

Calculating chemical speciation, pH, saturation index and calcium carbonate precipitation potential (CCPP) based on alkalinity and acidity using OpenModelica

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ABSTRACT

Of the most commonly used calcium carbonate (CaCO_3) saturation indices, the Calcium Carbonate Precipitation Potential (CCPP) most accurately describes CaCO_3 precipitation and dissolution. This paper illustrates how to write an OpenModelica programme that calculates the CCPP and other key water parameters starting from total alkalinity and CO_2 -acidity. It describes the calculation steps of all components of the developed OpenModelica package and explains how the components work together. Underlying chemical principles follow the German standard DIN 38404-10 and are presented along with the OpenModelica code. The developed programme considers 14 different dissolved species, including complex species of carbonate, calcium, magnesium and sulphate. Data of the six phosphate-free example waters from DIN 38404-10 is compared to the results of the developed programme and the results of a programme which neglects complexation. The developed programme reaches required accuracy for four of the six CCPP values; with the other programme, requirements cannot be met. By using OpenModelica, the developed package can be readily integrated into a Modelica model of, for example, a drinking water treatment plant. There, it can help to monitor legal and technical requirements, or to assess the dissolution capacity if neutralizing filters containing CaCO_3 are employed for pH adjustment.

Key words | calcite dissolution capacity, calcium carbonate precipitation capacity (CCPC), ion pairs, modelling, software

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INTRODUCTION

Calcium carbonate precipitation potential

The Calcium Carbonate Precipitation Potential (CCPP) is the amount of calcium carbonate (CaCO_3) that needs to precipitate or dissolve from water in order to reach equilibrium with CaCO_3 . In equilibrium, water is saturated with CaCO_3 and the CCPP equals zero. If water is oversaturated with CaCO_3 , the CCPP is positive; if it is undersaturated, the CCPP is negative (APHA/AWWA/WEF 2005).

Unlike other commonly used calcium carbonate saturation indices (such as the Saturation Index, the Relative Saturation and the Ryznar Index), the CCPP indicates

both the tendency of a water to precipitate or dissolve CaCO_3 and the quantity that may be precipitated or dissolved. In drinking water treatment, knowledge about the ability of water to deposit CaCO_3 is often used in connection with the control of corrosion and scale formation in water conduits (Rossum & Merrill 1983; APHA/AWWA/WEF 2005).

In the current German Drinking Water Regulation (TrinkwV 2001), the parameter used to monitor calcium carbonate saturation is the Calcite Dissolution Capacity (Calcitlösekapazität) D_c . D_c has the same absolute value as the CCPP, but opposite sign; hence positive D_c values

represent CaCO_3 -undersaturated water, while negative D_c values stand for CaCO_3 -oversaturated water. According to the TrinkwV, D_c must not exceed 5 mg/L at the outlet of a water works (for a description of the rationale behind this limit value see Nissing & Johannsen (2003)). Even though no minimum limit value is defined, practice shows that, preferably, water close to saturation should be distributed, as extensive precipitation of CaCO_3 may cause disruptions in the distribution network and equipment (Nissing & Johannsen 2003).

The TrinkwV further specifies that D_c is to be determined following the calculation method set out in the German standard DIN 38404-10 if the pH at the outlet is below 7.7 (water with a $\text{pH} \geq 7.7$ is considered to meet the limit value for D_c). For this purpose, DIN 38404-10 establishes chemical principles such as the reactions and thermodynamic constants that should be at the basis of any calculation. The newest version of DIN 38404-10 (DIN 38404-10:2012-12, hereafter referred to as DIN 38404-10) considers ion pairs and complex formation, including complexes with sulphate or phosphate (de Moel *et al.* 2013). The calculation of D_c starts out from data of the water chemistry analysis. To determine the reliability of this data, DIN 38404-10 lays down a procedure referred to as a plausibility test. To validate computer programmes, i.e. check whether their calculation of D_c is sufficiently accurate, DIN 38404-10 provides data sets of ten exemplary water samples (Stock & Johannsen 2013).

The developed programme

In the course of the present work, a computer programme which calculates the chemical speciation, pH, saturation index and eventually the CCPP based on the chemical principles established in DIN 38404-10 has been developed. The programme has been created in the form of an OpenModelica package. OpenModelica is an open-source modelling and simulation environment developed by the Open Source Modelica Consortium (Open Source Modelica Consortium 2017; OpenModelica can be downloaded free of charge from openmodelica.org). It is based on the object-oriented, equation-based programming language Modelica[®], devised by the Modelica Association (Modelica Association 2017). Modelica is especially useful to model and connect processes of different natural and technical domains. Moreover,

in Modelica, reuse of components and evolution of models is particularly convenient (Fritzson 2015). The developed package has been conceived to become part of an OpenModelica model which combines the chemical and physical processes inside a drinking water treatment plant. Therefore, OpenModelica is considered a suitable programming environment for this project.

The programme considers all aqueous species specified in DIN 38404-10 except from $\text{Ca}(\text{OH})^+$, $\text{Mg}(\text{OH})^+$, HSO_4^- and the ones containing phosphate. Like the standard, it applies to ‘waters, that are designated for the distribution as drinking water’ (DIN 38404-10, p. 6). Due to its intended application, the input parameters of the developed programme differ slightly from the ones in DIN 38404-10 (further details in the following section).

This paper serves readers as a guideline to develop their own programme. It follows in large part the approach presented in Eberle & Donnert (1991), but focusses on the implementation with OpenModelica. For this purpose, the six components of the developed OpenModelica package will be explained in detail, while concentrating on how the main steps of calculating the CCPP have been realised and how the different components work together. Where necessary, underlying chemical principles are elucidated. The thoroughly commented OpenModelica code of the entire package (as for example water 1) can be found in the appendix (available with the online version of this paper). From there, the code can be directly copied into the OpenModelica Connection Editor and run straightaway. In this project, OpenModelica version 1.9.6 was used.

To assess the accuracy of the developed programme, calculation results of six example waters from DIN 38404-10 will be compared to the values given in the standard and to those obtained with a programme based on a simplified model that does not consider ion pairs and complex formation.

METHODS

Input parameters of the developed programme and differences to DIN 38404-10

The input parameters of the developed programme are listed in Table 1. As mentioned earlier, the programme is

Table 1 | Input parameters of the developed programme

Parameter	Description	Unit
T	Water temperature	°C
IOS	Ionic strength at temperature T	mmol/L
Alk	Total alkalinity: $Alk = ([HCO_3^-] + [CaHCO_3^+] + [MgHCO_3^+]) + 2([CO_3^{2-}] + [CaCO_3] + [MgCO_3]) + [OH^-] - [H^+]$	mmol/L
Aci	CO ₂ -acidity: $Aci = [CO_2] - ([CO_3^{2-}] + [CaCO_3] + [MgCO_3]) - [OH^-] + [H^+]$	mmol/L
$tCa, tMg, tSO_4,$ tNa, tK, tCl, tNO_3	Total concentrations of calcium, magnesium, sulphate, sodium, potassium, chloride or nitrate, respectively	mmol/L

meant to be applied within some other larger model, for example of a drinking water treatment plant. For this reason, the developed programme starts out from the parameters ionic strength, total alkalinity and CO₂-acidity and not, like DIN 38404-10, from the pH, acid neutralising capacity with reference to pH 4.3, and base or acid neutralising capacity with reference to pH 8.2. Consequently, precision of the underlying data is also assumed to have been previously assessed. This particularly entails that the plausibility test set out in DIN 38404-10 is not within the scope of this programme. The programme also calculates the ionic strength (IOS_{Calc}), but only to enable comparison with the input ionic strength (IOS). For calculation of the CAPP, IOS is used. The total concentrations of sodium, potassium, chloride and nitrate are only needed to calculate IOS_{Calc} .

To simulate the effect of a specific treatment process (e.g. chlorination) on CaCO₃ precipitation or other output parameters of the programme, it is necessary to first identify how the regarded treatment process influences the programme's input parameters. This is different for each treatment process and has to be determined through measurements or models. Once the impact on the input parameters is known, the programme can be run and the process's effect on chemical speciation, pH, saturation index and CAPP evaluated.

Note that Ca(OH)⁺, Mg(OH)⁺, HSO₄⁻ as well as phosphate and its complexes are not considered within the programme. When carrying out the comparison in the end of this paper with and without considering Ca(OH)⁺, Mg(OH)⁺ and HSO₄⁻, their impact on the CAPP was

found to be in the range of 0.001 mg/L, thus far beneath the accuracy limit of 0.1 mg/L demanded in DIN 38404-10. Therefore, omission of Ca(OH)⁺, Mg(OH)⁺ and HSO₄⁻ does not entail any significant losses in precision, but helps to considerably decrease code complexity and increase its readability. The neglect of phosphate is justified as its concentrations inside drinking water treatment plants are usually very small, especially compared to phosphate dosages that might be added later to inhibit corrosion. However, the developed programme can be extended to include the omitted species and reactions without any difficulties.

Determining concentration-based equilibrium constants (function *Constants*)

The function *Constants* calculates the concentration-based equilibrium constants Kc in mmol/L at the temperature T . As input parameters, it requires the temperature T in °C and the ionic strength IOS in mmol/L. Output parameters are the array Kc containing the eleven concentration-based equilibrium constants and the activity coefficient fH of H⁺, which will be needed in the function *EqConc* to calculate the pH.

The function begins by calculating the decimal logarithm of the activity coefficients f of the considered species using the Debye-Hückel equation (DIN 38404-10):

$$\lg(f(i)) = -\frac{A \cdot z(i)^2 \sqrt{IOS/1000}}{1 + B \cdot g(i) \cdot \sqrt{IOS/1000}} \quad (1)$$

with

$$A = \frac{1824300}{(TK \cdot DK)^{1.5}} \quad (2)$$

$$B = \frac{50.248}{(TK \cdot DK)^{0.5}} \quad (3)$$

$$DK = 87.74 - 0.40008 \cdot T + 0.0009398 \cdot T^2 - 0.00000141 \cdot T^3 \quad (4)$$

where IOS is the ionic strength of the water in mmol/L; $z(i)$ is the charge of species i ; $g(i)$ is the ion size parameter of species i ; DK is the dielectric constant of the water; TK is the temperature in K ($TK = T + 273.15$), and T is the temperature in °C.

All considered species, their index i and their ion size parameter can be found on the right side of Table 3. For uncharged species, $\lg(f(i))$ is zero. The explicit activity coefficient is only calculated for H^+ , as it will be needed in the function *EqConc*.

The equilibrium constants K considered in the programme are listed in Table 2. They are defined based on the activities of the species involved in the respective reaction. However, for subsequent calculations it is convenient to use concentration-based constants Kc . The conversion procedure will be demonstrated exemplary for [1]. In the following,

brackets [] signalize concentrations (besides identifying indices within arrays), while braces {} symbolize activities.

[1] is defined as:

$$Kc[1] = \frac{[H^+][HCO_3^-]}{[CO_2]} \quad (5)$$

The activity a of a species i is:

$$a(i) = c(i) \cdot f(i) \quad (6)$$

where $c(i)$ is the concentration and $f(i)$ the activity coefficient of the species (DIN 38404-10). Combining Equations (5) and (6), one obtains:

$$Kc[1] = \frac{\{H^+\}\{HCO_3^-\}}{\{CO_2\}} \cdot \frac{f(CO_2)}{f(H^+) \cdot f(HCO_3^-)} \quad (7)$$

The left part of the right side of Equation (7) equals the activity-based constant $K[1]$ (cf. Table 2). Besides, CO_2 has no charge, therefore $f(CO_2) = 1$ and Equation (7) becomes:

$$Kc[1] = \frac{K[1]}{f(H^+) \cdot f(HCO_3^-)} \quad (8)$$

which is equal to:

$$Kc[1] = 10^{\lg(K[1]) - \lg(f(H^+)) - \lg(f(HCO_3^-))} \quad (9)$$

Table 2 | Definition of the activity-based equilibrium constants K , their decimal logarithm $\lg(K_0)$ at 25°C, the reaction enthalpy ΔH in J/mol and the heat capacity C_p of the reaction in J/(mol·K); values are adapted from DIN 38404-10; the indices listed correspond to the indices of Kc in the programme's array

Index	Activity-based equilibrium constant	$\lg(K_0)$	ΔH	C_p
1	$K[1] = \{H^+\}\{HCO_3^-\} / \{CO_2\}$	-6.356	9,250	-330
2	$K[2] = \{H^+\}\{CO_3^{2-}\} / \{HCO_3^-\}$	-10.329	14,950	-290
3	$K[3] = \{Ca^{2+}\}\{HCO_3^-\} / \{CaHCO_3^+\}$	-1.121	-7,950	0
4	$K[4] = \{Ca^{2+}\}\{CO_3^{2-}\} / \{CaCO_3\}$	-3.200	-16,000	-430
5	$K[5] = \{Ca^{2+}\}\{SO_4^{2-}\} / \{CaSO_4\}$	-2.310	-7,600	-170
6	$K[6] = \{Mg^{2+}\}\{HCO_3^-\} / \{MgHCO_3^+\}$	-1.068	-7,250	0
7	$K[7] = \{Mg^{2+}\}\{CO_3^{2-}\} / \{MgCO_3\}$	-2.947	-13,000	-70
8	$K[8] = \{Mg^{2+}\}\{SO_4^{2-}\} / \{MgSO_4\}$	-2.263	-18,000	-10
9	$K[9] = \{H^+\}\{OH^-\}$	-13.996	56,532	-197
10	$K[10] = \{Ca^{2+}\}\{CO_3^{2-}\}$	-8.481	-10,000	-250
11	$K[11] = \{H^+\}\{H^+\}\{CO_3^{2-}\} / p(CO_2)$	-18.156	4,150	-460

Table 3 | Components of the array *ec*; values for *g(i)* are taken from DIN 38404-10 and Eberle & Donnert (1991)

Total concentrations		Species concentrations		
Index	Component	Index	Component	Ion size parameter <i>g(i)</i>
1	tC	9	H ⁺	6.8
2	tCa	10	OH ⁻	4.2
3	tMg	11	CO ₂	3.0
4	tSO ₄	12	HCO ₃ ⁻	1.5
5	tNa	13	CO ₃ ²⁻	4.1
6	tK	14	Ca ²⁺	5.4
7	tCl	15	CaHCO ₃ ⁺	5.4
8	tNO ₃	16	CaCO ₃	3.0
		17	CaSO ₄	3.0
		18	Mg ²⁺	6.2
		19	MgHCO ₃ ⁺	6.2
		20	MgCO ₃	3.0
		21	MgSO ₄	3.0
		22	SO ₄ ²⁻	3.0

Following DIN 38404-10, $\lg(K[1])$ can be substituted using the Van't-Hoff equation and the parameters listed in Table 2:

$$\lg(K[1]) = \lg(K_0) + \frac{\Delta H}{\ln(10) \cdot R} \cdot TK_1 + \frac{C_p}{\ln(10) \cdot R} \cdot TK_2 \quad (10)$$

with

$$TK_1 = \frac{1}{298.15} - \frac{1}{TK} \quad (11)$$

$$TK_2 = \ln\left(\frac{TK}{298.15}\right) + \frac{298.15}{TK} - 1 \quad (12)$$

The value used for the universal gas constant *R* is 8.3144126 J/(mol K). Note that the resulting constants are in mol/L, except for *Kc*[9], *Kc*[10] and *Kc*[11], which are in (mol/L)². For the following calculations, they are converted to mmol/L.

Determining equilibrium concentrations (function *EqConc*)

The function *EqConc* calculates the equilibrium concentration *ec*[*i*] of each species in mmol/L. Required input

parameters are the pH, alkalinity (*Alk*) and acidity (*Aci*), the total concentrations of calcium, magnesium, sulphate, sodium, potassium, chloride and nitrate (*tCa*, *tMg*, *tSO₄*, *tNa*, *tK*, *tCl* and *tNO₃* respectively) as well as the outputs from the function *Constants* (*Kc* and *fH*). As the input pH of *EqConc* is needed but unknown, it has to be determined within an iteration in the following function (function *pH_Alk_Aci*). Output parameters of *EqConc* are the array *ec* containing the 22 equilibrium concentrations, the charge factor *FC*, the residual *D* of the charge balance and the calculated ionic strength *IOScal*. Table 3 lists all components of the array *ec*.

The function begins by calculating the concentrations of H⁺ and OH⁻ from the handed over pH, activity coefficient *fH* and equilibrium constant *Kc*[9]. Then the concentrations of the main constituents (constituents are the species that do not further dissolve under the examined conditions (Eberle & Donnert 1991)) CO₃²⁻, Ca²⁺, Mg²⁺ and SO₄²⁻ are calculated from the given total concentrations. The calculation will be presented taking the example of the carbonate ion CO₃²⁻.

The total carbon concentration *tC* is the sum of the concentrations of all species containing carbon and equals the sum of total alkalinity and CO₂-acidity (cf. Table 1):

$$tC = [CO_3^{2-}] + [HCO_3^-] + [CO_2] + [CaCO_3] + [CaHCO_3^+] + [MgCO_3] + [MgHCO_3^+] \quad (13)$$

$$= Alk + Aci \quad (14)$$

Using the concentration-based constants *Kc*, Equation (13) can also be expressed as follows:

$$tC = [CO_3^{2-}] + \frac{[H^+][CO_3^{2-}]}{Kc[2]} + \frac{[H^+][H^+][CO_3^{2-}]}{Kc[1]Kc[2]} + \frac{[Ca^{2+}][CO_3^{2-}]}{Kc[4]} + \frac{[Ca^{2+}][H^+][CO_3^{2-}]}{Kc[2]Kc[3]} + \frac{[Mg^{2+}][CO_3^{2-}]}{Kc[7]} + \frac{[Mg^{2+}][H^+][CO_3^{2-}]}{Kc[2]Kc[6]} \quad (15)$$

$$= [CO_3^{2-}] \cdot \left(1 + \frac{[H^+]}{Kc[2]} + \frac{[H^+]^2}{Kc[1]Kc[2]} + \frac{[Ca^{2+}]}{Kc[4]} + \frac{[Ca^{2+}][H^+]}{Kc[2]Kc[3]} + \frac{[Mg^{2+}]}{Kc[7]} + \frac{[Mg^{2+}][H^+]}{Kc[2]Kc[6]} \right) \quad (16)$$

$$= [CO_3^{2-}] \cdot S \quad (17)$$

As tC is given by Equation (14), $[CO_3^{2-}]$ can be calculated from tC by:

$$[CO_3^{2-}] = \frac{tC}{S} \quad (18)$$

Similar relations can be derived for Ca^{2+} , Mg^{2+} and SO_4^{2-} .

Since the constituent concentrations depend on one another, they must be calculated iteratively. In the programme, this is realised by a while-loop. As starting values for the sought concentrations, the respective total concentrations are taken. Each iteration step starts by 'saving' the constituent concentrations of the previous step in the local variables $c1$, $c2$, $c3$ and $c4$. These are later used to check the stopping criterion. Then new values for $[CO_3^{2-}]$, $[Ca^{2+}]$, $[Mg^{2+}]$ and $[SO_4^{2-}]$ are calculated from the total concentrations and the equilibrium constants as described before. The loop will be exited if:

$$\left| \frac{\sum \text{old values} - \sum \text{new values}}{\sum \text{new values}} \right| < 10^{-6} \quad (19)$$

If this is not the case, a new iteration step begins with the new values as starting values. Once $[CO_3^{2-}]$, $[Ca^{2+}]$, $[Mg^{2+}]$ and $[SO_4^{2-}]$ have been calculated with a sufficient precision, they are used together with the equilibrium constants to calculate the concentrations of the remaining species.

As a last step, FC , D and $IOScal$ are computed. FC and D are necessary to determine the pH in the function pH_Alk_Aci ; $IOScal$ is just calculated to enable comparison with the measured IOS . According to Eberle (1989), the relation between Alk and tC can be expressed by the linear equation:

$$Alk = tC \cdot FC + D \quad (20)$$

with

$$FC = \frac{2 \cdot ([CO_3^{2-}] + [CaCO_3] + [MgCO_3])}{[tC]} + \frac{[HCO_3^-] + [CaHCO_3^+] + [MgHCO_3^+]}{[tC]} \quad (21)$$

$$D = [OH^-] - [H^+] \quad (22)$$

$IOScal$ is computed via:

$$IOS = 0.5 \cdot \sum_i c(i) \cdot z(i)^2 \quad (23)$$

where $c(i)$ is the concentration and $z(i)$ the charge of the species i (DIN 38404-10).

Determining pH and SI (functions pH_Alk_Aci and $FunctSI$)

The function pH_Alk_Aci primarily determines the equilibrium pH from the input water data. A flowchart illustrating the sequence of necessary operations is given in Figure 1. As input variables, pH_Alk_Aci requires T , IOS , Alk , Aci , tCa , tMg , tSO_4 , tNa , tK , tCl and tNO_3 . The output variables are the equilibrium pH ($pHcal$), tC , the equilibrium concentrations ec of all considered species, $IOScal$ and SI . For the determination of the CCPP, the actual role of the function pH_Alk_Aci is to provide the saturation index SI . As described later, the other output variables do not necessarily have to be considered in the main programme; however, they are useful to determine the programme's accuracy and estimate the reliability of the resulting CCPP.

The function pH_Alk_Aci calls the two previously described functions ($Constants$ and $EqConc$). As stated before, the function $EqConc$ determines the equilibrium concentrations at any given pH. However, in the function pH_Alk_Aci , the output of $EqConc$ is actually used to determine the equilibrium pH. This is carried out iteratively by adapting the input pH of $EqConc$ until equilibrium state is reached with sufficient precision. Before entering the pH iteration loop, the function $Constants$ needs to be called to provide the equilibrium constants Kc for $EqConc$.

For the very first iteration step, the iteration pH ($pHit$) is assumed to be 7. Then the function $EqConc$ is called to determine ec , FC , D and $IOScal$. The returned values of FC and D are immediately used to evaluate Equation (20). If, for the current $pHit$, the auxiliary variable $zero$ is above 0, the current value of $tC \cdot FC - D$ is lower than Alk . In particular, the calculated FC and D are too low. Because

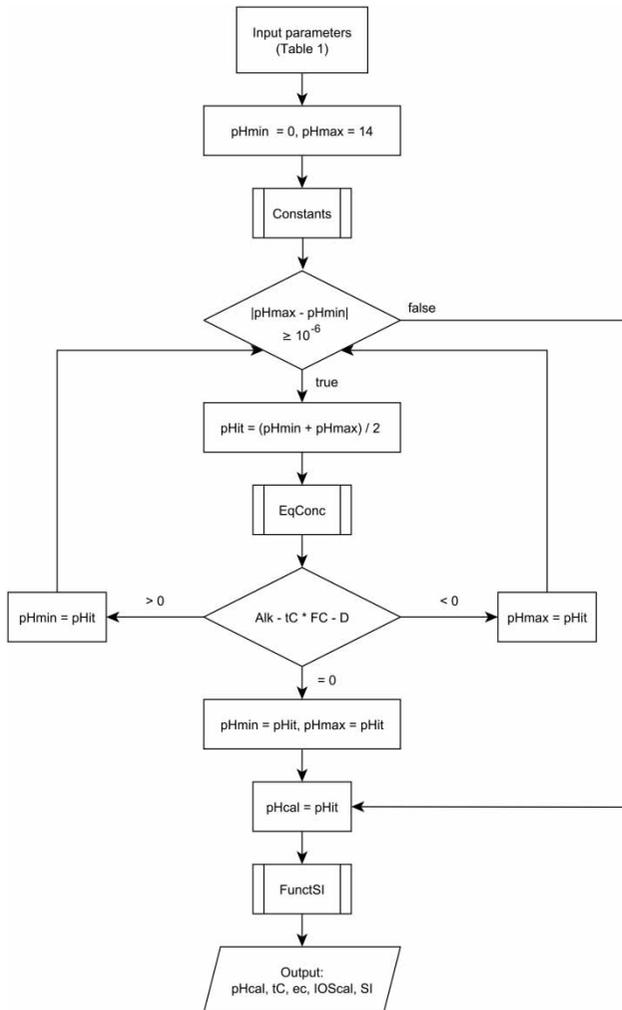


Figure 1 | Flowchart for function pH_Alk_Aci .

they both increase with increasing pH (and decrease with decreasing pH), the iteration pH of the next iteration step must be raised, which is realised by setting the lower boundary pH ($pHmin$) to $pHit$. If, on the other hand, $zero$ is beneath 0, the higher boundary pH ($pHmax$) is altered instead. This procedure is also known as the bisection method. For the (unlikely but possible) case that $zero$ is exactly 0, $pHit$ is the sought pH and both boundary pH values can be set to $pHit$. After each iteration step, the absolute difference between upper and lower boundary pH is evaluated. If it reaches the desired precision (here 10^{-6}), the while-loop is exited and the sought equilibrium pH ($pHcal$) is set to $pHit$ of the last iteration step. Note that, to enhance robustness, iteration has been limited to a pH

range between 0 and 14. As this programme is developed for applications in drinking water treatment, this should not cause any problems.

Subsequently, the saturation index SI is determined by calling the function $FunctSI$, which calculates SI according to DIN 38404-10 via:

$$SI = \lg \left(\frac{[Ca^{2+}][CO_3^{2-}]}{Kc[10]} \right) \quad (24)$$

An if-statement is added to the function to prevent misleading values of SI in case concentrations of Ca^{2+} or CO_3^{2-} are zero.

Determining the CCPP (function $CCPP_Alk_Aci$)

The function $CCPP_Alk_Aci$ finally determines the CCPP of the examined water. For this purpose, it needs the same input variables as the function pH_Alk_Aci (T , IOS , Alk , Aci , tCa , tMg , tSO_4 , tNa , tK , tCl and tNO_3). Aside from the CCPP, it also outputs pH_C , the pH of saturation with $CaCO_3$. Figure 2 shows the flowchart for $CCPP_Alk_Aci$.

There is no way to directly calculate the CCPP. Therefore, $CaCO_3$ precipitation has to be simulated by iteratively withdrawing virtual amounts of $CaCO_3$ from the water until saturation is reached. This virtual withdrawal is realised by altering given water parameters to the way they would react to precipitation of $CaCO_3$. For precipitation of X mmol/L of $CaCO_3$, alterations are as follows:

- IOS decreases by $4 \cdot X$, as both CO_3^{2-} and Ca^{2+} contribute to the ionic strength with two times their concentration (cf. Equation (23)),
- Alk decreases by $2 \cdot X$, because CO_3^{2-} contributes to it with two times its concentration (cf. Table 1),
- Aci increases by X , because CO_3^{2-} counteracts CO_2 -acidity with one time its concentration (cf. Table 1), and
- tCa decreases by X , as 1 mol of $CaCO_3$ contains the same amount of calcium.

The actual implementation of $CCPP_Alk_Aci$ is similar to pH_Alk_Aci . Iteration is again realised through a while-loop, but this time with $CCPPit$ as iteration variable. Inside the loop, the function pH_Alk_Aci is called. Here it is crucial to alter the input parameters using $CCPPit$ as

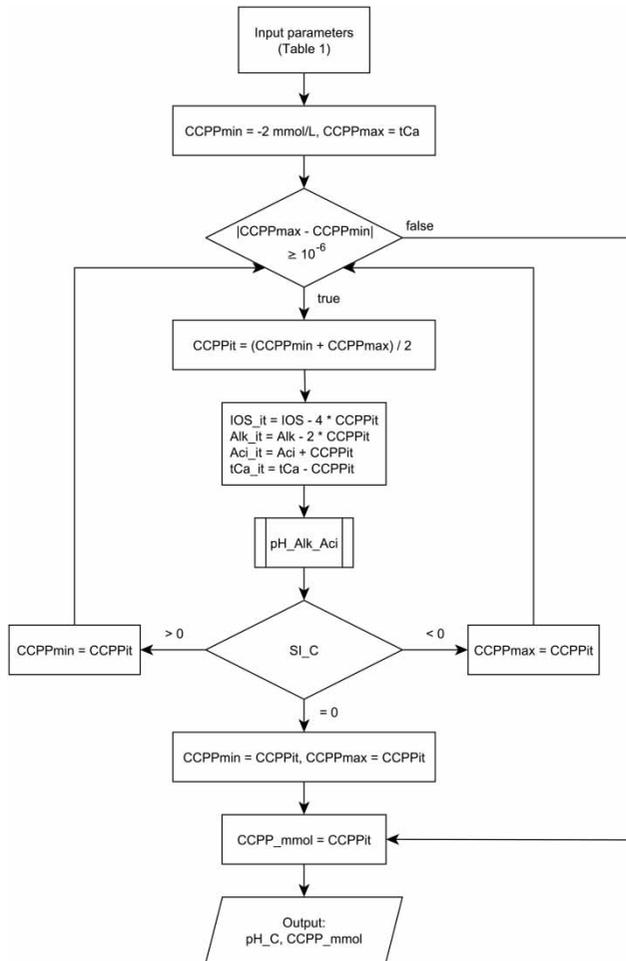


Figure 2 | Flowchart for function *CCPP_Alk_Aci*.

described above. The returned saturation index (*SI_C*) is then evaluated in order to determine whether saturation has been reached sufficiently. If *SI_C* is above 0, the altered water is still oversaturated and the current *CCPPit* is lower than the sought CCPP. Hence, *CCPPit* is raised for the next iteration step by setting the lower boundary CCPP (*CCPPmin*) to *CCPPit*. If, on the other hand, *SI_C* is beneath 0, the higher boundary CCPP is adapted. For the (unlikely but possible) case that *SI_C* = 0, the exact value of the CCPP is found. The loop is exited if the difference between upper and lower boundary CCPP reaches or underpasses 10^{-6} mmol/L. Eventually, the iteration CCPP of the last iteration step is taken as the actual CCPP (in mmol/L) of the examined water.

Note that, to enhance robustness, overall limit values for the CCPP have been set. The upper limit has been set to *tCa*,

meaning that only as much CaCO_3 can precipitate as calcium is contained in the water. The lower limit value has been set to -200 mg/L, as higher values are rarely found in drinking water treatment; yet it remains an arbitrary number.

Main model (model *MAIN_CCPP*)

The main model has to provide the input parameters listed in Table 1 in the specified units. Call the function *pH_Alk_Aci* in the main model to obtain the calculated pH (*pH_{cal}*), the sum of the concentrations of carbonic species (dissolved inorganic carbon, *tC*), the equilibrium concentrations (*ec*) of the examined water, the calculated ionic strength (*IOS_{cal}*) and the saturation index (*SI*). This is not required to calculate the CCPP, but provides a means to determine the accuracy of the programme when testing it and to assess the reliability of its results when employing it. To obtain the CCPP (in mmol/L), the function *CCPP_Alk_Aci* must be called. This function also outputs the pH of calcium carbonate saturation (*pH_C*). To obtain the CCPP in mg/L, multiply with the molar mass of CaCO_3 (here 100.09 g/mol are used). A scheme that illustrates how all described components are nested within the programme is shown in Figure 3.

RESULTS AND DISCUSSION

Comparison to DIN 38404-10 and a simplified model

To assess the accuracy of the developed programme, the *pH_C* and the CCPP were calculated for six example data sets of DIN 38404-10, and compared to the values given in the standard. DIN 38404-10 explicitly provides these data sets for validation of computer programmes. Data of the data sets is synthetically generated and represents analysis data of ten example waters, which mainly differ in temperature and ion content. As mentioned before, the developed programme does not consider any phosphate species. Contrary to this, the values for *Alk* and *Aci* of phosphate-containing waters given in the standard and required for programme execution do include these species; therefore, only the waters which do not contain phosphate (waters 1, 2, 3,

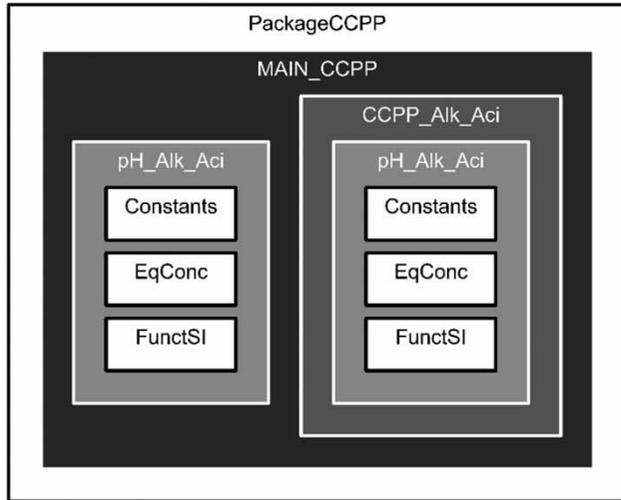


Figure 3 | Hierarchy of the developed programme's components.

4, 7, 9) are included in this study. Table 4 summarizes relevant data of these waters. While the temperature remains constant between 10 and 15°C for all regarded waters, the ionic strength ranges widely, with a minimum at 1.041 mmol/L (water 4) and a maximum at 15.167 mmol/L (water 3). With 3.50 mmol/L and 0.70 mmol/L, water 3 contains the highest total concentrations of calcium and magnesium respectively. The highest total sulphate concentration is 1.40 mmol/L and occurs in water 7. The lowest concentrations of these three constituents are contained in water 4, with 0.15 mmol/L for calcium, 0.05 mmol/L for magnesium and 0.05 mmol/L for sulphate. Regarding their CCPP, waters 2 and 7 can be characterised as slightly, and waters 1 and 3 as moderately, CaCO₃ dissolving. Water 4 is highly dissolving, whereas water 9 is the only one with a positive CaCO₃ precipitation potential.

Calculation results were furthermore compared to those obtained with a programme based on a simplified model. The simplified model neglects ion pairs and complex formation. Therefore, it assumes that all calcium is present as Ca²⁺ (i.e. $tCa = [Ca^{2+}]$) and only considers the equilibrium constants of the first and second dissociation of CO₂, the ion product of water, and the solubility product of calcite, which are equivalent to K[1], K[2], K[9] and K[10] in Table 2. In the simplified model, they are calculated using the formulas provided by Ball & Nordstrom (1991). To calculate activity coefficients, the following simpler version of the Debye-Hückel

equation is used:

$$\lg(f(i)) = -\frac{0.5 \cdot z(i)^2 \sqrt{IOS/100}}{1 + 1.4 \cdot \sqrt{IOS/100}} \quad (25)$$

and, when calculating *SI*, it is presumed that all alkalinity stems from HCO₃⁻.

Values and results of the three calculation methods are presented in Table 4. The comparison reveals that CCPP values calculated with the developed programme tend to be slightly too low; yet, four of the six calculated CCPP values meet the accuracy requirement of ±0.1 mg/L set out in DIN 38404-10. With neglect of ion pairs and complex formation, i.e. with the simplified programme, no CCPP value meets the requirement. Values of *pHcal* comply with the required accuracy of ±0.001 for five of the six waters if calculated using the developed programme; using the simplified programme, no *pHcal* value lies within limits of accuracy.

Results of the simplified programme are in accordance with findings described in APHA/AWWA/WEF (2005), which states that '[m]odels that do not consider [ion pairs] overestimate the amount of CaCO₃ that can be precipitated and underestimate the amount of CaCO₃ that can be dissolved' (pp. 2–34). As can be seen in Table 4, this behaviour is especially pronounced for waters with high ion concentrations (waters 3 and 9). Correspondingly, calculations for waters with low ion concentrations (waters 2 and 4) give relatively good results.

Results of the developed programme deviate from DIN 38404-10 because, contrary to what is assumed in the function *CCPP_Alk_Aci*, the ionic strength does not precisely decrease by four times the precipitated amount of CaCO₃. When CaCO₃ precipitates, the water's pH decreases, which affects speciation. Consequently, withdrawal of CaCO₃ not only results in lower concentrations of Ca²⁺ and CO₃²⁻, but also of other, lower charged species. Therefore, the ionic strength will generally decrease less than four times the precipitated amount of CaCO₃. To determine the exact decrease, it is necessary to additionally iterate over the ionic strength when calculating the CCPP in *CCPP_Alk_Aci*. However, within the additional iteration loop, *IOScal* has to serve as input parameter of *pH_Alk_Aci*. This is not desirable for this programme, as it shall also be applicable in situations in which not all constituent

Table 4 | Data of the six example waters and comparison of the pH of calcium carbonate saturation (pH_{LC}) and the CCPP obtained with the developed programme (Progr.) to the values provided in DIN 38404-10 (DIN), and the results of a programme based on a simplified model (Simpl.)

Input parameters	Unit	Water 1	Water 2	Water 3	Water 4	Water 7	Water 9
T	°C	10.0	15.0	10.0	10.0	12.0	15.0
IOS	mmol/L	5.362	3.125	15.167	1.041	7.173	8.886
Alk	mmol/L	2.445	1.577	5.392	0.168	1.092	4.194
Aci	mmol/L	0.292	0.054	1.333	1.207	0.067	0.478
tCa	mmol/L	1.40	0.75	3.50	0.15	1.30	2.65
tMg^*	mmol/L	0.23	0.10	0.70	0.05	0.25	0.20
$tSO4^*$	mmol/L	0.38	0.15	1.20	0.05	1.40	0.55
tNa^*	mmol/L	0.30	0.40	2.30	0.30	1.60	0.30
tK^*	mmol/L	0.05	0.10	0.30	0.10	0.15	0.06
tCl^*	mmol/L	0.25	0.30	2.70	0.34	0.85	0.75
$tNO3^*$	mmol/L	0.15	0.03	0.50	0.18	0.10	0.05

Results	Unit	DIN	Progr.	Simpl.	DIN	Progr.	Simpl.	DIN	Progr.	Simpl.	DIN	Progr.	Simpl.	DIN	Progr.	Simpl.	DIN	Progr.	Simpl.
pH_{LC}	-	7.660	7.661	7.634	8.050	8.051	8.029	7.080	7.081	7.048	7.775	7.787	7.770	8.092	8.093	8.035	7.229	7.228	7.203
Deviation from DIN	-	-	+0.001	-0.026	-	+0.001	-0.021	-	+0.001	-0.052	-	+0.014	-0.003	-	+0.001	-0.057	-	-0.001	-0.026
CCPP	mg/L	-14.5	-14.6	-12.9	-3.2	-3.2	-2.5	-16.3	-16.6	-6.5	-111.1	-111.6	-110.6	-5.5	-5.5	-4.6	7.1	7.1	11.1
Deviation from DIN	mg/L	-	-0.1	+1.9	-	0.0	+0.7	-	-0.3	+9.8	-	-0.5	+0.5	-	0.0	+0.9	-	0.0	+4.0

*Input parameters that are not considered in the simplified model

-0.026 Deviations that surpass the maximum deviation specified in DIN 38404-10.

concentrations listed in Table 1 are known, but IOS is assessable, for example through the electrical conductivity.

CONCLUSIONS

This work has shown how to programme calculation of species concentrations, pH, CaCO₃ saturation and the CCPP using OpenModelica. The advantage of using OpenModelica is that the developed package can easily be integrated into the model of, for example, a drinking water treatment plant, where it can be employed, for example, to estimate whether water leaving the plant meets the required CCPP, or to assess how much CaCO₃ dissolves if neutralizing filters containing calcium carbonate are employed to adjust the pH of the water.

The described approach adheres closely to the principles established in DIN 38404-10 and, as proven by comparison to six example waters, its results for the CCPP of phosphate-free waters nearly reach the degree of accuracy stipulated by the standard – a degree that cannot be met when neglecting ion pairs and complex formation.

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