Aquatic Chemistry for engineers

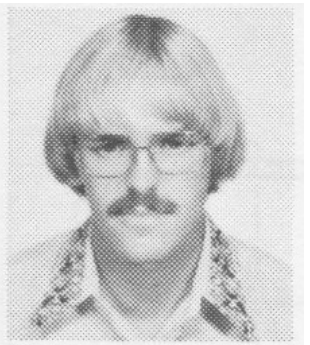
PHREEQC / PHREEQXCEL for water treatment

12 September 2013

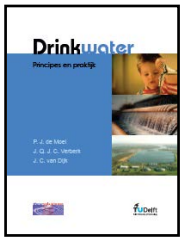
Peter de Moel – TU Delft

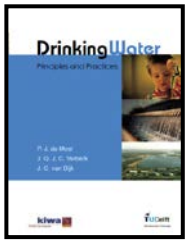
Personal introduction …

Record on water chemistry



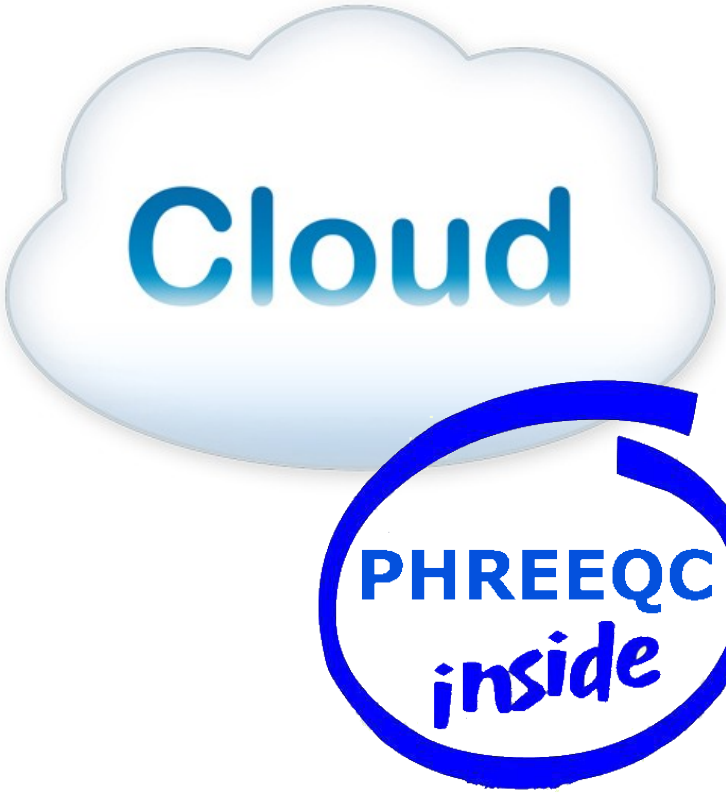
- 1979 - 1980 : KIWA
  - KIWA report and computer program aggressive water
- 1980 - 2000 : DHV
  - Patent softening Amsterdam (Graveland cs)
  - Publication / HP41 program on CaCO3 equilibrium
  - Publications / presentations (H2O - JAWWA – Las Vegas)
  - Design and build over 40 water treatment plants, wordwide
- 2000 - present : TU Delft (part-time)
  - BSc / MSc – education
  - OpenCourseWare (2007 -)
  - Aquatic Chemistry 4 Eng (2011 -)
  - Online MSc (2013/2014)
  - edX MOOC (16 Sept)

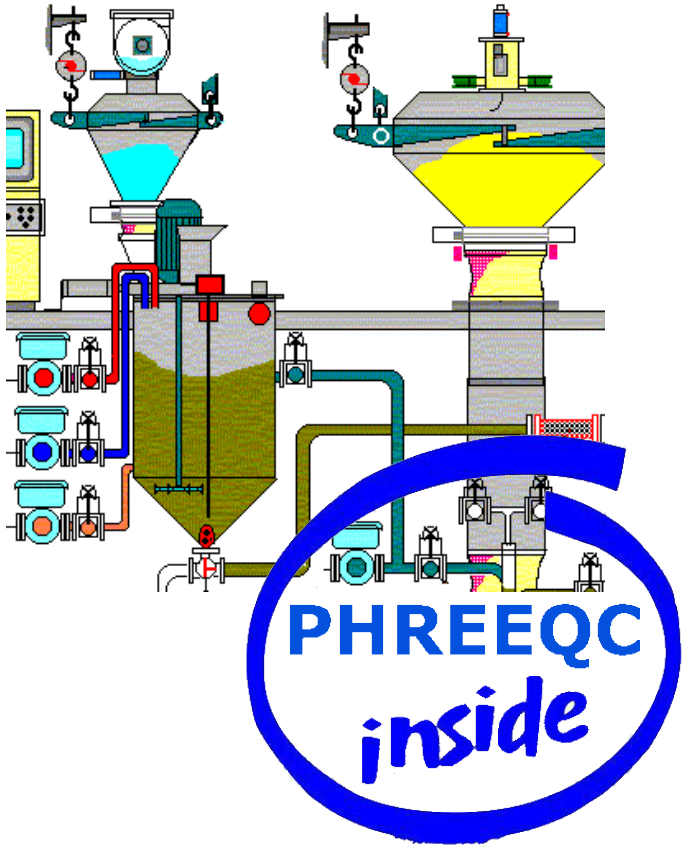




OCW CONSORTIUM

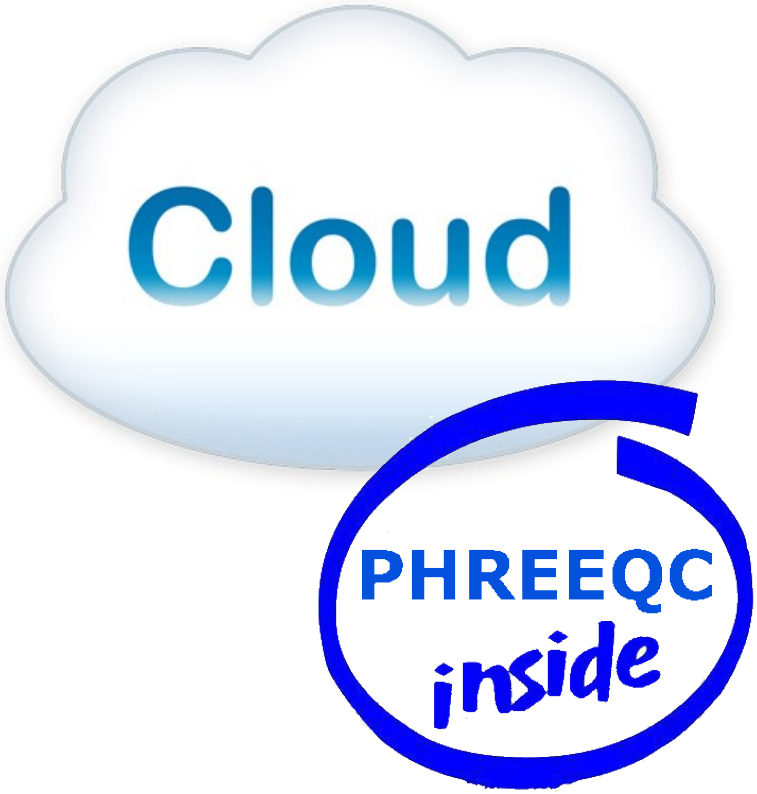
PHREEQC – Our focus points

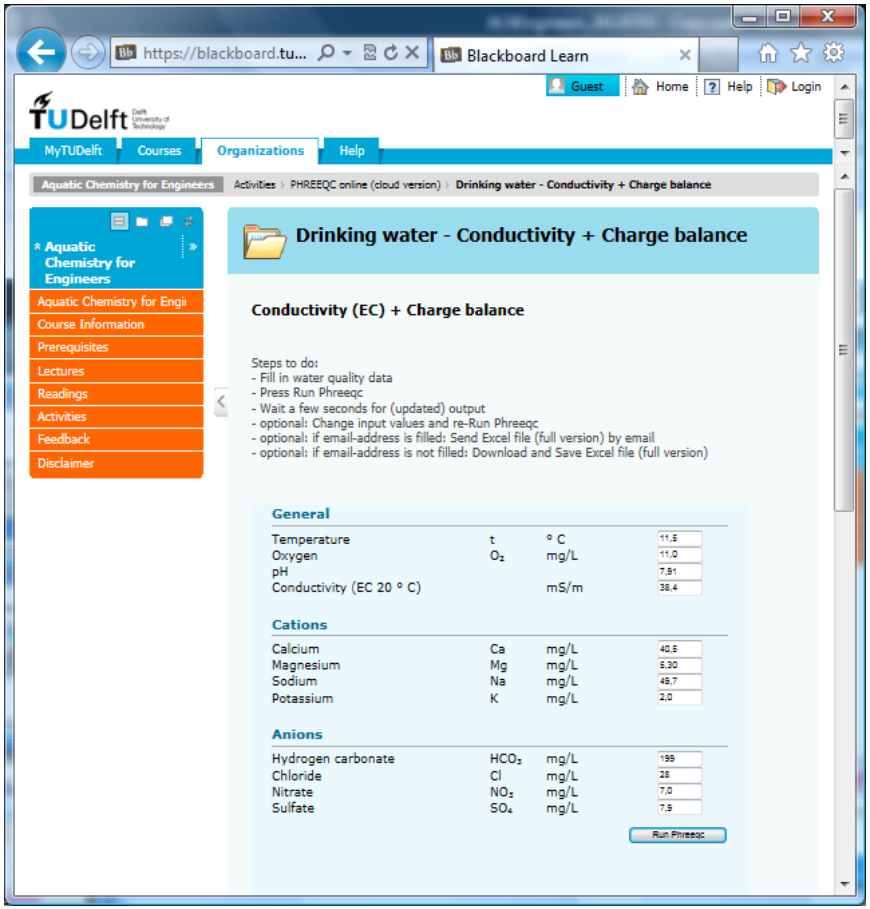




- Practical applications for drinking water and wastewater

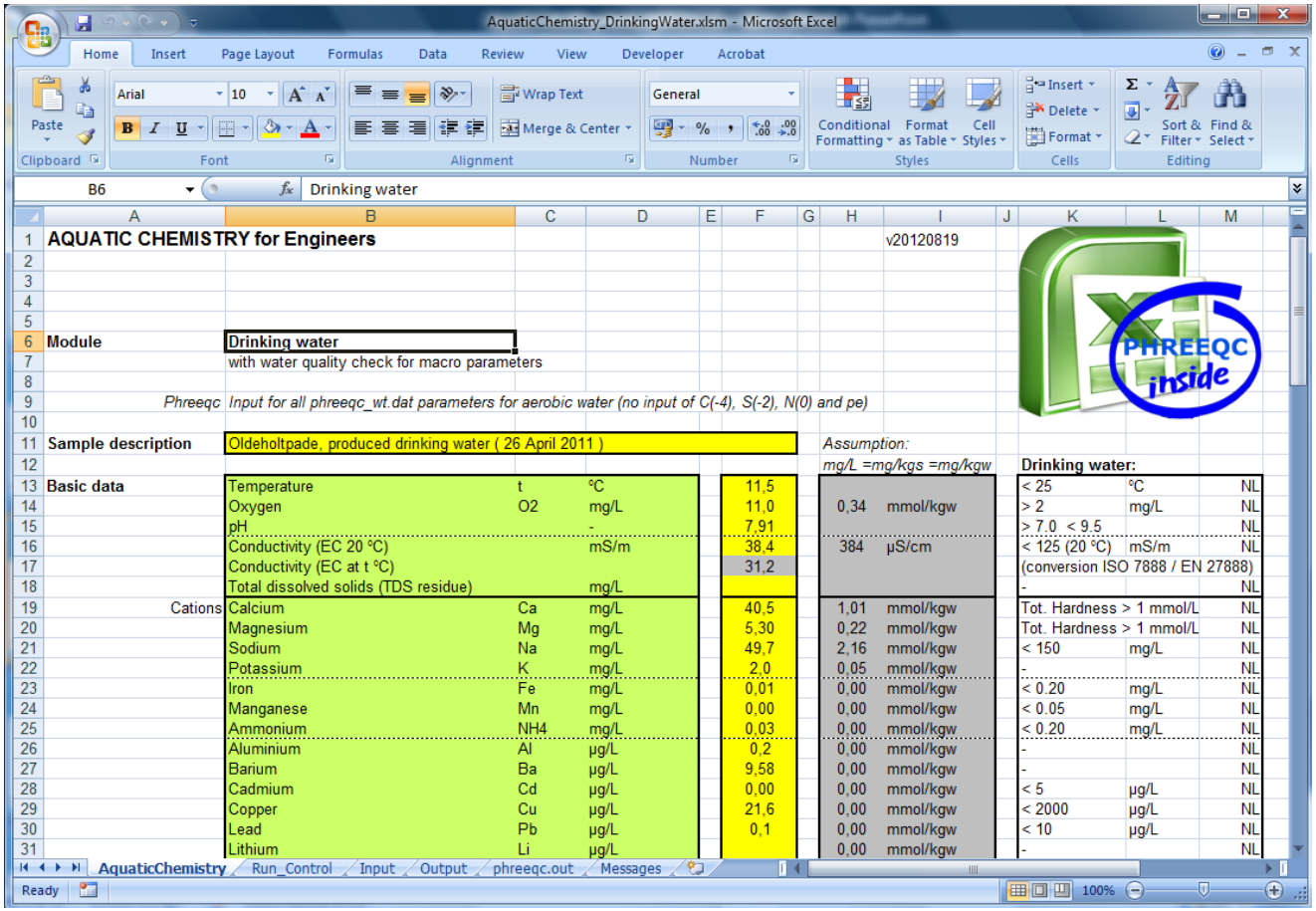
PHREEQC “in the cloud”





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

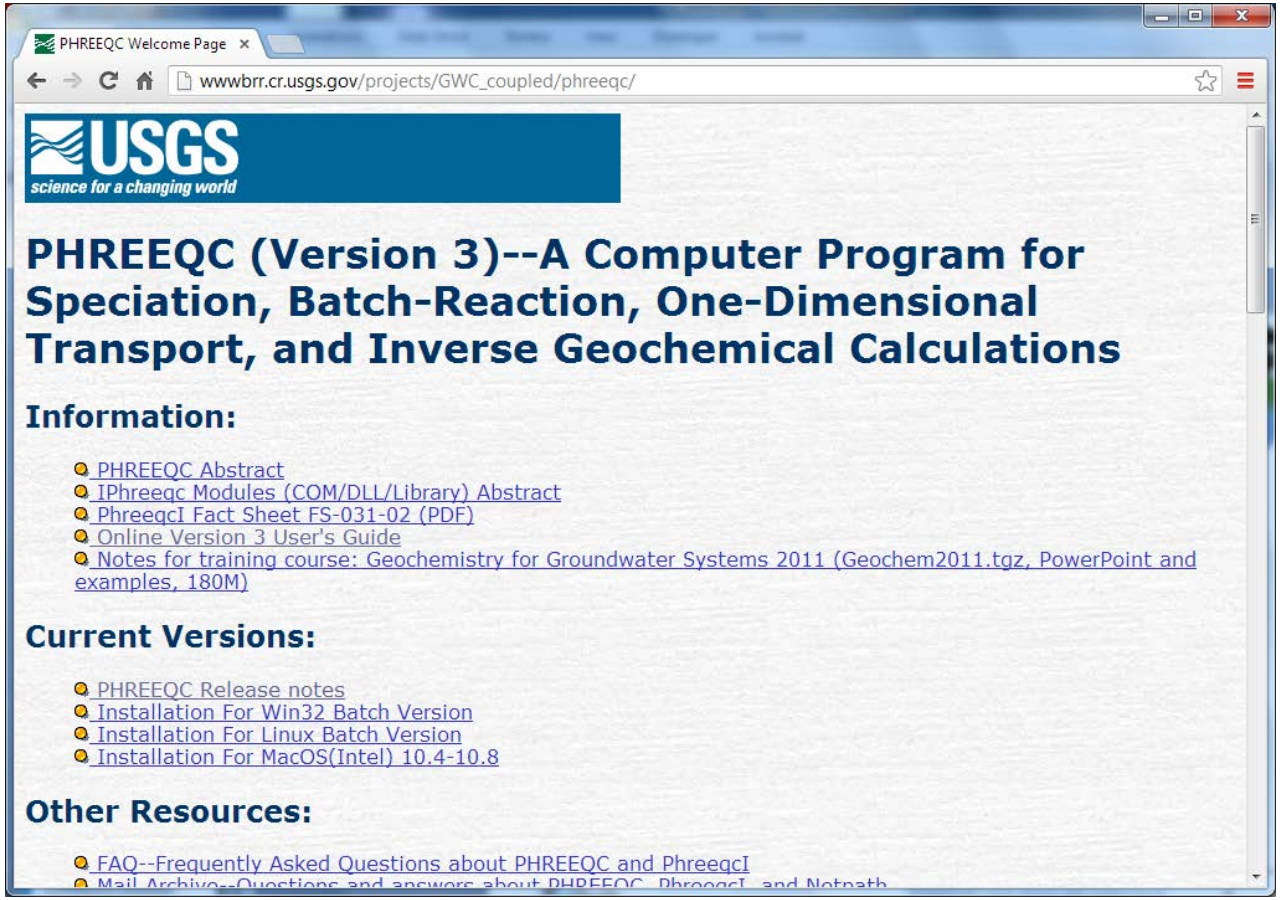
PHREEQC in Excel



- Demo ?

PHREEQC

Development since 1980

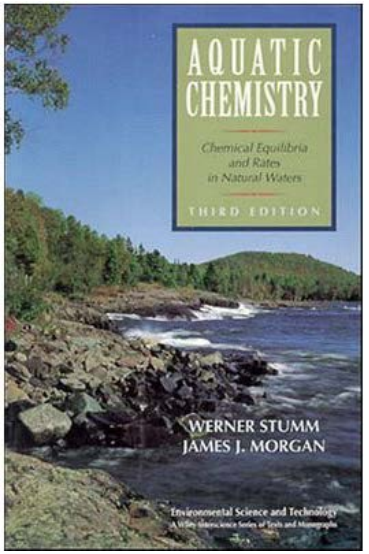


pH - Redox – Equilibrium - Calculations

PHREEQC

pH - Redox - Equilibrium Calculations

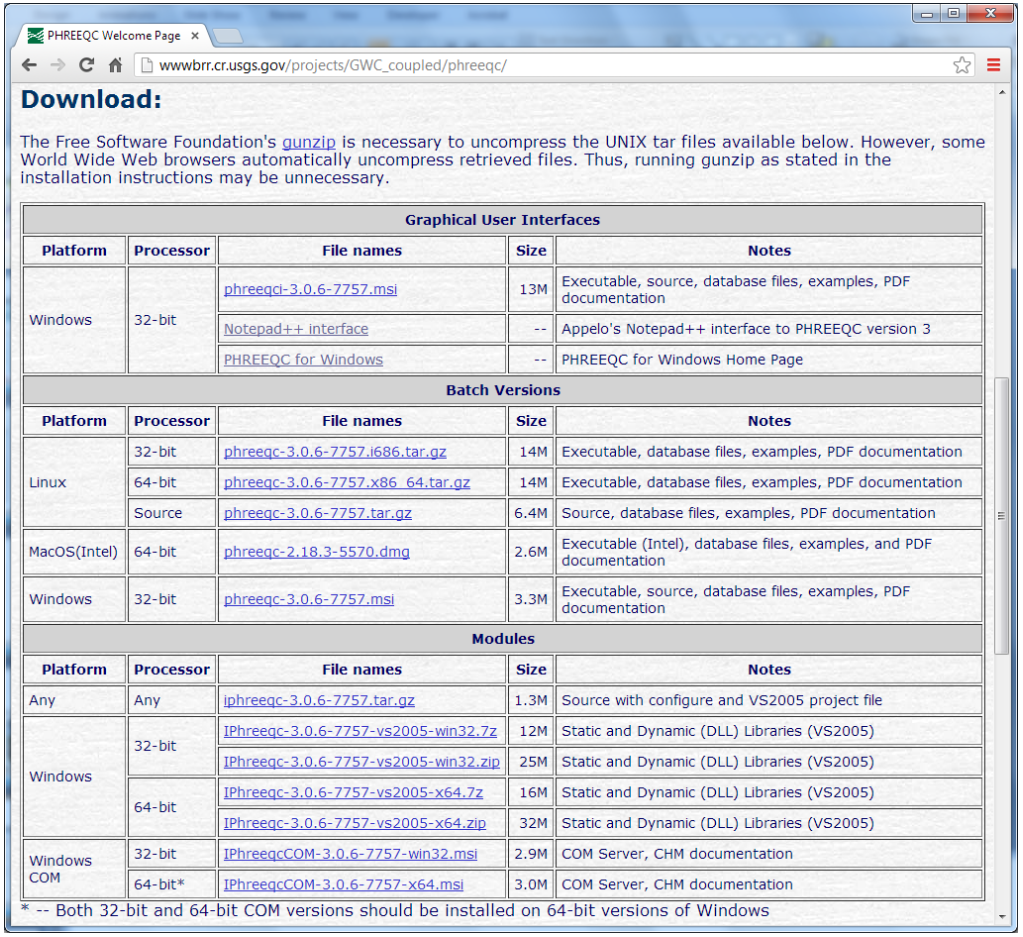
- 25 elements — C Ca Mg Na etc
- 21 redox states — C(+4) C(-4) etc
- 180 species — C(+4) : CO2 HCO3 CO3 etc; C(-4) : CH4 etc
- 72 solid phases — CaCO3 Fe(OH)3 etc
- 8 gas phases — CO2 H2S etc
- + Exchange eq. — (ion-exchange)
- + Surface eq. — (activated carbon)
- + Rates — (kinetics)
- 8 databases



Aquatic Chemistry (Stumm & Morgan) in your laptop

PHREEQC

Freely available



PHREEQC Welcome Page

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	phreeqci-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

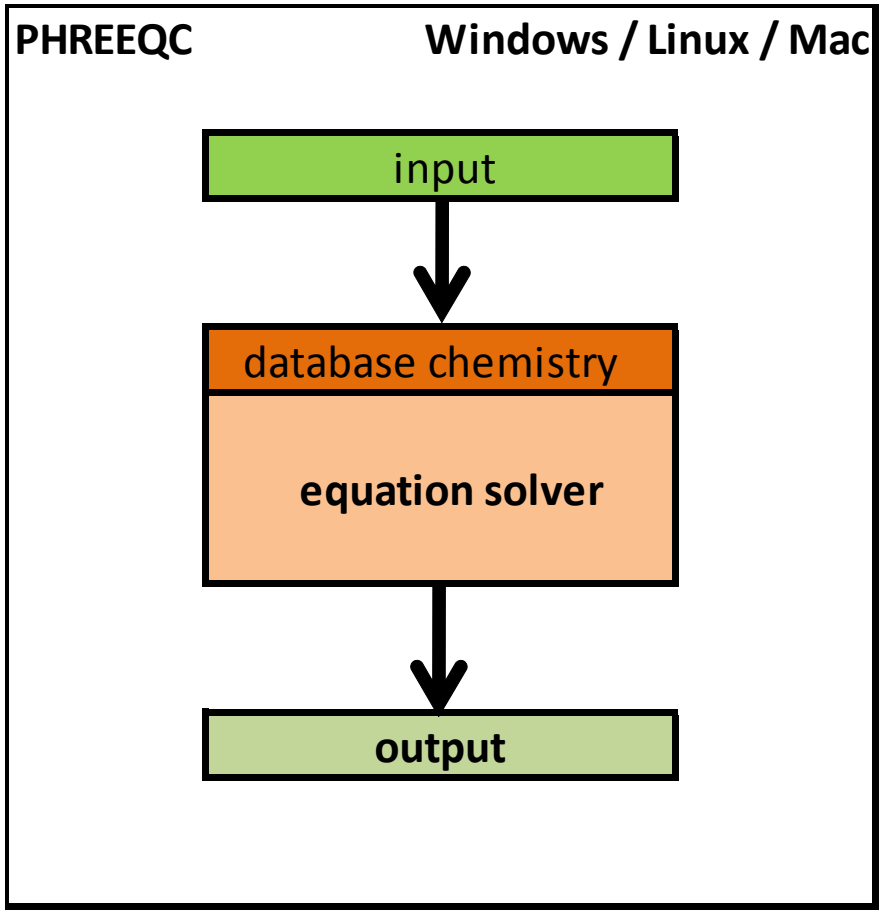
Modules

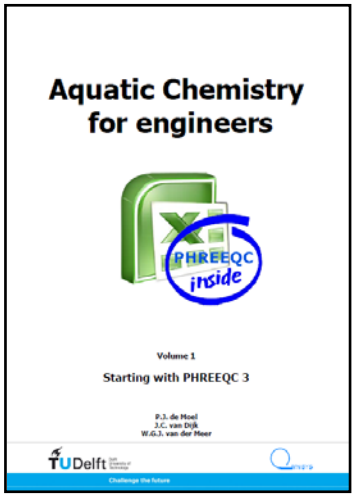
Platform	Processor	File names	Size	Notes
Any	Any	iphreeqc-3.0.6-7757.tar.gz	1.3M	Source with configure and VS2005 project file
Windows	32-bit	IPhreeqc-3.0.6-7757-vs2005-win32.7z	12M	Static and Dynamic (DLL) Libraries (VS2005)
		IPhreeqc-3.0.6-7757-vs2005-win32.zip	25M	Static and Dynamic (DLL) Libraries (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

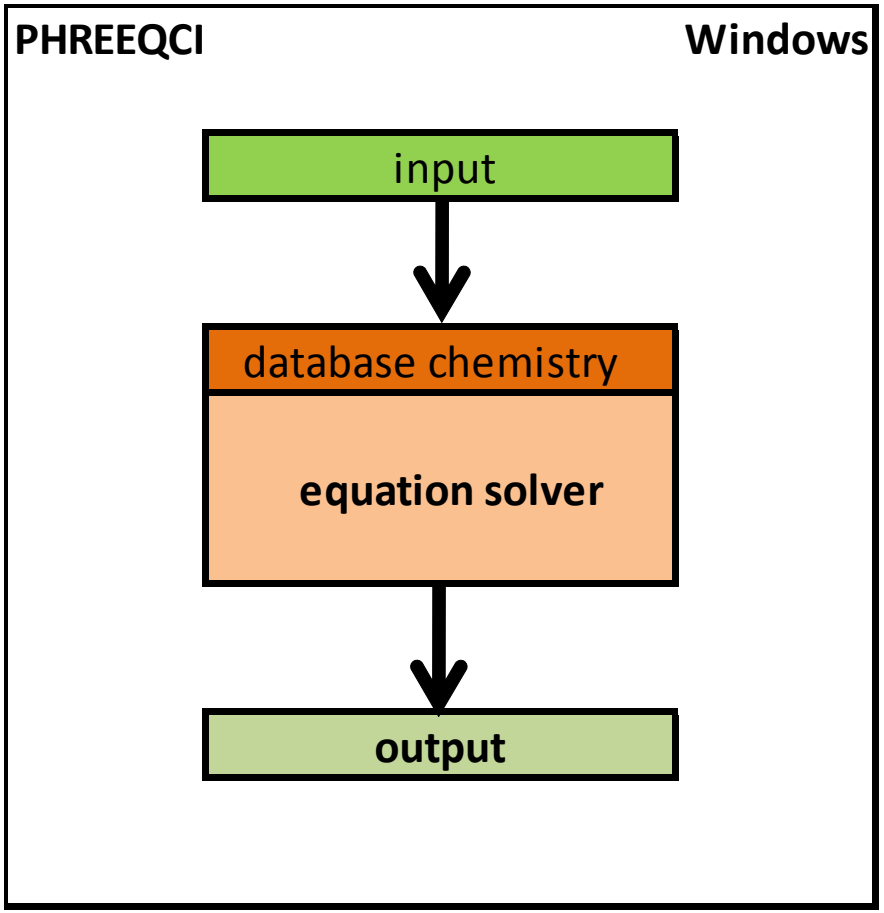
Batch version (text) - since 1980/1995

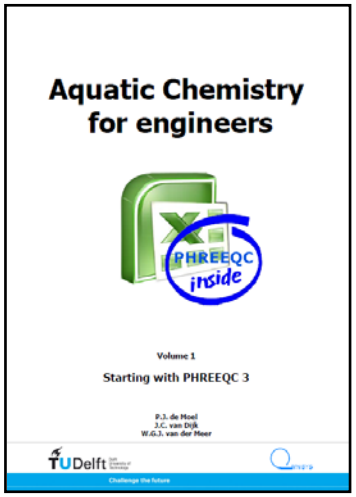




PHREEQC

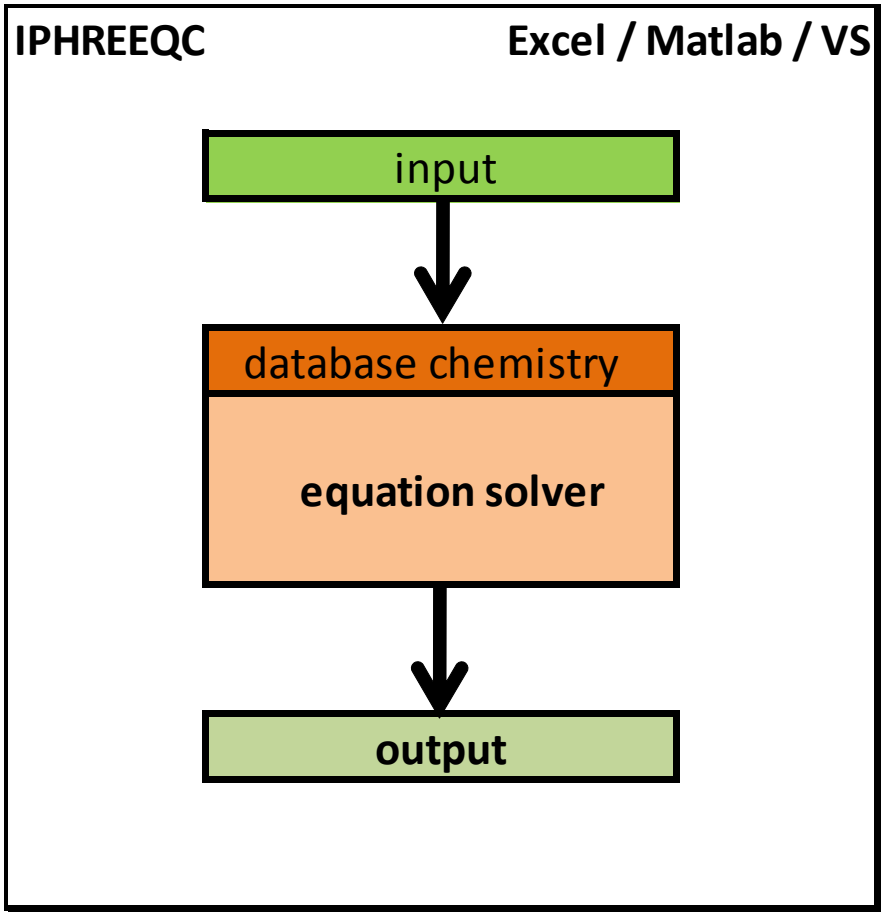
Graphical user interface - since 2001

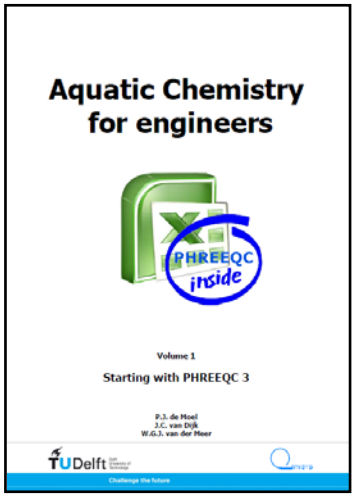




PHREEQC

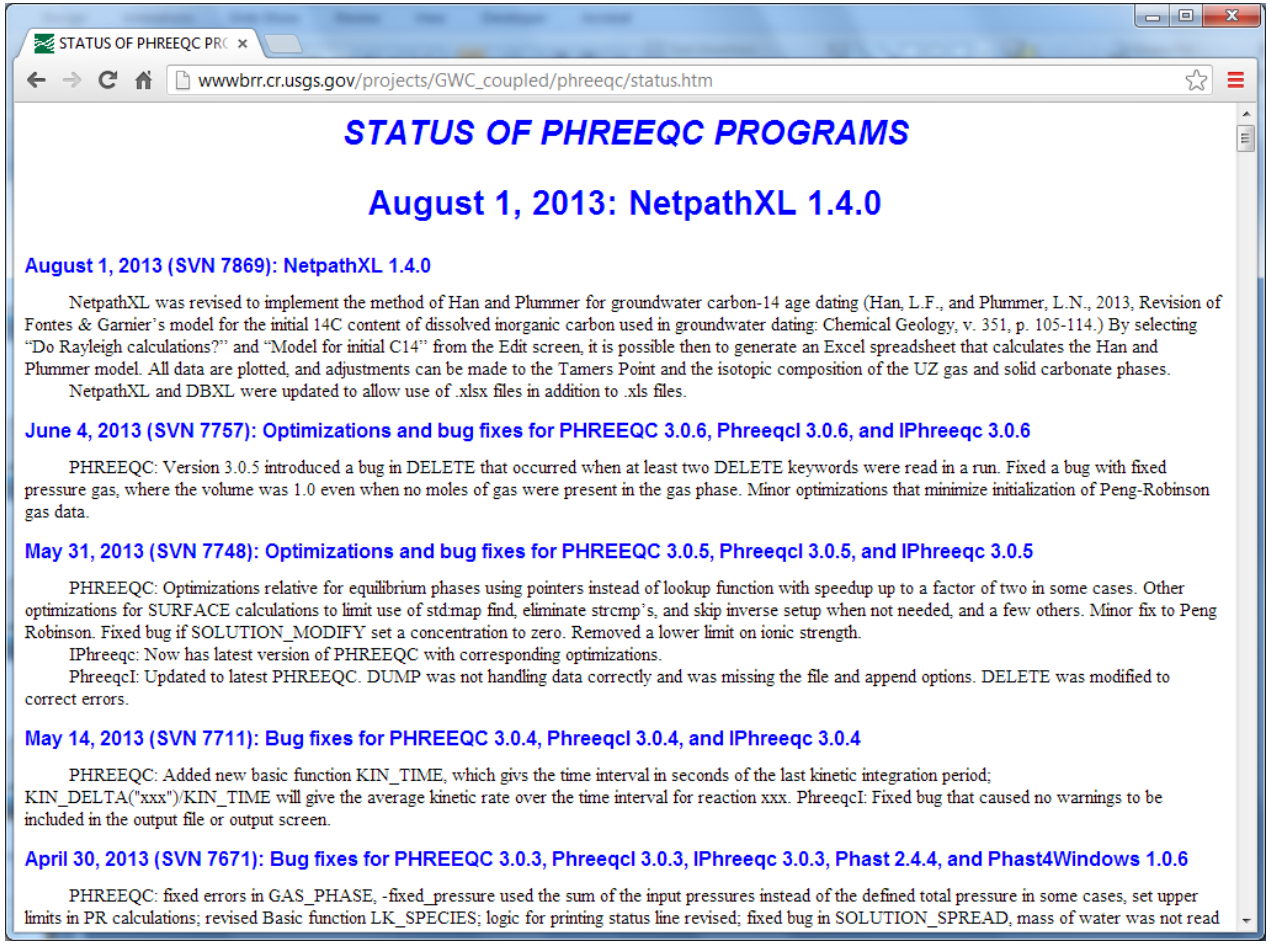
Modules (COM / VS) - since 2011





PHREEQC

Latest release PHREEQC: 3 month ago



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 ?

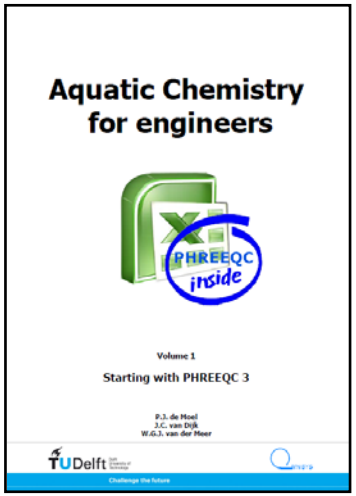
PHREEQC is now accessible for our SE students

- 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

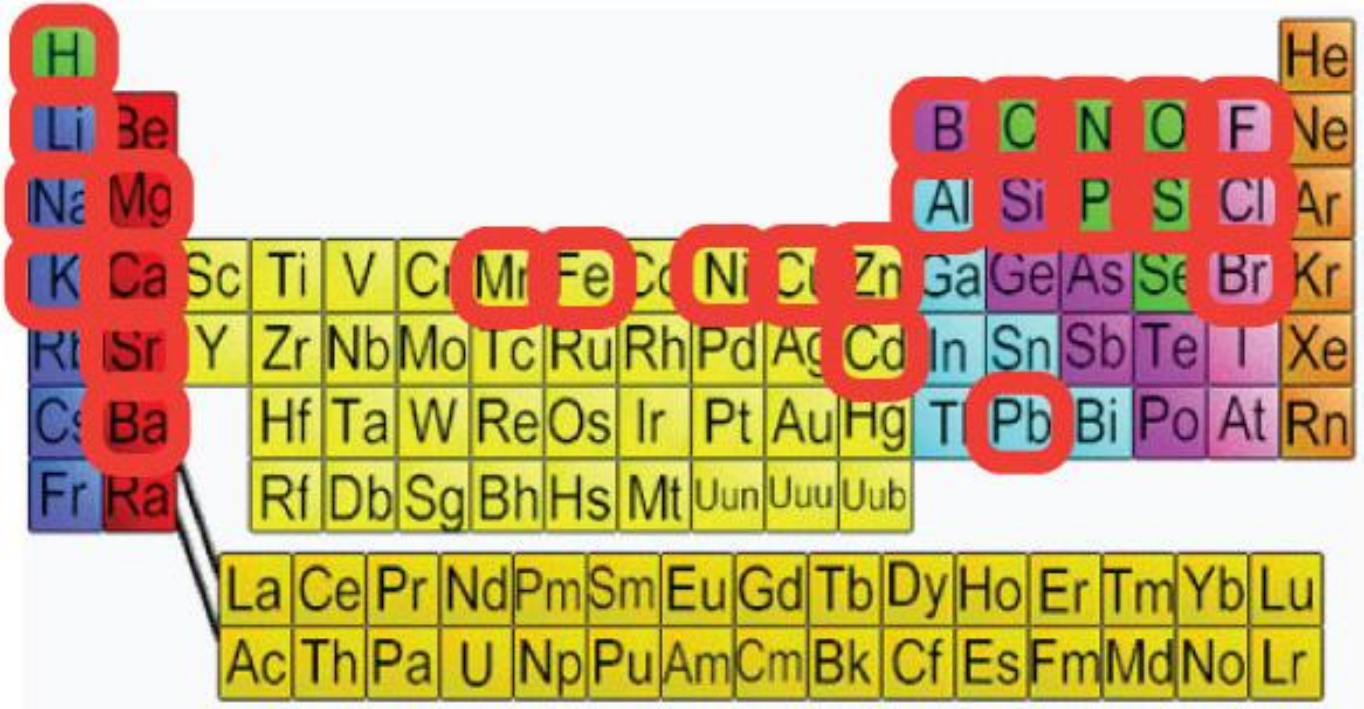
  (since September 2011)



PHREEQC

Basics: all elements – pe – pH - temperature

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

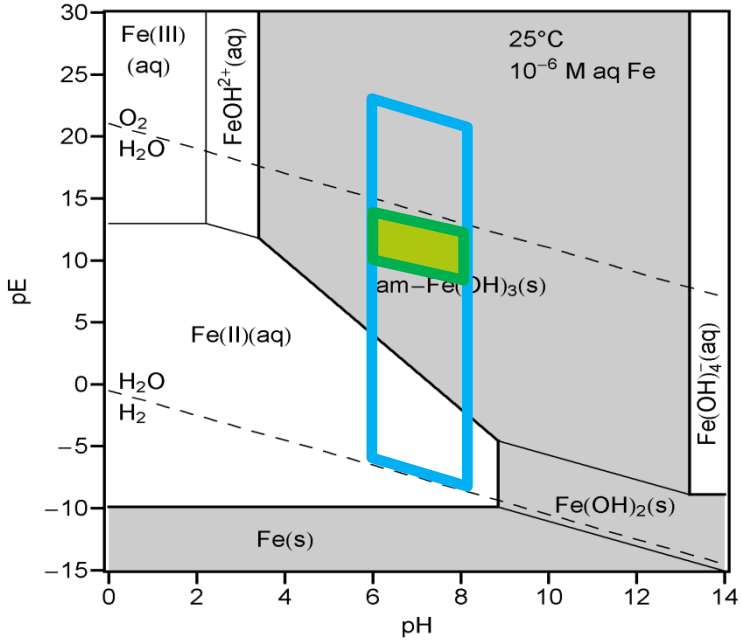


PHREEQC

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
  - CO_2 – HCO_3 – CO_3
- temperature:
  - natural water : temp = 0 – 25 ^{0}C

Fe:



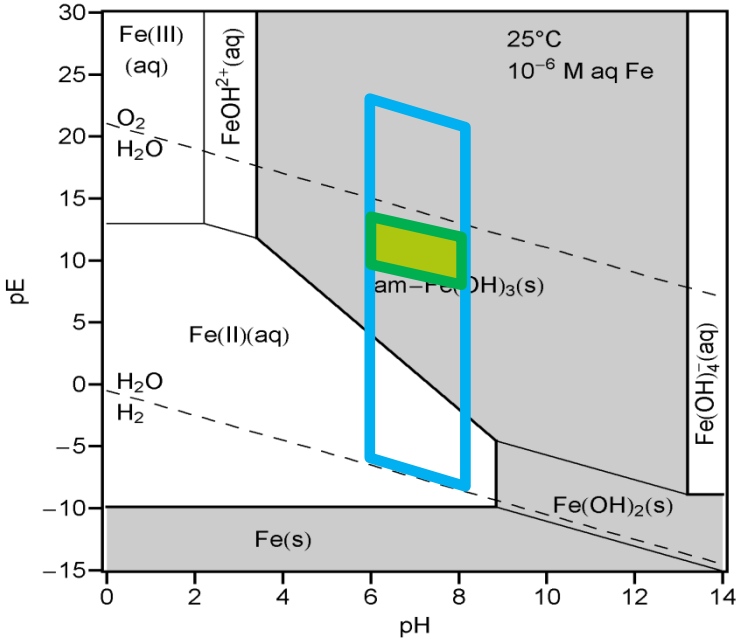
PHREEQC gives all species, and SI for all solids and gases

PHREEQC

Basics: green area for water treatment

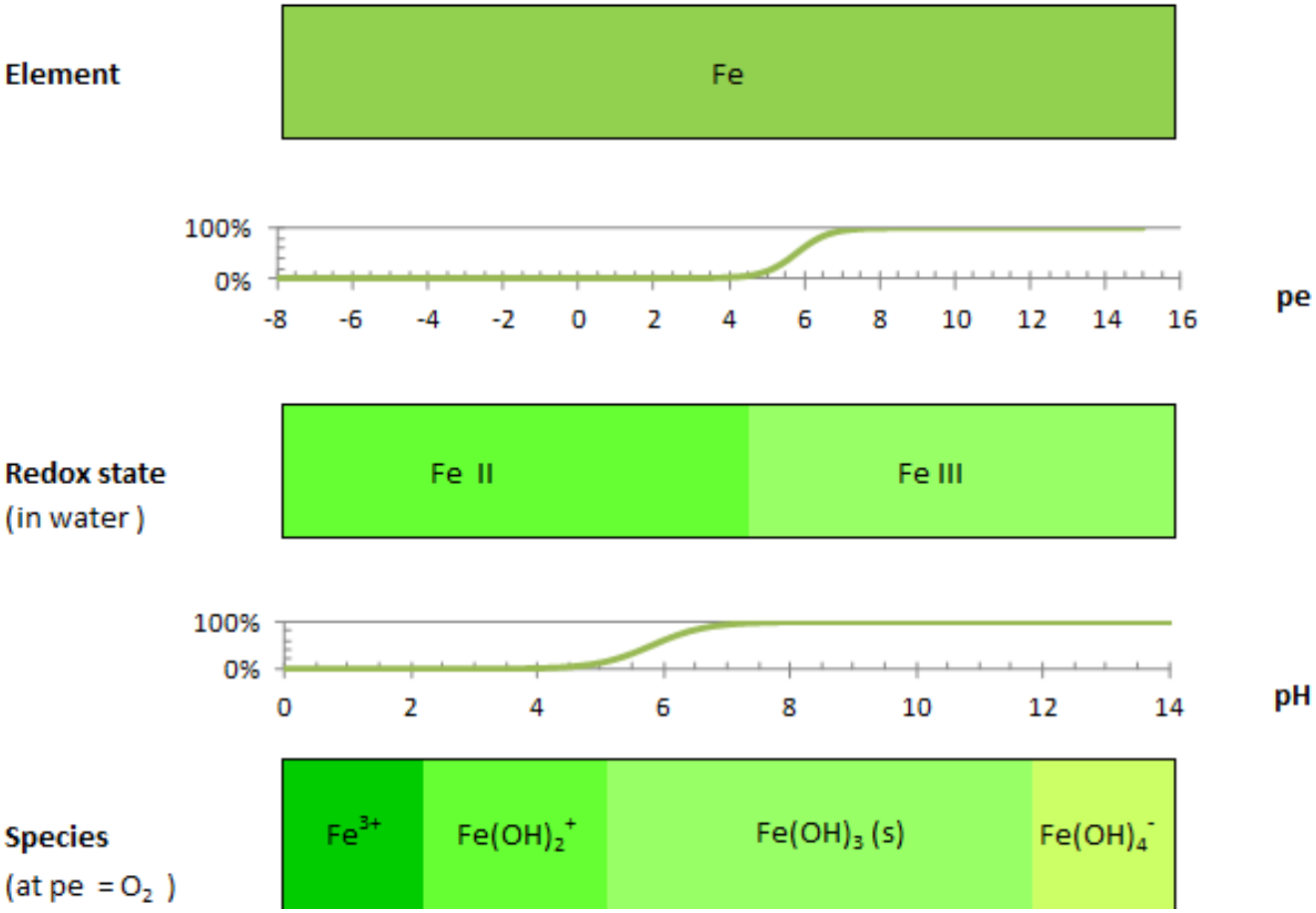
- acid – base
  - new pH after dosing and/or reactions
- gases
  - solubility
  - gas phase (bubbles / air)
- precipitation/dissolution
  - $CaCO_3$, $Fe(OH)_3$ etc
  - $CaCO_3$ (limestone filtration)
- modelling kinetics
  - to be developed in our research

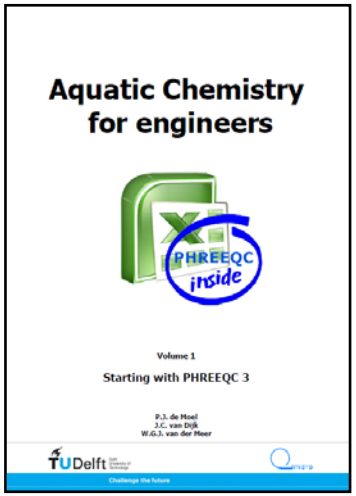
Fe:



PHREEQC

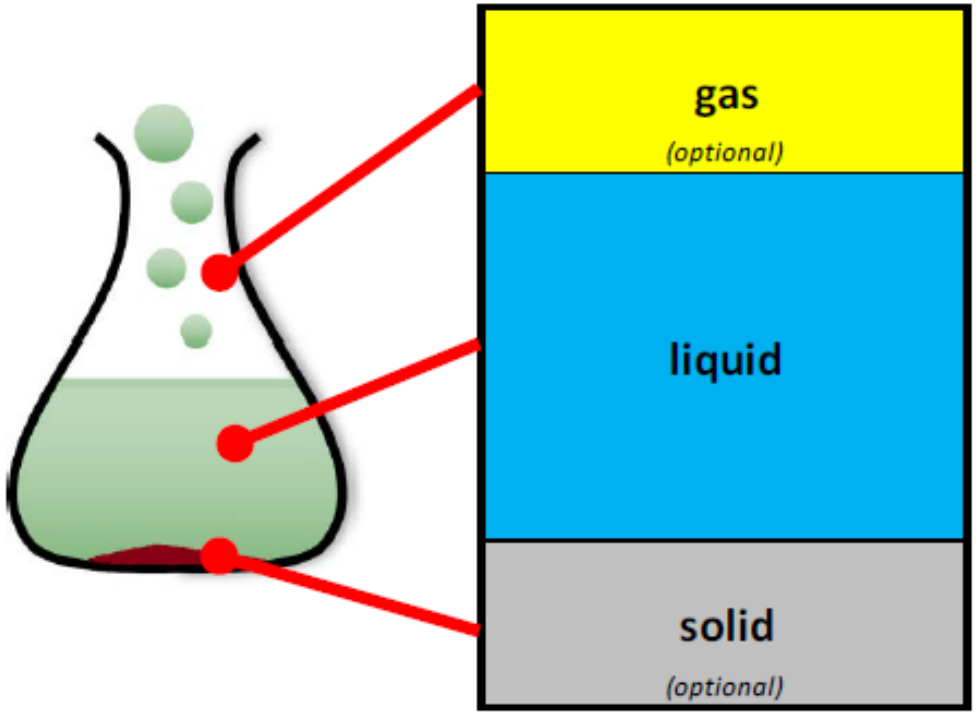
Basics: element – redox states - species





PHREEQC

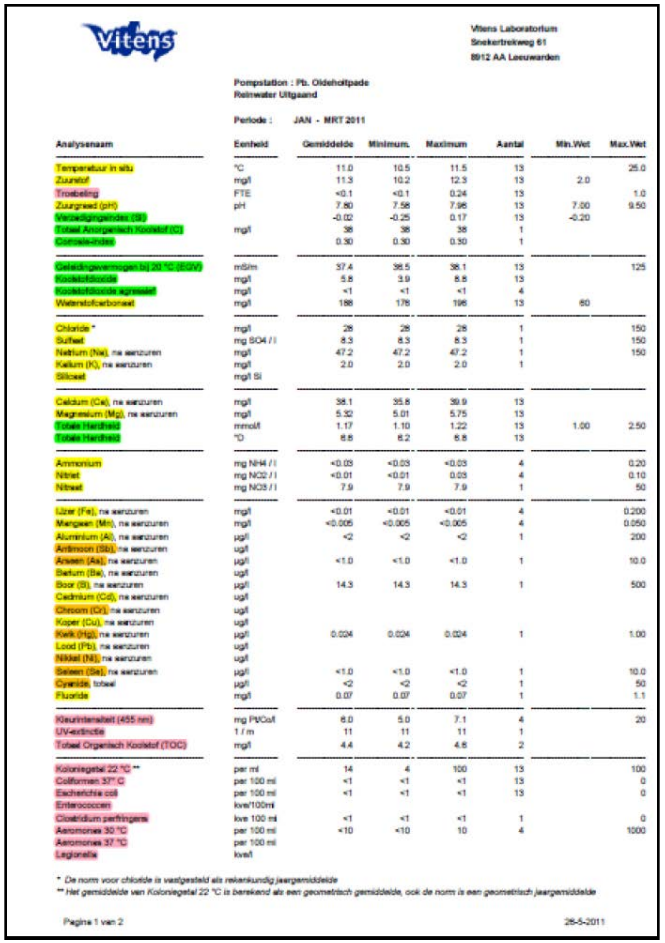
Basics: all equilibriums, full mass balances



PHASES	1 atm
(or EQUILIBRIUM_PHASES)	
(or GAS_PHASE)	
	1 kg of H2O
SOLUTION	temp 25 C
(or SOLUTION_SPREAD)	pH 7.0
	pe 4.0
	1 kg/L
PHASES	10 mol per solid
(or EQUILIBRIUM_PHASES)	

PHREEQC

Drinking water in PHREEQC



Vitens

Vitens Laboratorium
Snekertrekweg 61
8912 AA Leeuwarden

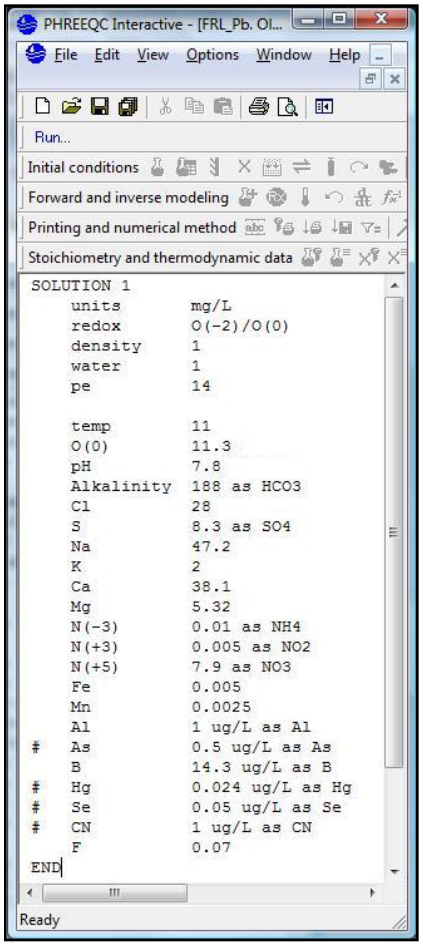
Pompstation : Pb. Oldeholtpade
Reinwater Uitgaand

Periode : JAN - MRT 2011

Analysenaam	Eenheid	Gemiddelde	Minimum	Maximum	Aantal	Min.Wet	Max.Wet
Temperatuur in situ	°C	11.0	10.5	11.5	13		25.0
Zuurstof	mg/l	11.3	10.2	12.3	13	2.0	
Troebeling	FTE	<0.1	<0.1	0.24	13		1.0
Zuurgraad (pH)	pH	7.80	7.56	7.96	13	7.00	9.50
Verzadigingsindex (SI)		-0.02	-0.25	0.17	13	-0.20	
Totaal Anorganisch Koolstof (IC)	mg/l	36	36	36	1		
Corrosie-index		0.30	0.30	0.30	1		
Geleidingsvermogen bij 20 °C (EGV)	mS/m	37.4	36.5	38.1	13		125
Koolstofdioxide	mg/l	5.8	3.9	8.8	13		
Koolstofdioxide agressief	mg/l	<1	<1	<1	4		
Waterstofcarbonaat	mg/l	188	178	196	13	80	
Chloride *	mg/l	28	28	28	1		150
Sulfaat	mg SO4 / l	8.3	8.3	8.3	1		150
Natrium (Na), na aanzuren	mg/l	47.2	47.2	47.2	1		150
Kalium (K), na aanzuren	mg/l	2.0	2.0	2.0	1		
Silicaat	mg/l Si						
Calcium (Ca), na aanzuren	mg/l	38.1	35.8	39.9	13		
Magnesium (Mg), na aanzuren	mg/l	5.32	5.01	5.75	13		
Totale Hardheid	mmol/l	1.17	1.10	1.22	13	1.00	2.50
Totale Hardheid	°D	6.6	6.2	6.8	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
Nitraat	mg NO3 / l	7.9	7.9	7.9	1		50
IJzer (Fe), na aanzuren	mg/l	<0.01	<0.01	<0.01	4		0.200
Mangaan (Mn), na aanzuren	mg/l	<0.005	<0.005	<0.005	4		0.050
Aluminium (Al), na aanzuren	µg/l	<2	<2	<2	1		200
Antimoon (Sb), na aanzuren	ug/l						
Arseen (As), na aanzuren	µg/l	<1.0	<1.0	<1.0	1		10.0
Barium (Ba), na aanzuren	ug/l						
Boor (B), na aanzuren	µg/l	14.3	14.3	14.3	1		500
Cadmium (Cd), na aanzuren	ug/l						
Chroom (Cr), na aanzuren	ug/l						
Koper (Cu), na aanzuren	ug/l						
Kwik (Hg), na aanzuren	µg/l	0.024	0.024	0.024	1		1.00
Lood (Pb), na aanzuren	ug/l						
Nikkel (Ni), na aanzuren	ug/l						
Seleen (Se), na aanzuren	µg/l	<1.0	<1.0	<1.0	1		10.0
Cyanide, totaal	µg/l	<2	<2	<2	1		50
Fluoride	mg/l	0.07	0.07	0.07	1		1.1
Kleurintensiteit (455 nm)	mg Pt/Co/l	6.0	5.0	7.1	4		20
UV-extinctie	1 / m	11	11	11	1		
Totaal Organisch Koolstof (TOC)	mg/l	4.4	4.2	4.6	2		
Kolonietal 22 °C **	per ml	14	4	100	13		100
Coliformen 37° C	per 100 ml	<1	<1	<1	13		0
Escherichia coli	per 100 ml	<1	<1	<1	13		0
Enterococcen	kve/100ml						
Clostridium perfringens	kve 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	kve/l						

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

Pagina 1 van 2 28-6-2011



PHREEQC Interactive - [FRL_Pb. Ol...

File Edit View Options Window Help

Run...

Initial conditions

Forward and inverse modeling

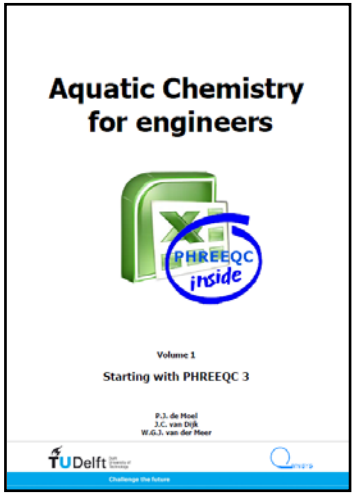
Printing and numerical method

Stoichiometry and thermodynamic data

```
SOLUTION 1
    units       mg/L
    redox       O(-2)/O(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
```

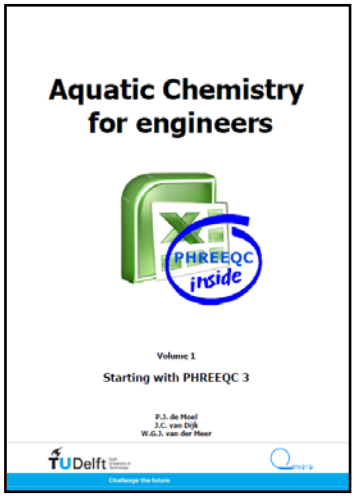
Ready



PHREEQC

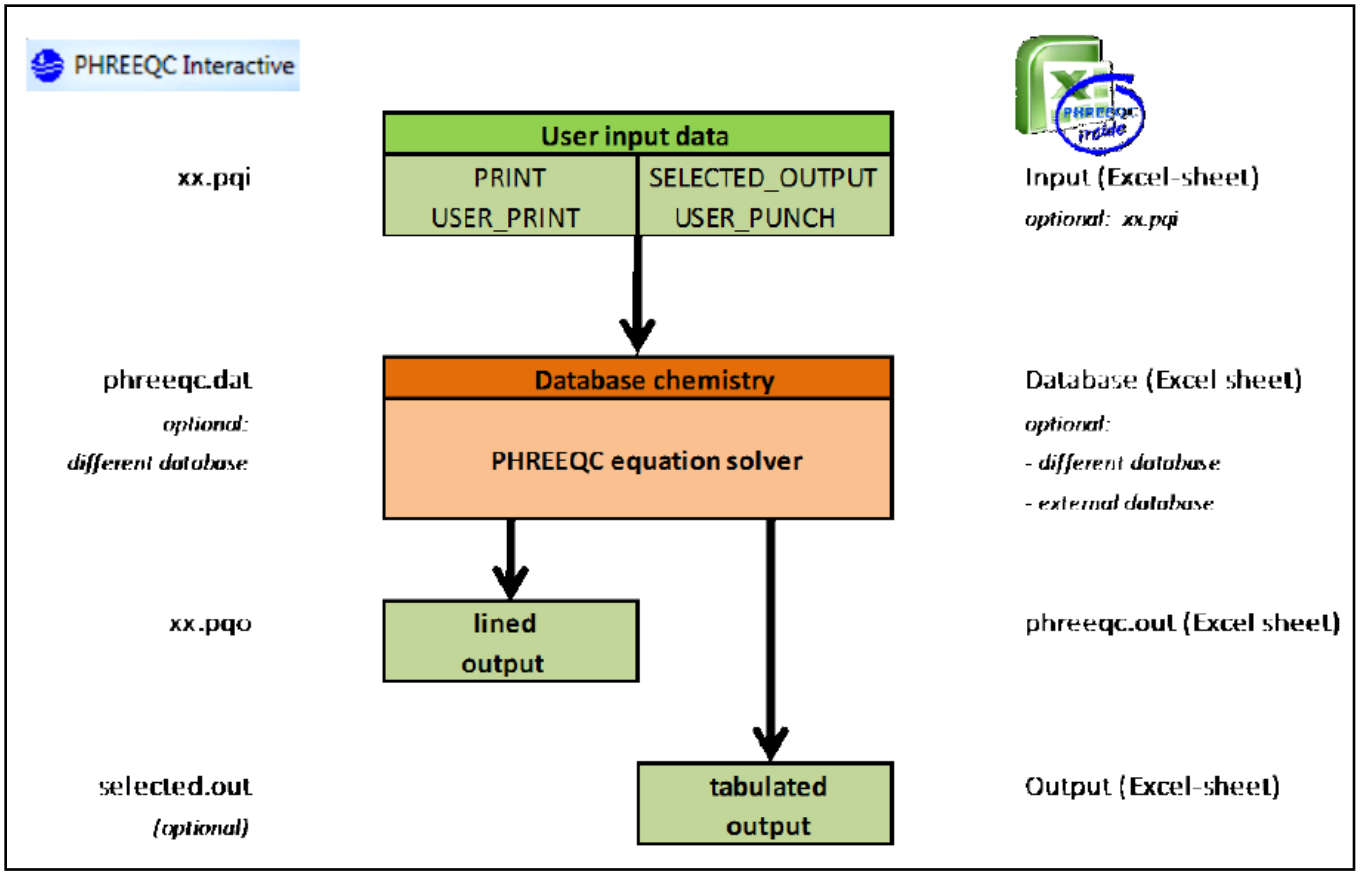
Basics: concentrations as mol/kgw

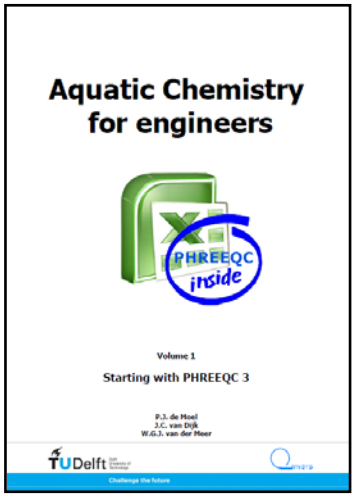
- Solution in kgw
  - not Liter — change with temperature
  - not kg solution — change by formation/use of H_2O
- Amount in mol:
  - not mg — stoichiometric reactions
  - not mmol — equilibrium constants
- Concentrations:
  - input amount as g / mg / µg or mol / mmol / µmol
  - input as /L (with density in kgs/L) or /kgs or /kgw
  - output always as mol/kgw
- [Concentrations] and {Activities}:
  - [Ca] = 40 mg/L = 1 mmol/L ≈ 1 mmol/kgw
  - {Ca} = gamma * [Ca]



PHREEQC

Basics: data flow

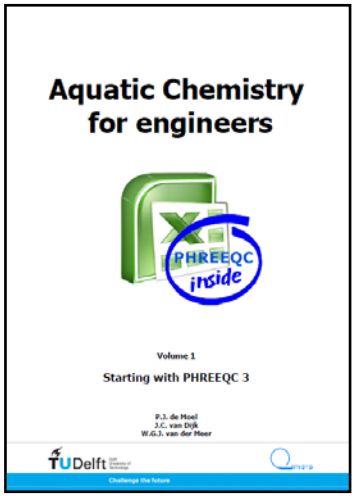




PHREEQC

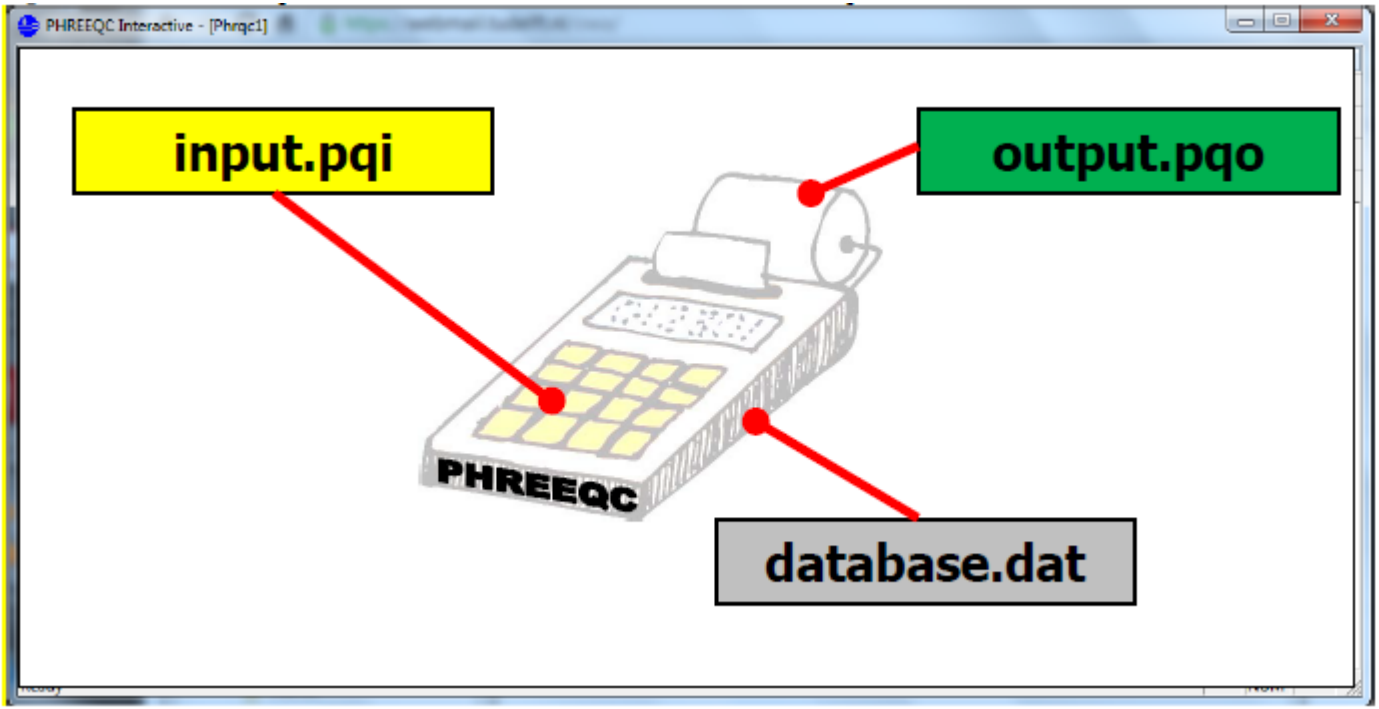
Basics: kinetics in phreeqc.dat

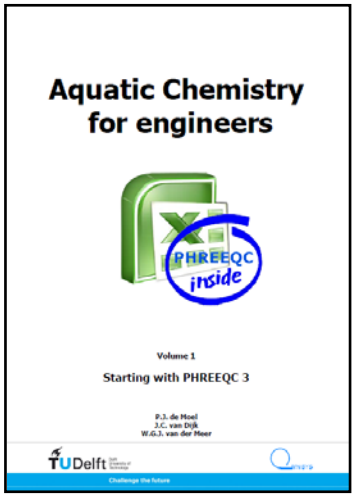
- Calcite ($CaCO_3$) (precipitation / dissolution)
  - PWP model (Plummer, Wigley, Parkhurst), 1978
  - Rate = f (temp H^+ CO_2 SI-calcite)
  - dMass = Rate x Area x Timestep
- Organic C (oxydation)
  - Additive Monod kinetics $\frac{dX}{dt} = \mu \cdot X \qquad \mu = \mu_{max} \cdot \frac{S}{K_s + S}$
  - Rate = f (O_2 NO_3 SO_4)
  - dMass = Rate x Mass x Timestep
- plus Pyrite, K-feldspar, Albite, Pyrolusite
- own models in user input



PHREEQC Interactive

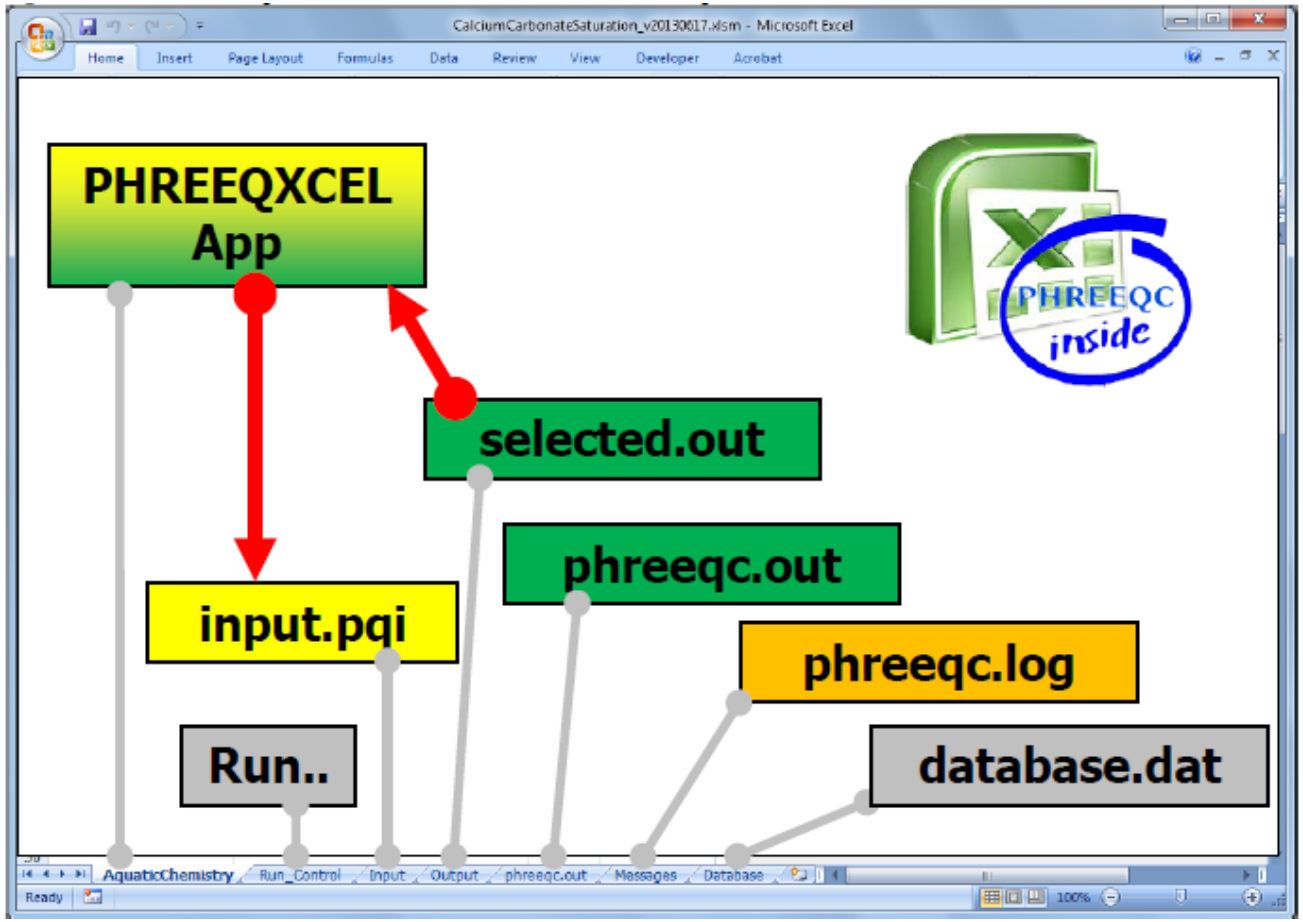
Basics: files

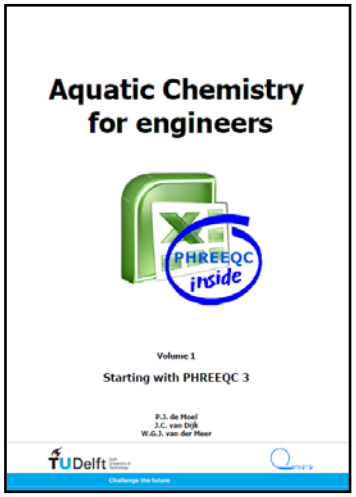




PHREEQXCEL

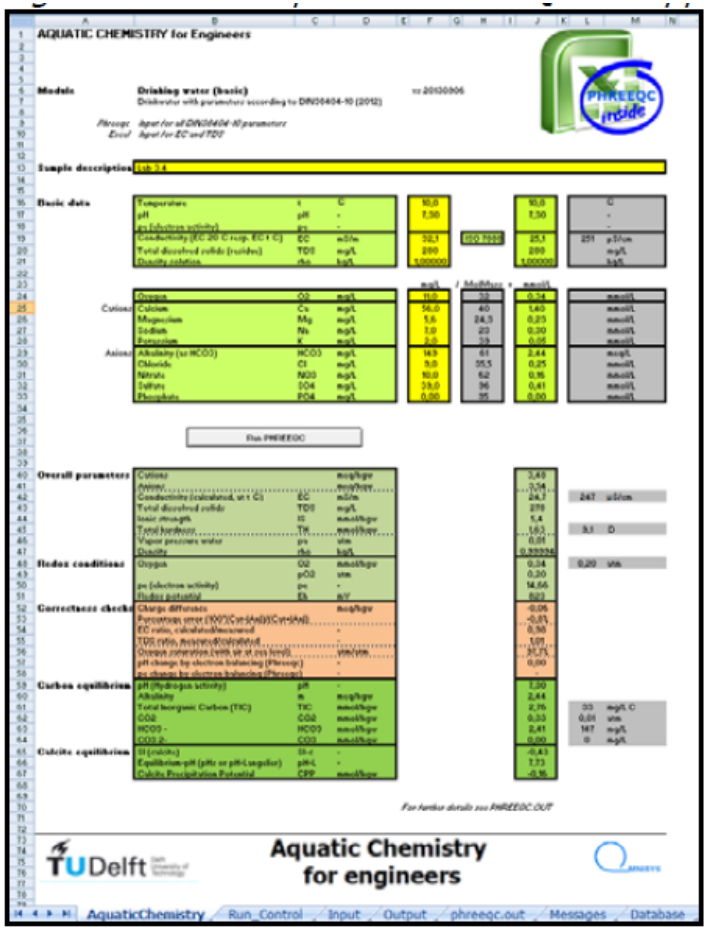
Basics: files

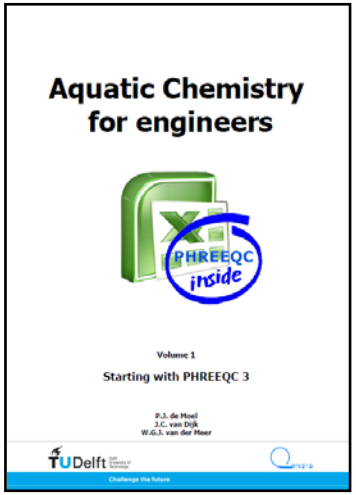




PHREEQXCEL

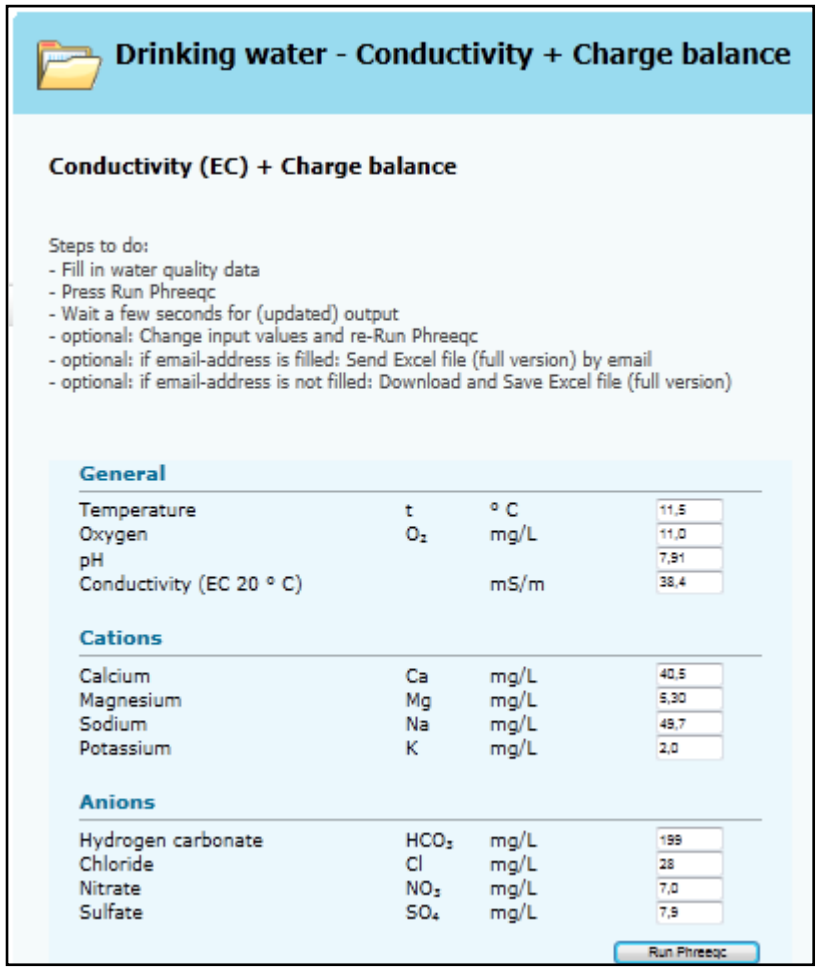
Input+output in Excel





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			7,91
Conductivity (EC 20 ° C)		mS/m	38,4

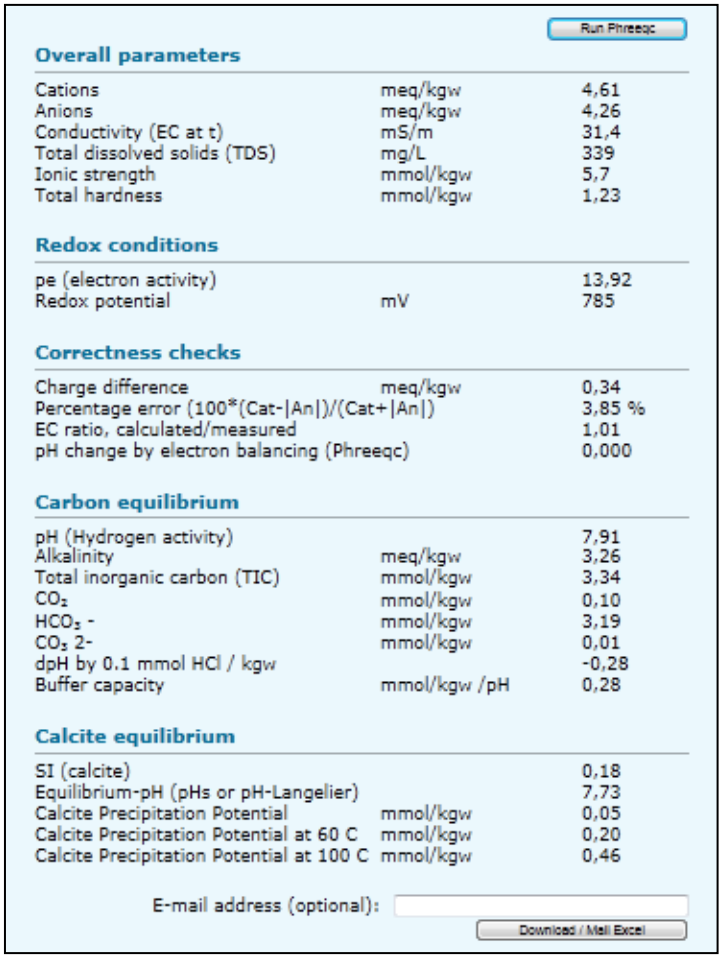
Cations

Calcium	Ca	mg/L	40,5
Magnesium	Mg	mg/L	5,30
Sodium	Na	mg/L	48,7
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

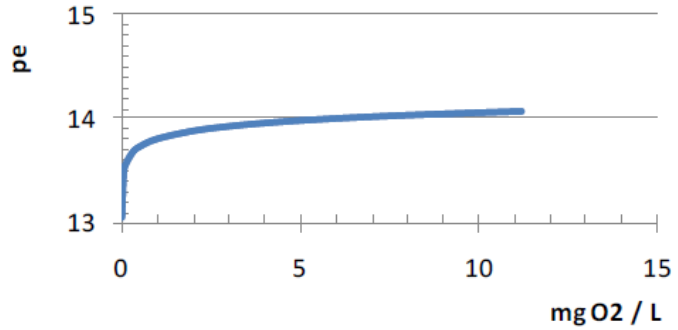
SI (calcite)		0,18
Equilibrium-pH (pHs or pH-Langelier)		7,73
Calcite Precipitation Potential	mmol/kgw	0,05
Calcite Precipitation Potential at 60 C	mmol/kgw	0,20
Calcite Precipitation Potential at 100 C	mmol/kgw	0,46

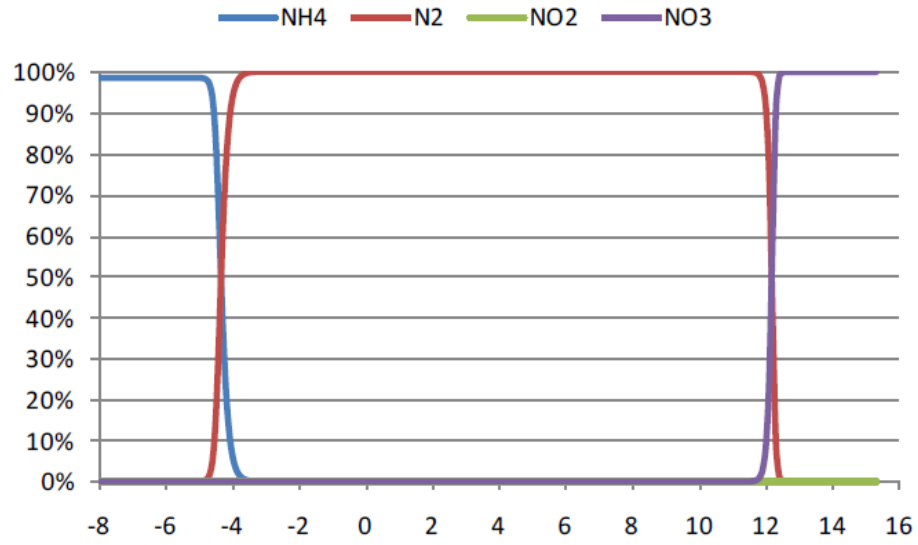
E-mail address (optional):

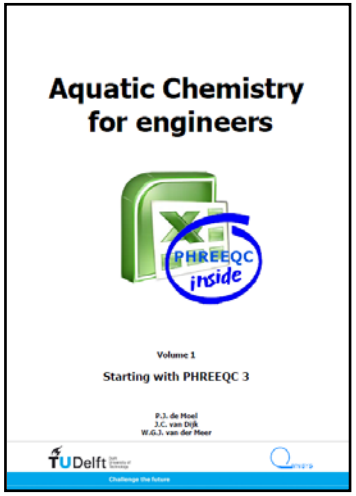
Download / Mail Excel

PHREEQC

Nitrogen - Equilibrium vs Kinetics



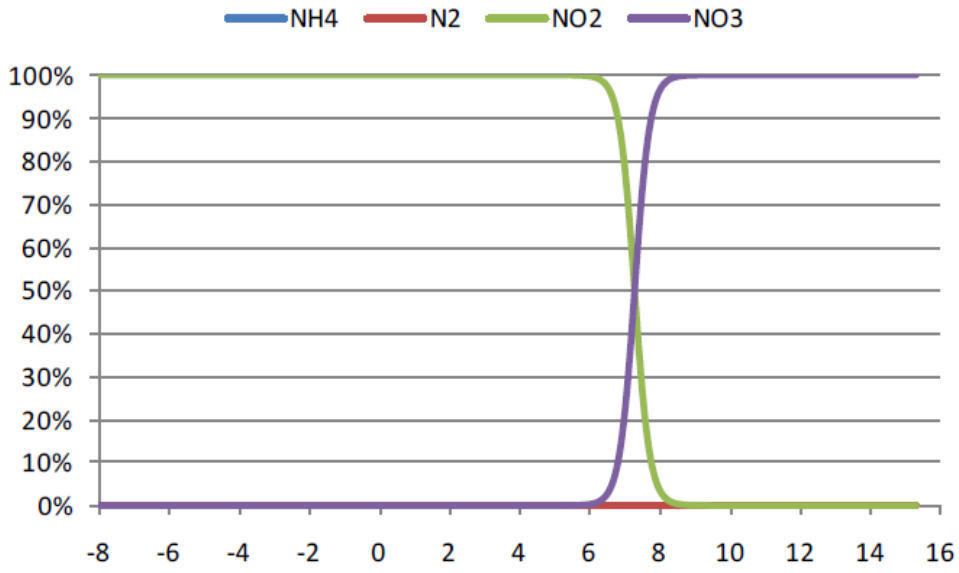


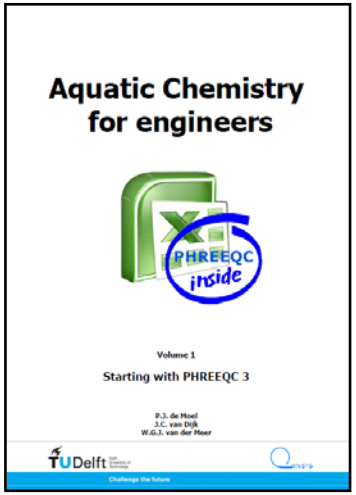


PHREEQC

Nitrogen - Inert NH4 / Inert N2

- 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

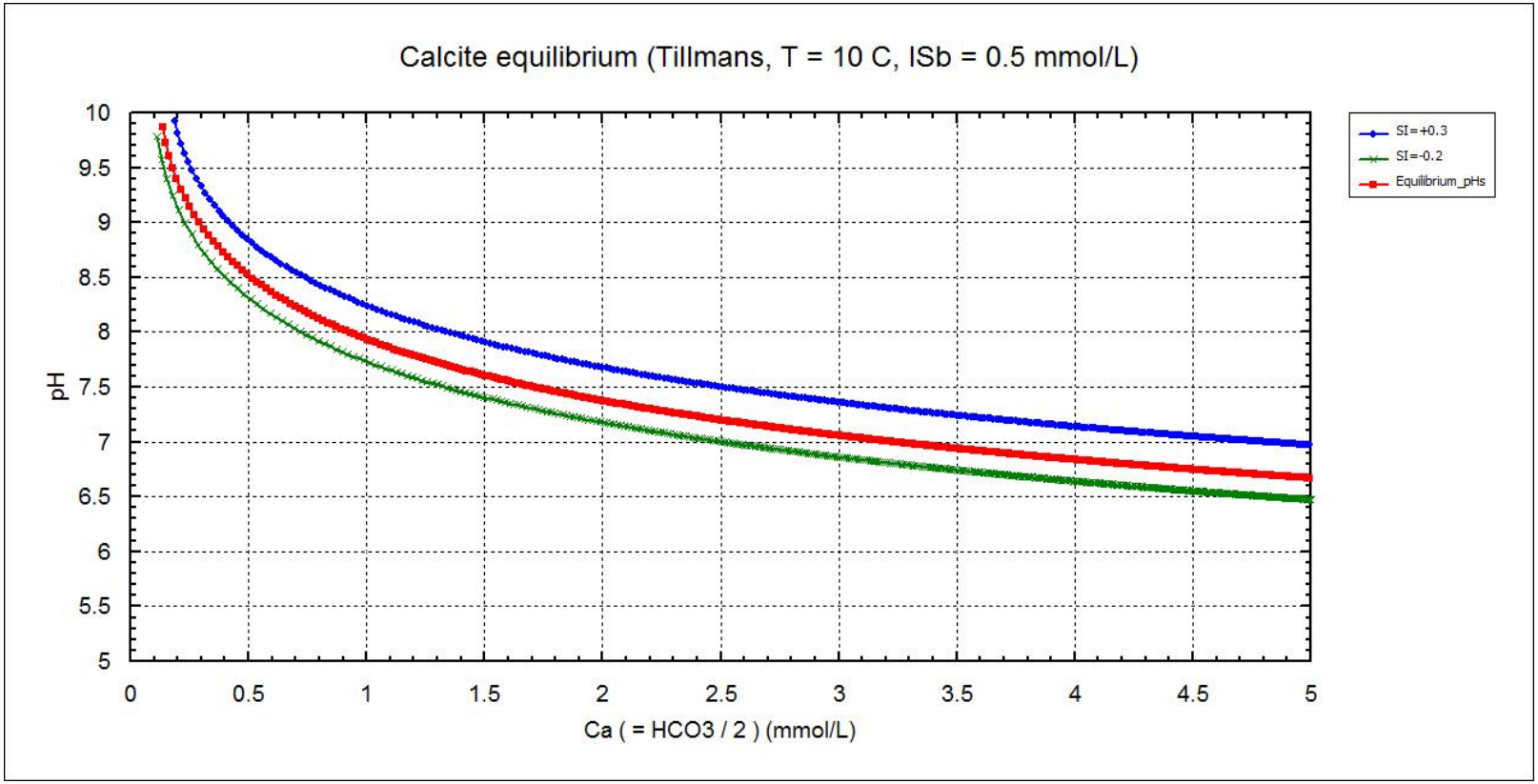




Examples

Calcite equilibrium

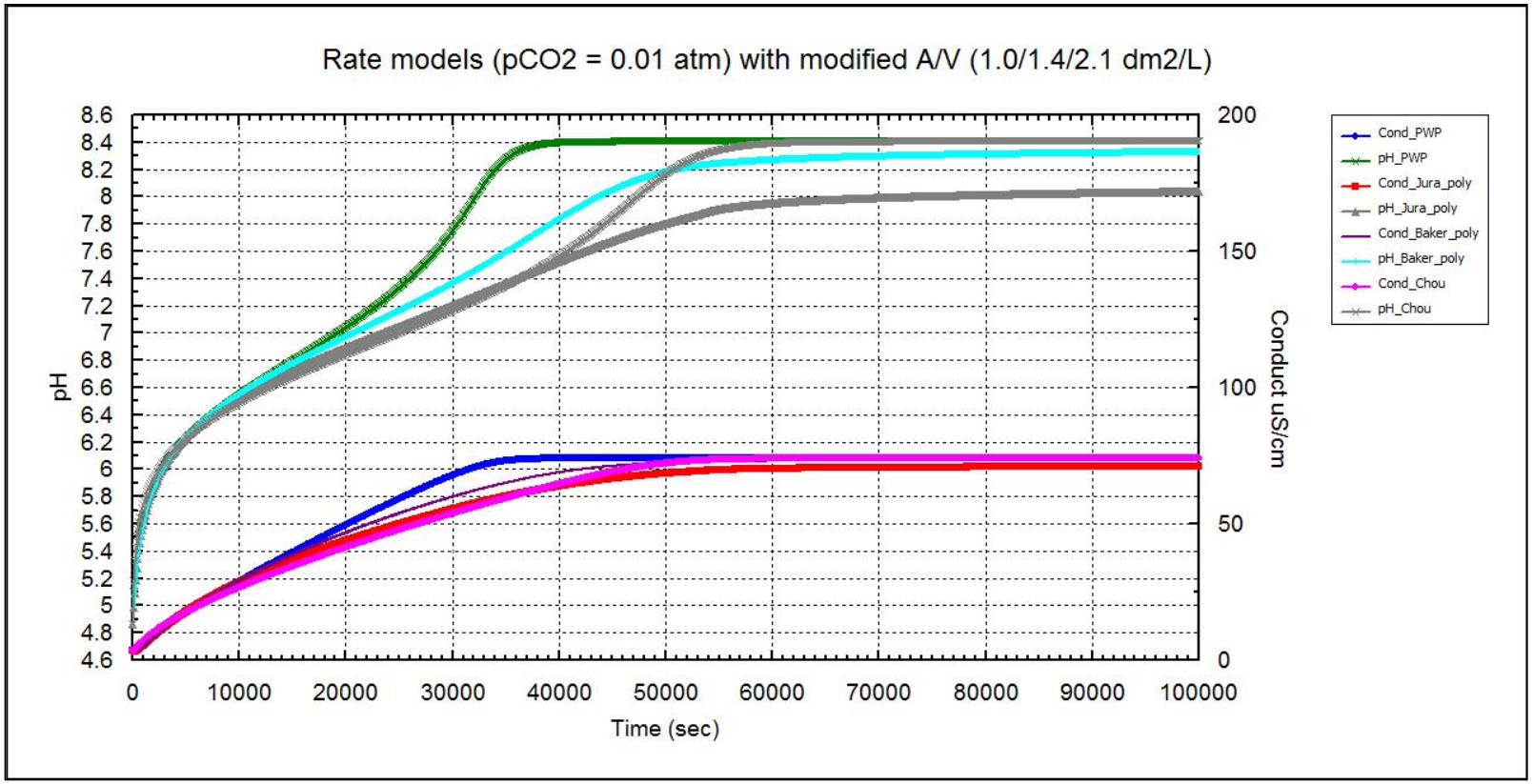
Phreeqc:



Examples

Dissolution rate CaCO3 (Lime stone filtration)

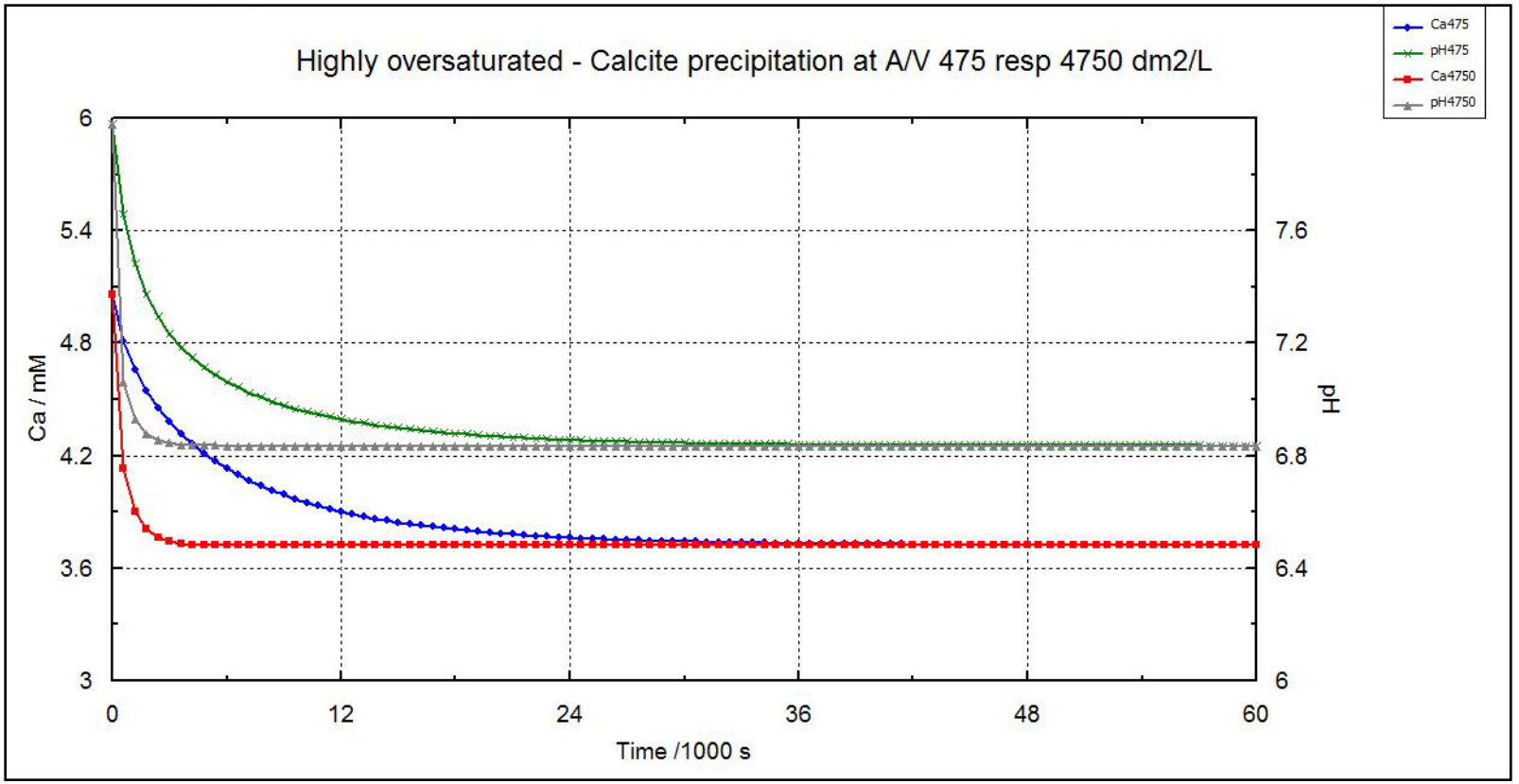
Phreeqc:



Examples

Precipitation rate CaCO3 (no seed material)

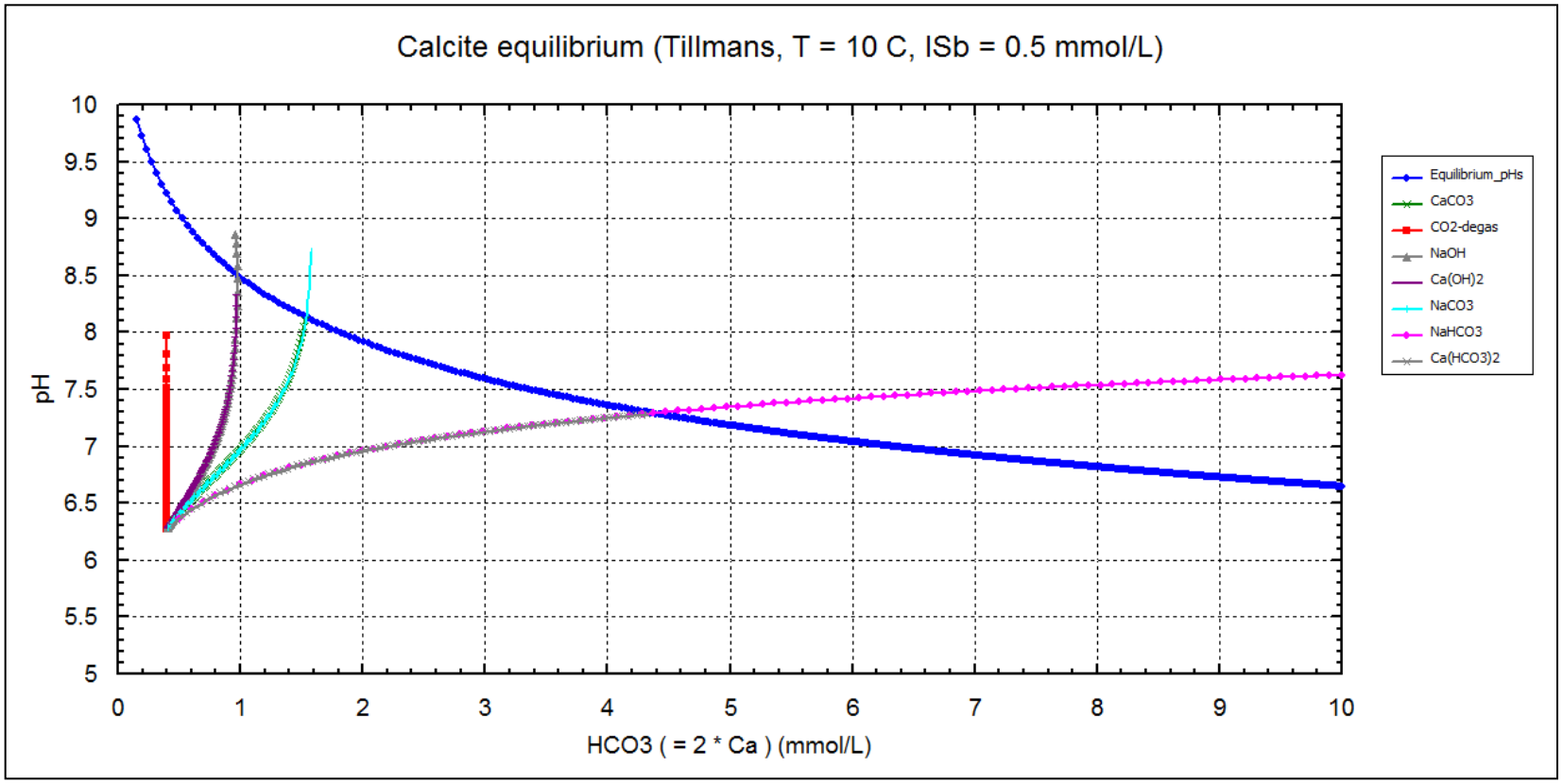
Phreeqc:



Examples

pH for different treatment methods

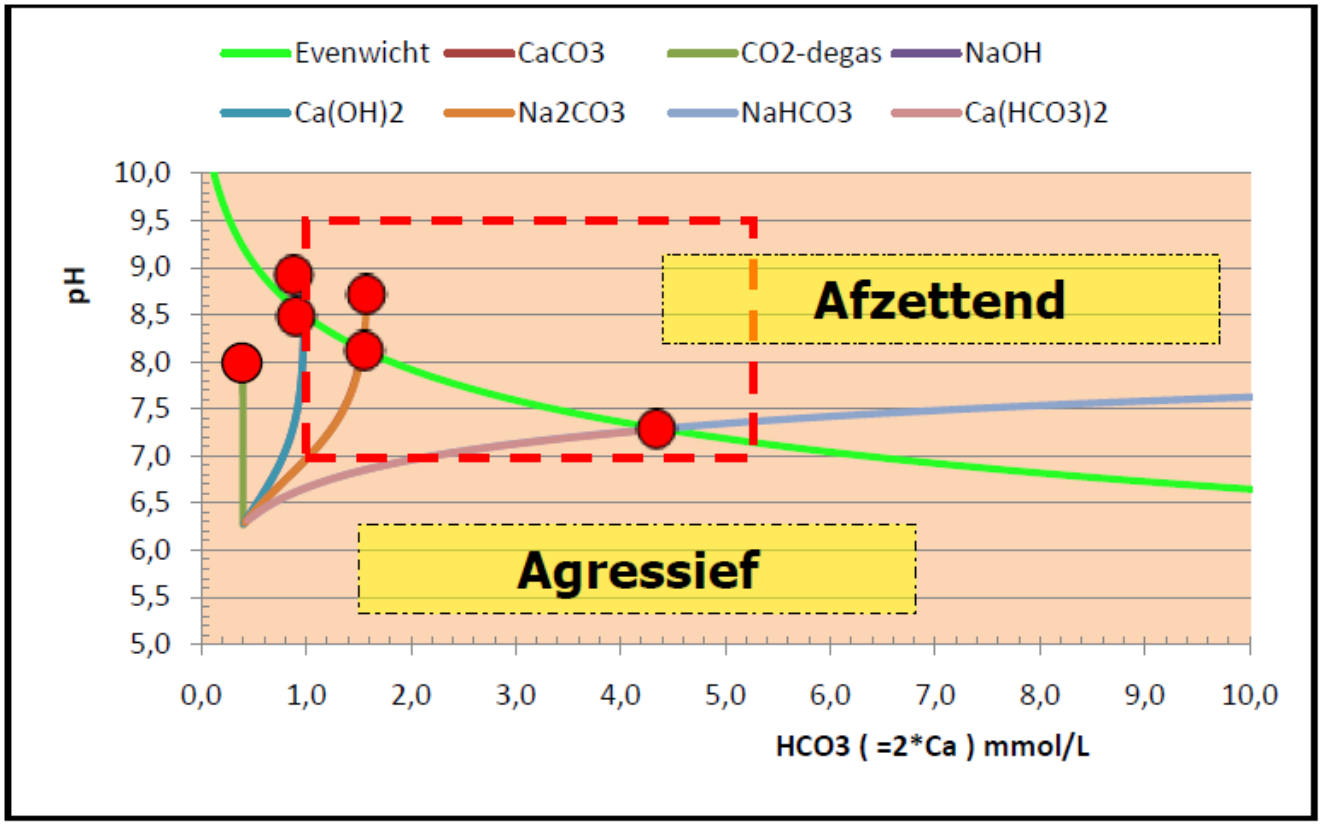
Phreeqc:



Examples

pH for different treatment methods (2)

Phreeqc:

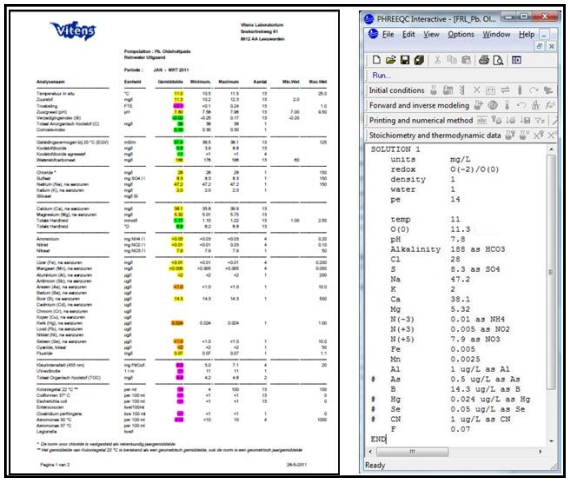


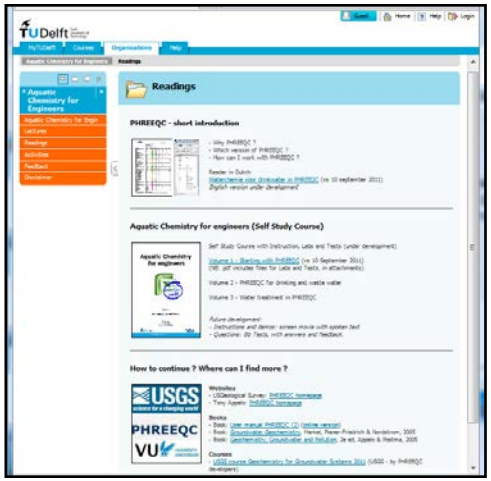
Aquatic chemistry for engineers

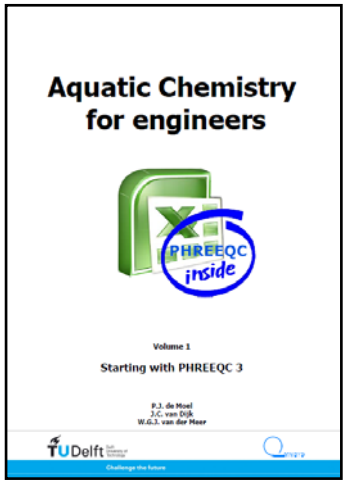
Status

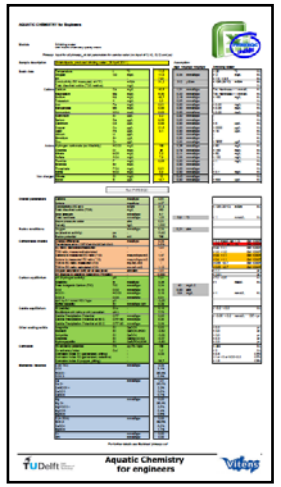
Completed:

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









Aquatic chemistry for engineers

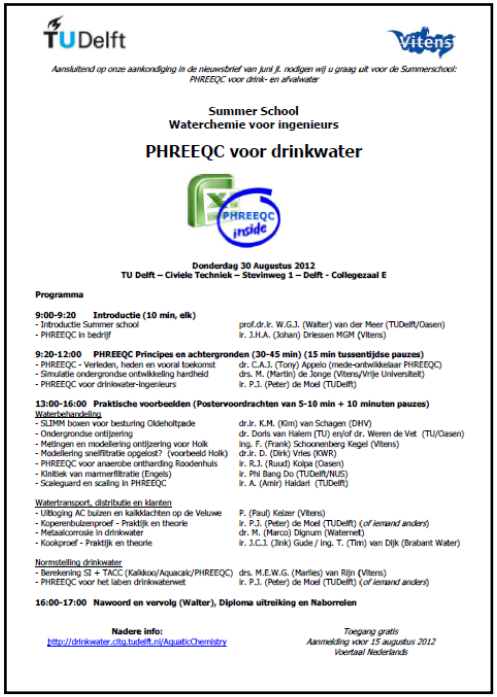
Recent and future developments

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

Aansluitend op onze aankondiging in de nieuwsbrief van juni jl. 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 – Stevinweg 1 – Delft - Collegezaal E

Programma

9:00-9:20 Introductie (10 min, elk)

- Introductie Summer school	prof.dr.ir. W.G.J. (Walter) van der Meer (TUDelft/Oasen)
- PHREEQC in bedrijf	ir. J.H.A. (Johan) Driessen MGM (Vitens)

9:20-12:00 PHREEQC Principes en achtergronden (30-45 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. (Martin) de Jonge (Vitens/Vrije Universiteit)
- PHREEQC voor drinkwater-ingenieurs	ir. P.J. (Peter) de Moel (TUDelft)

13:00-16:00 Praktische voorbeelden (Postervoordrachten van 5-10 min + 10 minuten pauzes)

Waterbehandeling

- SLIMM boxen voor besturing Oldeholtpade	dr.ir. K.M. (Kim) van Schagen (DHV)
- Ondergrondse ontijzering	dr. Doris van Halem (TU) en/of dr. Weren de Vet (TU/Oasen)
- Metingen en modellering ontijzering voor Holk	Ing. F. (Frank) Schoonenberg Kegel (Vitens)
- Modellering snelfiltratie opgelost? (voorbeeld Holk)	dr.ir. D. (Dirk) Vries (KWR)
- PHREEQC voor anaerobe ontharding Roodenhuis	ir. R.J. (Ruud) Kolpa (Oasen)
- Kinitiek van marmerfiltratie (Engels)	ir. Phi Bang Do (TUDelft/NUS)
- Scaleguard en scaling in PHREEQC	ir. A. (Amir) Haidari (TUDelft)

Watertransport, distributie en klanten

- Uitloging AC buizen en kalkkiachten op de Veluwe	P. (Paul) Kelzer (Vitens)
- Koperenbuizenproef - Praktijk en theorie	ir. P.J. (Peter) de Moel (TUDelft) (*of iemand anders*)
- Metaalcorrosie in drinkwater	dr. M. (Marco) Dignum (Waternet)
- Kookproef - Praktijk en theorie	ir. J.C.J. (Jink) Gude / Ing. T. (Tim) van Dijk (Brabant Water)

Normstelling drinkwater

- Berekening SI + TACC (Kalkkoo/Aquacalc/PHREEQC)	drs. M.E.W.G. (Marlies) van Rijn (Vitens)
- PHREEQC voor het laben drinkwaterwet	ir. P.J. (Peter) de Moel (TUDelft) (*of iemand anders*)

16:00-17:00 Nawoord en vervolg (Walter), Diploma uitreiking en Nabornelen

Nadere info:
http://drinkwater.citg.tudelft.nl/AquaticChemistry

Toegang gratis
Aanmelding voor 15 augustus 2012
Voertaal Nederlands

Aquatic chemistry for engineers

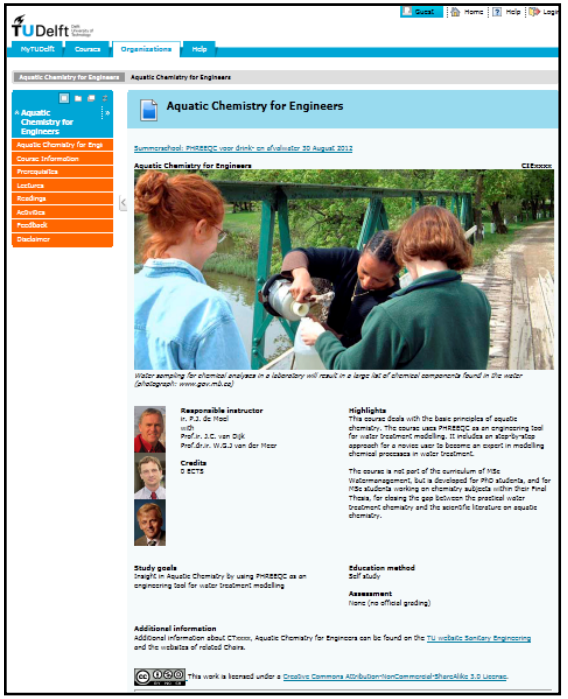
Treatment processes

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



Aquatic chemistry for engineers

Further information

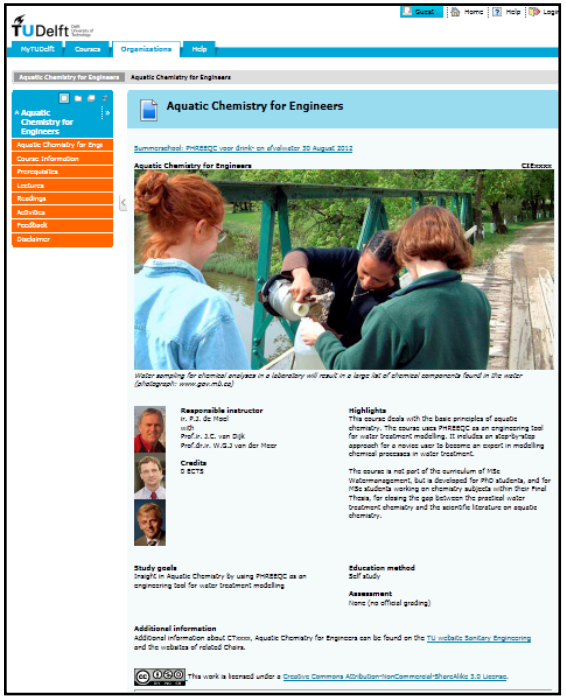
OpenCourseWare website

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

Contains

- Lectures
- Readings
- Activities (Labs and Tests)
- New developments

- Database stimela.dat
  (phreeqc.dat for Water Treatment, updated)



Questions?

Aquatic Chemistry for engineers

PHREEQC / PHREEQXCEL for water treatment

12 September 2013

Peter de Moel – TU Delft