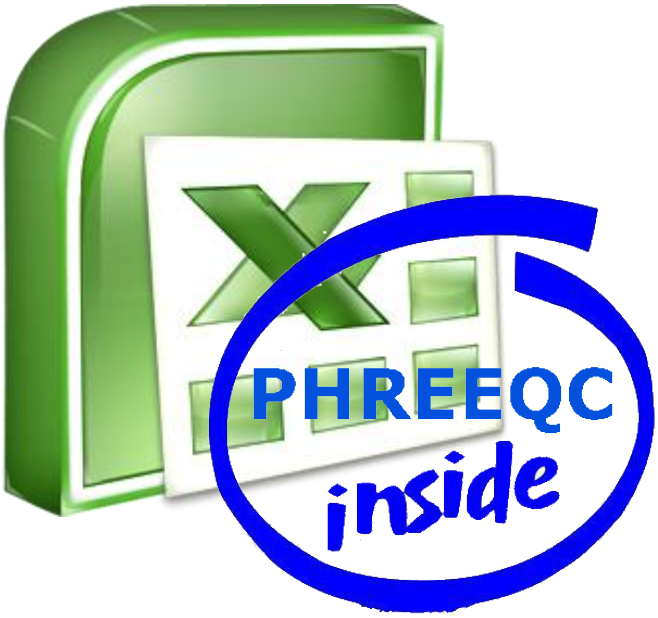
Aquatic Chemistry for engineers



Volume 1

Starting with PHREEQC for water treatment

P.J. de Moel
J.C. van Dijk
W.G.J. van der Meer

TU Delft Delft University of Technology

OMNISYS

Challenge the future

Aquatic Chemistry for engineers

Self-study course on PHREEQXCEL
for modelling water quality and water treatment

Volume 1

Starting with PHREEQC for water treatment

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Content

1. Introduction

PHREEQC
PHREEQC has become the 'de facto' standard for water chemistry in geohydrology. It is developed by the US Geological Survey (USGS), starting in 1980 with regular updates and extensions to date. Major aspects contributed to its success are:
- freely available (USGS website)
- active and continuous development
- scientific base, fully traceable
- adapted to newest scientific knowledge
- users can modify and extend the basics
- active interaction between developers and users (mostly scientists)
- large growing users group
- international assessment and recognition.

PHREEQC is famous in geohydrology but hardly known in water treatment. This might be caused by:
- requires above average skills in water chemistry
- high threshold for starters
- absence of scientific literature on water treatment with PHREEQC
- absence of educational material for using PHREEQC in water treatment
- requires modifications for practical application in water treatment (see Chapter 5 and 6).

PHREEQC has a large potential for application in water treatment. In its basic form all relevant chemical equilibriums for water chemistry are incorporated, including acid-base reactions, reactions for precipitation/dissolution, reactions for aeration/gas transfer, and redox reactions.

This course 'Aquatic Chemistry for engineers' will guide students at their learning path in using PHREEQC for water treatment.
The course assumes a minimum knowledge on water chemistry, as given in basic text books in water treatment (i.e. Drinking water - Principles and Practices, De Moel e.a., World Scientific 2006).
The course is presented in four volumes:
1. Starting with PHREEQC for water treatment
2. Drinking water with PHREEQC
3. Waste water with PHREEQC
4. Industrial water with PHREEQC

Starting with PHREEQC
This volume ('Starting with PHREEQC for water treatment') gives the first steps for students in using PHREEQC for water chemistry. This course uses PHREEQXCEL as a container application or 'Graphical User Interface' for PHREEQC (or the Excel interface for PHREEQC).
Chapter 2 gives the backgrounds of PHREEQC and an introduction for using PHREEQXCEL.
In chapter 3 the chemical composition of an example drinking water is used for showing the basic use of PHREEQC (program basics, input, output).
Chapter 4 shows how PHREEQXCEL allows for pre- and post-processing of data.
The application of PHREEQXCEL for water treatment is briefly demonstrated in Chapter 5. Further details on chemistry and scientific backgrounds are presented in Volume 2, 3 and 4.
Chapter 6 deals with the modification of the database phreeqc.dat for redox reactions in order to make PHREEQC applicable in water treatment.
All these chapters include Labs on specific aspects, with questions to evaluate the gained skills.
Chapter 7 shortly gives hints for further steps in using PHREEQXCEL and an overview of advanced resources on PHREEQC.

The following table gives an overview of the PHREEQC keywords introduced per paragraph and Lab:

Chap-ter	**Para-graph**	**PHREEQC keyword**	**Lab**
2	2.3	*PHREEQXCEL as container system for PHREEQC*	2.1
	2.4	*PHREEQXCEL in real life process control*	2.2
3	3.2	SOLUTION (*pure water*)	3.1
	3.3	SOLUTION (*drinking water*) SOLUTION_SPREAD (*drinking water*)	3.2 + 3.3 3.4
	3.4	SOLUTION (*output*)	3.5
4	4.1	PRINT / USER_PRINT	4.1
	4.2	SELECTED_OUTPUT / USER_PUNCH	4.2
	4.3	SELECTED_OUTPUT <n> / USER_PUNCH <n>	4.3
	4.4	CALCULATE_VALUES	4.4
	4.5	SELECTED_OUTPUT / USER_PUNCH *in Excel*	4.5
	4.6	USER_GRAPH *in Excel*	4.6
5	5.1	CHARGE *for a specific solution component*	5.1
	5.2	REACTION_TEMPERATURE	5.2
	5.3	MIX	5.3
	5.4	REACTION MIX	5.4 5.5
	5.5	EQUILIBRIUM_PHASES	5.6
	5.6	KINETICS / RATES	-
	5.7	GAS_PHASE	5.7
6	6.1	*Redox reactions with pE as master parameter*	-
	6.2	SOLUTION_MASTER_SPECIES / SOLUTION_SPECIES / PHASES SOLUTION (*anaerobic water*)	 6.1
	6.3	SOLUTION_SPREAD (*anaerobic water*) / MIX	6.2
	6.4	REACTION / KINETICS+RATES *for converting inert elements*	6.3
	6.5	-	6.4

PHREEQC functions for transport modelling (TRANSPORT, ADVECTION), adsorption or surface complexation (SURFACE_SPECIES) and ion-exchange (EXCHANGE_SPECIES) are not part of this volume 'Starting with PHREEQC for water treatment'. These items will be discussed in Volume 2, 3 and 4.

2. Using PHREEQXCEL

PHREEQC and its predecessor PHREEQE were originally developed as a batch program for modelling of aquatic chemistry in ground water, interacting with different solids and gas phases. Even after more than three decades of updates, extensions and modifications a PHREEQC batch version still exists, nowadays available for different platforms (Windows, Linux, MacOS).
More recently, container systems or 'Graphical User Interfaces' have been developed such as 'Phreeqc Interactive' (USGS) and 'PHREEQC in adapted Notepad++' (Tony Appelo).

Since 2011 PHREEQC is also available as modules which enables its application within other hosting environments on different platforms. In Microsoft Window the module IPhreeqcCOM allows the incorporation of PHREEQC in program languages such as C++, Visual Basic, Fortran, and Python, or in applications such as Matlab and Excel. PHREEQXCEL uses this IPreeqcCOM module allowing to run PHREEQC calculations within Microsoft Excel.

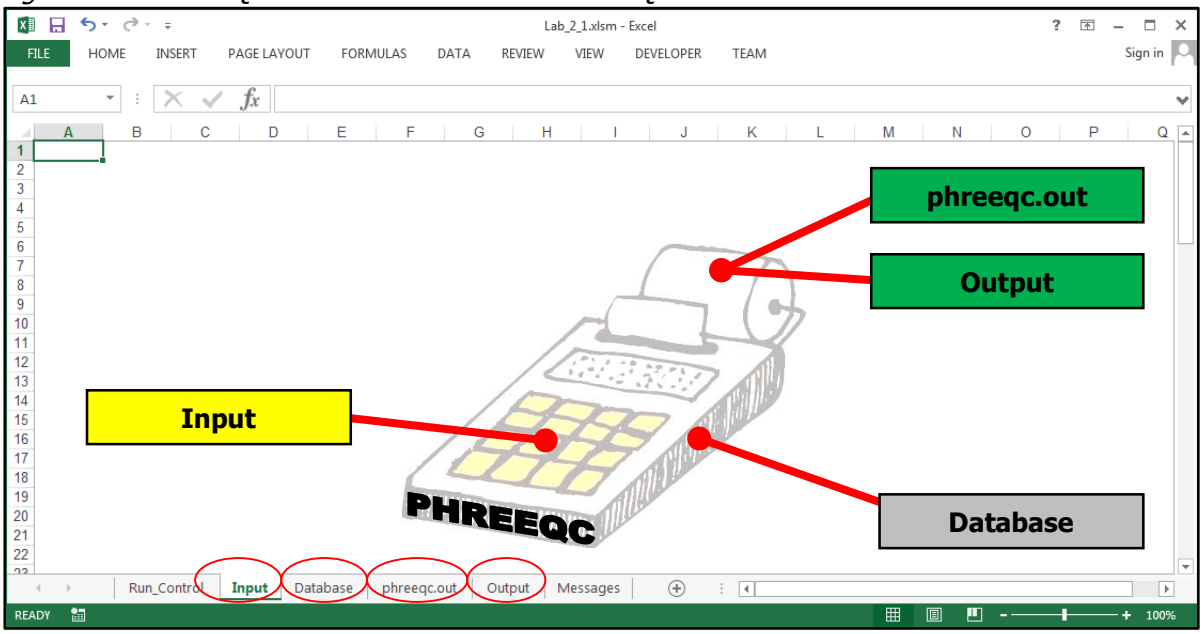
In this chapter the concept of PHREEQXCEL is introduced.
In paragraph 2.1 the basic components of PHREEQXCEL are shown. Paragraph 2.2 gives an instruction for installing the IPreeqcCOM module.
Paragraph 2.3 demonstrates PHREEQXCEL by using input code from external sources such as USGS and Tony Appelo or by using self-developed input code. In paragraph 2.4 the possibilities for developing specific applications in PHREEQXCEL are presented. Paragraph 2.5 gives a brief presentation of using PHREEQXCEL 'in the cloud'.

2.1 PHREEQXCEL as container system for PHREEQC

Files of a PHREEQC Run
Calculations in PHREEQC are called 'Simulations'. One or more simulations are done in a single 'Run'. These simulations are defined in an input file, having the extension 'pqi' in PhreeqcI. An input file has to be created by the user.
A single Run uses the chemical definitions collected in a database. The default database for PHREEQC is 'phreeqc.dat', but any other chemical definition in PHREEQC-format can be used.
A single Run creates output, by default as an output file, having the extension 'pqo' in PhreeqcI and the default file name 'phreeqc.0.out' in IPhreeqcCOM.

PHREEQXCEL as 'file container'
PHREEQXCEL is an alternative container system for PHREEQC. Its major components are shown in Figure 2.2. A PHREEQXCEL application contains all files of a single Run (.pqi, .dat, .pqo files in PhreeqcI) on different sheets in a single Excel file.

Figure 2.2 - PHREEQXCEL as container for the PHREEQC calculator



A PHREEQXCEL application is included in a macro-enabled Excel file (.xlsm file) containing 6 predefined sheets and 4 generic VBA (Visual Basic for Applications) subroutines. The Excel sheet names and VBA subroutines are shown in Table 2.1.

Table 2.1 - Components of PHREEQXCEL applications

Sheet name	**Function**	**IphreeqcCOM method or file**
Run_Control	Run settings and Start button	-
Input	PHREEQC input code	[Ex1].pqi
Database	Chemical database for PHREEQC	stimela.dat
phreeqc.out	Lined output (PRINT)	phreeqc.[id].out
Output	Tabulated output (SELECTED_OUTPUT)	selected.[id].out
Messages	PHREEQC warnings and errors	GetWarningString() GetErrorString()
VBA subroutines		
RunPhreeqc()	Generic VBA program code for PHREEQXCEL applications	RunFile() RunString()
Button1_Click()	Macro to start RunPhreeqc()	-
Button2_Click()	Macro to select an external Input file	-
Button3_Click()	Macro to select an external Database file	-

Running a PHREEQXEL application on a PC requires Microsoft Excel for Windows to be installed (Excel 2007 or later), as well as the IphreeqcCOM module for Windows (version 3.1.4 or later).

2.2 Installing the Windows COM module for PHREEQC

Download
The Windows COM module for PHREEQC can be downloaded from:
http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/

The Windows COM module for PHREEQC requires one install file on a 32-bits Windows system and two install files on a 64-bits Windows system, as shown in Table 2.2.

Table 2.2 - Install files for the Windows COM module for PHREEQC

Platform	Processor	File name
Windows COM	32-bit	IPhreeqcCOM-3.1.7-9213-win32.msi
	64-bit *	IPhreeqcCOM-3.1.7-9213-x64.msi

** Both 32-bit and 64-bit COM versions should be installed on 64-bit versions of Windows*

The install file names will be changed for succeeding releases. It is recommended to use the latest release, since these releases might include resolved bugs, updated databases etc.

Installation
Installing the downloaded .msi files will (by default) create the following maps:
- on 32 bits Windows: C:\Program Files\USGS\ IPhreeqcCOM 3.1.7-9213
- on 64 bits Windows: C:\Program Files\USGS\ IPhreeqcCOM 3.1.7-9213
  C:\Program Files (x86)\USGS\ IPhreeqcCOM 3.1.7-9213

The following sub maps will be created:
- bin IPhreeqcCOM dynamic link library (DLL) and type library (TLB) files
- database 9 chemistry database files in PHREEQC format, including phreeqc.dat
- doc documentation files (pdf, chm), release notes
- examples in sub map ./com/excel: runphreeqc.xls and phreeqc.dat.

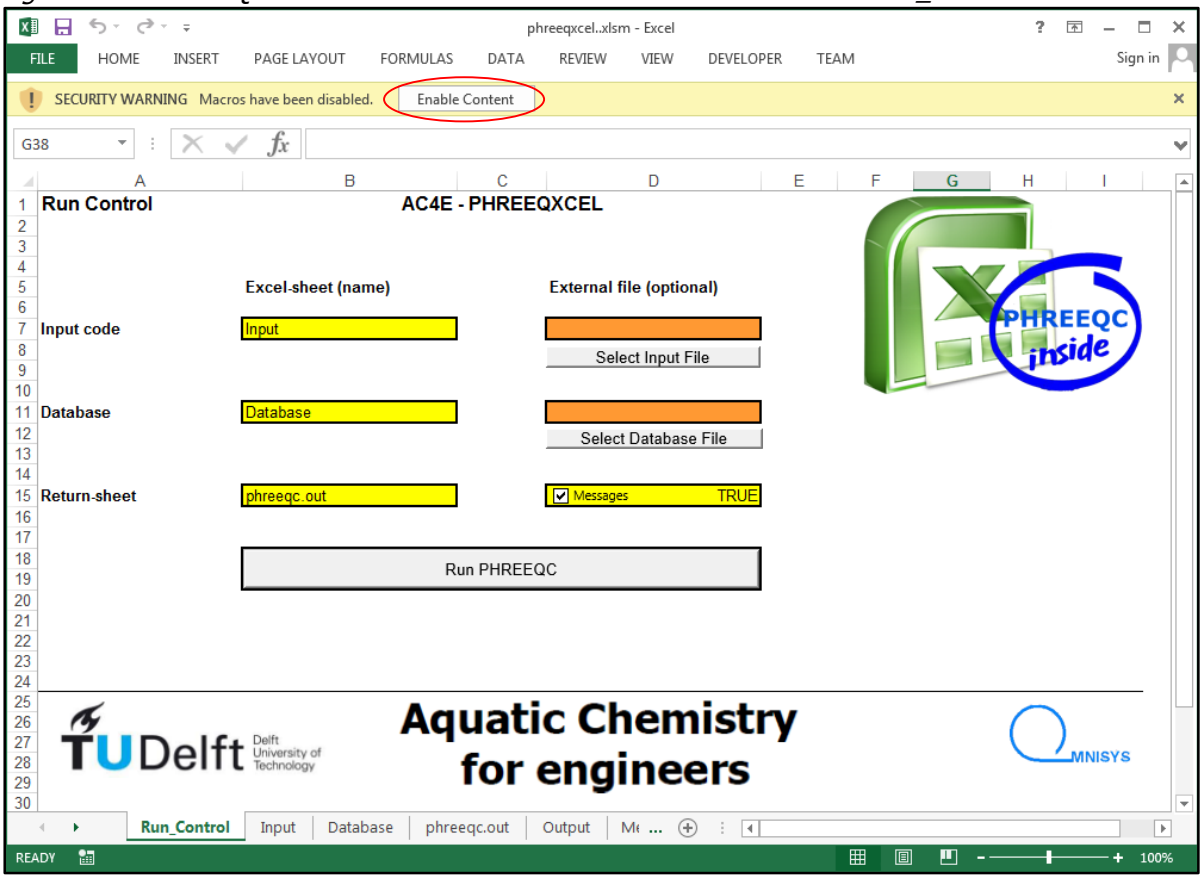
Updating an installed COM module results in the removal of the old version, including its folders.

2.3 Running PHREEQXCEL

PHREEQXCEL runs are defined on the sheet Run Control which also contains a 'Run PHREEQC' button to start the Run. Figure 2.3 shows the sheet Run_Control of PHREEQXCEL applications. It also shows an Excel warning message to 'Enable Content'. Enabling allows Excel to run the VBA code in this Excel file, which is required for PHREEQXCEL applications. Excel security warnings depends on user's security settings.

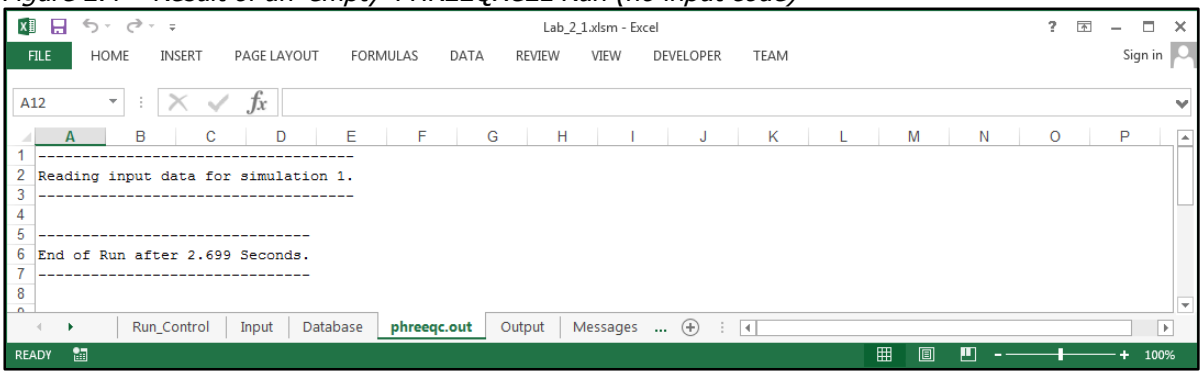
Starting the PHREEQXCEL application runs the simulations defined in the user input code on sheet 'Input' using the PHREEQC database on sheet 'Database'. The results are presented on the sheets 'Output' and 'phreeqc.out'. Users might modify the names of these sheets, might use alternative sheets, or might use external files for Input and/or Database. External files are imported in related sheets, in order to fulfil the 'single file' container concept.

Figure 2.3 - PHREEQC calculations are defined and initiated on the sheet Run_Control



Running an 'empty' PHREEQXCEL application (without any user input code, but with a valid Database) gives the output as shown in Figure 2.4. This empty application is distributed as AC4E-phreeqxcel.xlsm, which includes the default database for water treatment applications stimela.dat.

Figure 2.4 - Result of an 'empty' PHREEQXCEL Run (no input code)



Running external PHREEQC-code

PHREEQXCEL also runs external input code files generated in and for other container systems, such as 'Phreeqc Interactive' (USGS) and 'PHREEQC in adapted Notepad++' (Tony Appelo).
A huge number of example files for these containers systems are available, which can be used in PHREEQXCEL:

- USGS: http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/phreeqc3-html/phreeqc3-55.htm
- Tony Appelo: http://www.hydrochemistry.eu/exmpls/index.html

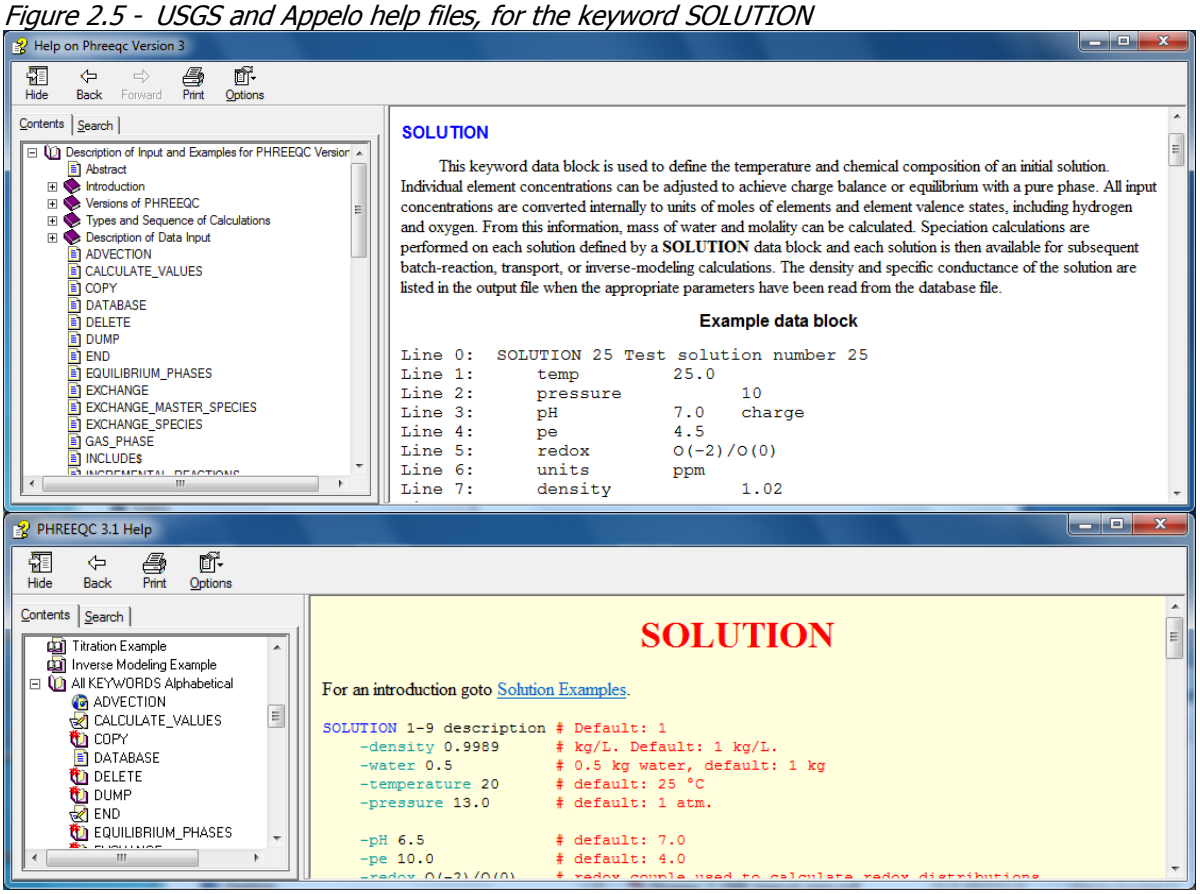
Student activity	**Lab 2.1 – Running PHREEQXCEL**
Study goals	- novice use of PHREEQXCEL - running external input files from other container systems (pqi, phr) - using different databases for PHREEQC

Creating PHREEQC-code

Both 'Phreeqc Interactive' (USGS) as 'PHREEQC in adapted Notepad++' (Tony Appelo) include extended support for creating PHREEQC code.
'Phreeqc Interactive' (USGS) has been developed for the novice PHREEQC user. 'PHREEQC in adapted Notepad++' is focussed on users with a basic understanding of the PHREEQC concept.

PHREEQXCEL does not include such support for code generation. PHREEQXCEL users might use one of these container systems for code generation and import the code lines in the PHREEQXCEL sheet 'Input'. Alternatively, users may directly create their own code in the PHREEQXCEL sheet 'Input' using the extended help files and manuals for PHREEQC as reference systems.
Syntax for PHREEQC code can be found in the PHREEQC 3.1 Help files (phreeqc_31_USGS.chm and phreeqc_31_Appelo, see PHREEQXCEL documentation). Figure 2.5 give examples of both Help files.

Figure 2.5 - USGS and Appelo help files, for the keyword SOLUTION



These Compiled HTML Help files are modified with PHREEQC language modifications (as in version 3.1, not for bug fix version as in version 3.1.2). The PHREEQC manuals (pdf version as well as online version) are not modified for language modifications.
The USGS help file gives the full explanation of syntax options for all keywords. The Appelo help file gives only examples of syntax options with minor comments.
Suggestion: Try out both versions of PHREEQC help file to find your most appropriate version

2.4 Running PHREEQXCEL apps

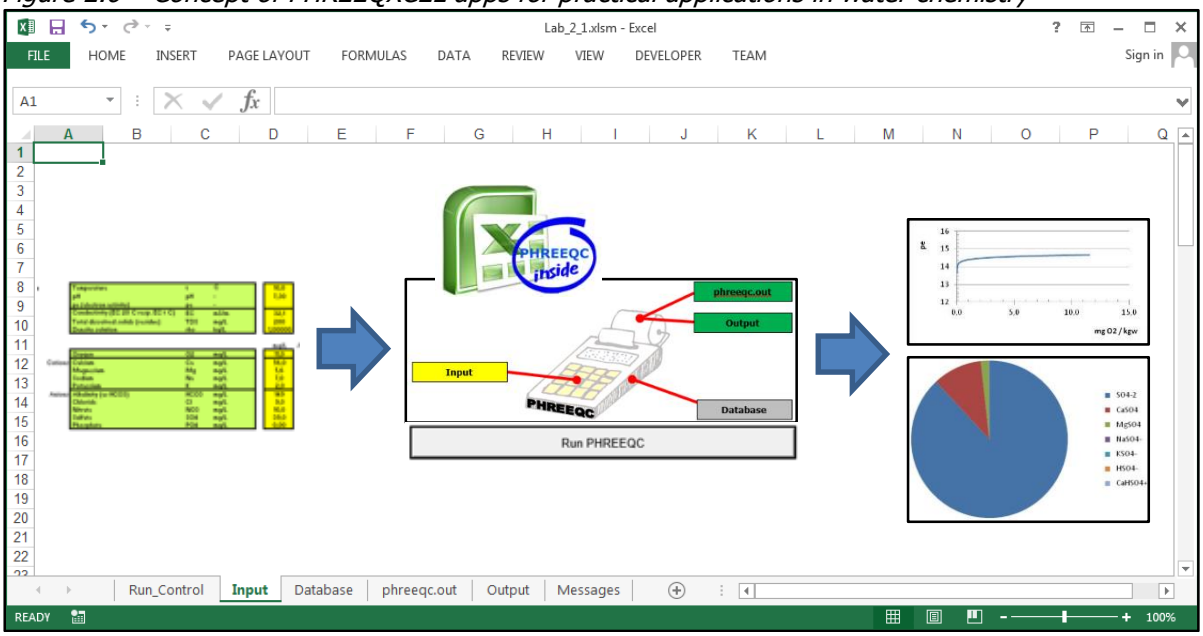
Within PHREEQXCEL the imported code lines and the directly created code lines might be extended with the specific pre-processing options of Excel, for creating PHREEQXCXEL apps. These apps might also include post-processing of the results in Excel which will improve the presentation and interpretation of the calculated results.

PHREEQXCEL apps might be used by its developer but also by users without any knowledge of PHREEQC. Running PHREEQXCEL apps includes the following 3 steps:

- input of user specific data
- running the PHREEQC simulations
- presenting the results.

This concept is shown in Figure 2.6.

Figure 2.6 - Concept of PHREEQXCEL apps for practical applications in water chemistry



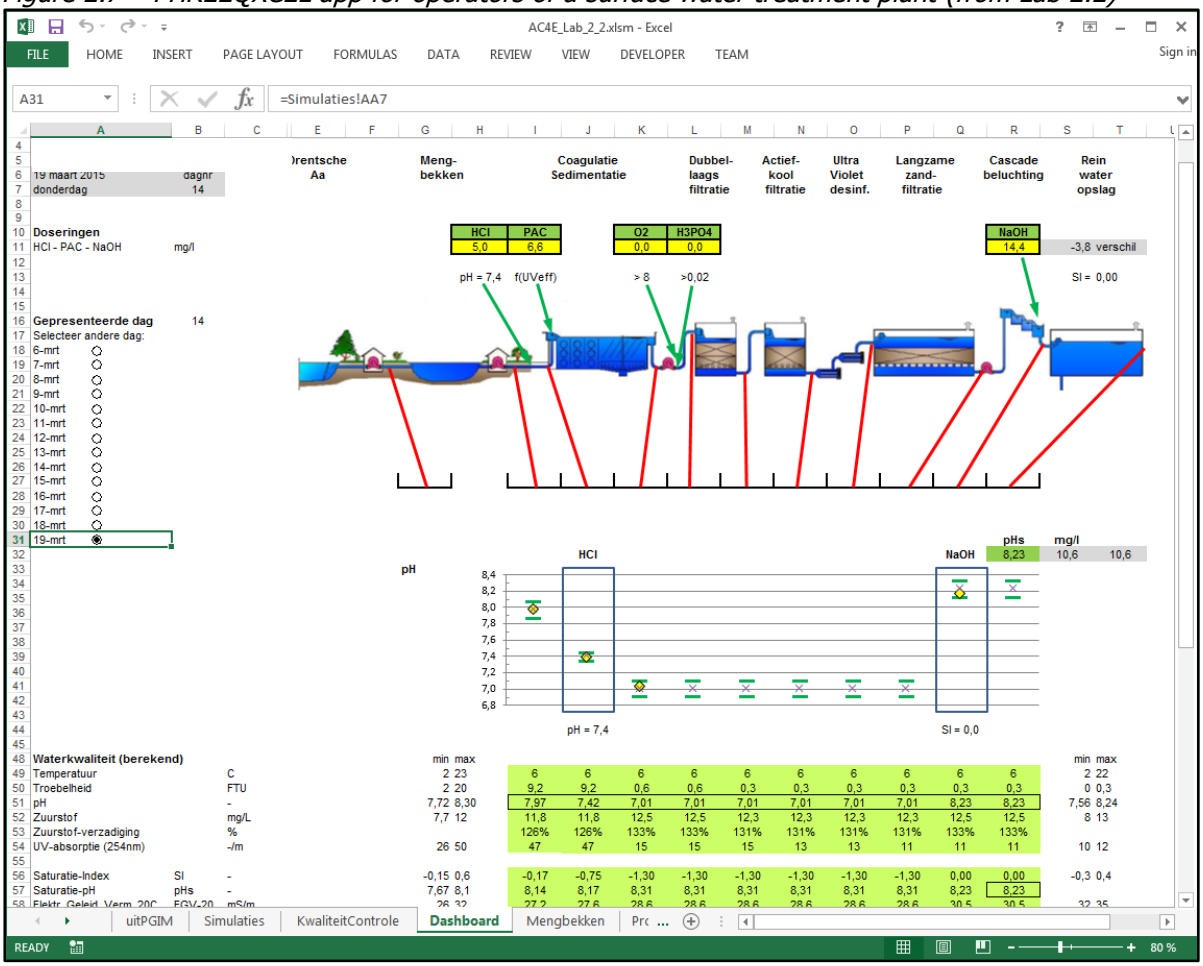
Student activity	**Lab 2.2 – Running PHREEQXCEL apps**
Study goals	- novice use of PHREEQXCEL - demonstrating the concept of PHREEQXCEL apps - demonstrating the use of PHREEQXCEL in process control

Figure 2.7 gives an impression of a PHREEQXCEL app(lication) in which the water quality in a surface water treatment plant is modelled (drinking water produced from river water after passing an equalizing reservoir with a detention time of some 60 days). The model calculates the water quality (macro-parameters) after each process step in the treatment plant, solely based on 25 raw water quality parameters and on 22 online flow measurements (9 for water and 13 for dosed chemicals, values for day-average). Each week the raw water quality is measured for 8 parameters, while the other 17 parameters are obtained from historical data, with internal validation. Each morning the model is used for the simulation of the plant performance during the last 14 days. The model results are used for:

- determination of set-points for pH control (SI calcite = 0) for the actual day
- presentation of plant performance during the last 14 days
- reference-values for all 27 inline water quality measurements, with alarms for excessive deviations

- reference-values for laboratory analyses for the model parameters, with a tendency for less analyses (less parameters, and less frequent)
- evaluation of alternative process operation (set-points, process parameters, etc.).

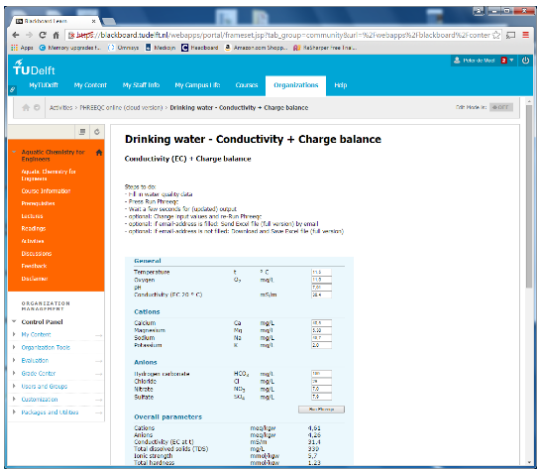
Figure 2.7 - PHREEQXCEL app for operators of a surface water treatment plant (from Lab 2.2)



More details on this applications are given in Lab 2.2.

2.5 PHREEQXCEL as a Web service ('in the Cloud')

PHREEQXCEL is also available as a web service. In this concept the Excel file of a PHREEQXCEL application is uploaded to the Stimela webserver, where the application is executed after which the completed file is returned to the user.
This concept avoids the installation of the IPhreeqcCOM object on the computer of the user.



3. Drinking water in PHREEQC

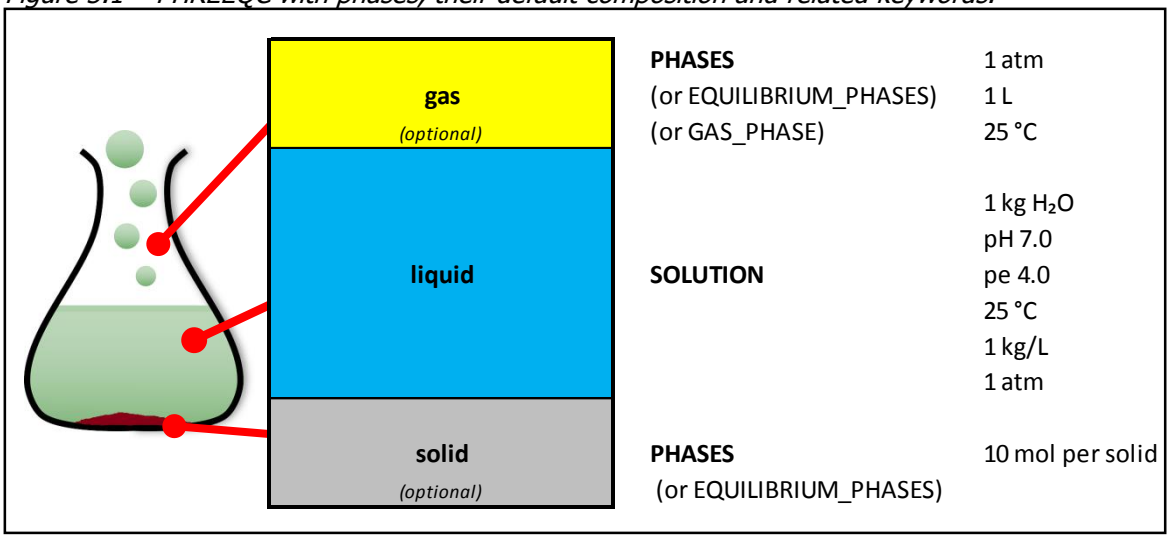
PHREEQC is developed for modelling of aquatic chemistry in ground water, interacting with different solids and gas phases. Its sophisticated modelling and its extended interaction functions creates an 'inaccessible jungle' for water treatment engineers who likes to start using PHREEQC in the field of water and wastewater. The initial question for this 'starter' will be "How can my water sample be defined as a PHREEQC solution?"

In this chapter the basic form of a solution is demonstrated using drinking water as water sample. In paragraph 3.1 the basis concept of PHREEQC is presented. Paragraph 3.2 describes the default solution in PHREEQC, introduced as 'Pure water'. Paragraph 3.3 presents how to specify a simple drinking water sample in PHREEQC code using the keyword SOLUTION. Paragraph 3.4 gives the results from PHREEQC for this example water showing the specific data for solutions.

3.1 Basic concept of PHREEQC

Water is the solvent for a solution in Aquatic chemistry, and therefore also in PHREEQC. PHREEQC starts with a known mass of water (in kilograms, indicated as kgw). This solution (liquid) may interact with gas phases and solid phases as shown in Figure 3.1. PHREEQC covers all equilibrium reactions in the solution, as well as all equilibrium reactions to and from the gas and solid phases. A full mass balance over these phases is maintained by PHREEQC. PHREEQC keywords and default conditions for each phase are also shown in Figure 3.1.

Figure 3.1 - PHREEQC with phases, their default composition and related keywords.



For all elements the total amount of substance (moles) should be known, in all phases (gas, liquid/solution and solid). PHREEQC keeps track on the mass balances for each element over all phases. Also the mass balance of water is maintained, either by formation or by consumption in chemical reactions.

Concentrations are defined on molality basis, calculated from the amount of a specific solute (moles of solute, or element) divided by the mass of the solvent (kg water).
For input and presentation of results PHREEQC uses degree Centigrade (°C) as unit for temperature. Internally the Kelvin temperature (K) is used (K = °C + 273.15).
PHREEQC uses the obsolete standard atmosphere (1 atm = 101.325 kPa) as standard pressure. In this course this is assumed to be equal to the modern standard state pressure of 1 bar (100 kPa).

PHREEQC uses elements as main component indicators. These elements might have more than one oxidation state (called valence state in PHREEQC documentation) forming different species (ions and dissolved complexes) and different phases (solids or gases).

3.2 Pure water as default solution

Default values for solutions
As shown in Figure 3.1 the default solution in PHREEQC is 1 kg of 'Pure water' (H_2O) with a density of 1 kg/L, a temperature of 25 °C, a pressure of 1 atm, a hydrogen activity of 10^{-7} (pH = 7) and an electron activity of 10^{-4} (pE = 4).
Moreover PHREEQC uses solution default values for the parameters units (mmol/kgw) and redox (pE).

The parameters density, units and redox are only used once, in the 'Initial calculation' of the solution composition.
Density is required for the calculation of mass concentrations (per kg solution, per kg water) from initial concentrations given by volume (per L, m^3 etc). Internally PHREEQC quantifies elements, species and phases by its total amount of substance (as mol) for 'bookkeeping' of mass balances per element. PHREEQC calculates concentrations in solutions from the amount of substance divided by the total mass of water (concentrations as mol/kgw, as in molality). PHREEQC gives its output per element, species and phases in molality (mol/kgw, relevant for equilibrium reactions) and in total amount of substance (moles, relevant for mass balances), regardless the parameter units.
In trailing simulations the values for density and redox (i.e. pE) are taken from the result of the preceding simulation/calculation.

Calculations steps
PHREEQC requires two calculation steps to determine the composition of a solution:
1. Initial solution calculation, to determine the amounts of substance per element
2. Final solution calculation including electron balancing, to determine single values for pE and pH being the master variables for the composition of the solution bases on the amounts of substance per element.

The keywords EQUILIBRIUM_PHASES or REACTION without any further data can be used as a dummy simulation to start the 'final calculation' for the solution.

Student activity	**Lab 3.1 – PHREEQXCEL for Pure water**
Study goals	- novice use of PHREEQC and PHREEQXCEL - learning PHREEQC's default Solution (pure water) - mass concept in PHREEQC with total amount of substances (mol), mass of water (kgw), and concentrations (mol/kgw) as in molality - additional calculation results such as electrical balance of ions, Electrical Conductivity (EC), density of solution, water vapour pressure

pH and pE as master variables for speciation
The parameters pH and pE are the master variables for speciation.
These parameters are defined as:
- $pH = - lg\{H^+\}$ with $\{H+\}$ = activity of $H^+ = \gamma_{H+} * [H^+]$
- $pE = - lg\{e^-\}$ with $\{e-\}$ = imaginary activity of free electrons in half-reaction.

These parameters and their representation in PHREEQC are:
- $\{H^+\}$ Activity of H+ (mol/kgw)
- $[H^+]$ Molality of H+ (mol/kgw)
- γ_{H+} Gamma as activity coefficient for H^+ (-)
- e^- E (as element) and e- (as species)
- lg Log (= $\log_{10}$)

The parameter pE is related to the reduction potential E_H as:

- $E_H = \ln(10)\ R\ T\ pE\ /\ F$ with E_H = reduction potential (V = J/C), R = gas constant (8.314 J/mol.K), T = temperature (K), F = charge of 1 mol of electrons (96,485 C/mol),

The default solution (25 °C = 298.15 K and pE = 4) has a reduction potential E_H of 237 mV.

Reactions in pure water

Chemical reactions in pure water are:

- Dissociation of water: H_2O <--> $H^+ + OH^-$
- Oxidation of water: $2\ H_2O$ <--> $O_2(aq) + 4\ H^+ + 4\ e^-$
- Reduction of water: $2\ H_2O + 2\ e^-$ <--> $H_2(aq) + 2\ OH^-$
  or $2\ H^+ + 2\ e^-$ <--> $H_2(aq)$.

From these chemical reactions PHREEQC calculates concentrations (molalities) for this water solution as:

- $[H^+] = 1.001 * 10^{-7}$ mol/kgw (extreme low concentration)
- $[OH^-] = 1.013 * 10^{-7}$ mol/kgw (extreme low concentration)

The calculated concentrations for H^+ and OH- should be equal for a proper Electrical charge balance. PHREEQC can be used to determine that charge balance is achieved at pH of 6.997 (see Lab 3.1). PHREEQC calculates for this pH value:

- $[H^+] = 1.006 * 10^{-7}$ mol/kgw (extreme low concentration)
- $[OH^-] = 1.006 * 10^{-7}$ mol/kgw (extreme low concentration)
- $[H_2(aq)] = 7.166 * 10^{-26}$ mol/kgw (negligible concentration)
- $[O_2(aq)] = 0$ mol/kgw (absent).
- $[H_2O] = 55.51$ mol/kgw (solution is nearly 'all water')

The calculated molality of H_2O reflects the molar mass (or gram formula weight gfw in PHREEQC): 1 mol H_2O = 1.008*2 + 16.0 = 18.016 g = 0.018016 kg, or 1/0.018016 = 55.50622 mol H_2O/kg water. This value is also reflected in the calculated concentrations of the elements O and H.

Equilibrium for gases

H_2O, H_2 and O_2 are also defined as gases $H_2O(g)$, $H_2(g)$ and $O_2(g)$ in stimela.dat (in PHASES) with their equilibrium reactions:

- Water vapour: H_2O <--> $H_2O(g)$
- Henry's law for H_2: $H_2(aq)$ <--> $H_2(g)$
- Henry's law for O_2: $O_2(aq)$ <--> $O_2(g)$.

PHREEQC calculates the SI values in the solution for these three gases. For dissolved ideal gases the saturation index (SI) is defined as: $SI = \lg(p_a)$, with p_a as the partial pressure of this gas in the gas phase. From the PHREEQC values for SI the partial pressure of these gases can be calculated:

- $H_2O(g)$: SI = -1.50 $p_a = 10^{-1.50} = 0.031$ atm
- $H_2(g)$: SI = -22.04 $p_a = 10^{-22.04} = 0.000$ atm (negligible)
- $O_2(g)$: SI = -39.20 $p_a = 10^{-39.20} = 0.000$ atm (negligible).

The solution is in equilibrium with a gas phase with a partial pressure for H_2O of 0.031 atm. This pressure is the vapour pressure of water at 25 °C.

This concept shows that the concentration of a gas in a solution (aq) can also be expressed as a gas pressure being the equilibrium partial pressure of that gas in the gas phase (g).

Parameters for other temperatures

Density, pH, vapour pressure and Electrical Conductivity (EC) depend on the temperature of the solution. Table 3.1 shows the calculated values for these parameters in Pure water (see Lab 3.1).

Table 3.1 - Composition of Pure water at different temperatures, as calculated with PHREEQC

Parameter		Temperature		
		0 ˚C	**25 ˚C**	**100 ˚C**
pH	-	7.469	6.997	6.119
Density	kg/L	0.99984	0.99704	0.95835
Vapour pressure	atm	0.006	0.031	0.989
Electrical Conductivity (EC)*	µS/m	0.93	5.51	131.32

* Specific Conductance (SC) in PHREEQC output and documentation

Freezing and boiling are not included in PHREEQC. It is assumed that water is a solution at all temperatures.

3.3 Drinking water as solution (input)

The chemical composition of an example drinking water is given in Table 3.2.
With respect to water chemistry drinking water is much 'simpler' than (anaerobic) groundwater with its more complicated redox reactions, or natural seawater with its large content of dissolved solids.

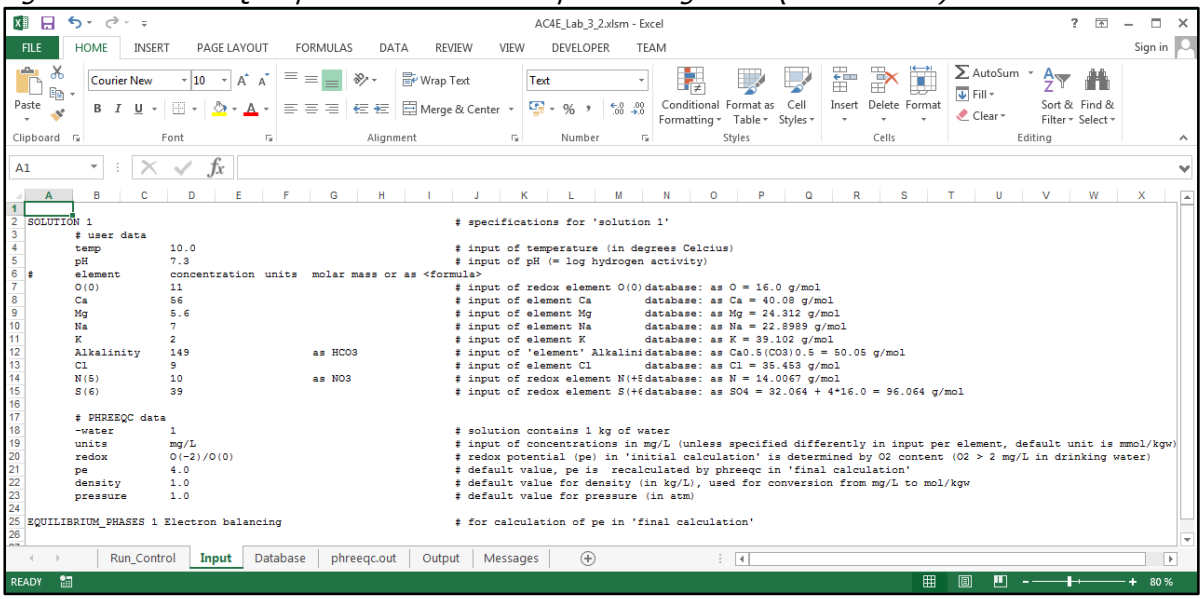
Table 3.2 - Composition of example drinking water

Parameter / Element		Unit	Value
Temperature	t	˚C	10
Hydrogen ion activity	pH	-	7.3
Oxygen	O_2	mg/L as O_2	11
Calcium	Ca^{2+}	mg/L as Ca	56
Magnesium	Mg^{2+}	mg/L as Mg	5.6
Sodium	Na^{+}	mg/L as Na	7
Potassium	K^{+}	mg/L as K	2
Bicarbonate *	HCO_3^{-}	mg/L as HCO_3	149
Chloride	Cl^{-}	mg/L as Cl	9
Nitrate	NO_3^{-}	mg/L as NO_3	10
Sulphate	SO_4^{2-}	mg/L as SO_4	39

* Assume: [HCO_3^{-}] = Alkalinity

PHREEQC input code
The example drinking water of Table 3.2 should be converted into a PHREEQC input file as shown in Figure 3.2 (from Lab 3.2).

Figure 3.2 - PHREEQC input code for the example drinking water (from Lab 3.2)



PHREEQC uses the keyword SOLUTION and SOLUTION_SPREAD for defining a solution, including its temperature, pressure and chemical composition. PHREEQC uses concentrations of chemical elements, such as Ca, Mg, Na, N and S as prime input parameters. These elements might be subdivided into oxidation states of an element, such as N(+5), S(+6) and O(0). The elements, oxidation states and their specifications are defined in the PHREEQC database (stimela.dat).

PHREEQC uses amount of substance (mole) as prime quantity for elements, and mass of water (kg, or kgw) as prime quantity for the solvent. The amount of substance for an element in solution is calculated from its molal concentration (molality in mol/kgw) and the mass of water (default 1 kg). Next to molal concentration PHREEQC accepts concentrations per mass of solution (kgs) or per volume of solution (L). The latter uses the density of solution (default 1 kg/L) to convert into molality. Within the SOLUTION data block all concentrations should be in the same group (either /kgw, /kgs, or /L). Within a group, either grams or moles may be used, and prefixes milli (m) and micro (u) are acceptable. The abbreviations for parts per thousand, "ppt"; parts per million, "ppm"; and parts per billion, "ppb", are acceptable in the "per kilogram solution" group.
The conversion from mass concentration (g, mg) to molal concentrations (mol, mmol) is based on the molar mass (g/mol) of the element as specified in the PHREEQC database. It is recommended to include the chemical formula in the input for mass concentration, by example for 39 mg/L sulphate: 'S(6) 39 mg/L as SO4'. Special attention should be given to dissolved oxygen ('element O(0)') since PHREEQC uses moles O and not moles O_2, so 11 mg/L O_2 should be specified as 'O(0) 11 mg/L as O'.

Some elements in the drinking water analysis are defined in stimela.dat as a single oxidation state (Ca, Mg, Na, K and Cl), and others are defined in multiple oxidation states (C, N, S, H and O). The latter elements can be specified as total concentration for this element either or as concentration of (one or more of) its oxidation states.
The elements H and O have a special status in PHREEQC because of their multiple appearances (H_2O, H^+, OH^-, O_2, H_2) in the solution, and H_2O being the solvent in PHREEQC. Their data will always be within the output of PHREEQC.

The speciation of elements is calculated in PHREEQC based on pH and pE. The initial value for pE can be given either as input value or as the value for a specific redox couple. It is recommended to use 'redox O(-2)/O(0)' for drinking water solutions since drinking water always contains a minimum amount of dissolved oxygen O(0), which highly determines the pE-value in water. The O(-2) oxidation state is always included in PHREEQC being the oxidation state of oxygen in H_2O.

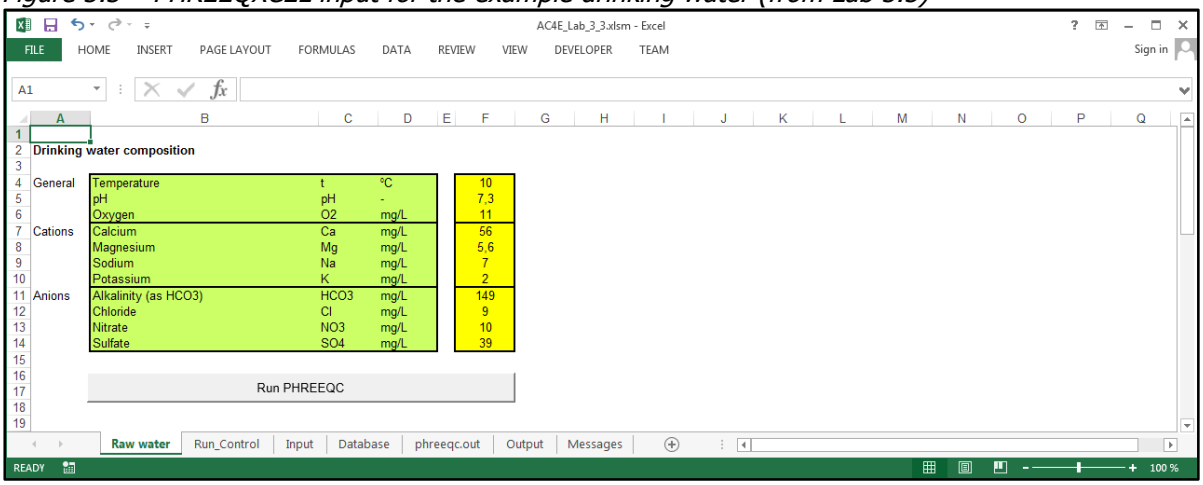
The keyword END marks the end of the input of a simulation, and starts the calculation/simulation. The 'end of the input file' is also regarded as END marker.

Student activity	**Lab 3.2 - PHREEQC input with SOLUTION**
Study goals	- novice use of PHREEQC and PHREEQXCEL - solution quantities in PHREEQC (/L, /kgs, /kgw) - element qualities in PHREEQC (g, mol with optional prefixes milli (m) and micro (u)) - specific input items (Alkalinity, N(5), S(6), O(0)) - PHREEQC comment marker (#) - simulation input delimiter (END, (end-of-file))

Input in Excel

Previous section shows that PHREEQC requires extended programming skills in order to transform chemical data of a water analysis into code for PHREEQC. For novice users or infrequent users this input code might be avoided by using Excel as 'input assistant' as shown in Figure 3.3 (from Lab 3.3).

Figure 3.3 - PHREEQXCEL input for the example drinking water (from Lab 3.3)



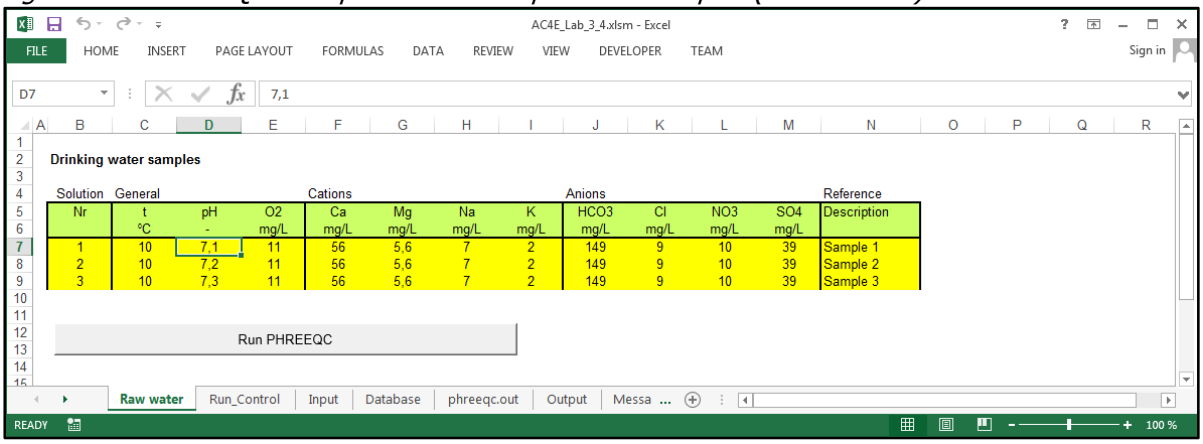
The PHREEQXCEL file has been extended with an additional sheet 'Raw water'. The green section in this sheet (see Figure 3.3) includes the input parameters and their respective units, the yellow section contain the input values. The input values are linked to the PHREEQC code on sheet 'Input', converting of the numeric values into text strings.
The 'Run PHREEQC' button enables the start of the PHREEQC calculations.

Student activity	**Lab 3.3 - PHREEQXCEL input with SOLUTION**
Study goals	- novice use of PHREEQC and PHREEQXCEL - Excel as 'input assistant' for PHREEQC

Input of multiple solutions

With the keyword SOLUTION_SPREAD concentrations of solutions can be inputted in a column-based setup, which is useful for input of multiple solutions. This input feature is shown in Figure 3.4 (from Lab 3.4).

Figure 3.3 - PHREEQXCEL input for the multiple water samples (from Lab 3.4)

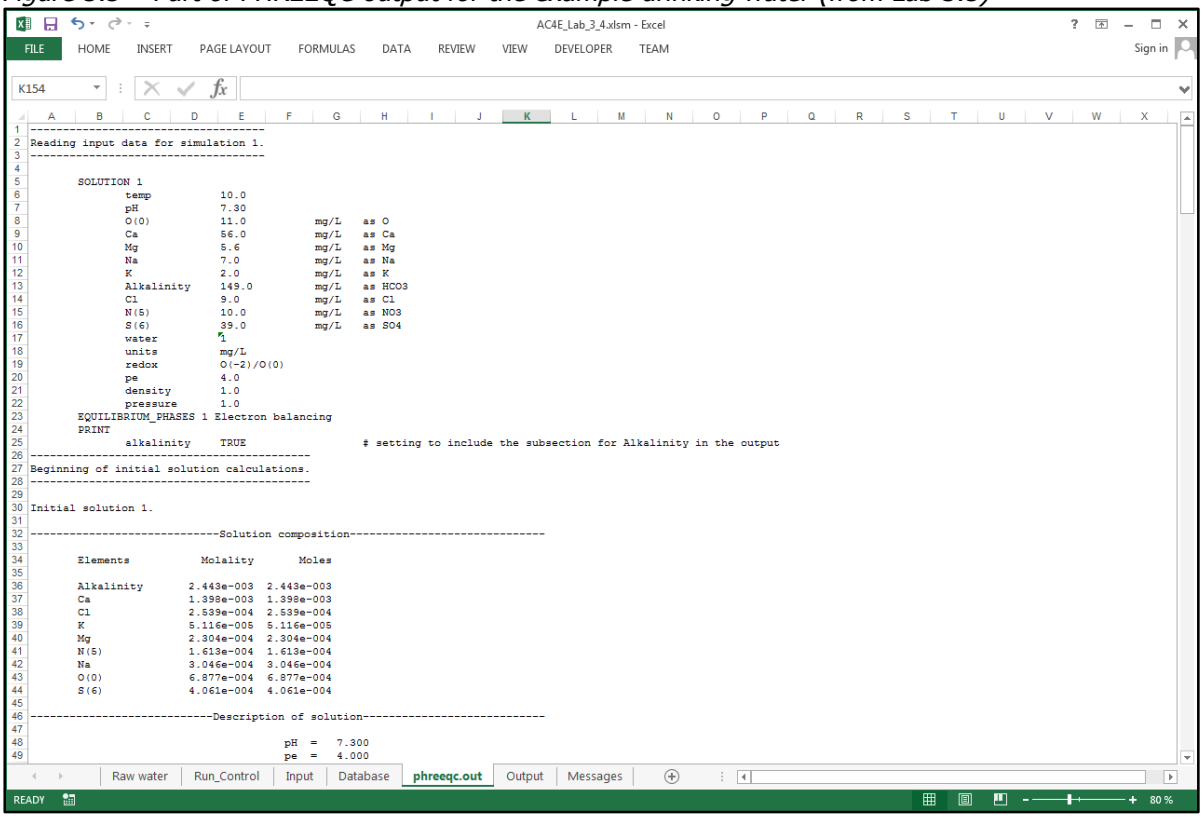


Student activity	**Lab 3.4 - PHREEQXCEL input with SOLUTION_SPREAD**
Study goals	- novice use of PHREEQC and PHREEQXCEL - Excel as 'input assistant' for PHREEQC

3.4 Drinking water as solution (output)

The results of the PHREEQC calculations are presented on sheet 'phreeqc.out' as shown in Figure 3.5 (from Lab 3.5).

Figure 3.5 - Part of PHREEQC output for the example drinking water (from Lab 3.5)



The output shows blocks from the consecutive stages in the Run:
- reading input data (per simulation)
- results of the initial solution calculations
- results of the final solution calculation (within 'batch-reaction calculations').

The final solution calculation gives in a 'real' PHREEQC solution, which is only characterized by its mass of water, total amount per Element (moles), pH, pE, temperature and pressure. All properties of the solution, such as speciation and saturation states, are diverted from these parameters and all further changes in the solution are reflected in changed values for these parameters.

The results of the solution calculations are divided into sections as presented in Table 3.3.

Table 3.3 - Output sections of solution calculations

Output section	**Description**	**Main purpose**
Solution composition	Molality and moles for all elements [3]	Input check for elements
Description of solution	Values for pH, pE, mass of water, temperature and pressure [4] Calculated overall parameters [5]	Input check for basic parameters Overall parameters
Redox couples [1]	pE and redox potential (Eh) for all redox couples	Electron balance in input
Distribution of species	Molality, activity, gamma and molar volume of all species, with total molality per oxidation state of an element [3]	Speciation
Distribution of alkalinity [2]	Contribution in alkalinity per dissolved species, as well as molality and Alkalinity-molality ratio	Acid-base buffering
Saturation indices	SI, IAP and K values for all phases	Saturation state related to gas and solid phases

[1] Only in initial calculation, when unbalanced redox couples are present
[2] Only in output if PRINT setting 'alkalinity = true'
[3] In initial calculation: values only for the oxidation state given in the input code
[4] Pressure is only printed if it differs from the default pressure of 1.0 atm.
[5] In initial calculation: Total CO2 is included, if Alkalinity is given in the input

Student activity	**Lab 3.5 - PHREEQC output for SOLUTION**
Study goals	- learning sections in PHREEQC output - learning output parameters in each section - learning the differences between initial and final solution calculation

Solution composition
The section 'Solution composition' gives molality (mol/kgw) and amount of substance (moles) for each element, or its oxidation state. The 'initial calculation' converts the input values of each element (in mg/L) into molality (in mol/kgw) and into amount (in moles) based on the molar mass of each element (from input code or database), mass of water (from input code) and density of the solution (from input code).

Description of solution
The section 'Description of solution' includes some general parameters as presented in Table 3.4.

Table 3.4 - Some results from Description of solution section for the example drinking water

Parameter	Unit	Value	Remark
Hydrogen activity	pH	7.300	From final calculation (reaction result)
Electron activity	pE	14.663	From final calculation (reaction result)
Electrical Conductivity (EC) (at actual water temperature)	mS/m	24.6	As Specific Conductance (SC) in µS/cm
Water temperature	°C	10.00	From input
Density of solution	kg/L	0.99994	In g/cm^3 (calculated)
Volume of solution	L	1.00036	
Mass of water in solution	kg	1.000	From final calculation (reaction result)
Ionic strength	mmol/kgw	5.425	In mol/kg
Total alkalinity	meq/kgw	2.443	In eq/kg (calculated)
Total inorganic carbon (TIC)	mmol/kgw	2.764	Total CO2 in mol/kg
Electrical balance in solution	meq	-0.058	Total balance in solution in eq Not as concentration in eq/kg
Percent error (Cat-An) / (Cat+An)	%	-0.83	Not as (Cat-An) / (Cat+An)/2

PHREEQC uses parameter names and units which are not always equally used in the field of water treatment, as par example defined in 'Standard Methods for the Examination of Water and Wastewater', or other local standards and regulations.
PHREEQXCEL can overcome this hurdles since user specific parameters names and unit conversions can easily be applied in Excel.

Redox couples
The section 'Redox couples' in only presented in the 'initial solution calculation', and gives the calculated electron activity (as pE=lg{e^-}) and redox potential (in volts) for all redox couples.
The example water only includes the O(-2)/O(0) redox couple as O(-2) is the oxidation state of oxygen in H_2O, and O(0) in dissolved O_2.
In the 'final solution calculations' all electrons are balanced over all redox elements, since free electrons cannot exist in a solution. Electron balancing forces chemical reactions to a single redox potential for the solution. These reactions might significantly change the composition of the solution which is reflected in a significant change of pH. A pH change of 0.01 or higher should be regarded as an unstable solution.
For the example water the final solution calculation did not change pH and resulted in a single pE-value of 14.663 which equals a redox potential of 824 mV (E_H = pE * ln(10) * R * T / F).

Distribution of species
The largest section in the output is the Distribution of species, which gives all the ion forms ('species') of the elements in the solution, also known as 'speciation'. Table 3.5 gives the number of species for each element, and its major species.

Table 3.5 - Speciation for the elements in solution

Element * (Oxidation state)	Molality (mmol/kgw)	Number of species	Major species	
O (0)	0.688	1	O_2	50.0%
Ca	1.398	6	Ca^{2+}	95.3%
Mg	0.230	5	Mg^{2+}	95.1%
Na	0.305	5	Na^+	99.7%
K	0.051	2	K^+	99.9%
C (+4)	2.764	9	HCO_3^-	87.1%
Cl	0.254	1	Cl^-	100.0%
N (+5)	0.161	1	NO_3^-	100.0%
S (+6)	0.406	7	SO_4^{2-}	88.1%

* Excluded negligible redox elements C(-4), H(0), N(-3), N(0), N(+3), S(-2) and water elements

Table 3.5 shows that most elements have more than one species, with one dominant species (>85%). By example for Calcium the dominant species is Ca^{2+}, but also $CaHCO_3^-$, $CaSO_4^0$ (aq), $CaCO_3^0$ (aq) are found.
In water analyses most often the concentration of an element is reported by its major species. Multiple species per element are ignored but the method of analysis actually measures the concentration of an element. For example the reported analysis for sulphate includes the dissolved species SO_4^{2-}, $CaSO_4$ (aq), $MgSO_4$ (aq) etc. Discarding this phenomenon will result in overestimating the saturation state of the solid phase $CaSO_4$ (s), since the real or actual concentrations of Ca^{2+} and SO_4^{2-} are lower than the reported values.

The Distribution of species section also shows Log Molality, Activity, Log Activity and Log Gamma which are related as: {Activity} = γ * [Molality] or Log Activity = Log Gamma + Log Molality . Activities are used in all equilibrium calculations, while Molalities are used in all mass balance calculations.
Gamma (γ) is the scientific symbol for 'Activity coefficient' or 'Fugacity coefficient' for gases. Several model have been developed for determining this Activity coefficient. By default PHREEQC uses the 'Extended Debye-Hückel model' but other models might be used, depending on the settings and values of the applied database.
The activity coefficient in the example water is around 0.93 for monovalent ions (such as Na^+, HCO_3^-, and Cl^-), around 0.74 for divalent ions (such as Ca^{2+}, Mg^{2+}, and SO_4^{2-}) and around 1.002 for gases and uncharged complexes.

Molar volumes in the Distribution of species section are used for calculating density and volume of the solution and for pressure related parameters.

Distribution of Alkalinity
The section Distribution of Alkalinity is by default not included in the PHREEQC output file.
Alkalinity is defined as the acid consumption (in meq/kgw) for titration to the 'end-point pH', which is around 4.5. Alkalinity can be calculated from:

$$\text{Alkalinity} = [HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-] - [H^+] + [CaHCO_3^+] + [MgHCO_3^+] + 2\,[CaCO_3^0] + \ldots$$

In laboratory practices the result of an Alkalinity measurement is often reported as HCO_3^- concentration.
The Alkalinity in the example water is 2.44 meq/kgw, while the sum of all HCO_3 species amounts to 2.43 mmol/kgw). This indicates the correctness of the applied assumption $[HCO_3^-]$ = Alkalinity.

Saturation indices
The section Saturation indices gives the relation of the solution to solids and gases, defined under PHASES in the database. Saturation indices are calculated from:
- for solids: $SI = lg(IAP/K_s)$ with IAP as Ion Activity Product and K_s as Solubility Product
- for gases: SI = lg(fugacity) with fugacity equals partial pressure, for ideal gases in equilibrium with the solution.

The section gives the name and the chemical formula (last column) for solids and gases defined in the database under PHASES. This section presents calculated values for SI, lg(IAP) and $lg(K_s)$ having the relation:

$$SI = LOG\ IAP - LOG\ K$$

A supersaturated solution contains ions for which the Activity Product IAP is larger than the Solubility Product K_s of a solid phase ($IAP > K_s$ or $SI > 0.0$). An undersaturated solution will dissolve a solid in case this solid is in contact with the solution.
The SI value indicates the driving force to dissolution or precipitation of solids.
The example solution is undersaturated to all solids, since all values for SI are negative.

4. Controlling output

The output of PHREEQC is a huge dump of calculated values, as shown in previous chapter, which lacks easy access for user specific information.
PHREEQC has 2 basis routes for creating user controlled output:
- lined output included in the standard output file (such as phreeqc.out)
- tabulated output in a separate user defined output file (such as selected.out).

PHREEQXCEL presents the lined output in sheet 'phreeqc.out' and the tabulated output in sheet 'Output'. Tabulated output can be used for further data processing, like presentation in tables with user defined units and names, or using the extended possibilities of graphical presentation in Excel. Since December 2013 (version 3.1) multiple tabulated output streams can be defined.

PHREEQC uses four keywords for two output flows:
- lined output is controlled with keywords PRINT and USER_PRINT
- tabulated output is controlled with keywords SELECTED_OUTPUT and USER_PUNCH.

In this chapter the output options in PHREEQXCEL will be discussed.
In paragraph 4.1 the possibilities of lined output will be presented. The options for tabulated output will be explained in paragraph 4.2 and 4.3. Both output options might use user-defined functions (CALCULATE_VALUES) which is discusses in paragraph 4.4. Post-processing of data within Excel is touched lightly in paragraph 4.5. Paragraph 4.6 shows the creation of user defined graphs in Excel without the USER_GRAPH option in PHREEQC.

4.1 Lined output

Lined output of PHREEQC is controlled with keywords PRINT and USER_PRINT.
PRINT and USER_PRINT controls the output starting with the simulation in which they are declared. Lined output is not suitable for further data processing.

In PHREEQXCEL lined output is used as a full report of all calculation results. This full report can be used to find relevant data or model mistakes which might be missed by looking only to user defined tabulated output.

Student activity	**Lab 4.1 – Lined output from PHREEQC**
Study goals	- learning to control output sections (PRINT) - learning to create user defined lined output (USER_PRINT)

PRINT
Settings following the PRINT keyword controls whether or not complete blocks such as 'Distribution of species' are printed in the output. Lab 4.1 gives a brief overview of the options available under the keyword PRINT.

USER_PRINT
The USER_PRINT keyword marks a -start/-end block in which BASIC statements can be used for printing to the output file. This allows for printing of additional text, user-defined quantities as well as user defined functions (via CALCULATE_VALUES). Lab 4.1 gives a brief overview of the concept of creating output using the Basis Interpreter in PHREEQC with its specific statements and functions for PHREEQC.

4.2 Tabulated output

PHREEQC also allows for tabulated output in which TAB separated items are displayed, with a new line for consecutive simulations and/or simulation steps. The content of this tabulated output can be set in the PHREEQC input file under the keywords SELECTED_OUTPUT and USER_PUNCH.

Student activity	**Lab 4.2 – Tabulated output from PHREEQC**
Study goals	- learning to control tabulated output (SELECTED_OUTPUT) - learning to create tabulated output (USER_PUNCH)

SELECTED_OUTPUT
Settings following the SELECTED_OUTPUT keyword controls whether or not specific items should be printed, such as simulation number, solution number, pH, temperature and charge balance. Moreover specific items can be indicated as output such as the total concentration of specified elements, the concentration of specified species and the saturation indexes of specified phases. Lab 4.2 gives a brief overview of the options available under the keyword SELECTED_OUTPUT.

Items from the SELECTED_OUTPUT section are printed in a fixed order, regardless their order in the input block. List items such as Totals, Molalities, and Saturation indexes are printed in their order within these lists.

USER_PUNCH
The USER_PUNCH keyword marks a -start/-end block in which BASIC statements can be used for printing to the tabulated output. This allows for printing user-defined quantities as well as user defined functions (via CALCULATE_VALUES). Lab 4.2 gives a brief overview of the options available under the keyword USER_PUNCH.

Items of USER_PUNCH are always printed after the SELECT_OUTPUT items.
Items from the USER_PUNCH sections are printed in their order in the Basic statements.

4.3 Multiple output

PHREEQC allows for diverting tabulated output into separate streams (since December 2013, version 3.1). These streams are defined by adding a number to the keywords SELECTED_OUTPUT and USER_PUNCH. For each additional output stream a new Excel sheet should be created named Output2, Output3 etc. Lab 4.3 shows how to work with multiple tabulated output streams.

Separated output might be beneficial for grouping parameters (columns) or for grouping simulations (rows). This concept allows for output tables which are specific for a group of simulations with different columns, enabling better post-processing of data in tables and/or graphs.

Student activity	**Lab 4.3 – Multiple tabulated output streams from PHREEQC**
Study goals	- learning to control multiple output streams (SELECTED_OUTPUT <n>) - learning to create multiple output streams (USER_PUNCH <n>)

4.4 User defined functions

PHREEQC allows for creation of user defined functions, collected under the keyword CALCULATE_VALUES. PHREEQC Basic statements are used to calculate additional parameters. Lab 4.4 shows how to create and print the results of user defined functions.

User defines functions might be beneficial for either unit conversion, such as Specific Conductance in mS/m, or creating parameters which are missing in PHREEQC, such as 'Redox potential' and concentrations for 'Total Anion' and 'Total Cation'.

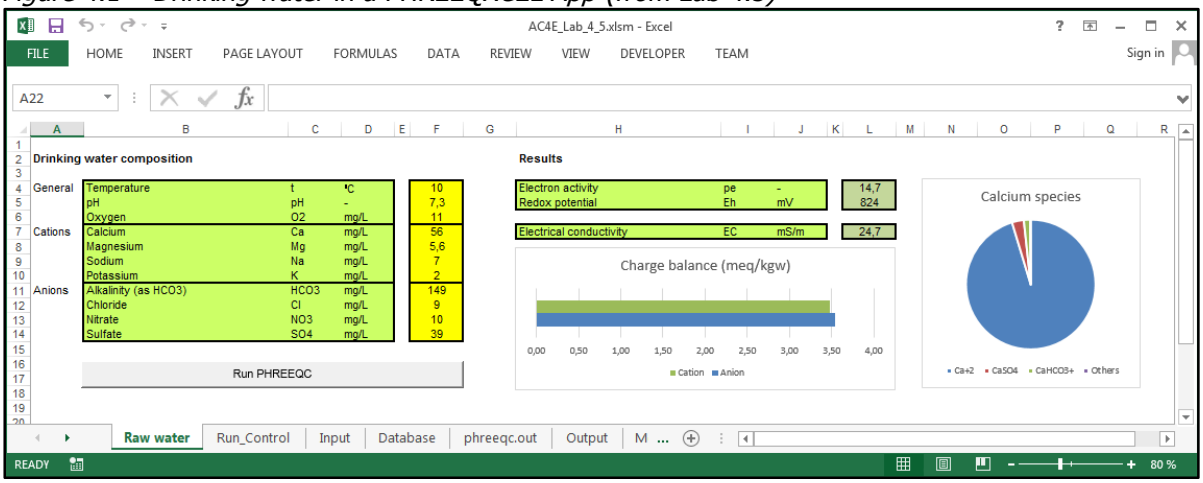
Student activity	**Lab 4.4 – User defined functions in PHREEQC**
Study goals	- learning to create user defined functions (CALCULATE_VALUES) - learning to print the results of user defined values

4.5 Output processing in Excel

Excel allows for post-processing of PHREEQC results including calculations, text and number formatting, as well as graphical presentation of data.
This setup enables users to modify these results to their own personal preferences in language, parameter names, units etc. without any modification in the PHREEQC code.
Lab 4.5 shows how to use Excel for output processing and to create PHREEQXCEL applications for non-PHREEQC users. Figure 4.1 gives this single input-output application from this Lab, which resembles a typical PHREEQXCEL App.

Student activity	**Lab 4.5 – Output processing in Excel**
Study goals	- learning to use Excel functions and graphs for output processing - learning to create PHREEQXCEL apps for non-PHREEQC users

Figure 4.1 - Drinking water in a PHREEQXCEL App (from Lab 4.5)



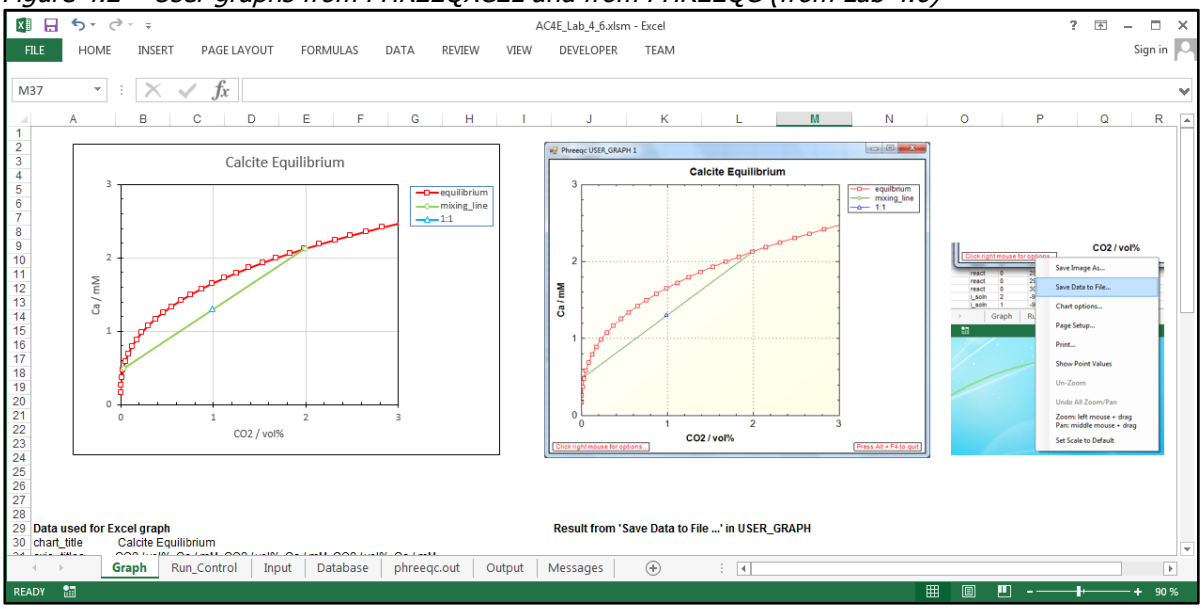
4.6 User graphs in Excel

Excel provides a great range of functions for graphical presentation of data.
Lab 4.6 shows how to use Excel for user defined graphs without using the keyword USER_GRAPH as build-in option in PHREEQC. Figure 4.2 shows the graph from this Lab as well as the graph that has

been created using the keyword USER_GRAPH. The background of this graph will be discussed in paragraph 5.6.
Creating graph in Excel is more flexible than creating graphs in PHREEQC itself. Moreover most Excel users are already familiar with creating graphs.

Student activity	**Lab 4.6 – User graphs in Excel**
Study goals	- learning to use Excel graphs as user defined graphs for PHREEQC - showing the differences between Excel and USER_GRAPH

Figure 4.2 - User graphs from PHREEQXCEL and from PHREEQC (from Lab 4.6)



5. Water treatment

The development of PHREEQC is focussed on water chemistry in aquifers, dealing with its specific chemical conditions but also dealing with the specific language and habits in geochemistry. Water treatment has some different chemical conditions, and also its specific language and habits.
In this course we will show how to apply some typical aspects of water treatment in PHREEQC.
In this chapter we will deal only with aerobic water such as drinking water and surface water, in which redox reactions are not significant. Redox reactions will be discussed in Chapter 6.

In paragraph 5.1 we will discuss how the typical concentration units as applied in the water treatment industry (mg/L, ppm) can be obtained from PHREEQC concentration results (mol/kgw). In addition the aspects of charge balance will be appointed as a validation method for water quality analysis or a method for estimating non-measured components.
Paragraph 5.2 deals with Electrical Conductivity (EC) which can be calculated in PHREEQC and might be compared to a measured value as an important validation method for water quality analysis.
Mixing water, a common phenomenon in water treatment and drinking water distribution, is discussed in paragraph 5.3.
Paragraph 5.4 gives some options for dosing chemicals in PHREEQC.
Equilibrium reactions as applied in softening and neutralization will be demonstrated in paragraph 5.5.
Paragraph 5.6 gives a short notice on process kinetics in PHREEQC.
Interaction between gases and water as applied in aeration and gas transfer are discussed in paragraph 5.7.

This volume of the course only presents a brief overview in how to use PHREEQC for water treatment. Water treatment applications will be discussed into more detail in Volume 2, 3 and 4. These volumes will be focused on aquatic chemistry in water treatment itself, without detailed instruction for program coding.

5.1 Concentration units

Concentration units
PHREEQC uses Molality (mol/kgw) as concentration unit, both for calculations and output.
PHREEQXCEL allows for post-processing of these 'uncommon' concentration unit into units which are more familiar to the individual water treatment engineer.
PHREEQC accepts for input also mass concentrations (such as mg/L) and mass ratio concentrations (such as mg/kgs or ppm). Both types of concentration units require proper molar masses for conversion to amount of substance (mol), while the first type also require a proper value for the density of the solution.

Molar mass
Molar masses of elements, or 'Standard Atomic Weights' are published by CIAAW under the auspices of the International Union of Pure and Applied Chemistry (IUPAC) with bi-annual updates. (http://www.ciaaw.org/abridged-atomic-weights.htm). Data of their most recent version (2013) is included in the PHREEQC database stimela.dat. This database also shows values as used in the database phreeqc.dat.

Density
PHREEQC uses a sophisticated model for the density of a solution, based on molar volumes (see http://www.hydrochemistry.eu/exmpls/molar_vol.html). PHREEQC might be used to calculate this density, if mass concentrations (mg/L) are used as input values.

For conversion of Molality output (mol/kgw) into Molarity (mol/L) a 'Molality to molarity' factor can be calculated by PHREEQC. Further conversion into mass concentrations (mg/L) can be done using molar masses of elements and species.

Charge balance
Concentrations might also be expressed as molar equivalent (eq/L) or molal equivalent (eq/kgw) indicating the electric charge of dissolved components. The total equivalents in a solution should be zero.
The charge balance is an important indicator for the completeness and correctness of chemical analyses for a solution. According to Standard Methods 1030E a difference up to 2% of the total equivalent value is accepted if the anion charge is between 3.0 and 10.0 meq/L.
Charge balancing might be used to determine the concentration of a non-measured component, or to correct a dubious analysis. The PHREEQC keyword 'CHARGE' can be used to determine these concentrations.

The obsolete unit mg/L $CaCO_3$ for hardness and Alkalinity is a mass equivalent concentration (1 meq/L equals 50.043 mg/l as CaCO3).
Unit conversions can easily be done in PHREEQXCEL, both for input as output values.

Student activity	**Lab 5.1 - Concentrations, density and charge balance**
Study goals	- learning to determine the density of a solution - learning to convert from and into molal concentrations - learning to calculate the charge balance of a solution for validation - learning to charge balance by additional or modified concentrations

5.2 Electrical Conductivity (EC) and Total Dissolved Solids (TDS)

Electrical Conductivity (EC)
PHREEQC includes a sophisticated model for the calculation of Electrical Conductivity (EC) whenever diffusion coefficients are included in the applied database (parameter -dw under SOLUTION_SPECIES). EC is called Specific Conductance (SC) in PHREEQC (see for further details http://www.hydrochemistry.eu/exmpls/sc.html).
The calculated EC-value is the conductivity at the actual temperature of the water.

Conductivity in water treatment is normalized to a standard temperature of 25 °C. Converting PHREEQC output to 25 °C can be done by either using the conversion table/formula as given by ISO 7888 in Excel, or by changing the 'REACTION_TEMPERATURE' in PHREEQC. The results of both methods will be different. The first method is recommended since its results are in compliance with the international accepted standard ISO 7888.

The calculated Electrical Conductivity can be an important indicator for the completeness and correctness of chemical analyses for a solution, if the Electrical Conductivity has been measured. According to Standard Methods 1030E the calculated over measured ratio should be between 0.9 and 1.1 for validated analyses.

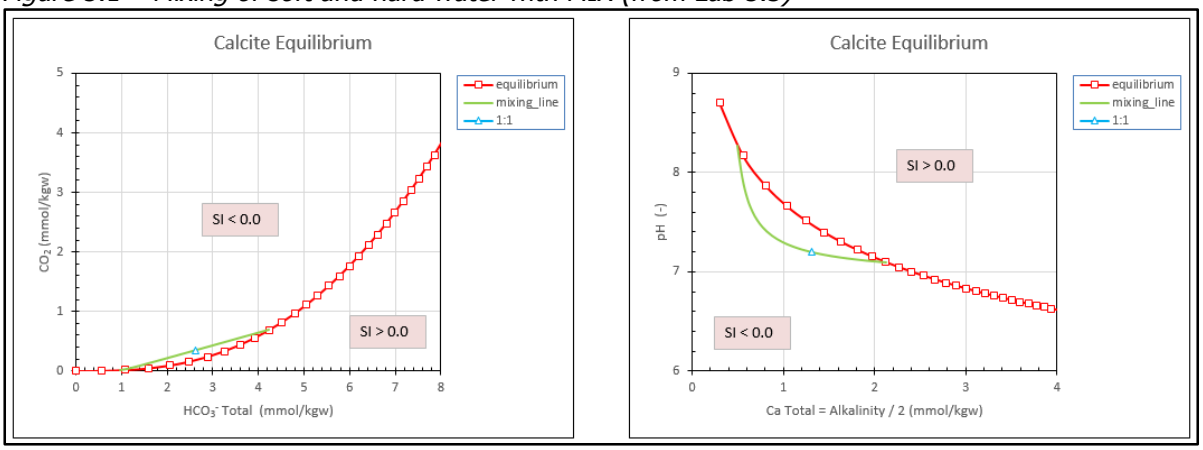
Total dissolved solids (TDS)
PHREEQC lacks a function for the calculation of Total Dissolved Solids (TDS in mg/L). A user function for the calculation of TDS from molalities of all dissolved solids (non-gaseous components) is considered here as 'too elaborated'. Also the calculated density, volume and mass of water from PHREEQC will not give an accurate result for TDS.
With input concentrations in mg/L the Total Dissolved Solids can be easily be calculated in Excel.

Student activity	**Lab 5.2 - Electrical Conductivity and Total Dissolved Solids**
Study goals	- learning to determine the Electrical Conductivity at 25 °C (EC-25) - learning to apply the calculated EC-25 for validation - learning to calculate the Total Dissolved Solids content

5.3 Mixing waters

Mixing waters is a common phenomenon in water treatment and drinking water distribution. PHREEQC includes the keyword MIX which allows for mixing two or more solutions. The quantity of each solution might be specified as fractional part of that solution.
A classic example in drinking water is mixing of soft and hard water, both in equilibrium to calcite (SI = 0.0) resulting in aggressive water (SI < 0.0). This might be showed in a 'Tillmans' diagram' or in a hardness-pH diagram, both presented in Figure 5.1 being alternative diagrams for Figure 4.2.

Figure 5.1 - Mixing of soft and hard water with MIX (from Lab 5.3)



Student activity	**Lab 5.3 – Mixing waters with MIX**
Study goals	- learning the basic use of MIX for mixing waters - learning to understand and present calculation results

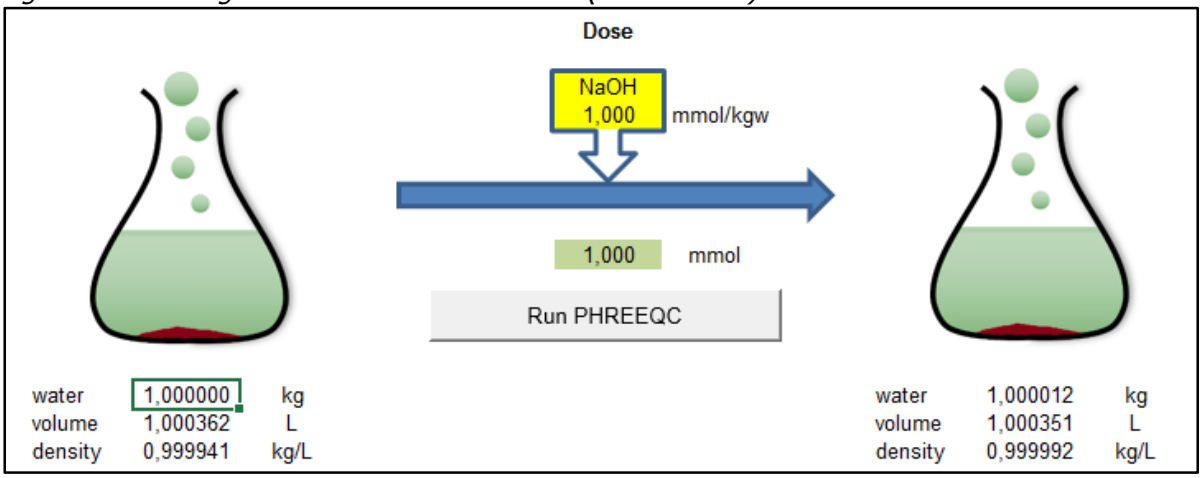
5.4 Dosing of chemicals

Dosing methods in PHREEQC
PHREEQC includes three basic methods for dosing of chemicals to a solution, each under a specific keyword:
- REACTION, for adding moles of any chemical to a solution
- MIX, for mixing a chemical solution with a water solution
- EQUILIBRIUM_PHASES, for adding a chemical until equilibrium is reached, or a given SI.

This paragraph will discuss the first two keywords. The third keyword will be discussed in chapter 5.5.

Dosing with REACTION
Under the keyword REACTION a certain amount of substance (moles) of a chemical is added to the solution. The added amount of substance will also influence the volume and density of the solution because of the molar volume and electric forces of its ions. Additionally the mass of water might be changed if H_2O is formed or consumed by the reactions. The changes in these parameters are calculated by PHREEQC in order to determine the changes in concentrations (molalities) and activities (see Figure 5.2).
Since the chemical formula of a chemical is used as input value, any chemical can be dosed with REACTION, i.e. NaOH, $FeCl_3$, but even fractional formulas such as $Al_{0.2}Fe_{0,8}(OH)_3$ etc.

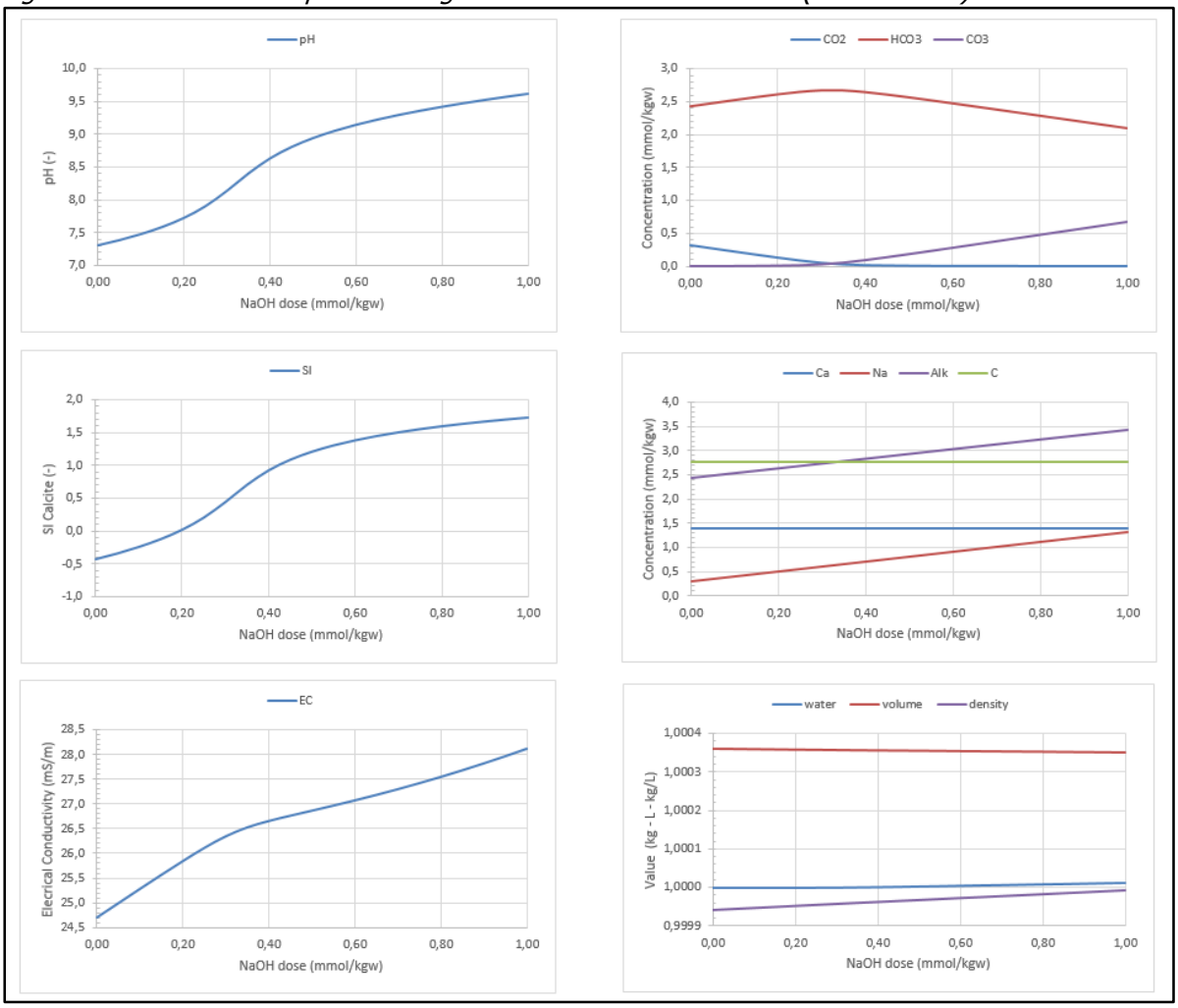
Figure 5.2 - Dosing of chemicals with REACTION (from Lab 5.4)



In water treatment chemical dosing is expressed as a concentration (in mmol/L or mg/L). This concentration have to be multiplied by the volume of the solution to obtain the added amount.
For practical reasons the added dose might be expressed as mmol/kgw, since we use 1 kg of water as the basic component of solutions. In this way the added dose (in mmol/kgw) equals the added amount of substance (in mmol).

With the keyword REACTION a mixture of chemicals can be added to the solution. This mixture is defined by the relative stoichiometry of each chemical. The added amount is defined by a list of reaction amounts, which might also be given as 'dosing steps'. The latter method allows for detailed calculations of all chemical changes caused by the reaction, as is shown in Figure 5.3.
Not only can chemicals be added, also components can be removed from the solution, by adding a negative amount.
Excel allows for further combining calculated results with actual measured data, in tabular and graphical form.

Figure 5.3 - Results of stepwise dosing of chemicals with REACTION (from Lab 5.4)



Student activity	**Lab 5.4 - Dosing of chemicals with REACTION**
Study goals	- learning the basic use of REACTION for chemical dosing - learning to understand and present calculation results

Dosing with MIX

Under the keyword MIX two or more solutions can be mixed. The quantity of each solution is defined by the fractions of the original solutions. The MIX concept has been developed for mixing two or more water streams or solutions, but can also be applied for dosing chemicals on the base of volumes or masses instead of concentrations as in REACTION.

A typical example is the measurement of Alkalinity by a titration method in which a strong HCl solution is added to the water sample until a certain pH (around 4.5) is reached (see Figure 5.4). The alkalinity is directly related to the volume or mass of dosed HCl. With stepwise mixing the change in water quality parameters can be visualized as is done Figure 5.4, which also includes so-called Gran-plots (http://en.wikipedia.org/wiki/Gran_plot) which might be based on H^+-activity (as 10^{6-pH}) or EC. The Gran-plots show a switch-point at 24.4 mL HCl 0.1N corresponding to an Alkalinity of 2.44 meq/L.

Figure 5.4 - Dosing of chemicals with MIX (from Lab 5.5)

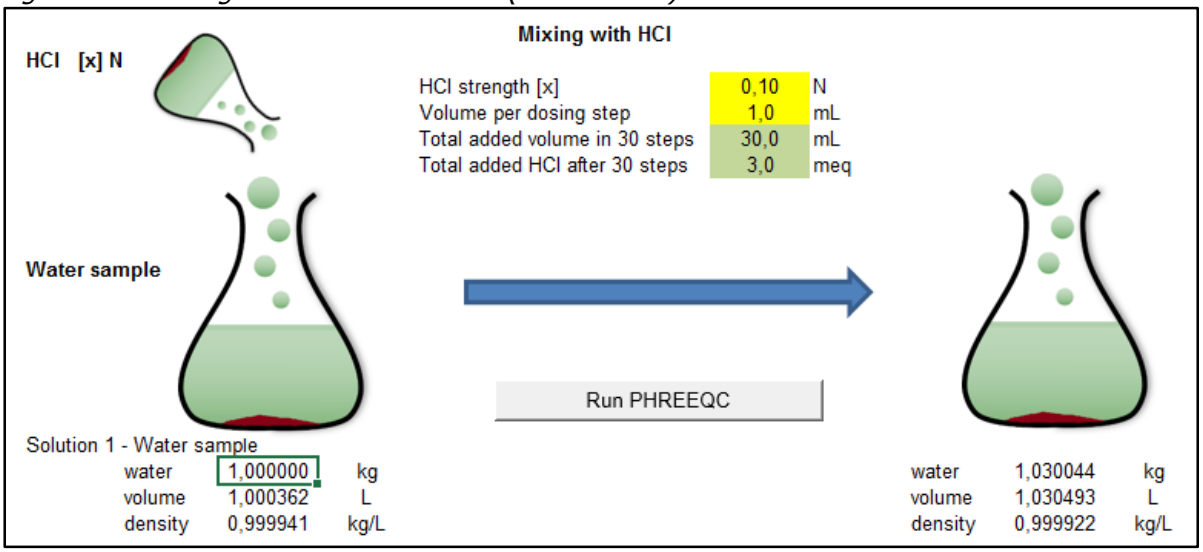
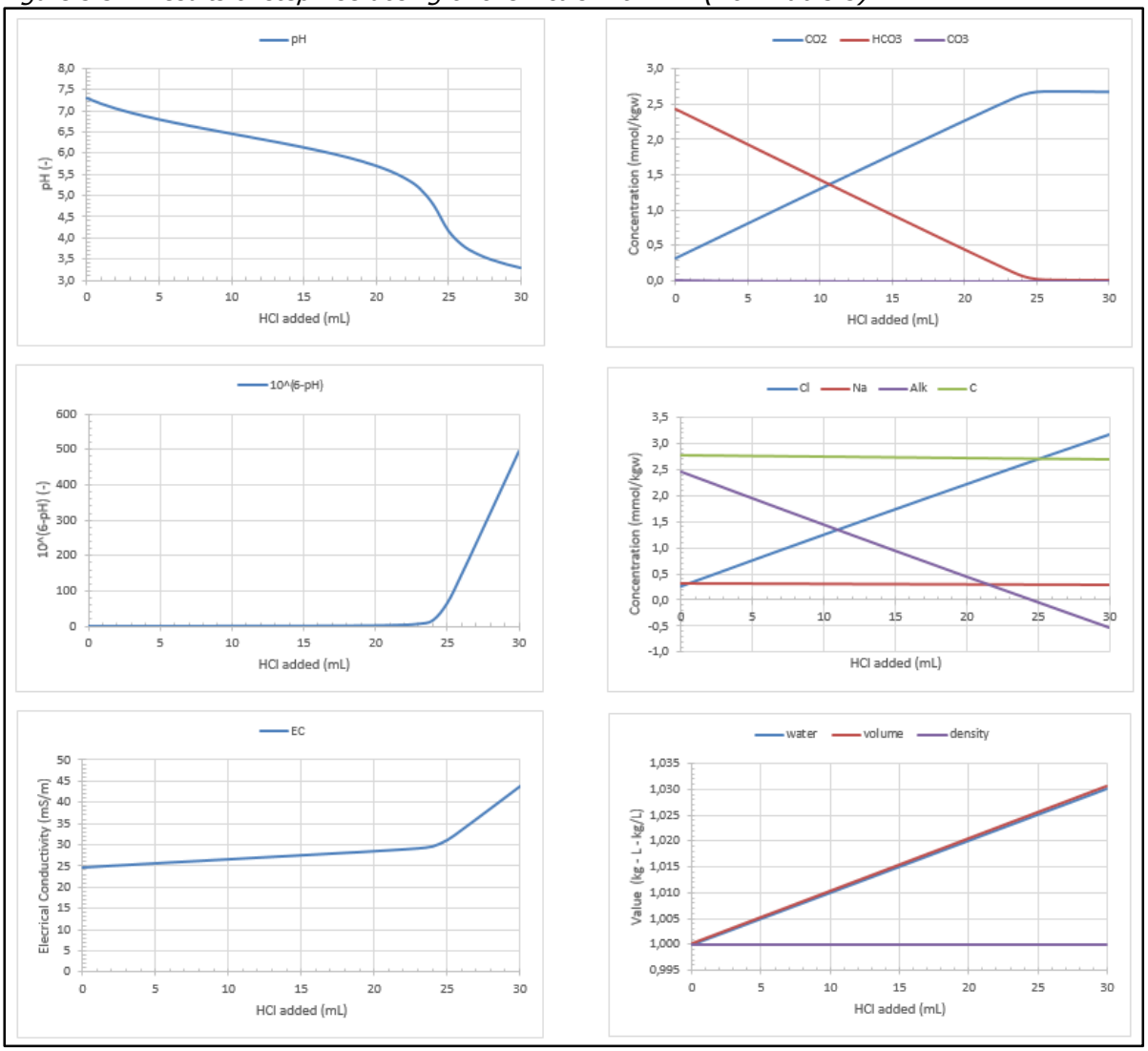


Figure 5.5 - Results of stepwise dosing of chemicals with MIX (from Lab 5.5)



Student activity	**Lab 5.5 - Dosing of chemicals with MIX**
Study goals	- learning the basic use of MIX for chemical dosing - learning to understand and present calculation results

5.5 Neutralization and softening

Reactions with EQUILIBRIUM_PHASES
Under the keyword EQUILIBRIUM_PHASES reactions will be initiated until equilibrium with the specified solid or gas is reached. This keyword also allows for specifying a certain Saturation Index (SI) instead of SI=0 at equilibrium.
Two basis reaction types might be applied:
- the specified solid or gas phase is the reactant
- an alternative solid, gas or chemical is the reactant.

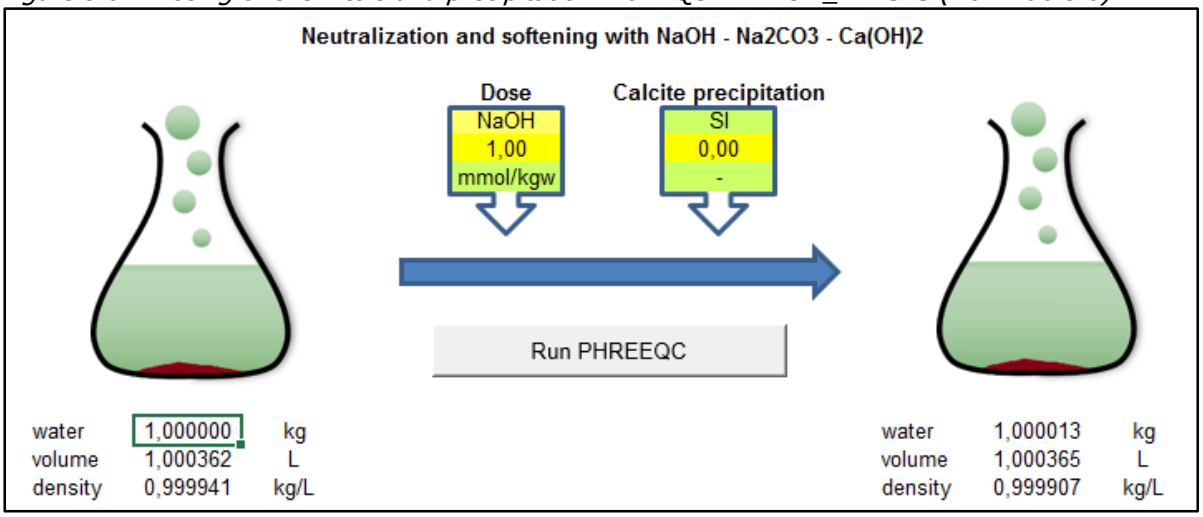
Both reaction types might be considered a special type of dosing chemicals (adding or removing) as applied in water treatment. Examples are dissolution of calcium carbonate grains ($CaCO_3$ calcite) for neutralization of acid water and precipitation of calcium carbonate ($CaCO_3$ calcite) in chemical softening.
The keyword EQUILIBRIUM_PHASES might also be applied for pH control to a specified pH.

This type of reactions includes both solid phases as well as gas phases. However, equilibrium with gases will be discussed in paragraph 5.7.

Solid as reactant
In paragraph 5.4 alkaline chemicals were dosed in order to increase the pH of the water. However, the dosed amounts were much larger than required for neutralization (SI calcite = 0.0). A positive SI value indicates a precipitation potential of calcium carbonate, with a larger potential at higher SI values. Theoretically such precipitation of calcite (softening) might continue until equilibrium is reached (SI calcite = 0.0), in practice a certain super-saturation will remain (SI calcite 0.7-1.2).
Under the keyword EQUILIBRIUM_PHASES four items per solid might be specified:
- the saturation value after reaction (as SI-value)
- the initial quantity of the solid phase (in moles)
- the 'freedom' of the reaction (precipitation, dissolution or both)

Figure 5.6 gives an example of using EQUILIBRIUM_PHASES in which only SI might be set by the user. The 'initial quantity' (0.01 moles) and 'freedom' (precipitation only) have been set in the PHREEQC code.

Figure 5.6 - Dosing of chemicals and precipitation with EQUILIBRIUM_PHASES *(from Lab 5.6)*



Student activity	**Lab 5.6 – Reaction with solids in EQUILIBRIUM_PHASES**
Study goals	- learning some basics of EQUILIBRIUM_PHASES for chemical reactions - learning to understand and present calculation results

The amount of calcium carbonate that might precipitate until equilibrium is called 'calcium carbonate precipitation potential' (CCPP), as defined in Standard Methods 2330C.
PHREEQC and PHREEQXCEL are successfully applied for the calculation of CCPP (see Annex 4).

Limestone filtration is a typical water treatment process in which limestone (calcite) is both the chemical as the 'controlling solid'. Neutralization or dissolution of calcite will only take place as long as the water is under-saturated in respect to calcite (SI calcite < 0.0).

Chemical as reactant
Under the keyword EQUILIBRIUM_PHASES also alternative solids or chemicals might be applied to reach the specified equilibrium, as in:
EQUILIBRIUM_PHASES 1 ; Calcite 0.0 NaOH 0.01
This code specifies a required SI value for calcite (SI = 0.0 or equilibrium) which should be achieved by dosing NaOH for which the available amount is set at 0.01 moles, or 10 mmoles. The latter corresponds to a concentration with a fixed mass of the solution (1 kg of water).

With this code the required dose of NaOH can be calculated in order to neutralize the water (SI = 0.0).

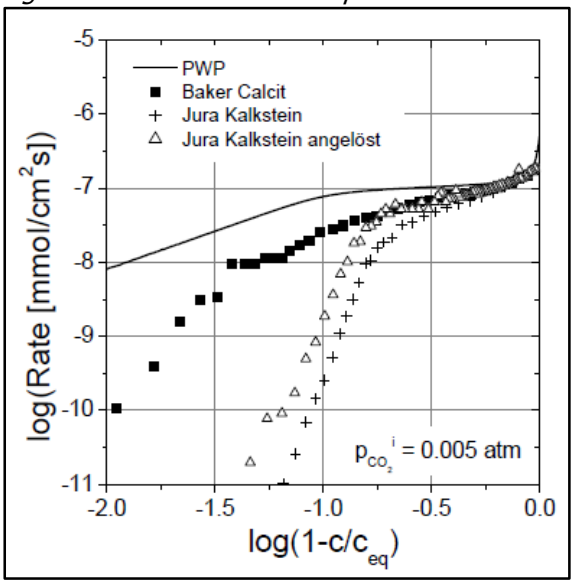
Chemical as reactant for pH control
Sometimes not a certain SI for calcite is required for neutralization but a specified pH.
For such case PHREEQC uses an imaginary solid pH-Fix, as in:
EQUILIBRIUM_PHASES 1 ; pH_Fix -8.0 NaOH 0.01
This code specifies a pH value of 8.0 which should be achieved by dosing NaOH for which the available amount is set at 0.01 moles, or 10 mmoles. This type of code is applied in Lab 5.7.
More details on the application of this imaginary solid can be found in the PHREEQC documentation.

5.6 Kinetics of processes

PHREEQC is focussed on Equilibrium calculations as is reflected by the letters EQ in its name.
The time required to obtain equilibrium is not primarily part of PHREEQC but can be provided by using conversion or reaction rates based on the (changing) composition of the solution.
Kinetic processes can be defined under the keyword RATES, in which the relation between reaction rate and quality parameters can be specified.
In the input code reference to such rate-formula is made under the keyword KINETCS.

Under the keyword RATES extended Basic programs might be developed, in order to calculate the amount of reactant that is converted in a specific time step.
As an example references is made to the PWP-model for calcite dissolution and precipitation which is included in the PHREEQC databases phreeqc.dat and stimela.dat.
However, this model does not give reliable results under near-equilibrium conditions (-1.0 < SI calcite < 1.0) in particular when applied for modelling dissolution of natural limestone (see Figure 5.7). Improved kinetic models for calcite dissolution and precipitation will be presented in Volume 2.

Figure 5.7 - PWP model compared to dissolution of synthetic (Baker) and natural (Jura) calcite



Source: Vosbeck 2004

The concept of RATES can also be applied for non-timed calculations in which iterative adding of chemicals is to be applied until certain conductions are obtained. An example of this is the calculation of NaOH required in chemical softening to obtain a certain total hardness.

Kinetics of processes in water treatment will be discussed in Volume 2, 3 and 4. These volumes will be focused on aquatic chemistry in water treatment, without detailed instruction for program coding.

5.7 Aeration and gas transfer

PHREEQC also includes equilibrium reactions with gases, for solubility and speciation of dissolved gases as well as mass balances for interaction between a solution phase and a gas phases. PHREEQC provides for four methods to specify the concentration of a gas in a solution:

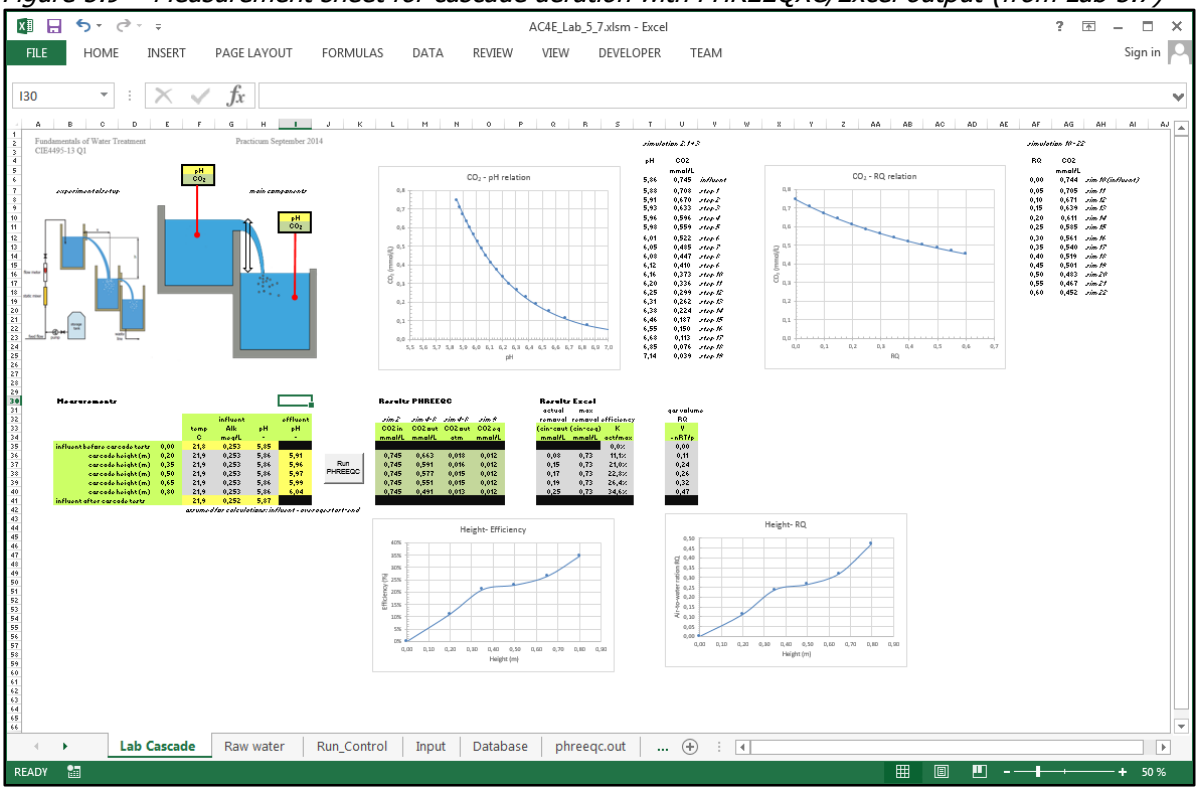
- input of the concentration of a gas under SOLUTION (such as mg/L, mmol/kgw etc.)
- input of the equilibrium pressure of a gas (as SI) under SOLUTION
- input by interaction under EQUILIBRIUM_PHASES
- input by interaction with a gas phase under GAS_PHASE.

Applying PHREEQC for aeration and gas transfer processes require specification of a GAS_PHASE in order to keep track on mass balances in phase transfer, from gas to solution and visa versa.

All these forms of specifying gas concentrations and gas-solution interaction in PHREEQC are applied in the practicum of TU Delft course 'Fundamentals of water treatment'. Figure 5.8 and 5.9 give an impression of this practicum and the application of PHREEQC within this practicum. Further details are presented in Lab 5.7.

Figure 5.8 - TU Delft Lab course on cascade aeration for CO_2 removal (with pH measurement)

Figure 5.9 - Measurement sheet for cascade aeration with PHREEQXC/Excel output (from Lab 5.7)



Student activity	**Lab 5.7 – Gas transfer with GAS_PHASE**
Study goals	- learning different options to specify a gas concentration in a solution - learning to use GAS_PHASE for mass balances in water-gas exchange

6. Groundwater and redox reactions

Previous chapter discussed application of PHREEQC for aerobic water such as drinking water and surface water, in which redox reactions are not significant. In this chapter redox reactions as found in groundwater treatment schemes will be discussed.
In paragraph 6.1 some basics of redox conditions in water are presented, using pE as the determining parameter, based on thermodynamic equilibria. However several redox reactions never reach their thermodynamic equilibrium in water treatment, because of kinetic limitations. Nearly all oxidation states of nitrogen are simultaneously encountered in groundwater treatment (NO_3^-, NO_2^-, N_2 and NH_4^+). This is in contradiction with results obtained from PHREEQC.
Paragraph 6.2 discusses the application of PHREEQC for groundwater treatment, showing the differences between the databases phreeqc.dat, amm.dat and stimela.dat in particular the application of redox-uncoupled elements to deal with non-equilibrium conditions.
The practical application of the stimela.dat database for groundwater treatment is presented in three paragraphs. Paragraph 6.3 shows the mixing of water from multiple wells, paragraph 6.4 presents the modelling of groundwater treatment by aeration and filtration, while paragraph 6.5 deals with the biological nitrate removal in anaerobic conditions using methanol.

6.1 Redox conditions in water

As demonstrated in Chapter 3 speciation in water is mainly determined by the hydrogen activity (pH) and the electron activity (pE) or redox potential. In theory the value of pH varies from 0 to 14 (and even wider) but in water treatment practices pH is between 6 and 8 in over 99% of the cases. The variation in water treatment practices for pE is much larger, as shown in Figure 6.1. In here three zones are distinguished:

- drinking water with disinfectant, with 14<pE<22, determined by the disinfectant
- drinking water and aerobic water, with 12<pE<15, determined by O_2 content
- anaerobic groundwater, with -8<pE<13, determined by reduction products

Aerobic water is defined here as water with an oxygen content of over 0.001 mmol/L O_2 (0.03 mg/L). Drinking water and nearly all kinds of surface water, like rivers, lakes, canals belong to this water type. Also some groundwaters fall into this category, often to be recognized by the absence of dissolved iron and dissolve manganese.

Figure 6.1 - pH-pe areas relevant for water treatment (in the background: dominant Fe species)

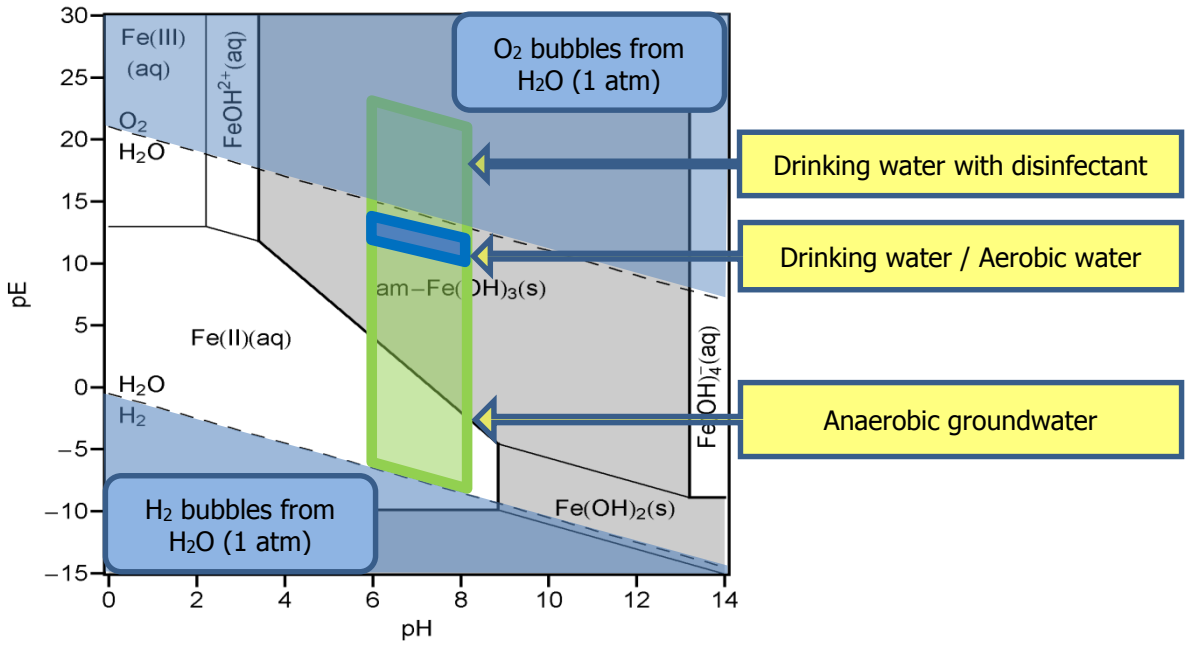
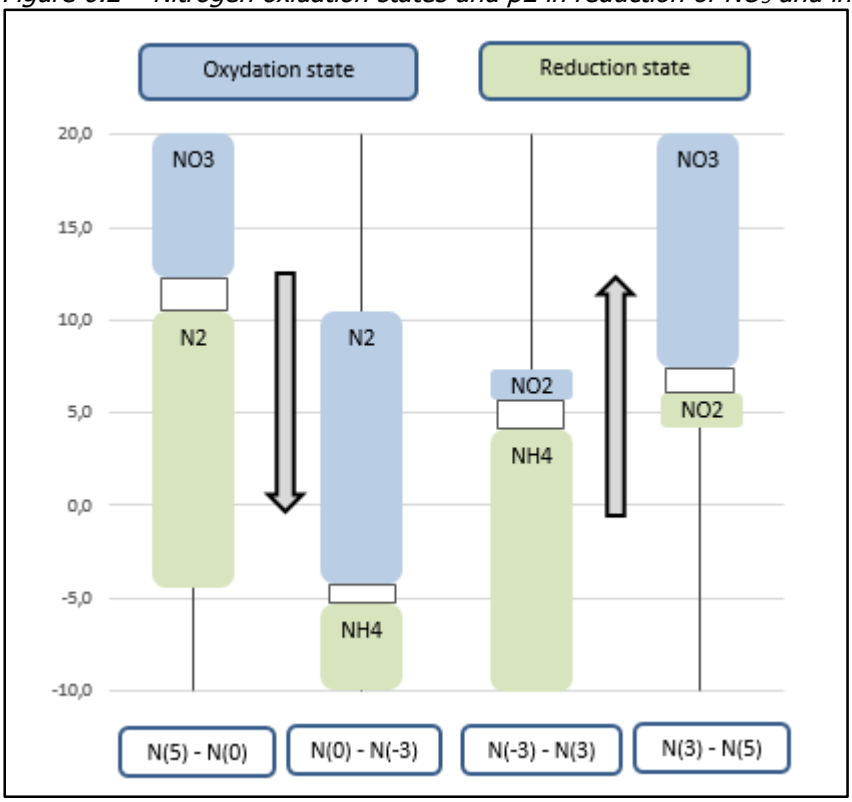


Figure 6.1 also shows that the value of pE is slightly influenced by pH, with lower pE at higher pH. Temperature has a similar effect on pE, with lower pE at higher temperature.

Oxidation states of nitrogen

In the natural environment nitrogen is found in four oxidation states: N(5), N(3), N(0) and N(-3). Major species for these states are respectively NO_3^-, NO_2^-, N_2 and NH_4^+.
In aerobic water the dominant oxidation state is N(5) with NO_3^- as main representative species. However such water will also contain N(0) in the form of dissolved nitrogen gas N_2.
Under anaerobic conditions NO_3^- is converted into N_2, which is the chemical reaction in biological nitrate removal processes, and also the reaction in the natural environment at places where organic material 'rottens'. With ongoing conversion of organic matter N_2 is converted into NH_4^+, being the typical component of anaerobic groundwater. This reduction process of nitrate is shown in the left part of Figure 6.2 with the related pe-values.
Theoretically, oxidation of NH_4^+ should follow the reversed reaction path. However due to kinetic constraints this is not the case. In practice (biological) oxidation of NH_4^+ will results in the formation of NO_2^- and NO_3^- as shown in the right part of Figure 6.2.

Figure 6.2 - Nitrogen oxidation states and pE in reduction of NO_3 and in oxidation of NH_4^+

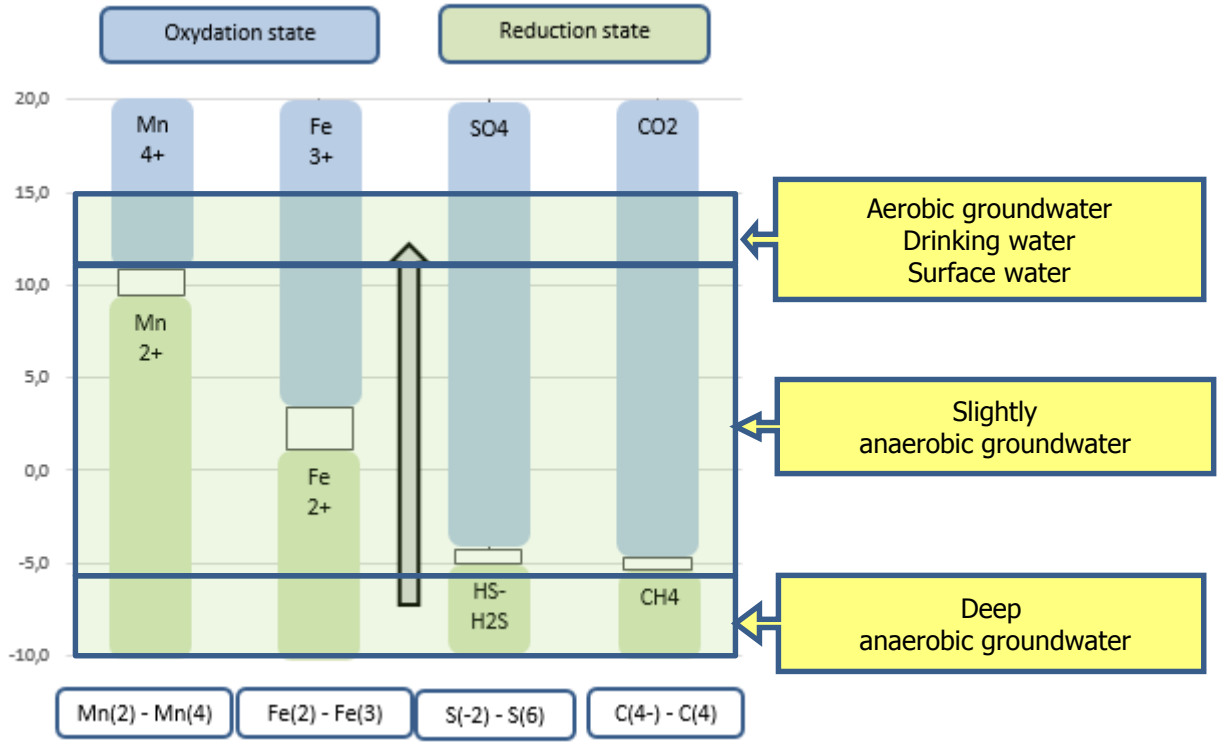


Temperature 10-25 °C, pH 7.2-8.2

Oxidation states of other groundwater components

The major components in treatment of anaerobic groundwater are, beside aforementioned forms of nitrogen, dissolved iron (Fe^{2+}) and manganese (Mn^{2+}) and the dissolved gases methane (CH_4) and H_2S. Figure 6.3 shows their dominant oxidation states. Based on the presence of these components the text book 'Drinking water – Principles and Practices' distinguishes on 'slightly anaerobic water' and 'deep anaerobic water'.

Figure 6.3 - Dominant oxidation states and pE for Mn, Fe, S and C



Temperature 10-25 °C, pH 7.2-8.2

6.2 Groundwater in PHREEQC

Redox reactions in PHREEQC
PHREEQC has been developed for groundwater flows in which redox reactions play a very important role. The original concept was based on single equilibrium constants for the conversion from one oxidation state into another, and on electron balancing over all elements and oxidation states as implicit part of all simulations, except for the 'initial solution'. As a consequence electron balancing might involve many unrealistic reactions. This drawback was overcome by modelling only one or two elements.
Aforementioned different reaction path in reduction and oxidation of nitrogen has resulted in the development of an additional database amm.dat in which NH_4^+ was introduced as an inert, or redox-uncoupled element Amm. This database is distributed with PHREEQC next to its default database phreeq.dat.
PHREEQC version 3 has introduced redox-uncoupled elements for all gasses, to get more control over redox reactions, especially nitrogen gas (N_2) which is otherwise fully converted into Nitrate (NO_3^-) when oxygen is present. These redox-uncoupled elements are also included in the database amm.dat.

For water treatment modelling a restricted set of elements is considered unrealistic. Moreover the reaction times in treatment plant is too short to reach equilibrium states incomparable to the long retention times in groundwater flows. This has resulted into the development of the PHREEQC database stimela.dat, in which major groundwater species can be modelled as redox-uncoupled elements. This database allows for controlling the oxidation of these redox-uncoupled elements according to realistic reaction patterns in groundwater treatment plants.
Table 6.1 gives an overview of the major redox reaction in groundwater treatment processes, and the redox-uncoupled elements in the three named databases, under the keywords SOLUTION_MASTER_SPECIES, SOLUTION_SPECIES AND PHASES. The formation reactions show that redox reactions not only include electrons (e-) but also hydrogen ions (H+), either as part of the reaction itself or as part of the oxygen reaction (O(0) to O(-2)), which alters pH.

Table 6.1 - Redox reactions for major groundwater elements, in databases for PHREEQC

Element (with species)		**Formation reactions for species** (under SOLUTION_SPECIES)	**Additional redox-uncoupled elements** phreeqc .dat	amm .dat	stimela .dat
N	NO3-	-			
N(5)	NO3-	NO3-			
N(3)	NO2-	NO3- + 2 H+ + 2 e- = NO2- + H2O			[N+3]
N(0)	N2	2 NO3- + 12 H+ + 10 e- = N2 + 6 H2O	Ntg	Ntg	Ntg
N(-3)	NH4+	NO3- + 10 H+ + 8 e- = NH4+ + 3 H2O		Amm	Amm [N-3]
Mn	Mn+2	-			
Mn(2)	Mn+2	Mn+2			[Mn+2]
Mn(3)	Mn+3	Mn+2 = Mn+3 + e-			
Mn(4)	Mn+4	MnO2:H2O + 4 H+ + 2 e- = Mn+2 + 3 H2O			
Fe	Fe+2	-			
Fe(2)	Fe+2	Fe+2			[Fe+2]
Fe(3)	Fe+3	Fe+2 = Fe+3 + e-			
S	SO4-2	-			
S(6)	SO4-2	SO4-2			
S(-2)	HS-	SO4-2 + 9 H+ + 8 e- = HS- + 4 H2O	Sg	Sg	Sg [S-2]
C	CO3-2	-			
C(4)	CO3-2	CO3-2			
C(-4)	CH4	CO3-2 + 10 H+ + 8 e- = CH4 + 3 H2O	Mtg	Mtg	Mtg [C-4]
O	H2O	-			
O(-2)	H2O	H2O			
O(0)	O2	2 H2O = O2 + 4 H+ + 4 e-	Oxg	Oxg	Oxg

Redox modelling with stimela.dat

The stimela.dat database allows to run all input files originally developed for phreeqc.dat and /or for amm.dat, without any modification, as demonstrated in Chapter 2.

However, modelling water treatment processes including all measured species in a groundwater sample requires the application of the database stimela.dat. Based on extensive use of PHREEEQC for modelling water treatment processes, the following approach is highly recommended:
- modelling includes all species measured in the water sample to give realistic models
- all reduced species are modelled as redox-uncoupled elements
- preventing uncontrolled redox reactions by keeping pE>12, by assuming pO2 = 0.000001 atm
- checking that the change in pH in the 'final solution calculation' is below 0.01 (no pH reactions)
- successive reactions per element convert the redox-uncoupled state to redox-coupled state.

This approach will be demonstrated in the following paragraphs.

Redox potential

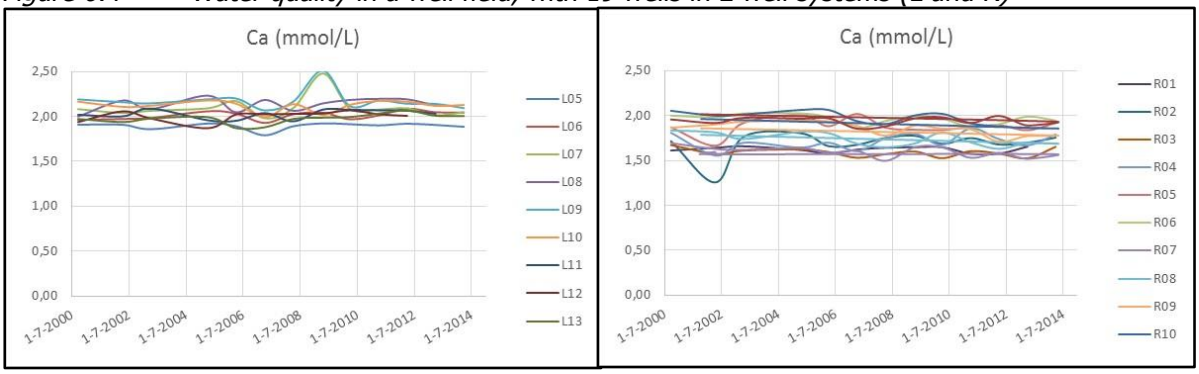
Above mentioned modelling approach gives unrealistic pE values (or redox potential) in anaerobic (or anoxic) conditions. This prevents comparison of model values with measured redox potential values.
For these cases the redox couple which dominates the redox potential reading might be set to a redox-coupled element, in a single simulation, only for determining the redox potential according to PHREEQC.

Student activity	**Lab 6.1 – Groundwater in PHREEQC**
Study goals	- introducing modelling groundwater (SOLUTION) - evaluating redox-coupled versus and redox-uncoupled elements - showing pE values for different water compositions - demonstrating a 'dashboard' for model input and model results

6.3 Mixing water from groundwater wells

Nearly all groundwater treatment plants for the production of drinking water treat groundwater abstracted by more than one single well. Well fields containing 4 to 30 abstraction wells are commonly found. The water quality obtained from these wells will be different, even when these wells abstract water from the same aquifer (see Figure 6.4).

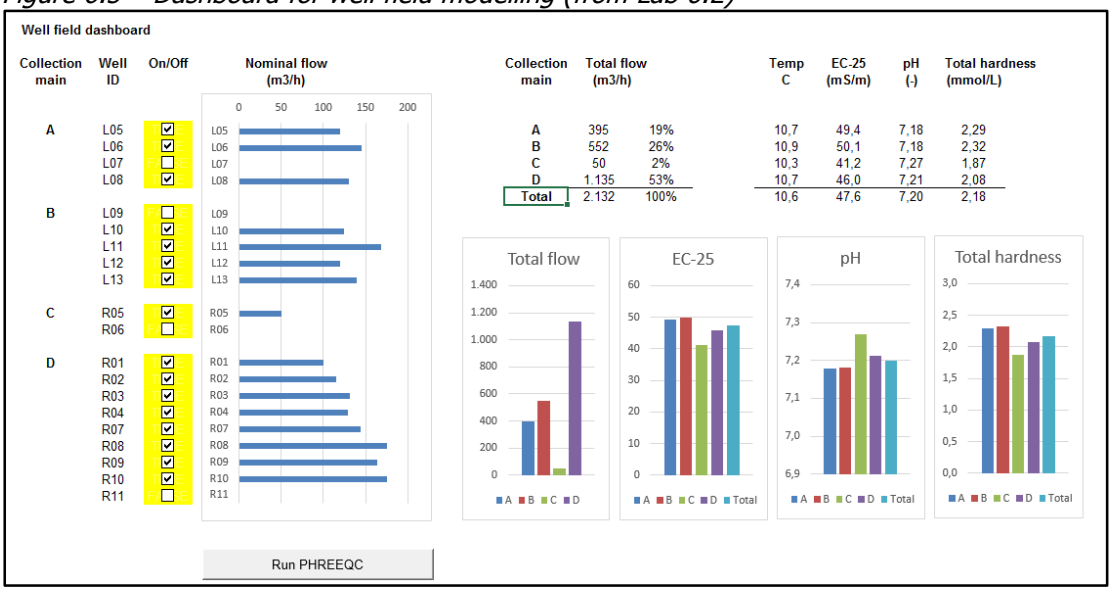
Figure 6.4 - Water quality in a well field, with 19 wells in 2 well systems (L and R)



The actual production capacity of these groundwater treatment plants is controlled by regulating the number of wells in operation. As a consequence the water quality entering the groundwater treatment plant alters with each change of production capacity disturbing the treatment processes especially when chemicals are dosed at levels related to water quality parameters.

PHREEQC can be used to predict the actual water quality entering the groundwater treatment plant. The outcome of the model might be validated by inline measurements such as pH, EC and redox potential. These sensors measure 'sum parameters' lacking information on each individual parameter such as the content of calcium, alkalinity, iron, manganese, carbon dioxide, methane etc. A validated model will give detailed information on each relevant parameter.
PHREEQC models for a well field will use the keyword SOLUTION_SPREAD for the raw water quality, with redox-uncoupled elements except for oxygen. The water quality entering the treatment plant can be determined using the keyword MIX.
The actual capacity of each well as well as the model result can be presented in a 'dashboard' as shown in Figure 6.5.

Figure 6.5 - Dashboard for well field modelling (from Lab 6.2)



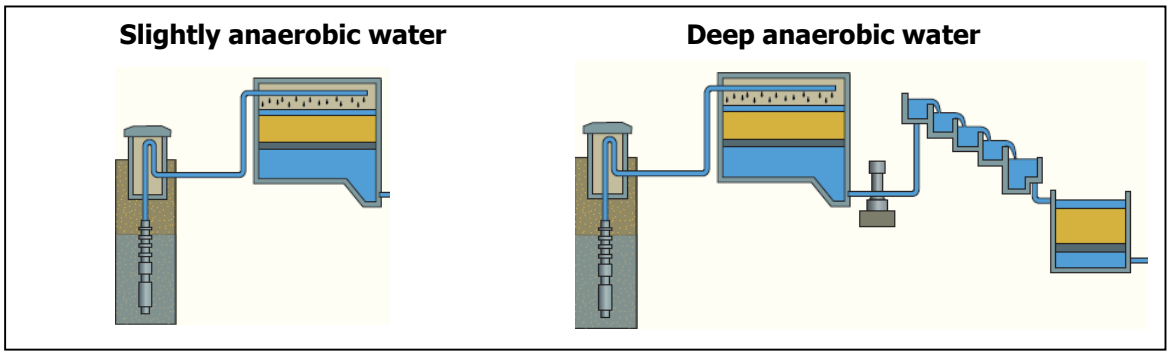
Student activity	**Lab 6.2 – Groundwater well fields**
Study goals	- introducing tabulated input for several wells (SOLUTION_SPREAD) - introducing mixing of water from a well field (MIX) - demonstrating a 'dashboard' for model input and model results

6.4 Aeration and filtration

Natural treatment of anaerobic groundwater for the production of drinking water will include aeration and filtration. In the aeration process oxygen (O_2) from atmospheric air is introduced in the water, while the content of other gases such as carbon dioxide (CO_2), methane (CH_4) and hydrogen sulfide (H_2S) will be reduced. In the filtration process dissolved iron (Fe2+) and manganese (Mn) are oxidized by O_2 and removed by precipitation of formed solids, enhanced by adsorption. Ammonium (NH_4^+), Nitrite (NO_2^-) and remaining methane (CH_4) and hydrogen sulfide (H_2S) are oxidized by bacteria. This clearly illustrates the need for a multi-parameter approach as offered by the database stimela.dat. The common approach is to start with redox-uncoupled elements except for oxygen.

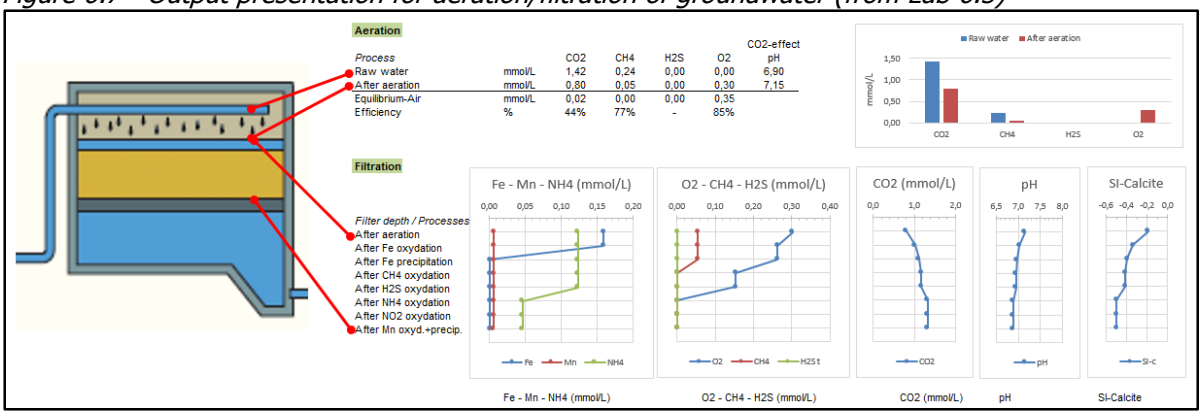
Figure 6.6 gives typical natural treatment schemes for slightly anaerobic groundwater and for deep anaerobic groundwater. Further information on these treatment schemes are given in the text book 'Drinking water - Principles and Practices' (de Moel a.o., 2006).

Figure 6.6 - Natural treatment schemes for anaerobic groundwater



Modelling groundwater treatment processes in PHREEQC uses the same keywords as discussed in Chapter 5. Conversion of redox-uncoupled elements into redox-coupled elements can be done with the keyword REACTION or with more sophisticated Basic-programming using the keywords KINETCS with RATES.
PHREEQXCEL provides for extensive options for output presentation as shown in Figure 6.7. The presented concentrations are the sum of the redox-uncoupled and redox-coupled elements.

Figure 6.7 - Output presentation for aeration/filtration of groundwater (from Lab 6.3)



Student activity	**Lab 6.3 – Groundwater treatment with aeration and filtration**
Study goals	- introducing groundwater treatment in a combined model - conversing redox-uncoupled elements (REACTION / KINETICS+RATES) - demonstrating a 'dashboard' for model input and model results

7. Next steps

After studying the previous chapters and finalizing the labs and tests the basic principles of using PHREEQXCEL for water chemistry modelling will be understood.
More advanced modelling is discussed in the trailing volumes of the series 'Aquatic Chemistry for engineers':

- Volume 2: Drinking water with PHREEQC
- Volume 3: Waste water with PHREEQC
- Volume 4: Industrial water with PHREEQC

These volumes deal with equilibrium and mass balance of most chemical reactions found in the respective fields of water treatment. The kinetics in water chemistry will be presented for some treatment processes. More detailed information on these volumes is given as last section of this Volume.

Further and actual information on 'Aquatic Chemistry for engineers' can be found on the TU Delft OpenCourseWare website for this course: http://drinkwater.citg.tudelft.nl/AquaticChemistry.
Further information on the background of PHREEQC and additional literature is given in Annex 3.

ANNEXES

Annex 1 **Keywords for PHREEQC user input**

Annex 2 **Databases for PHREEQC**

Annex 3 **Additional information**

Annex 4 **PHREEQXCEL**

Annex 1 Keywords for PHREEQC user input

(adapted from PhreeqcI and PhreeqcI Fact Sheet)

Data for PHREEQC are entered through a series of keyword data blocks, each of which provides a specific type of information. For example, the SOLUTION keyword data block defines the chemical composition of a solution. PhreeqcI provides tabbed dialog boxes for each PHREEQC keyword. Data entry in PhreeqcI is grouped within in the following blocks (Toolbars):

- initial conditions
- forward and inverse modelling
- printing and numerical method
- stoichiometry and thermodynamic data

Initial conditions

	SOLUTION	Define the chemical composition of a solution
	SOLUTION_SPREAD	Define the chemical composition of multiple solutions in a spreadsheet format
	EQUILIBRIUM_PHASES	An assemblage of minerals and gases that react to equilibrium (or until exhausted)
	GAS_PHASE	A finite reservoir of gas that reacts with a solution
	SOLID_SOLUTIONS	Solids that precipitate as mixtures of minerals, an important reaction for radio nuclides and other trace metals
	EXCHANGE	One or more sets of reaction sites for exchangeable ions, an important reaction for major cations
	SURFACE	One or more sets of sites that react by surface complexation, a major reaction for phosphorus, arsenic, and other trace elements
	USE	Use the composition of previously defined or saved data block
	COPY	Allows a data entity to be copied from one index to a new index or to a range of indices
	DELETE	Delete reactants, including solutions, phases etc.
	RUN_CELLS	For running simulations in a specified set of cells
	END	Ends the data input for a simulation step, starts the calculation for the preceding input, and prints the results

Forward and inverse modelling

	REACTION_TEMPERATURE	Changing the temperature of the reaction system
	REACTION_PRESSURE	Changing the pressure of the reaction system
	MIX	Mixing together specified fractions of solutions
	REACTION	Addition and removal of specified elements from solution
	INCREMENTAL_REACTIONS	Setting whether or not reaction steps for REACTION and time steps for KINETICS data blocks are incremental added to previous reactions steps
	RATES	BASIC language statements define rate expressions for kinetic reactions

K	KINETICS	Any non-equilibrium reaction, for which a rate expression can be formulated
	TRANSPORT	1D advection, dispersion, and reaction modelling
	ADVECTION	1D advection and reaction modelling
	INVERSE_MODELING	Deduce mixing, mineral, and gas reactions that account for the chemical evolution of waters
	SAVE	Save the composition following the batch reaction for use in subsequent reactions

Printing and numerical method

abc	TITLE	To include a comment for a simulation in the output file
	PRINT	To select which results are written to the output file
	SELECTED_OUTPUT	To produce a selected-output file that is suitable for processing by spreadsheets and other data-management software
	USER_PRINT	To define Basic programs that print user-defined quantities to the output file
	USER_PUNCH	To define Basic programs that print user-defined quantities to the selected-output file
	DUMP	To write complete definitions of reactants to a specific file
	KNOBS	To redefine parameters that affect convergence of the numerical method during speciation, batch-reaction, and transport calculations
	USER_GRAPH	To create charts of simulation results

Stoichiometry and thermodynamic data

	SOLUTION_MASTER_SPECIES	To define the correspondence between element names and aqueous primary and secondary master species, including the alkalinity contribution of the master species, the gram formula weight used to convert mass units, and the element gram formula weight
	SOLUTION_SPECIES	To define aqueous species with its chemical reaction, log K, and activity-coefficient parameters
(s)	PHASES	To define a name, chemical reaction, log K , and temperature dependence of log K for each gas component and mineral
	EXCHANGE_MASTER_SPECIES	To define the correspondence between the name of an exchange site and an exchange species that is used as the master species in calculations
	EXCHANGE_SPECIES	To define a half-reaction and relative log K for each exchange species
	SURFACE_MASTER_SPECIES	To define the correspondence between surface binding-site names and surface master species
	SURFACE_SPECIES	To define a reaction and log K for each surface species, including surface master species
Pitz	PITZER	Invokes the Pitzer activity coefficient model
SIT	SIT	Invokes the Specific ion Interaction Theory (SIT) activity coefficient model

Annex 2 Databases for PHREEQC

The basis chemical data for PHREEQC is collected in a database (.dat) file, in which data are entered through a series of keyword data blocks, similar to the user input file.
All input files for PHREEQC are white-space delimited (tabs and/or spaces) ASCII text files.

Available databases
PHREEQC comes with 9 databases:

Database	Short description *)	Remark
phreeqc.dat	Derived from PHREEQE (Parkhurst and others, 1980), which is consistent with wateq4f.dat, but has a smaller set of elements and aqueous species	Default databases for Phreeqc.
amm.dat	The same as phreeqc.dat, except that ammonia oxidation state has been uncoupled from the rest of the nitrogen system; that is, ammonia has been defined as a separate component	Called phreeqc.dat in 'Notepad++ interface to PHREEQC version 3' (Tony Appelo)
wateq4f.dat	Derived from WATEQ4F (Ball and Nordstrom, 1991)	
llnl.dat	Derived from databases for EQ3/6 and Geochemist's Workbench that uses thermodynamic data compiled by the Lawrence Livermore National Laboratory	Since vs. 2.3 (2001)
minteq.dat	Derived from the databases for the program MINTEQA2 (Allison and others, 1990) (solubility of gases are not included)	No longer supported by U.S. Environmental Protection Agency
minteq.v4.dat	Derived from MINTEQA2 version 4 (U.S. Environmental Protection Agency, 1998) (solubility of gases are not included)	Since vs. 2.11 (2005)
pitzer.dat	Database for the specific-ion-interaction model of Pitzer (Pitzer, 1973) as implemented in PHRQPITZ (Plummer and others, 1988)	Since vs 2.12 (2005) For modelling highly saline, SO_4^{2-}-rich solutions
sit.dat	Database implementing the Specific ion Interaction Theory (SIT) as described by Grenthe and others (1997)	Since vs 2.17 (2010)
iso.dat	Partial implementation of the individual component approach to isotope calculations as described by Thorstenson and Parkhurst (2002, 2004)	Since vs 2.7 (2003)

*) Source: Parkhurst and Appelo (2013), p. 27

Database	Responsible source	File ID *)
phreeqc.dat	USGS	-
amm.dat	USGS	-
wateq4f.dat	USGS	# $Id: wateq4f.dat 6895 2012-08-21 18:10:05Z dlpark $
llnl.dat	Lawrence Livermore National Lab	# $Id: llnl.dat 4023 2010-02-09 21:02:42Z dlpark $
minteq.dat	EPA	# $Id: minteq.dat 3568 2009-07-13 16:15:14Z dlpark $
minteq.v4.dat	EPA	# $Id: minteq.v4.dat 794 2006-02-27 21:06:22Z dlpark $
pitzer.dat	USGS	-
sit.dat	Amphos 21 /ANDRA	# Update note: ThermoChimie v.8.0 September 2011.
iso.dat	USGS	-

*) as supplied with PHREEQC vs 3.1.7

Databases used at TU Delft
The general rule of thumb at TU Delft is: always use stimela.dat (see Chapter 5 and 6). This database includes additional inert elements for NH_4^+, NO_2^-, Fe^{2+} and Mn^{2+} and is maintained at TU Delft, as an inherited and updated version of phreeqc.dat. Moreover, it includes additional RATES for typical water treatment processes (under development).
Only if more elements and/or species are required it is recommended to use other databases, while realizing the consequences of the implicit redox reactions in PHREEQC to the redox equilibrium state (see Chapter 6).
Moreover it is recommended not to change one of the distributed phreeqc databases with own data, but include adjustments in user input files (via additional elements and definitions).

Content of PHREEQC databases
A PHREEQC database contains several sections. Each section starts with a PHREEQC keyword:

Keyword	Description
SOLUTION_MASTER_SPECIES SOLUTION_SPECIES	Defines elements, oxidation states, species, as well as chemical reactions of formation and redox reactions
PHASES	Defines minerals (solids) and gases, and their dissolution reaction
EXCHANGE_MASTER_SPECIES EXCHANGE_SPECIES	Defines exchange sites, exchange species and their exchange reaction
SURFACE_MASTER_SPECIES SURFACE_SPECIES	Defines surface sites, surface species and their surface reaction
RATES	Defines kinetics for reactions
END	Delimiter for simulations, starts the calculation of a simulation

SOLUTION_MASTER_SPECIES
SOLUTION_MASTER_SPECIES is used to define element names and oxidation states, atomic weights and the master species in a solution.
Master species are the ones primarily used in the calculations. They function as basis species for defining other ones in reactions with keyword SOLUTION_SPECIES.

Example lines:

```
#1            2       3      4              5
O             H2O     0.0    O              15.999
O(0)          O2      0.0    O
O(-2)         H2O     0.0    0.0
Ca            Ca+2    0.0    Ca             40.078
Mg            Mg+2    0.0    Mg             24.305
Fe            Fe+2    0.0    Fe             55.845
Fe(+2)        Fe+2    0.0    Fe
Fe(+3)        Fe+3    -2.0   Fe
Cl            Cl-     0.0    Cl             35.45
C             CO3-2   2.0    HCO3           12.011
C(+4)         CO3-2   2.0    HCO3
C(-4)         CH4     0.0    CH4
Alkalinity    CO3-2   1.0    Ca0.5(CO3)0.5  50.043
S             SO4-2   0.0    SO4            32.06
S(6)          SO4-2   0.0    SO4
S(-2)         HS-     1.0    S
```

#	Item	Description
1	Element name	Elements with various oxidation states must be given as element followed by all related oxidation states. Element names must start with a capital letter, followed by lower case letters or underscores (no numbers, except for defining oxidation state)
2	Master species	Must be repeated with an identity reaction under SOLUTION_SPECIES
3	Contribution to alkalinity	Master species' contribution to the alkalinity when titrating down to pH = 4.5
4	Mass-mole conversion	Chemical formula or gram formula weight for converting mass units in SOLUTION to mol
5	Atomic weight	Atomic weight of the element in column 1

Each master species should be repeated under SOLUTION_SPECIES to specify its parameters for the activity coefficient, the diffusion coefficient, and the molar volume.

SOLUTION_SPECIES

SOLUTION_SPECIES is used to define:

- the chemical (association) reaction
- log K and reaction enthalpy (or analytical expression for log K versus T)
- activity-coefficient parameters (-gamma)
- tracer diffusion coefficient (-dw) for aqueous species
- parameters for calculating the density of the solution (-Millero, -Vm)
- enrichment in the diffuse double layer (-erm_ddl)
- parameters for isotopic species.

The SOLUTION_SPECIES section starts with the identity reaction for master species, as in H+ = H+. Example lines:

```
SOLUTION_SPECIES
H+ = H+
        -gamma  9.0     0.0
        -dw      9.31e-9
e- = e-
H2O = H2O
Ca+2 = Ca+2
        -gamma  5.0     0.1650
        -dw      0.793e-9
        -Vm   -0.3456  -7.252   6.149   -2.479   1.239   5   1.60   -57.1   -6.12e-3   1

# aqueous species
H2O = OH- + H+
        -analytic   293.29227   0.1360833   -10576.913   -123.73158   0   -6.996455e-5
        -gamma  3.5     0.0
        -dw      5.27e-9
        -Vm   -9.66   28.5   80.0 -22.9 1.89 0 1.09 0 0 1 # supcrt modified
2 H2O = O2 + 4 H+ + 4 e-
        -log_k  -86.08
        -delta_h 134.79 kcal
        -dw      2.35e-9
        -Vm   5.7889   6.3536   3.2528   -3.0417   -0.3943 # supcrt
```

PHREEQC can calculate the temperature dependence of log K with:

- Van 't Hoff's equation:
  $\log K_T = \log K_{298} + \Delta H_r / (2.303 * 8.314e\text{-}3) * (1 / 298 - 1 / T)$
  where $\log K_T$ is log K at temperature T (Kelvin), $\log K_{298}$ is log K at 298 K (= 25 °C), ΔH_r is the reaction enthalpy (kJ/mol), entered after -delta_h.
- a polynomial, with coefficients following -analytical_expression.

PHREEQC adds the pressure term to log_k: -= delta_v * (P - 1) / (2.3RT).

Gas-pressures and fugacity coefficients are calculated with Peng-Robinson's equation of state (EOS).

For definition of the activity coefficients see Parkhurst and Appelo (2013) and Parkhurst and Appelo (1999) .
If gamma is not entered, the Davies equation will be used. To make the activity coefficient equal to 1, write: -gamma 1e5 0

The diffusion coefficient is used for calculating:
- multicomponent diffusion of individual solutes with keyword TRANSPORT
- the specific conductance (electrical conductivity) of the solution.

The density of the solution is calculated using the molar volumes of species, or alternatively using functions developed by Millero (2001).
Temperature- and pressure-dependent volumina of aqueous species are calculated with a Redlich-type equation (cf. Redlich and Meyer, Chem. Rev. 64, 221), from parameters entered with:
-Vm a1 a2 a3 a4 W a0 i1 i2 i3 i4 .
The Millero function V(i) = a + b * tC + c * tC^2 + s(I) * I^0.5 + (d + e * tC + f * tC^2) * I
for calculating the molar volume of species i, is entered with -millero a b c d e f,
where a - f are the 6 parameters in the input file, tC is the temperature in °C, s(I) is the Debye-Hueckel limiting slope, and I is the ionic strength.

Identifiers no_check and mole_balance are used for a reaction that needs coefficients in the law of mass action which differ from the ones required by mass- and charge-balance.

PHASES
PHASES is used to defines the name, the dissolution reaction, log K, and temperature dependence of log K for minerals and gases, as well as the molar volume.
Example lines:

```
PHASES
Calcite
       CaCO3 = CO3-2 + Ca+2
       -log_k  -8.48
       -delta_h -2.297 kcal
       -analytic      -171.9065      -0.077993      2839.319       71.595
       -Vm 36.9 cm3/mol # MW (100.09 g/mol) / rho (2.71 g/cm3)
CO2(g)
       CO2 = CO2
       -log_k  -1.468
       -delta_h -4.776 kcal
       -analytic  109.534  1.9913e-2  -6986.04  -40.83  669370
       -T_c  304.2 # critical T, K
       -P_c   72.86 # critical P, atm
       -Omega 0.225 # acentric factor
```

PHREEQC can calculate the temperature dependence of log K with:
- Van 't Hoff's equation:
  $\log K_T = \log K_{298} + \Delta H_r / (2.303 * 8.314e\text{-}3) * (1 / 298 - 1 / T)$
  where $\log K_T$ is log K at temperature T (Kelvin), $\log K_{298}$ is log K at 298 K (= 25 °C), ΔH_r is the reaction enthalpy (kJ/mol), entered after -delta_h.
- a polynomial, with coefficients following -analytical_expression

The molar volume of solids is derived from the density of the solid and its molair mass.
The molar volume of a gas is used to calculate the pressure dependence of log_k, using the critical temperature (-T_c), critical pressure (-P_c) and the acentric factor (-omega) in the Peng-Robinson's equation of state (EOS).

Elements, oxidation states and species in stimela.dat

The most relevant elements, oxidation states and species in stimela.dat are:

Element	Molar mass (g/mol)	Master species	Major species
Elements with single oxidation state:			
Ca	40.078	Ca+2	Ca^{2+}
Mg	24.305	Mg+2	Mg^{2+}
Na	22.990	Na+	Na^{+}
K	39.098	K+	K^{+}
Cl	35.45	Cl-	Cl^{-}
P	30.974	PO4-3	PO_4^{3-} HPO_4^{2-} $H_2PO_4^{-}$
F	18.998	F^{-}	F^{-}
Si	28.085	H4SiO4	H_4SiO_4 (= $SiO_2.2H_2O$)
Elements with multi oxidation states:			
C	12.011	CO3-2	CO_2 $CO_2(g)$ HCO_3^{-} CO_3^{2-} CH_4
C(+4) = C(4)		CO3-2	CO_2 $CO_2(g)$ HCO_3^{-} CO_3^{2-}
Alkalinity		CO3-2	HCO_3^{-} CO_3^{2-}
C(-4)		CH4	CH_4
Fe	55.845	Fe+2	Fe^{2+} FeS $FeCO_3$ $Fe(OH)_3$
Fe(+2) = Fe(2)		Fe+2	Fe^{2+} FeS $FeCO_3$
Fe(+3) = Fe(3)		Fe+3	Fe^{3+} $Fe(OH)_3$
Mn	54.938	Mn+2	Mn^{2+} MnOOH MnO_2 Mn_3O_4
Mn(+2) = Mn(2)		Mn+2	Mn^{2+} Mn_3O_4 (= $2MnO.MnO_2$)
Mn(+3) = Mn(3)		Mn+3	Mn^{3+} MnOOH
Mn(+4) = Mn(4)		-	MnO_2 Mn_3O_4 (= $2MnO.MnO_2$)
S	32.06	SO4-2	SO_4^{2-} H_2S HS^{-} $H_2S(g)$
S(6)		SO4-2	SO_4^{2-}
S(-2)		HS-	H_2S HS^{-} $H_2S(g)$
N	14.007	NO3-	NO_3^{-} NO_2^{-} N_2 $N_2(g)$ NH_4^{+}
N(+5) = N(5)		NO3-	NO_3^{-}
N(+3) = N(3)		NO2-	NO_2^{-}
N(0)		N2	N_2 $N_2(g)$
N(-3)		NH4+	NH_4^{+} NH_3 $NH_3(g)$
H	1.008	H+	H_2O H_2 H^{+} OH^{-}
H(0)		H2	H_2
H(1)		H+	H^{+} OH^{-}
O	15.999	H2O	H_2O $H_2O(g)$
O(0)		O2	O_2 $O_2(g)$
O(-2)		H2O	H_2O
Elements with inert (redox-uncoupled) state:			
Hdg	2.016	Hdg	H_2 $H_2(g)$ (inert)
Oxg	31.998	Oxg	O_2 $O_2(g)$ (inert)
Ntg	28.014	Ntg	N_2 $N_2(g)$ (inert)
[C-4]	12.011	[C-4]H4	CH_4 $CH_4(g)$ (inert)
[Fe+2]	55.845	[Fe+2]+2	Fe^{+2} (inert)
[Mn+2]	54.938	[Mn+2]+2	Mn^{+2} (inert)
[S-2]	32.06	H2[S-2]	H_2S $H_2S(g)$ (inert)
[N-3]	14.007	[N-3]H4+	NH_4^{+} NH_3 $NH_3(g)$ (inert)
[N+3]	14.007	[N+3]O2-	NO_2^{-} (inert)

Table does not include the single oxidation state elements (with master species) E (e-), Al (Al+3), Ba (Ba+2), Sr (Sr+2), B (H3BO3), Li (Li+), Br (Br-), Zn (Zn+2), Cd (Cd+2), Pb (Pb+2)
Table does not include the multi oxidation state elements (with master species) Cu (Cu+2), Cu(+2) (Cu+2), Cu(+1) (Cu+1)
Table does not include the redox-uncoupled gases Mtg (Methane, CH_4) and Sg (Hydrogen sulfide, H_2S), specified as single element species.

All elements and element oxidation states can be found in the first column of the SOLUTION_MASTER_SPECIES. The related master species are given in the second column. All solute species (master species and other species) can be found following the '=' sign in each reaction line of SOLUTION_SPECIES.

Annex 3 Additional information

Further and actual information on 'Aquatic Chemistry for engineers' can be found on the TU Delft OpenCourseWare website for this course: http://drinkwater.citg.tudelft.nl/AquaticChemistry.

Further information on PHREEQC can be found in the following sources:
Websites:
- USGS – PHREEQC: (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/)
  This website also includes FAQs, edited by David Parkhurst.
- Tony Appelo: (http://www.hydrochemistry.eu/)

Books:
- User's Guide to PHREEQC (Version 3) (Parkhurst & Appelo, 2013)
  Available as 'PHREEQC version 3 Documentation (4.2 M)' at the PHREEQC website
  Available as Help file in PhreeqcI (phreeqci.chm)
- User's Guide to PHREEQC (Version 2) (Parkhurst & Appelo, 1999)
  Available as 'PHREEQC version 2 Documentation (2.3 M)' at the PHREEQC website
  Still relevant for Version 3: pages 9-63
- Hydrogeochemical modeling with PHREEQC (Appelo & Parkhurst, 2011)
  Available as updated Help file at website of Tony Appelo (phreeqc.chm)
- Groundwater Geochemistry (Merkel, Planer-Friedrich & Nordstrom, 2005)
- Geochemistry, Groundwater and Pollution, 2e ed (Appelo & Postma, 2005)

Papers (peer reviewed):
- Assessment of calculation methods for calcium carbonate saturation in drinking water for DIN 38404-10 compliance (de Moel et al., 2013)
  Drinking Water Eng. Science, 6, 115-124, 2013 (doi:10.5194/dwes-6-115-2013)
  (http://www.drink-water-eng-sci.net/6/115/2013/)

Courses:
- USGS course Geochemistry for Groundwater Systems 2011
  Presentations, examples, exercises and literature of a 5-days course (USGS website)

Tony Appelo uses an adapted version of Notepad++ for writing, editing and running PHREEQC3 input files. This Notepad+ version is available as free download at his website.
The book Geochemistry, Groundwater and Pollution, 2e ed (Appelo & Postma, 2005) uses the obsolete PHREEQC version 'PHREEQC for Windows' (Vincent Post 2010: http://pfw.antipodes.nl/).

Additional information on Iphreeqc (COM modules) can be found in the documentation supplied with the Iphreeqc download:
- Modules Based on the Geochemical Model PHREEQC for Use in Scripting and Programming Languages (Charlton & Parkhurst, 2011)
- IPhreeqcCOM reference (supplied as Help file IPhreeqcCOM.chm).

Annex 4 PHREEQXCEL

PHREEQXCEL has been developed as a container application or 'Graphical User Interface' for PHREEQC for all types of chemical simulations within the online MSc course Aquatic Chemistry for Engineers, given at Delft University of Technology (The Netherlands).
The generic approach allows for all kinds of tailor made simulations and calculations making the power of PHREEQC available to engineers, students, laboratory personnel and many others who lack the programming skills previously required for PHREEQC.
PHREEQXCEL applications are freely available at the website of the course. The public availability of this framework allows for the development of similar applications by experienced PHREEQC users for their own research and using their findings and modelling for all kind of engineering applications.

1. Introduction

PHREEQC has become the 'de facto' standard for geochemical calculations. It has been developed by the US Geological Survey (USGS), starting in 1980 with regular updates and extensions to date. The program is freely available for users, and can be downloaded from the USGS website.
Since April 2011 PHREEQC is also available as a COM-module, which allows running PHREEQC within Windows programs such as Excel and MATLAB (Charlton, S.R. and Parkhurst, D.L., 2011).
This makes the power of PHREEQC available to engineers, students, laboratory personnel and many others who lack the programming skills previously required for PHREEQC.
This article describes the Visual Basis code for Excel (VBA) for using Excel as a one-stop application (PHREEQXCEL) unleashing the powerful chemistry of PHREEQC within the widely known flexible and user friendly environment of Excel with all its powerful graphical and tabular features.
PHREEQXCEL applications can be created by an experienced PHREEQC user and used by all kind of professionals, such as researchers, students, treatment plant operators, laboratory staff etc.
PHREEQXCEL applications can also be used by external Windows applications such as Web servers, allowing for online applications ('in the cloud') without installing PHREEQC at the user-PC. The all-in-one setup creates an Excel file containing all relevant data, which can easily be downloaded or emailed to the online user, as an add-on to the summary results shown in the browser itself.
PHREEQXCEL applications have been developed for the MSc course Aquatic Chemistry at Delft University of Technology, in both Excel versions as well as online versions.
Since February 2013 PHREEQC version 3 is available, with an updated COM-module. This updated version is used in PHREEQXCEL.

2. Basic setup

The PHREEQC COM-module (IPHREEQC, version 3) can be downloaded from the USGS website and should be installed on a Windows PC. Excel files showing the setup as described in this article can be downloaded from the TU Delft site for the online course Aquatic Chemistry for Engineers.

PHREEQXCEL applications contains at minimum 6 predefined sheets and 4 generic VBA subroutines. The Excel sheet names and VBA subroutines are shown in Table 1.
In PHREEQXCEL all related files are contained in a single Excel file, including the in- and output files, the chemical database file and eventually error messages.

In the minimum setup PHREEQXCEL can run all input code files generated in and for other container systems, such as 'Phreeqc Interactive' (USGS) and 'PHREEQC in adapted Notepad++' (Tony Appelo). A huge number of example files for these containers systems are available, which can be used in PHREEQXCEL:
- USGS: http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/phreeqc3-html/phreeqc3-55.htm
- Tony Appelo: http://www.hydrochemistry.eu/exmpls/index.html

In a more elaborated setup PHREEQXCEL applications contain one or more user defined input sheets which on one hand provides for a user friendly input sheets and on the other hand a direct relation to the PHREEQC code in the PHREEQXCEL sheet 'Input'. User defined input sheets might also contain results from PHREEQC simulations.
The novice user will only use such user defined front sheet being a tailor made sheet for a specific application, such as calculation of the Electrical Conductivity (EC) or Calcium Carbonate Saturation (SI and CCPP) in drinking water (Standard Methods, 2010).
The output in this sheet might be tabular and/or graphical.
This novice user can fill in the specific data within a self-explaining Excel sheet, start the PHREEQC calculation by clicking the 'Run PHREEQC' button, and overview the results, all within the same front-end sheet.

Experienced PHREEQC users can modify the specific PHREEQXCEL application, or draft a complete new application without modifying the VBA code in PHREEQXCEL
Only 'normal' Excel skills are required to create or modify the application to the specific requirements in a company, department, or project.

Table 1 - Minimum components of PHREEQXCEL applications

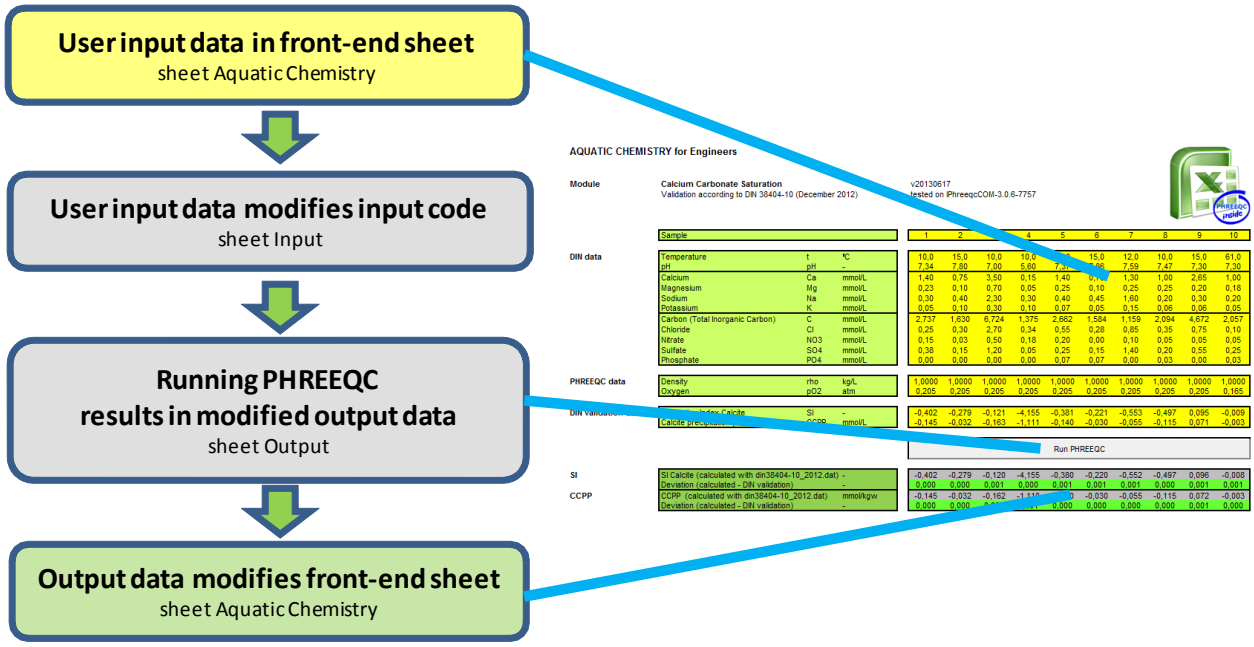
Sheet name	**Function**	**IphreeqcCOM method or file**
Run_Control	Run settings and Start button	-
Input	PHREEQC input code	[Ex1].pqi
Database	Chemical database for PHREEQC	stimela.dat
phreeqc.out	Lined output (PRINT)	phreeqc.[id].out
Output	Tabulated output (SELECTED_OUTPUT)	selected.[id].out
Messages	PHREEQC warnings and errors	GetWarningString() GetErrorString()
VBA subroutines		
RunPhreeqc()	Generic VBA program code for PHREEQXCEL applications	RunFile() RunString()
Button1_Click()	Macro to start RunPhreeqc()	-
Button2_Click()	Macro to select an external Input file	-
Button3_Click()	Macro to select an external Database file	-

3. VBA code and data flow

The heart of PHREEQXCEL is the universal VBA subroutine called RunPhreeqc(), which is called by clicking the 'Run PHREEQC' button. This code can be divided into five steps:
1. Initialize application, including COM-object
2. Loading database in COM-object (from sheet Database or from external file)
3. Running PHREEQC with user input (from sheet Input or from external file)
4. Saving output (to sheet Output, sheet Messages and sheet phreeqc.out)
5. Returning to a specified front-end sheet.
The subroutine code also includes Error handling.
The optional items are controlled by settings in the sheet Run_Control, which allows for selecting the chemical database, and user input. These might be read from sheets in the Excel file either or from external files.

The data flow in PHREEQXCEL is shown in Fig. 1. The user input in the front-end sheet (yellow cells) is directly related to the input code in the sheet Input.
After running PHREEQC the (updated) output data in the sheet Output is directly shown in the front-end sheet (non-yellow cells) underneath the 'Run PHREEQC' button.

Figure 1. Data flow in PHREEQXCEL applications, with an example application.



The Input sheet contains the full input code for PHREEQC simulations, as in 'normal' .pqi or .phr files. This input sheet is converted into an input string, which can be used in the COM-method Phreeqc.RunString(). The conversion into a string allows for putting part of a PHREEQC statement into separate Excel cells. Such cells can be references to cells on the front-end sheet.
The Output sheet is filled by writing the result array from the COM-method Phreeqc.GetSelectedOutputArray() into the Output sheet. Its tabulated output can be used as references in cells on the front-end sheet.
The content of the tabulated Output sheet is determined by the PHREEQC keywords SELECTED_OUTPUT and USER_PUNCH.

The VBA code is started by its macro-call RunPhreeqc(<Boolean>). With Boolean=TRUE all internal screen messages are ignored allowing for use by external programs without user dialogs.
The full VBA code can be seen in PHREEQXCEL applications, as available at the TU Delft Aquatic Chemistry website. All PHREEQXCEL applications have the same VBA code.

4. Details of PHREEQXCEL applications

Details of PHREEQXCEL application will be discussed here for four aspects:
- typical Excel functions
- typical PHREEQC simulations
- dynamic simulations with PHREEQC
- running PHREEQXCEL applications in the Cloud.

Typical Excel functions

PHREEQXCEL applications can be customized by 'normal' Excel routines and formulas. Excel functions should give direct modifications from the front-end sheet into the Input sheet, as well as from the Output sheet into the front-end sheet.

The main object is to 'translate' the user input on the front-end sheet into proper PHREEQC code on the Input sheet. This requires some typical conversions to change numeric data types into proper strings, with points as decimal separator and without thousands separators.
The Excel function FIXED(<number>;3;TRUE) gives text showing the number with 3 decimals with no_commas. The Excel function SUBSTITUTE(<number-text>;",";".") changes all decimal commas into points, in case the international setting of the user creates decimal commas. Combining these 2 functions gives a generic number conversion into proper PHREEQC code.
Using the # symbol, the comment indicator in PHREEQC code, as initial line cell allows for conditional statements in the code.

The PHREEQC output in the Output sheet can often be shown directly into the front-end sheet. For showing results in mmol/kgw instead of the mol/kgw (as PHREEQC default) requires a <result>*1000 formula. Similar unit conversions can be made in Excel into operating units such as mg/L, mS/m etc.
SI values of gases can be converted into partial pressure in Excel with the formula $p_a=10^{SI}$.

Typical PHREEQC simulations
Some water quality parameters require two PHREEQC simulations, as the difference in results gives the requested parameter. Typical examples are Calcium Carbonate Precipitation Potential (CCPP) and Buffer capacity.
Calcium Carbonate Precipitation Potential can be calculated from the difference in Calcium concentration in a simulation with EQUILIBRIUM_PHASES; Calcite, or by the amount of reacted calcite (EQUI_DELTA) divided by the mass of water either volume of the solution.
Buffer capacity can be calculated using REACTION for adding a very small amount of HCl (0.01 mmol/kgw) and by subtracting the pH before and after.

Some water quality parameters are not directly calculated by PHREEQC but require additional formulas or functions (CALCULATE_VALUES) to get their values. Typical examples are total Cation and Anion concentration, which can be calculated from Charge Balance difference (CHARGE_BALANCE=Cation-Anion) and Percentage error (PERCENT_ERROR=(Cation-Anion)/(Cation+Anion)).

Kinetic and transport simulations in PHREEQC often give a huge amount of data in the Output sheet. In this case the presentation in the front-end sheet is preferably given as a graph, either directly from the output sheet or via an intermediate transformation calculation in Excel.

Dynamic simulations with PHREEQC
The VBA code in RunPhreeqc includes a one-time-run of PHREEQC, in which the full output array is written into the Excel file, only after ending the full code in the input sheet.
Multiple runs are required if calculation results are required for sequential runs. Solutions with input concentrations in mg/L require the density of the solution as input value. This density can be calculated by PHREEQC, and used in a re-run of the calculation. Such double-runs can be achieved by calling twice the VBA function/procedure RunPhreeq in StartCalc_Click(). This approach is applicable for simulations which require a known number of runs.
More dynamic simulations can be made by using the PHREEQC option INCLUDE$ in the input file/code. This option allows for writing input code 'on the run', which can be used in trailing simulations, based on the results of previous simulations.

Running PHREEQXCEL applications in the Cloud
Modern web server can use other applications for external processes. This makes PHREEQXCEL applications available for web applications without installation of PHREEQC, the IPREEQC-COM module or even Excel on the electronic device of the user.
Data in a web application can be put on the web server into a PHREEQXCEL application, the VBA macro RunPhreeqc(true) can be called and the (summary of) results from the Excel file can be

shown in the browser. Eventually the whole Excel file including all data can be forwarded to the client, as download and/or email attachment.
For experienced web designers this is a 'standard procedure' which is not described here in more detail.

5. Example: Calcium carbonate saturation in drinking water

Calcium carbonate saturation in drinking water is presented here as an example of a practical application of PHREEQXCEL. This application is shown in Fig. 1 (right) and attached to this paper as Supplementary Material. The application deals with the calcium carbonate saturation according to the German standard DIN 38404-10 (2012). The purpose of this standard is to calculate the Saturation Index for calcite (SI) and the Calcium Carbonate Precipitation Potential (CCPP) or its counterpart Calcitlösekapazität (D_C).
The user can fill in the yellow data fields in the front-end sheet and click on the Run PHREEQC button below the input fields to start the PHREEQC calculation. The main results are also presented on the front-end sheet, as 'refreshed values'.

Input parameters
DIN 38404-10 (2012) requires the validation of computer programs on 10 water samples, with given water temperature, pH, and the concentrations of Calcium, Magnesium, Sodium, Potassium, Inorganic carbon, Chloride, Nitrate, Sulphate and Phosphate. Inorganic carbon is used in this example instead of Alkalinity.
In order to use these samples in PHREEQC the Oxygen content (as pO2) and Density (in kg/L) are added.
Moreover the validation values for SI and CCPP are included.

Simulations
The input parameters are transferred to the PHREEQC input code in the Excel sheet Input, under SOLUTION_SPREAD, in which the 10 'initial solutions' are calculated.
After these 'Initial calculations' all samples are recalculated by dummy calculations for electron balancing (to redox equilibrium including calculation of pE).
In these 10 simulations the Saturation Index (SI) SI of all samples is determined (as SI for Calcite). SI is a standard output parameter of each simulation in PHREEQC.
For CCPP additional simulations are required including EQUILIBRIUM_PHASES to Calcite.

Post processing
The calculation results are presented on the front-end sheet, showing the differences between calculated values and validation values.
The example application shows several additional post-processing calculations.

6. Conclusions

PHREEQXCEL makes the power of PHREEQC available to engineers, students, laboratory personnel and many others who lack the programming skills previously required for PHREEQC.
PHREEQXCEL applications can be created by an experienced PHREEQC user and used by all kind of professionals, such as researchers, students, treatment plant operators, laboratory staff etc.
PHREEQXCEL applications unleash the powerful chemistry of PHREEQC within the widely known flexible and user friendly environment of Excel with all its powerful graphical and tabular features.
PHREEQXCEL applications can be used on a Windows PC with Excel and installed IPHREEQC-COM module, but also on all electronic devices as laptops, tablet PCs, iPads, smart phones, etc. as online applications in a web browser ('in the cloud').

References

Charlton, S.R. and Parkhurst, D.L.: Modules based on the geochemical model PHREEQC for use in scripting and programming languages, Computers & Geosciences, 37, 1653–1663, 2011.

De Moel, P.J., Van der Helm, A.W.C., Van Rijn, M., Van Dijk, J.C. and Van der Meer, W.G.J.: Assessment of calculation methods for calcium carbonate saturation in drinking water for DIN 38404-10 compliance, Drinking Water Eng. Science, 6, 115-124, 2013 (doi:10.5194/dwes-6-115-2013), available at http://www.drink-water-eng-sci.net/6/115/2013/.

DIN 38404-10: German standard methods for the examination of water, waste water and sludge - Physical and physico-chemical parameters (group C) - Part 10: Calculation of the calcit saturation of water (C 10), DIN Deutsches Institut für Normung, 2012.

PHREEQXCEL application: AquaticChemistry_CalciumCarbonateSaturation_v20130617.xlsm

Standard Methods 1030E: Checking Analyses' Correctness, in: Standard Methods for the Examination of Water and Wastewater, 22nd Edition, APHA/AWWA/WEF, 2012, SM1030E: 2011.

Standard Methods 2330: Calcium carbonate saturation, in: Standard Methods for the Examination of Water and Wastewater, 22nd Edition, APHA/AWWA/WEF, 2012, SM2330: 2010.

TU Delft: Aquatic Chemistry for Engineers (Online MSc-PhD course in Watermanagement), available at: http://drinkwater.citg.tudelft.nl/AquaticChemistry.

USGS: http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/.

Generic VBA code in PHREEQXCEL

```
Sub RunPhreeqc(Optional Server As Boolean)
  ' Call examples: RunPhreeqc or RunPhreeqc False or Call RunPhreeqc() or Call RunPhreeqc(False)
  ' No user messages if Server = True (default = False)


  ' Requirements (installed items):
  ' - PHREEQC COM-module (version 3, latest download from USGS website)
  ' - MS Forms library (part of Windows OS)
  ' MS-Windows clipboard is used for fast copy/paste actions
  ' This requires (MSForms.)DataObject from the MS Forms Library
  ' For loading this library: include Forms in the VBA project,
  ' and select MS Forms library in References under menu option Tools
  ' included Form might be removed afterwards

  ' Initialize application, including COM-object
  Dim starttime, endtime As Single
  starttime = Timer

  On Error Resume Next                    ' ChDrive gives error running on a UNC-system (i.e. Citrix)
  ChDrive Left(ActiveWorkbook.Path, 1)        ' set drive of Excel file as default drive
  ChDir ActiveWorkbook.Path                ' set path of Excel file as default directory
  On Error GoTo ErrHandler:                ' set Error handler

  Set phreeqc = CreateObject("IPhreeqcCOM.Object")
  phreeqc.OutputStringOn = True              ' default = False
  phreeqc.OutputFileOn = False               ' default value
  phreeqc.SelectedOutputFileOn = False        ' default value
  phreeqc.CurrentSelectedOutputUserNumber = 1  ' default = 1

  Worksheets("Messages").Activate
  ActiveSheet.Cells.ClearContents            ' clear (old) Messages
  InputSheet = Worksheets("Run_Control").Range("InputSheet").Value
  DatabaseSheet = Worksheets("Run_Control").Range("DatabaseSheet").Value
  ReturnSheet = Worksheets("Run_Control").Range("ReturnSheet").Value
  ' User messages only in non-server mode
  If Not Server And Not Worksheets("Run_Control").Range("Messages").Value Then
    Server = True
  End If


  ' Define input file and database file (might be empty)
  File_In = Worksheets("Run_Control").Range("InputFile").Value
  ' Iphreeqc generates an error if File_In can not be read
  DatabaseFile = Worksheets("Run_Control").Range("DatabaseFile").Value
  ' Iphreeqc generates an error if DatabaseFile can not be read
  ' Include full path name if not in default directory (= location of Excel file)

  ' Load database in COM-object
  If DatabaseFile <> "" Then  'use DatabaseFile if filled
     phreeqc.LoadDatabase (DatabaseFile)  'method loads database (returns number of errors)

     ' database dump to sheet Database (with switch True/False for users preference)
     If True Then  'allways fast version
        ' Import database file in Excel-sheet (fast version, requires MS Forms Library)
        ' Fast copy/paste from database file via Clipboard (with TAB = next column, new rows etc)
        Worksheets(DatabaseSheet).Activate
        ActiveSheet.Cells.ClearContents
        Open DatabaseFile For Input As #2
        Dim MyData2 As MSForms.DataObject  'from MS Forms Library
        Set MyData2 = New MSForms.DataObject
        MyData2.SetText Input(LOF(2), #2)
```

```
      MyData2.PutInClipboard
      Close #2
      ActiveSheet.Paste Destination:=Worksheets(DatabaseSheet).Range("A1")
    End If
Else  ' use DatabaseSheet
    ' From sheet Database into string for COM-module
    ' Copy content sheet Database to Clipboard
    Sheets(DatabaseSheet).Select
    Cells.Select
    Selection.Copy
    ' Copy Clipboard to String
    Dim IstringDB As String
    Dim MyData1 As MSForms.DataObject  'from MS Forms Library
    Set MyData1 = New MSForms.DataObject
    MyData1.GetFromClipboard
    IstringDB = MyData1.GetText   'or GetText(1)
    ' use string in COM-module
    phreeqc.LoadDatabaseString (IstringDB)  'method loads database (returns number of errors)
End If
' Iphreeqc generates an error if Database is not loaded in COM-object
' Iphreeqc generates an error if file Db cannot be opened or read (as proper PHREEQC database)
' Iphreeqc ignores the database file specified with DATABASE in the input file (.pqi)
' This is also shown in the warning in phreeqc.out:
'  DATABASE <filename>
'  WARNING: DATABASE keyword is ignored by IPhreeqc.


' Run PHREEQC with user input
If File_In <> "" Then  'use File_In if filled
    phreeqc.RunFile (File_In)  'method runs PHREEQC (returns number of errors)

    ' input file dump to sheet Input (with switch True/False for users preference)
    If True Then  'allways fast version
      ' Import input file in Excel-sheet (fast version, requires MS Forms Library)
      ' Fast copy/paste from database file via Clipboard (with TAB = next column, new rows etc)
      Worksheets(InputSheet).Activate
      ActiveSheet.Cells.ClearContents
      Open File_In For Input As #3
      Dim MyData3 As MSForms.DataObject  'from MS Forms Library
      Set MyData3 = New MSForms.DataObject
      MyData3.SetText Input(LOF(3), #3)
      MyData3.PutInClipboard
      Close #3
      ActiveSheet.Paste Destination:=Worksheets(InputSheet).Range("A1")
    End If
Else  ' use InputSheet as String

    Dim Istring As String
    ' Content from from InputSheet into Clipboard
    Worksheets(InputSheet).Activate
    Cells.Select
    Selection.Copy
    ' Copy Clipboard to String
    Dim MyData4 As MSForms.DataObject  'from MS Forms Library
    Set MyData4 = New MSForms.DataObject
    MyData4.GetFromClipboard
    Istring = MyData4.GetText   'or GetText(1)
    phreeqc.RunString (Istring) 'method runs PHREEQC (returns number of errors)
End If


' Save output string in phreeqc.out sheet (fast version, requires MS Forms Library)
' Fast copy/paste from outputstring via Clipboard (with TAB = next column, new rows etc)
Worksheets("phreeqc.out").Activate
```

```
  ActiveSheet.Cells.ClearContents
  Dim MyData As MSForms.DataObject  'from MS Forms library
  Set MyData = New MSForms.DataObject
  MyData.SetText phreeqc.GetOutputString()
  MyData.PutInClipboard
  ActiveSheet.Paste Destination:=Worksheets("phreeqc.out").Range("A1")


  ' Save Selected_Output data to output sheets Output, Output2, Output 3 etc.
  Dim num, nums
  nums = phreeqc.GetNthSelectedOutputUserNumberList()
  For Each num In nums
    phreeqc.CurrentSelectedOutputUserNumber = num
    If num = "1" Then num = ""  'Name OutputSheet is Output (n=1) else Output<n>
    OutputSheet = "Output" & num
    Worksheets(OutputSheet).Activate
    ActiveSheet.Cells.ClearContents
    ' check for empty output array to avoid Excel error in Range copy
    If phreeqc.GetSelectedOutputValue(0, 0) <> "" Then
      arr = phreeqc.GetSelectedOutputArray()
      Range(Cells(1, 1), Cells(phreeqc.RowCount, phreeqc.ColumnCount)) = arr
    End If
  Next


  ' Messages
  If Server = False Then  'no messageboxes in server
    endtime = Timer
    MsgBox ("Phreeqc ran successfully." + Chr(13) + "IPreeqcCOM " + phreeqc.Version + Chr(13) + "End of
Run after  " + Format((endtime - starttime), "#,##0.00 "" Seconds."""))
  End If
  If phreeqc.GetWarningString() <> "" Then
    Worksheets("Messages").Activate
    Cells(1, 1) = "Phreeqc errors: " & phreeqc.GetWarningString()
    If Server = False Then  'no messageboxes in server
      MsgBox phreeqc.GetWarningString()  'PHREEQC warnings (from COM-object)
    End If
  End If


  ' Show Excel return sheet
  On Error Resume Next                  ' Prevents VBA-error if ReturnSheet does not exist
  Worksheets(ReturnSheet).Activate
Exit Sub


ErrHandler:
  If Server = False Then  'no messageboxes in server
    If phreeqc.GetErrorString() = "" Then
      MsgBox ("Iphreeqc error:" + Chr$(13) + "Excel-VBA error")
    Else
      MsgBox ("Phreeqc errors: " + Chr$(13) + phreeqc.GetErrorString())
    End If
  End If
  Worksheets("Messages").Activate
  If phreeqc.GetErrorString() = "" Then
    Cells(3, 1) = "Iphreeqc error:" + Chr$(13) + "Excel-VBA error"
  Else
    Cells(3, 1) = "Phreeqc errors: " + Chr$(13) + phreeqc.GetErrorString()
  End If

End Sub
```

LABS AND TESTS

Using PHREEQC in PHREEQXCEL

Lab 2.1	Running PHREEQC in PHREEQXCEL	
Lab 2.2	Running PHREEQXCEL apps	

Drinking water in PHREEQC

Lab 3.1	PHREEQXCEL for Pure water	with Test
Lab 3.2	PHREEQC input for SOLUTION	with Test
Lab 3.3	PHREEQXCEL input for SOLUTION	with Test
Lab 3.4	PHREEQXCEL input for SOLUTION_SPREAD	with Test
Lab 3.5	PHREEQC output for SOLUTION	with Tests

Controlling output

Lab 4.1	User controlled output	with Test
Lab 4.2	Tabulated output from PHREEQC	with Test
Lab 4.3	Multiple output streams from PHREEQC	with Test
Lab 4.4	User defined functions in PHREEQC	with Test
Lab 4.5	Output processing in Excel	with Test
Lab 4.6	User graphs in PHREEQXCEL	with Test

Water treatment

Lab 5.1	Concentrations, density and charge balance	with Test
Lab 5.2	Electrical Conductivity and Total Dissolved Solids	with Test
Lab 5.3	Mixing water	
Lab 5.4	Dosing of chemicals with REACTION	with Test
Lab 5.5	Dosing of chemicals with MIX	with Test
Lab 5.6	Reaction with solids in EQUILIBRIUM_PHASES	
Lab 5.7	Gas transfer with GAS_PHASE	

Groundwater and redox reactions

Lab 6.1	Groundwater in PHREEQC	with Test
Lab 6.2	Groundwater well fields	
Lab 6.3	Groundwater treatment with aeration and filtration	

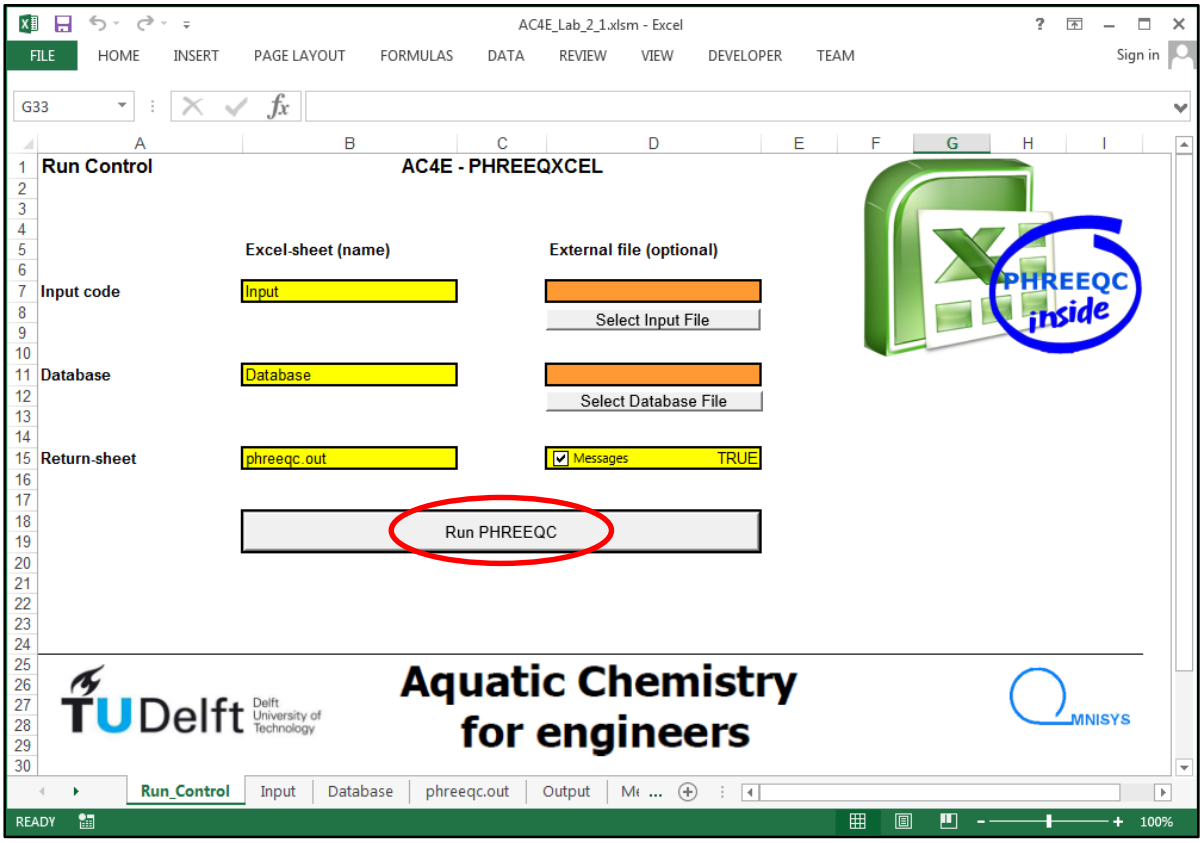
Answer sheets for Labs

Sheets for students

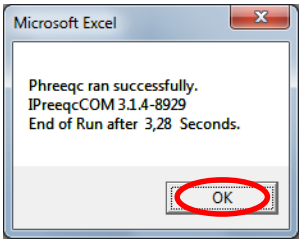
Sheets with correct answers

Lab 2.1 Running PHREEQC in PHREEQXCEL

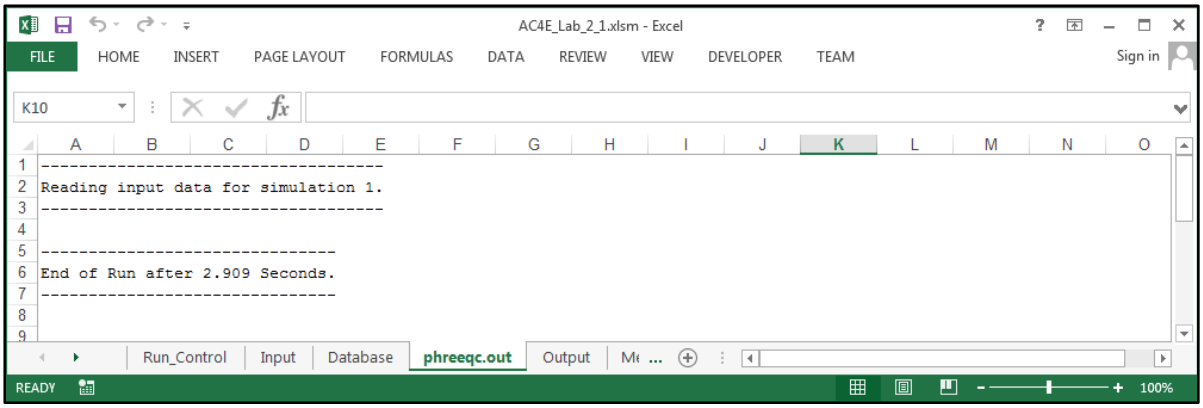
Open AC4E_Lab_2_1.xlsm.
Enable Macros, if requested.
Look to the content of each sheet, and notice that all sheets are empty, except for sheet Database, which includes stimela.dat, the default database for water treatment in PHREEQC.
Click on 'Run PHREEQC' to start the PHREEQC calculation:



After completion of the Run, the user is informed by an Excel message, since the Messages check box on Run_Control is set on TRUE.
Click OK to continue:



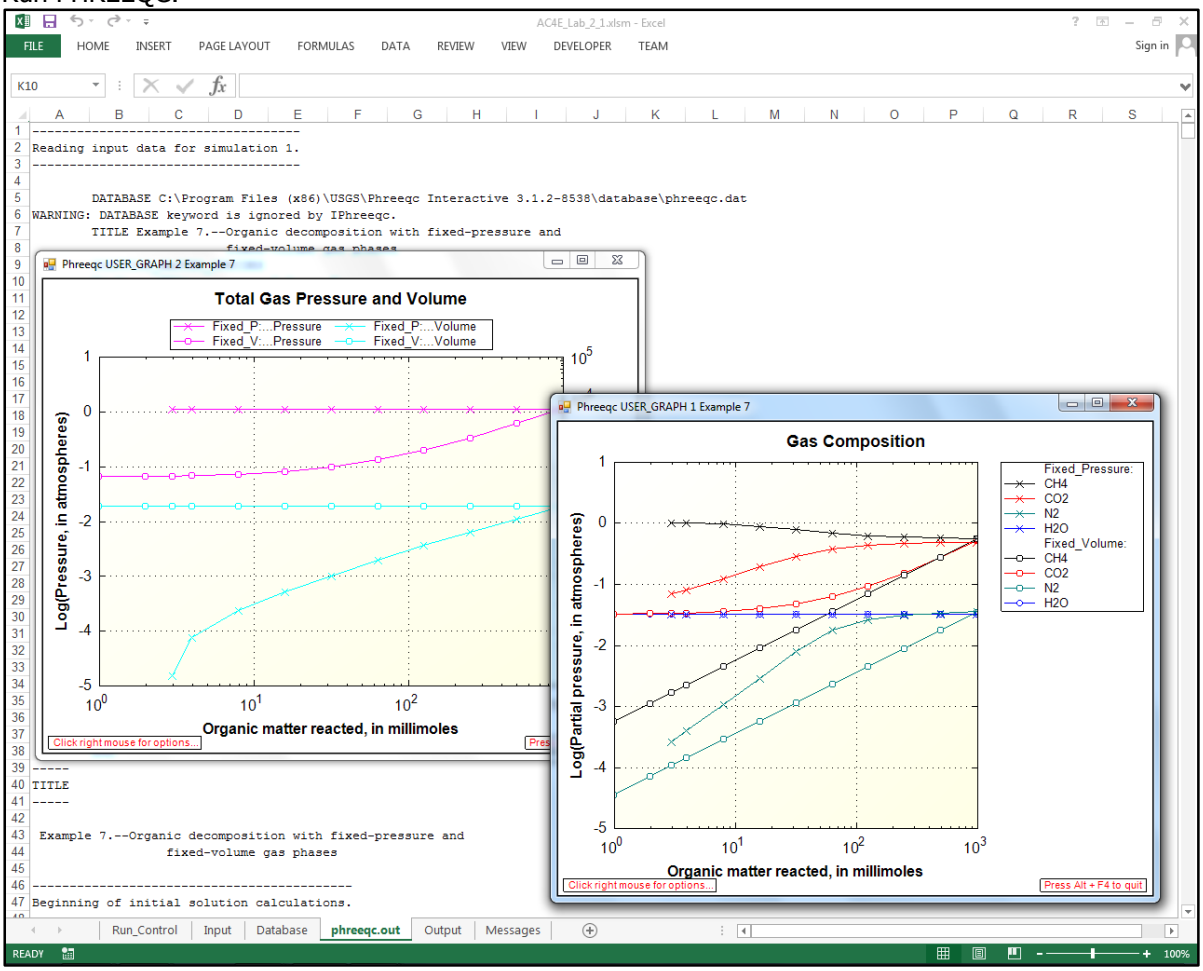
The Return-sheet phreeqc.out is shown, containing the PHREEQC PRINT results.
The 'empty' content of the sheet Input code results in only 'Reading input data for simulation 1' followed by 'End of Run after x Seconds.' :



Go to sheet Run_Control.
Set Messages to FALSE, and Run PHREEQC again.
Notice that Run takes less running time since the IphreeqcCOM object was already loaded. The End of Run gives the time after the first start of this COM object.

Go to sheet Run_Control.
Set Return sheet to 'Run_Control', and Run PHREEQC again.
Notice that actual Run is hardly notice by lacking the Excel Message box of completion of the Run.

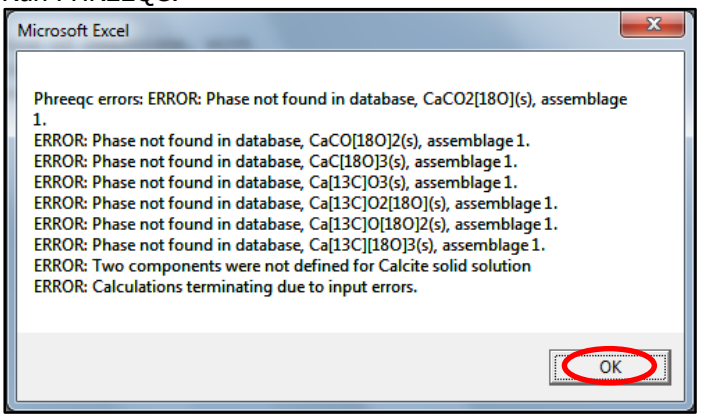
USGS: Example 7
Ref: http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/phreeqc3-html/phreeqc3-62.htm
Set Return sheet to 'phreeqc.out'.
Select an Input file by clicking the button 'Select Input File'. Select 'ex7.pqi'.
Run PHREEQC:



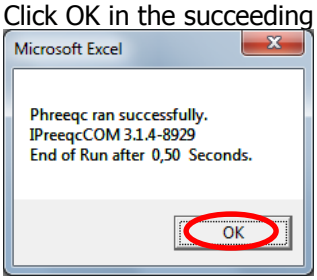
Notice the two user graphs, and close both graphs.
Observe the content of sheets phreeqc.out (=ex7.pqo), Output (=ex7.sel), Messages (=phreeqc.log and Warnings in ex7.pqo) and Input (=ex7.pqi).
Select the sheet Run_Control, and empty the cell D7 (=InputFile). Run PHREEQC.
The result is equal to previous run since the content of file ex7.pqi is stored in the sheet Input.
Close both graphs.

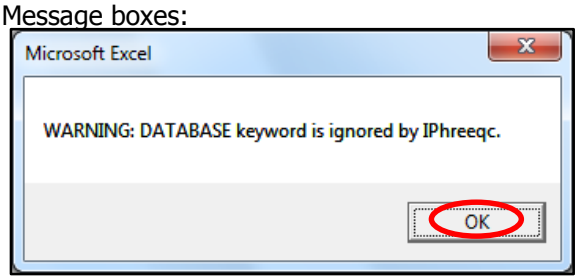
USGS: Example 20a
Ref: http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/phreeqc3-html/phreeqc3-75.htm

Select sheet Run_Control.
Type in Input code / External file: ex20a.pqi (assuming this file is located in the map of the .xlsm file), or select this file via button 'Select Input File'.
Set Messages to FALSE.
Run PHREEQC:



Click OK to continue.
Select sheet Run_Control.
Type in Database / External file: iso.dat (assuming this file is located in the map of the .xlsm file), or select this file via button 'Select Database File'.
Run PHREEQC.
Click OK in the succeeding Message boxes:





IphreeqcCOM uses the database set in the sheet Run_Control , instead of the file defined by the Keyword DATABASE in the input code.
Observe the content of sheets Database (=iso.dat), phreeqc.out (=ex20a.pqo), Output (=empty), Messages (=phreeqc.log and Warnings in ex20a.pqo) and Input (=ex20a.pqi).

This examples demonstrates that PHREEQC input code in written for a specific database, as defined by the keyword DATABASE. PHREEQC databases are not freely interchangeable they differs in (names and number of) elements, species, phases etc.

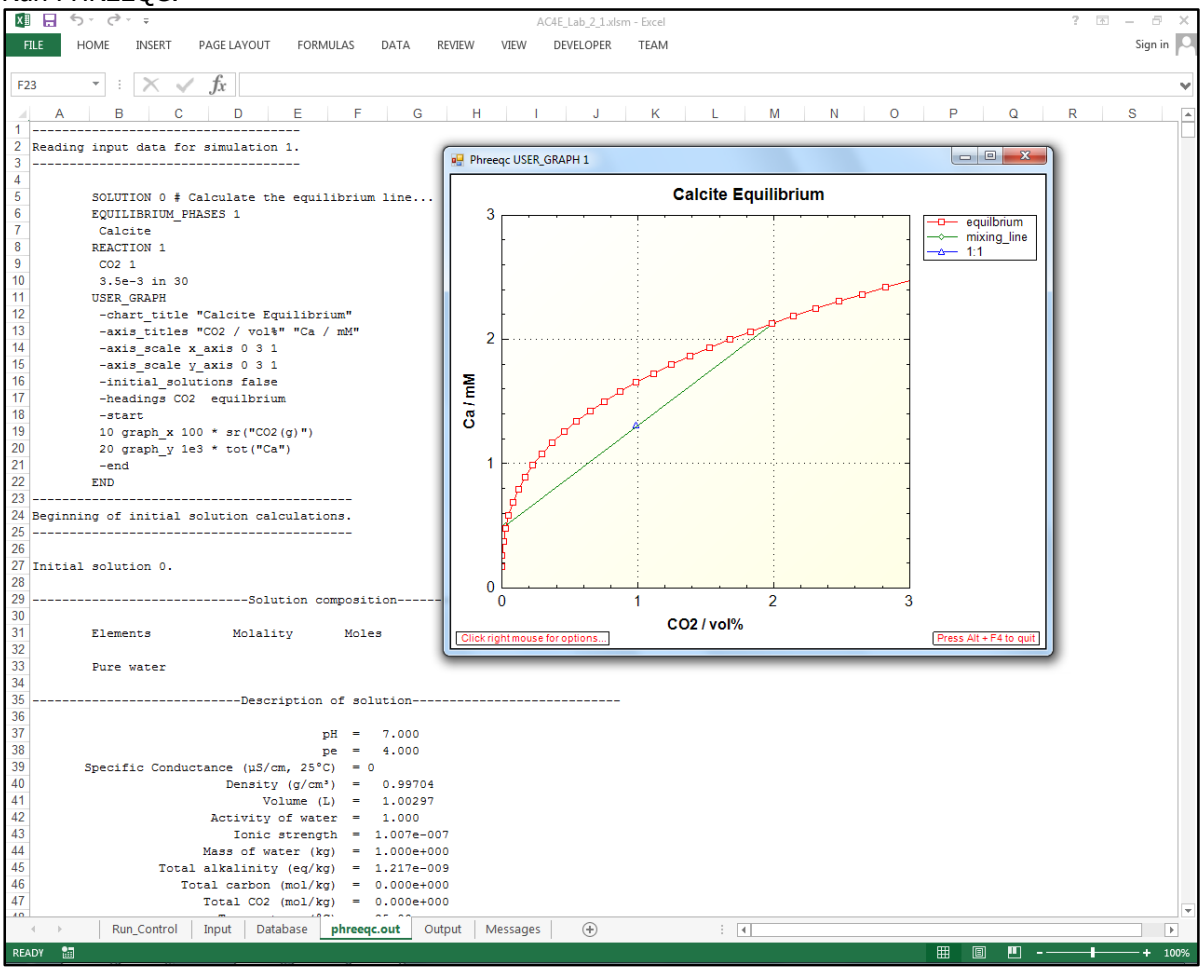
The content of sheet Database is overwritten by the content of iso.dat.
This behaviour could be avoided by creating a new sheet in Excel, with the name Database2 (or iso.dat), and defining on Run_Control the sheet Database as Database2 (or iso.dat).

Multiple databases in a PHREEQXCEL file might be considered in case the input code properly functions with the databases included. This scenario is beneficial for comparing results of different databases.
(Suggestion: repeat this example by adding and using an additional Excel sheet for iso.dat)

To restore the original content of the sheet Database:
- select sheet Run_Control
- empty the content on cell D7 (=InputFile)
- fill cell D11 (=DatabaseFile) with 'stimela.dat'
- empty the content of sheet Input
- Run Phreeqc,
- click OK
- empty the cell D11 (=DatabaseFile).

Appelo: Example 5.5
Ref: http://www.hydrochemistry.eu/exmpls/calcite.html
Ref: http://www.hydrochemistry.eu/a&p/5/ex_5_5.phr

Select sheet Run_Control.
Type in Input code / External file: ex_5_5.phr (assuming this file is located in the map of the .xlsm file), or select this file via button 'Select Input File'.
Set Return sheet to phreeqc.out.
Set Messages to FALSE.
Run PHREEQC:



Observe the content of sheets Input (=ex_5_5.phr), phreeqc.out (=ex_5_5.out), Output (=empty), Messages (=empty).

Select sheet Run_Control.
Empty the content on cell D7 (=InputFile).
Run PHREEQC.
The same result is obtained as the input code in already in sheet Input, and no other external Input file has been specified.
Close window User_Graph.

Select and empty the content of sheet Input
Select sheet Run_Control.
Set Return sheet on phreeqc.out.
Set Messages to TRUE.
Run PHREEQC.

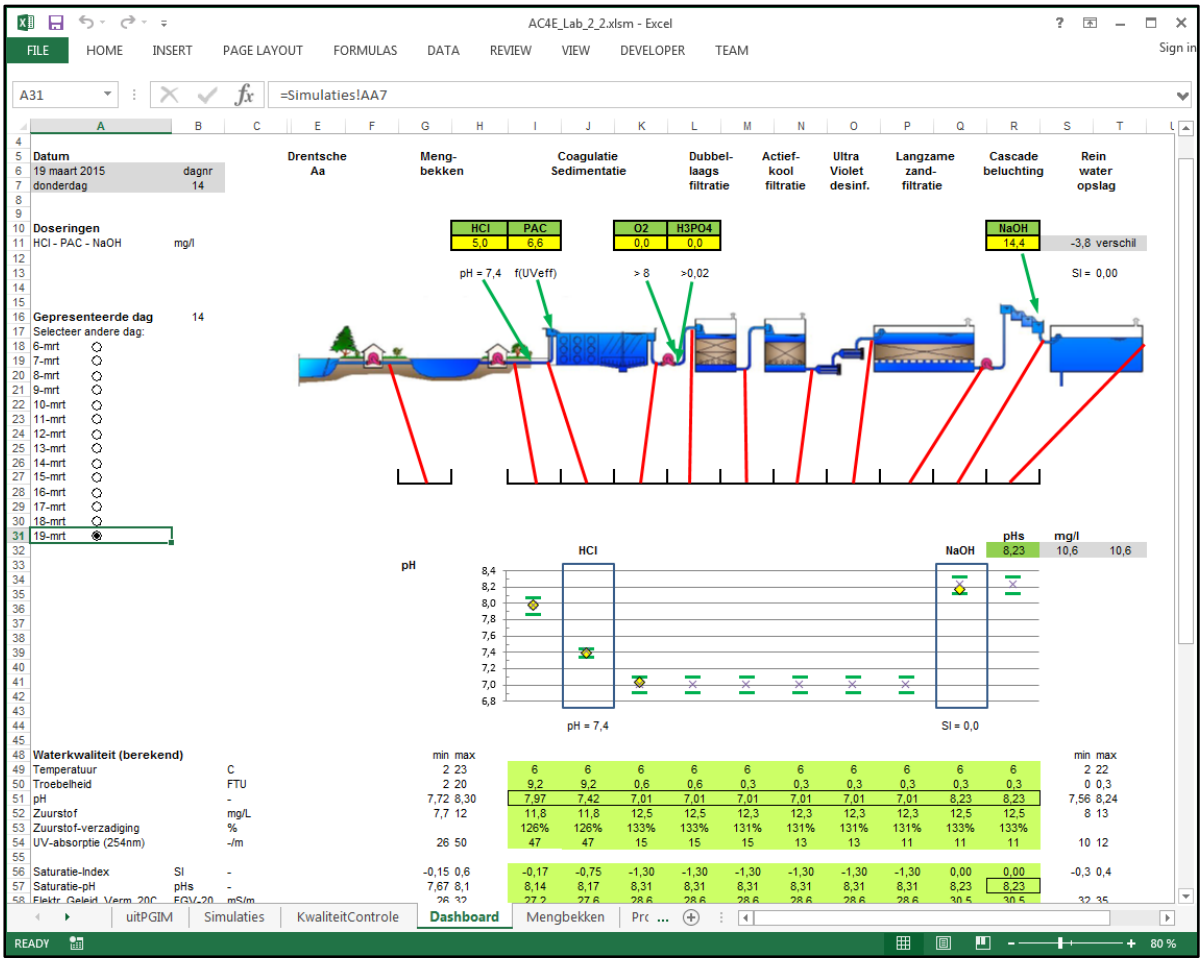
The initial result of this Lab is obtained.

Note 1:
The present version of 'AC4E-phreeqxcel.xlsm' does not allow for the use of selected output for the creation of input code for #INCLUDE.
This functionality might be obtained by multiple running of the IPhreeqcCOM-object, or by using the AccumulateLine Method of IPhreeqcCOM, or by using different selected output files with the CurrentSelectedOutputUserNumber Property of IPhreeqcCOM.

Note 2:
Appelo uses a modified version of the database phreeqc.dat, in which ammonium (NH_4^+) is defined as redox-uncoupled or inert $AmmH^+$ ('element' Amm = NH_3) and the element N(-3) is absent. USGS calls this database amm.dat.
PHREEQXCEL uses stimela.dat as default database, which includes both definitions and therefore allows for using input files from both sources.

Lab 2.2 Running PHREEQXCEL apps

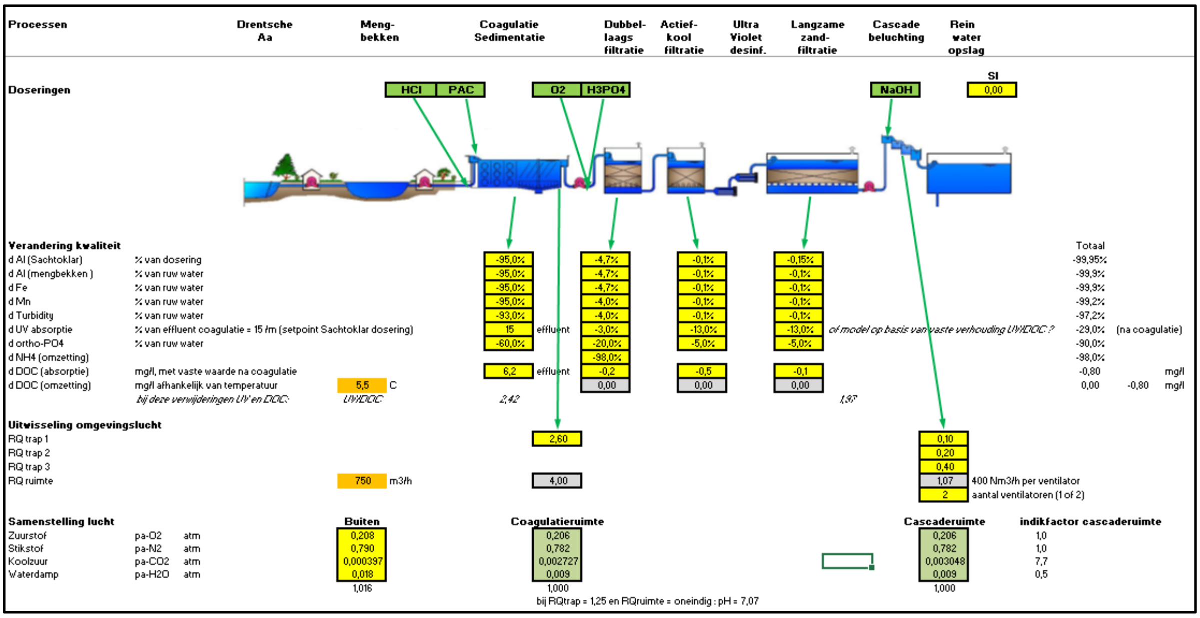
Open AC4E_Lab_2_2.xlsm.
Enable Macros, if requested.
Select sheet 'Dashboard'.
This sheet shows a process scheme for a surface water treatment plant for drinking water produced from river water after passing an equalizing reservoir with a detention time of some 60 days.
The model calculates the water quality (macro-parameters) after each process step in the treatment plant for the last 14 days (average day-values).



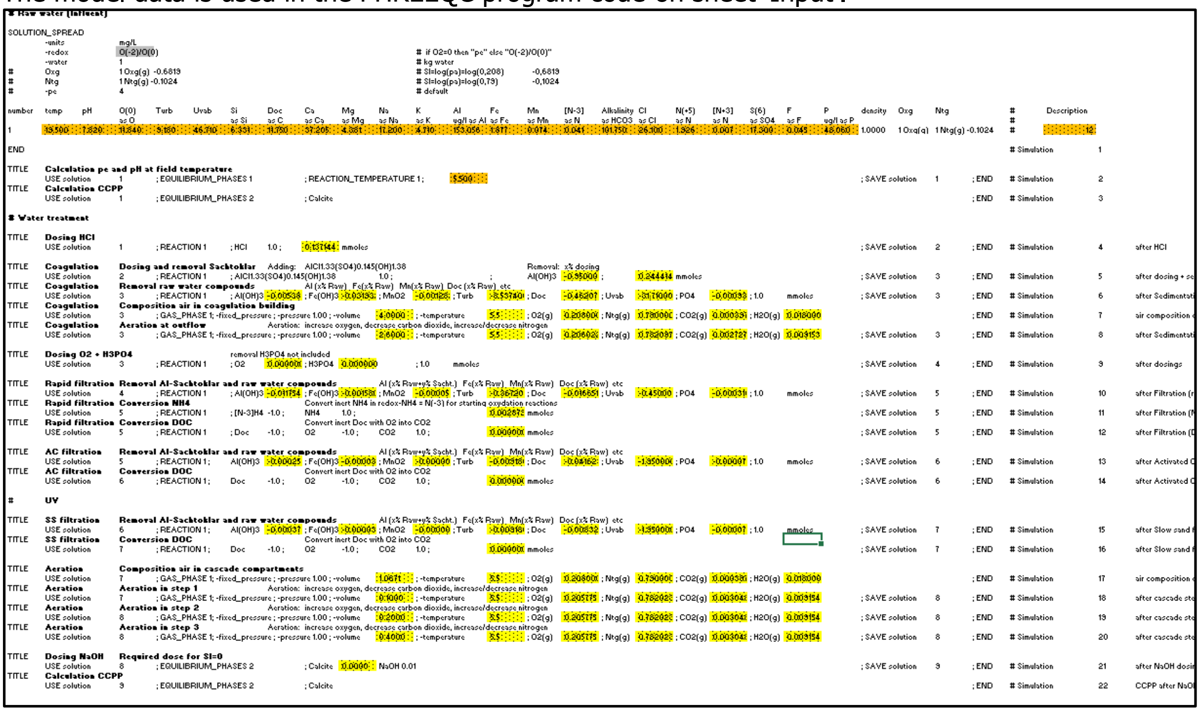
Treatment process
The 'Dashboard' sheet shows the treatment process scheme, with the chemical dosing points and the laboratory sample points. Below the process scheme the water quality at each sample point is shown (31 parameters). The value for pH is shown graphically, with calculated values, measured values (day-average values from inline measurements) as well as the acceptable operational range (min-max values).
At start-up the values for the last of the 14-day time span is shown.

Click on the first (upper) day, at the left site of the process scheme. This initiates the model calculation for the selected day, after which the data on this sheet is updated.

The process parameters used in this model are presented on sheet 'Proces'. Select this sheet and overview the data and set-up. This example model uses simple removal efficiencies based on historical performance of the plant.

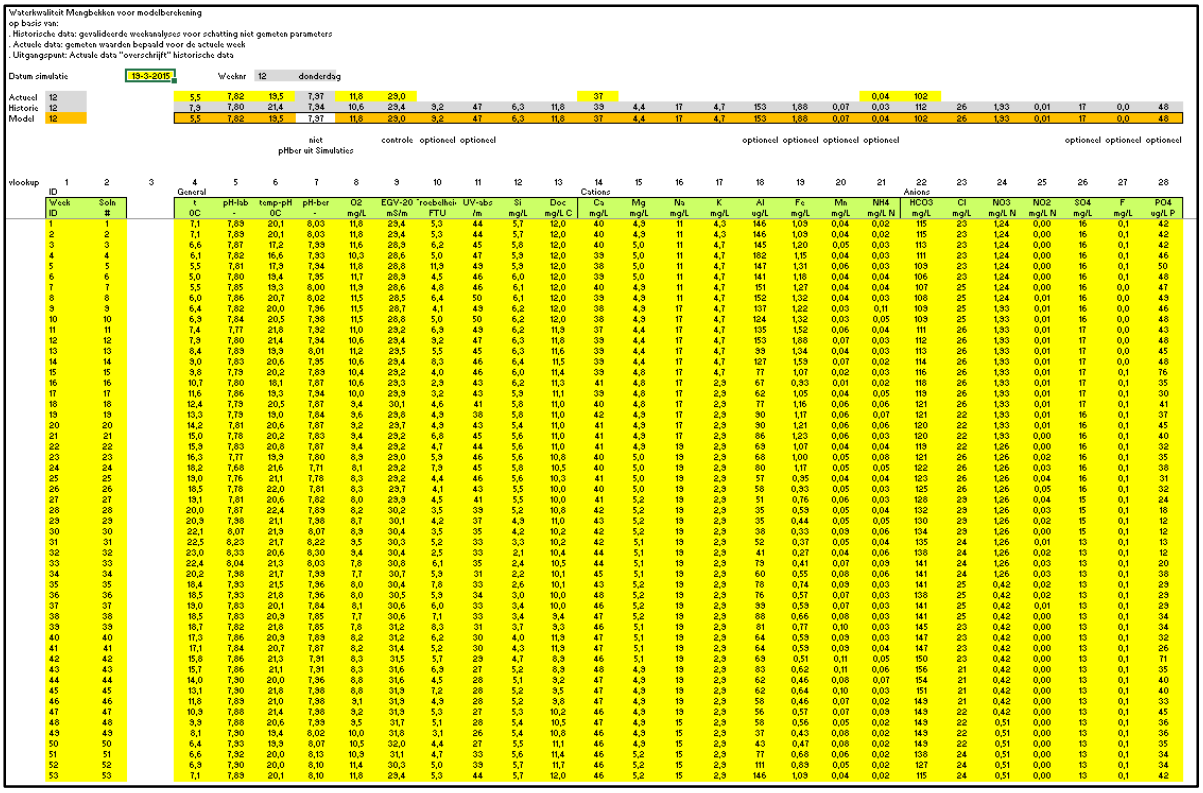


The model data is used in the PHREEQC program code on sheet 'Input'.



The orange cells in the program code show the raw water quality (effluent equalization reservoir) obtained from the sheet 'Mengbekken'. The yellow cells show the process parameters from the sheet 'Proces'.
The treatment process is modelled in 22 calculation steps ('Simulations' in PHREEQC nomenclature).

Select sheet 'Mengbekken'. Overview how the most recent water quality measurements for 9 parameters are completed and compared with historical data for 25 parameters. Previous model validations has shown that this combination of actual and historical data is adequate for the required accuracy of the model.



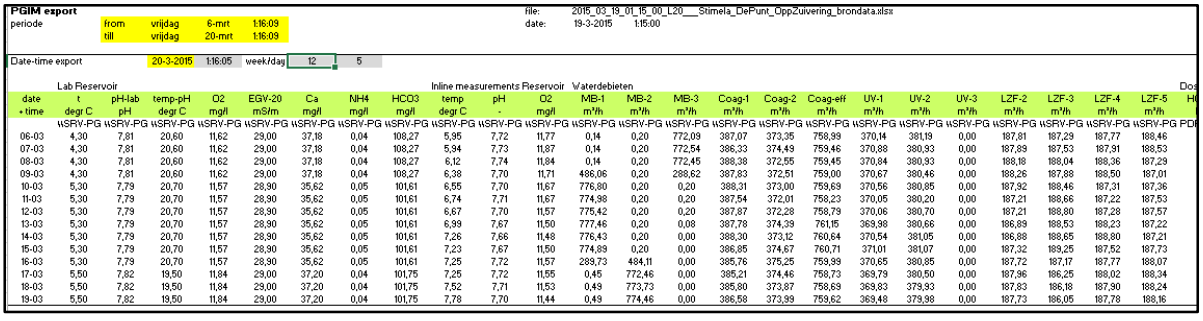
Waterkwaliteit Mengbekken voor modelberekening
op basis van:
. Historische data: gevalideerde weeksanalyses voor schatting niet gemeten parameters
. Actuele data: gemeten waarden bepaald voor de actuele week
. Uitgangspunt: Actuele data "overschrijft" historische data

Datum simulatie: 19-3-2015 Weeknr 12 donderdag

Actueel	12			5,5	7,82	19,5	7,97	11,8	29,0						37							0,04	102						
Historic	12			7,3	7,80	21,4	7,94	10,6	29,4	9,2	47	6,3	11,8	39	4,4	17	4,7	153	1,88	0,07	0,03	112	26	1,93	0,01	17	0,0	48
Model	12			5,5	7,82	19,5	7,97	11,8	29,0	9,2	47	6,3	11,8	37	4,4	17	4,7	153	1,88	0,07	0,04	102	26	1,93	0,01	17	0,0	48
						niet pHber uit Simulatics		controls	optioneel	optioneel							optioneel	optioneel	optioneel	optioneel				optioneel	optioneel	optioneel			
vlookup	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	
	ID			General										Cations								Anions							
	Week	Soln		t	pH-lab	temp-pH	pH-ber	O2	EGV-20	Troebelheid	UV-abs	Si	Doc	Ca	Mg	Na	K	Al	Fe	Mn	NH4	HCO3	Cl	NO3	NO2	SO4	F	PO4	
	ID	#		0C	-	0C	-	mg/L	mS/m	FTU	/m	mg/L	mg/L C	mg/L	mg/L	mg/L	mg/L	ug/L	mg/L	mg/L	mg/L N	mg/L	mg/L	mg/L N	mg/L N	mg/L	mg/L	ug/L P	
	1	1		7,1	7,89	20,1	8,03	11,8	29,4	5,3	44	5,7	12,0	40	4,9	11	4,3	146	1,09	0,04	0,02	115	23	1,24	0,00	16	0,1	42	
	2	2		7,1	7,89	20,1	8,03	11,8	29,4	5,3	44	5,7	12,0	40	4,9	11	4,3	146	1,09	0,04	0,02	115	23	1,24	0,00	16	0,1	42	
	3	3		6,6	7,87	17,2	7,99	11,6	28,9	6,2	45	5,8	12,0	40	5,0	11	4,7	145	1,20	0,05	0,03	113	23	1,24	0,00	16	0,1	42	
	4	4		6,1	7,82	16,6	7,93	10,3	28,6	5,0	47	5,9	12,0	39	5,0	11	4,7	182	1,15	0,04	0,03	111	23	1,24	0,00	16	0,1	46	
	5	5		5,5	7,81	17,9	7,94	11,8	28,8	11,9	49	5,9	12,0	38	5,0	11	4,7	147	1,31	0,06	0,03	109	23	1,24	0,00	16	0,1	50	
	6	6		5,0	7,80	19,4	7,95	11,7	28,9	4,5	46	6,0	12,0	39	5,0	11	4,7	141	1,16	0,04	0,04	106	23	1,24	0,00	16	0,1	48	
	7	7		5,5	7,85	19,3	8,00	11,9	28,6	4,8	46	6,1	12,0	40	4,9	11	4,7	151	1,27	0,04	0,04	107	25	1,24	0,00	16	0,0	47	
	8	8		6,0	7,86	20,7	8,02	11,5	28,5	6,4	50	6,1	12,0	39	4,9	11	4,7	152	1,32	0,04	0,03	108	25	1,24	0,01	16	0,0	49	
	9	9		6,4	7,82	20,0	7,96	11,5	28,7	4,1	49	6,2	12,0	38	4,9	17	4,7	137	1,22	0,03	0,11	109	25	1,93	0,01	16	0,0	46	
	10	10		6,9	7,84	20,5	7,98	11,5	28,8	5,0	50	6,2	12,0	38	4,9	17	4,7	124	1,32	0,03	0,05	109	25	1,93	0,01	16	0,0	48	
	11	11		7,4	7,77	21,8	7,92	11,0	29,2	6,3	49	6,2	11,9	37	4,4	17	4,7	135	1,52	0,06	0,04	111	26	1,93	0,01	17	0,0	43	
	12	12		7,3	7,80	21,4	7,94	10,6	29,4	9,2	47	6,3	11,8	39	4,4	17	4,7	153	1,88	0,07	0,03	112	26	1,93	0,01	17	0,0	48	
	13	13		8,4	7,83	19,9	8,01	11,2	29,5	5,5	45	6,3	11,6	39	4,4	17	4,7	99	1,34	0,04	0,03	113	26	1,93	0,01	17	0,0	45	
	14	14		9,0	7,83	20,6	7,95	10,6	29,4	8,3	46	6,4	11,5	39	4,4	17	4,7	127	1,59	0,07	0,02	114	26	1,93	0,01	17	0,0	48	
	15	15		9,8	7,79	20,2	7,89	10,4	29,2	4,0	46	6,0	11,4	39	4,8	17	4,7	77	1,07	0,02	0,03	116	26	1,93	0,01	17	0,1	76	
	16	16		10,7	7,80	18,1	7,87	10,6	29,3	2,9	43	6,2	11,3	41	4,8	17	2,9	67	0,93	0,01	0,02	118	26	1,93	0,01	17	0,1	35	
	17	17		11,6	7,86	19,3	7,94	10,0	29,9	3,2	43	5,9	11,1	39	4,8	17	2,9	62	1,05	0,04	0,05	119	26	1,93	0,01	17	0,1	30	
	18	18		12,4	7,79	20,5	7,87	9,4	30,1	4,6	41	5,8	11,0	40	4,8	17	2,9	77	1,16	0,06	0,06	121	26	1,93	0,01	17	0,1	41	
	19	19		13,3	7,79	19,0	7,84	9,6	29,8	4,9	38	5,8	11,0	42	4,9	17	2,9	90	1,17	0,06	0,07	121	22	1,93	0,01	16	0,1	37	
	20	20		14,2	7,81	20,6	7,87	9,2	29,7	4,9	43	5,4	11,0	41	4,9	17	2,9	90	1,21	0,06	0,06	120	22	1,93	0,01	16	0,1	45	
	21	21		15,0	7,78	20,2	7,83	9,4	29,2	6,8	45	5,6	11,0	41	4,9	17	2,9	86	1,23	0,06	0,03	120	22	1,93	0,00	16	0,1	40	
	22	22		15,9	7,83	20,8	7,87	9,4	29,2	4,7	44	5,6	11,0	41	4,9	19	2,9	69	1,07	0,04	0,04	119	22	1,26	0,00	16	0,1	32	
	23	23		16,3	7,77	19,9	7,80	8,9	29,0	5,9	45	5,6	10,8	40	5,0	19	2,9	68	1,00	0,05	0,08	121	26	1,26	0,02	16	0,1	35	
	24	24		16,2	7,68	21,6	7,71	8,1	29,2	7,9	45	5,8	10,5	40	5,0	19	2,9	60	1,17	0,05	0,05	122	26	1,26	0,03	16	0,1	38	
	25	25		19,0	7,76	21,1	7,78	8,3	29,2	4,4	46	5,6	10,3	41	5,0	19	2,9	57	0,95	0,04	0,04	123	26	1,26	0,04	16	0,1	31	
	26	26		18,5	7,78	22,0	7,81	8,3	29,7	4,1	43	5,5	10,0	40	5,0	19	2,9	58	0,93	0,05	0,03	125	26	1,26	0,05	16	0,1	32	
	27	27		19,1	7,81	20,6	7,82	8,0	29,9	4,5	41	5,5	10,0	41	5,2	19	2,9	51	0,76	0,06	0,03	128	29	1,26	0,04	15	0,1	24	
	28	28		20,0	7,87	22,4	7,83	8,2	30,2	3,5	39	5,2	10,8	42	5,2	19	2,9	35	0,59	0,05	0,04	132	29	1,26	0,03	15	0,1	18	
	29	29		20,3	7,86	21,1	7,86	8,7	30,1	4,2	37	4,9	11,0	43	5,2	19	2,9	35	0,44	0,05	0,05	130	29	1,26	0,02	15	0,1	12	
	30	30		22,1	8,07	21,9	8,07	8,9	30,4	3,5	35	4,2	10,2	42	5,2	19	2,9	38	0,33	0,09	0,06	134	29	1,26	0,00	15	0,1	12	
	31	31		22,5	8,23	21,7	8,22	9,5	30,3	5,2	33	3,3	10,2	42	5,1	19	2,9	52	0,37	0,05	0,04	135	24	1,26	0,01	13	0,1	13	
	32	32		23,0	8,33	20,6	8,30	9,4	30,4	2,5	33	2,1	10,4	44	5,1	19	2,9	41	0,27	0,04	0,06	138	24	1,26	0,02	13	0,1	12	
	33	33		22,4	8,04	21,3	8,03	7,8	30,8	6,1	35	2,4	10,5	44	5,1	19	2,9	79	0,41	0,07	0,09	141	24	1,26	0,03	13	0,1	20	
	34	34		20,2	7,86	21,7	7,93	7,7	30,7	5,9	31	2,2	10,1	45	5,1	19	2,9	60	0,55	0,08	0,06	141	24	1,26	0,03	13	0,1	38	
	35	35		18,4	7,93	21,5	7,96	8,0	30,4	7,8	33	2,6	10,1	43	5,2	19	2,9	78	0,74	0,09	0,03	141	25	0,42	0,02	13	0,1	29	
	36	36		18,5	7,83	21,8	7,96	8,0	30,5	5,9	34	3,0	10,0	48	5,2	19	2,9	76	0,57	0,07	0,03	138	25	0,42	0,02	13	0,1	23	
	37	37		19,0	7,83	20,1	7,84	8,1	30,6	6,0	33	3,4	10,0	46	5,2	19	2,9	99	0,59	0,07	0,03	141	25	0,42	0,01	13	0,1	29	
	38	38		18,5	7,83	20,9	7,85	7,7	30,6	7,1	33	3,4	9,4	47	5,2	19	2,9	88	0,66	0,08	0,03	141	25	0,42	0,00	13	0,1	34	
	39	39		18,7	7,82	21,8	7,85	7,6	31,2	8,3	31	3,7	9,3	46	5,1	19	2,9	81	0,77	0,10	0,03	145	23	0,42	0,00	13	0,1	34	
	40	40		17,3	7,86	20,9	7,89	8,2	31,2	6,2	30	4,0	11,3	47	5,1	19	2,9	64	0,59	0,09	0,03	147	23	0,42	0,00	13	0,1	32	
	41	41		17,1	7,84	20,7	7,87	8,2	31,4	5,2	30	4,3	11,9	47	5,1	19	2,9	64	0,59	0,09	0,04	147	23	0,42	0,00	13	0,1	26	
	42	42		15,8	7,86	21,3	7,91	8,3	31,5	5,7	29	4,7	8,9	46	5,1	19	2,9	69	0,51	0,11	0,05	150	23	0,42	0,00	13	0,1	71	
	43	43		15,7	7,86	21,1	7,91	8,3	31,6	6,9	27	5,2	8,9	48	4,9	19	2,9	83	0,62	0,11	0,06	156	21	0,42	0,00	13	0,1	35	
	44	44		14,0	7,90	20,0	7,96	8,8	31,6	4,5	28	5,1	9,2	47	4,9	19	2,9	62	0,46	0,08	0,07	154	21	0,42	0,00	13	0,1	40	
	45	45		13,1	7,90	21,8	7,96	8,8	31,9	7,2	28	5,2	9,5	47	4,9	19	2,9	62	0,64	0,10	0,03	151	21	0,42	0,00	13	0,1	40	
	46	46		11,8	7,89	21,0	7,98	9,1	31,9	4,9	28	5,2	9,8	47	4,9	19	2,9	58	0,46	0,07	0,02	149	21	0,42	0,00	13	0,1	33	
	47	47		10,9	7,88	21,4	7,96	9,2	31,9	5,3	27	5,3	10,2	46	4,9	19	2,9	56	0,57	0,07	0,03	149	22	0,42	0,00	13	0,1	45	
	48	48		9,9	7,88	20,6	7,93	9,5	31,7	5,1	28	5,4	10,5	47	4,9	15	2,9	59	0,56	0,05	0,02	149	22	0,51	0,00	13	0,1	36	
	49	49		8,1	7,90	19,4	8,02	10,0	31,8	3,1	26	5,4	10,8	46	4,9	15	2,9	37	0,43	0,08	0,02	149	22	0,51	0,00	13	0,1	36	
	50	50		6,4	7,93	19,9	8,07	10,5	32,0	4,4	27	5,5	11,1	46	4,9	15	2,9	43	0,47	0,08	0,02	149	22	0,51	0,00	13	0,1	35	
	51	51		6,6	7,92	20,0	8,13	10,9	31,1	4,7	33	5,6	11,4	46	5,2	15	2,9	77	0,66	0,06	0,02	138	24	0,51	0,00	13	0,1	34	
	52	52		6,9	7,90	20,0	8,10	11,4	30,3	5,0	39	5,7	11,7	46	5,2	15	2,9	111	0,89	0,05	0,02	127	24	0,51	0,00	13	0,1	34	
	53	53		7,1	7,89	20,1	8,10	11,8	29,4	5,3	44	5,7	12,0	46	5,2	15	2,9	146	1,09	0,04	0,02	115	24	0,51	0,00	13	0,1	42	

Simulations

In previous description the model calculation for a single day has been given. Simulations for a 14 days period are based on a data export (day-average values) from the process control computer, as presented on sheet 'uit PGIM'. For all 14 days, day-average values for 8 weekly measured water quality parameters from the reservoir, 27 online water quality measurements and 22 online flow measurements (9 for water and 13 for dosed chemicals) are imported.
This data update is programmed in Excel-VBA code, which checks for the most recent data-export file, loads the data and starts the simulation calculations for all 14 days, after start-up of the Excel file.

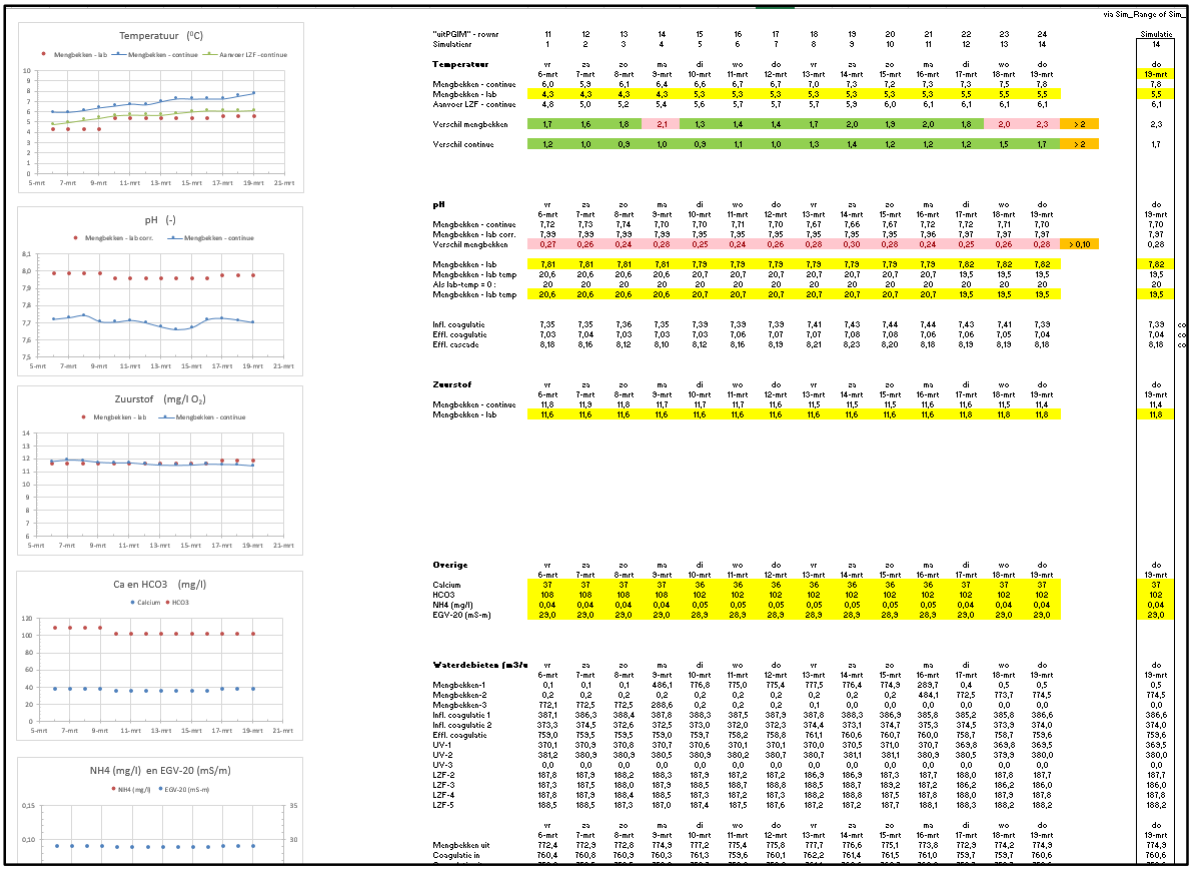


PGIM export file: 2015_03_19_01_15_00_L20___Stimela_DePunt_OppZuivering_brondata.mlsx
periode from vrijdag 6-mrt 1:16:09 date: 19-3-2015 1:15:00
till vrijdag 20-mrt 1:16:09

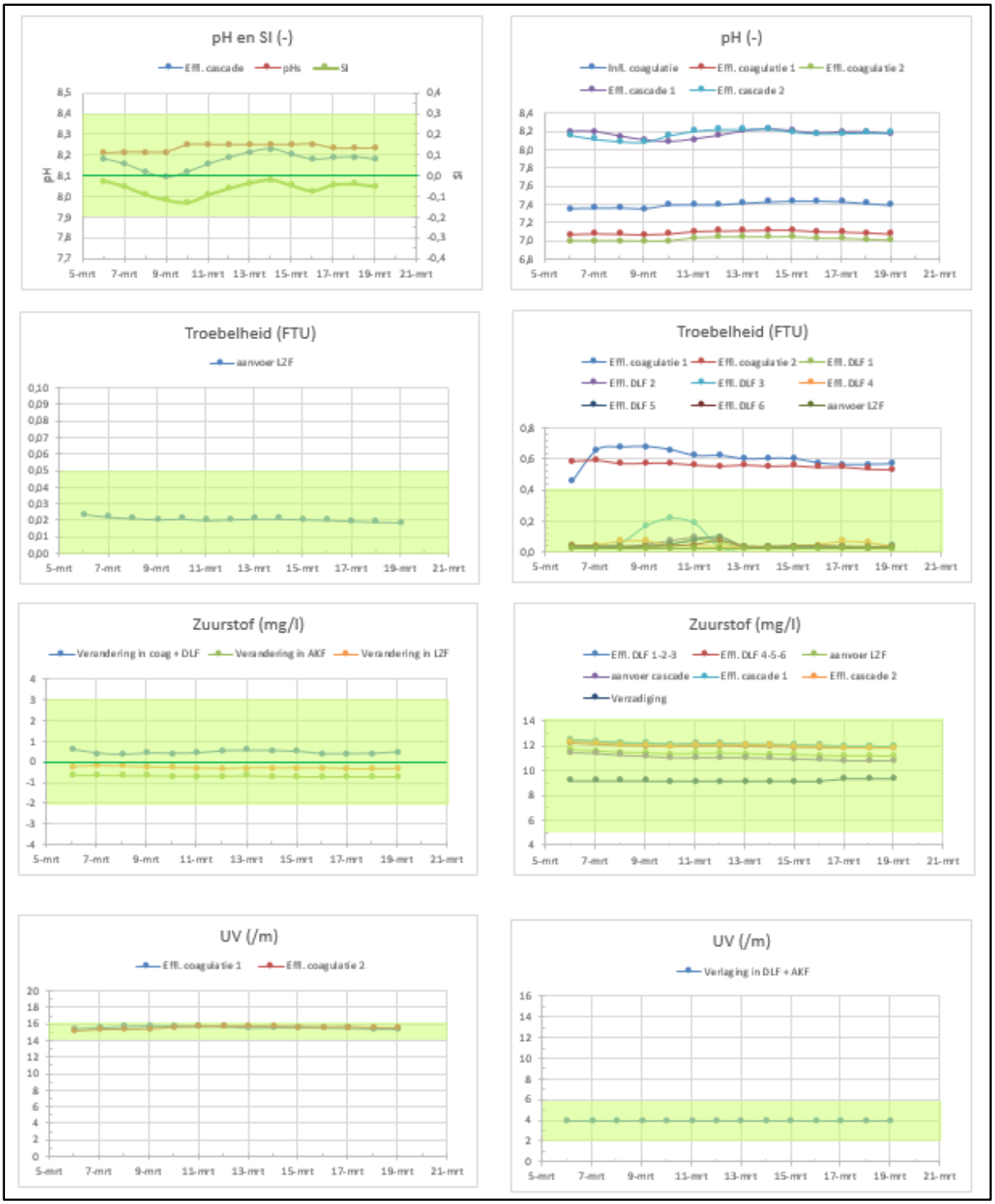
Date-time export 20-3-2015 1:16:05 week/dag 12 5

	Lab Reservoir								Inline measurements Reservoir			Waterdebieten																Dos
date	t	pH-lab	temp-pH	O2	EGV-20	Ca	NH4	HCO3	temp	pH	O2	MB-1	MB-2	MB-3	Coag-1	Coag-2	Coag-eff	UV-1	UV-2	UV-3	LZF-2	LZF-3	LZF-4	LZF-5	H
+ time	degr C	pH	degr C	mg/l	mS/m	mg/l	mg/l	mg/l	degr C	-	mg/l	m³/h	m³/h	m³/h	m³/h	m³/h	m³/h	m³/h	m³/h	m³/h	m³/h	m³/h	m³/h	m³/h	m³/h	
	\SRV-PG	\SRV-PG	\SRV-PG	\SRV-PG	\SRV-PG	\SRV-PG	\SRV-PG	\SRV-PG	\SRV-PG	\SRV-PG	\SRV-PG	\SRV-PG	\SRV-PG	\SRV-PG	\SRV-PG	\SRV-PG	\SRV-PG	\SRV-PG	\SRV-PG	\SRV-PG	\SRV-PG	\SRV-PG	\SRV-PG	\SRV-PG	\SRV-PG	PDI
06-03	4,30	7,81	20,60	11,62	29,00	37,18	0,04	108,27	5,95	7,72	11,77	0,14	0,20	772,09	387,07	373,35	759,99	370,14	381,19	0,00	187,81	187,29	187,77	188,46	
07-03	4,30	7,81	20,60	11,62	29,00	37,18	0,04	108,27	5,94	7,73	11,87	0,14	0,20	772,54	386,33	374,49	759,46	370,88	380,93	0,00	187,89	187,53	187,91	188,53	
08-03	4,30	7,81	20,60	11,62	29,00	37,18	0,04	108,27	6,12	7,74	11,84	0,14	0,20	772,45	388,38	372,55	759,45	370,84	380,93	0,00	188,18	188,04	188,36	187,29	
09-03	4,30	7,81	20,60	11,62	29,00	37,18	0,04	108,27	6,38	7,70	11,71	486,06	0,20	288,62	387,83	372,51	759,00	370,67	380,46	0,00	188,26	187,88	188,50	187,01	
10-03	5,30	7,79	20,70	11,57	28,90	35,62	0,05	101,61	6,55	7,70	11,67	776,80	0,20	0,20	388,31	373,00	759,69	370,56	380,85	0,00	187,92	188,46	187,31	187,36	
11-03	5,30	7,79	20,70	11,57	28,90	35,62	0,05	101,61	6,74	7,71	11,67	774,98	0,20	0,20	387,54	372,01	758,23	370,05	380,20	0,00	187,21	188,66	187,22	187,53	
12-03	5,30	7,79	20,70	11,57	28,90	35,62	0,05	101,61	6,67	7,70	11,57	775,42	0,20	0,20	387,87	372,28	758,79	370,06	380,70	0,00	187,21	188,80	187,28	187,57	
13-03	5,30	7,79	20,70	11,57	28,90	35,62	0,05	101,61	6,99	7,67	11,50	777,46	0,20	0,08	387,78	374,39	761,15	369,98	380,66	0,00	186,89	188,53	188,23	187,22	
14-03	5,30	7,79	20,70	11,57	28,90	35,62	0,05	101,61	7,26	7,66	11,48	776,43	0,20	0,00	388,30	373,12	760,64	370,54	381,05	0,00	186,88	188,65	188,80	187,21	
15-03	5,30	7,79	20,70	11,57	28,90	35,62	0,05	101,61	7,23	7,67	11,50	774,89	0,20	0,00	386,85	374,67	760,71	371,01	381,07	0,00	187,32	189,25	187,52	187,73	
16-03	5,30	7,79	20,70	11,57	28,90	35,62	0,05	101,61	7,25	7,72	11,57	289,73	484,11	0,00	385,76	375,25	759,99	370,65	380,85	0,00	187,72	187,17	187,77	188,07	
17-03	5,50	7,82	19,50	11,84	29,00	37,20	0,04	101,75	7,25	7,72	11,55	0,45	772,46	0,00	385,21	374,46	758,73	369,79	380,50	0,00	187,96	186,25	188,02	188,34	
18-03	5,50	7,82	19,50	11,84	29,00	37,20	0,04	101,75	7,52	7,71	11,53	0,49	773,73	0,00	385,80	373,87	758,69	369,83	379,93	0,00	187,83	186,18	187,90	188,24	
19-03	5,50	7,82	19,50	11,84	29,00	37,20	0,04	101,75	7,78	7,70	11,44	0,49	774,46	0,00	386,58	373,99	759,62	369,48	379,98	0,00	187,73	186,05	187,78	188,16	

The imported data as wells as the simulation results are shown on sheet 'Simulaties', partly also in graphs using standard Excel functions for graphs.
This sheets also indicates out-of-range data for all inline measurements, by using Excel's 'Conditional Formatting'.



A combination of measured and calculated data is used for water quality control, in which data is shown graphically within the accepted operational range (green areas).

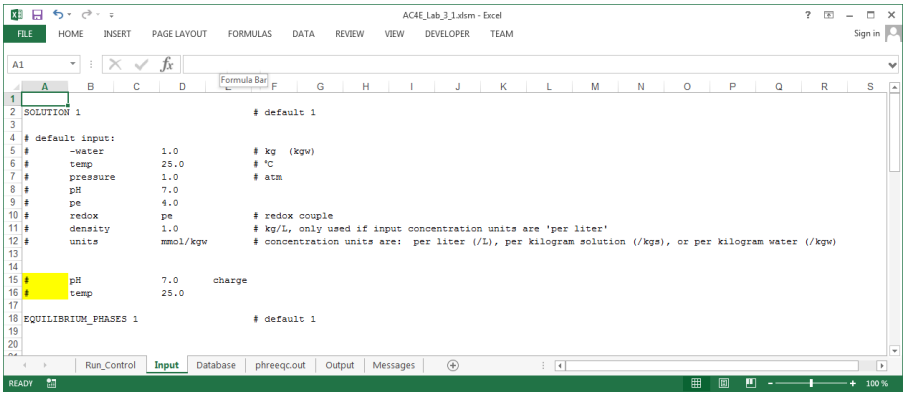

pH en SI (-)
Eff. cascade
pHs
SI
pH (-)
Infl. coagulatie
Eff. coagulatie 1
Eff. coagulatie 2
Eff. cascade 1
Eff. cascade 2
Troebelheid (FTU)
aanvoer LZF
Troebelheid (FTU)
Eff. coagulatie 1
Eff. coagulatie 2
Eff. DLF 1
Eff. DLF 2
Eff. DLF 3
Eff. DLF 4
Eff. DLF 5
Eff. DLF 6
aanvoer LZF
Zuurstof (mg/l)
Verandering in coag + DLF
Verandering in AKF
Verandering in LZF
Zuurstof (mg/l)
Eff. DLF 1-2-3
Eff. DLF 4-5-6
aanvoer LZF
aanvoer cascade
Eff. cascade 1
Eff. cascade 2
Verzadiging
UV (/m)
Eff. coagulatie 1
Eff. coagulatie 2
UV (/m)
Verlaging in DLF + AKF

Lab 3.1 PHREEQXCEL for Pure water

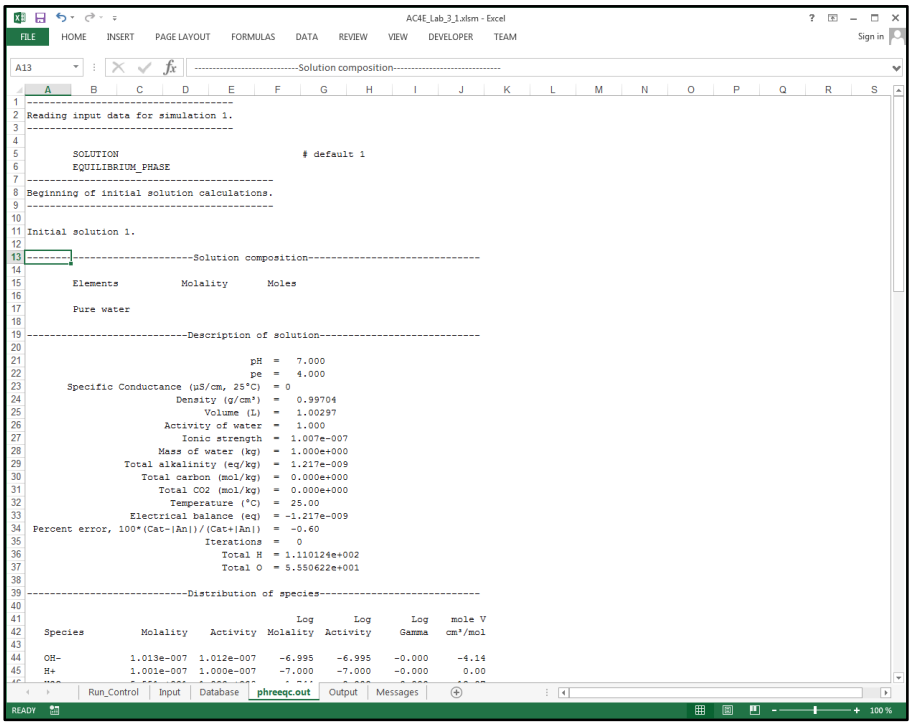
Open AC4E_Lab_3_1.xlsm.
Enable Macros, if requested.
Select sheet 'Input'.
PHREEQC uses the keyword SOLUTION for defining a solution with a trailing number to distinguish between several solutions. Default values for a solution might be omitted. In this example all default values have been 'commented', by # at the beginning of each line, being the PHREEQC symbol for comment.

PHREEQC requires two calculation steps to determine the composition of a solution:
1. Initial solution calculation, to determine the composition per element
2. Final solution calculation, to determine species after electron balancing (fixed pH and pE).

The keyword EQUILIBRIUM_PHASES is used as a dummy simulation to start the 'final calculation' for the solution:



Select sheet 'Run_Control'.
Click on 'Run PHREEQC' to start the PHREEQC calculation (and 'Ok' in case Messages are set TRUE).
The calculation results are shown on sheet 'phreeqc_out':



View the content of sheet 'phreeqc_out' and find the following marker lines:
- Reading input data for simulation 1.
- Beginning of initial solution calculations.
- Beginning of batch-reaction calculations.
- End of simulation.
- Reading input data for simulation 2.
- End of Run after xx.x Seconds.

The proper composition of the solution is obtained after the 'final calculation' (here the batch-reaction calculation). The differences between both calculations will be explained in Lab 3.4.

Both calculation sections contain the following subsections:
- Solution composition
- Description of solution
- Distribution of species
- Saturation indices.

Overview the content of these subsections to get familiar with its contents.

Charge balance

The final calculation shows a small error in the Electrical balance (-1.217 10^{-9} eq, or 0.60%). However this is still a relevant error compared to the (very low) concentrations of H^+ and OH^-. Electrical balance for H^+ and OH^- can be defined by adding the word 'charge' after pH indicating that pH is to be adjusted to achieve charge balance.

Select sheet 'Input'.
Empty the yellow marked cell at the beginning of the line for pH (so remove #).
Select sheet 'Run_Control'.
Click on 'Run PHREEQC' to start the PHREEQC calculation (and 'Ok' in case Messages are set TRUE).
The results on sheet 'phreeqc_out' show that the charge balance is achieved at pH 6.997.

Composition of Pure water at 25 °C

Description of solutions shows:
- pH of 6.997
- Temperature of 25 °C
- Specific Conductance 0 µS/cm, at the actual water temperature (now 25 °C)
  Specific Conductance is also known as Electrical conductivity (EC)
- Density of 0.99704 g/cm^3 (or kg/L)
- Volume of the solution of 1.00297 L
  Volume is related to density, amount of substances and mass of water (1 kg)
- Ionic strength of 1.006 * 10^{-7} mol/kgw
- Very low Alkalinity, caused by H^+ and OH^-
- Perfect Electrical balance (percentage error 0.00 %).

Distribution of species shows:
- Values for Molality, Activity and Molar volume (mole V) per species, and log-values for Molality, Activity and Activity coefficient (Gamma).
- Substantial value for H_2O molality: [H_2O] = 55.51 mol/kgw (1 kg of water)
- Very low concentrations for H^+ and OH^-, related to the dissociation of water:
  [H^+] = [OH^-] = 1.006 * 10^{-7} mol/kgw (pKw =13.995)
- Nearly absence of dissolved O_2 and H_2, from the natural redox reaction of water

Saturation indices show:
- Values for Saturation Index (SI), Ion Activity Product (lg IAP) and Equilibrium constant (lg K) for each phase (by phase name), and the chemical formula of that phase
- Saturation Index for $H_2O(g)$ of -1.50
- Vapour pressure of water (p_a - H_2O) from $p_a = 10^{SI} = 10^{-1.50} = 0.0316$ atm (assuming ideal gas)
- Negligible gas pressures for dissolved O_2 and H_2 (from its SI values).

Density, pH and vapour pressure for other temperatures
The density and pH of Pure water depends on its temperature. This can easily be shown by altering the temperature of the solution.

Select sheet 'Input'.
Empty the yellow marked cell at the beginning of the line for temperature (so remove #).
Give 0.0 as temperature.
Select sheet 'Run_Control'.
Click on 'Run PHREEQC' to start the PHREEQC calculation (and 'Ok' in case Messages are set TRUE).
The results on sheet 'phreeqc_out' show that at 0 °C charge balance is achieved at pH 7.469, and the density is now 0.99984 kg/L (3.88 % less than at 25 °C).

Repeating this for 100 °C gives a pH of 6.119, and a density of 0.95835 kg/L (0.25 % more than at 25 °C. The vapour pressure can be calculated from $p_a = 10^{SI} = 10^{-0.00} = 1.00$ atm (assuming an ideal gas). Water boils when this vapour pressure exceeds the actual pressure.

Note 1:
The calculation of pE for Pure water is unreliable with the used default settings. This is caused by the absence of stable redox-couple in the solution.
The accuracy for pE might be improved by:
- setting a lower convergence tolerance for iterations (see Help/Manual under keywords SELECTED_OUTPUT (-high_precision true) and/or KNOBS (-convergence_tolerance 1e-12)
- introducing a dummy species H2O-0.01 (see Help/Manual under keyword KNOBS).

For Pure water the latter option has the largest impact.

Note 2:
More precise values for Specific Conductance and SI (for vapour pressure of water) can be obtained with SELECTED_OUTPUT and/or USER_PRINT.
The vapour pressure of water can also be calculated by defining a gas phase, with PR_P("H2O(g)").

Test

Answer the following questions using the content of sheet 'phreeqc.out':

#	Questions		Answers
1	How many calculations steps are needed to determine the composition of a solution? (*select 1*)	A B C D	1 2 3 4
2	What are the internal quantities in PHREEQC for solutions? (*select 1*)	A B C D	quantities conform input values and units molality + moles mg/L + g molarity + moles
3	What is the unit of Molality? (*select 1*)	A B C D	mol/kgw mol/L g/kgw g/L
4	Which calculated (not input) parameters are includes in the Description of the solution section? (*select 1 or more*)	A B C D	Density (g/cm^3) Specific Conductance (µS/cm) Ionic strength (mol/kgw) Electrical balance (eq)
5	What is the pH of pure water at 25 °C? (*select 1*)	A B C D	7.469 7.0 6.997 6.119
6	How many elements are presented in the Distribution of species section? (*select 1*)	A B C D	1 2 3 4
7	How many species are presented in the Distribution of species section? (*select 1*)	A B C D	2 3 4 5
8	How many gases are presented in the Saturation indices section? (*select 1*)	A B C D	1 2 3 4

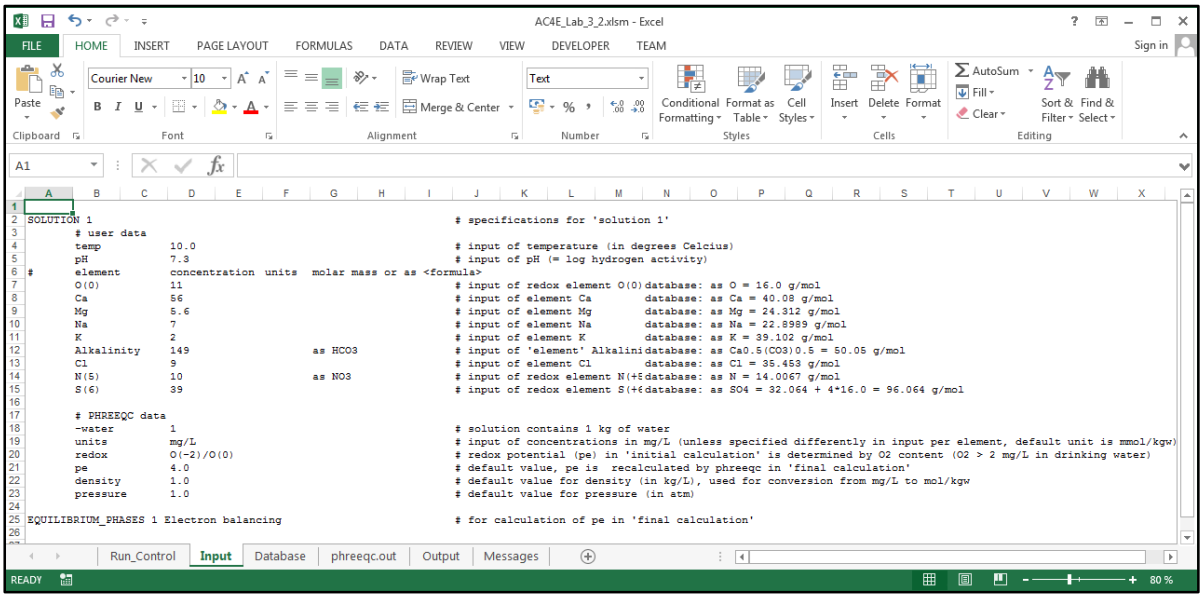
Lab 3.2 PHREEQC input for SOLUTION

The composition of the example drinking water for this Lab is:

Parameter / Element		Unit	Value
Temperature	t	˚C	10
Hydrogen ion activity	pH	-	7.3
Oxygen	O_2	mg/L as O_2	11
Calcium	Ca^{2+}	mg/L as Ca	56
Magnesium	Mg^{2+}	mg/L as Mg	5.6
Sodium	Na^{+}	mg/L as Na	7
Potassium	K^{+}	mg/L as K	2
Bicarbonate *	HCO_3^{-}	mg/L as HCO_3	149
Chloride	Cl^{-}	mg/L as Cl	9
Nitrate	NO_3^{-}	mg/L as NO_3	10
Sulphate	SO_4^{2-}	mg/L as SO_4	39

* Assume: [HCO_3^{-}] = Alkalinity

Open AC4E_Lab_3_2.xlsm.
Enable Macros, if requested.
Select sheet 'Input'.
This sheet shows the PHREEQC code for this example, with explanation for each line of code (after #):



PHREEQC uses the keyword SOLUTION for defining a solution with a trailing number to identify the solution. The composition of the solution is specified in the solution data block. Concentrations per elements requires the element name, the concentration, the concentration unit and the molar mass (or its chemical formula). Units might be omitted if they corresponds with the specified general unit (mg/L in this case), molar masses might be omitted if they corresponds with the specification in the database. In this example other molar mass specifications should be set for Alkalinity and Nitrate. Molar masses are required for calculating mg into moles.

The 'elements' Nitrogen, Sulphate and Oxygen are included as their respective oxidation states N(+5) as in NO_3^-, S(+6) as in SO_4^{2-} and O(0) as in O_2. In the database stimela.dat these elements are defined with multi oxidation states.
The elements Ca, Mg, Na, K, and Cl are defined as single oxidation state elements. Alkalinity is defined as a special 'element'.

Select sheet 'Database'.
Look into the section SOLUTION_MASTER_SPECIES to check the specifications (name, prime species, molar mass and/or chemical formula) of aforementioned elements and oxidation states ('redox elements'). Special attention should be given to all forms of nitrogen (N) with their molar mass of N (default unit 'as mg/L N').

PHREEQC requires two calculation steps to determine the composition of a solution:
1. Initial solution calculation, to determine the composition per element
2. Final solution calculation, to determine species after electron balancing (fixed pH and pE).

The keyword EQUILIBRIUM_PHASES is used as a dummy simulation to start the 'final calculation' for the solution.
Both calculation steps are included in a single 'simulation'. PHREEQC Runs can be divided into several simulations, separated by the keyword END. The 'End of file' of the input file always starts a 'simulation'. To avoid an 'empty simulation' the keyword END should not be included as the last line of the input file.

Read the input code for this example. Further information on the syntax can be obtained in the PHREEQC Help files and documentation.

Test

Answer the following questions using the text of Paragraph 3.3 and the PHREEQC code in this example:

#	Questions		Answers
1	What is de PHREEQC keyword for the input of the water composition? (*select 1*)	A B C D	WATER SOLIDS COMPONENTS SOLUTION
2	All units in the input should be in the same group. What are the 3 groups of concentration units in PHREEQC input? (*select 3*)	A B C D	per litre (/L) per kg solution (/kgs) per m^3 (/m3) per kg water (/kgw)
3	The input sets Units as mg/L. What are valid element quantity units? (*select 1 or more*)	A B C D	g, mg, µg kg, g, mg, µg mol, mmol, µmol kmol, mol, mmol, µmol
4	Units are set as mg/L. What are valid input units for solutions? (*select 1 or more*)	A B C D	µg/L mg/kgw ppm (used as m/m in mg/kgs) ppm (used as m/v in mg/L)
5	Oxygen concentration is mol O / kgw. The mean oxygen content is 11 mg/L. How should the oxygen content of 11 mg/L be coded in PHREEQC, with units set as mg/L? (*select 1*)	A B C D	O2 11 O2 11 mg/L O(0) 11 as O O(0) 11 as O2
6	How is HCO_3^- given in this PHREEQC input? (*select 1 or more*)	A B C D	C(4) HCO3 Alkalinity C
7	What is the PHREEQC comment marker? (*select 1 or more*)	A B C D	# Rem ` Comment
8	What is de PHREEQC keyword for the end of the simulation input, which starts the calculation/simulation? (*select 1 or more*)	A B C D	CALCULATE END (end of input file) END_SOLUTION

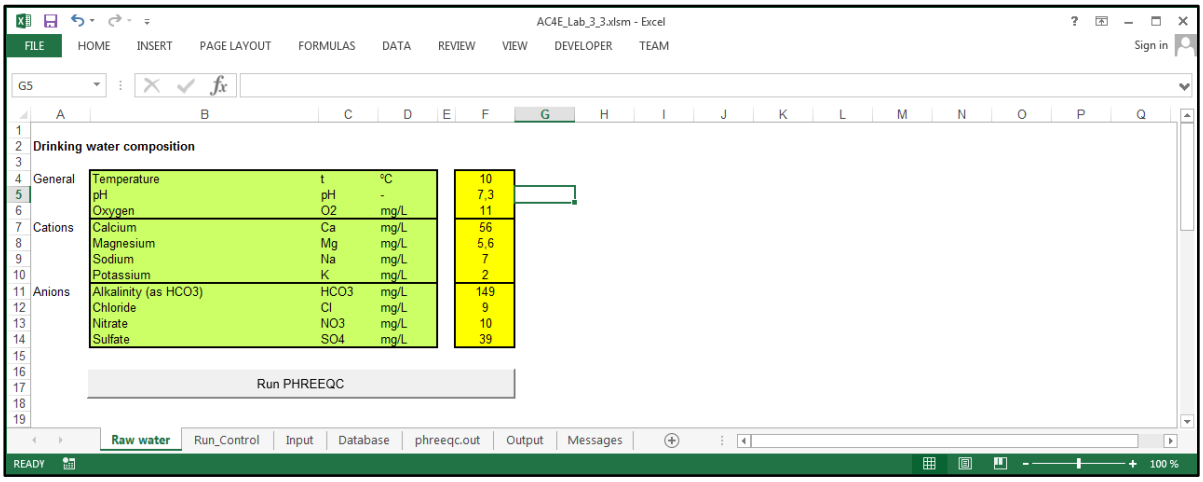
Lab 3.3 PHREEQXCEL input for SOLUTION

The composition of the example drinking water for this Lab is identical to Lab 3.2:

Parameter / Element		Unit	Value
Temperature	t	˚C	10
Hydrogen ion activity	pH	-	7.3
Oxygen	O_2	mg/L as O_2	11
Calcium	Ca^{2+}	mg/L as Ca	56
Magnesium	Mg^{2+}	mg/L as Mg	5.6
Sodium	Na^{+}	mg/L as Na	7
Potassium	K^{+}	mg/L as K	2
Bicarbonate *	HCO_3^{-}	mg/L as HCO_3	149
Chloride	Cl^{-}	mg/L as Cl	9
Nitrate	NO_3^{-}	mg/L as NO_3	10
Sulphate	SO_4^{2-}	mg/L as SO_4	39

* Assume: [HCO_3^{-}] = Alkalinity

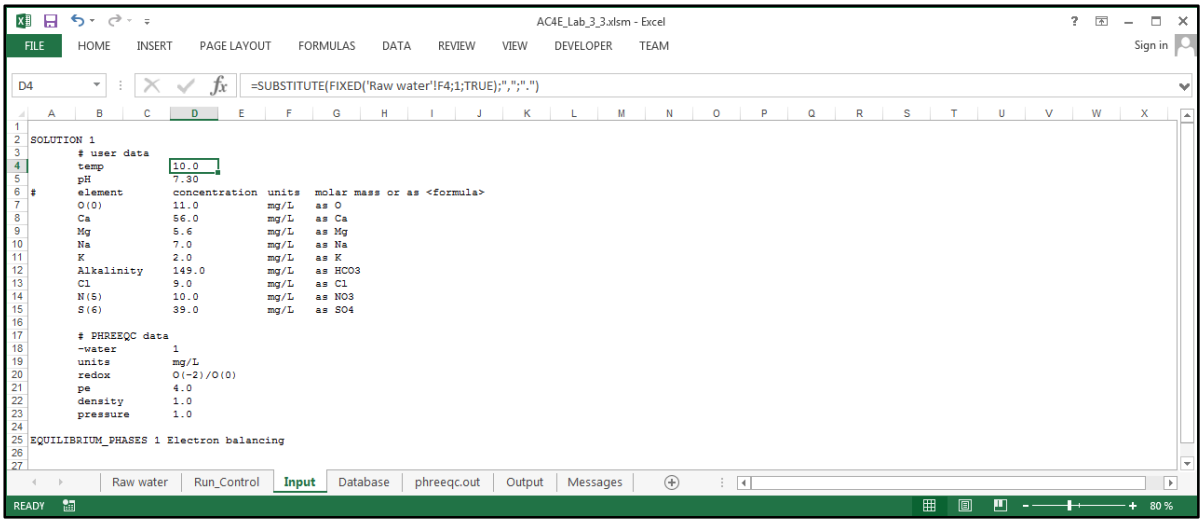
Open AC4E_Lab_3_3.xlsm.
Enable Macros, if requested.
Select sheet 'Raw water'.
This sheet shows a PHREEQXCEL input sheet for this example:



The green section includes the input parameters and their respective units, the yellow section contain the input values. The input values are linked to the PHREEQC code on sheet 'Input', converting of the numeric values into text strings, with points as decimal sign and without thousands separators. This conversion is performed by the Excel functions FIXED and SUBSTITUTE. The function FIXED(<number>;<x>;TRUE) creates text for <number> with <x> decimals and 'no_commas'. The function SUBSTITUTE(<number-text>;",";".") changes all decimal commas into points, in case the international setting of the user creates decimal commas. Combining these 2 functions gives a generic number conversion into proper PHREEQC code.

The 'Run PHREEQC' button has been copied from the sheet 'Run_Control'. This enables the user to start the PHREEQC Run without shifting to the sheet 'Run_Control'.

Select sheet 'Input':



Compare the input code with the input code of Lab 3.2.
The extended comments in the input code has been deleted.
The concentration values have been linked to their corresponding cells on sheet 'Raw water'.
All elements are specified with their chemical formula for the calculation of the molar masses as well as the units, which corresponds with the units on the sheet 'Raw water'. This method prevents common mistakes caused by omitting this information forcing PHREEQC to use the data from the database and the general setting for units.
All other items in the input code are identical the input code of Lab 3.2.

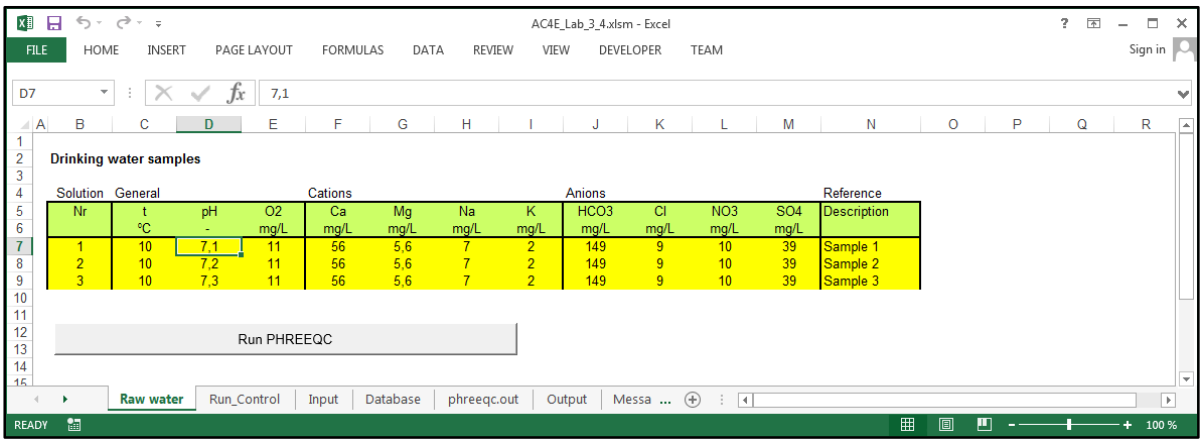
Test

Answer the following questions using the text of Paragraph 3.3 and this Lab, and the PHREEQC code in this example:

#	Questions		Answers
1	What value for the NO_3^- content should be entered as value in the input table? (*select 1 or more*)	A B C D	Nitrate as mg NO3 per Litre NO3 in mg/L NO3 in mg N/L NO3 in mg/kgw
2	How is NO_3^- given in this PHREEQC input code? (*select 1 or more*)	A B C D	NO3 NO3-1 N N(5)
3	Assume that the input code was N instead of N(5). Which concentration was set by that value? (*select 1 or more*)	A B C D	N(5) + N(3) + N(0) + N(-3) NO3- + NO2- + N2 + NH4+ N(+5) + N(+3) + N(0) + N(-3) Sum of all oxidation states of N
4	Assume that the user likes to give the Nitrate concentration as mg/L N. What should be the corresponding input code? (*select 1*)	A B C D	mg/L as N(5) mg/L as N-total mg/L as N mg/L NO3 as N
5	Which EXCEL function converts a number to text? (*select 1*)	A B C D	CHAR FIXED STRING SUBSTITUTE
6	Which EXCEL function is used to convert decimal commas to decimal points? (*select 1*)	A B C D	CHAR FIXED STRING SUBSTITUTE
7	The input code for SOLUTION contains the line "-water 1". What does this mean? (*select 1*)	A B C D	SOLUTION nr. 1 All solutions in 1 bottle Solution contains 1 kg of water Solution volume is 1 litre
8	The input code for SOLUTION contains the line "density 1". What does this mean? (*select 1*)	A B C D	Density type is 1 Density of solution is 1 kg/L Density of water is 1 kg/L Density should be calculated by PHREEQC

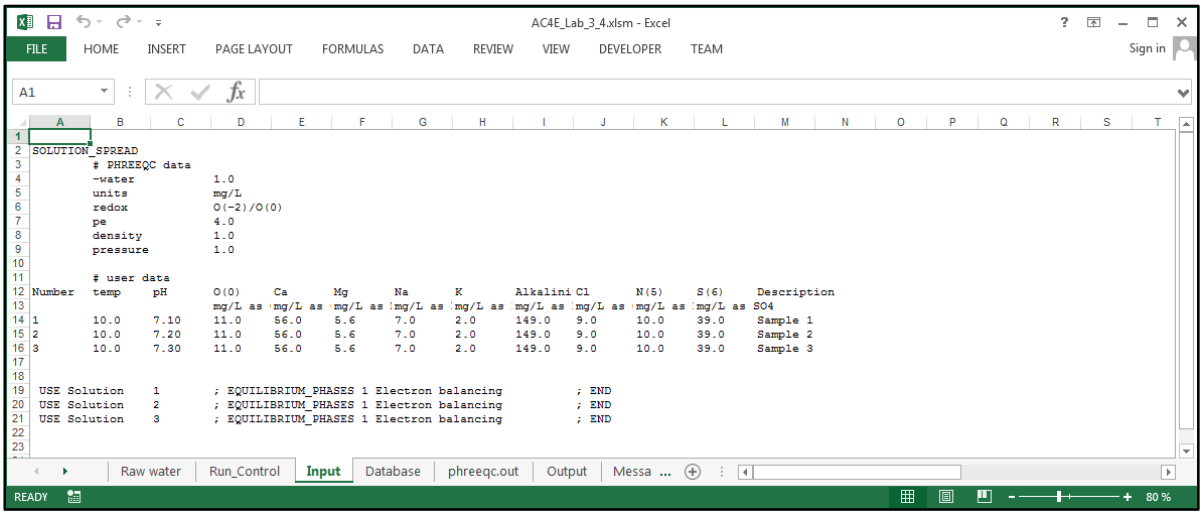
Lab 3.4 PHREEQXCEL input for SOLUTION_SPREAD

Open AC4E_Lab_3_4.xlsm.
Enable Macros, if requested.
Select sheet 'Raw water'.
This sheet shows a PHREEQXCEL input sheet for 3 water samples:



The water samples are presented in a spread-sheet layout with columns for water quality parameters. Again, the green section includes the input parameters and their respective units, the yellow section contain the input values. The input values are linked to the PHREEQC code on sheet 'Input' as in Lab 3.3.

Select sheet 'Input':



The keyword SOLUTION_SPREAD is used to define all samples as PHREEQC solutions, including general data settings followed by specific data per sample.
Electron balancing is done by 'final calculations' per solution. In these code lines the symbol ';' indicates an end-of-line marker, allowing for single line coding per calculation/simulation.
Both the raw water sheet and the input sheet might be extended with new lines in case more samples exist. This can be done by simple copy/paste of lines, in both sheets. The relative cell addressing in Excel provide for proper cell references between raw water sheet and input code lines.

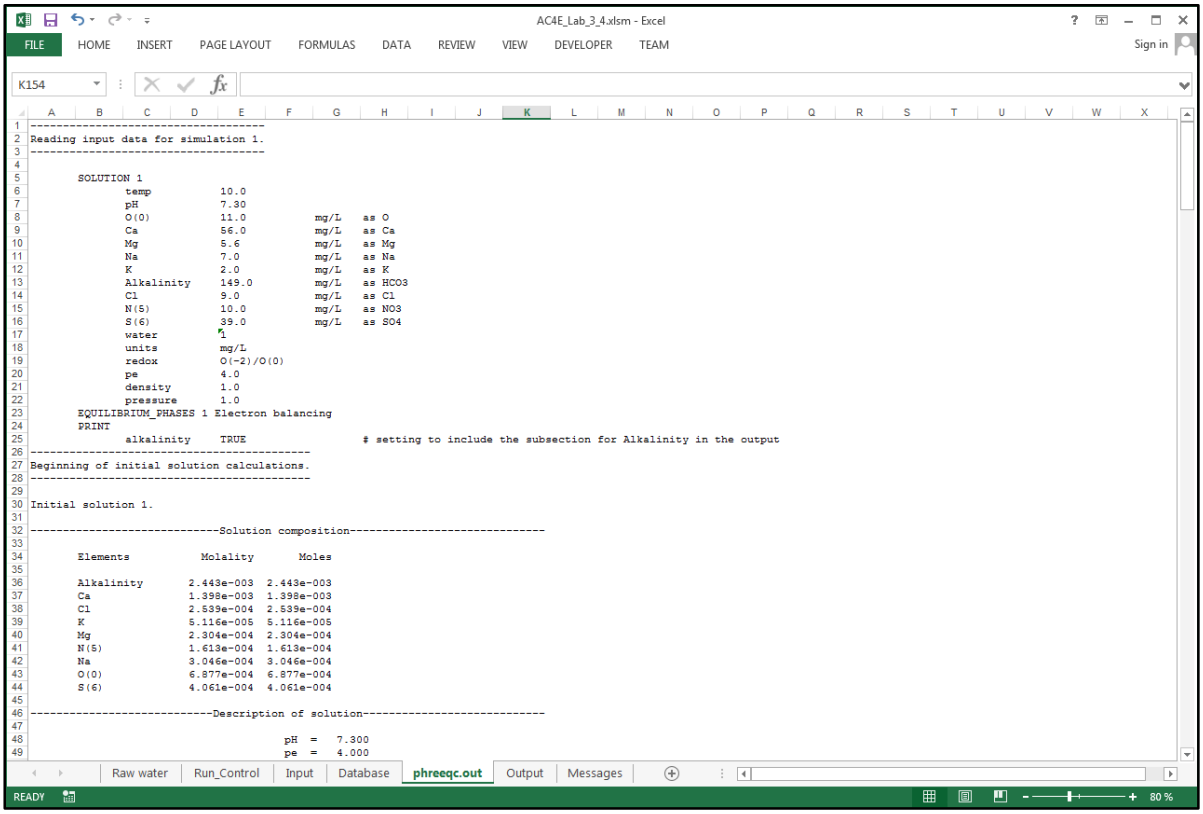
Test

Answer the following questions using the text of this Lab, and the PHREEQC code in this example:

#	Questions		Answers
1	How is the solution number specified here? (*select 1*)	A B C D	USE SOLUTION <x> In column Number In column Description Automatically by each new line
2	How is HCO_3^- given in the PHREEQC input code? (*select 1 or more*)	A B C D	C(4) HCO3 Alkalinity C
3	How many solutions can be entered via SOLUTION_SPREAD? (*select 1*)	A B C D	3 20 Limited by PHREEQC version Limited by computer memory
4	What is given in the first column heading per solution parameter? (*select 1*)	A B C D	Element names from applied database Species names from applied database Free names Chemical elements from periodic table
5	How many decimal digits are allowed in input values? (*select 1 or more*)	A B C D	0 2 > 2 > 10
6	All units in the input should be in the same group. What are the 3 groups of concentration units in PHREEQC input? (*select 3*)	A B C D	per litre (/L) per kg solution (/kgs) per m^3 (/m3) per kg water (/kgw)
7	What is the PHREEQC 'end-of-line' marker? (*select 1 or more*)	A B C D	# EOL ; `
8	What is de PHREEQC keyword for the end of the simulation input, which starts the calculation/simulation? (*select 1 or more*)	A B C D	CALCULATE END (end of input file) END_SOLUTION

Lab 3.5 PHREEQC output for SOLUTION

Open AC4E_Lab_3_5.xlsm (AC4E_Lab_3_3.xlsm with additional setting to print Alkalinity).
Enable Macros, if requested.
Select sheet 'Raw water'.
Press the button 'Run PHREEQC' to start the calculations. The calculation results are shown on sheet 'phreeqc.out' which is the Return-sheet as specified on the sheet 'Run_Control'.




```
----------------------------------------
Reading input data for simulation 1.
----------------------------------------

       SOLUTION 1
              temp            10.0
              pH              7.30
              O(0)            11.0            mg/L    as O
              Ca              56.0            mg/L    as Ca
              Mg              5.6             mg/L    as Mg
              Na              7.0             mg/L    as Na
              K               2.0             mg/L    as K
              Alkalinity      149.0           mg/L    as HCO3
              Cl              9.0             mg/L    as Cl
              N(5)            10.0            mg/L    as NO3
              S(6)            39.0            mg/L    as SO4
              water           1
              units           mg/L
              redox           O(-2)/O(0)
              pe              4.0
              density         1.0
              pressure        1.0
       EQUILIBRIUM_PHASES 1 Electron balancing
       PRINT
              alkalinity      TRUE                    # setting to include the subsection for Alkalinity in the output
-------------------------------------------
Beginning of initial solution calculations.
-------------------------------------------

Initial solution 1.

-----------------------------Solution composition------------------------------

       Elements           Molality       Moles

       Alkalinity       2.443e-003  2.443e-003
       Ca               1.398e-003  1.398e-003
       Cl               2.539e-004  2.539e-004
       K                5.116e-005  5.116e-005
       Mg               2.304e-004  2.304e-004
       N(5)             1.613e-004  1.613e-004
       Na               3.046e-004  3.046e-004
       O(0)             6.877e-004  6.877e-004
       S(6)             4.061e-004  4.061e-004

----------------------------Description of solution----------------------------

                                    pH  =   7.300
                                    pe  =   4.000
```

View the content of sheet 'phreeqc_out' and find the following marker lines:
- Reading input data for simulation 1.
- Beginning of initial solution calculations.
- Beginning of batch-reaction calculations.
- End of simulation.
- Reading input data for simulation 2.
- End of Run after xx.x Seconds.

The proper composition of the solution is obtained after the 'final calculation' (here the batch-reaction calculation). Simulation 2 is an 'empty simulation' without input code and without calculation results. This additional 'empty simulation' was initiated by the 'end-of-file' of the input code.

Solution calculation results are presented in the following sections:
- Solution composition
- Redox couples (only for initial calculations)
- Description of solution
- Distribution of species
- Distribution of alkalinity
- Saturation indices.

Overview the content of these subsections to get familiar with its contents.

Test A

Answer the following questions using Paragraph 3.4 and content of the 'initial solution calculation' block in sheet 'phreeqc.out':

#	Questions		Answers
1	In the Solution composition section all input concentrations are recalculated to which quantities? (*select 1*)	A B C D	quantities conform input values and units molality + moles mg/L + g molarity + moles
2	How many elements are given in the Solution composition section? (*select 1*)	A B C D	16 14 10 9
3	This section also includes calculated values for Total Carbon and Total CO2. Which statement is true? (*select 1 or more*)	A B C D	Different terms for the same parameter Total CO2 is CO_2 content in solution Total CO2 includes CH_4 Total CO2 is Total Inorganic Carbon
4	The Redox couples section gives combinations of oxidation states for elements as defined in SOLUTION_SPECIES in stimela.dat, for elements given in the input. Which redox couples are given? (*select 1 or more*)	A B C D	N(0)/N(5) N(-3)/N(5) O(-2)/O(0) S(-2)/S(6)
5	In the Distribution of species section the calculation is based on which pe-value? (*select 1*)	A B C D	4.000 0.8238 14.6627 Average value of Redox couples
6	Which input elements are distributed into more oxidation states? (*select 1 or more*)	A B C D	C Ca S O
7	Which element has the most species? (*select 1*)	A B C D	Ca S C Na
8	What kind of components are in the Saturation indices section? (*select 1 or more*)	A B C D	Dissolved gases Ion pairs Gases in gas phase Components with defined solid phases

In the final solution calculation redox reactions are allowed to proceed until an electron balance is achieved, for which a single value for pE can be reported.

The main differences between the initial and final solution calculations are:

- Alkalinity, under Solid composition in initial calculation, is replaced by data for the Element C in final calculation
- all oxidation states under Solution composition in initial calculation, are changed to Elements in final calculation
- total mass (or moles) per element is identical for initial and final calculation
- pH is recalculated in final calculation ('Charge balance' by redox reactions)
- pE is calculated in final calculation ('Adjusted to redox equilibrium')
- the 'Redox couples' section is absent in Simulation 2 (not relevant)
- all oxidation states per Element are included in the Distribution of species in final calculation, with additional new species
- new Saturation indices are included in final calculation, related to the additional new species.

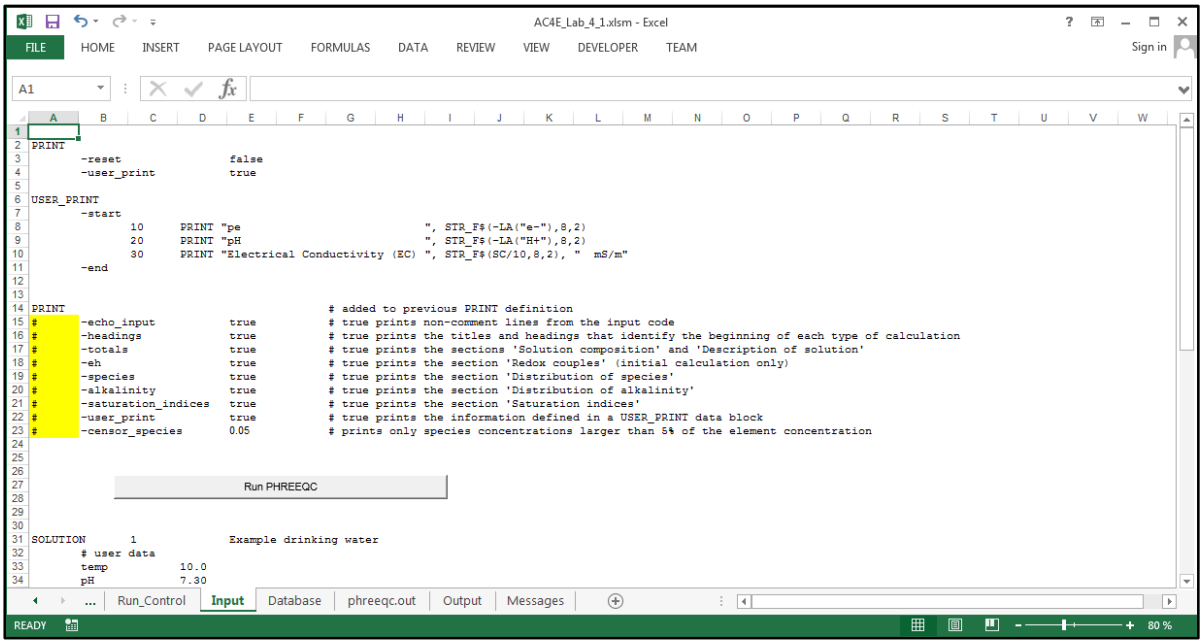
Test B

Answer the following questions using Paragraph 3.4 and content of the 'final solution calculation' (or 'batch reaction calculation') block in sheet 'phreeqc.out':

#	Questions		Answers
1	How many simulations are included in the input code and how many solution calculations were done? (*select 1*)	A B C D	2 and 2 1 and 2 2 and 1 1 and 1
2	Which keyword triggers the start of the final solution calculation (with electron balancing)? (*select 1*)	A B C D	USE END EQUILIBRIUM_PHASES SOLUTION
3	Which elements are included in the 'Solution composition' of the initial solution calculation which are not included in final solution calculation? (*select 1 or more*)	A B C D	Alkalinity S(6) Ca O(0)
4	Which values under Description of solution are unchanged in the final solution calculation? (*select 1 or more*)	A B C D	Percent error pE Specific Conductance Volume
5	Which oxidation states of element N are included in the final calculation? (*select 1 or more*)	A B C D	N(-3) N(0) N(+3) N(+5)
6	Which equations for the concentration of Nitrogen (N) are true (by definition)? (*select 1 or more*)	A B C D	N(5) initial = N(5) final N(5) initial = N final N(5) initial = N(5)+N(3)+N(0)+N(-3) final N(3) initial = N(3) final
7	How many oxidation states (or redox elements) are included in the 'Solution composition' of final calculation? (*select 1*)	A B C D	3 2 1 0
8	Which species has the largest visual change in molar concentration in the final calculation? (*select 1*)	A B C D	NO_2^- SO_4^{2-} NO_3^- N_2

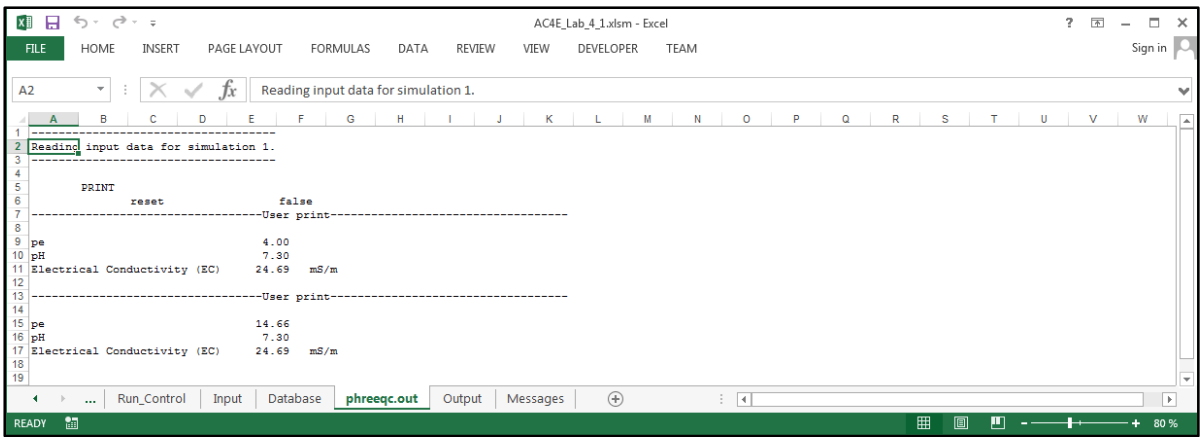
Lab 4.1 Lined output from PHREEQC

Open AC4E_Lab_4_1.xlsm.
Enable Macros, if requested.
Select sheet 'Input':



Overview the code lines under PRINT and USER_PRINT. Detailed information on the syntax of both Keywords and PHREEQC BASIC can be found in the Help-files and documentation for PHREEQC.

Press the button 'Run PHREEQC' to start the calculations. The output results are shown on sheet 'phreeqc.out' which is the Return-sheet as specified on the sheet 'Run_Control'.



Try out the effect of removing one or more comment markers (#) in the yellow section of sheet 'Input' and rerun PHREEQC to see the effect in the output.

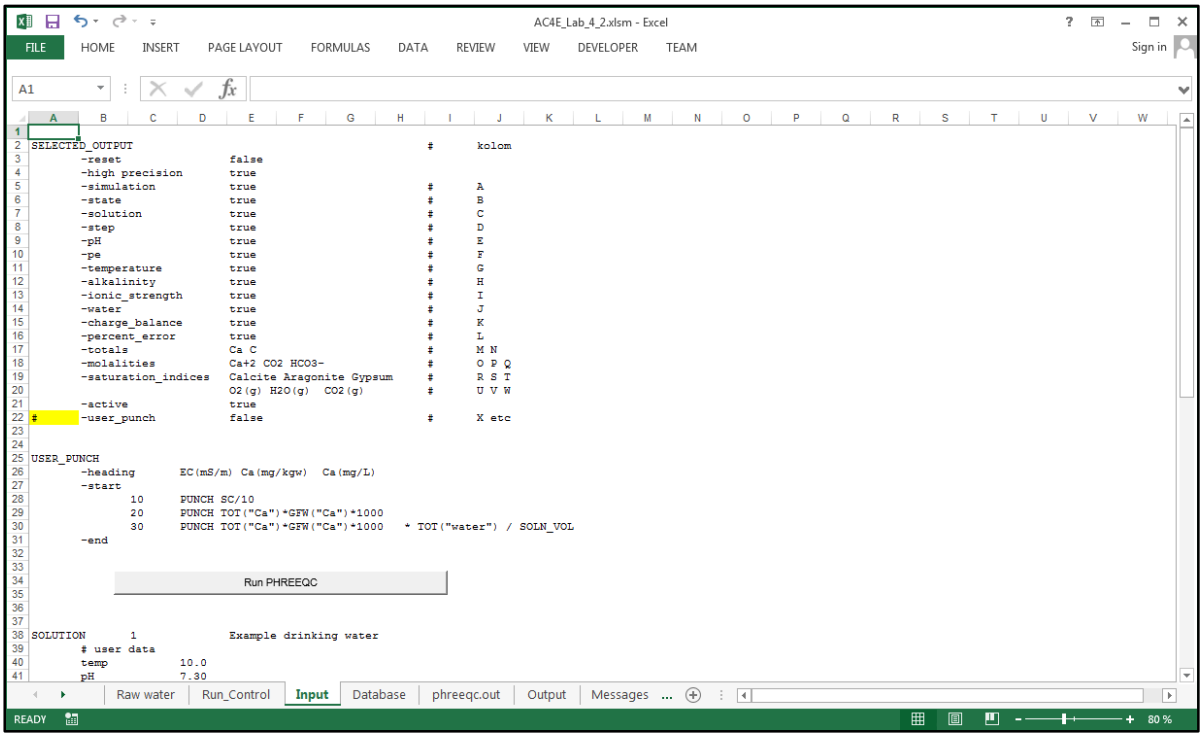
Test

Answer the following questions using data from sheets 'Input' and 'phreeqc.out':

#	Questions		Answers
1	Which keyword masters the printing to the lined output in sheet 'phreeqc.out'? (*select 1*)	A B C D	USER_OUTPUT PRINT USER_PRINT SELECTED_OUTPUT
2	Which setting controls the printing of the section 'Description of solution' to the output? (*select 1*)	A B C D	-totals -eh -alkalinity -saturation_indices
3	Which setting controls the printing of the section 'Distribution of alkalinity' to the output? (*select 1*)	A B C D	-totals -eh -alkalinity -saturation_indices
4	Which setting prints a limited number of species instead of all species? (*select 1*)	A B C D	-species -max_species -part_species -censor_species
5	What marks begin and end of BASIC statements in the USER_PRINT block? (*select 1*)	A B C D	begin / end - begin / -end start / end -start / -end
6	Which operations can be defined in de USER_PRINT block? (*select 1 or more*)	A B C D	Print internal values Print formatted values Change solution composition Calculate values
7	Which BASIC function gives pH? (*select 1*)	A B C D	PH LOG("H+") -LA("H+") LA("H+")
8	Which setting for censor-species results in 2 species in Alkalinity? (*select 1 or more*)	A B C D	5% 0.05 0.01 0.001

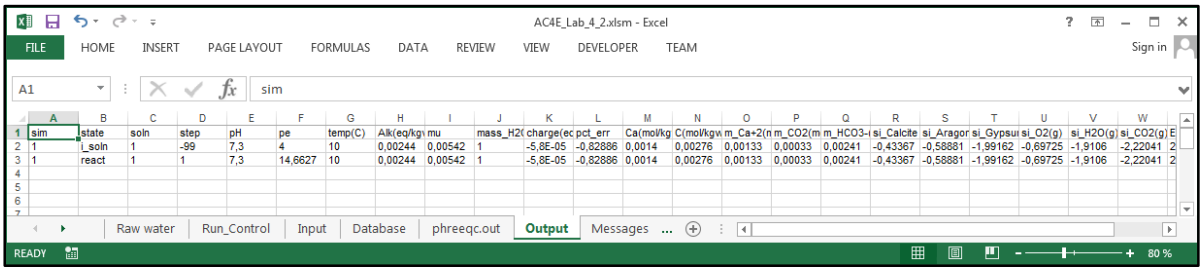
Lab 4.2 Tabulated output from PHREEQC

Open AC4E_Lab_4_2.xlsm.
Enable Macros, if requested.
Select sheet 'Input'.



Overview the code lines under SELECTED_OUTPUT and USER_PUNCH. Detailed information on the syntax of both Keywords and PHREEQC BASIC can be found in the Help-files and documentation for PHREEQC. USER_PUNCH functions allow formatting of numbers with is not applied in PHREEQXCEL, since it has better and easier formatting options within Excel.

Press the button 'Run PHREEQC' to start the calculations. The output results are shown on sheet 'Output' which is the Return-sheet as specified on the sheet 'Run_Control'.



Remove the comment marker (#) in the yellow cell of input code. Rerun the code and notice the effect in the output stream. The USER_PUNCH headings are still printed but the values are omitted.

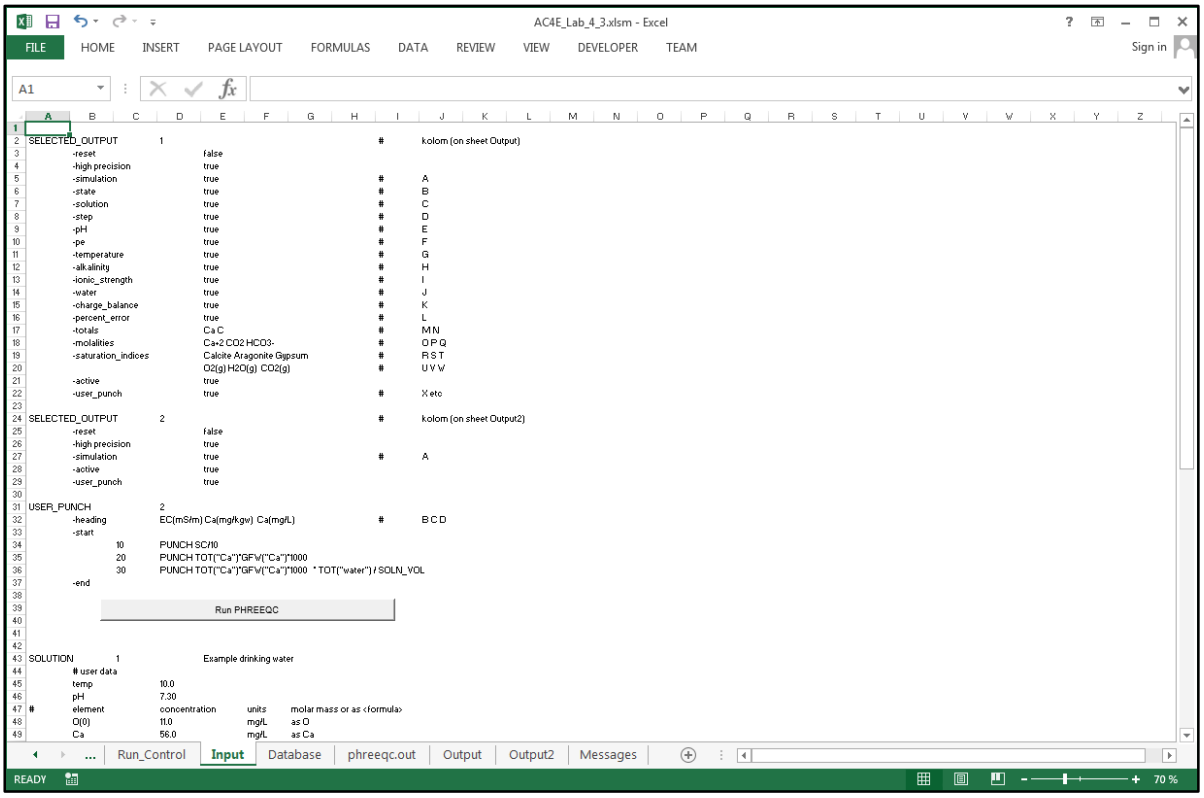
Test

Answer the following questions using data from sheets 'Input' and 'Output':

#	Questions		Answers
1	What is the sheet name for the tabulated output of this Lab? (*select 1*)	A B C D	selected.out Output phreeqc.out output.out
2	What is shown in the column 'mu'? (*select 1*)	A B C D	Ionic strength (mmol/L) Ionic strength (mmol/kgw) Ionic strength (mol/L) Ionic strength (mol/kgw)
3	What is the 'state' of the solution in the initial solution calculation? (*select 1*)	A B C D	i_soln soln solution react
4	What is the printed unit for the total Alkalinity (Alk)? (*select 1*)	A B C D	eq/L meq/kgw eq/kgw mol/L
5	Which parameter value has been changed in the final calculation? (*select 1*)	A B C D	sim pH pE Any concentration
6	Which pE value is printed for the initial solution? (*select 1*)	A B C D	Value pE from previous run Internal PHREEQC default value Calculated from redox-couple O(-2)/O(0) Value pE from input code
7	Which parameters were unchanged in the final calculation? (*select 1 or more*)	A B C D	pE pct_err si_H2O(g) Ca (mg/L)
8	How many PHREEQC BASIC functions were needed to calculate the calcium concentration in mg/L? (*select 1*)	A B C D	5 4 3 2

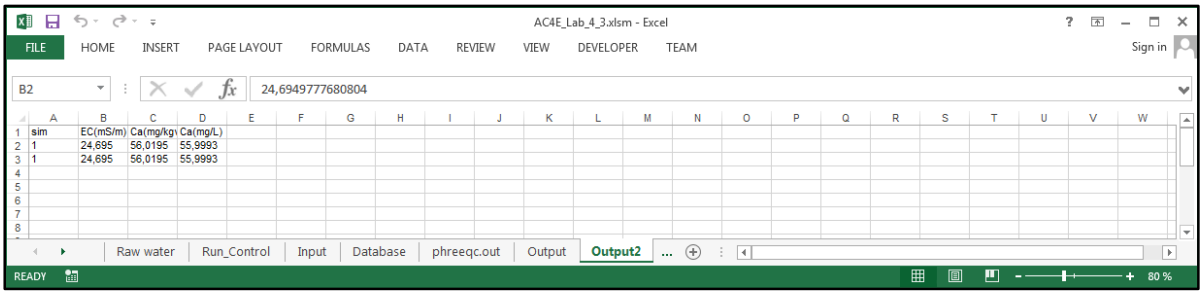
Lab 4.3 Multiple output streams from PHREEQC

Open AC4E_Lab_4_3.xlsm.
Enable Macros, if requested.
Select sheet 'Input'.



Overview the code lines under SELECTED_OUTPUT and USER_PUNCH and notice the output streams 1 and 2. Detailed information on the syntax of both Keywords and PHREEQC BASIC can be found in the Help-files and documentation for PHREEQC.

Press the button 'Run PHREEQC' to start the calculations. The output results in sheet 'Output2' are shown since this is the Return-sheet as specified on the sheet 'Run_Control'.



Look into sheet 'Output' for the other results.

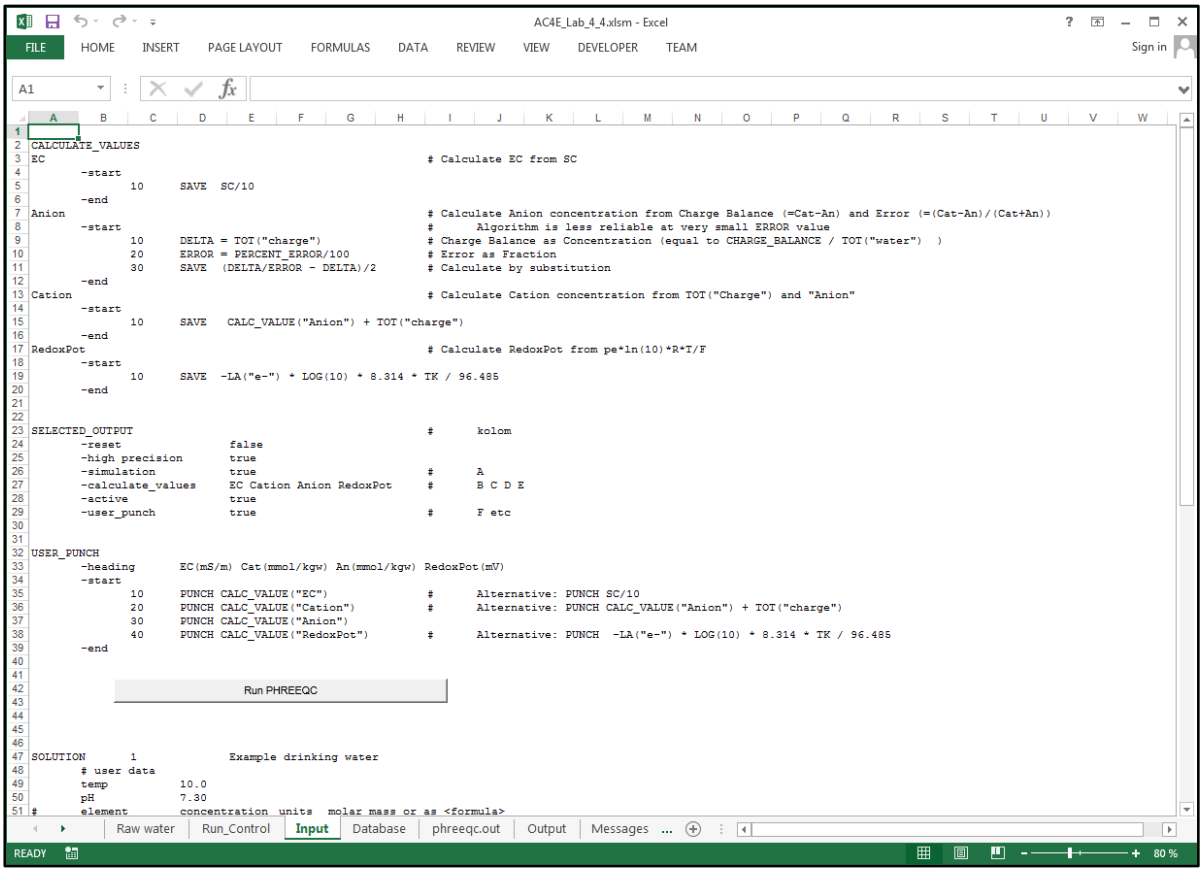
Test

Answer the following questions using data from sheets 'Input', 'Output' and 'Output2':

#	Questions		Answers
1	What is the sheet name for the USER_PUNCH output of this Lab? (*select 1*)	A B C D	Output Output2 phreeqc.out output.out
2	What is shown in the column 'mu'? (*select 1*)	A B C D	Ionic strength (mmol/L) Ionic strength (mmol/kgw) Ionic strength (mol/L) Ionic strength (mol/kgw)
3	What is the 'state' of the solution in the initial solution calculation? (*select 1*)	A B C D	i_soln soln solution react
4	What is the printed unit for the total Alkalinity (Alk)? (*select 1*)	A B C D	eq/L meq/kgw eq/kgw mol/L
5	Which parameter value has been changed in the final calculation? (*select 1*)	A B C D	sim pH pE Any concentration
6	Which pE value is printed for the initial solution? (*select 1*)	A B C D	Value pE from previous run Internal PHREEQC default value Calculated from redox-couple O(-2)/O(0) Value pE from input code
7	Which parameters were unchanged in the final calculation? (*select 1 or more*)	A B C D	pE pct_err si_H2O(g) Ca (mg/L)
8	How many PHREEQC BASIC functions were needed to calculate the calcium concentration in mg/L? (*select 1*)	A B C D	5 4 3 2

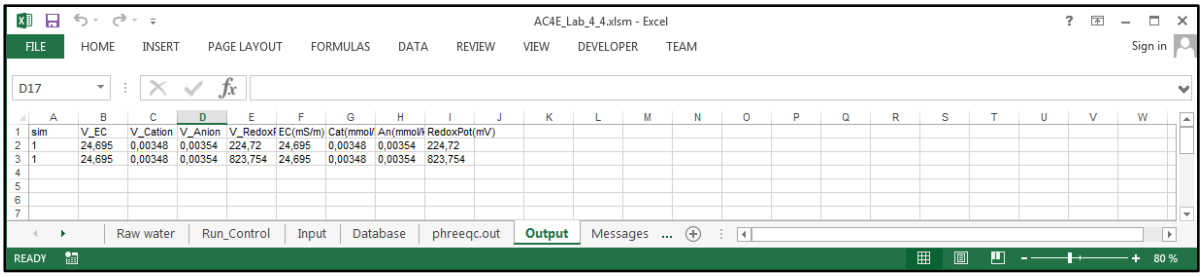
Lab 4.4 User defined functions in PHREEQC

Open AC4E_Lab_4_4.xlsm.
Enable Macros, if requested.
Select sheet 'Input'.



Overview the code lines under CALCULATE_VALUES with four user defined functions: EC, Anion, Cation and RedoxPot. Detailed information on the syntax of this Keyword and PHREEQC BASIC can be found in the Help-files and documentation for PHREEQC.
The results of the user defined functions are printed with SELECTED_OUTPUT and USER_PUNCH. It should be noticed that USER_PUNCH functions are identical to CALCULATE_VALUE. The latter is beneficial for functions used in other input code sections and/or simulations.

Press the button 'Run PHREEQC' to start the calculations. The output results on sheet 'Output' are shown since this is the Return-sheet as specified on the sheet 'Run_Control'.



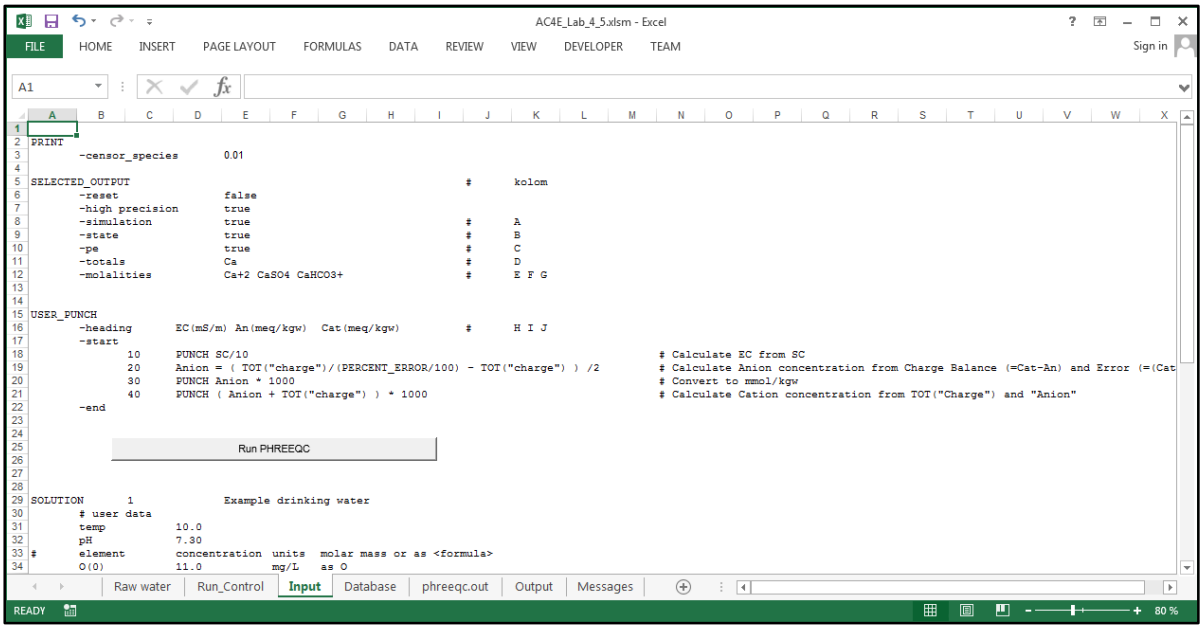
Test

Answer the following questions using also the PHREEQC Help file on the Basic Interpreter:

#	Questions		Answers
1	What is the keyword for user defined functions in the input code? (*select 1*)	A B C D	USER_FUNCTIONS CALCULATE_VALUES USER_FUNCTION FUNCTION
2	What marks begin and end of BASIC statements of a user defined function? (*select 1*)	A B C D	begin / end - begin / -end start / end -start / -end
3	The result of the user defined function is given on the last BASIC code line. Which keyword is used in this line? (*select 1*)	A B C D	RESULT CALCULATE_VALUE SAVE FUNCTION
4	The result of user defined functions can be printed in different output blocks. Under which keyword? (*select 1 or more*)	A B C D	PRINT USER_PRINT SELECTED_OUTPUT USER_PUNCH
5	Which BASIC function is user to recall the result of a user defined function? (*select 1*)	A B C D	CALC_VALUE() FUNCTION() UDF() CALCULATED_VALUE()
6	What is the unit for CHARGE_BALANCE in the BASIC code? (*select 1*)	A B C D	mol/kgw mol eq/kgw eq
7	What is the unit for TOT() in the BASIC code? (*select 1*)	A B C D	mol/kgw mol eq/kgw eq
8	What is the unit for TOT("water") in the BASIC code? (*select 1*)	A B C D	mol/kgw mol kg eq

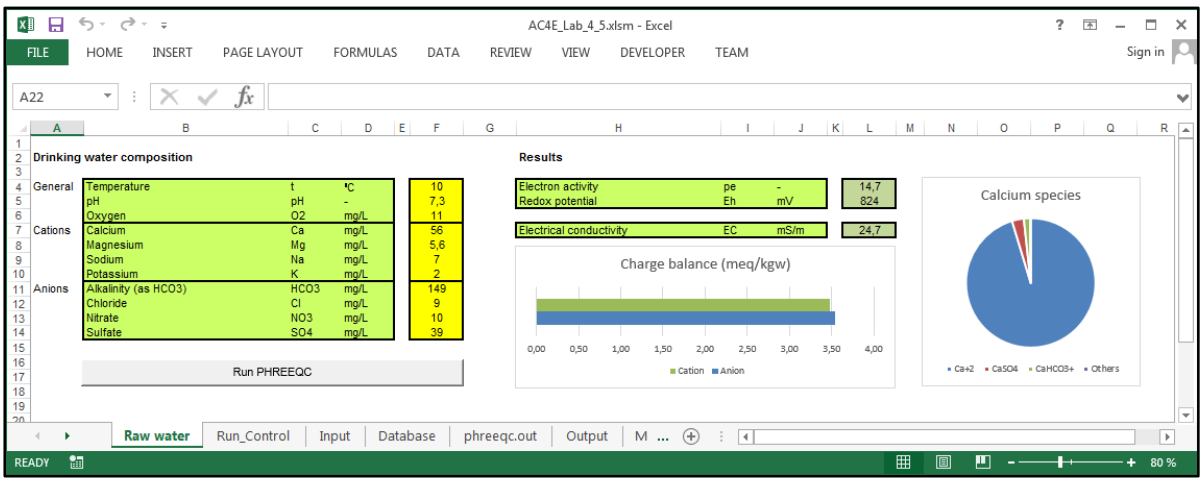
Lab 4.5 Output processing in Excel

Open AC4E_Lab_4_5.xlsm.
Enable Macros, if requested.
Select sheet 'Input'.



Overview the code lines under SELECTED_OUTPUT and USER_PUNCH. Detailed information on the syntax of both Keywords and PHREEQC BASIC can be found in the Help-files and documentation for PHREEQC.

Press the button 'Run PHREEQC' to start the calculations. The output results are shown on sheet 'Raw water' which is the Return-sheet as specified on the sheet 'Run_Control'.



The PHREEQC results in sheet 'Output' have been post-processed using Excel options for calculations, text and number formatting, as well as graphical presentation of data.
This setup enables users to modify these results to their own personal preferences in language, parameter names, units etc. without any modification in the PHREEQC code.

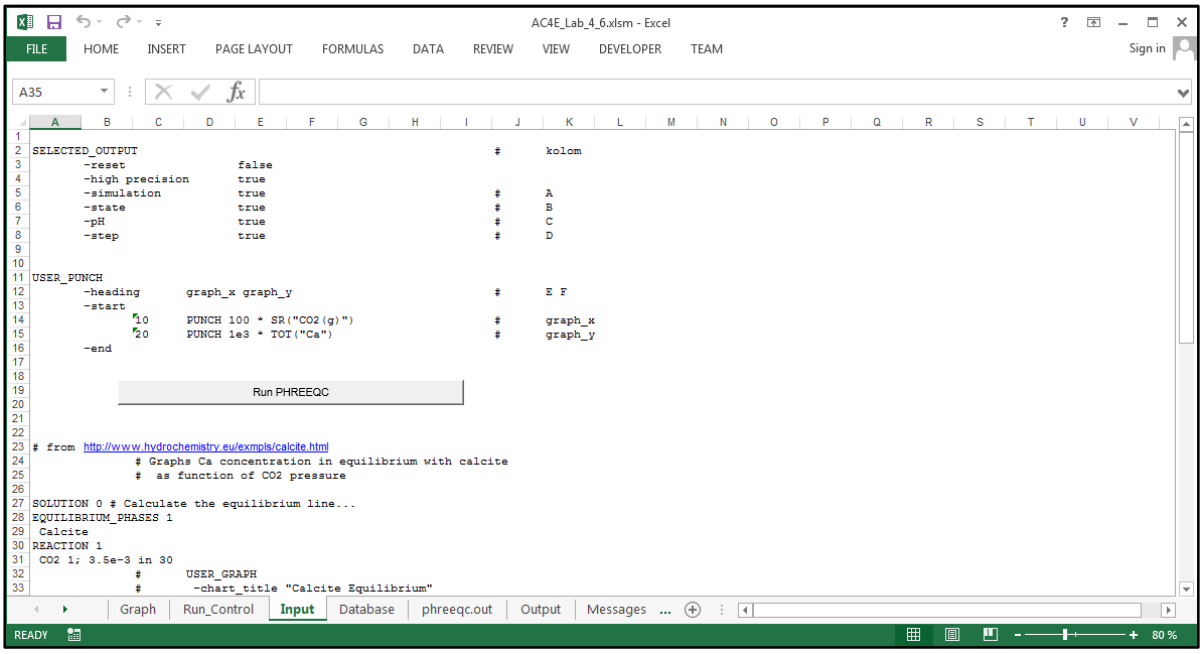
Test

Answer the following questions using the input code and results in the Excel of this Lab:

#	Questions		Answers
1	How many rows are printed by the SELECTED_OUTPUT and USER_PUNCH blocks? (*select 1*)	A B C D	1 2 3 4
2	How many columns are printed by the SELECTED_OUTPUT block? (*select 1*)	A B C D	3 5 7 10
3	How many columns are printed by the USER_PUNCH block? (*select 1*)	A B C D	3 5 7 10
4	How is the sequence of output from the SELECTED_OUTPUT block? (*select 1 or more*)	A B C D	According to the input line According to internal setting of PHREEQC In random order In alphabetic order
5	How is the sequence of output from -totals and -molalities in the SELECTED_OUTPUT block? (*select 1 or more*)	A B C D	According to the input line According to internal setting of PHREEQC In random order In alphabetic order
6	What is the unit for -totals and -molalities in the SELECTED_OUTPUT block? (*select 1*)	A B C D	mol/kgw mol mmol/kgw mmol
7	What is the benefit of presenting PHREEQC results in Excel? (*select 1 or more*)	A B C D	Formatting of data Calculated values from data Combined in- and output Data presentation in different chart forms
8	What are the options for unit conversion of PHREEQXCEL? (*select 1 or more*)	A B C D	Using user defined functions in PHREEQC Using formulas under USER_PUNCH Using formulas in Excel Using formulas under SELECTED_OUTPUT

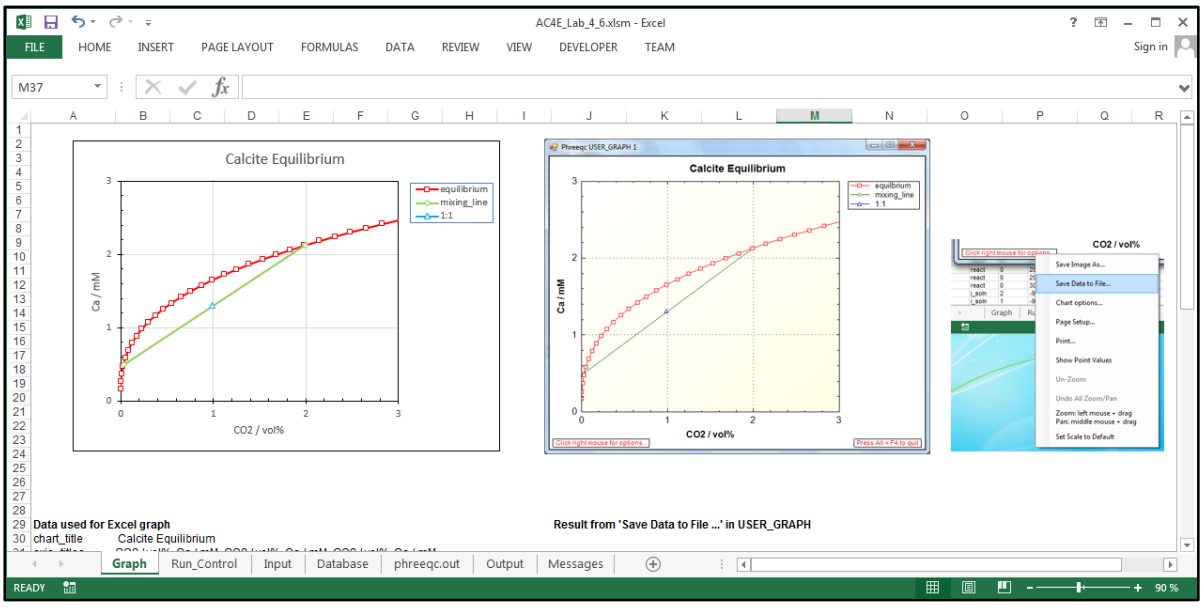
Lab 4.6 User graphs in PHREEQXCEL

Open AC4E_Lab_4_6.xlsm.
Enable Macros, if requested.
Select sheet 'Input'.



Overview the code lines under USER_PUNCH and # USER_GRAPH.

Press the button 'Run PHREEQC' to start the calculations. The output results are shown on sheet 'Graph' which is the Return-sheet as specified on the sheet 'Run_Control'. This sheet also includes the data used for this graph and the graph that would have been created by the keyword USER_GRAPH.



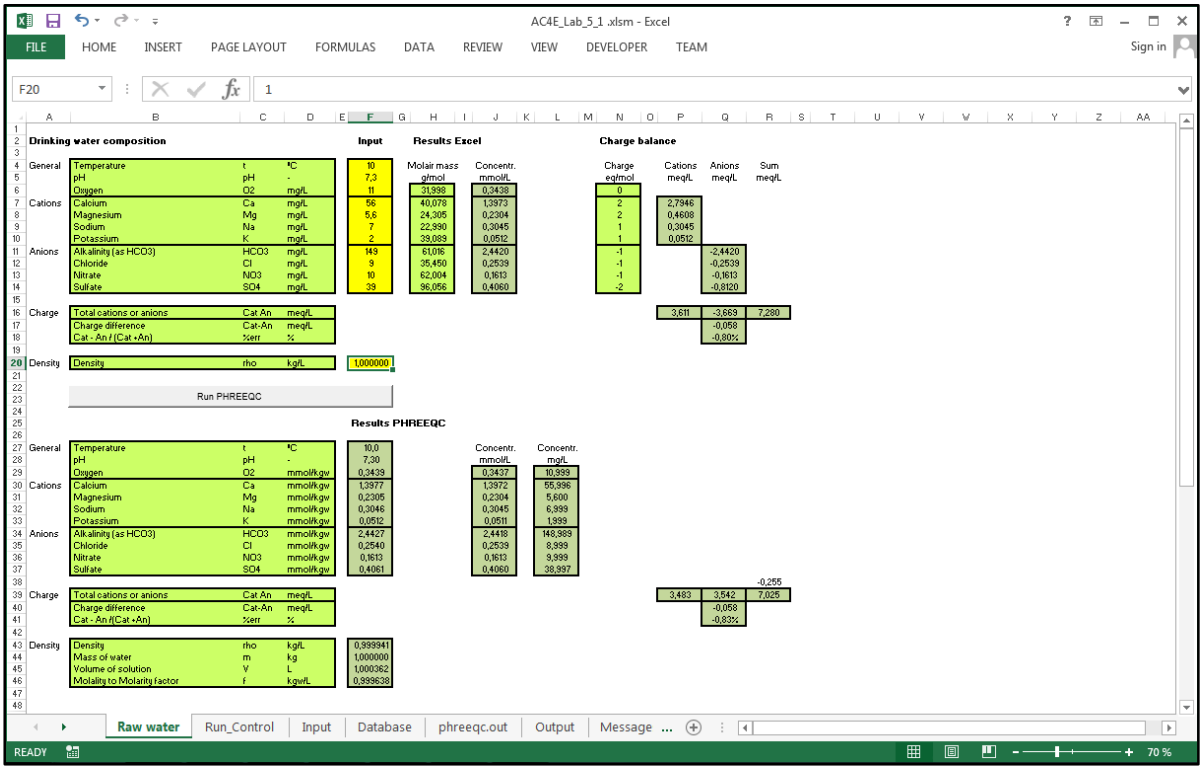
Test

Answer the following questions:

#	Questions		Answers
1	Which keyword is used to get the data for the graph (x and values)? (*select 1*)	A B C D	PRINT USER_PUNCH USER_PRINT SELECTED_OUTPUT
2	Which columns of sheet Output contains the x and y values for the graph? (*select 1*)	A B C D	A and B C and D E and F F and G
3	What determines in which the columns these x and y values are printed? (*select 1*)	A B C D	Internal PHREEQC settings Random selected by PHREEQC User code on sheet Input User code under USER_GRAPH
4	How many simulations were done in the PHREEQC calculation Run? (*select 1*)	A B C D	1 2 4 34
5	How many solution calculations were done in the PHREEQC calculation Run? (*select 1*)	A B C D	1 2 4 34
6	How many graph lines (x-y sets) are defined in the Excel graph? (*select 1*)	A B C D	1 2 3 4
7	Which Excel chart type was used to create the graph? (*select 1*)	A B C D	Line X Y (Scatter) Pie Bar
8	What determines the graph format, font, colours etc. for the graph? (*select 1*)	A B C D	Internal PHREEQC setting Internal Excel setting (fixed) User defined format settings User input in PHREEQC code

Lab 5.1 Concentrations, density and charge balance

Open AC4E_Lab_5_1.xlsm.
Enable Macros, if requested.
Select sheet 'Raw water'.
This water sample is equal to the sample of Chapter 3, with an additional input field for Density of the solution.



The input values are given in mg/L (mass per volume of solution). PHREEQC converts the values to mol/kgw (molality as amount of substance per mass of water) using the density of the solution, for which the input value is estimated at 1.000000 kg/L.

Press the button 'Run PHREEQC' to start the calculations. The output results are shown on sheet 'Raw water' which is the Return-sheet as specified on the sheet 'Run_Control'.
PHREEQC calculates a density of 0.999941 kg/L.
Use this amount as input value, and press the button 'Run PHREEQC' again. Now the calculated density equals the estimated input value.
The molality concentrations of PHREEQC can be calculated as molarity concentrations (mol/L) using the 'Molality to Molarity factor' of 0.999638 kgw/L. Molarity concentrations have also been calculated in Excel using the input values and the molar masses of each component. Comparing the values shows equal values (in 4 decimals). The mg/L values show only differences in the third decimal of three components.

In practical applications for water treatment the differences between Molality and Molarity are often ignored. This approach seems to be acceptable at temperatures between 0 and 50 °C and low salinity, limiting the differences to less than 1-2%.

Charge balance
The charge balance can be calculated in Excel ignoring ion-pairs and assuming a fixed molar charge. Comparing the results of Excel and PHREEQC shows a charge difference of -0.058 meq/L for both calculation methods.

However the cations and anions in PHREEQC are both 0.127 meq/L lower, caused by ion-pairs. Ion-pairs work equal to cations and anions, keeping the difference the same but reducing the total charge. Therefor also the 'percent error' is lower (0.80% versus 0.83%) since this error is relative to the total charge.
As can be seen in sheet 'phreeqc.out' the dominant ion-pairs in this sample are $CaSO_4$ and $CaHCO_3^+$ causing half of the difference between Excel and PHREEQC.

Charge balancing
PHREEQC can be used to balance the charge using the keyword 'CHARGE' for the component which is appointed to balance the charge.
Select sheet 'Input'.
Place a comment marker before the line 'Ca 56.0 mg/L as Ca' which activates the line 'Ca 56.0 mg/L as Ca charge'. In this case the calcium concentration will be modified to a value giving a full balance in charge.
Press the button 'Run PHREEQC' to start the calculations. The output shows a Calcium content of around 57.2 mg/L, which is 1.2 mg/L or some 2% higher as the original input value. Such a deviation falls within the accuracy range of most analyse methods.
Charge balancing might also be applied for estimating the concentration of a non-measured component.

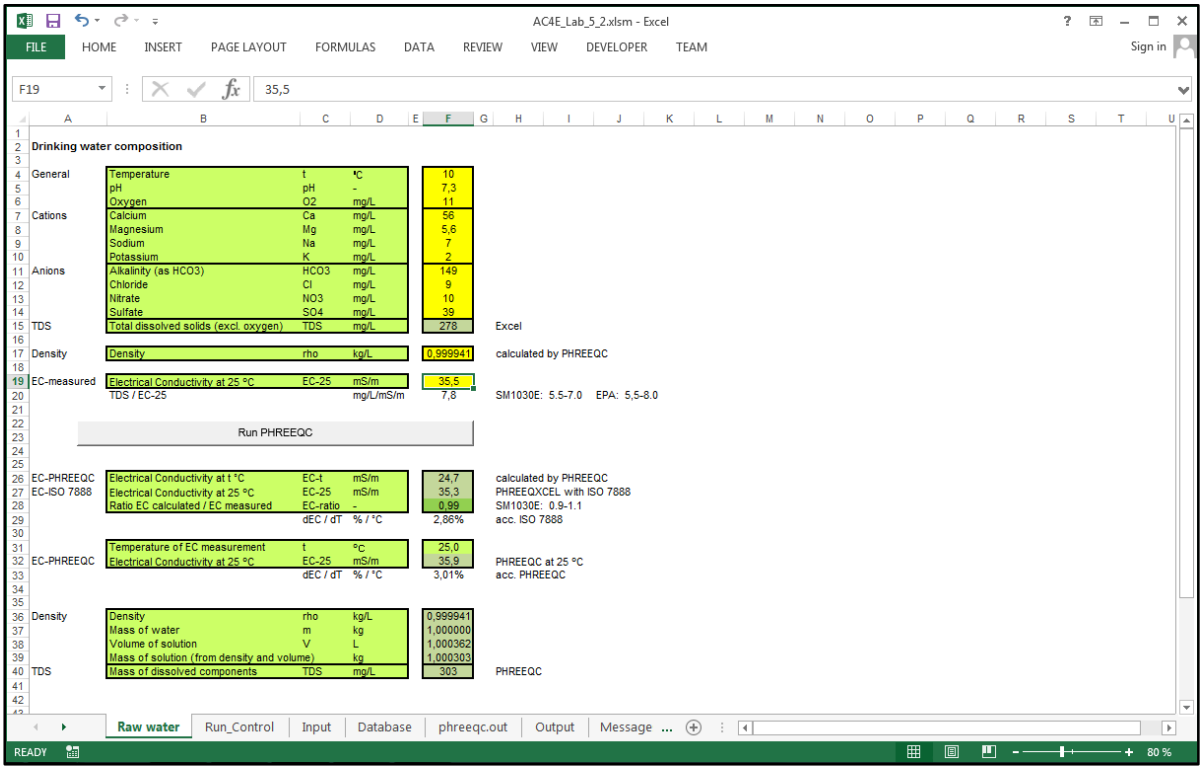
Test

Answer the following questions:

#	Questions		Answers
1	With molar masses in the database, and input concentrations in mg/L, which additional input parameter is applied by PHREEQC for the conversion into Molality? (*select 1*)	A B C D	Volume of solution Mass of water Atomic weights Density of solution
2	What are the calculated concentrations for oxygen at a density of 1 kg/L versus 0.999994 kg/L from PHREEQC? (*select 1*)	A B C D	10.999 / 11.000 mg/L 0.3437 / 0.3438 mg/L 0.3439 / 0.3439 mg/L 0.3438 / 0.3438 mg/L
3	Which concentration unit is applied by PHREEQC in the sheet 'Output'? (*select 1*)	A B C D	mmol/kgw mg/L mol/kgw mg/kgw
4	How is the Molality to Molarity factor calculated by PHREEQC? (*select 1*)	A B C D	MolalToMolar TOT("water")/SOLN_VOL Molal/Molar SOLN_VOL/TOT("water")
5	Which component has the largest effect on charge balance in this example? (*select 1*)	A B C D	Alkalinity Calcium (Ca) Bicarbonate (HCO_3) Sulphate (SO_4)
6	What is the effect of ion-pairs on the charge balance in a solution? (*select 1 or more*)	A B C D	Nett balance (eq) stays the same Cation and Anion (eq) stay the same Percent error decrease Percent error increase
7	What is an acceptable percent error in charge balance according to Standard Methods 1030E (for this anion charge)? (*select 1*)	A B C D	2.5% 1.0% 2.0% 4.0%
8	What is the keyword to discard the input concentration and calculate the value to obtain full charge balance? (*select 1*)	A B C D	charge balance balance charge charging

Lab 5.2 Electrical Conductivity and Total Dissolved Solids

Open AC4E_Lab_5_2.xlsm.
Enable Macros, if requested.
Select sheet 'Raw water'.
This water sample is equal to the sample of Lab 5.1, with an additional input field for measured Electrical Conductivity (EC-25).



Press the button 'Run PHREEQC' to start the calculations. The output results are shown on sheet 'Raw water' which is the Return-sheet as specified on the sheet 'Run_Control'.

Electrical Conductivity (EC)
For the sample water PHREEQXCEL calculates a value of 24.7 mS/m as being the conductivity at the actual water temperature of 10 °C.
In water treatment the Electrical Conductivity is normalized at 25 °C.
The EC at 25 °C is calculated at 35.3 mS/m with the temperature conversion formula of ISO 7888.
This temperature factor amounts to 2.86% per °C.

The ratio EC calculated over EC measured amounts to 0.99, showing a very good compliance. The acceptable range according to Standard Methods 1030E is 0.9 - 1.1.

ISO 7888 promotes the measurement of Electrical Conductivity in a temperature controlled water bath at 25 °C. Changing the water temperature will not only change the diffusion and conductivity, but also the equilibrium constants of all related reactions.
This measurement procedure is simulated in PHREEQC (simulation 2) with the keyword 'REACTION_TEMPERATURE' with 25 °C. The simulation gives an EC value of 35.9 mS/m, with a temperature factor of 3.01% per °C.

Total Dissolved Solids
From the input concentrations in mg/L the Total Dissolved Solids (TDS) can be calculated in Excel as 278 mg/L.
PHREEQC lacks a function for the calculation of TDS. An attempt has been made to obtain TDS from PHREEQC values for solution density, solution volume and mass of water. This method gives a TDS value of 303 mg/L (109%) showing that the density model of PHREEQC cannot be applied for calculation of TDS. The calculation of TDS from molalities of all dissolved solids (non-gaseous components) is considered as 'too elaborated'.

Standard Methods 1030E proclaims the TDS over EC ratio as validation method for which an acceptable ratio between 5.5 and 7.0 (mg/L / mS/m) is mentioned. EPA gives a ratio range between 5.5 and 8.0. These wide ranges indicate a less appropriate validation method.
Our sample water has a TDS over EC ratio of 7.8.

Test

Answer the following questions:

#	Questions		Answers
1	Which parameter is required in the PHREEQC database for calculating Electrical Conductivity? (*select 1*)	A B C D	Specific molar conductivity Diffusion coefficient Valance Ionic strength
2	What is the PHREEQC function for Electrical Conductivity (see sheet Input)? (*select 1*)	A B C D	EC Conduct SC SpecCond
3	What is the temperature for which EC is calculated in PHREEQC for this sample? (*select 1*)	A B C D	25 °C 20 °C 15 °C 10 °C
4	Why is the Electrical Conductivity changed at a different temperature? (*select 1 or more*)	A B C D	Diffusion coefficient change Viscosity change Mean valance per element change Concentration change
5	What factor (% per °C) gives a reliable estimate for EC change from 10 to 25 °C? (*select 1*)	A B C D	1% 2% 3% 4%
6	What is the acceptable range for EC calculated over EC measured according to SM 1030E? (*select 1*)	A B C D	0.99-1.01 0.98-1.02 0.95-1.05 0.90-1.10
7	What is the most reliable calculation method for TDS in this sample? (*select 1*)	A B C D	PHREEQC function TDS Excel from input values PHREEQC combined with Excel Internal Excel function
8	What is the acceptable range for TDS over EC measured (in mg/l / mS/m) according to EPA? (*select 1*)	A B C D	5.0-7.0 5.0-8.0 0.9-1.1 0.5-0.8

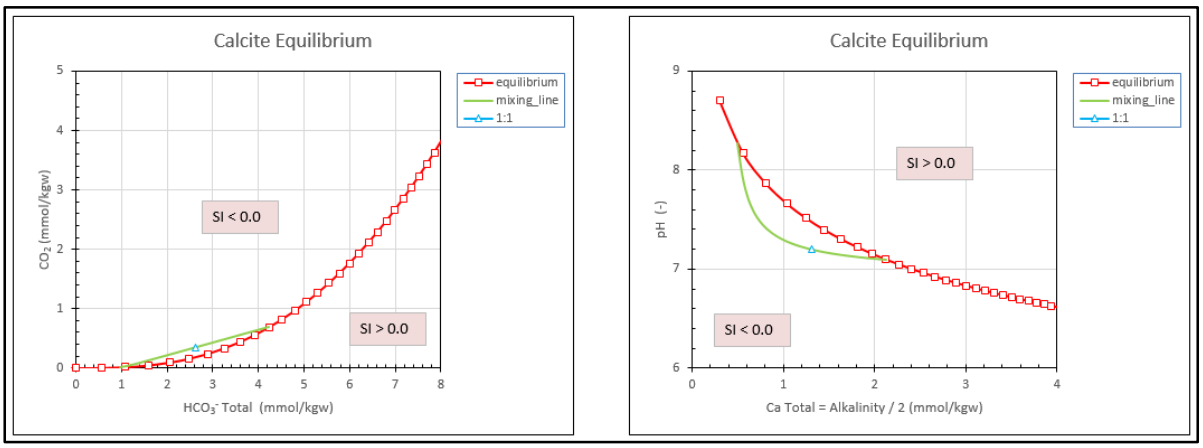
Lab 5.3 Mixing water

Open AC4E_Lab_5_3.xlsm.
Enable Macros, if requested.
Select sheet 'Input'.
Overview the code lines which are identical to the code lines of Lab 4.6, with the addition of 31 lines in which 31 mixing fractions are applied:

```
70
71 MIX     21      ;1      0.0000  ;2      1.0000  ;END            #       0
72 MIX     22      ;1      0.0333  ;2      0.9667  ;END            #       0,0333
73 MIX     23      ;1      0.0667  ;2      0.9333  ;END            #       0,0667
74 MIX     24      ;1      0.1000  ;2      0.9000  ;END            #       0,1
```

etc.
The 31 mixing fractions are calculated by formulas in Excel.

Press the button 'Run PHREEQC' to start the calculations. The output results are shown on sheet 'Graph' which is the Return-sheet as specified on the sheet 'Run_Control'.



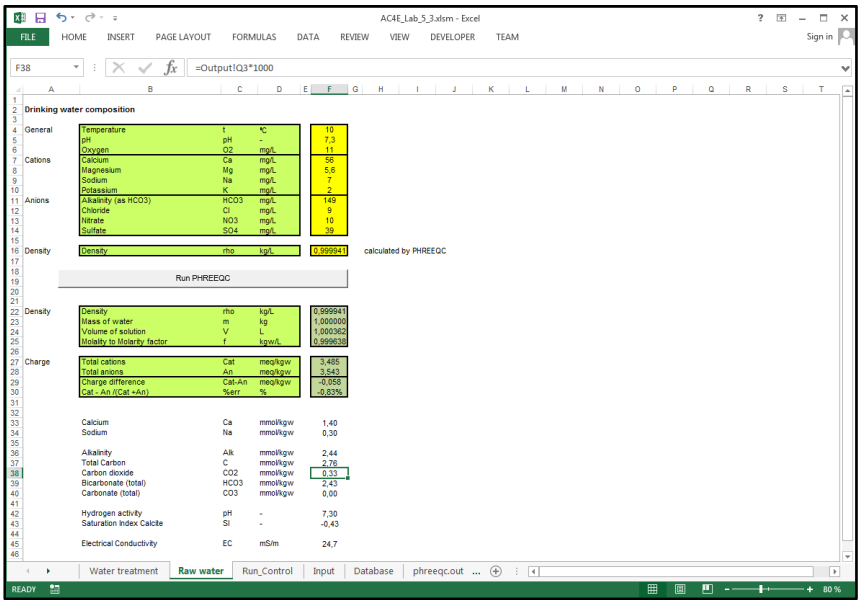
In this Lab the green line for mixed solutions has been calculated. In Lab 4.6 a straight line between the 2 solutions points was assumed. In a HCO_3-CO_2 diagram this is actually true as is shown in the diagram on the left (Tillman's diagram). In a hardness-pH diagram the mixing line is a curve line showing that mixing soft water with a small amount of hard water has a large influence on pH and therefor on SI.
It also shows that soft water should have a higher pH than hard water, when both are in equilibrium with calcite. The background and consequences of these graphs will be discussed in Volume 2 and 3.

Notice that the column 'soln' in sheet 'Output' suggests that each mixed solution is numbered and Saved as Solution, which is not ('use solution 21' will result in a PHREEQC error).

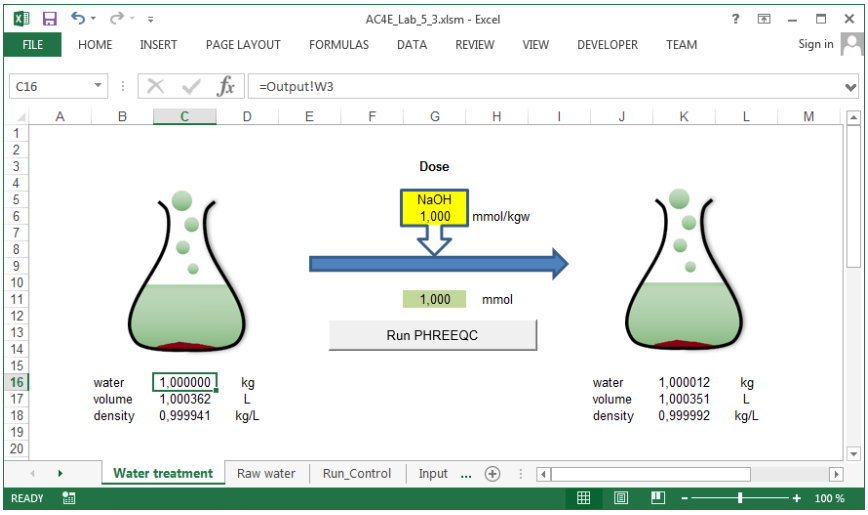
Lab 5.4 Dosing of chemicals with REACTION

Open AC4E_Lab_5_4.xlsm.
Enable Macros, if requested.
Select sheet 'Raw water'. This water sample is equal to the sample of Lab 5.1 and Lab 5.2.

The input values on the upper part of this sheet are left unchanged. The lower part of this sheet gives some basis results of the calculated values for this 'raw water'. In this way this sheet is focussed on the raw water itself including validation of input data, which allows for checking of values for density, charge balance, Electrical Conductivity (if measured), molality (or concentrations) of relevant elements, saturation index (SI) for calcite etc.

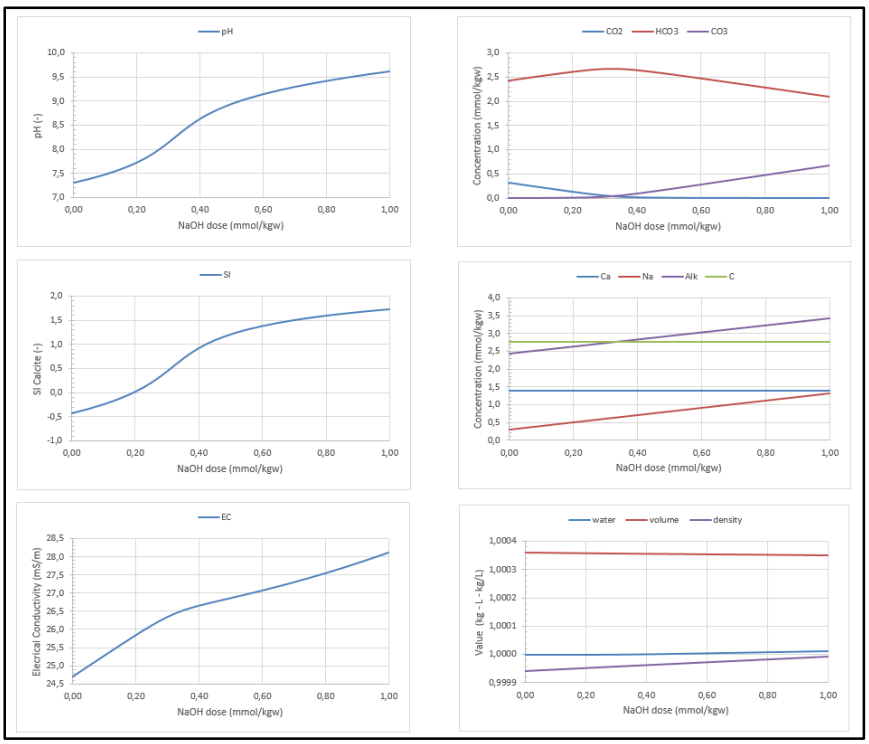


Select sheet 'Water treatment'. This sheet contains input values for the added chemical and its dose.
Fill in at the yellow input cells 'NaOH' as dosed chemical and a dosing level of 1.0 mmol/kgw.
The total dosed amount is calculated in Excel as 1.00 mmol, from this dosing level multiplied by 1 kg of water.



The sheet 'Water treatment' also contains the calculated results, in tabular and graphical form. The latter is achieved by dividing the dosed amount into 20 steps via the input code line:
REACTION 1 ; NaOH 1.00 ; 1.00000 mmol in 20 steps (see sheet 'Input')

Press the button 'Run PHREEQC' to start the calculations.
Excel returns on the same sheet 'Water treatment' being the Return-sheet as specified on the sheet 'Run_Control'.



Look to the non-linear graphs for pH, SI Calcite and EC, and explain their forms.
Look to the linear graphs for CO_2-HCO_3-CO_3, Ca-Na-Alkalinity-Ctotal, and water-volume-density and explain their forms.
(*Hint: Reactions are* $CO_2 + OH^- \rightarrow HCO_3^-$ *and* $CO_3^{2-} + OH^- \rightarrow CO_3^{2-} + H_2O$)

Repeat the calculations for the following doses:
- Na_2CO_3 adding 1.0 mmol/L
- $CaCO_3$ adding 1.0 mmol/L
- $Ca(OH)_2$ adding 0.5 mmol/L
- CO_2 removing 0.3 mmol/L (by adding -0.3 mmol/L)
- CO_2 removing 1.0 mmol/L (by adding -1.0 mmol/L)

Notice for the latter example that the amount of CO_2 is more than in the raw water. Nevertheless PHREEQC calculates the quality. Why?

Test

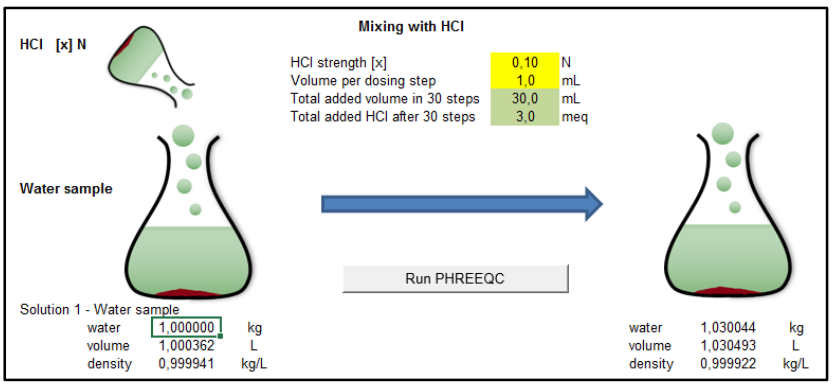
Answer the following questions:

#	Questions		Answers
1	How many simulations were done by PHREEQC in each Run? (*select 1*)	A B C D	1 2 21 22
2	Which amount of NaOH (in mmol) was dosed in the first step for the example with NaOH? (*select 1*)	A B C D	0.0 1.0 0.95 0.05
3	In which column of the sheet 'Output' is pH 'printed'? (*select 1*)	A B C D	D E F G
4	Which parameter is linear with the dosed amount of NaOH? (*select 1 or more*)	A B C D	pH Na molality Total Carbon molality Mass of water
5	The graph for Electrical Conductivity shows 2 different ranges. What causes the breakpoint in this graph? (*select 1*)	A B C D	Reaction temperature pH CO_3^{2-} formation Na molality
6	The graph for mass of water shows 2 different ranges. What causes the breakpoint in this graph? (*select 1*)	A B C D	Reaction temperature pH CO_3^{2-} formation H_2O formation
7	Which parameters are unchanged with increasing NaOH dosing? (*select 1 or more)*	A B C D	Na molality Total Carbon molality Alkalinity Ca molality
8	Which parameters are unchanged with increasing $Ca(OH)_2$ dosing? (*select 1 or more)*	A B C D	Na molality Total Carbon molality Alkalinity Ca molality

Lab 5.5 Dosing of chemicals with MIX

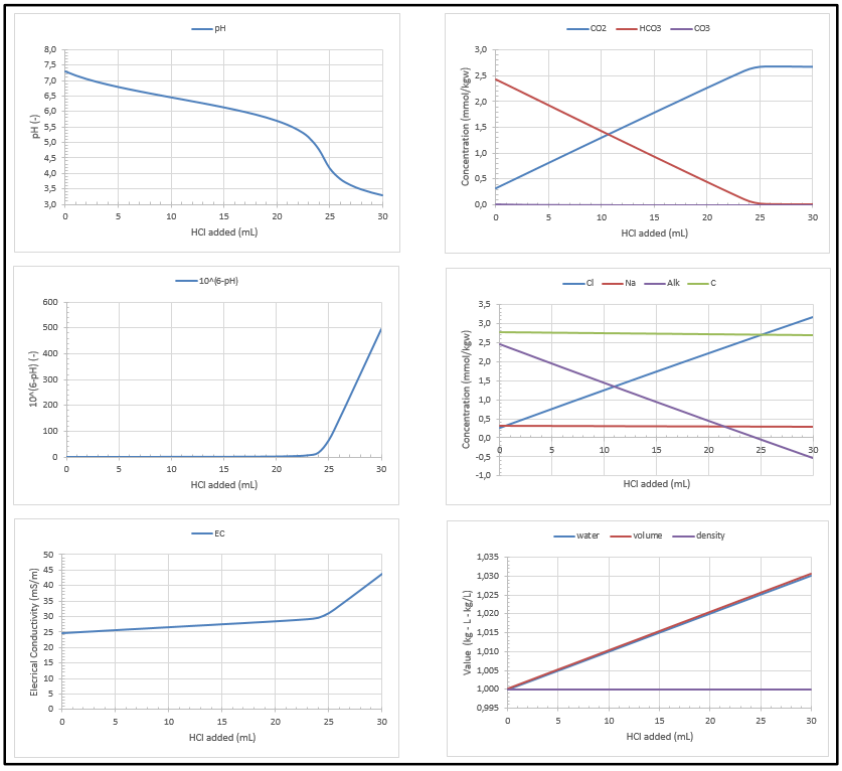
Open AC4E_Lab_5_5.xlsm.
Enable Macros, if requested.
Select sheet 'Raw water'. This water sample is equal to the sample of Lab 5.1, Lab 5.2 and Lab 5.4.

Select sheet 'Water treatment'. This sheet contains input values for the strength of HCl and the volume per dosing step.
Fill in at the yellow input cells '0.10' as HCl strength (Normality 0.10 mol/L) and a volume per step of 1.0 mL. The added volume after 30 steps is calculated in Excel as 30.0 mL.



The sheet 'Water treatment' also contains the calculated results, in tabular and graphical form. The applied PHREEQC code per step is: MIX 1; 1 1.0 ; 2 0.0010 ; END
with increasing amount of volume for Solution 2 (see sheet 'Input', without volume/mass correction for densities of these two solutions).

Press the button 'Run PHREEQC' to start the calculations.
Excel returns on the same sheet 'Water treatment' being the Return-sheet as specified on the sheet 'Run_Control'.



Look to the graphs, and explain their forms.

Fill in at the yellow input cells '0.20' as HCl strength (Normality 0.2 mol/L).
Press the button 'Run PHREEQC' to start the calculations.
Now the graphs show the same shape but at half the volume.

Fill in at the yellow input cells '0.02' as HCl strength (Normality 0.02 mol/L) and 5 mL per step.
Press the button 'Run PHREEQC' to start the calculations.
Modify in Excel the x-axes of the graphs in order to show the equivalence points in each graph.

Test

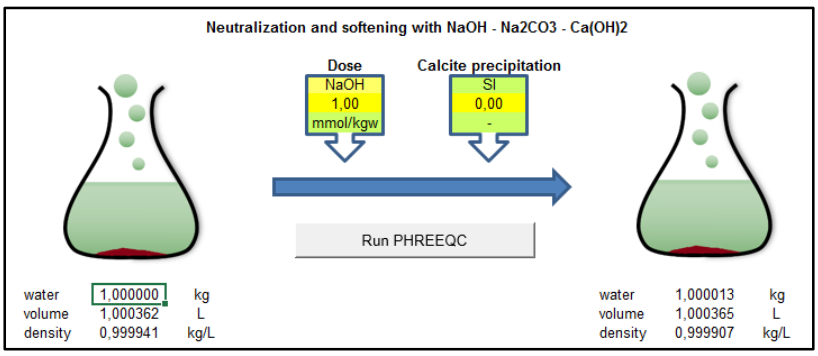
Answer the following questions:

#	Questions		Answers
1	How many simulations were done by PHREEQC in each Run? (*select 1*)	A B C D	2 3 32 33
2	Which amount of HCl (in mL) was dosed in the first step for the first example? (*select 1*)	A B C D	0,10 1,0 30,0 3,0
3	In which column of the sheet 'Output' is pH 'printed'? (*select 1*)	A B C D	D E F G
4	Which parameter is linear with the mixed amount of HCl? (*select 1 or more*)	A B C D	pH Cl molality Total Carbon molality Mass of water
5	The graph for Electrical Conductivity shows 2 different ranges. What causes the breakpoint in this graph? (*select 1*)	A B C D	Reaction temperature H^+ increase CO_2 formation Cl molality
6	The graph for HCO_3 shows 2 different ranges. What causes the breakpoint in this graph? (*select 1*)	A B C D	Reaction temperature H^+ increase CO_2 formation Cl molality
7	Which parameters are unchanged with increasing HCl dosing, disregarding the dilution effect? (*select 1 or more)*	A B C D	Cl molality Total Carbon molality Alkalinity Ca molality
8	Which parameters might be used for determination of equivalence point in Alkalinity measurements? (*select 1 or more)*	A B C D	pH EC 10^{-pH} Cl

Lab 5.6 Reaction with solids in EQUILIBRIUM_PHASES

Open AC4E_Lab_5_6.xlsm.
Enable Macros, if requested.
Select sheet 'Raw water'. This water sample is equal to the sample of Lab 5.4 and 5.5.

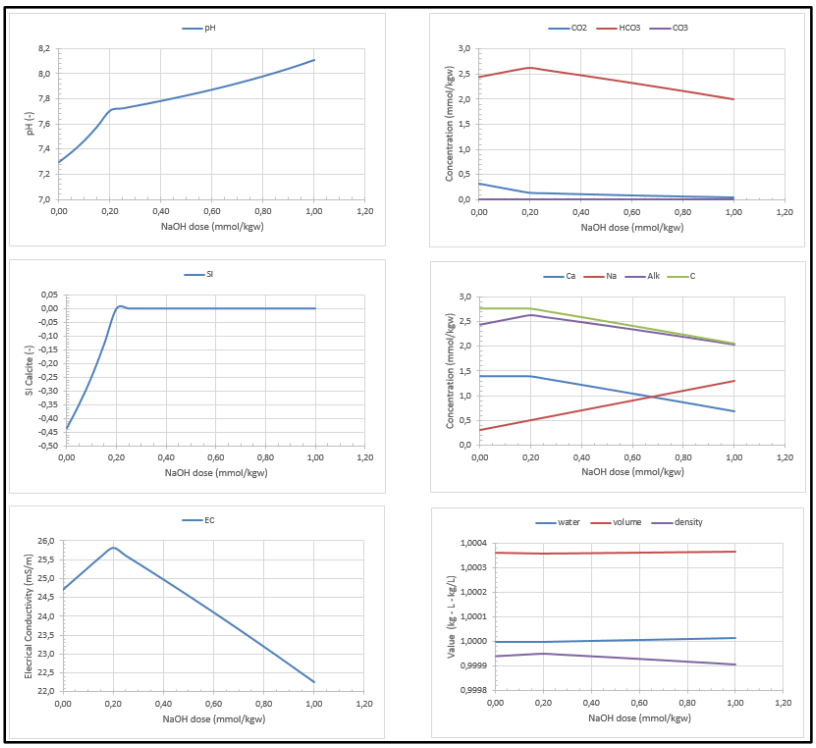
Select sheet 'Water treatment'. This sheet contains input values for the applied chemical (NaOH, Na_2CO_3 or $Ca(OH)_2$) and the super-saturation after precipitation of calcite (SI-value).
Fill in at the yellow input cells 'NaOH' as chemical, '1.00' as dose (in mmol/kgw) and '0.00' as SI after precipitation.



The sheet 'Water treatment' also contains the calculated results, in tabular and graphical form. The applied PHREEQC code for precipitation is:
EQUILIBRIUM_PHASES 1; Calcite 0.000 0.01 precipitate_only (see sheet 'Input').
Further details on this keyword can be found in the PHREEQC documentation.

Press the button 'Run PHREEQC' to start the calculations. Excel returns on the same sheet 'Water treatment' being the Return-sheet as specified on the sheet 'Run_Control'.

Try out the alternative chemicals, dosing's and SI-values as indicated on sheet "Water treatment'.



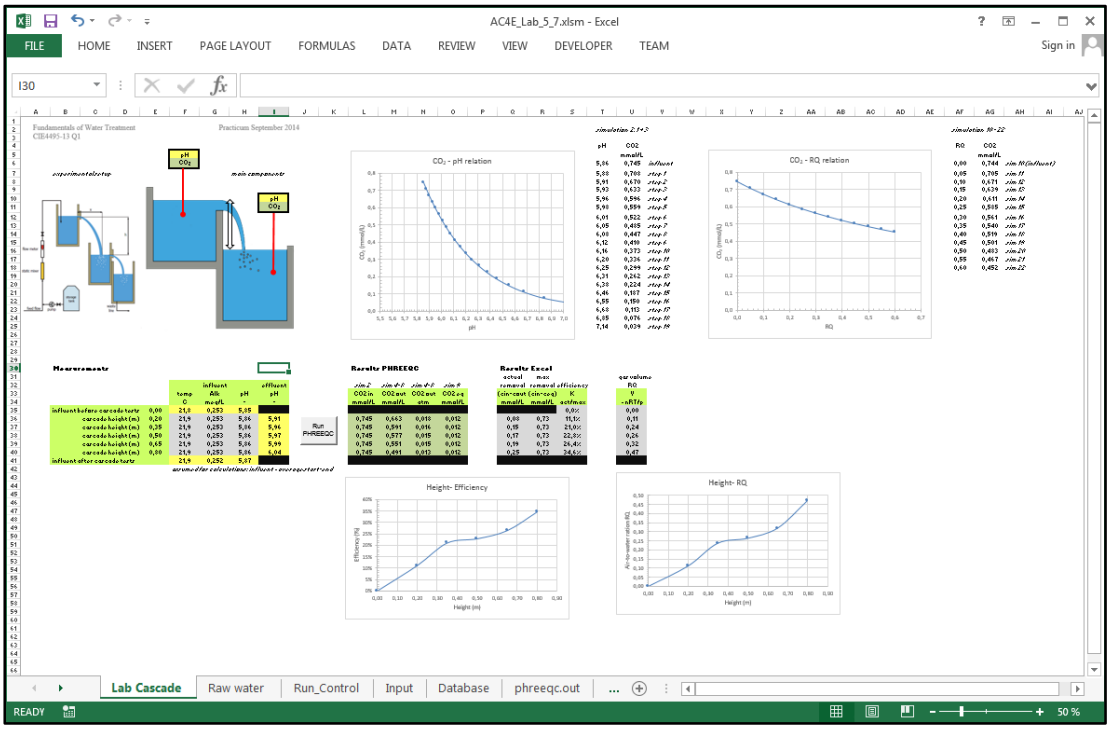
Lab 5.7 Gas transfer with GAS_PHASE

Open AC4E_Lab_5_7.xlsm.
Enable Macros, if requested.
This lab is used in the practicum part of TU Delft course 'Fundamentals of water treatment' in which CO_2 removal in a single step cascade aerator is measured with variable falling height. The experiment uses Delft drinking water which is acidified by HCl to convert HCO_3 into CO_2. This CO_2 is partly removed by cascade aeration. This removal can easily be measured by an increase of pH. PHREEQC is used for calculation of the relation between pH and CO_2 content, and to determine the apparent air-to-water ratio in cascade aeration.

Select sheet 'Raw water'.
The quality of Delft drinking water is obtained by using data from Evides. These parameters are mainly used by the course staff for estimating the required HCl dose. PHREEQC uses this data for calculating the ionic strength, for which the exact value is not very sensitive for the lab results. Relevant parameters for CO_2 removal (temperature, Alkalinity, and pH) are measured as part of the practicum.

Select sheet 'Input'.
Delft drinking water is entered as Solution 1 (Simulation 1), the influent of the cascade aeration as Solution 2 (Simulation 2). Simulation 3 determines the relation between removed CO_2 (negative dosing of CO_2) and pH. Simulation 4 to 8 calculates the CO_2 contents for the measured pH values, as concentration and as gas pressure (from $p_a = 10^{SI}$). Simulation 9 calculated the CO_2 content of water in equilibrium with atmospheric air (CO_2 eq), being the lowest CO_2 which can be achieved by aeration in an atmospheric environment (unlimited air-to-water ratio and full equilibrium between gas and water). Simulation 10-22 determines the relation between remaining CO_2 and air-to-water volume ratio RQ.

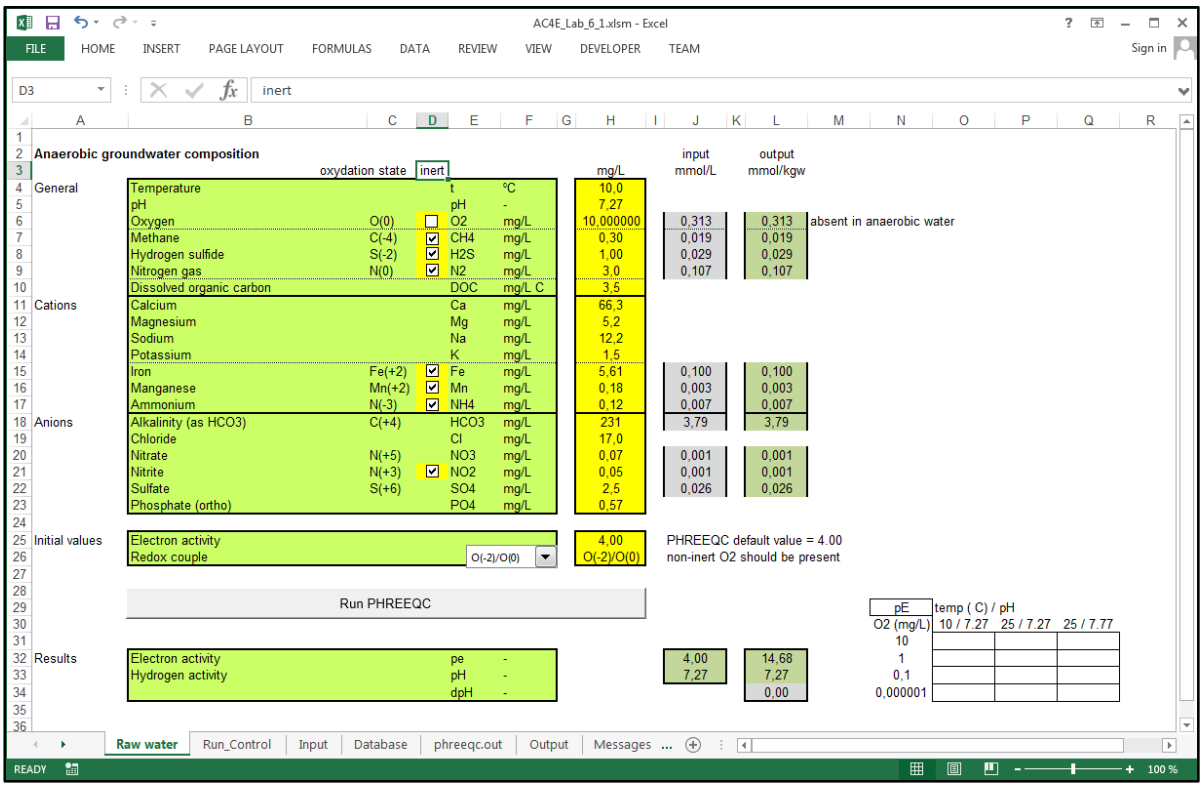
Select sheet 'Water treatment'.
This sheet contains input values and calculated results for this practicum.



Study this Excel workbook to understand its setup and the use of PHREEQC simulations.

Lab 6.1 Groundwater in PHREEQC

Open Lab_6_1.xlsm.
Enable Macros, if requested.
Select sheet 'Raw water', overview its content and notice the check-boxes for selecting inert or non-inert elements (or redox-uncouples or redox-coupled elements) as well is the combo-box for selecting the leading redox couple for the 'initial calculation':



This lab shows a typical composition of 'deep anaerobic groundwater', with the exception of an additional oxygen content of 10 mg/L (pO_2 = 0.18 atm at 10 °C). The latter resembles a realistic oxygen content after aeration, being the initial treatment process in natural groundwater treatment.

This lab starts with the determination of the relation between oxygen content and pE, with all other components set as inert elements.
Execute consecutive simulations (by pressing the 'Run PHREEQC' button) with input values for O_2 as 10, 1, 0.1 respectively 0.000001 mg/L. Write down the calculated pE values.
Repeat these calculations for a water temperature of 25 °C, with the same pH of 7.27.
Repeat these calculations for a water temperature of 25 °C, with a pH of 7.77.

Reset the input data to the original values (10 °C, 7.27 and 10.0 mg/L), and uncheck all inert components. Execute the simulation by pressing the 'Run PHREEQC' button.
Notice the changes and try to explain the differences for each component.
Repeat these simulations with individual components set as inert, and with different redox couples for the 'initial calculation'.

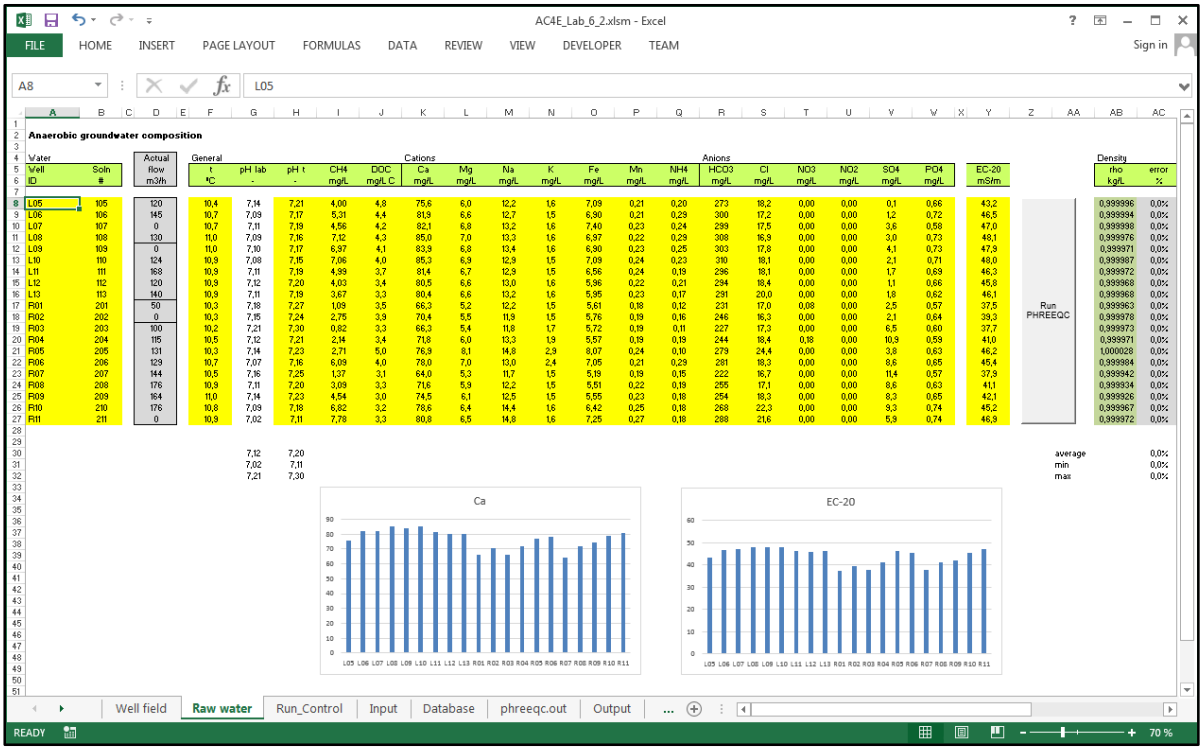
Test

Answer the following questions:

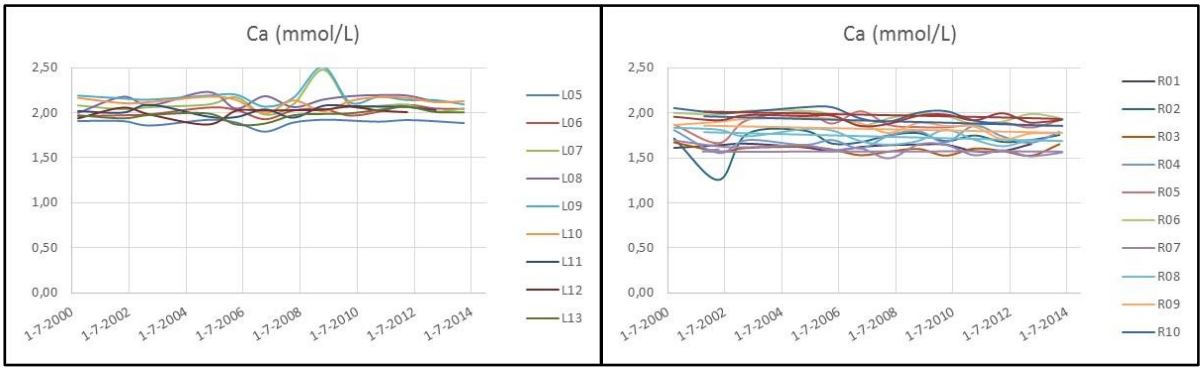
#	Questions		Answers
1	What are the minimum and maximum pE values obtained in the simulations with oxygen and inert components? (*select 1*)	A B C D	13.06 - 14.68 11.00 - 15.00 11.25 - 14.68 11.81 - 13.37
2	Temperature and pH influences pE. What gives lower pE values? (*select 1*)	A B C D	Higher temperature, lower pH Higher temperature, higher pH Lower temperature, lower pH Lower temperature, higher pH
3	Which oxidation states are not enabled as inert in this Lab? (*select 1 or more*)	A B C D	C(+4) S(+6) N(0) N(+5)
4	Which concentrations are changed in the simulations when all components are redox-coupled (not inert)? Why and how? (*select 1 or more*)	A B C D	Mn(+2) pH Alkalinity S(+6)
5	Which concentrations are increased in the simulations when all components are redox-coupled (not inert)? Why and how? (*select 1 or more*)	A B C D	O(0) N(+5) S(+6) Alkalinity
6	What made methane (CH4) to be absent in simulations with redox-coupled oxygen? (*select 1*)	A B C D	Removed by aeration Absorbed in Alkalinity Removed by bacteria Converted into CO2
7	Change O2 to 0.00, C(-4)/C(4) as redox couple and all components as redox-coupled (no inert). Which pE is obtained? (*select 1*)	A B C D	Depends on the initial pE value -3,65 -3,69 Depends on the initial redox couple
8	And which pE is obtained if all but C(-4) are set as redox-uncoupled (inert)? (*select 1*)	A B C D	Depends on the initial pE value -3,65 -3,69 Depends on the initial redox couple

Lab 6.2 Groundwater well fields

Open Lab_6_2.xlsm.
Enable Macros, if requested.
Select sheet 'Raw water', overview its content and notice the column with the actual flow calculated from data and On/Off settings on sheet 'Well field'. Also notice the column with measured values for EC (Electrical Conductivity) at 20 °C.

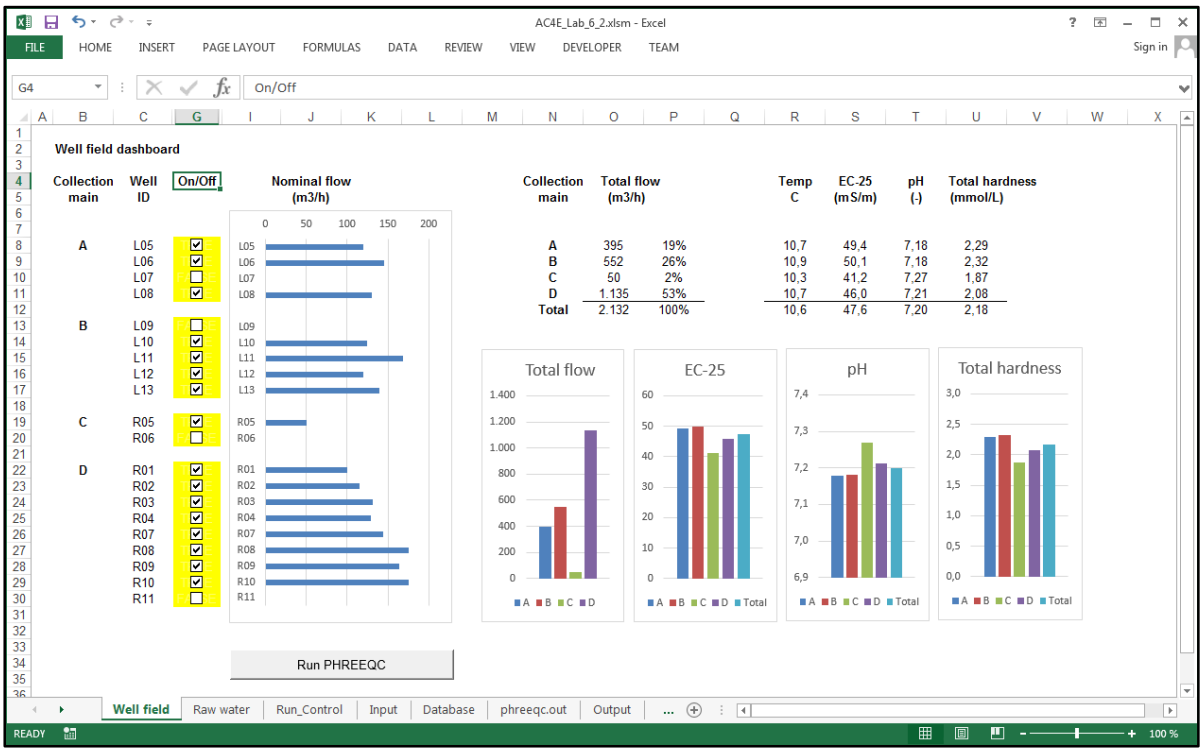


The graphs represent the calcium content respectively Electrical Conductivity of each individual well. It was shown by analyses of data from over 14 years of operation that the water quality of each well is nearly constant, but specific for each well:



This enables the prediction of the actual water quality based on their assumed quality and their actual flow.

Select sheet 'Well field', overview its content and notice the column with On/Off settings of each well. The actual flow of each well is nearly constant because of the characteristics of each well pump, and the hydraulics in the pipe system to the treatment plant.
The constant flow and quality of each well allow for predicting the actual water quality only based on the operating status (On/Off) of each well. This status can be set in the 'dashboard':



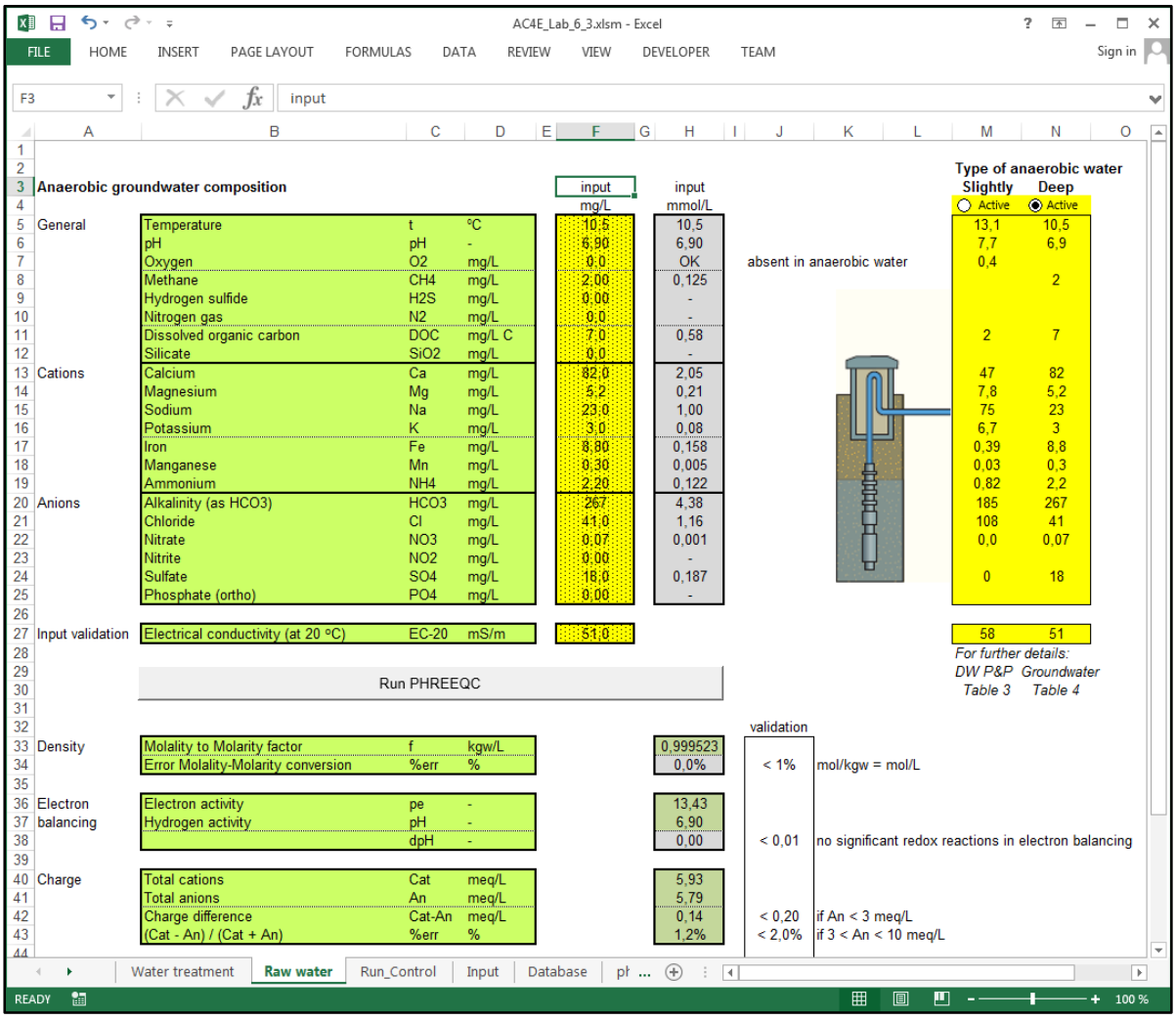
The PHREEQC model for this well field uses the MIX function with the actual flow (as m3/h) in the mixing fraction. Switch to the sheet 'Input' to overview the PHREEQC code for the simulations. The model simulations might be done at each change in pump status. This automated start-up is not included in this Lab.

Some parameters of the calculated water quality are shown in the 'dashboard'. The calculated values can permanently be compared to inline measurements being part of the treatment plant control system. This plant includes chemical softening in pellet reactors using lime. The lime dosing level depends on the actual water quality, which changes by each change in actual production or change in number and specific wells in operation.

Try out several pump settings to see the variation in water quality entering the treatment plant.

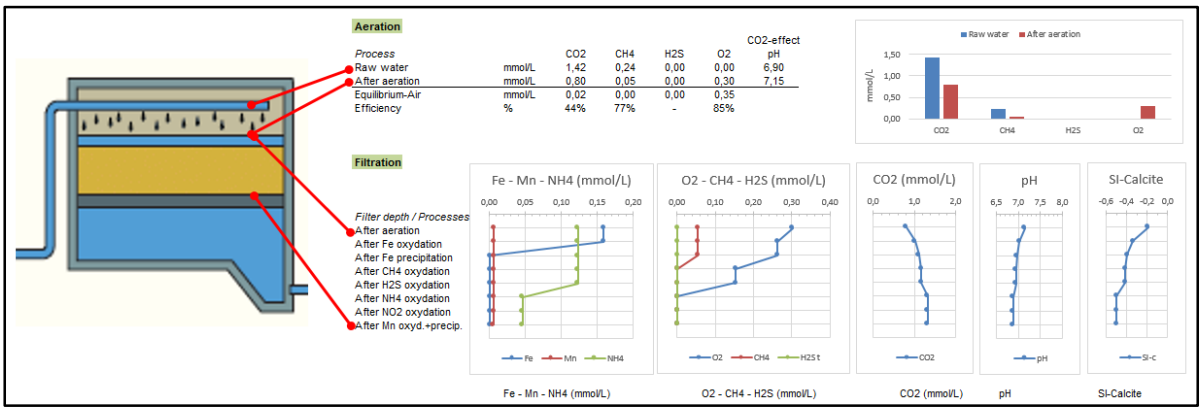
Lab 6.3 Groundwater treatment with aeration and filtration

Open Lab_6_3.xlsm.
Enable Macros, if requested.
Select sheet 'Raw water', overview its content and notice the two columns with yellow cells showing the water quality for slightly anaerobic groundwater respectively deep anaerobic groundwater.
Further details on these examples can be found in the text book 'Drinking water - Principles and Practices' (de Moel a.o., 2006)
Select the radio button for 'Slightly'. The data is copied to the input cells for PHREEQXCEL (yellow with pixel pattern). Notice also the output from Excel calculations (grey cells), and output from PHREEQC (dark green cells). This data might support the user in validating the 'raw water quality'.



Press the button 'Run PHREEQC' to start the calculations. Excel returns on the sheet 'Water treatment' being the Return-sheet as specified on the sheet 'Run_Control'.
This sheets show the results of 15 simulations, dealing with the processes within aeration and filtration of anaerobic groundwater. Overview all results.

Select sheet 'Raw water', and select the radio button for 'Deep'.
Press the button 'Run PHREEQC' to start the calculations
The results on the sheet 'Water treatment' shows that ammonium and manganese are not fully removed because of oxygen shortage for oxidation of these compounds. Further backgrounds of these phenomena will be discussed in Volume 2.



Select sheet 'Input', and overview the PHREEQC code for this Lab.
The input code contains a 'Water treatment' section.
Notice the code for aeration of each individual gas allowing for fine-tuning the composition of atmospheric air, as well as the removal efficiency of each gas by applying an 'effective RQ' (gas-to-water-volume ratio).
The filtration sections deals with all oxidation and precipitation processes. The conversion from redox-inert elements into redox-coupled elements is done with KINETICS+RATES. This conversion is based on the actual contents of the related element as well as the actual oxygen content.

Try out your own 'raw water quality' to see its behaviour in a water treatment plant using natural groundwater treatment processes.

Aquatic Chemistry for engineers - Volume 1

Answer sheet for Lab-test

Name	
Email	
Subject of thesis	

Lab	Question	Answer				Points 0 or 1
Lab 3.1	1	A	B	C	D	
	2	A	B	C	D	
	3	A	B	C	D	
	4	A	B	C	D	
	5	A	B	C	D	
	6	A	B	C	D	
	7	A	B	C	D	
	8	A	B	C	D	
Lab 3.2	1	A	B	C	D	
	2	A	B	C	D	
	3	A	B	C	D	
	4	A	B	C	D	
	5	A	B	C	D	
	6	A	B	C	D	
	7	A	B	C	D	
	8	A	B	C	D	
Lab 3.3	1	A	B	C	D	
	2	A	B	C	D	
	3	A	B	C	D	
	4	A	B	C	D	
	5	A	B	C	D	
	6	A	B	C	D	
	7	A	B	C	D	
	8	A	B	C	D	
Lab 3.4	1	A	B	C	D	
	2	A	B	C	D	
	3	A	B	C	D	
	4	A	B	C	D	
	5	A	B	C	D	
	6	A	B	C	D	
	7	A	B	C	D	
	8	A	B	C	D	
Lab 3.5a	1	A	B	C	D	
	2	A	B	C	D	
	3	A	B	C	D	
	4	A	B	C	D	
	5	A	B	C	D	
	6	A	B	C	D	
	7	A	B	C	D	
	8	A	B	C	D	
Lab 3.5b	1	A	B	C	D	
	2	A	B	C	D	
	3	A	B	C	D	
	4	A	B	C	D	
	5	A	B	C	D	
	6	A	B	C	D	
	7	A	B	C	D	
	8	A	B	C	D	
Total Labs 3						

Aquatic Chemistry for engineers - Volume 1

Answer sheet for Lab-test

Name	
Email	
Subject of thesis	

Lab	Question	Answer				Points 0 or 1
Lab 4.1	1	A	B	C	D	
	2	A	B	C	D	
	3	A	B	C	D	
	4	A	B	C	D	
	5	A	B	C	D	
	6	A	B	C	D	
	7	A	B	C	D	
	8	A	B	C	D	
Lab 4.2	1	A	B	C	D	
	2	A	B	C	D	
	3	A	B	C	D	
	4	A	B	C	D	
	5	A	B	C	D	
	6	A	B	C	D	
	7	A	B	C	D	
	8	A	B	C	D	
Lab 4.3	1	A	B	C	D	
	2	A	B	C	D	
	3	A	B	C	D	
	4	A	B	C	D	
	5	A	B	C	D	
	6	A	B	C	D	
	7	A	B	C	D	
	8	A	B	C	D	
Lab 4.4	1	A	B	C	D	
	2	A	B	C	D	
	3	A	B	C	D	
	4	A	B	C	D	
	5	A	B	C	D	
	6	A	B	C	D	
	7	A	B	C	D	
	8	A	B	C	D	
Lab 4.5	1	A	B	C	D	
	2	A	B	C	D	
	3	A	B	C	D	
	4	A	B	C	D	
	5	A	B	C	D	
	6	A	B	C	D	
	7	A	B	C	D	
	8	A	B	C	D	
Lab 4.6	1	A	B	C	D	
	2	A	B	C	D	
	3	A	B	C	D	
	4	A	B	C	D	
	5	A	B	C	D	
	6	A	B	C	D	
	7	A	B	C	D	
	8	A	B	C	D	
Total Labs 4						

Aquatic Chemistry for engineers - Volume 1

Answer sheet for Lab-test

Name	
Email	
Subject of thesis	

Lab	Question	Answer				Points 0 or 1
Lab 5.1	1	A	B	C	D	
	2	A	B	C	D	
	3	A	B	C	D	
	4	A	B	C	D	
	5	A	B	C	D	
	6	A	B	C	D	
	7	A	B	C	D	
	8	A	B	C	D	
Lab 5.2	1	A	B	C	D	
	2	A	B	C	D	
	3	A	B	C	D	
	4	A	B	C	D	
	5	A	B	C	D	
	6	A	B	C	D	
	7	A	B	C	D	
	8	A	B	C	D	
Lab 5.3						
Lab 5.4	1	A	B	C	D	
	2	A	B	C	D	
	3	A	B	C	D	
	4	A	B	C	D	
	5	A	B	C	D	
	6	A	B	C	D	
	7	A	B	C	D	
	8	A	B	C	D	
Lab 5.5	1	A	B	C	D	
	2	A	B	C	D	
	3	A	B	C	D	
	4	A	B	C	D	
	5	A	B	C	D	
	6	A	B	C	D	
	7	A	B	C	D	
	8	A	B	C	D	
Lab 5.6						
Lab 5.7						
Total Labs 5						

Aquatic Chemistry for engineers - Volume 1

Answer sheet for Lab-test

Name	
Email	
Subject of thesis	

Lab	**Question**	**Answer**				**Points** 0 or 1
Lab 6.1	1	A	B	C	D	
	2	A	B	C	D	
	3	A	B	C	D	
	4	A	B	C	D	
	5	A	B	C	D	
	6	A	B	C	D	
	7	A	B	C	D	
	8	A	B	C	D	
Lab 6.2						
Lab 6.3						
Total Labs 6						

Aquatic Chemistry for engineers - Volume 1

Answer sheet for Lab-test

Name	
Email	
Subject of thesis	

Lab	Question	Answer				Points 0 or 1
Lab 3.1	1	A	**B**	C	D	1
	2	A	**B**	C	D	1
	3	**A**	B	C	D	1
	4	**A**	**B**	**C**	**D**	1
	5	A	B	**C**	D	1
	6	A	**B**	C	D	1
	7	A	B	C	**D**	1
	8	A	B	**C**	D	1
Lab 3.2	1	A	B	C	**D**	1
	2	**A**	**B**	C	**D**	1
	3	**A**	B	**C**	D	1
	4	**A**	**B**	**C**	D	1
	5	A	B	**C**	D	1
	6	A	B	**C**	D	1
	7	**A**	B	C	D	1
	8	A	**B**	**C**	D	1
Lab 3.3	1	**A**	**B**	C	D	1
	2	A	B	C	**D**	1
	3	**A**	B	**C**	**D**	1
	4	A	B	**C**	D	1
	5	A	**B**	C	D	1
	6	A	B	C	**D**	1
	7	A	B	**C**	D	1
	8	A	**B**	C	D	1
Lab 3.4	1	A	**B**	C	D	1
	2	A	B	**C**	D	1
	3	A	B	C	**D**	1
	4	**A**	B	C	D	1
	5	A	B	**C**	**D**	1
	6	**A**	**B**	C	**D**	1
	7	A	B	**C**	D	1
	8	A	**B**	**C**	D	1
Lab 3.5a	1	A	**B**	C	D	1
	2	A	B	C	**D**	1
	3	A	B	C	**D**	1
	4	A	B	**C**	D	1
	5	A	B	**C**	D	1
	6	**A**	B	**C**	**D**	1
	7	A	B	**C**	D	1
	8	**A**	B	C	**D**	1
Lab 3.5b	1	A	**B**	C	D	1
	2	A	B	**C**	D	1
	3	**A**	**B**	C	**D**	1
	4	**A**	B	**C**	**D**	1
	5	**A**	**B**	**C**	**D**	1
	6	A	**B**	**C**	D	1
	7	A	B	C	**D**	1
	8	**A**	B	C	D	1
Total Labs 3						48

Aquatic Chemistry for engineers - Volume 1

Answer sheet for Lab-test

Name	
Email	
Subject of thesis	

Lab	Question	Answer				Points 0 or 1
Lab 4.1	1	A	**B**	C	D	1
	2	**A**	B	C	D	1
	3	**A**	B	C	D	1
	4	A	B	C	**D**	1
	5	A	B	C	**D**	1
	6	**A**	**B**	C	**D**	1
	7	A	B	**C**	D	1
	8	A	**B**	**C**	D	1
Lab 4.2	1	A	**B**	C	D	1
	2	A	B	C	**D**	1
	3	**A**	B	C	D	1
	4	A	B	**C**	D	1
	5	A	B	**C**	D	1
	6	A	B	C	**D**	1
	7	A	**B**	**C**	**D**	1
	8	A	**B**	C	D	1
Lab 4.3	1	A	**B**	C	D	1
	2	A	B	C	**D**	1
	3	**A**	B	C	D	1
	4	A	B	**C**	D	1
	5	A	B	**C**	D	1
	6	A	B	C	**D**	1
	7	A	**B**	**C**	**D**	1
	8	A	**B**	C	D	1
Lab 4.4	1	A	**B**	C	D	1
	2	A	B	C	**D**	1
	3	A	**B**	C	D	1
	4	A	**B**	**C**	**D**	1
	5	**A**	B	C	D	1
	6	A	B	C	**D**	1
	7	**A**	B	C	D	1
	8	A	B	**C**	D	1
Lab 4.5	1	A	B	**C**	D	1
	2	A	B	**C**	D	1
	3	**A**	B	C	D	1
	4	A	**B**	C	D	1
	5	**A**	B	C	D	1
	6	**A**	B	C	D	1
	7	**A**	**B**	**C**	**D**	1
	8	**A**	**B**	**C**	D	1
Lab 4.6	1	A	**B**	C	D	1
	2	A	B	C	**D**	1
	3	A	B	**C**	D	1
	4	A	B	**C**	D	1
	5	A	B	C	**D**	1
	6	A	B	**C**	D	1
	7	A	**B**	C	D	1
	8	A	B	**C**	D	1
Total Labs 4						48

Aquatic Chemistry for engineers - Volume 1

Answer sheet for Lab-test

Name	
Email	
Subject of thesis	

Lab	Question	Answer				Points 0 or 1
Lab 5.1	1	A	B	C	**D**	
	2	**A**	B	C	D	
	3	A	B	**C**	D	
	4	A	**B**	C	D	
	5	A	**B**	C	D	
	6	**A**	B	C	**D**	
	7	A	B	**C**	D	
	8	A	B	**C**	D	
Lab 5.2	1	A	**B**	C	D	
	2	A	B	**C**	D	
	3	A	B	C	**D**	
	4	**A**	B	**C**	**D**	
	5	A	B	**C**	D	
	6	A	B	C	**D**	
	7	A	**B**	C	D	
	8	A	**B**	C	D	
Lab 5.3						
Lab 5.4	1	A	**B**	C	D	
	2	A	B	C	**D**	
	3	**A**	B	C	D	
	4	A	**B**	**C**	D	
	5	A	B	**C**	D	
	6	A	B	C	**D**	
	7	A	**B**	C	**D**	
	8	**A**	**B**	C	D	
Lab 5.5	1	A	B	**C**	D	
	2	A	**B**	C	D	
	3	A	**B**	C	D	
	4	A	**B**	**C**	D	
	5	A	**B**	C	D	
	6	A	B	**C**	D	
	7	A	**B**	C	**D**	
	8	**A**	**B**	**C**	D	
Lab 5.6						
Lab 5.7						
Total Labs 5						

Aquatic Chemistry for engineers - Volume 1

Answer sheet for Lab-test

Name	
Email	
Subject of thesis	

Lab	**Question**	**Answer**				**Points** 0 or 1
Lab 6.1	1	A	B	C	D	
	2	A	B	C	D	
	3	A	B	C	D	
	4	A	B	C	D	
	5	A	B	C	D	
	6	A	B	C	D	
	7	A	B	C	D	
	8	A	B	C	D	
Lab 6.2						
Lab 6.3						
Total Labs 6						

VOLUMES

Volume 1 Starting with PHREEQC for water treatment

1. Introduction
2. Using PHREEQXCEL
3. Drinking water in PHREEQC
4. Controlling output
5. Water treatment
6. Groundwater and redox reactions
7. Next steps

Volume 2 Drinking water with PHREEQC (*under development*)

1. Introduction
2. Drinking water quality (*includes DW – P&P chapter Water quality*)
    1 Concentrations (WQ 3.2)
    2 Ions in water (WQ 3.3)
    3 Gases in water (WQ 3.4)
    4. Acid - base reaction (WQ 3.5 plus 'Ionization of water')
    5. Precipitation reactions (WQ 3.6)
    6. Redox reactions (WQ 3.7)
3. Validation of water analyses
4. Groundwater treatment (*includes DW – P&P chapter Groundwater*)
    1. Treatment schemes (GW 4.1 - 4.2 - 4.3)
    2. Aeration and gas transfer (GW 4.5 plus 'Gases in water')
    3. Groundwater filtration (GW 4.6)
    4. Neutralization (GW 4.7)
    5. Softening (GW 4.8)
    6. Membrane filtration (GW 4.9)
    7. Ion exchange
5. Surface water treatment (*includes DW – P&P chapter Surface water*)
    1. Coagulation (flocculation-sedimentation-filtration)
    2. Activated carbon filtration
    3. Disinfection
6. Kinetics of treatment processes
    1. Softening in pellet reactors
    2. Limestone contactors
7. Next steps

Volume 3 Waste water with PHREEQC (*under development*)

1. Introduction
2. Waste water quality
3. Biological treatment
4. Physical-chemical treatment

etc.

Volume 4 Industrial water with PHREEQC (*under development*)

1. Introduction
2. Cooling water systems
3. Boiler water systems

etc.