.221	−0.553	−0.497	0.095	−0.009
CCPP		$\text{mmol}\,\text{L}^{-1}$	−0.145	−0.032	−0.163	−1.111	−0.140	−0.030	−0.055	−0.115	0.071	−0.003

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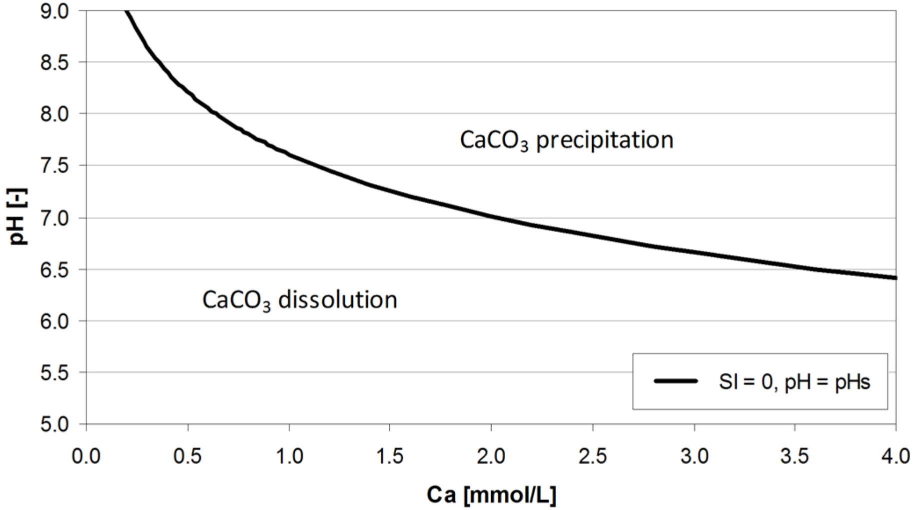

Fig. 1. Calcium carbonate equilibrium or saturation (SI = 0, at 25 °C and $\{HCO_3^-\} = 2\ \{Ca^{2+}\}$) with over- and under-saturation i.e. calcium carbonate precipitation and dissolution.

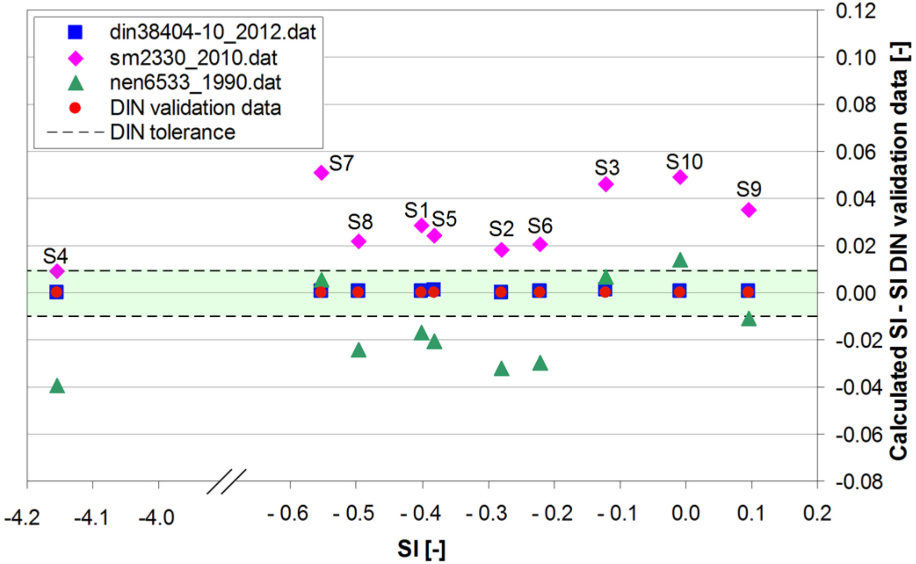

Fig. 2. Deviations of the SIs calculated in PHREEQC according to the DIN, SM and NEN standards, from the SIs given in the DIN validation data set for the 10 water quality samples S1 to S10 (see Table 5).

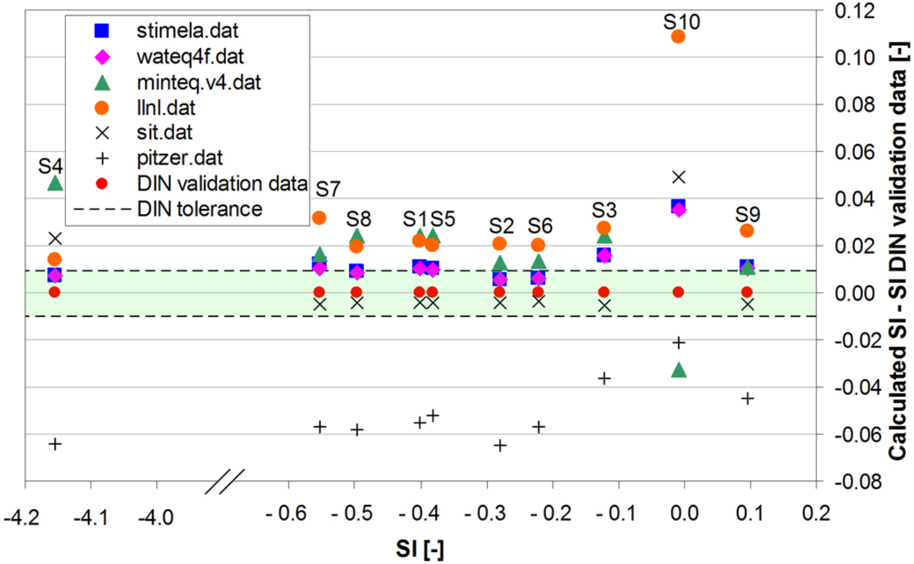

Fig. 3. Deviations of the SIs calculated in PHREEQC with internationally accepted chemical databases, from the SIs given in the DIN validation data set for the 10 water quality samples S1 to S10 (see Table 5).

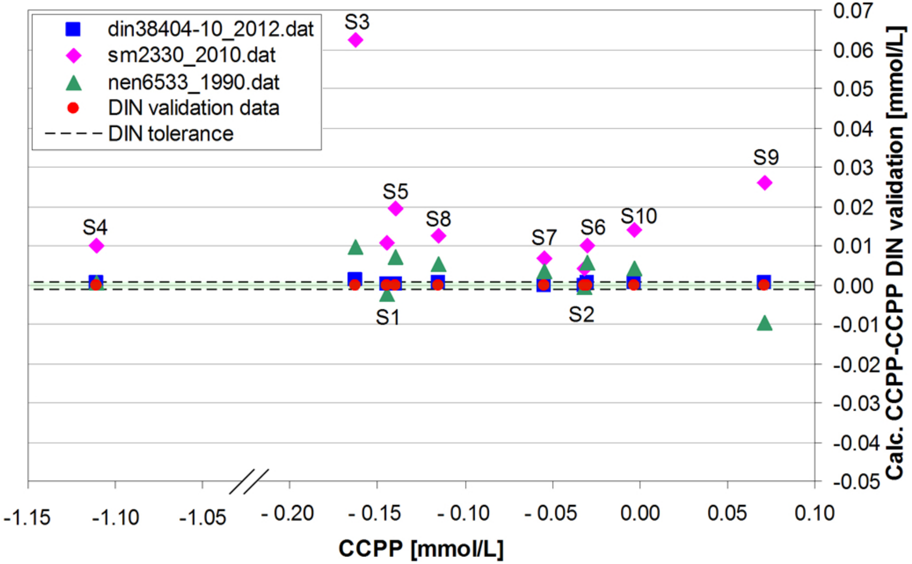

Fig. 4. Deviations of the CCPPs calculated in PHREEQC according to the DIN, SM and NEN standards, from the CCPPs given in the DIN validation data set for the 10 water quality samples S1 to S10 (see Table 5).

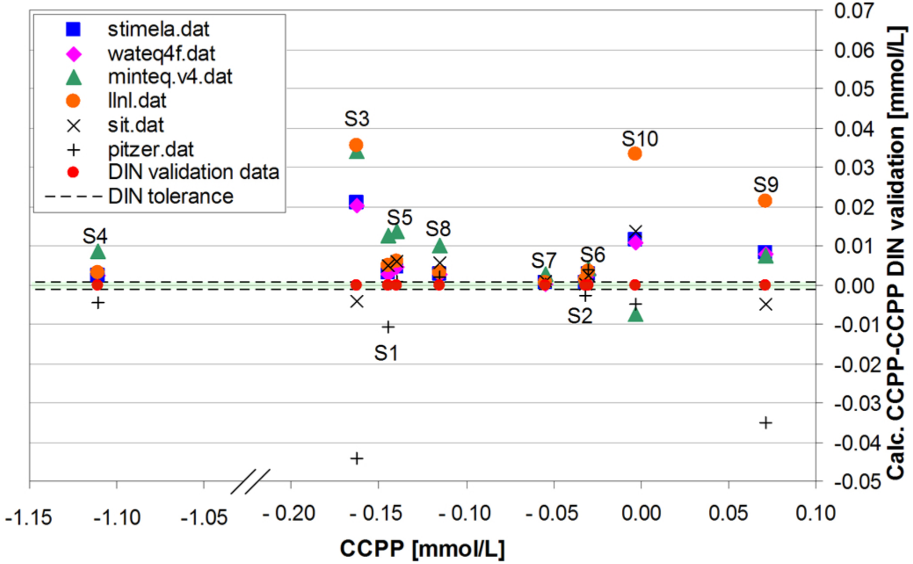

Fig. 5. Deviations of the CCPPs calculated in PHREEQC with the internationally accepted chemical databases, from the CCPPs given in the DIN validation data set for the 10 water quality samples S1 to S10 (see Table 5).

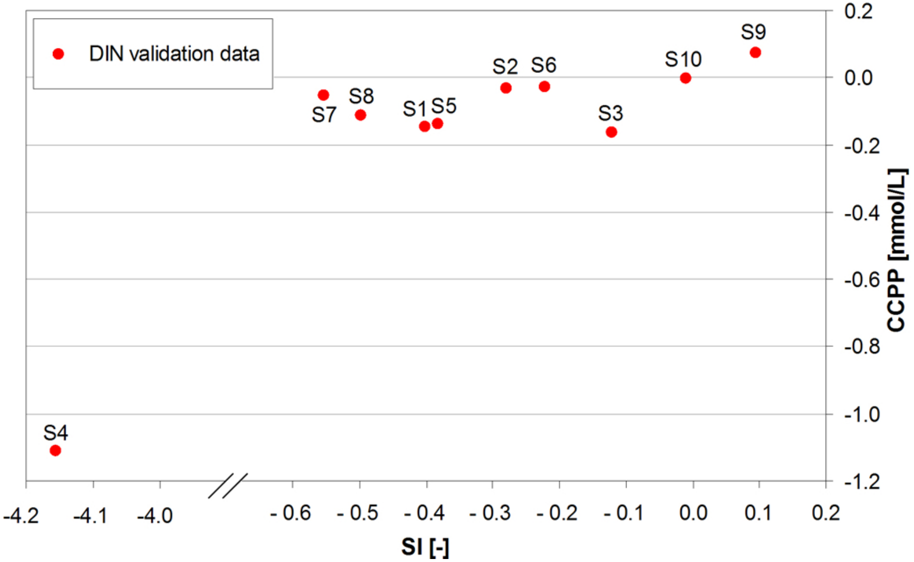

Fig. 6. CCPP values plotted against the SI (data from the DIN validation data set, see Table 5).