

Aquatic Chemistry for engineers

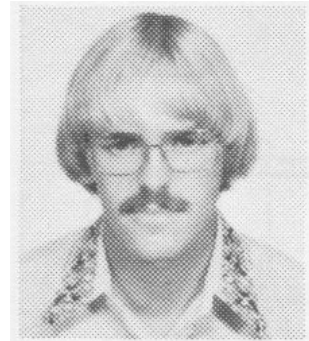
PHREEQC / PHREEQXCEL for water treatment

12 September 2013

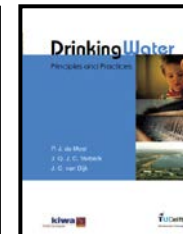
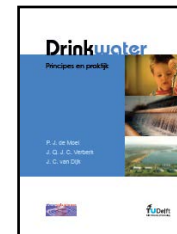
Peter de Moel – TU Delft

Personal introduction ...


Record on water chemistry



- 1979 - 1980 : KIWA
 - KIWA report and computer program aggressive water
- 1980 - 2000 : DHV
 - Patent softening Amsterdam (Graveland cs)
 - Publication / HP41 program on CaCO_3 equilibrium
 - Publications / presentations (H_2O - JAWWA – Las Vegas)
 - Design and build over 40 water treatment plants, worldwide
- 2000 - present : TU Delft (part-time)
 - BSc / MSc – education
 - OpenCourseWare (2007 -)
 - Aquatic Chemistry 4 Eng (2011 -)
 - Online MSc (2013/2014)
 - edX MOOC (16 Sept)

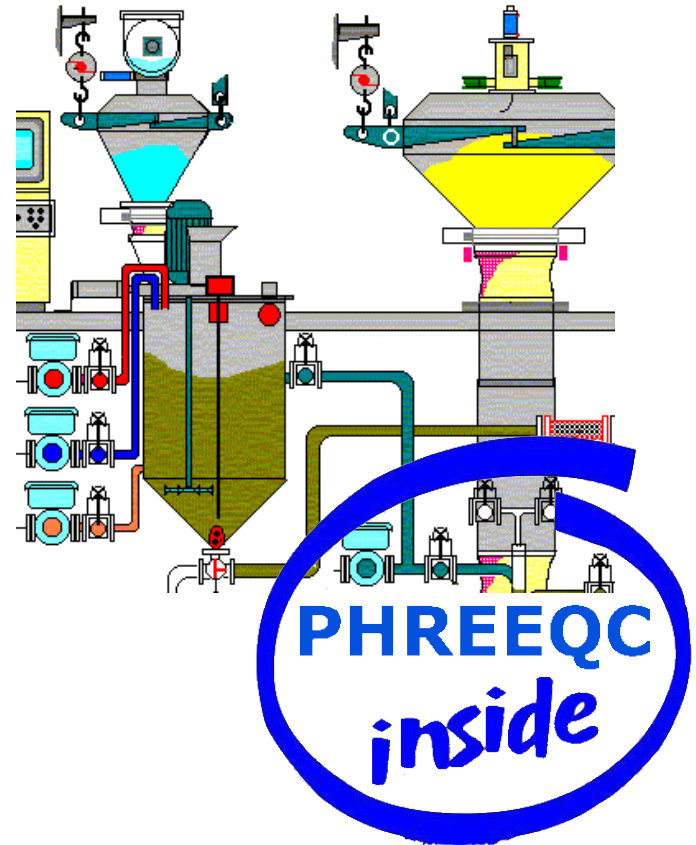
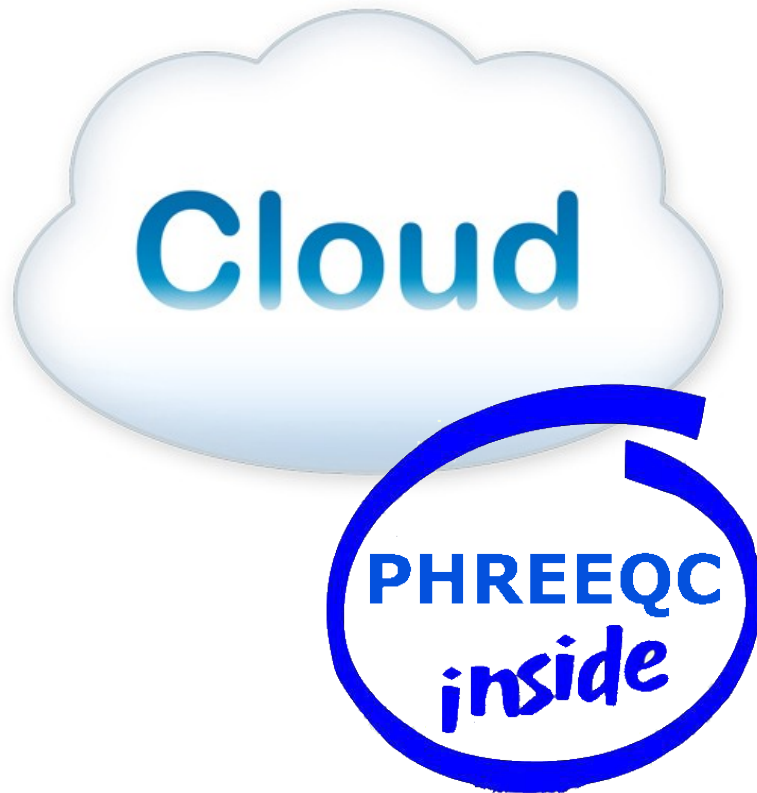


CTB3365x: Introduction to Water Treatment
Learn about urban water services, focusing on basic drinking water and wastewater treatment technologies [MORE](#)
STARTS: 16 Sep 2013 • INSTRUCTORS: Jules van Lier • DelftX



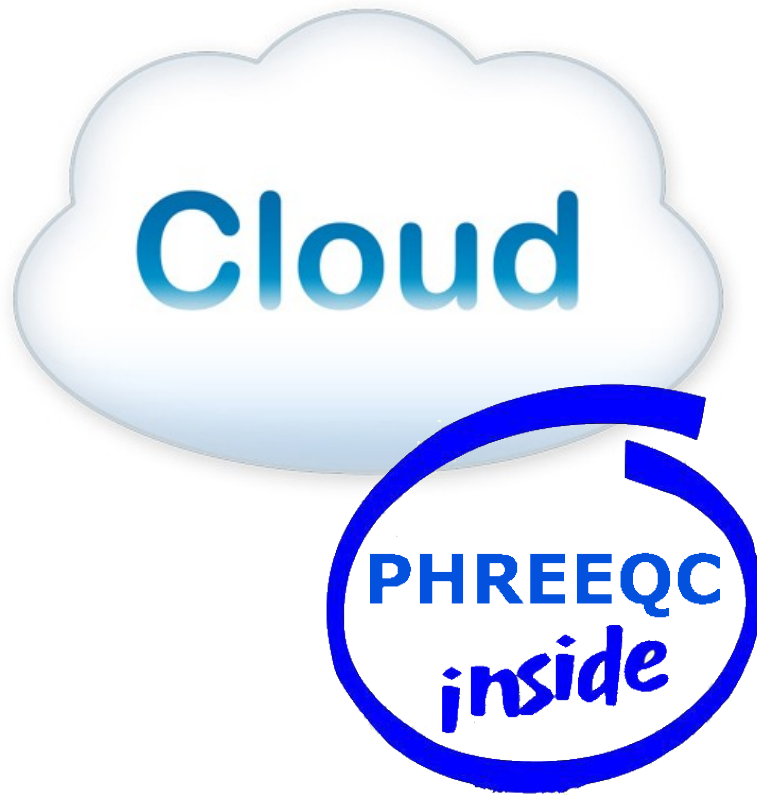
access courseware

PHREEQC – Our focus points



- Practical applications for drinking water and wastewater

PHREEQC “in the cloud”



The screenshot shows a Blackboard Learn interface for a course titled 'Aquatic Chemistry for Engineers'. The main content area is titled 'Drinking water - Conductivity + Charge balance' and contains instructions for running the simulation. Below the instructions are three tables of input parameters: General, Cations, and Anions. Each table has columns for the parameter name, units, and a numerical value in a text input field. A 'Run Phreeqc' button is located at the bottom right of the input fields.

Steps to do:

- Fill in water quality data
- Press Run Phreeqc
- Wait a few seconds for (updated) output
- optional: Change input values and re-Run Phreeqc
- optional: if email-address is filled: Send Excel file (full version) by email
- optional: if email-address is not filled: Download and Save Excel file (full version)

General

| | | | |
|--------------------------|----------------|------|------|
| Temperature | t | ° C | 11.5 |
| Oxygen | O ₂ | mg/L | 11.0 |
| pH | | | 7.91 |
| Conductivity (EC 20 ° C) | | mS/m | 38.4 |

Cations

| | | | |
|-----------|----|------|------|
| Calcium | Ca | mg/L | 40.5 |
| Magnesium | Mg | mg/L | 5.30 |
| Sodium | Na | mg/L | 45.7 |
| Potassium | K | mg/L | 2.0 |

Anions

| | | | |
|--------------------|------------------|------|-----|
| Hydrogen carbonate | HCO ₃ | mg/L | 199 |
| Chloride | Cl | mg/L | 38 |
| Nitrate | NO ₃ | mg/L | 7.0 |
| Sulfate | SO ₄ | mg/L | 7.9 |

Run Phreeqc

- Demo <http://drinkwater.citg.tudelft.nl/AquaticChemistry>

PHREEQC in Excel

AQUATIC CHEMISTRY for Engineers

Module: **Drinking water**
with water quality check for macro parameters

Phreeqc Input for all phreeqc_wt.dat parameters for aerobic water (no input of C(-4), S(-2), N(0) and pe)

| Sample description | Oldeholtgade, produced drinking water (26 April 2011) | | | Assumption: | Drinking water: |
|--------------------|---|-----|------|--|-------------------------------------|
| | | | | mg/L =mg/kg _s =mg/kg _w | |
| Basic data | Temperature | t | °C | 11,5 | < 25 °C NL |
| | Oxygen | O2 | mg/L | 11,0 | > 2 mg/L NL |
| | pH | - | - | 7,91 | > 7,0 < 9,5 NL |
| | Conductivity (EC 20 °C) | - | mS/m | 38,4 | < 125 (20 °C) mS/m NL |
| | Conductivity (EC at t °C) | - | - | 31,2 | (conversion ISO 7888 / EN 27888) NL |
| | Total dissolved solids (TDS residue) | - | mg/L | - | - NL |
| Cations | Calcium | Ca | mg/L | 40,5 | Tot. Hardness > 1 mmol/L NL |
| | Magnesium | Mg | mg/L | 5,30 | Tot. Hardness > 1 mmol/L NL |
| | Sodium | Na | mg/L | 49,7 | < 150 mg/L NL |
| | Potassium | K | mg/L | 2,0 | - NL |
| | Iron | Fe | mg/L | 0,01 | < 0,20 mg/L NL |
| | Manganese | Mn | mg/L | 0,00 | < 0,05 mg/L NL |
| | Ammonium | NH4 | mg/L | 0,03 | < 0,20 mg/L NL |
| | Aluminium | Al | µg/L | 0,2 | - NL |
| | Barium | Ba | µg/L | 9,58 | - NL |
| | Cadmium | Cd | µg/L | 0,00 | < 5 µg/L NL |
| | Copper | Cu | µg/L | 21,6 | < 2000 µg/L NL |
| | Lead | Pb | µg/L | 0,1 | < 10 µg/L NL |
| | Lithium | Li | µg/L | 0,00 | - NL |

- Demo ?

PHREEQC

Development since 1980



The screenshot shows a web browser window with the URL www.brr.cr.usgs.gov/projects/GWC_coupled/phreeqc/. The page features the USGS logo with the tagline "science for a changing world". The main heading is "PHREEQC (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations". Below this, there are three sections: "Information:" with links to an abstract, module abstract, fact sheet, user's guide, and training notes; "Current Versions:" with links to release notes and installation instructions for Win32, Linux, and MacOS; and "Other Resources:" with links to a FAQ and a mail archive.

pH - Redox – Equilibrium - Calculations



PHREEQC

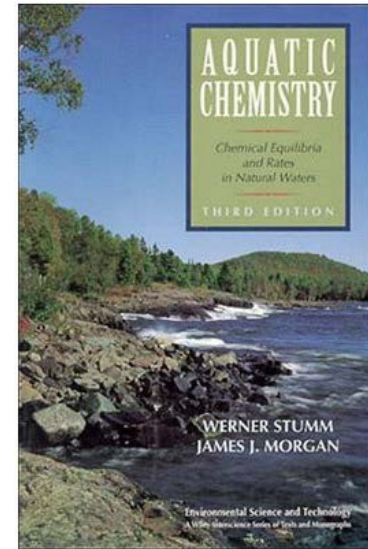
pH - Redox - Equilibrium Calculations

- 25 elements
- 21 redox states
- 180 species

- 72 solid phases
- 8 gas phases
- + Exchange eq.
- + Surface eq.
- + Rates

- 8 databases

C Ca Mg Na etc
C(+4) C(-4) etc
C(+4) : CO₂ HCO₃ CO₃ etc
C(-4) : CH₄ etc
CaCO₃ Fe(OH)₃ etc
CO₂ H₂S etc
(ion-exchange)
(activated carbon)
(kinetics)



Aquatic Chemistry (Stumm & Morgan) in your laptop

PHREEQC

Freely available



PHREEQC Welcome Page x

wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/

Download:

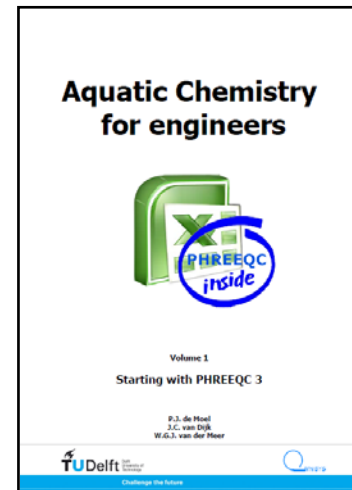
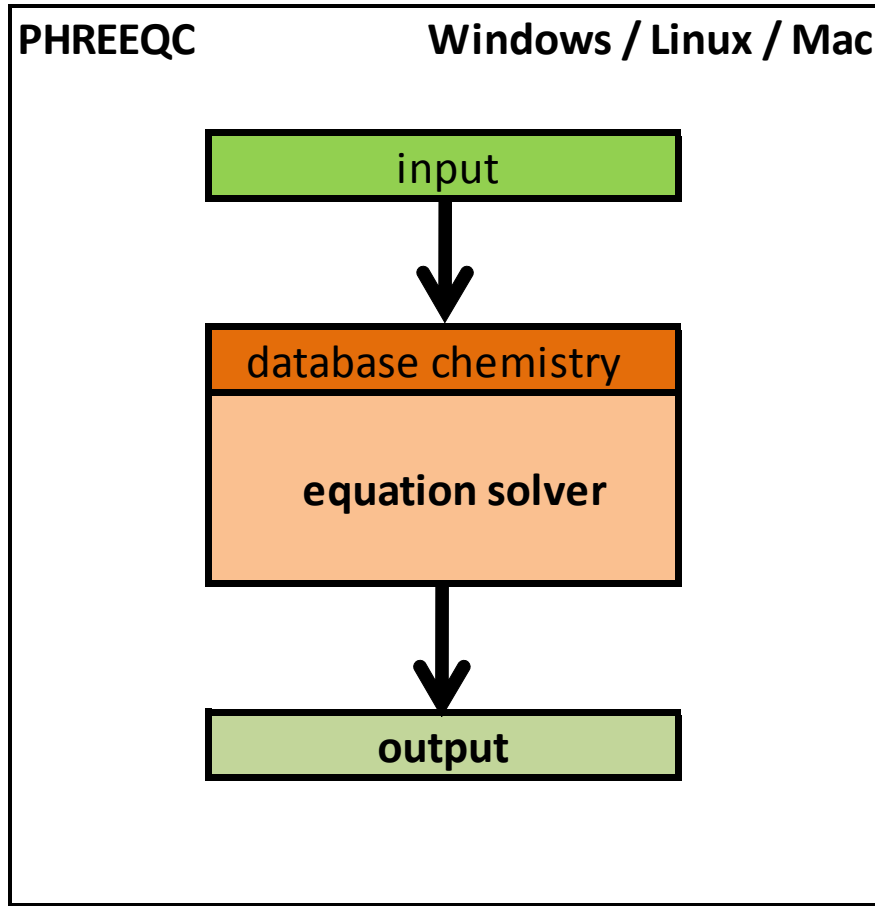
The Free Software Foundation's [gunzip](#) is necessary to uncompress the UNIX tar files available below. However, some World Wide Web browsers automatically uncompress retrieved files. Thus, running gunzip as stated in the installation instructions may be unnecessary.

| Graphical User Interfaces | | | | |
|---------------------------|-----------|--|------|---|
| Platform | Processor | File names | Size | Notes |
| Windows | 32-bit | phreeqc-3.0.6-7757.msi | 13M | Executable, source, database files, examples, PDF documentation |
| | | Notepad++ interface | -- | Appelo's Notepad++ interface to PHREEQC version 3 |
| | | PHREEQC for Windows | -- | PHREEQC for Windows Home Page |
| Batch Versions | | | | |
| Platform | Processor | File names | Size | Notes |
| Linux | 32-bit | phreeqc-3.0.6-7757.i686.tar.gz | 14M | Executable, database files, examples, PDF documentation |
| | 64-bit | phreeqc-3.0.6-7757.x86_64.tar.gz | 14M | Executable, database files, examples, PDF documentation |
| | Source | phreeqc-3.0.6-7757.tar.gz | 6.4M | Source, database files, examples, PDF documentation |
| MacOS(Intel) | 64-bit | phreeqc-2.18.3-5570.dmg | 2.6M | Executable (Intel), database files, examples, and PDF documentation |
| Windows | 32-bit | phreeqc-3.0.6-7757.msi | 3.3M | Executable, source, database files, examples, PDF documentation |
| Modules | | | | |
| Platform | Processor | File names | Size | Notes |
| Any | Any | iphreeqc-3.0.6-7757.tar.gz | 1.3M | Source with configure and VS2005 project file |
| Windows | 32-bit | Iphreeqc-3.0.6-7757-vs2005-win32.7z | 12M | Static and Dynamic (DLL) Libraries (VS2005) |
| | | Iphreeqc-3.0.6-7757-vs2005-win32.zip | 25M | Static and Dynamic (DLL) Libraries (VS2005) |
| | 64-bit | Iphreeqc-3.0.6-7757-vs2005-x64.7z | 16M | Static and Dynamic (DLL) Libraries (VS2005) |
| | | Iphreeqc-3.0.6-7757-vs2005-x64.zip | 32M | Static and Dynamic (DLL) Libraries (VS2005) |
| Windows COM | 32-bit | IphreeqcCOM-3.0.6-7757-win32.msi | 2.9M | COM Server, CHM documentation |
| | 64-bit* | IphreeqcCOM-3.0.6-7757-x64.msi | 3.0M | COM Server, CHM documentation |

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

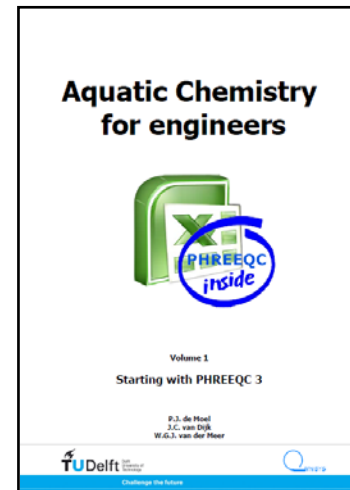
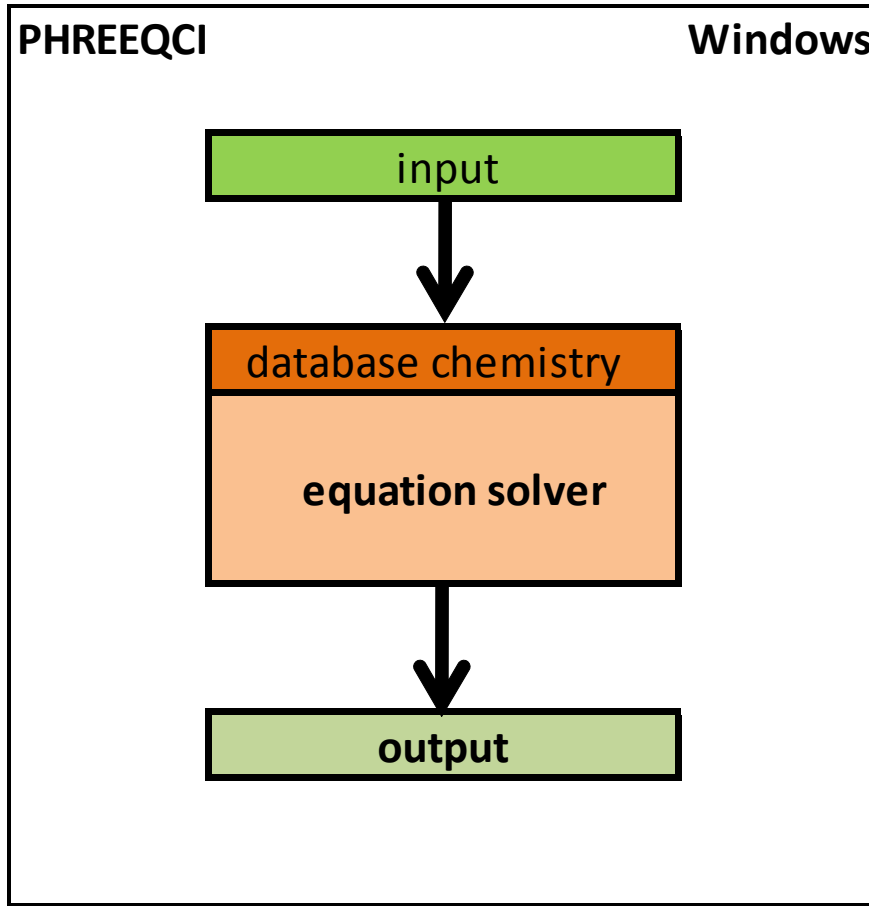
PHREEQC

Batch version (text) - since 1980/1995



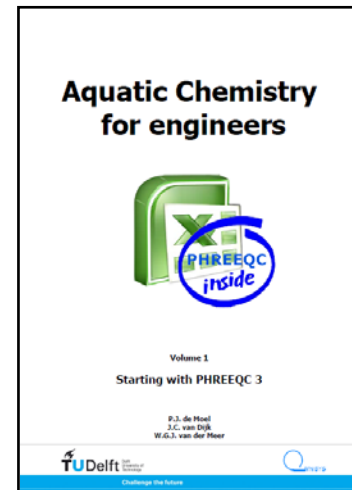
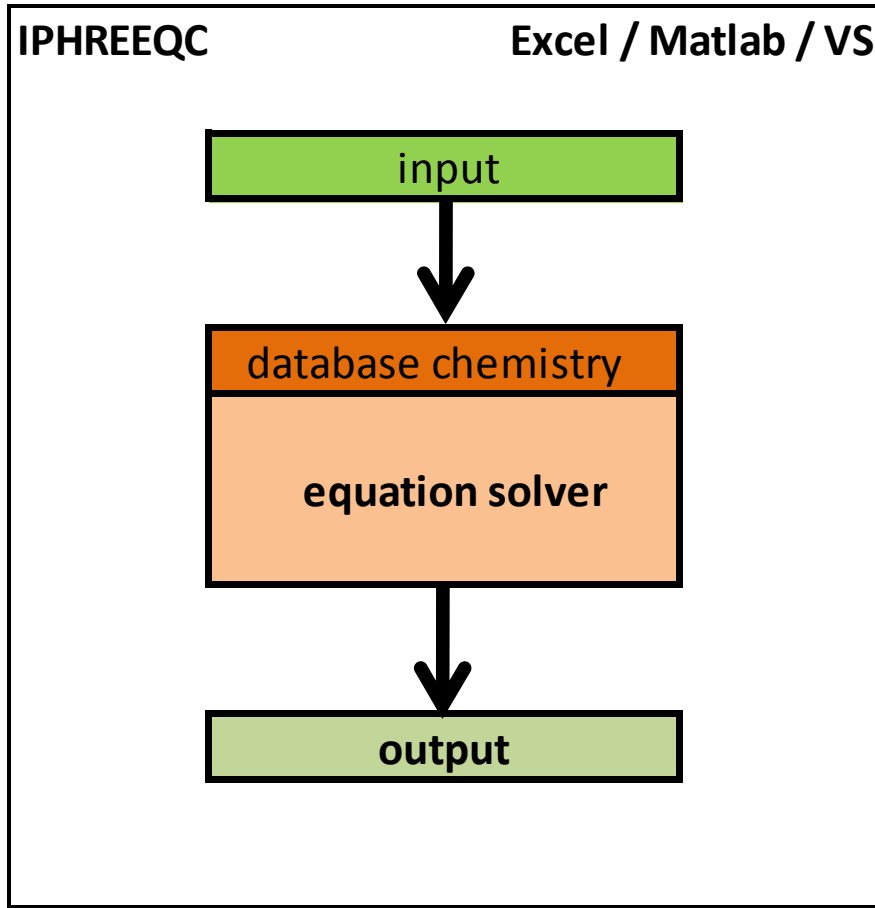
PHREEQC

Graphical user interface - since 2001



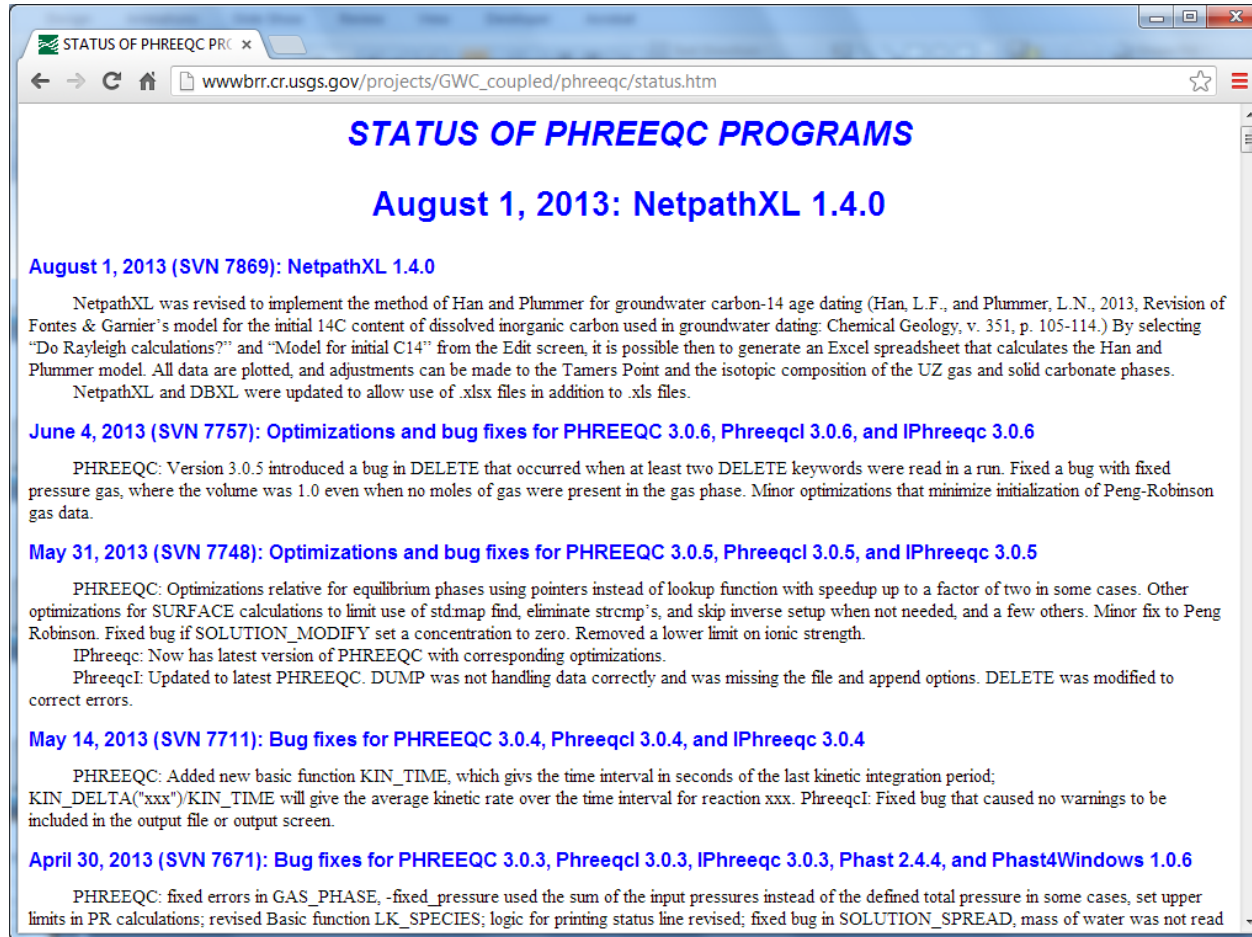
PHREEQC

Modules (COM / VS) - since 2011



PHREEQC

Latest release PHREEQC: 3 month ago



The screenshot shows a web browser window with the address bar displaying `www.brr.cr.usgs.gov/projects/GWC_coupled/phreeqc/status.htm`. The page title is "STATUS OF PHREEQC PROGRAMS". The main heading is "August 1, 2013: NetpathXL 1.4.0". Below this, there are several sections of updates:

- August 1, 2013 (SVN 7869): NetpathXL 1.4.0**

NetpathXL was revised to implement the method of Han and Plummer for groundwater carbon-14 age dating (Han, L.F., and Plummer, L.N., 2013, Revision of Fontes & Garnier's model for the initial ^{14}C content of dissolved inorganic carbon used in groundwater dating: *Chemical Geology*, v. 351, p. 105-114.) By selecting "Do Rayleigh calculations?" and "Model for initial C^{14} " from the Edit screen, it is possible then to generate an Excel spreadsheet that calculates the Han and Plummer model. All data are plotted, and adjustments can be made to the Tamers Point and the isotopic composition of the U^{238} gas and solid carbonate phases. NetpathXL and DBXL were updated to allow use of .xlsx files in addition to .xls files.
- June 4, 2013 (SVN 7757): Optimizations and bug fixes for PHREEQC 3.0.6, Phreeqcl 3.0.6, and IPhreeqc 3.0.6**

PHREEQC: Version 3.0.5 introduced a bug in DELETE that occurred when at least two DELETE keywords were read in a run. Fixed a bug with fixed pressure gas, where the volume was 1.0 even when no moles of gas were present in the gas phase. Minor optimizations that minimize initialization of Peng-Robinson gas data.
- May 31, 2013 (SVN 7748): Optimizations and bug fixes for PHREEQC 3.0.5, Phreeqcl 3.0.5, and IPhreeqc 3.0.5**

PHREEQC: Optimizations relative for equilibrium phases using pointers instead of lookup function with speedup up to a factor of two in some cases. Other optimizations for SURFACE calculations to limit use of std::map find, eliminate strcmp's, and skip inverse setup when not needed, and a few others. Minor fix to Peng Robinson. Fixed bug if SOLUTION_MODIFY set a concentration to zero. Removed a lower limit on ionic strength. IPhreeqc: Now has latest version of PHREEQC with corresponding optimizations. Phreeqcl: Updated to latest PHREEQC. DUMP was not handling data correctly and was missing the file and append options. DELETE was modified to correct errors.
- May 14, 2013 (SVN 7711): Bug fixes for PHREEQC 3.0.4, Phreeqcl 3.0.4, and IPhreeqc 3.0.4**

PHREEQC: Added new basic function KIN_TIME, which gives the time interval in seconds of the last kinetic integration period; KIN_DELTA("xxx")KIN_TIME will give the average kinetic rate over the time interval for reaction xxx. Phreeqcl: Fixed bug that caused no warnings to be included in the output file or output screen.
- April 30, 2013 (SVN 7671): Bug fixes for PHREEQC 3.0.3, Phreeqcl 3.0.3, IPhreeqc 3.0.3, Phast 2.4.4, and Phast4Windows 1.0.6**

PHREEQC: fixed errors in GAS_PHASE, -fixed_pressure used the sum of the input pressures instead of the defined total pressure in some cases, set upper limits in PR calculations; revised Basic function LK_SPECIES; logic for printing status line revised; fixed bug in SOLUTION_SPREAD, mass of water was not read

PHREEQC

Why is it so successful (in geohydrology) ?

PHREEQC is the 'de facto' standard in geohydrochemistry

- Freely available
- 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
- Large growing user group (mostly scientists)
- International assessment and recognition

PHREEQC

Why is it not (yet) used in water treatment ?

PHREEQC is hardly/not known in water treatment

- Requires above average skills in water chemistry
- Redox potential is not known/used as chemical concept in treatment
- High threshold for starters
- Absence of scientific literature on water treatment with PHREEQC
- Absence of educational material on PHREEQC for water treatment
- Requires modification for practical application (N-chemistry)

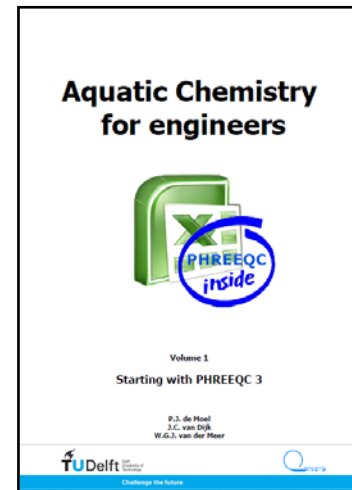
PHREEQC

Why is it accessible now ?

PHREEQC is now accessible for our SE students

- Applied in PhD Weren de Vet + Doris van Halem (groundwater)
- Applied in MSc Harmen van der Laan + Laia Moré Roca + Jink Gude + Amir Haidari + Do Phi Bang
- Applied in BSc Tim van Dijk

- Available as module for MatLab and Excel
(since April 2011)
- Self study course TU Delft Sanitary Engineering:
Aquatic Chemistry for engineers
(since September 2011)



PHREEQC

Basics: all elements – pe – pH - temperature

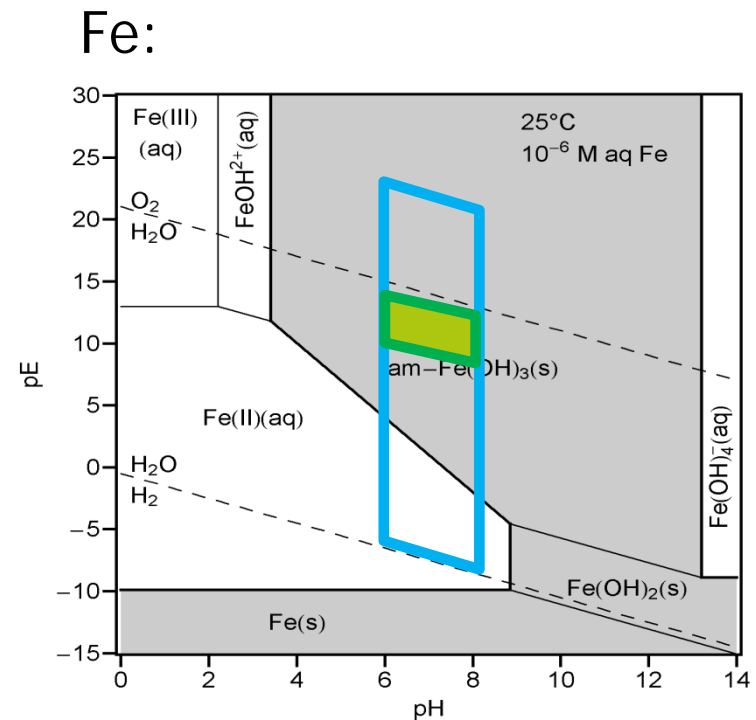
- elements (not species):
 - Ca, Fe, C, S, P etc

The image shows a periodic table with several elements highlighted by red circles. The highlighted elements are: H, Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra, B, C, N, O, F, Al, Si, P, S, Cl, Br, I, At, Pb, and various transition metals including Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg, Pt, Au, Ag, Pd, Rh, Ru, Tc, Mo, Nb, Zr, Y, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr, Rf, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Xe, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, At, Rn, Rf, Db, Sg, Bh, Hs, Mt, Uun, Uuu, Uub, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr.

PHREEQC

Basics: all elements – pe – pH - temperature

- elements (not species):
 - Ca, Fe, C, S, P etc
- pe (redox state):
 - natural water : pe = -8 – 15
 - with Oxygen: pe > 12
- pH (acidity):
 - natural water : pH = 6 – 8
 - CO₂ – HCO₃ – CO₃
- temperature:
 - natural water : temp = 0 – 25 °C

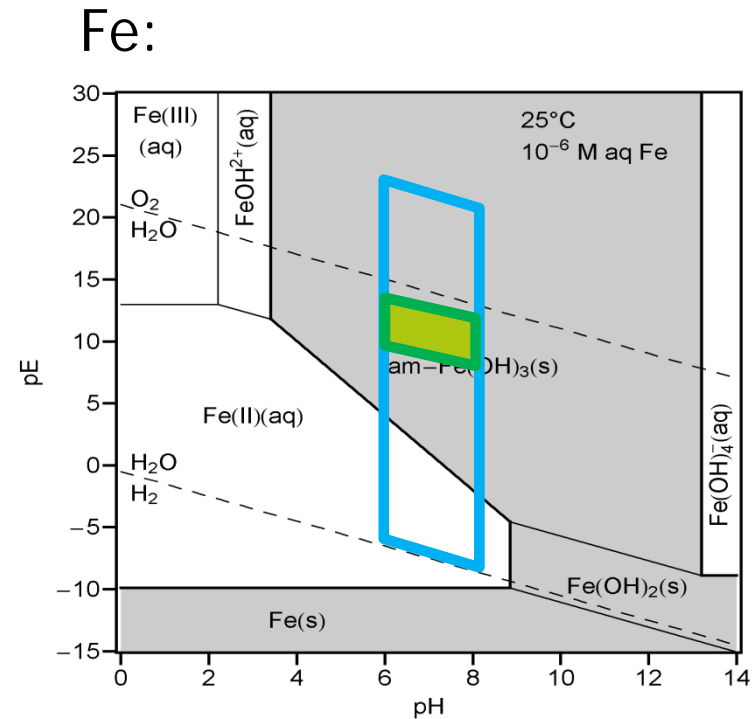


PHREEQC gives all species, and SI for all solids and gases

PHREEQC

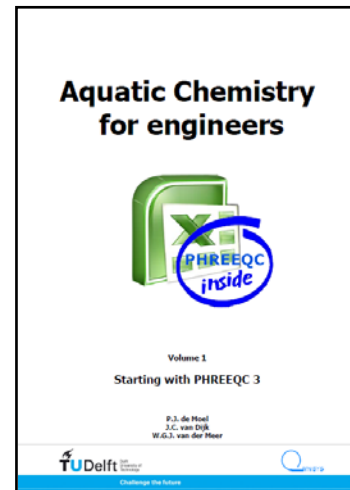
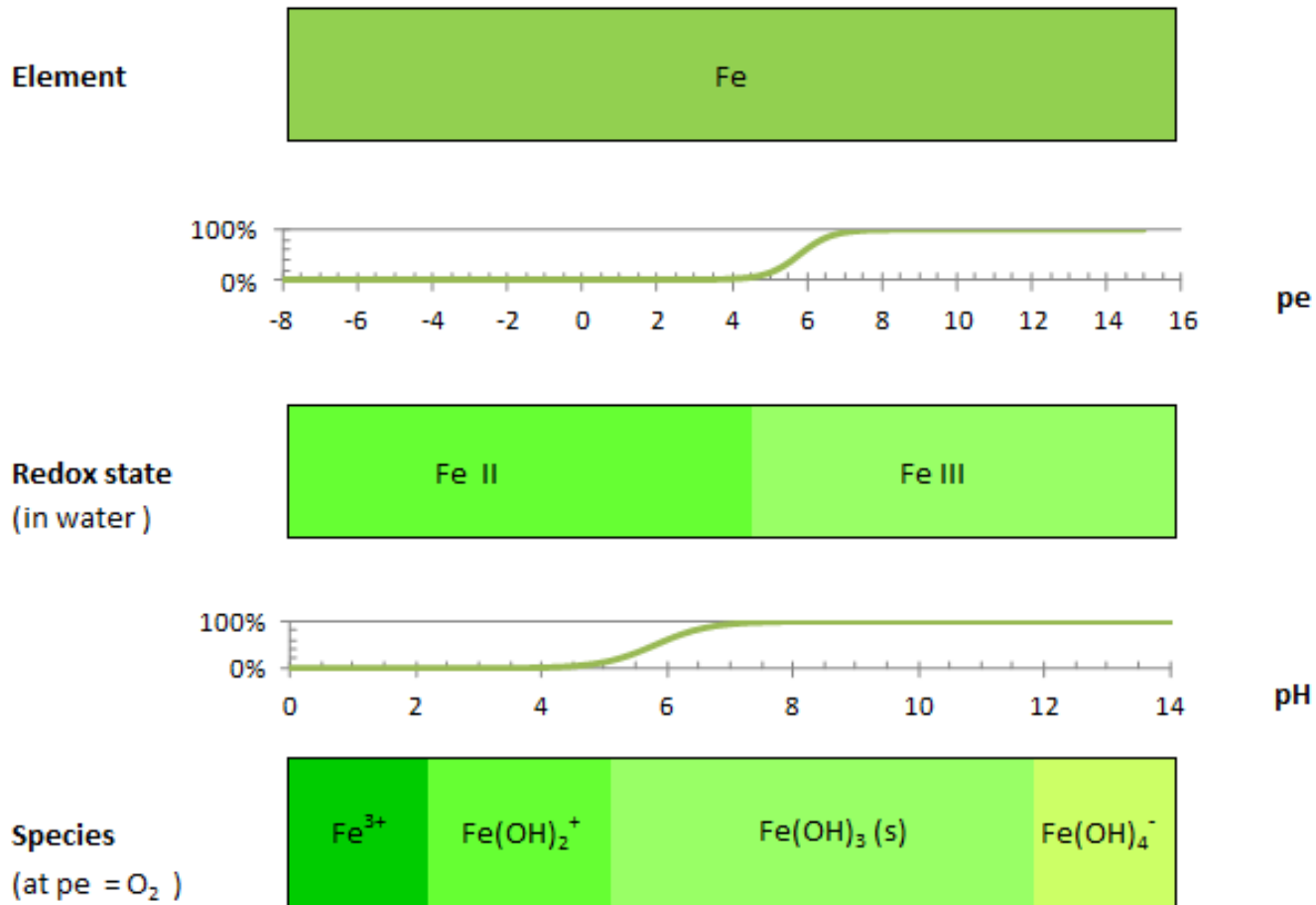
Basics: green area for water treatment

- acid – base
 - new pH after dosing and/or reactions
- gases
 - solubility
 - gas phase (bubbles / air)
- precipitation/dissolution
 - CaCO_3 , $\text{Fe}(\text{OH})_3$ etc
 - CaCO_3 (limestone filtration)
- modelling kinetics
 - to be developed in our research



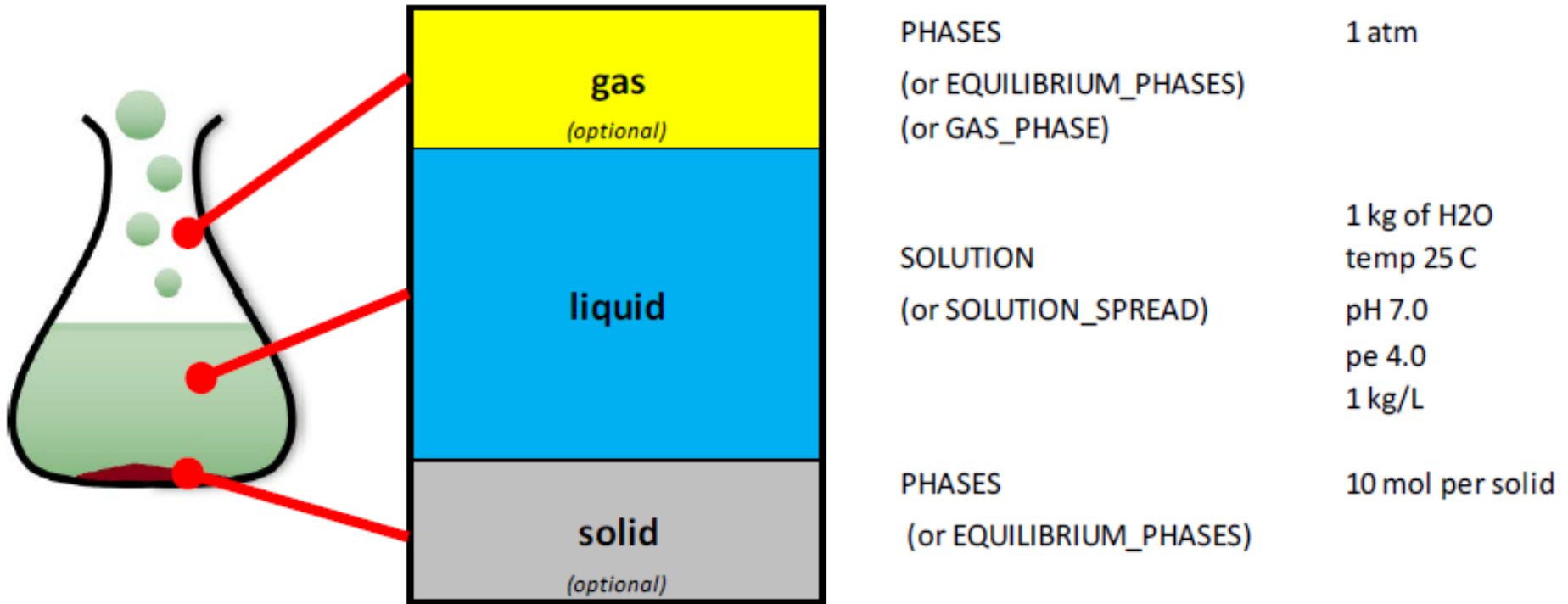
PHREEQC

Basics: element – redox states - species



PHREEQC

Basics: all equilibriums, full mass balances



PHREEQC

Drinking water in PHREEQC

Vitens
 Milieu Laboratorium
 Steenkerkeweg 81
 8912 AA Leeuwarden

Pompstation : Pb. Oudehoopside
 Reinwater Uitgaard

Periode : JAN - MRT 2011

| Analysenaam | Eenheid | Gemiddelde | Minimum | Maximum | Aantal | Mn.Wet | Max.Wet |
|---------------------------------------|-------------|------------|---------|---------|--------|--------|---------|
| Temperatuur in situ | °C | 11.0 | 10.5 | 11.5 | 13 | | 26.0 |
| Zuurnut | mg/l | 11.3 | 10.2 | 12.3 | 13 | 2.0 | |
| Turbiditeit | FTE | <0.1 | <0.1 | 0.24 | 13 | | 1.0 |
| Zuurgraad (pH) | pH | 7.80 | 7.58 | 7.98 | 13 | 7.00 | 9.50 |
| Totaal opgelost ijzer(II) | mg/l | <0.02 | <0.25 | 0.17 | 13 | | |
| Totaal opgelost ijzer(III) | mg/l | .38 | .38 | .38 | 1 | | |
| Totaal opgelost koper | mg/l | 0.30 | 0.30 | 0.30 | 1 | | |
| Totaal opgelost nikkel | mg/l | 37.4 | 38.5 | 38.1 | 13 | | 125 |
| Totaal opgelost koper | mg/l | 5.8 | 3.9 | 8.8 | 13 | | |
| Totaal opgelost nikkel | mg/l | <1 | <1 | <1 | 4 | | |
| Totaal opgelost zink | mg/l | 188 | 178 | 198 | 13 | 80 | |
| Chloride* | mg/l | 28 | 28 | 28 | 1 | | 150 |
| Sulfiet | mg SO4 / l | 8.3 | 8.3 | 8.3 | 1 | | 150 |
| Natrium (Na), ne verzuren | mg/l | 47.2 | 47.2 | 47.2 | 1 | | 150 |
| Kalium (K), ne verzuren | mg/l | 2.0 | 2.0 | 2.0 | 1 | | |
| Silica | mg/l Si | | | | | | |
| Calcium (Ca), ne verzuren | mg/l | 38.1 | 38.8 | 38.9 | 13 | | |
| Magnesium (Mg), ne verzuren | mg/l | 5.32 | 5.01 | 5.75 | 13 | | |
| Totaal Hardheid | mmol/l | 1.17 | 1.10 | 1.22 | 13 | 1.00 | 2.50 |
| Totaal Hardheid | °D | 8.8 | 8.2 | 8.8 | 13 | | |
| Ammonium | mg NH4 / l | <0.03 | <0.03 | <0.03 | 4 | | 0.20 |
| Nitriet | mg NO2 / l | <0.01 | <0.01 | 0.03 | 4 | | 0.10 |
| Nitriet | mg NO3 / l | 7.9 | 7.8 | 7.9 | 1 | | 50 |
| Izer (Fe), ne verzuren | mg/l | <0.01 | <0.01 | <0.01 | 4 | | 0.200 |
| Manganees (Mn), ne verzuren | mg/l | <0.005 | <0.005 | <0.005 | 4 | | 0.050 |
| Kobalt (Co), ne verzuren | µg/l | <2 | <2 | <2 | 1 | | 200 |
| Arseen (As), ne verzuren | µg/l | <1.0 | <1.0 | <1.0 | 1 | | 50.0 |
| Bor (B), ne verzuren | µg/l | 14.3 | 14.3 | 14.3 | 1 | | 500 |
| Broom (Br), ne verzuren | µg/l | | | | | | |
| Chroom (Cr), ne verzuren | µg/l | | | | | | |
| Cadmium (Cd), ne verzuren | µg/l | | | | | | |
| Cobalt (Co), ne verzuren | µg/l | | | | | | |
| Cu(II), ne verzuren | µg/l | 0.024 | 0.024 | 0.024 | 1 | | 1.00 |
| Lead (Pb), ne verzuren | µg/l | | | | | | |
| Merkel (Hg), ne verzuren | µg/l | | | | | | |
| Selen (Se), ne verzuren | µg/l | <1.0 | <1.0 | <1.0 | 1 | | 10.0 |
| Silver (Ag), totaal | µg/l | <2 | <2 | <2 | 1 | | 50 |
| Fluoride | mg/l | 0.07 | 0.07 | 0.07 | 1 | | 1.1 |
| Koolstofdioxide (CO2 sat) | mg PCO2 / l | 6.0 | 5.0 | 7.1 | 4 | | 20 |
| UV-vervalende | 1 / m | 11 | 11 | 11 | 1 | | |
| Totaal opgelost koolstof (TOC) | mg/l | 4.4 | 4.2 | 4.8 | 2 | | |
| Koloniegel 22 °C ** | per ml | 14 | 4 | 100 | 13 | | 100 |
| Coliformen 37 °C | per 100 ml | <1 | <1 | <1 | 13 | | 0 |
| Staphylococcus | per 100 ml | <1 | <1 | <1 | 13 | | 0 |
| Enterococcus | lee/100ml | | | | | | |
| Chloridum zierfrees | lee 100 ml | <1 | <1 | <1 | 1 | | 0 |
| Aeromonas 30 °C | per 100 ml | <10 | <10 | 10 | 4 | | 1000 |
| Aeromonas 37 °C | per 100 ml | | | | | | |
| Legionella | lee/l | | | | | | |

* De norm voor chloride is vastgesteld als rekenkundig jaargemiddelde
 ** Het gemiddelde van Koloniegel 22 °C is berekend als een geometrisch gemiddelde, ook de norm is een geometrisch jaargemiddelde

Page 1 van 2
 28-5-2011

PHREEQC Interactive - [FRL_Pb. OI...]

File Edit View Options Window Help

Run...

Initial conditions

Forward and inverse modeling

Printing and numerical method

Stoichiometry and thermodynamic data

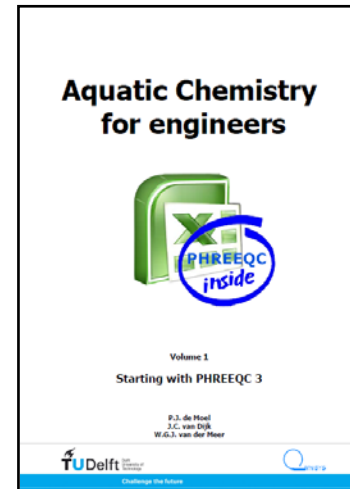
```

SOLUTION 1
units          mg/L
redox          0(-2)/0(0)
density        1
water          1
pe             14

temp           11
O(0)           11.3
pH             7.8
Alkalinity     188 as HCO3
Cl             28
S              8.3 as SO4
Na             47.2
K              2
Ca             38.1
Mg             5.32
N(-3)         0.01 as NH4
N(+3)         0.005 as NO2
N(+5)         7.9 as NO3
Fe             0.005
Mn             0.0025
Al             1 ug/L as Al
# As          0.5 ug/L as As
# B           14.3 ug/L as B
# Hg          0.024 ug/L as Hg
# Se          0.05 ug/L as Se
# CN         1 ug/L as CN
# F           0.07

END
  
```

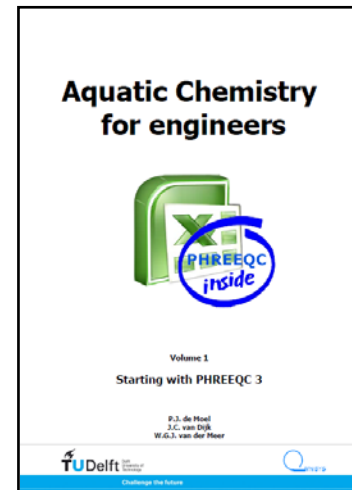
Ready



PHREEQC

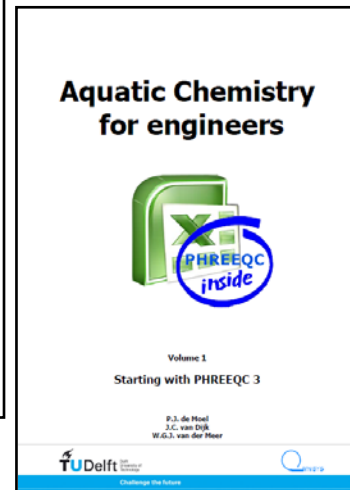
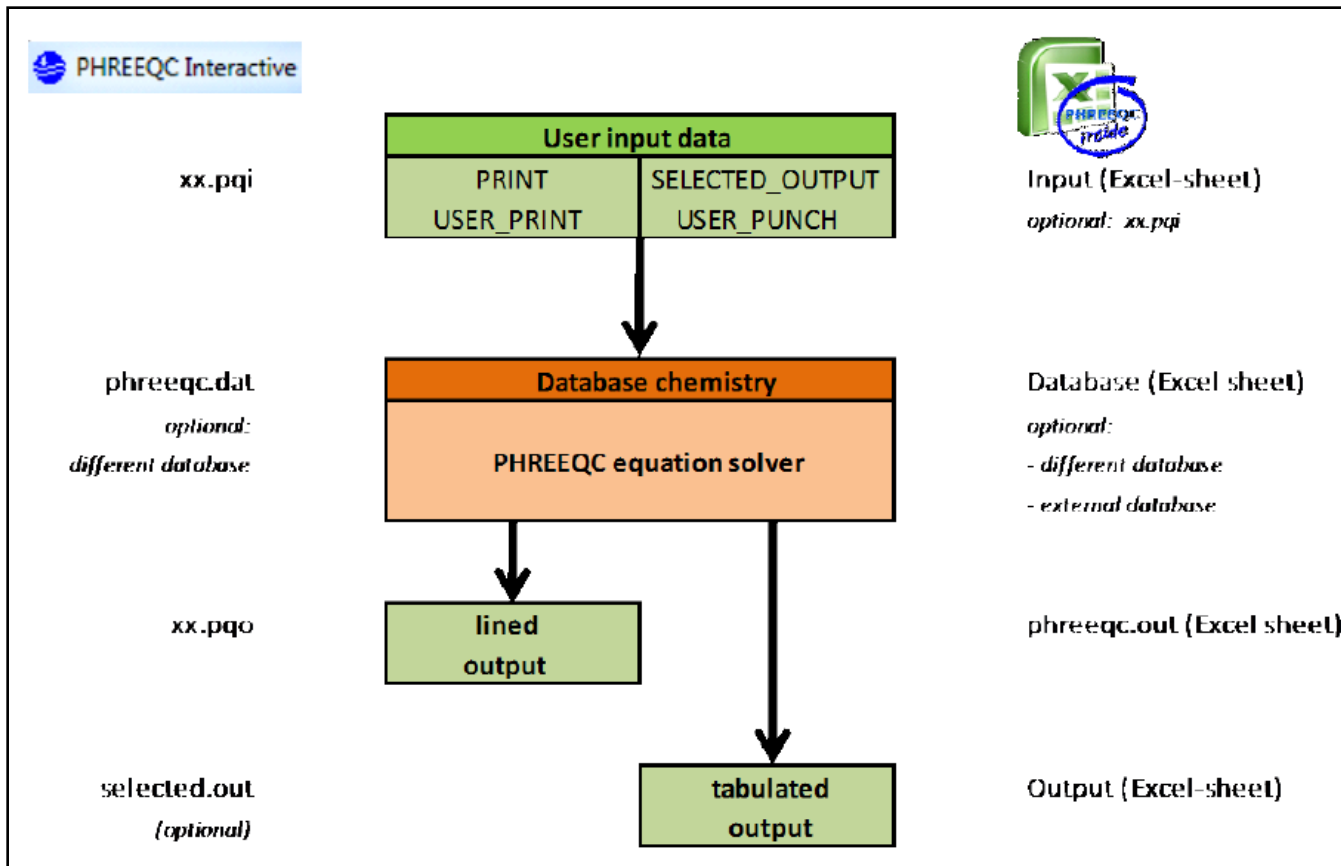
Basics: concentrations as mol/kgw

- Solution in kgw
 - not Liter change with temperature
 - not kg solution change by formation/use of H₂O
- Amount in mol:
 - not mg stoichiometric reactions
 - not mmol equilibrium constants
- Concentrations:
 - input amount as g / mg / μ g or mol / mmol / μ mol
 - input as /L (with density in kgs/L) or /kgs or /kgw
 - output always as mol/kgw
- [Concentrations] and {Activities}:
 - [Ca] = 40 mg/L = 1 mmol/L \approx 1 mmol/kgw
 - {Ca} = gamma * [Ca]



PHREEQC

Basics: data flow



PHREEQC

Basics: kinetics in phreeqc.dat

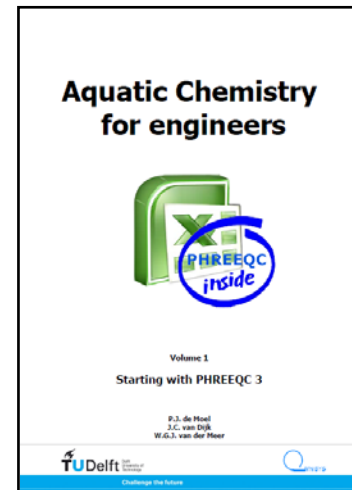
- Calcite (CaCO_3) (precipitation / dissolution)
 - PWP model (Plummer, Wigley, Parkhurst), 1978
 - Rate = f (temp H^+ CO_2 SI-calcite)
 - $\text{dMass} = \text{Rate} \times \text{Area} \times \text{Timestep}$

- Organic C (oxydation)

- Additive Monod kinetics
- Rate = f (O_2 NO_3 SO_4)
- $\text{dMass} = \text{Rate} \times \text{Mass} \times \text{Timestep}$

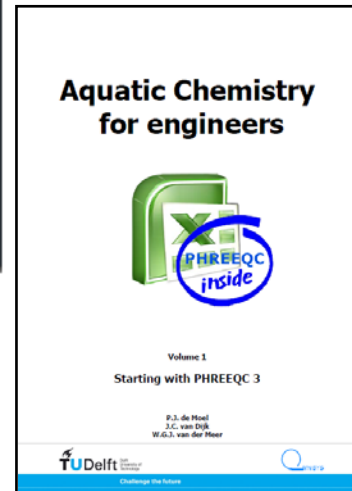
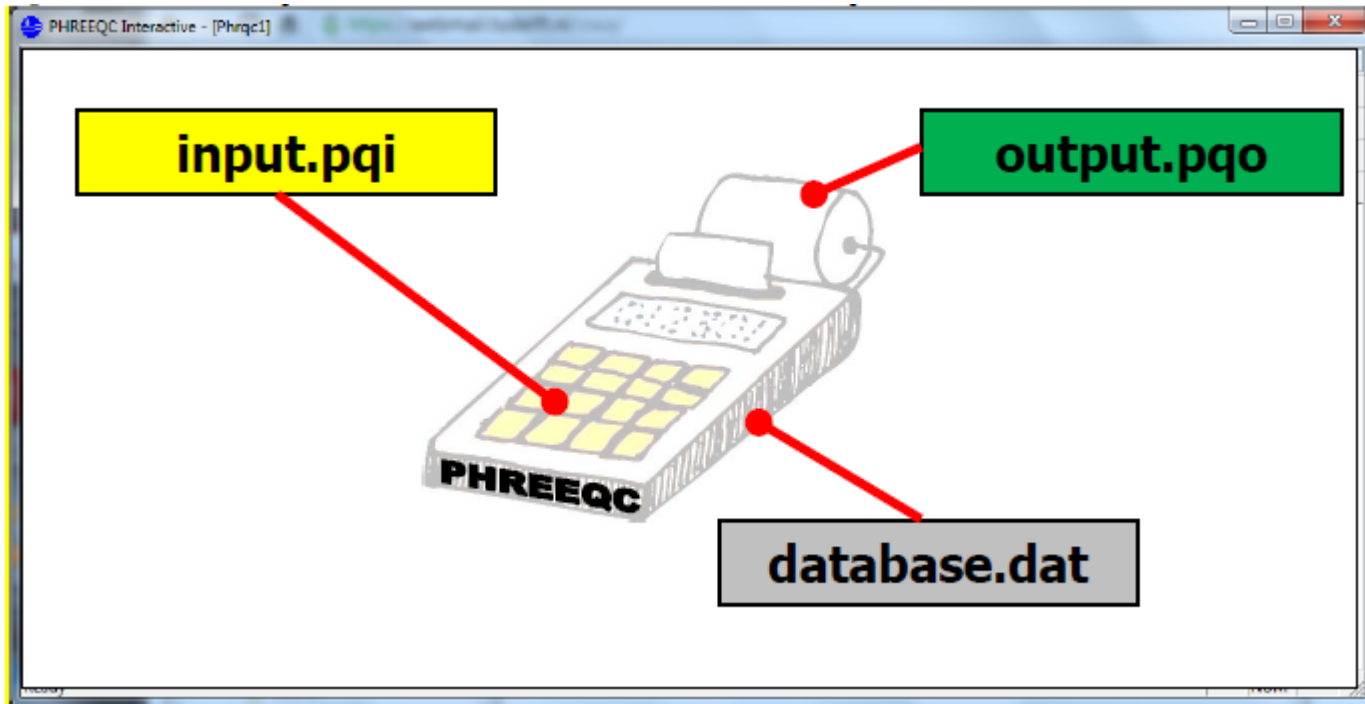
$$\frac{dX}{dt} = \mu \cdot X \quad \mu = \mu_{\max} \cdot \frac{S}{K_s + S}$$

- plus Pyrite, K-feldspar, Albite, Pyrolusite
- own models in user input



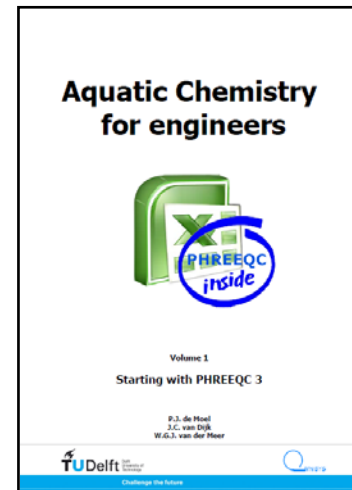
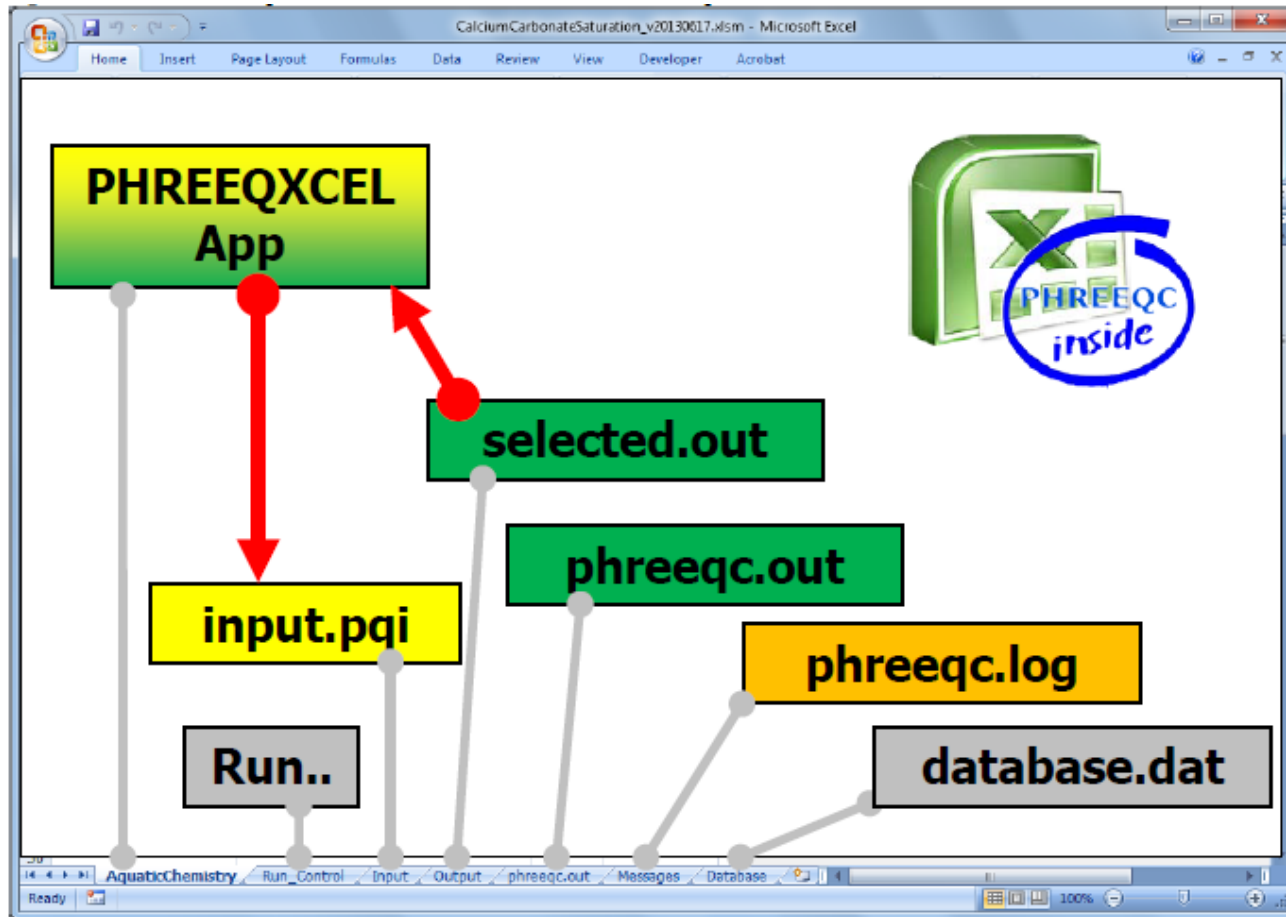
PHREEQC Interactive

Basics: files



PHREEQXCEL

Basics: files





PHREEQC

Input+output in Excel

AQUATIC CHEMISTRY for Engineers

Models: **Drinking water (basic)** vs 20100006
 Description: Drinking water with parameters according to DIN20404-10 (2010)
 Please: Input for all DYNAMIC parameters
 End: Input for EC and TDS

Sample description: Lab 1.1

Basic data

| | | | | | |
|---------------------------------------|-----|-------|--------|--------|-----------|
| Temperature | t | °C | 15.0 | 15.0 | °C |
| pH | pH | - | 7.30 | 7.30 | - |
| qs (electro activity) | qs | - | | | |
| Conductivity (EC 20) (or temp. EC 10) | EC | mS/cm | 241 | 241 | 241 µmhos |
| Total dissolved solids (TDS) | TDS | mg/L | 289 | 289 | mg/L |
| Dissolved silica | ds | mg/L | 100000 | 100000 | mg/L |

Cations

| | | | | | |
|-----------|----|------|------|------|-------------|
| Oxygen | O2 | mg/L | 10 | 10 | 0.34 mg/L |
| Calcium | Ca | mg/L | 56.0 | 40 | 1.60 mmol/L |
| Magnesium | Mg | mg/L | 1.5 | 24.5 | 0.25 mmol/L |
| Sodium | Na | mg/L | 1.2 | 62 | 0.30 mmol/L |
| Potassium | K | mg/L | 3.0 | 59 | 0.07 mmol/L |

Anions

| | | | | | |
|----------------------|------|------|------|------|-------------|
| Alkalinity (as HCO3) | HCO3 | mg/L | 183 | 61 | 2.44 mmol/L |
| Chloride | Cl | mg/L | 7.0 | 95.5 | 0.25 mmol/L |
| Nitrate | NO3 | mg/L | 8.0 | 62 | 0.16 mmol/L |
| Sulfate | SO4 | mg/L | 23.0 | 36 | 0.41 mmol/L |
| Fluoride | FO4 | mg/L | 0.00 | 05 | 0.00 mmol/L |

Run PHREEQC

Overall parameters

| | | |
|------------------------------------|--------|---------|
| Calcium | mg/kgp | 1.43 |
| Alkalinity | mg/kgp | 7.54 |
| Conductivity (calculated, at 1 °C) | EC | 24.7 |
| Total dissolved solids | TDS | 278 |
| Total strength | IS | 3.4 |
| Total hardness | TH | 183 |
| Dissolved silica | ds | 0.00000 |
| Oxygen | O2 | 0.24 |
| qs (electro activity) | qs | 0.20 |
| Dissolved silica | ds | 0.00000 |

Redox conditions

| | | |
|---|--------|------|
| Charge difference | mg/kgp | 0.06 |
| Percentage error (W/Cr/Sr/Hr/Cr/Hr) | mg/kgp | 0.03 |
| EC ratio, calculated/measured | mg/kgp | 0.30 |
| TDS ratio, calculated/measured | mg/kgp | 0.97 |
| Oxygen saturation level, wt. at 101 kPa | mg/kgp | 12.3 |
| pH change by electro balancing (Please) | mg/kgp | 0.00 |
| qs change by electro balancing (Please) | mg/kgp | 0.00 |

Carbon equilibria

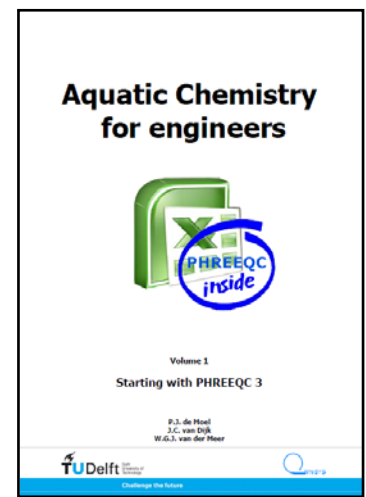
| | | |
|------------------------------|--------|------|
| pH (redox activity) | pH | 7.30 |
| Alkalinity | mg/kgp | 2.44 |
| Total inorganic Carbon (TIC) | mg/kgp | 2.76 |
| CO2 | mg/kgp | 0.81 |
| HCO3- | mg/kgp | 1.67 |
| CO3 2- | mg/kgp | 0.00 |

Sulfate equilibria

| | | |
|------------------------------------|--------|-------|
| S (solid) | mg/kgp | -0.43 |
| Equilibrium pH (pH or pH Legation) | pH | 7.3 |
| Calcite Precipitation Potential | mg/kgp | -0.35 |

For further details see PHREEQC.OUT

TU Delft Aquatic Chemistry for engineers





PHREEQC

Drinking water in PHREEQC – in the cloud

Drinking water - Conductivity + Charge balance

Conductivity (EC) + Charge balance

Steps to do:

- Fill in water quality data
- Press Run Phreeqc
- Wait a few seconds for (updated) output
- optional: Change input values and re-Run Phreeqc
- optional: if email-address is filled: Send Excel file (full version) by email
- optional: if email-address is not filled: Download and Save Excel file (full version)

| General | | | |
|--------------------------|----------------|------|------|
| Temperature | t | ° C | 11,5 |
| Oxygen | O ₂ | mg/L | 11,0 |
| pH | | | 7,31 |
| Conductivity (EC 20 ° C) | | mS/m | 38,4 |

| Cations | | | |
|-----------|----|------|------|
| Calcium | Ca | mg/L | 40,5 |
| Magnesium | Mg | mg/L | 5,30 |
| Sodium | Na | mg/L | 49,7 |
| Potassium | K | mg/L | 2,0 |

| Anions | | | |
|--------------------|------------------|------|-----|
| Hydrogen carbonate | HCO ₃ | mg/L | 199 |
| Chloride | Cl | mg/L | 28 |
| Nitrate | NO ₃ | mg/L | 7,0 |
| Sulfate | SO ₄ | mg/L | 7,9 |

Run Phreeqc

Run Phreeqc

Overall parameters

| | | |
|------------------------------|----------|------|
| Cations | meq/kgw | 4,61 |
| Anions | meq/kgw | 4,26 |
| Conductivity (EC at t) | mS/m | 31,4 |
| Total dissolved solids (TDS) | mg/L | 339 |
| Ionic strength | mmol/kgw | 5,7 |
| Total hardness | mmol/kgw | 1,23 |

Redox conditions

| | | |
|------------------------|----|-------|
| pe (electron activity) | | 13,92 |
| Redox potential | mV | 785 |

Correctness checks

| | | |
|--|---------|--------|
| Charge difference | meq/kgw | 0,34 |
| Percentage error (100*(Cat-[An])/(Cat+[An])) | | 3,85 % |
| EC ratio, calculated/measured | | 1,01 |
| pH change by electron balancing (Phreeqc) | | 0,000 |

Carbon equilibrium

| | | |
|-------------------------------|--------------|-------|
| pH (Hydrogen activity) | | 7,91 |
| Alkalinity | meq/kgw | 3,26 |
| Total inorganic carbon (TIC) | mmol/kgw | 3,34 |
| CO ₂ | mmol/kgw | 0,10 |
| HCO ₃ ⁻ | mmol/kgw | 3,19 |
| CO ₃ ²⁻ | mmol/kgw | 0,01 |
| dpH by 0.1 mmol HCl / kgw | | -0,28 |
| Buffer capacity | mmol/kgw /pH | 0,28 |

Calcite equilibrium

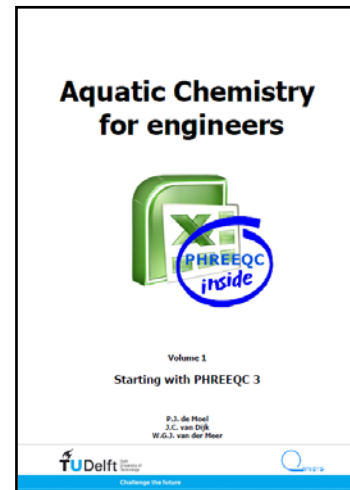
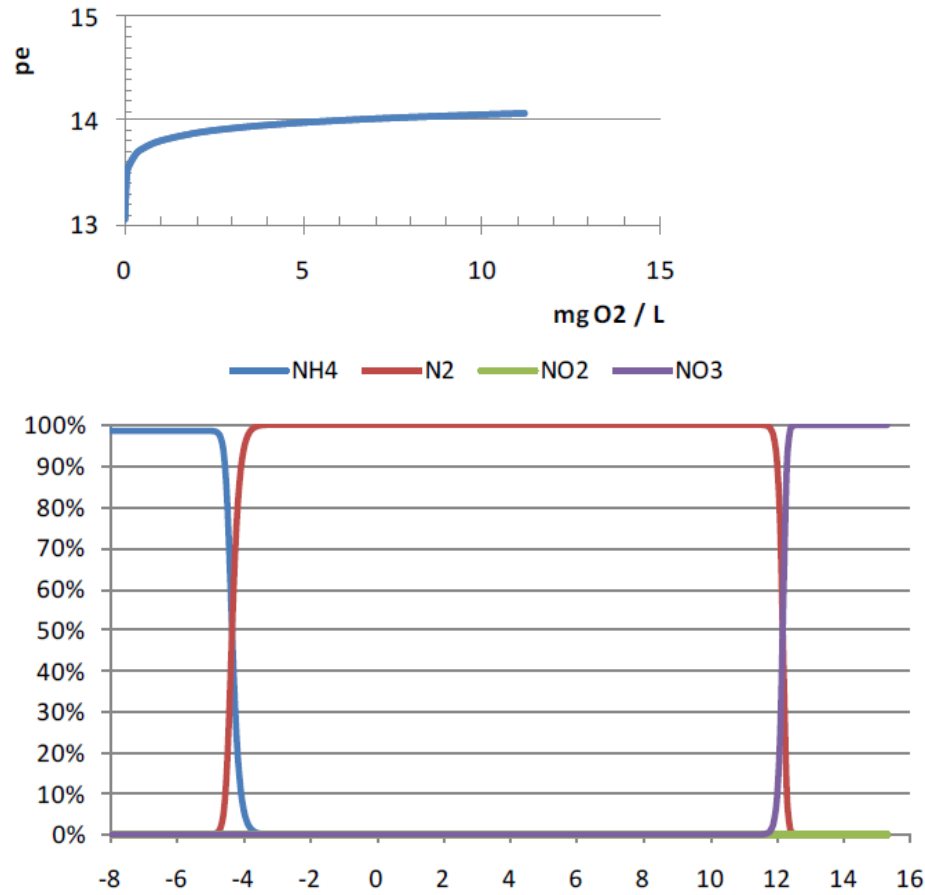
| | | |
|--|----------|------|
| SI (calcite) | | 0,18 |
| Equilibrium-pH (pHs or pH-Langelier) | | 7,73 |
| Calcite Precipitation Potential | mmol/kgw | 0,05 |
| Calcite Precipitation Potential at 60 C | mmol/kgw | 0,20 |
| Calcite Precipitation Potential at 100 C | mmol/kgw | 0,46 |

E-mail address (optional):

Download / Mail Excel

PHREEQC

Nitrogen - Equilibrium vs Kinetics

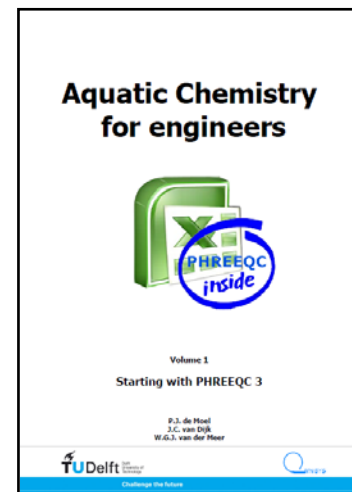
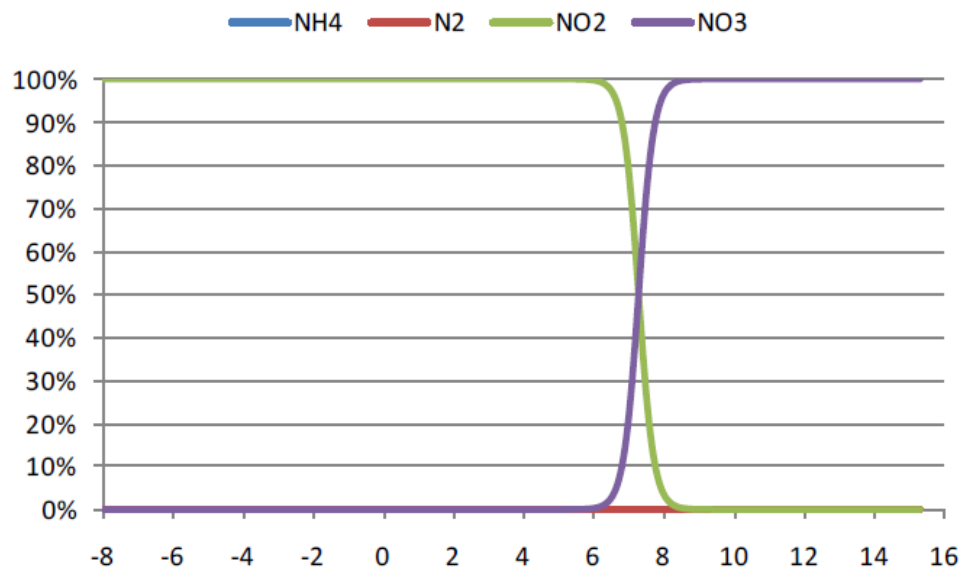




PHREEQC

Nitrogen - Inert NH_4 / Inert N_2

- Modified database for water treatment: phreeqc_wt.dat
- Inert N : Namm as inert NH_4^+ / Nga as inert N_2
- To be expended for water treatment kinetics

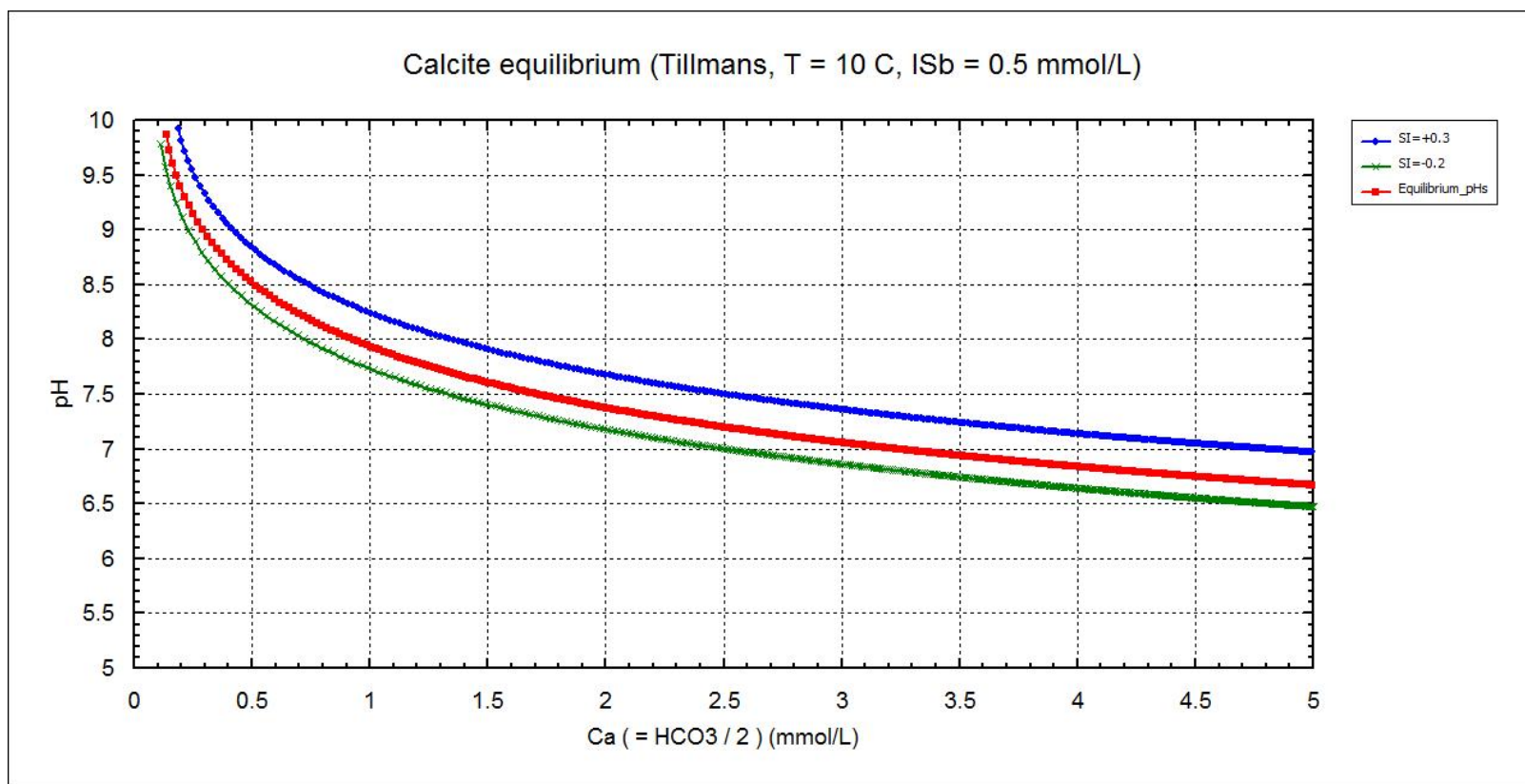




Examples

Calcite equilibrium

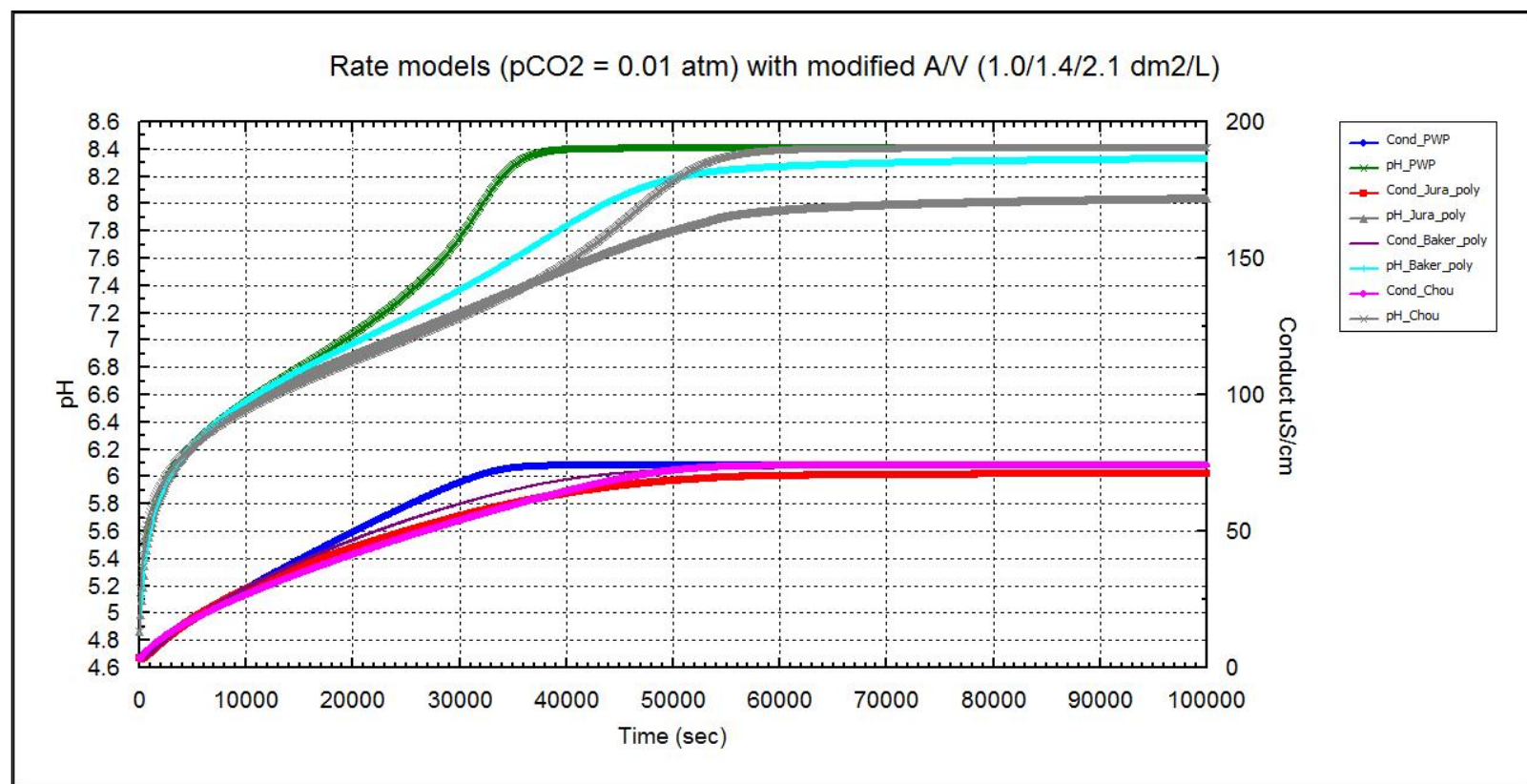
Phreeqc:



Examples

Dissolution rate CaCO₃ (Lime stone filtration)

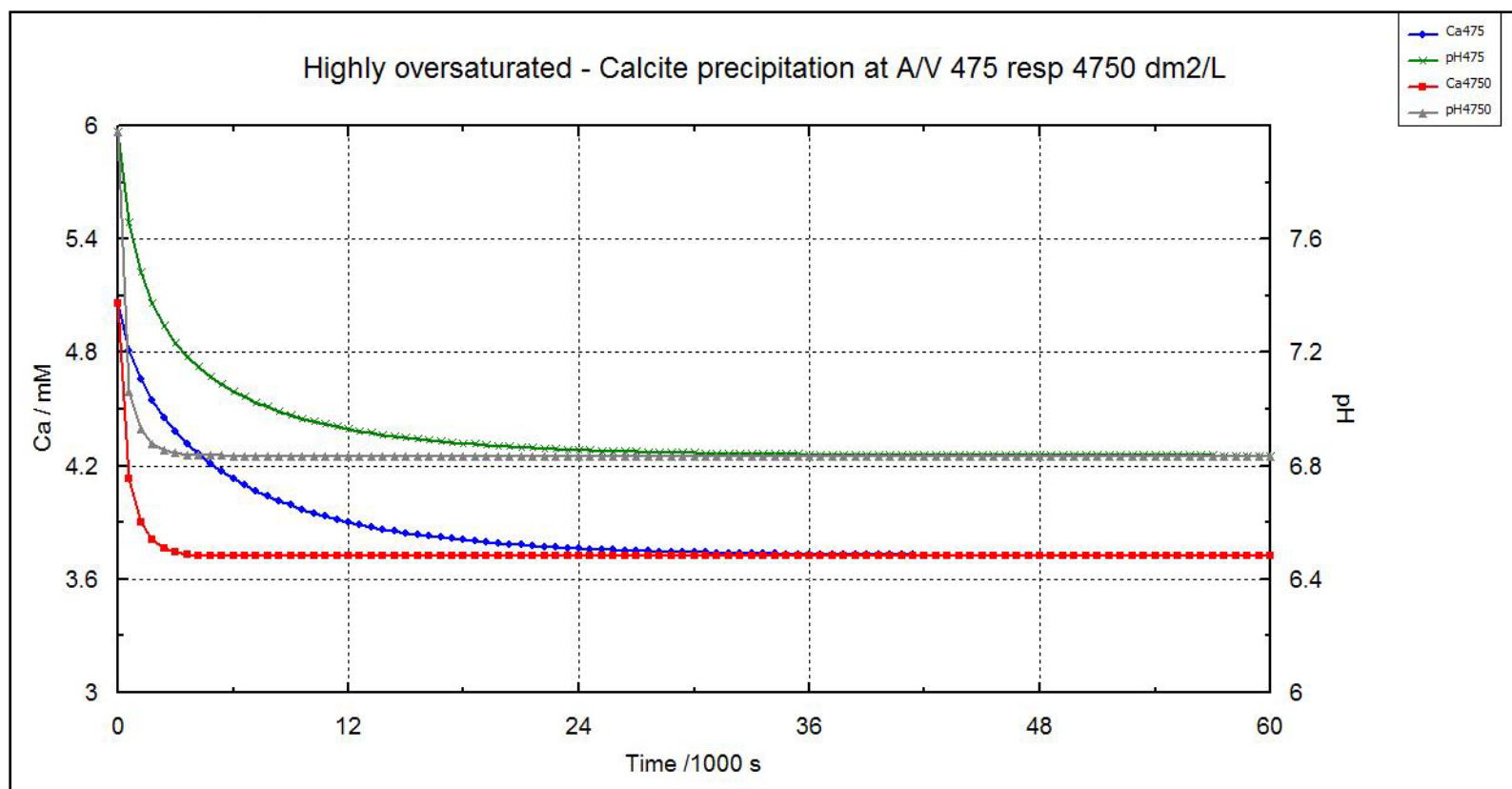
Phreeqc:



Examples

Precipitation rate CaCO_3 (no seed material)

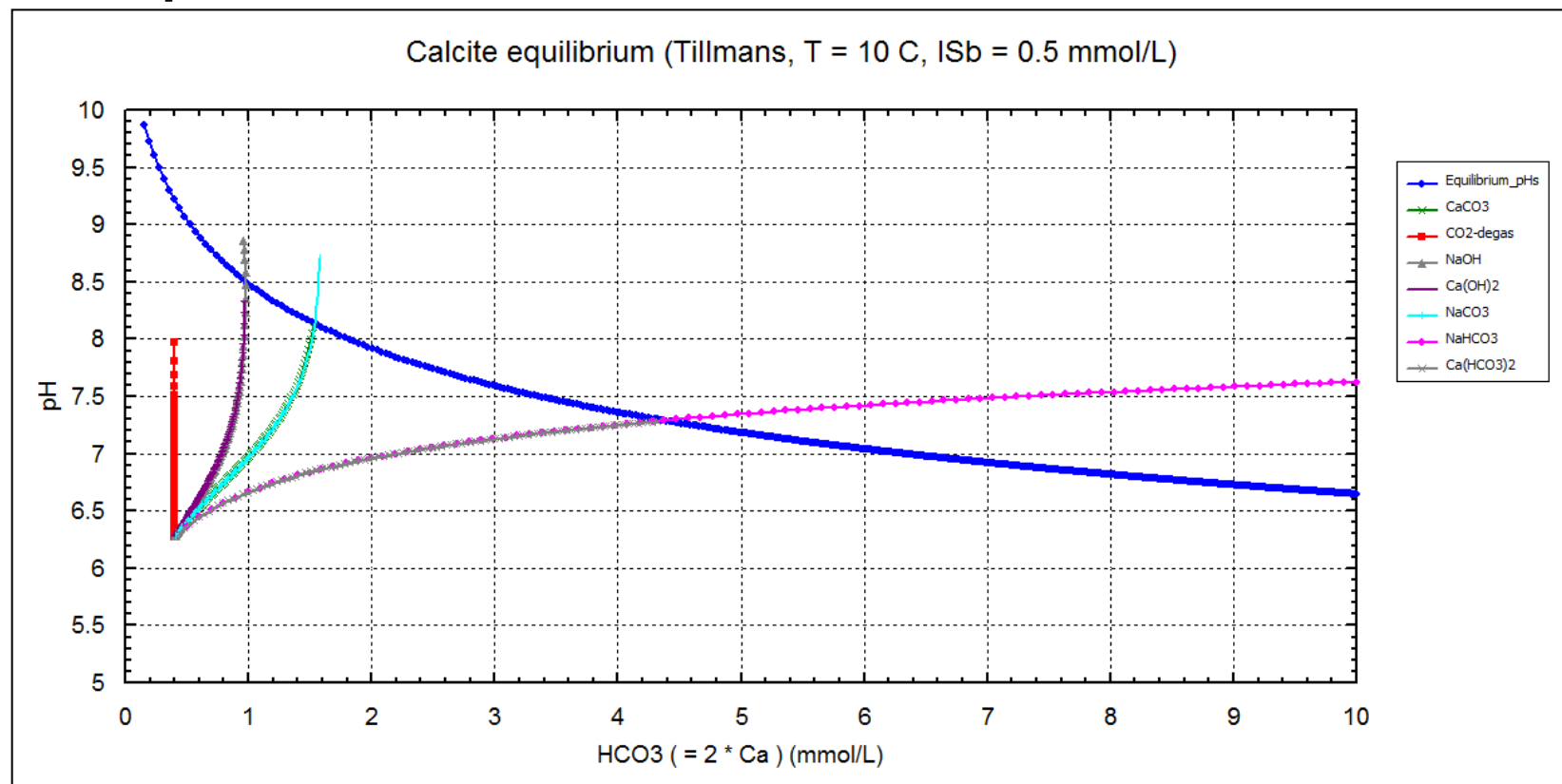
Phreeqc:



Examples

pH for different treatment methods

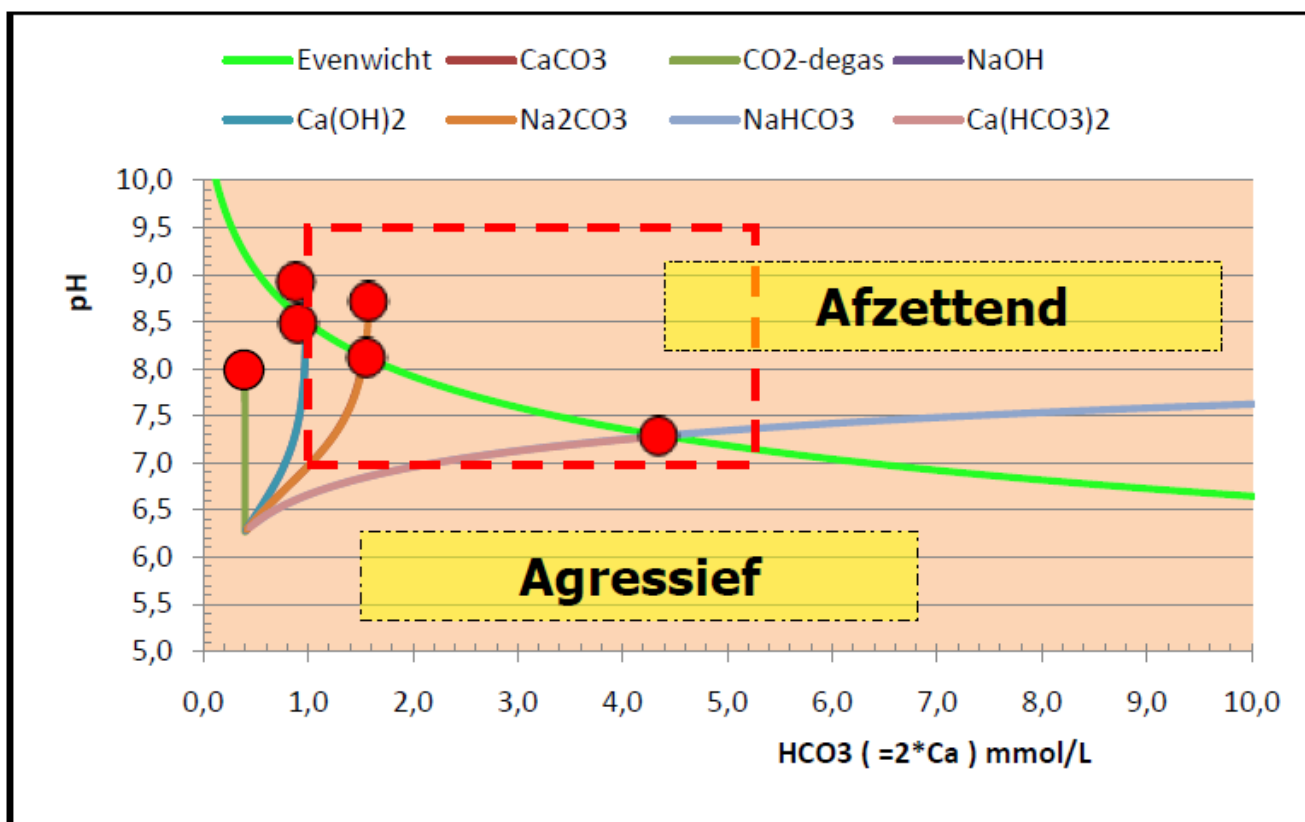
Phreeqc:



Examples

pH for different treatment methods (2)

Phreeqc:



Aquatic chemistry for engineers

Status



Completed:

- Waterchemistry for drinking water (H2O-Dutch)
- OCW website: Aquatic Chemistry for engineers
- Volume 1: Starting with PHREEQC
- 9+ Excel sheets / PHREEQC "in the cloud"

Waterchemie voor drinkwater modelleren met PHREEQC

Van grondstof tot drinkwater: de rol van waterchemie in de drinkwaterproductie. Dit boek is bedoeld voor ingenieurs en technici die met waterchemie te maken hebben. Het behandelt de basisprincipes van de waterchemie en de toepassing van PHREEQC in de praktijk.

| Species | Concentration | Units |
|---------|---------------|-------|
| Ca | 100.00 | mg/L |
| Mg | 50.00 | mg/L |
| Na | 10.00 | mg/L |
| K | 5.00 | mg/L |
| Cl | 20.00 | mg/L |
| SO4 | 15.00 | mg/L |
| HCO3 | 10.00 | mg/L |
| CO3 | 5.00 | mg/L |
| OH | 1.00 | mg/L |
| H+ | 1.00 | mg/L |
| Fe | 0.01 | mg/L |
| Mn | 0.01 | mg/L |
| Zn | 0.01 | mg/L |
| Cu | 0.01 | mg/L |
| Pb | 0.01 | mg/L |
| Ni | 0.01 | mg/L |
| Cr | 0.01 | mg/L |
| As | 0.01 | mg/L |
| Sr | 0.01 | mg/L |
| Ba | 0.01 | mg/L |
| Li | 0.01 | mg/L |
| Rb | 0.01 | mg/L |
| Cs | 0.01 | mg/L |
| Ag | 0.01 | mg/L |
| Hg | 0.01 | mg/L |
| Cd | 0.01 | mg/L |
| Co | 0.01 | mg/L |
| Ni | 0.01 | mg/L |
| Cu | 0.01 | mg/L |
| Pb | 0.01 | mg/L |
| Zn | 0.01 | mg/L |
| Mn | 0.01 | mg/L |
| Fe | 0.01 | mg/L |
| Al | 0.01 | mg/L |
| Si | 0.01 | mg/L |
| Cl | 0.01 | mg/L |
| SO4 | 0.01 | mg/L |
| HCO3 | 0.01 | mg/L |
| CO3 | 0.01 | mg/L |
| OH | 0.01 | mg/L |
| H+ | 0.01 | mg/L |

SOLUTION 1

units mg/L

redox O(2)/O(1)

density 1

water 1

DS 1.4

temp 11

O(2) 11.3

pH 7.8

Alkalinity 100 as HCO3

Cl 28

Na 5.3 as SO4

K 2

Ca 38.1

Mg 5.32

S(-3) 0.01 as HS4

S(+3) 0.005 as SO2

S(+5) 7.9 as SO3

Fe 0.005

Mn 0.0025

Al 3. ug/L as Al

As 0.5 ug/L as As

B 14.3 ug/L as B

Ba 0.024 ug/L as Ba

Cd 0.03 ug/L as Cd

Co 1. ug/L as Co

Zn 0.07

PHREEQC - short introduction

- Why PHREEQC?
- How to use PHREEQC?

Aquatic Chemistry for engineers (Self Study Course)

Self Study Course with Introduction, Labs and Tests (under development)

Volume 1: PHREEQC for drinking and waste water

Volume 2: PHREEQC for drinking and waste water

Volume 3: Water treatment in PHREEQC

Future development

- Introduction and domain driven model with application
- Questions: 20 Tests, 100 answers and feedback.

How to continue? Where can I find more?

PHREEQC VU logo

Aquatic Chemistry for engineers

Volume 1

Starting with PHREEQC 3

P.J. de Hoel
J.C. van Diek
W.G.A. van der Meer

TU Delft logo

| Parameter | Value | Unit |
|-----------|--------|------|
| Ca | 100.00 | mg/L |
| Mg | 50.00 | mg/L |
| Na | 10.00 | mg/L |
| K | 5.00 | mg/L |
| Cl | 20.00 | mg/L |
| SO4 | 15.00 | mg/L |
| HCO3 | 10.00 | mg/L |
| CO3 | 5.00 | mg/L |
| OH | 1.00 | mg/L |
| H+ | 1.00 | mg/L |
| Fe | 0.01 | mg/L |
| Mn | 0.01 | mg/L |
| Zn | 0.01 | mg/L |
| Cu | 0.01 | mg/L |
| Pb | 0.01 | mg/L |
| Ni | 0.01 | mg/L |
| Cr | 0.01 | mg/L |
| As | 0.01 | mg/L |
| Sr | 0.01 | mg/L |
| Ba | 0.01 | mg/L |
| Li | 0.01 | mg/L |
| Rb | 0.01 | mg/L |
| Cs | 0.01 | mg/L |
| Ag | 0.01 | mg/L |
| Hg | 0.01 | mg/L |
| Cd | 0.01 | mg/L |
| Co | 0.01 | mg/L |
| Ni | 0.01 | mg/L |
| Cu | 0.01 | mg/L |
| Pb | 0.01 | mg/L |
| Zn | 0.01 | mg/L |
| Mn | 0.01 | mg/L |
| Fe | 0.01 | mg/L |
| Al | 0.01 | mg/L |
| Si | 0.01 | mg/L |
| Cl | 0.01 | mg/L |
| SO4 | 0.01 | mg/L |
| HCO3 | 0.01 | mg/L |
| CO3 | 0.01 | mg/L |
| OH | 0.01 | mg/L |
| H+ | 0.01 | mg/L |

Aquatic chemistry for engineers

Recent and future developments



Summer school 2012

- Conference for drinking water treatment experts
- Cases with PHREEQC for drinking water

Further development

- Volume 2: PHREEQC for drinking and waste water
- Volume 3: Water treatment in PHREEQC

TU Delft Vitens

Aankondiging in de nieuwsbrief van juni 8, nodigen wij u graag uit voor de *Summerschool PHREEQC voor drink- en afvalwater*.

**Summer School
Waterchemie voor ingenieurs
PHREEQC voor drinkwater**

Donderdag 30 Augustus 2012
TU Delft – Civiele Techniek – Steuwinweg 1 – Delft - Colledgezaal E

Programma

9:00-9:20 Introductie (10 min, elk)
- Introductie Summerschool prof.dr.ir. W.G.J. (Walter) van der Meer (TU Delft/Oasen)
- PHREEQC in bedrijf ir. J.H.A. (Johan) Driessen MGM (Vitens)

9:20-12:00 PHREEQC Principles en achtergronden (20-45 min) (15 min tussentijdse pauzes)
- PHREEQC - Verleden, heden en vooral toekomst dr. C.A.J. (Tony) Appelo (mede-ontwikkelaar PHREEQC)
- Simulatie ondergrondse ontwikkeling hardheid drs. M. (Marlies) de Jonge (Vitens/Wrije Universiteit)
- PHREEQC voor drinkwater-ingenieurs ir. P.J. (Peter) de Moel (TU Delft)

13:00-16:00 Praktische voorbeelden (Postervoordrachten van 5-10 min + 10 minuten pauzes)
Waterbehandeling
- SLMH boeien voor besturing Oudehoopside dr. J.M. (Kim) van Schagen (OHV)
- Ondergrondse ontginning dr. Doris van Ieperen (TU) en/of dr. Weren de Vet (TU/Oasen)
- Metingen en modellering ontzilting voor Hok ing. F. (Frank) Schoonenberg Kegel (Vitens)
- Modelleren inerteisatie opgevoerd (voorbeeld Hald) dr. J. D. (Dink) Vries (NWR)
- PHREEQC voor anemobie ontzanding Bovenhuis ir. S.J. (Sjoerd) Koken (Oasen)
- Kinetiek van marmertfiltratie (Engels) ir. Phi Bang Do (TU Delft/NUS)
- Schaalgevoel en scaling in PHREEQC ir. A. (Anne) Halder (TU Delft)

Watertransport, distributie en slatten
- Uitloging AC buizen en kalkaanslag op de Veluwe P. (Paul) Kober (Vitens)
- Koperniobozonproef - Praktijk en theorie ir. P.J. (Peter) de Moel (TU Delft) (of iemand anders)
- Medakonzemie in drinkwater dr. M. (Marco) Dignum (Waterland)
- Koolstof - Praktijk en theorie ir. J.C.J. (Jink) Guile / Ing. T. (Tim) van Dijk (Brabant Water)

Normstelling drinkwater
- Berekening SI + TACC (Kalkoos/Aquacalc/PHREEQC) drs. M.E.W.G. (Marlies) van Rijn (Vitens)
- PHREEQC voor het luten drinkwater ir. P.J. (Peter) de Moel (TU Delft) (of iemand anders)

16:00-17:00 Navoord en vervolg (Walter), Diploma uitreiking en Naborrelen

Nadere info: <http://drinkwater.civ.technic.tu/delft.nl/AquaticChemistry> *Toegang gratis*
Aankomst voor 15 augustus 2012
kwartiel Nederland

Aquatic chemistry for engineers

Treatment processes

Drinking water

- Acid/Base dosing
- Aeration and gas transfer
- Fe/Mn/NH₄/CH₄ oxydation (redox reactions)
- Precipitation/Crystallization
- Ion-exchange (exchange equilibrium)
- Activated carbon (surface equilibrium)
- Membrane filtration (scaling)

Waste water

- Aeration and gas transfer
- Biological conversion (chemistry)
- PO₄/Heavy metal removal



The screenshot shows the course page for 'Aquatic Chemistry for Engineers' on the TU Delft website. The page includes a navigation menu on the left with options like 'Course Information', 'Introduction', 'Lectures', 'Readings', 'Activities', 'Feedback', and 'Instructor'. The main content area features a header with the course title, a sub-header 'Aquatic Chemistry for Engineers', and a date 'Summer school PHREEQC user drink on 8/10/2013'. Below this is a photograph of three people in a laboratory setting, with one person using a pipette. A caption below the photo reads: 'Water sampling for chemical analysis in a laboratory will result in a large list of chemical components found in the water (photograph: www.gov.mb.ca)'. The page also lists the responsible instructor as P.J. de Haad with Prof. J.C. van Dijk and Prof. Dr. Ir. H.G.J. van der Meer. It mentions the course is part of the curriculum of the Watermanagement and is designed for MSc students and for PhD students working on chemistry analysis with Prof. Theun. The page also lists the education method as 'Self study' and the assessment as 'None (no official grading)'. There is an 'Additional information' section at the bottom with a link to 'Additional information about PHREEQC' and a Creative Commons license notice.

Aquatic chemistry for engineers

Further information

OpenCourseWare website

- <http://drinkwater.citg.tudelft.nl/AquaticChemistry>

Contains

- Lectures
- Readings
- Activities (Labs and Tests)
- New developments
- Database stimela.dat
(phreeqc.dat for Water Treatment, updated)



The screenshot shows the TU Delft OpenCourseWare website for the course 'Aquatic Chemistry for Engineers'. The page includes a navigation menu on the left with options like 'Aquatic Chemistry for Engineers', 'Course Information', 'Introduction', 'Lectures', 'Readings', 'Activities', 'Feedback', and 'Attendance'. The main content area features a header for the course, a summary paragraph, a photograph of students in a lab setting, and detailed information sections including 'Responsible instructor' (Prof. J.C. van Dijk), 'Credits' (5 ECTS), 'Study goals', 'Education method' (Self study), and 'Assessment' (None, no official grading). There is also an 'Additional information' section and a Creative Commons license notice at the bottom.

Questions?



Aquatic Chemistry for engineers

PHREEQC / PHREEQXCEL for water treatment

12 September 2013

Peter de Moel – TU Delft